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I N D I C E

(Continúa del Primer Tomo)

(Continúa en el Tercer Tomo)

II—GEOCHEMICAL AND BIOGEOCHEMICAL METHODS OF PROSPECTING

(Continuación)

ADVANCES IN BOTANICAL MEHODS OF PROSPECTING FOR URANIUM IN WESTERN UNITED STATES *

H. L. CANNON * *

ABSTRACT

The use of botany in prospecting for uranium has been investigated by the U. S. Geological Survey during the past eight years, and botanical techniques in conjunction with trace analyses are now widely used. Two methods of botanical prospecting have proved successful in the discovery of shallow ore bodies.

The first is based upon the absorption of anomalous amounts of uranium by plants rooted in ore. Tree foliage is collected systematically and analyzed for its content. Trees rooted in ore commonly contain one to two parts per million (ppm) in the ash compared to an average of 0.5 ppm in trees rooted in barren ground. Trees of deep root habit have been used effectively to outline mineralized ground at depths of 70 feet.

Mapping the distribution of key indicator plants rooted in ore-bearing formations is an effective prospecting method. Distinctive plants requiring selenium and sulfur may indicate associated uraniferous ores. *Astragalus pattersoni* delineated ore bodies to depths of 68 feet. Where the ground-water table is shallow, sulfur plants such as mustards, onions, and species of *Eriogonum* are useful.

These methods of botanical prospecting are useful in both detailed exploration and reconnaissance.

INTRODUCCION

Botanical methods of prospecting have been developed by the U. S. Geological Survey under the auspices of the Atomic Energy Commission in the search for uranium on the Colorado Plateau in Western United States.

Studies in this uranium province were begun in 1947 to discover whether plants rooted in ore differ chemical or ecologically from those rooted in barren ground, and whether these differences can be used in prospecting.

The Colorado Plateau is a semi-arid country of deeply dissected tablelands that are penetrated here and there by isolated mountain masses. The average

* *Publication authorized by the Director, U. S. Geological Survey and by the U. S. Atomic Energy Commission.*

* * *U. S. Geological Survey.*

level of the plateau is about 6500 feet and the rainfall is about 10 inches a year. The ore deposits are generally tabular in outline and lie roughly parallel to the bedding. Carnotite is the principal ore in the oxidized zone, but uraninite associated sulfides are common at depth. The flora is commonly affected along the outcrop of an ore-bearing formation due to variations in texture, moisture content, or salinity associated with the introduction or redistribution of the mineral constituents.

Two methods of botanical prospecting have been used successfully to locate ore-bodies in flat-lying sediments under a cover of as much as 70 feet thick of barren sandstone. On ore-bearing sandstones at lower altitudes where the cover is open, the appearance and grouping of certain plant species may be a clue to changes in soil chemistry and even to the location of ore deposits not otherwise revealed at the ground surface. A method of using these indicator plants in prospecting has been perfected for such areas. At higher altitudes where the forest cover is dense and no ground cover exists, tree sampling for uranium content has proved successful in outlining mineralized areas.

During the past six years, a thorough evaluation has been made of the relative effectiveness of these methods. Reports are being prepared for publication by A. J. Fraelich, P. F. Narteu, F. S. Kleinhampl, and the author on the results of these studies. A positive correlation has been shown to exist between botanical anomalies and mineralized ground.

PROSPECTING BY TREE ANALYSIS

Prospecting by tree analysis is based on the detection of unusual amounts of uranium in trees rooted in mineralized ground. Plant ash normally contains from 2 tenths to 1 ppm or .0001 percent uranium. Trees rooted in sandstone-type uranium deposits of the Colorado Plateau have an average content of 1.5 ppm and may contain 100 ppm or more in areas where the ore is highly oxidized. There are many reasons for slight variations in the concentration of uranium in vegetation. Seasonal differences, and differences in the part of the tree and the side of the tree sampled may be overcome by sampling only leaves or end branches from the entire circumference of the tree, and sampling on a day-to-day basis in any one area. It is more difficult to deal with variations due to changes in availability of ions in the soil solution. Control experiments on the absorption of metals by plants were made as an aid in standardizing our methods. Plants were grown in plots of desert soil salted with combinations of ore metals and plant nutrients over a three year period. Twenty species of plants were grown in these plots, or and analyzed for as many critical elements as possible. The amounts of watersoluble uranium and vanadium were

increased in the presence of sulfur or selenium, and selenium and sulfur were more available in a carnotite environment. We believe this oxidizing reaction to be due to irradiation as shown by Dale (1954, p. 258) in experiments concerning the irradiation of ferrous sulfate. Plants, then, should absorb uranium

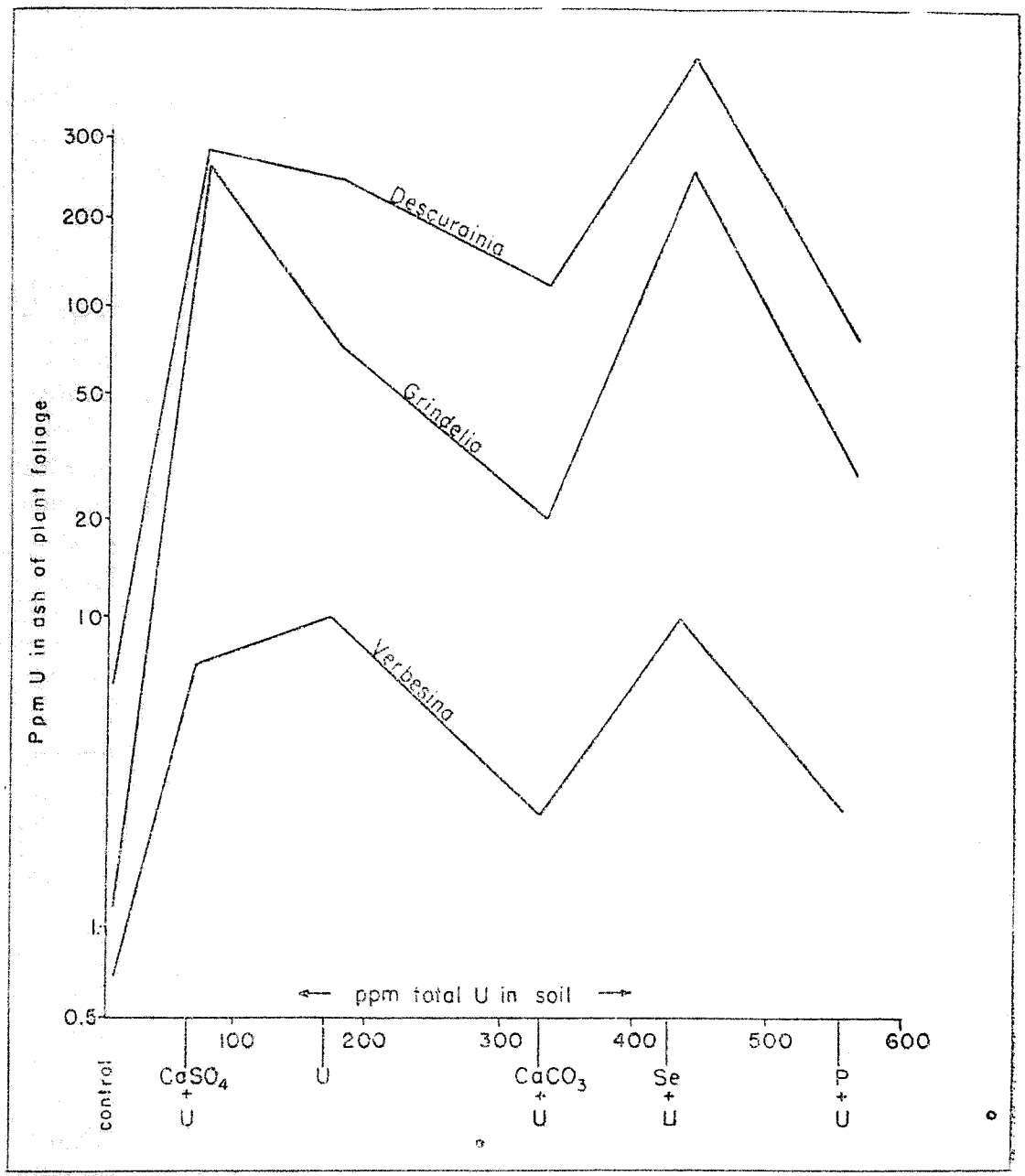

FIGURE 1. A GRAPH SHOWING ABSORPTION OF URANIUM BY 3 PLANT SPECIES GROWN IN 6 SOIL PLOTS VARYING IN URANIUM CONTENT AND AVAILABILITY

easily from ores having a high selenium or sulfur content, and selenium and sulfur from radioactive deposits.

The amount of uranium absorbed varies also with the species as individual relation with potassium held for most species studied. Generally more uranium and vanadium absorption by 10 species grown at one time in experimental plats was between *Verbesina* (goldweed) and *Descurainia* (tansy mustard). (Fig. 1). The foliage of goldweed contained the largest amount of potassium, and the smallest amount of uranium and vanadium. Tansy mustard contained the most uranium, vanadium, and also sodium, phosphorus, calcium, and sulfur. A positive correlation between the concentration of uranium in plant ash and that of sodium, phosphorus, and either sulfur or selenium and a negative correlation with potassium held for most species studied. Generally more uranium is found in the roots than in the tops of the plants. The amount of uranium in the branch tips, nevertheless, bears a definite relation to that available in the soil, and branches or foliage have been used in all wide-scale sampling programs. Evergreens of deep-rooted habit are a satisfactory sampling medium and in areas of wide-scale sampling where it is necessary to use several species of tree, the variations between species can be lessened by adjusting for each species the cutoff value used to delineate mineralizd ground. Information accumulated by Fraelich and Kleinhampl (in preparation) on the average contents of uranim coniferous species on Elk Ridge, Utah, is shown in Table 1.

TABLE 1

URANIUM CONTENT OF TREES SAMPLED ON ELK RIDGE, UTAH

Species	Percent Ash	Average U in ash barren ground (ppm)	Average U in ash mineralized (ppm)
Juniper	4.7	0 33	1.74
Pinyon	2.8	0.56	1.31
Fir	3.4	0.35	2.18
Ponderosa pine	2.6	0.63	1.28

The depth to wich roots of various species penetrate is important in botanical prospecting. In many areas of the Colorado Plateau the ore-bearing bed is also a water-bearing horizon and the roots of desert trees and shrubs penetrate long distances through cracks and crevices to reach this source of moisture. Generally plant analysis is an effective tool in delineating mineralized ground at depths as much as 70 feet beneath the ground surface.

In a flat country having a uniform forest cover, systematic sampling at intervals of 100 to 200 feet is recommended. The end branch sample may be shipped to a central laboratory for analysis or analyzed by a field test at a field base camp.

A fluorimetric method of analysis (Grimaldi, May, Fletcher, and Titcomb, 1952) was used for the determination of uranium in the plant ash in most of our evaluation studies. Both the collection of smaples and analysis in the laboratory by this method are costly.

PROSPECTING BY INDICATOR PLANTS

Mapping the distribution of herbaceous plants that are more abundant in the vicinity of uranium deposits is a second method of prospecting on the Plateau. The plants that are used as indicators of uranium ore are actually controlled by the increased availability of selenium, sulfur, or some one of the major plant nutrients. They are common weeds, but weeds that bear watcking an area considered to be favorable for finding ore. In addition to ecologic field studies in some 10 districts, many of these plants were grown in experimental plots and differences in tolerance and preference were recorded.

In each new area, that species is used as an indicator whose distribution correlates best with mineralized ground. In general, the most useful plants are selenium indicator species of deep tap root habit. The most important group of selenium-absorbers falls in the genus *Astragalus* belonging to the vetch family. The species *Astragalus pattersoni* is the most realiable indicator of uranium ore in the Colorado Plateau. This indicator is an efficient concentrator of molybdenum and selenium both of which are toxic in large quantities to sheep and cattle. In plot experiments, more than 11,00 ppm of selenium was found in the ash of plants collected from soil containing only 30 ppm. We found also that the addition of carnotite doubled the absorption of selenium, and the addition of selenium tripled the absorption of uranium. *Astragalus pattersoni* acts as an indicator of carnotite deposits containing as little as 1 ppm Se. *Astragalus preussi*, a closely related form with purple flowers, is also useful in prospecting, but appears to have a more restricted range. Several other species are indicative of deposits of lower selenium content. *Aster venustus*, a selenium bearing woody aster with daisy-like heads, i scommon on alluvium and wash down slope from uranium deposits. *Stanleya pinnata* (Prince's Plume), which requires both sulfur and selenium, is common on the Plateau but has not been useful in pinpointing the location of uranium deposits; we included this plant in our plot experiments to determine the cause of this variance. *Stanleya* grew to magnificent maturity in the selenium plot, but growth and the absorption of selen-

ium were restricted by the addition of carnotite. In addition, the spikes produced only imperfect flowers with no petals or stamena and greatly enlarged sepals. To determine whether this phenomenon was due to irradiation, normal *Stanleya* plants were "fertilized" with thorium ore. In a few weeks time imperfect apetalous flowers began to appear. This suggests that *Stanleya* is not able to perpetuate itself in irradiated soil. Its reaction to soils of high carnotite content and its sensitiveness to irradiation, explain the peculiar distribution of the species in many districts and why the plant can be used as a selenium and sulfur tracer downstream from deposits, but is not a plant to be used in drilling for ore.

Many uranium ores contain sulfides that weather to gypsum above the water table. Sulfur —and calcium— absorbing annuals may act as indicators where the gypsum moves upward into the surface soils.

Lepidium, and other plants of the mustard family are excellent indicators of uranium ores of high gypsum content. The family is capable of absorbing large amounts of sulfur, calcium, and sodium and thus is well adapted to life in an alkaline desert environment. *Descurainia* ranked first among the experimental plants in uranium and vanadium absorption.

Plants of the lily family are also indicative of high gypsum soils. The Sego lily and wild onion are the most useful indicator plants of this group.

No one calcium or sulfur indicator plant should be considered to be indicative of mineralized ground, as many of the plants are common roadside weeds A dense population of several of these genera is, however, commonly indicative of the soluble salts leaching from a uranium deposit.

Indicator plant prospecting is rapid. inexpensive, and therefore preferred over prospecting by plant analysis if the area is in the proper ecologic zone to permit unobstructed development of the plant association.

EVALUATION OF METHODS

Botanical prospecting studies have been made in 10 districts of the Colorado Plateau and mineralized ground has been located both by plant analysis and indicator plant techniques. Prospecting by indicator plants was tested in Grand County, Utah, where 1660 holes were drilled on a grid pattern in an area of 6 square miles after the distribution of plants had been carefully mapped. The holes ranged in depth from 10 to 250 feet. The plant distribution data was correct in delineating barren and mineralized ground at 81 percent of the drill sites. Five ore-bodies were found solely because of the plant data in areas not tested by the random drilling pattern. One of these is shown in Figure 1. Indicator plants were found to reflect mineralized ground to an average depth

of 68 feet. *Astragalus pattersoni* was the most efficient indicator plant in the district and has proved to be the most dependable species in all districts of the Plateau where indicator plants occur. Gypsum plants are useful where the water table is very near the sur face and the ore is not more than 35 feet in depth.

Prospecting by plant analysis has been tested in several districts and nearly 11,000 samples have been collected (Table 2). Over 60 anomalous areas were located on Elk Ridge, Utah, and of the anomalies that hace been tested by drilling, more than 80 percent have indicated mineralized ground. The conifers sampled were effective in indicating ore as much as 70 feet in depth.

TABLE 2

EXTENT OF SURVEY TREE SAMPLING PROGRAM

Localites	No. of tree samples analyzed
Grants, New Mexico	4000
Elk Ridge, Utah	4100
San Rafael, Utah	700
Gateway, Colorado	600
Carrizo Mtns., Arizona	500
Thompson, Utah	400
La Ventana, New Mexico	200
Meeker, Colorado	200
Circle Cliffs, Utah	100
	10,800

SUMMARY

The use of botanical prospecting is recommended in advance of exploration for uraniferous deposits in sedimentary rocks. In open country where the uranium ores average from .001 to 0.01 percent selenium and lie at an average depth of 40 feet or less, the more inexpensive method of indicator plant mapping may be advantageous. *Astragalus pattersoni* is a most reliable indicator of uranium ore. Where the tree cover is continuous and the ores lies at a depth of 70 feet or less, prospecting by tree sampling on a grid pattern may be useful.

ON PEAT-CHEMICAL PROSPECTING IN FINLAND

M. SALMI *

ABSTRACT

To clarifiy the practicability of the peat-chemical prospecting methods, various ore occurrences covered by bogs were investigated. Research was carried out on materials containing vanadium-bearing titanic iron ore, antimonite, molybdenite, and zinc-copper-lead ore. The metal content of the peat ash was spectrographically determined in the first three cases, and of the plant ash in the last.

INTRODUCTION

The author started the development of his peat-chemical prospecting method in Finland and published investigations (Salmi, 1950) on trace elements in peats in general and later on (Salmi, 1955, 1956) detailed investigations concerning the Otanmäki and Vihanti ore field. Part of the latter will be presented in this paper. Thus far the author has dealt with more than ten points of investigation, four of wich will be trated here.

Investigations were performed in some areas where the location of the ores was already known. As an example research work in the Otanmäki iron ore field will be presented. On the other hand, peat-chemical investigations were performed in such areas where prospecting was simultaneously carried on by other methods. Two cases will be described, the antimonite occurence of Seinäjoki and the molybdenite of Rautio. The last investigation presented here was done in the zinc-copper-lead ore area of Vihanti. It enables us to make comparisons with the occurrences of metals in peat and in bog plants.

Investigations were carried out in collaboration with the prospecting department of the Geological Survey and various ore prospecting companies. At least three prospecting companies have adopted the peat chemical prospecting method using it independent in addtion to their other methods.

The materials of Otanmäki and Rautio were analyzed spectrographically at the laboratory of the Valmet Co. in Jyväskylä, that of Seinäjoki at the laboratory

* *Geological Survey of Finland, Helsinki.*

of the Geological Survey and the Vihanti material at the laboratory of the Technical Institute of Helsinki.

THE TITANIC IRON ORE OF OTANMÄKI

There are several smaller ore bodies besides the main one at the Otanmäki iron ore field. Some of them are studied in detail, like the occurrence at Malmisuo. Its location under the bog provides an appropriate impetus for peat-chemical investigation. Magnetic measurements and drilling were carried out earlier at the site, and the location of the occurrence was thus precisely known.

The sample line (Fig. 1) was placed on the bog parallel to the drill hole R 57. Its total length is 250 m. The bog lies on a slope, whose inclination from the left is 3 m for the first 100 metres and 4.5 m for the whole line of investigation.

In the lower part of figure 1 the bedrock is shown with the various rock types and ores. The best ore is exposed at the 60 m site and consists of compact ore. The corresponding ore in the mining area contains, according to Vaasjoki (1947), 18.85 percent TiO_2 and 0.42 percent V_2O_3. The locations of the ores are clearly shown by the peaks in the magnetic curve over the best ore outcrops.

Quaternary deposits total 4-7 m along the line of investigation. Above the rock there is first till and then shore sand. Bith are mixed deposits. Peat lies uppermost in layers 0.4-2.0 m thick.

The geology is well known at the investigation site, and the sample sites were placed alternately above ores and barren rock. In this way it was possible to test how precisely the location of the ores could be determined from the peat layer. The spacing between the sites was 5-50 m horizontally, being most dense above the ore zone, and 10-30 cm vertically.

The iron, titanium, and vanadium content of the peat ash over the Otanmäki ore is shown in Figure 1. Iron is given in percent; titanium and vanadium in ppm.

The vanadium content is highest in the profile at the 60 m site, i.e., above the best exposure of the ore. Here in some samples the content is 1,200-5,000 ppm. The solid black area on the figure represents the location of the highest vanadium content. From there the vanadium contents decrease gradually horizontally and vertically to an average of probably less than 200 ppm. To the left of the locality mentioned before, there is another anomalous vanadium occurrence in the peat layers. This is smaller than the former, reflecting the small lensed ore bodies below it. Between these occurrences the peat is quite poor

in vanadium. At the same site the bedrock consists of an amphibolite, and there is a steep decline in the magnetic curve.

The occurrence of titanium in the peat resembles that of vanadium. High contents exist at the 60 m point, even 3,100-5,100 ppm. Nearly as strong an anomaly occurs at the 40 m point, and further to the left of it in the profile, the amount of titanium is above average. The titanium seems to have moved downward along the slope in the peat layers from above the ore at the 10-30 m points to the 40 m point, where no ore exists. An increased titanium content generally occurs in the lower peat layers, especially above the granite. As other investigations show no corresponding increase in titanium content above the granites, the phenomenon must here be considered as a secondary. In all probability titanium-bearing shore sand was washed down along the slope at the time that an ancient shore line existed at the level of Malmisuo. Most abundantly it accumulated on the benches of the slope, where it appears as a strong titanium anomaly. The titanium occurrence in the peat layers differs from that above the ores, where high contents that form individual peaks in the profile occur in many samples along the same vertical line.

The iron content is high compared with the former metals. Its occurrence shows an interesting agreement with the ore body underneath the bog. The solid black area on the figure represents the highest iron content (more than 20 percent) and lies horizontally in the middle part of the profile. It is significant that the left side of this area coincides with the best outcrop. From there it continues down the slope and merges with the surface of the bog at its steepest point. The iron content decreases gradually to background, which must be estimated to be less than 10 percent here. The second outcrop of the ore along the line of sampling causes a separate area of increased iron content in the peat layers that is situated on the left side of the profile. It is much smaller than the other. This area has likewise moved down the slope. Between these peaks a zone poor in iron reveals the amphibolite in the bedrock, as was clearly seen in the case of vanadium.

The occurrence of titanium and vanadium resemble each other in that the highest contents never extend to the surface of the bog even above the best exposure of the ore. The content of the surface samples is fairly close to background. On the contrary, the iron content is at its highest in the surface samples, and the values are rather low in the bottom samples, even directly above the ore body.

Two more localities have been investigated in the Otanmäki ore district by chemical analyses of peat samples. The results obtained correspond to those mentioned (Salmi, 1955).

THE ANTIMONITE OF SEINÄJOKI

The occurrence of antimonite in bedrock in Seinäjoki facilitated the study of the behavior of antimony in peat. The bedrock is covered by till 0.5-1 m thick overlain by 75 cm of peat. A stretch of bog about 20 m broad lies along a small brook.

Samples were taken of the peat at three points, which were spaced 5 meters from each other and situated on a line crosswise to the river bed. Point 1 in Table 1 is furthest from the brook. About 10 m from it is an outcrop containing antimonite. Diamond drilling performed later and directed below the stretch of bog, showed antimonite only at that locality. All sampling sites are at 10-20 m from the antimony-bearing rock and at the foot of a steeply inclined slope.

TABLE I

RESULTS FROM THE INVESTIGATED LOCALITIES AT SEINÄJOKI

Sample site	Depth in cm	Ash (percent)	Element in ppm					
			Sb	Pb	Ag	Ni	Zn	Cu
	0–25	61.48	600	20	170	30	1300	—
1	25–50	34.55	1500	50	40	30	—	—
	50–75	76.28	300	10	5	20	—	—
	0–25	27.59	2500	60	30	100	—	—
2	25–50	30.78	4000	30	30	50	—	—
	50–75	35.06	4000	50	60	100	—	—
	0–25	25.03	4000	150	250	100	600	2000
3	25–50	28.28	4500	70	60	50	—	—
	50–75	38.90	1500	10	30	100	—	—
	0–10	2.89	—	700	120	10	2500	800
4	10–25	6.69	—	700	120	80	1000	—
	0–20	2.31	—	1000	500	250	2500	1800
5	20–40	1.43	—	500	40	400	500	400
	40–60	4.75	—	350	20	200	200	400
	0–20	1.60	—	600	80	60	3000	800
6	20–40	1.38	—	600	70	200	1500	500

The metal content of peat samples from sites 1-3, which are from the vicinity of the antimonite occurrence, are shown in Table 1. For the sake of comparison, peat samples were also taken about 1 Km from the occurrences, sites 4-6. The sites 4-6 belong to the same zone of magnetic anomalies, and they form a line across the anomalous zone. No diamond drilling was performed at that locality. The above analyses justify the conclusion that no antimony exists there. The

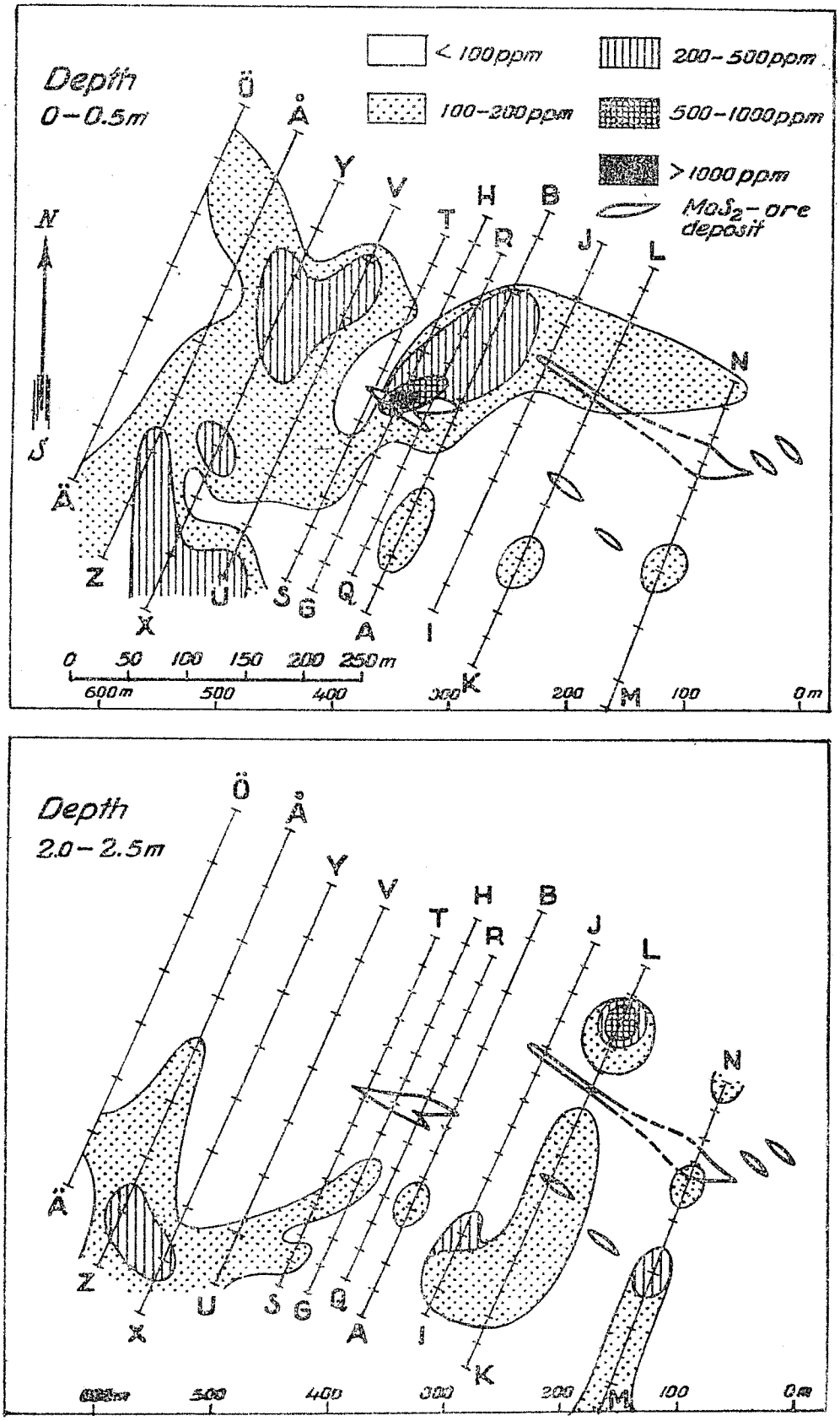

Fig. 2. Sampling net from the Susineva bog in Rautio.

somewhat high contents of zinc, copper, and silver indicate that black schists may possibly cause the anomalies. Graphite schist, not studied there earlier, might also be considered.

The influence of antimonite in the bedrock is clearly revealed in the high antimony content of samples at points 1-3. There is more antimony than any other element analyzed, and the results are high.

THE MOLYBDENITE OF RAUTIO

In collaboration with Suomen Malmi Co. the occurrence of molybdenum in peat layers was investigated at the Susineva bog in Rautio. Blocks rich in molybdenite were found, especially at the southeast border of the bog. Bearing in mind the transportation by the continental ice and its direction, these blocks were assumed to originate from below the bog nearby. Geophysical measurements on the bog and its surroundings did not indicate the occurrence of molybdenite, as did, on the other hand, the drilling. By means of drilling a deposit, 200 m in length and in places quite narrow and broken, it was ascertained to lie under the bog. Its position is marked near the eastern border of the maps in Fig. 2.

While the Suomen Malmi Co. was carrying on the drilling, the author was requested to investigate the peat in the Susineva district in order to find possible new occurrences of molybdenite. Samples were taken from the bog during three different periods of the years 1954-55 along the lines shown in Fig. 2. The peat layers are mostly 2-3 m thick. Underneath is mostly till. The samples were taken at 0.5 m apart vertically. In addition to molybdenum some other elements were tested, but they are not to be presented at this time. The molybdenum content in peat ashes varies greatly in various samples. The lowest content is less than 10 ppm and the highest one exceeds 2,000 ppm. The background could be estimated to be below 100 ppm. It is an interesting phenomenon that the molybdenum content is smaller in the lower samples than in the surface samples of the bog. This feature is striking where the molybdenum content exceeds background. This is clearly shown in Fig. 2, where the molybdenum content of the samples is presented. Separate maps are drawn for the surface layer to a depth of 0.5 m, and for the depths between 2 and 2.5 m.

The high molybdenum content (exceeding 2,000 ppm) in a surface sample from the sample line GH was noted. The surface samples around it were also above background as shown on the upper map (Fig. 2). Diamond drilling was performed along this line to clarify the source of molybdenum in the peat.

Fig. 3 shows the geologic conditions at the drilling site. The surface sample at the 175 m site has a high molybdenum content. To the side and downward

the values decrease. Above the bedrock there is about 4 m of till, which is overlain by 3 m of peat. Two drill holes were drilled parallel to the line GH. They revealed the bedrock geology of the area. The drill holes are shown schematically in Fig. 3, according to the data given by the Suomen Malmi Co., and revealed molybdenite as an impregnate and as compact lumps, as was

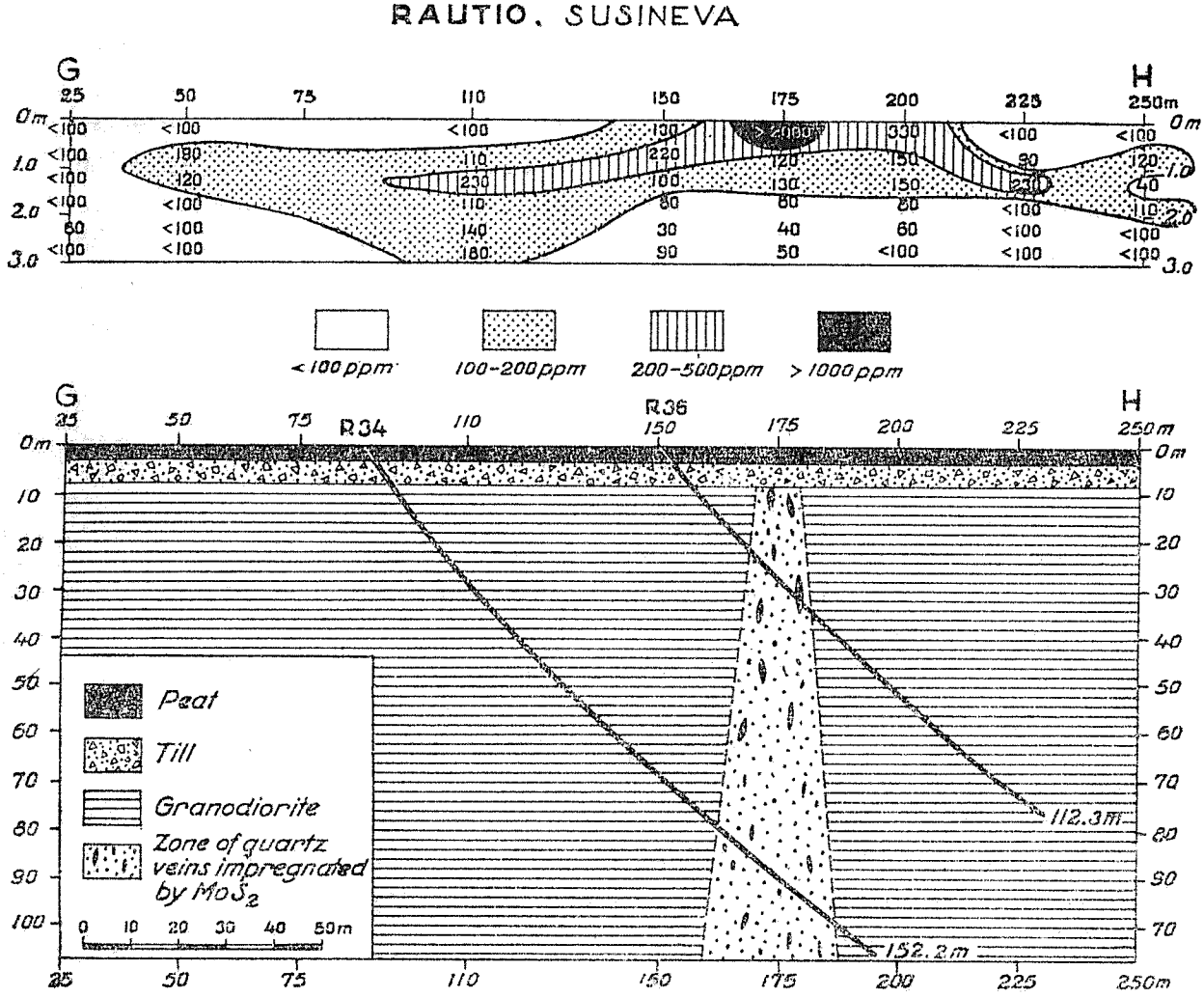

Fig. 3. The line of investigation from the Susineva bog in Rautio.

confirmed by the aid of the latter hole. By means of this and other drilling in the vicinity, a quartz zone could be defined. It is of greatest interest from the present point of view to note that it reaches the surface of the bedrock as an outcrop, and is situated on the line GH exactly at the same place where the surface samples of the peat showed an exceptionally high content of molyb-

denum. Thus a new molybdenite ore body was found in the bog area by means of peat-chemical prospecting. According to the drill cores analyzed from the quartz zone, the average molybdenum content is 0.02 percent.

Fig. 2 shows all the ore bodies confirmed by drilling. They are marked on the detailed maps. The one found by the peat-chemical prospecting lies approximately in the middle of the map, the others are eastward from it. It may be noted that a narrow, elongate and broken ore body was also detected by peat investigations. Only two sampling sites occur in this area, and it is evident that none of them hit the broken ore body, leaving it thus undiscovered.

The middle ore body seems to have spread molydbenum into the sorrounding area. This can be seen most distinctly toward the northeast and east. The natural explanation of it is the surface slope of the bog. Directly above the ore body and around it no sign of outstanding molybdenum content exists in the bottom samples of the bog. Westward from the ore body, near the north end of the sample lines UV and XY the surface samples show remarkably high molybdenum content. Its source has not been discovered by drilling, but is probably due to the molybdenite content of the underlying bedrock. It lies along the same line with the ore bodies southeast of it. The anomalous molybdenum content found at the south ends of UV and XY are also caused by the underlying bedrock, as was shown by drilling.

Molybdenum differs from titanium and vanadium in that the highest amounts of molybdenum are found at the surface of the bog, whereas the highest amounts of titanium and vanadium occur in the bottom layers of the peat. Molybdenum and iron are alike in this respect.

THE SPHALERITE OF VIHANTI

In the Lampinsaari area of the parish of Vihanti the Outokumpu Co. has mined zinc-copper-lead ore since 1954. Before that various investigations were carried out in the area where the mining began (Hyyppä, 1948; Isokangas, 1954). In 1950 and 1951 when the author collected peat and plant samples from the Vihanti area for his chemical research work, the area had already been generally investigated. Yet it was not until a later date that the Outokumpu Co. found the main ore body being mined at the present time in the western part of the area. Before this discovery the results of the investigation by the author seemed contradictory (Salmi, 1956).

As bog is scarce in the area and appears in thin layers only, *Ledum palustre* leaves and twigs were collected at every sampling site to be examined and compared with the results obtained from the peat. For this reason the results of the investigation along only one sample line, which crosses the ore district

from east to west, are presented. This line is 2,400 m long and comprises peat and till deposits (Fig. 4). The thickness of the soil totals 1-10 m, and decreases to the west.

The known ore bodies of the area lie on the sampling line approximately between the 1,700 m an 2,700 m sites. The surface along this part of the line consists of till, covered in places by thin layers of peat. A zinc ore body, situated between the 2,300 and 2,500 m sites, is mined at present. It is not known to reach the surface of the bedrock (Isokangas, 1954). It also contains some copper and lead. East of it several small zinc ore bodies crop out on both sides of the line of sampling around the 1,700 m — 2,000 m sites. Pyrite, the other ore of the area, is seen in numerous outcrops along the line or in its immediate vicinity around the 2,000 m — 2,700 m sites. These outcrops also contain copper.

The copper, zinc, and lead contents of the samples investigated are presented in Fig. 4 as ppm in the ash. Each element is presented twice, on top there is the bog profile with peat analyses, and below are the results of analyses of leaf and twig samples of *Ledum palustre*.

Attention is arrested first by the western part of the area where ore is known to exist. It can be noted that the copper and zinc contents are so low in the thin peat layers, that they are not able to indicate a neighboring ore. Lead contents are slightly above background, 300-600 ppm.

On the contrary, the leaf and twig samples of *Ledum palustre* show contents of quite another order of magnitude. The copper content of leaf samples, with one exception, is 1,000 ppm, and of twig samples near the best ore, up to 3,000 ppm. Both stand out distinctly from background. The zinc content of the leaf and twig samples exceeds background at the zinc occurrences. The highest values are 1,000-3,000 ppm. Likewise the lead content above the best ore body, and that of one twig sample from the middle of the line of sampling are above normal, both being 300 ppm. Here the nearness of the ore body is indicated by plant samples whereas the thin and watery peat layers do not give any indication of the ore body.

Strikingly high metal contents occur along the eastern part of the line of sampling where the peat cover is thickest. No ores are now known to exist there. It is true, however, that the site has not been thoroughly investigated. The high copper content, 1,000-3,000 ppm, from the bottom to the surface samples of the peat, especially deserves attention on both sides of the 1,000 m site. At the same place the twig samples contain 1,000 ppm copper, but the leaves much less. The corresponding peat layer is deficient in zinc, but at the 1,000 m site the content of leaf and twig samples, 3,000 ppm and 6,000 ppm, respective-

ly, are exceptionally high. In general, twigs contained more zinc than the leaves from corresponding sampling sites. The lead content, 600 ppm, appears at the 1,000 m site both in surface peat and in twig samples. It differs clearly from the lead content of the other samples along the eastern part of the line. Here, as is the case at most sites along the line of sampling, the twigs seem to gather more lead than the leaves.

On the basis of what has been presented above on the result of peat chemical prospecting, it seems apparent that in the present case the high copper, zinc, and lead contents of the peat, leaf and twig samples refer to the occurrence of these elements in abnormal amounts with respect to normal background in the underlying rock. Similar results were obtained from the 100 m and 200 m sampling sites, respectively, to the south and east from the aforementioned site. Thus these elements would seem to occur in a rather large area. The question whether they would be of economic importance could be solved by means of diamond drilling.

CONCLUSION

The chief importance of the investigations presented here is that the elements of the ore minerals in the bedrock occur in greatest abundance in the overlying peat layers above the ore bodies. This takes place in spite of the covering layers of till, several meters in thickness and transported to the site by the continental ice from other areas; or of shore sand, mixed by water; or of clay sediment, once deposited in water; and of peat situated above these deposits. This phenomenon occurs almost undisturbed even in tilted bogs.

It can be concluded from the succession of loose deposits in the cases presented here that transportation of metal ions must have taken place from the bedrock and its ore deposits through the soil after the bog was formed at the site. The author (Salmi, 1955) has discussed the question earlier in more detail and came to the conclusion that the formation of the bog was the factor which enabled penetration of the metals from the bedrock to the surface of the soil. The entire soil layer is then saturated by water, and the metal ions can move upward, mainly due to capillarity. The suction of the plant roots of the living vegetation on the surface of the bog is apt to accelerate this movement, and above all, the strong evaporation at the surface of the bog during the season of growth will accelerate the movement. In Finland the period June-August exceeds many times the corresponding rainfall of the rest of the months, as was stated by Homén (1917) in his investigation. The absence of water in the surface layers of the bog strives to be supplied by the water from the lower layers, thus there is a constant flow from below upwards.

The fact that the main occurrence of different elements takes place in different parts of the peat layers is due to their varying ability to react to the humic acids. Titanium and vanadium seem to gather by the influence of humic matters in anaerobic conditions in the bog, as they are most frequently found in the lower parts of the bog. Molybdenum, as well as lead, iron, and apparently zinc, on the contrary accumulate first in the aerobic conditions, thus ocurring most abundantly in the surface of the bog. They are easily transported by the surface waters of the bog and spread, according to the sloping of the bog, perhaps widely around the source. Copper and antimony are found to be rather evenly distributed in the peat layer; they apparently react with the humic matters both in aerobic and anaerobic conditions. Such elements, and above all, those found mainly in the surface parts of the bog are most easily reached by the roots of bog plants. Thus their abundance in the plants of bogs with thick peat layers is easily explained and therefore, bog plants are adaptable for prospecting for some ores. The case of Vihanti shows that the twigs of *Ledum palustre* concentrate copper, zinc and lead more abundantly than its leaves, and with the best results where the peat layer is thick.

The cases described above are markedly clear examples of peat chemical prospecting and as such are apt to give too optimistic an impression of the usefulness of the method. The examples were chosen for the purpose of elucidating the method. It must be borne in mind that disturbing factors always occur in nature. One appeared in connection with the Vihanti investigation. It was stated there that the thin and wet peat layer, in spite of the closeness of the ore, did not contain ores above background amount of metal. Bog plants gave better results. It has been proved that peat layers 1-3 m in thickness are best for peat-chemical prospecting.

The method excels when searching for ores which do not cause any geophysical anomalies. A preliminary investigation of rather large bog areas can be made with a coarse sampling net. Large barren areas might be eliminated and favorable sites can be searched more throughly before diamond drilling is started. The advantage of the method is that, at least in favorable cases, ore deposits covered by bog can be located fairly accurately, even in the areas once covered by the continental ice sheet.

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PATHFINDING ELEMENTS IN GEOCHEMICAL PROSPECTING

H. V. WARREN * and R. E. DELAVAUT *

ABSTRACT

Experience in searching for hidden mineralization has shown that important deposits may, on the surface at least, be betrayed only by comparatively modest anomalies, which indeed can be so inconspicuous that their recognition in the field becomes economically impractical.

The sensitivity of geochemical methods may be much increased if, instead of searching for the halo of such elements as copper or zinc whose natural backgrounds are relatively high, one investigates the halo of some other element with which the copper or zinc may be associated. The other element which is selected should have either a much lower-background, and hence provide a more conspicuous anomaly, or alternately by its manner of occurrence offer greater simplicity either in sampling or in analyzing. Such an element is termed a "pathfinder".

A porphyry copper, unless covered by a shallow residual soil, may provide only a weak anomaly. However, molybdenum usually is associated with porphyry copper deposits and, normally being more soluble and present in the earth's crust in smaller amounts than copper, it is apt to provide larger and more obvious anomalies.

The U. S. Geological Survey has provided an excellent example of the use of a pathfinder in an area where it was found expedient to search for cobalt by means of associated arsenic.

In biogeochemical or hydrogeochemical prospecting, epithermal gold or silver deposits may be sought by means of associated manganese or zinc.

THE PROBLEM

Geochemical prospecting consists of attempting to detect by one or more techniques, appropriate to a particular set of conditions, anomalous amounts of some element. Geochemical prospecting falls into two phases, searching for an anomalous locality, and attempting to determine the cause and source of an anomaly: any technique which will aid either of the above phases is obviously of interest to those engaged in searching for hidden ore bodies. Anomalies are part and parcel of the haloes which are associated with ore bodies. Haloes may be classified as either genetic or dispersion. Pathfinder

* *University of British Columbia, Canada.*

elements may be defined as elements which, because of some particular property or properties, provide anomalies, or haloes, more readily usable than the sought-after element with which they are associated. This paper describes some examples of the successful use of pathfinders.

SEARCHING FOR AN ANOMALOUS LOCALITY

Today one seldom embarks on geochemical exploration without first of all selecting, on the basis of acceptable geological theories, an area considered to be favourable for the discovery of some particular metal. A careful examination of air photographs is made to learn something of the nature of the vegetation and overburden in the area in which exploration is planned, and to ascertain the nature of its drainage pattern. It may be easy to find an anomalous area if rusty outcrops are available. A mineralized area by its chemical or physical weathering may betray its presence by easily detected evidence in downstream water or silt. However, where the going is difficult, outcrops scarce, and no evidence of mineralization is visible to the eye, it may well be that only a systematic search will provide better than a gamblers chance of finding evidence of some dispersion halo.

It may usually be assumed, even in the general exploration of a new area, that there is some idea of the type of mineralization which may be expected. The geochemist is immediately faced with one pertinent problem. Is the metal being sought susceptible to being spread far enough from its source and in sufficient quantities, to justify direct geochemical search? Will normal variations in the background of the area render any geochemical method abortive? Some elements, such as lead and columbium, travel but little; others, such as manganese and iron, are so abundant everywhere that variations caused by geochemical dispersion haloes can be observed merely by local variations in the normal background: this latter condition applies equally well to plants, soils, or waters where they are used as prospecting media.

In order to have the best chance of discovering a halo in some new area it may be wise to base investigation, not on the element which is the actual object of the search, but on some other element which stands a better chance of being detected at a distance. A good illustration of the use of this principle is provided in the Coast Range Mountains of British Columbia.

Here at one well known mine, the Britannia, copper is known to be associated with varying amounts of zinc. In general the area has a high rainfall and natural stream waters are usually further diluted by melting snow. Sphalerite and chalcopyrite are the two minerals of particular interest at Britannia and the former is much more easily attacked by acid waters than the latter.

In ascending a creek below mineralization in the mine area zinc is detectable long before copper. Indeed, in many cases copper can only be detected a few hundred yards below mineralization whereas zinc, although in some ores present in amounts of only one tenth that of the copper, may appear in the water at five to ten times that distance. Taking advantage of this fact water testing for zinc has been responsible for the discovery of some new copper bearing mineral occurrences. In this example we would speak of zinc being used as a pathfinder element for copper.

SEARCHING FOR OREBODIES IN AN ANOMALOUS AREA

Our experience suggests that the discovery of an anomalous area is a relatively modest part of the problem of finding an ore body. Once an anomaly has been found there remains the task of discovering the source of the anomaly and deciding on actual drilling sites. This task may prove to be exceedingly difficult.

An anomaly may extend over a large areas, possibly several square miles, and this area would be far too large to attempt systematically to drill it. In such a case it may be wise to make use of some pathfinder element, either because the chemistry of the pathfinder is such that it allows the use of simpler field techniques than would otherwise be possible, or because the geochemistry of the area is such that the pathfinder element provides a better contrast between areas of commercial mineralization and the general background. One other condition which calls for the use of a pathfinder occurs where one is dealing with such elements as lead, silver, or columbium. These elements tend to travel little and could easily be missed in any search which involved sampling on a widely spaced grid system. In the case of silver and lead it is usually possible to use zinc in exploratory work, turning to lead and silver only in the final stages of the search. In some areas it is not necessary ever to turn to the element which is sought: the pathfinder leads to a geological feature which provides the obvious place to drill.

It may be well to remember that neither the central nor the strongest part of an anomaly may overlie the strongest mineralization. Both Russian (Sergeev, 1941) and United States (Hawkes, 1951) geochemists have pointed out what now seems obvious, namely that many anomalies lie below their original source largely because of the effects of gravity.

In the fulness of time it may be possible, by making a series of simple determinations on a small number of pathfinder elements, to assess the mineral possibilities of an area where little geological data are available. Then it might be practical to eliminate large areas from further exploration. Unfortunately

the present state of our geochemical knowledge is such that, to us at least, it seems prudent to restrict our use of pathfinder elements to a few well known associations examples of which follow. Doubtless other examples will be forthcoming just as soon as other workers make their knowledge available.

MOLYBDENUM AS A PATHFINDER FOR "PORPHYRY" COPPER

When preliminary studies of the biogeochemistry of molybdenum were being made we found that some species of trees and lesser plants effectively reflected anomalous contents of molybdenum in some soils. Furthermore, we noted that the normal molybdenum content of soils frequently was only one one-hundredth to one four-hundredth that of the copper in the same soil. The fact that the porphyry coppers usually contain small amounts of molybdenum immediately suggested the possibilities inherent in using molybdenum as a pathfinder for copper. Fortunately we had, through the kindness of Mr. J. S. Scott and the officials of Kennco Explorations (Canada) Ltd. excellent suites of samples both from an operating "Porphyry" copper mine in New Mexico and from an undeveloped prospect in British Columbia. Biogeochemical studies of suites of trees and lesser plants from these two areas provided much useful information. In general, anomalous vegetation from New Mexico contained from six to eight times the copper and molybdenum content of normal samples. However, because of much lower background of molybdenum in vegetation, relative to copper, it is usually much easier to spot anomalous molybdenum in vegetation than it is to discover anomalous copper.

Honesty compels us to admit that some pitfalls do exist. Molybdenum is selectively accumulated by some trees and lesser plants, such as alders, lupins, and probably some pines. Molydenum is mobilized and made more easily absorbable by phosphorous in some forms. Small and uneconomic occurrences of molybdenum may occur near "porphyry" copper deposits. All of these facts should be taken into account by any geochemist.

After taking all the above factors into account it still seems that a "porphyry" copper may be more easily "run to earth" by using molybdenum rather than copper in geochemical studies. Possibly this is because, except in some favourable circumstances, copper does not weather as readily as molybdenum and consequently does not tend to give such easily recognizable haloes.

Finally molybdenum provides one other use as a pathfinder for copper. In some areas there is a halo of molybdenum, partly genetic and partly dispersive, outside at least one section of the copper mineralization. This molybdenum halo, in some areas at least, can easily be detected over the regional background, and this, in effect, may appreciably enlarge the target area. This

molybdenum halo is probably caused by molybdenum being more soluble than copper under both hydrothermal and weathering conditions.

ARSENIC AS A PATHFINDER FOR COBALT

In nature cobalt normally occurs in very small amounts, whether in rocks, soils, or vegetal matter. Even in ores its normal occurrence is such that, without using very refined methods, its geochemical halo is apt to be too low to be readily detectible.

In the Blackbird District of Central Idaho the U. S. Geological Survey (Lovering, 1955) has found it convenient to detect cobalt, not directly, but by the arsenic which in this area is closely associated with it.

In soil arsenic migrates less easily than cobalt. Arsenic is, therefore, more likely to pinpoint a mineralized area. In the above area the maximum cobalt content of the soil is 300 ppm, or ten times background: the arsenic content of the soil is 1000 ppm, or one hundred times the background. Furthermore with suitable apparatus it is easier and safer to look for small amounts of arsenic then for the same amount of cobalt, if they are mixed with all possible elements in a soil.

MANGANESE AND ZINC AS PATHFINDERS FOR GOLD AND SILVER

Although the gold pan probably remains one of the best tools in prospecting for gold there are localities where it may not be as efficient as some geochemical technique. Where gold occurs largely as a telluride, panning below and even close to, the outcrop may not be effective. In such circumstances the fact that manganese is commonly associated with epithermal gold deposits and zinc, albeit in modest amounts, with both gold and silver deposits, may be used to advantage. Manganese and zinc can readily be detected in both soils, stream silts, and in vegetal matter. In view of the present economic position of gold the use of manganese and zinc as pathfinder elements is likely to be useful only for silver; however, times may change.

OTHER PATHFINDER POSSIBILITIES

The few examples of pathfinders mentioned above are far from being exhaustive. It is to be expected that in the near future more will be found and described. As our fundamental knowledge and practical experience expands we should find more and more use for pathfinder techniques. Such associations as gallium in bauxite and cadmium in zinc point to obvious new fields for fruitful investigation. In the latter case we ourselves have found, by spectro-

graphic methods, much more cadmium in the ash of trees in some zinc areas where cadmium is conspicuous. The background cadmium content of vegetal matter appears to be relatively low and anomalies relatively easy to spot. Possibly cadmium could be used in the search for zinc.

CONCLUSIONS

Pathfinder techniques can be useful in searching for ore. As our knowledge of geochemistry grows we may anticipate further applications of this technique.

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ГЕОХИМИЯ ВРОМА В ПРОЦЕССАХ ГАЛОГЕНЕЗА И ИСПОЛЬЗОВАНИЕ СОДЕРЖАНИЯ ВРОМА В КАЧЕСТВЕ ГЕНЕТИЧЕСКОГО И ПОИСКОВОГО КРИТЕРИЯ

М. Г. Валяшко

ABSTRACT

During the halogenation process, bromine does not give independent minerals but precipitates with chlorides as an isomorphous mixture. This distinguishes bromine from other components.

The bromide-ion content in solid chloride is determined by its nature and by the bromide-ion content in the solution. During simultaneous crystallization of two or more chlorides, the bromide-ion is distributed between them in agreement with the distribution coefficient. The most probable values of the distribution coefficient are 0.037 for halite, 0.20 for sylvite, 0.32 for carnallite, and 0.47 for bischofite. The normal bromide content of halite, sylvite, carnallite, and bischofite at various stages in the condensation of ocean waters has been computed from the distribution coefficients and the bromide-ion content of the ocean water at each stage. The computed data provides scales of normal bromine content (rather its relation to chlorine) for the individual chloride minerals crystallizing from the ocean. Such scales have been determined for rocks, too.

By the means of these scales it is possible a) to determine the stratigraphic position of the "mutue" habite rocks, b) to determine the probability of the existence of postassium salt ratios at a given place among halites, and c) to determine the existence of redeposition processes in the history of a given deposit.

The analysis of a large amount of material for the bromine content in deposits of various salts from all geological periods has shown that a) the value of the B:Cl ratio in the ocean water has practically not changed during geological time; b) there are many processes in the nature which decrease this ratio, but there are nearly no processes which increase it; c) it has been shown that a number of salt deposits were redeposited; and d) the possibility of an existence of potassius salts confirmed by boring, has been predicted.

ВВЕДЕНИЕ

Среди элементов, составляющих соляную массу океанической воды, бром занимает особое место. В отличие от других компонентов, порою содержащихся даже в меньших количествах (например, бор), бром при испарении морской воды не образует собственных минералов, а выделяется в твердую фазу вместе с хлоридами в виде изоморфной примеси к ним.

NOTA DEL EDITOR: No se acompañaron las figuras citadas en el texto.

Как известно, первым из хлоридов выделяется галит, затем при дальнейшем концентрировании к нему присоединяется сильвин, который в последующем переходит в карналлит или каинит. Каинит в последующем также переходит в карналлит. В эвтонической точке к этим минералам присоединяется бишофит. Все эти хлориды увлекают с собою в твердую фазу бром.

Если посмотреть на изменение содержания брома в океанической воде при ее концентрировании, то, как можно видеть из данных табл. 2, содержание брома по мере концентрирования все возрастает, несмотря на то, что идет садка перечисленных хлоридов, увлекающих бром в твердую фазу. Таким образом, в процессе испарения морской воды бром с момента начала кристаллизации первого хлорида — галита — все время распределяется между раствором и одной или несколькими твердыми фазами. Распределение это идет таким образом, что в твердую фазу его увлекается меньше, чем остается в растворе.

Выяснением закономерностей, управляющих распределением брома между кристаллами и раствором, занимался ряд исследователей. Эти работы, начатые в 1908 г. (Бекке), получили широкое развитие и свое завершение благодаря трудам Ю. В. Морачевского (1928, 1950), В. И. Николаева (1932, 1936), Н. А. Шлезингера с Ф. П. Зоркиным и А. В. Новоженовой и др. (1935, 1939), С. К. Чиркова (1935, 1946), В. П. Ильинского, В. М. Филиппео, Д. И. Сапирштейна (1928, 1948), М. Г. Валяшко с Е. М. Петровой и Т. В. Мандрыкиной (1943, 1949).

В 1946 году сводка всех наших знаний в этой области сделана С. К. Чирковым; им же разработана теория распределения иона брома между кристаллами и раствором. Поэтому можно не останавливаться здесь на рассмотрении истории вопроса и обзоре всех работ в этой области, а перейти к основным выводам относительно закономерностей, управляющих этим процессом.

Главнейшие из этих выводов следующие:

1. Бром [1] изоморфно смешивается с твердыми хлоридами.

2. Содержание брома в твердом хлориде определяется содержанием брома в растворе, из которого происходит кристаллизация.

3. Для каждого данного хлорида характерен свой коэфициент распределения

$$J = \frac{C_{тв}}{C_{с.о.}},$$

[1] Здесь и везде в дальнейшем подразумевается ион брома.

где: $C_{ТВ}$ — концентрация брома в твердых кристаллах (вес. %),

$C_{С.О.}$ — концентрация брома в сухом (солевом) остатке жидкой фазы (вес. %).

Для небольших концентраций бромида по сравнению с хлоридом, какие мы имеем в природных рассолах и в морской воде, коэфициент распределения, как показал С. К. Чирков, есть величина постоянная.

При графическом изображении кривой распределения $C_{ТВ} = f(C_{С.О.})$,

$J = \frac{C_{ТВ}}{C_{С.О.}}$ есть tg угла наклона касательной к кривой распределения.

4. Как показывает опыт, для всех хлоридов, кристаллизующихся из морской воды, $J < 1$. Следствием этого будет то обстоятельство, что при кристаллизации из раствора хлорида — носителя брома, несмотря на увлечение им части брома в твердую фазу, концентрация брома в растворе растет.

5. Если из раствора кристаллизуются одновременно два хлорида, с которыми бром образует изоморфные смеси, распределение брома происходит так, как будто другого хлорида нет.

Иными словами, содержание брома в каждом хлориде будет определяться своим коэфициентом распределения и содержанием брома в растворе.

Перечисленные здесь закономерности позволяют сделать следующие важные в практическом отношении выводы:

1. При сгущении морской воды содержание брома в ней будет постепенно возрастать и каждой определенной концентрации морской воды будет соответствовать определенное содержание брома.

2. При кристаллизации какого-либо хлорида, происходящей всегда на определенном интервале концентраций, содержание брома в первых порциях выделенного хлорида будет более низким и по мере дальнейшей кристаллизации должно постепенно возрастать, поскольку растет концентрация брома в морской воде, а коэфициент распределения остается постоянным.

3. При одновременной кристаллизации двух хлоридов из морской воды — содержание брома в каждом из них будет определяться свойственным ему коэфициентом распределения и концентрацией брома в растворе.

4. Последующая перекристаллизация хлорида в случае потери маточных растворов будет вести к обеднению хлорида бромом, поскольку $J < 1$.

Таким образом, содержание брома в соляных породах и минералах определяется их историей и, следовательно, может явиться индикатором на условия их образования.

Как хорошо известно, большинство, во всяком случае, крупных соляных месторождений образовалось в результате концентрирования морской воды. Поэтому можно все компоненты соляных отложений рассматривать как продукты кристаллизации из морской воды. Если установить содержания брома, характерные для каждой стадии сгущения морской воды, то, зная коэфициенты распределения для каждого хлорида, можно будет установить те нормальные содержания брома, какие должны быть у хлоридов, выделившихся из морской воды при ее концентрировании, или так называемую *шкалу нормальных концентраций брома в хлоридах.*

Это даст нам возможность, на основании содержания брома и его отношения к хлору, определить ту стадию, на которой происходило выделение данной соляной породы, а также установить наличие процессов перекристаллизации. Содержание брома в галите может явиться и поисковым признаком на отложения калийных солей.

Отношение $\frac{Br^1 \cdot 10^3}{Cl^1}$ в океане и морях близко к 3,30 (табл. 2).

Содержание брома в морях и океанах, хотя и испытывает в отдельных случаях колебания, давая более низкие значения для отдельных станций и отдельных проб, но эти колебания, скорее всего, вызываются местными причинами. Отношение же $\frac{Br^1 \cdot 10^3}{Cl^1}$ можно считать характерной постоянной для морской воды (А. П. Виноградов, 1944) не только в настоящее время, но и на протяжении длительного отрезка геологического времени [2].

I. БРОМ В ПРОДУКТАХ КОНЦЕНТРИРОВАННОЙ МОРСКОЙ ВОДЫ

Для выяснения поведения брома в процессе сгущения морской воды и установления его содержания на разных стадиях сгущения мы использовали материалы Крымской соляной станции и наши собственные данные опытов испарения в природных условиях воды Черного и Азовского морей и рассолов прибрежных соляных озер, питающихся морской водой.

Отношение $Br^1 : Cl^1$ и химический состав этих водоемов весьма близки

[2] Последнее утверждение весьма важно для дальнейших выводов. Анализ данных по содержанию брома в соляных отложениях (см. ниже) показывает, что на протяжении длительной части геологической истории Земли это отношение для океана было близко к современному.

к составу морской воды, как это следует из табл. 1. Выборочные данные из всех использованных материалов представлены в табл. 2 и на графике рис. 1 [3]. Рассмотрение всех данных позволяет сделать следующие выводы:

1. Вром в процессе испарения морской воды накапливается в жидкой фазе. Содержание его первоначально является прямолинейной функцией концентрации.

2. Первый излом на кривой: содержание брома – концентрация рапы – отмечается в момент начала кристаллизации NaCl. Следующий излом характеризует начало выделения в твердую фазу эпсомита $MgSO_4.7H_2O$, затем мы наблюдаем излом в момент появления в твердой фазе карналлита KCl. $MgCl_2.6H_2O$ и, наконец, при достижении эвтонической точки (Э) — начала садки бишофита.

Интересно отметить, что интенсивность накопления брома в процессе испарения морской воды все возрастает, кривая с появлением каждой новой твердой фазы становится все более и более крутой. Это связано с тем, что выделение каждой новой твердой фазы не прекращает выделения предшествующей, а присоединяется к ней, тем самым скорее сокращается объем жидкой фазы и увеличивается содержание в ней солей.

Для наших целей весьма существенным является установление содержания брома в узловых точках. Сравнение данных по этим точкам для различных озер показывает некоторое различие в содержании в них брома. Отличны также величины отрезков кривой, отвечающие кристаллизации отдельных твердых фаз. Это обусловлено небольшими отличиями в составе рассолов этих озер и различным количеством выделяющихся солей на определенных интервалах концентраций.

В табл. 3 сведены содержания брома, отвечающие узловым точкам кристаллизации растворов этих озер.

Мы видим, что максимальные отличия в содержании брома наблюдаются в эвтонических точках, затем меньшие в точке начала кристаллизации карналлита. Очень близко совпадают по содержанию брома точки начала кристаллизации эпсомита. Немного больше отличаются между собой точки начала кристаллизации галита.

В дальнейшем мы не считаем нужным усреднять эти данные, поскольку все они характеризуют концентрирование морской воды в несколько отличных условиях взаимодействия с водами суши.

Такое взаимодействие будет всегда наблюдаться в природе, и поэтому эти данные дадут нам естественный разброс точек, который мы должны

[3] Подробно см. (2).

Таблица 2

Содержание брома и значение бром-хлорного коэфициента в продуктах испарения морской воды в озере № 5

№№ П/П	Уд. вес	°Б	Cl^1 %	Br^1 %	$\frac{Br \cdot 10^3}{Cl^1}$	Твердая фаза
1	1,01	1,0	1,01	0,0035	3,48	
2	1,075	10,0	5,49	0,018	3,28	
3	1,091	12,0	6,62	0,022	3,33	
4	1,108	14,0	7,77	0,026	3,22	
5	1,162	20,0	11,83	0,039	3,29	
6	1,199	24,0	14,33	0,047	3,28	
7	1,220	26,1	15,72	0,051	3,24	NaCl
8	1,231	27,0	15,57	0,083	5,34	,,
9	1,252	29,0	15,26	0,137	9,00	,,
10	1,273	31,0	15,29	0,179	11,70	,,
11	1,291	32,6	15,63	0,214	13,70	,,
12	1,300	33,4	15,77	0,226	14,30	,,
13	1,308	34,0	15,93	0,236	14,80	$NaCl+MgSO_4 \cdot 7H_2O(KCl)$
14	1,315	34,6	17,93	0,296	16,50	,,
15	1,323	35,3	19,10	0,334	17,50	,,
16	1,325	35,5	19,23	0,342	17,80	$NaCl+MgSO_4 \cdot 7H_2O+KCl \cdot MgCl_2 \cdot 6H_2O$
17	1,331	35,9	20,97	0,421	20,01	,,
18	1,336	36,5	21,91	0,469	21,40	,,
19	1,350	37,5	23,10	0,516	22,40	
20	1,359	38,3	23,68	0,520	22,00	

Таблица 3

Содержание брома (вес. %) в узловых точках

№№ III	Озеро	Начало садки галита		Начало садки эпсомита (сильвин)		Начало садки карналлита		Эвтонита	
		Уд.вес	B	Уд.вес	B	Уд.вес	B	Уд.вес	B
1	Озеро № 8	1,224	0,062	1,308	0,222	1,319	0.259	1,361	0,431
2	Озеро № 5	1,220	0,051	1,308	0,236	1,325	0,342	1,359	0,520
3	Азовское море	1,221	0,044	1,308	0,223	1,321	0,317	1,357	0,608
4	Залив	1,220	0,033	—	—	—	—	—	—

принять во внимание при установлении шкалы нормальных содержаний брома в соляных отложениях морского происхождения.

Прежде чем перейти к решению нашей основной задачи, сделаем еще один вывод из этого материала, который может оказаться полезным при определении принадлежности того или иного соляного водоема по своему происхождению к морскому типу.

Величина отношения брома к хлору, по предложению акад. А. П. Виноградова, может явиться удобным генетическим признаком для природных вод. Однако постоянство этого отношения для вод морского происхождения будет сохраняться лишь до момента начала кристаллизации первого хлорида, каковыми будет NaCl. С этого момента величина отношения $\frac{Br^1 \cdot 10^3}{Cl^1}$ начинает резко возрастать. Следовательно, величина этого отношения может использоваться лишь для определенного интервала минерализации.

Более универсально пользование графиком, показывающим зависимость между величиной отношения $\frac{Br^1 \cdot 10^3}{Cl^1}$ и содержанием хлор-иона как показателя степени минерализации, при этом содержание хлор-иона откладывается на оси абсцисс. Такой график представлен на фиг. 2. Линия O a b d представляет собой усредненную кривую для вод морского происхождения. Ниже и правее ее располагаются воды, более бедные бромом, а выше и левее — более богатые.

При бурении одной скважины в Сибири на глубине 1410 м была встречена минерализованная вода с отношением бромхлорного коэфициента, равным 19.05 при содержании хлор-иона 19,3%. Если сравнивать значение бромхлорного коэфициента этих вод с таковыми для моря, то вода явно обогащена бромом. Нанесение же на наш график позволяет рассматривать эту воду как маточный раствор морского генезиса. Точка (x) попадает как раз на кривую.

Как можно видеть, озера морского происхождения, отмеченные на диаграмме D и V, хорошо укладываются на эту кривую. Озера континентальные располагаются, как правило, ниже и правее. Выше этой кривой расположено несколько точек, относящихся к соляным озерам Керченского полуострова, для которых вероятна связь с сопочными водами, показывающими повышенное содержание брома. Судя по этим данным, океан является местом максимального концентрирования брома. Миграция вод суши рассеивает бром. Другим источником его концентрирования является живое вещество, чем можно объяснить более высокое содержание брома в сопочных и некоторых нефтяных водах.

II. КОЭФИЦИЕНТЫ РАСПРЕДЕЛЕНИЯ БРОМА

Установление, по возможности, точных значений коэфициентов распределения брома между твердыми хлоридами и раствором $J = \frac{C_{тв}}{C_{с.о.}}$ чрезвычайно существенно для указанных выше целей.

Это заставило нас предпринять специальное экспериментальное исследование для установления значения этих коэфициентов и влияния на их величину путей и условия образования. Такое исследование выполнено нами и Е. М. Петровой для двух главнейших минералов — галита и сильвина.

При выборе окончательных значений коэфициента распределения учтены и все имевшиеся литературные данные, а для галита также результаты расчета из данных определения брома в новосадке галита и рассолах ряда соляных озер.

Для карналлита и бишофита мы воспользовались для выбора коэфициентов только литературными данными.

Подробно все эти расчеты приведены в нашей работе с Т. В. Мандрыкиной (1952). Здесь же приводим только окончательные результаты, приведенные в табл. 4.

Таблица 4

Коэфициенты распределения брома между твердой и жидкой фазами для главнейших хлоридов

Минерал-хлорид	$J = \frac{C_{тв}}{C_{с.о.}}$
Галит (NaCl)	0,037
Сильвин (KCl)	0,200
Карналлит ($KMgCl_3 6H_2O$)	0,320
Бишофит ($MgCl_2 6H_2O$)	0,420

Эти величины коэфициентов и положены нами в основу всех дальнейших расчетов и рассуждений.

III. БРОМ В ХЛОРИДАХ МОРСКОГО ПРОИСХОЖДЕНИЯ

Зная содержание брома в рассолах — продуктах концентрирования морской воды и зная коэфициенты распределения $J = \frac{C_{тв}}{C_{с.о.}}$ для отдельных хлоридов, можно рассчитать то содержание брома ($C_{тв}$), которое должно быть в хлориде, кристаллизующемся из морской воды в процессе ее сгущения. Условимся называть это содержание брома нормальным.

Расчет ведет из уравнения:

$$C_{тв.} = J\ C_{с.о.}$$

Если, например, содержание брома в рассоле в момент начала садки NaCl 0,051%, а сумма солей 27,49, то $C_{с.о.} = \frac{0{,}051 \cdot 100}{27{,}49} = 0{,}185\%$, а $C_{тв} = J\ C_{с.о.} = 0{,}037 \cdot 0{,}185 = 0{,}0068\%$. Этим же способом, только беря соответствующие коэфициенты, рассчитываем нормальные содержания брома в сильвине, карналлите и бишофите. Рассмотрим эти данные для отдельных мынералов:

Галит.—Галит, начиная кристаллизоваться из морской воды при достижении ею 26-27% суммы солей ($J = \sim 1{,}220$), продолжает кристаллизоваться до полного ее усыхания. Это делает галит весьма удобным минералом для определения стратиграфического положения отдельных пачек немых соляных пород.

Как следует из табл. 5, где приведены содержания брома и величины бромхлорного коэфициента в галите, в первых кристаллах галита нормальное содержание брома будет 0,005 — 0,006%, а в галите, кристаллизующемся из эвтонических рассолов, 0,05 — 0,06%, т.е. в 10 раз выше. Если изобразить эту зависимость графически, то мы получим кривую, представленную на рис. 3. Изломы на этой кривой отвечают появлению в осадке новых твердых фаз.

Еще удобнее рассматривать не содержание брома, а величину его отношения к хлору $\left(\frac{Br \cdot 10^3}{Cl^1}\right)$; такой график представлен на рис. 4.

Зная распределение по шкале концентраций полей кристаллизации калийных и магнезиальных солей, а, следовательно, положение отдельных зон,

можно использовать содержание брома в галите или, лучше, величину бромхлорного коэфициента галитовой породы как указатель стратиграфического положения данной пачки галитовых пород, а также как поисковый признак на калийно-магнезиальные соли. Если содержание брома в галите (в расчете на 100% хлорида) близко к 0,02% или величина бромхлорного коэфициента около 0,04, то этот галит выделился где-то в начале зоны калийных солей (зона сильвина) и, следовательно, наличие такого галита будет говорить о вероятности нахождения здесь калийных солей.

Таблица 5

Нормальные содержания брома и величина отношения $\frac{Br \cdot 10^3}{Cl^1}$ в галите, сильвините и карналлите, выделившихся из морской воды (выборочные данные (2)).

№№ П/П	Жидкая фаза $\frac{Br^1 \cdot 10^3}{Cl^1}$	Галит		Сильвин		Карналлит	
		Br^1 % весов.	$\frac{Br^1 \cdot 10^3}{Cl^1}$	Br^1 % весов.	$\frac{Br^1 \cdot 10^3}{Cl^1}$	Br^1 % весов.	$\frac{Br^1 \cdot 10^3}{Cl^1}$
1	3,24	0,0068	0,11				
2	5,34	0,011	0,18				
3	9,00	0,017	0,288				
4	11,70	0,022	0,36				
5	13,70	0,025	0,41				
6	14,30	0,026	0,43				
7	14,80	0,027	0,44	0,137	2,9		
8	16,50	0,033	0,54	0,176	3,70		
9	17,50	0,037	0,61	0,190	4,00		
10	17,80	0,037	0,60	0,199	4,20	0,318	8,3
11	20,01	0,045	0,74	(0,242)	(5,10) [4]	0,387	10,1
12	21,40	0,049	0,81	(0.266)	(5,60)	0,425	11,3
13	22,40	0,052	0,86	—	—	0,523	13,7
14	26,7	0,063	1,03	—	—	0,544	14,1

[4] В скобки взяты значения для сильвина, если предположить его выделение в карналлитовой зоне.

Сильвин.—Выделение сильвина из океанической воды, как показали наши с Е. Ф. Соловьевой исследования, начинается при составе рассола Cl — 16,28%, SO_4'' — 6,03%, Mg — 5,8%, K — 1,94%, что весьма близко к началу садки эпсомита при летних температурах. Поэтому мы с достаточной степенью приближения можем считать начало садки эпсомита за начало садки сильвина. Исходя из данных содержания брома в рассолах, начиная с этой концентрации и кончая началом кристаллизации карналлита, и принимая J = 0,20 рассчитаны нормальные содержания брома в сильвине (табл. 5).

Как следует из этих расчетов, нормальное содержание брома в сильвине, выделившемся из рассолов морского происхождения, будет колебаться в пределах 0,13-0,20. Бромхлорный коэфициент для сильвина меняется в пределах 2,9 - 4,2. Меньшие содержания брома в сильвине будут свидетельствовать о выделении из обедненных бромом рассолов или о процессах перекристаллизации.

По определению Д'Анса и Кюна, содержание брома в сильвине из северной калийной залежи 0,21 — 0,28%, а для сильвина из области Верра — 0,13%. Эти величины свидетельствуют о первичной кристаллизации соли.

По определению Т. В. Мандрыкиной, сильвин из Соликамска содержит брома 0,06 — 0,08%, значительно ниже нормального, что говорит об имевших место процессах перекристаллизации (после потери маточных рассолов). Но сильвин, как правило, не образует мономинеральных образований, а чаще всего встречается в ассоциации хлорида с галлитом, много реже с карналлитом и каннитом, о чем ниже.

Карналлит.—В определенный момент, когда в растворе накопится достаточное количество хлористого магния, начинается выделение карналлита. Для рассолов морского происхождения это наступает при достижении плотности 1,320 – 1,325 (сумма солей 34–35%). Пользуясь коэфициентом распределения 0,32 и содержанием брома в рассолах морского происхождения, нормальное содержание брома в карналлите определится от 0,24 в начале кристаллизации и до ~ 0,6% – в момент начала появления бишофита (табл. 5). Соответствующий бромхлорный коэфициент для карналлитов будет колебаться от 6 до 15. Более высокие содержания брома в карналлитах могут быть встречены при кристаллизации карналлита из эвтонических рассолов.

В ископаемых месторождениях мы находим карналлиты с довольно резко отличающимся содержанием брома, однако они не выходят за пределы нормальных содержаний. Максимальное содержание брома обнаружено у индерских карналлитов (скв. 244). Нормальные содержания брома обнаруживают и карналлиты германских месторождений. Заметно более низким

оказывается содержание брома в соликамских карналлитах, озинских и ряде других. Причин этого мы коснемся ниже.

Бишофит.—Является последним минералом-хлоридом, кристаллизующимся из морской воды в процессе ее испарения. Из-за своей гигроскопичности он редко встречается в соляных месторождениях.

Исходя из содержания брома в эвтонической ране морского происхождения и J = 0,42, нормальное содержание брома бишофита определяется 0,5 – 0,7%, а при дальнейшем испарении эвтонити может достигнуть 1%. Бромхлорный коэфициент для бишофита будет 14-20 и выше.

В бишофите из отечественных месторождений нормальные содержания брома известны в бишофите Индерского месторождения и резко понижены в бишофите из Озинского месторождения.

Каинит.—В ряде месторождений калийных солей и, особенно, в наших предкарпатских месторождениях полупает широкое развитие каинит. К сожалению, у нас нет определений коэфициента распределения J, поэтому мы лишены возможности дать нормальное содержание брома в этом интервале. Определения брома произведены Д'Ансом и Кюном для германских месторождений и Предкарпатья, автором для Индера и автором, Ю. В. Морачевским и Т. В. Мандрыкиной для каинита из Калуша. По этим данным, брома в каините меньше, чем в сопровождающем его сильвине. Но больше, приблизительно, в среднем, в 1,5 раза того количества, какое должно было в нем находиться, если бы содержащийся в нем KCl сохранил свой коэфициент распределения J = 0,2. Таким образом, коэфициент распределения из этих данных можно считать 0,3, считая на KCl, содержащийся в каините, или 0,1 на всю молекулу каинита. Но это лишь косвенные соображения, требующие экспериментальной проверки.

Соляные породы.—Из многочисленных соляных пород мы рассмотрим только главнейшие: галитовые сильвинитовые и карналлитовые.

Главным породообразующим минералом галитовых пород является галит, сопровождаемый обычно ангидритом, реже полигалитом, небольшим количеством карбонатов кальция и магния. Ни сульфаты, ни карбонаты брома не содержат и поэтому примесь их к галиту только снижает общее содержание брома, но совершенно не отражается на величине бромхлорного коэфициента. Поэтому при использовании содержания брома в галитовых породах для установления стратиграфического положения данной породы, для поисковых и генетических целей можно пользоваться приведенным выше графиком нормальных значений бромхлорного коэфициента (см. рис. 4).

Главными породообразующими минералами сильвинитовых пород являются галит и сильвин. Оба эти минерала – носители брома. Величина

бромхлорного коэфициента такой породы, состоящей из смеси сильвина и галита, будет какой то промежуточной, и определится составом смеси и содержанием брома в этих минералах.

Для использования содержания брома в сильвинитовой породе для генетических построений, без выделения отдельных составляющих ее минералов, или определения в них брома косвенным путем (Д'Анс и Кюн, 1940; М. Г. Валяшко, 1944) необходимо определить нормальное содержание брома в сильвинитовой породе. Удобнее всего сделать это графически [5]. Отрезок прямой, принятый за 100%, изображает состав смесей галита и сильвина от 0 до 100%. По вертикальной оси откладывается величина бромхлорного коэфициента (см. рис. 5).

Выделение сильвина из морской воды начинается при достижении ею ~ 32% суммы солей, когда содержание брома в сухом остатке рассола $C_{с.о.} = 0{,}69$. Выделяющийся при этом сильвин характеризуется величиной бромхлорного коэфициента, равной 2,9, а сопровождаемый ею галит ~ 0,4. Исходя из этих величин, рассчитано содержание брома и хлора в смесях галита и сильвина и величина бромхлорного коэфициента. Значение бромхлорного коэфициента нанесено на график [6]. Соединив эти точки, получаем кривую $\Gamma_1 C_0$ нормальных значений бромхлорного коэфициента в смесях галита и сильвина в начале кристаллизации последнего.

Заканчивается выделение сильвина при достижении рассолом $C_{с.о} = 1{,}0$. Величина бромхлорного коэфициента для сильвина и галита, кристаллизующихся в этот момент, будет соответственно 4,2 и 0,57. Рассчитав значения бромхлорного коэфициента для смесей этих двух минералов и нанеся на тот же график, получаем вторую кривую $\Gamma_2 C_1$, – показывающую нормальные значения бромхлорного коэфициента для смесей галита и сильвина в конце кристаллизации последнего. Область диаграммы заключенная между кривыми $\Gamma_1 C_0$ и $\Gamma_2 C_1$ будет отвечать нормальным значениям бромхлорного коэфициента для всех возможных смесей галита и сильвина, выделившихся из морской воды при ее сгущении.

Реальные породы содержат зачастую, помимо этих двух минералов, другие, не содержащие брома (кизерит, полигалит и т.д.), которые будут снижать содержание брома во всей породе, но не отразятся на величине бромхлорного коэфициента. Для таких пород перед нанесением на график

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[5] Есть и другой путь, предложенный и примененный в нашей лаборатории Н. С. Спиро, – путь расчета по данным химического анализа галитовых эквивалентов для сильвина, карналлита и пр. Этот путь удобен для пород сложного состава.

[6] При построении данного графика по ряду соображений для галита принято несколько более низкое значение бромхлорного коэфициента.

необходимо рассчитать процент KCl от суммы NaCl и KCl и эту величину отложить по оси составов нашего графика.

На рис. 6 приведен аналогично построенный график нормальных значений бромхлорного коэфициента для карналлитовых пород (галит + карналлит). Область диаграммы между кривыми $Г_2К_0$ и $Г_3К_1$ отвечает нормальным значениям бромхлорного коэфициента для всех возможных составов карналлитовых пород, выделившихся из морской воды в карналлитовую стадию.

Карналлит, так же как и галит, является так называемым конгруентным минералом и продолжает кристаллизоваться и в бишофитовую стадию из эвтонических рассолов. Для таких карналлитовых пород значение бромхлорного коэфициента будет выше, чем указанное здесь на графике.

Эти графики дают возможность использовать содержание брома, вернее, величину бромхлорного коэфициента для ряда генетических построений.

Выше мы говорили о том, что солевые минералы не хлориды не содержат брома. Как показали наши исследования, бромид в адсорбированном состоянии может находиться в мелкодисперсном глинистом материале, нередко загрязняющем соляные породы, причем для месторождений Предкарпатья содержание брома в глинистой части таково же, как и в сильвине. Поэтому, если имеют дело с солевыми породами, содержащими глинистый материал, необходимо учитывать его как возможный носитель брома.

Как следует из всего изложенного, обработка всего накопленного фактического материала по содержанию и распределению брома в солях под определенным углом зрения позволила установить так называемую шкалу нормальных содержаний брома и нормальных значений бромхлорного коэфициента для соляных минералов и главнейших соляных пород, и разработать приемы пользования ими.

IV. ЗАКЛЮЧЕНИЕ

В заключение рассмотрим несколько примеров использования значений бромхлорного коэфициента.

1. *Определение стратиграфического положения галитовой породы*

Выше мы уже отмечали, что содержание брома в галите будет зависеть от того, на какой стадии сгущения морской воды он выделился. Это дает возможность определить по величине бромхлорного коэфициента "стратиграфическое" положение данной пачки галита. Для этого рассчитывают $\frac{Br^1 \cdot 10^3}{Cl^1}$

для данной пробы галита и наносят его на кривую $\Gamma_0\Gamma_1\Gamma_2\Gamma_3$ рис. 4. Место на этой кривой определяет стратиграфическое положение данной пробы или пачки солей. Если точка находится между Γ_0–Γ_1, то мы находимся в галитовой зоне, если на участке Γ_1-Γ_2 – то в зоне сильвина, Γ_2-Γ_3 – карналлита. Если ближе к Γ_0 – то это начало галитовой зоны, если ближе к Γ_1 – то это верх галитовой зоны. Так, например, в скв. 6 в Верхнекамском месторождении Т. В. Мандрыкиной были определены следующие значения бромхлорного коэфициента:

глуб.:	528 м	491 м	458 м	430 м
$\frac{Br^1 \cdot 10^3}{Cl^1}$	0,08	0,12	0,14	0,17
№ точки:	1	2	3	4

Нанеся эти значения на график (фиг. 4), выясняем, что здесь вскрыта бурением нижняя часть галитовой зоны.

Для Индерского месторождения галитовые (Е. М. Петрова) породы обнаружили следующие значения бромхлорного коэфициента:

Скв. №	1134	1137	1141	1989
$\frac{Br^1 \cdot 10^3}{Cl^1}$	0,422	0,40	0,46	0,69
№ точки	5	6	7	8

Точки 5, 6 и 7 располагаются около Γ_1 и отвечают самому верху галитовой зоны (т. 6) и началу сильвинитовой зоны. Наконец, т. 8 лежит в зоне карналлита.

Положение точек 5, 6, 7, а также 8 может служить поисковым признаком на калийные соли. Действительно, невдалеке от скв. 1134 и 1141 обнаружен сильвинит, а в скв. 1989 включения карналлита.

Возможны случаи столь низких значений величины бромхлорного коэфициента для галита, что точка ложится левее Γ_0. Такое положение свидетельствует о размыве и последующем повторном отложении галита. Напомним, что никогда нельзя судить по анализу единичной пробы, если не желают впасть в ошибку.

2. *Первичность и вторичность сильвинитовых и карналлитовых отложений*

Попробуем определить, пользуясь значением бромхлорного коэфициента, историю сильвинитовых и карналлитовых пород ряда месторождений. Для этого нанесем значения бромхлорного коэфициента для сильвинитовых пород на график рис. 5, а карналлитовых пород – на график рис. 6.

Как показывает рассмотрение этого графика "нормальными" являются сильвиниты месторождений Стассфурта, обл. Верра, Калуша и Стебника. Некоторые сильвиниты Индера (скв. 273, 221) располагаются на нижней границе этой области. Большая часть сильвинитов Индера и особенно сильвиниты скв. 238, по аналогии с соликамскими, называемыми "пестрыми", безусловно, подвергались растворению и перекристаллизации, о чем свидетельствует низкое значение бромхлорного коэфициента при высоком содержании KCl.

Сильвиниты Соликамска лежат в большинстве своем ниже нижней границы, что заставляет предполагать вторичный переотложенный – характер этого месторождения. Пестрые сильвиниты Соликамска также являются перекристаллизованными и потерявшими при этом бром.

Особенно низко располагаются по значению бромхлорного коэфициента сильвиниты из Озинского месторождения.

Сильвиниты Гаурдака по значению бром-хлорного коэфициента оказываются также ниже нижней границы нормальных сильвинитов.

Выше верхней границы области нормальных содержаний попадают некоторые сильвиниты германских месторождений. Следует думать, что эти сильвиниты образовались за счет разложения карналлита.

Рассмотрение графика для карналлитовых пород различных месторождений показывает, что нормальными являются карналлиты германских месторождений Стассфурта и области Верра. К первичным карналлитам относятся также и карналлиты Индера. Они лежат в большинстве своем выше верхней границы. Это свидетельствует о выделении их из эвтонических рассолов. Об этом же, как мы знаем, говорит присутствие в карналлитах Индера и боратов. Интересно заметить, что бораты встречены также и в германских месторождениях, которые, судя по всем данным, является первичными, выделившимися из морской воды и заметно не измененными последующими процессами.

Карналлиты Соликамска по значениям бром-хлорного коэфициента лежат заметно ниже нижней границы нормальных содержаний брома.

Так же низко расположены и карналлитовые и бишофитовые породы Озинок.

Отдельные анализы для карналлитсодержащей породы из Калуша располагаются в области нормальных содержаний брома.

Таким образом, с построением этих графиков мы получаем объективный метод, позволяющий судить о первичности и вторичности отдельной породы и всего месторождения.

Справедливость и соответствие этих данных фактическому положению вещей определяется достаточно тщательным обоснованием, с одной стороны, коэфициентов распределения для каждой из пород, а с другой – обширным материалом, на котором нами выведены нормальные содержания брома в продуктах концентрирования морской воды.

Нанесение на построенные для сильвинитовых и карналлитовых пород графики значений бром-хлорного коэфициента для всех доступных нам калийных месторождений Мира показало, что все они легли или в области бром-хлорного коэфициента для нормальных пород, или же ниже ее. Такое расположение точек является вполне закономерным и вытекает из существа природы вероятных процессов и указывает на них. Расположение точек выше границ нормальных содержаний брома почти не наблюдается.

Для сильвинитов такое превышающее норму значение мы отмечаем для сильвинитовых пород Стебника и Калуша, бедных сильвином и вообще хлоридами, но обогащенных глинистым материалом.

Выше располагаются отдельные точки для германских месторождений. Следует думать, что это – сильвиниты, образованные из карналлитов в высоким содержанием брома при разложении их раствором, относительно богатым бромом. В этом случае, как показали наши с Е. М. Петровой опыты, наблюдается повышенное содержание брома в сильвине. Таким образом, также и это отклонение находит себе экспериментально подтвержденное объяснение.

Наконец, на карналлитовой диаграмме выше нормальных значений располагаются карналлиты Индера. Их богатство бромом следует объяснить кристаллизацией из высококонцентрированных эвтонических рассолов.

Как следует из всего здесь изложенного, разработанный и изложенный в настоящей работе способ использования величины бром-хлорного коэфициента в соляных породах дает в руки исследователя объективный метод, позволяющий вскрывать те преобразования, которые претерпели месторождения, отыскивать среди галитовых полей отложения калийных солей и устанавливать стадию выделения отдельных пачек галитовых пород. Применение этого метода позволило автору и его сотрудникам предсказывать в ряде мест нахождение калийных солей, что затем было подтверждено бурением.

Наконец, приведенный анализ позволяет сделать еще один общий вывод. Расположение значений бром-хлорного коэфициента для сильвинитовых и карналлитовых пород в области нормальных и пониженных значений указывает нам на то весьма важное обстоятельство, что величина бром-хлорного коефициента для океанической воды на протяжении того геологического времени, для которого известны месторождения солей (начиная с кембрия) была весьма близкой к современному.

Разобранные здесь данные позволяют также утверждать, что в природе широко распространены процессы снижающие величину отношения $\frac{Br^1 \cdot 10^3}{Cl^1}$ и много реже процессы концентрирования брома, повышающие значение $\frac{Br^1 \cdot 10^3}{Cl^1}$. Главными из этих факторов будут: галогенез, живое вещество и в отдельных случаях адсорбция.

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GEOCHEMISTRY AND RADIATION SURVEYING FOR OIL AND GAS

J. W. MERRITT *

ABSTRACT

The purpose of this paper is to trace the operational history of and problems connected with the use of soil chemistry and soil radiation in exploring for oil and gas. It is not our purpose to give any space to instrumentation either in the field or laboratory, but rather to discuss the theories involved and their application in practical oil and gas exploration.

Many years ago chemists and geologists began to observe what they considered as significant patterns in the distribution of hydrocarbon in the surface soils above oil and gas production. These patterns were observed both in the form of solid and liquid hydrocarbons. Subsequently, certain inorganic compounds were found to follow in this same category. Still later, it was observed that similar patterns could be developed by measuring relative density patterns of surface radiation.

Unfortunately in the case of each of the above methods the earlier proponents were too optimistic. They failed to give proper weight and attention to the interference patterns caused by various natural conditions. As a result, the density patterns developed were irregular and often undependable. It is our purpose in this paper, therefore, to discuss some of these problems and to suggest remedies which will permit the use of these methods with a much greater degree of success.

INTRODUCTION

Some of the earliest records of human history refer to the presence of bituminous material and gas escapes which we know now were related to oil and gas reaching the surface from subterranean deposits.

Early American oil exploration following the first oil discovery in Pennsylvania and also leading to discoveries in other states was frequently based upon the known presence of oil or gas seeps. These occurrences were not common enough to lead to widespread exploration and development. Furthermore, the direct relationship between surface phenomena and the actual location of the related subterranean deposits was often not clear. It became necessary at an early date to find a more dependable method upon which to base a drill-

* *Merrit Radiation Surveys, U. S. A.*

ing of test wells. The anticlinal theory was developed, therefore, from natural observations relative to relationship of oil structures to oil production. The method was first applied by the mapping of surface formations. This work was highly successful in the early days when Class A prospects were abundant and dependable surface data were available. However, there came a time when surface beds were not available or continuous enough for mapping purposes. The oil operator then turned to core drilling and other subsurface methods. But before long there came the problem of finding suitable markers at depths shallow enough to permit economical core exploration. This problem was then largely overcome by the development of geophysical methods —particularly seismograph and gravity meter.

As exploration gradually expanded across the country and the best prospects available for the above methods were tested, successful exploration became increasingly complicated and expensive. All during those years the oil operator kept thinking how wonderful it would be if someone would discover a method of exploration that was directly related to the oil rather than indirectly related through structure. From the very beginning, of course, "doodle bug" operators abounded and sufficient credulity existed among oil operators to give the "doodle bugger" a chance to show his wares. Nevertheless, scientists kept at work trying to find some surface phenomena that would be useful as a guide to oil exploration.

DEVELOPMENT OF SURFACE GEOCHEMICAL METHODS

HYDROCARBON METHOD:

Early in the history of American oil exploration it was observed that in addition to oil and gas seeps indicating the presence of oil and gas somewhere in the neighborhood there was a fairly common occurrence of paraffin in the surface soil. This substance was especially abundant above salt domes in the gulf coast area. Many oil operators considered the presence of paraffin to be significant but it was not until about the second decade of this century that the paraffin phenomena were studied with the view of determining a density pattern. European scientists were busy at the same time with the same thought in mind regarding hydrocarbon symptoms. Some of them, particularly in Germany, went a step beyond the paraffin concept and analyzed the soil for the presence of any light hydrocarbons which could be related in origin to petroleum or natural gas (Fig. 1). Through these studies it was observed that in many cases both light and heavy hydrocarbons found in surface soil showed a tendency to develop a density pattern in the form of a band of high

values following the approximate borders of the oil or gas production. Thus the "halo theory" came into existence.

After a considerable amount of experimentation, organizations were formed offering geochemical service to oil operators. Both the wax and the ligh hydrocarbon methods were exploited. Some of the early surveys were strikingly suc-

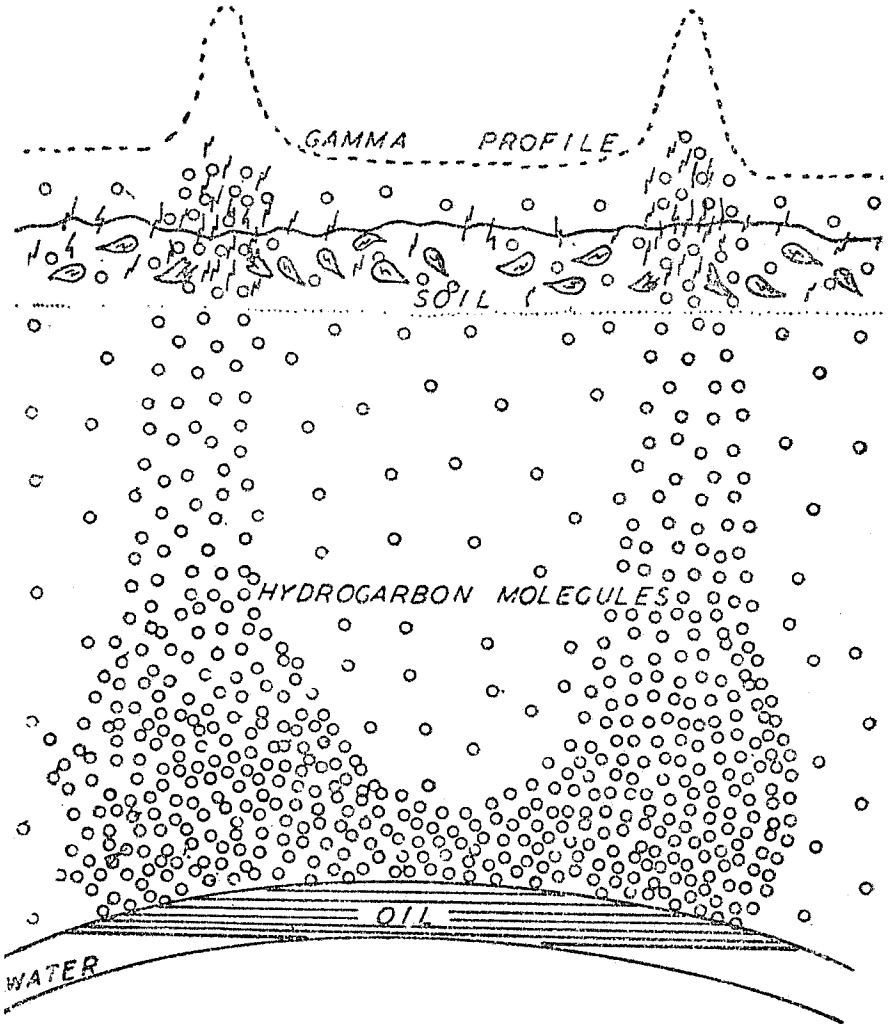


Fig. 1. Hypothetical cross section through oil structure, showing pattern of hydrocarbon gas molecular movement from oil body to surface and movement of ground water carrying radioactive elements in solution to build up concentration over margins of oil. (Leaf-like symbols indicate ground-water, angular escaping radiation. *World Oil*, July 1, 1952).

cessful in going beyond the then conventional methods of exploration and correctly predicting oil or gas production ahead of the drill. Oil operators sought these new methods with such avidity that the available service organizations were swamped with orders and were often several months behind in filling them. It looked like the oil man's Utopia had arrived. The only fear was that

such a simple method of finding oil would lead to rapid development and over-production!

Utopia, however, is not so easily attained. Mother Nature is generous with us human beings but only if we do our share of the work. It was only a short time after the development of this new geochemical method, which the trade called "soil analysis", that failures came more rapidly than success. The oil man is a peculiar creature. He is quick to accept a new idea, hoping for perfection. If perfection is not attained, he is just as quick to reject it. As a result of the many early failures of "soil analysis", the method fell into such disfavor that the words "soil analysis" elicited only frowns or smiles of derision. Scientists, interested in geochemical exploration and believing that the method must have a sound basis, were first to go back into the field and laboratory to find the cause of the excessive number of failures.

Then began the agonizing re-appraisal. Were the interpretative errors due to failure in laboratory technique? Evidently not because the chemical methods then used had been long established, the equipment used was capable of sensitive differentiation, and analytical results were repeatable. If not the chemical laboratory, then the conditions in the field must be to blame. One of the first improvements in field technique came with the discovery that soil chemical density patterns as contoured were not clean-cut and uniform due to improper sampling. On this account careful studies were made of sample density and patterns until an optimum spacing arrangement had been determined for each type of production. Up to that time sampling had been too widely scattered or too poorly arranged to make it possible to connect points of high value into a conclusive pattern. After this, one at a time, additional problems appeared to plague the geochemist. Sealed samples or surface soils lost their hydrocarbon because of the destructive effect of bacteria present in the sample container. The effect of differential atmospheric temperatures, barometric pressures and moisture in the soils made it almost impossible to obtain check readings at the same point at different times and seasons (Fig. 2). In the case of light hydrocarbon surveys surface sampling in the heat of summer often yielded very low values compared with those obtained from the same sample points tested in the winter. Some of the latter difficulties have been overcome by taking samples of soil ten or twelve feet below the surface but this method is impossible in areas of shallow bed rock and often impractical from the point of view of cost.

Early in the development of the light hydrocarbon method, it was discovered that the grain size of the soil sample had a profound effect upon the quantity of light hydrocarbon absorbed on the surface of the soil particles. On top of all this the interpreter was often plagued by the fact that where multiple sand

production occurred each producing sand tended to form its own surface pattern. Since no clue as to the depth of the various pay horizons was obtainable, the resultant pattern of a multiple-sand field would naturally be a composite of all the individual patterns.

ELECTRICAL CONDUCTIVITY METHOD

During the later years of the development of the hydrocarbon theory of oil exploration a method making use of the application of electrical earth conductivity was developed. By this method it was thought that a charge of electrical current could be sent into the surface of the earth and a pick-up of the return current obtained. It was thought that there would be blanketing effect of the petroleum deposits due to their natural insulating qualities. The resultant conductivity patterns of such surveys over production closely followed the halo pattern obtained by the hydrocarbon surveys. Finding a low conductivity value above oil or gas deposits and a high value margin, the operators concluded that the above mentioned theory was correct. However, the conductivity method was rendered almost useless after heavy rain storms. This fact indicated to the writer that the conductivity measurements represented only superficial conditions, and the pattern obtained was a surface pattern.

INORGANIC GEOCHEMICAL METHOD

Thinking along this line, we decided that the conductivity pattern indicated that there must be a surface concentration of inorganic compounds soluble in water that would follow the hydrocarbon pattern. The conductivity in such places would be increased by the increase in dissolved matter. We then sought for a relationship between such inorganic concentration and the hydrocarbon concentration. We knew from thousands of analyses that the hydrocarbon density pattern could be traced downward to its source at the margin of the oil production. We knew that the movement of light hydrocarbon was vertical and continuous. We also knew that the movement of gas through water stimulated water evaporation. Since the greater the quantity of gas passing through water, the greater the evaporation, it would be logical to assume that there would be a proportionally heavy water loss in the gas halo zones. Since there would be greater water loss in the halo zone it would be logical to expect that the areas touching the halo zone and, containing more water due to lesser water loss, would yield water to the halo zone by capillary action. Furthermore, every drop of water leaving the halo zone by evaporation must leave behind it its soluble contents. To these would be added the additional soluble

contents of waters entering this zone from the sides. As long as gas continues to escape from below, therefore, there is a constant buildup of evaporites in the halo zone. Putting this theory into practice we then developed an inorganic method of geochemical surveying following the same interpretative

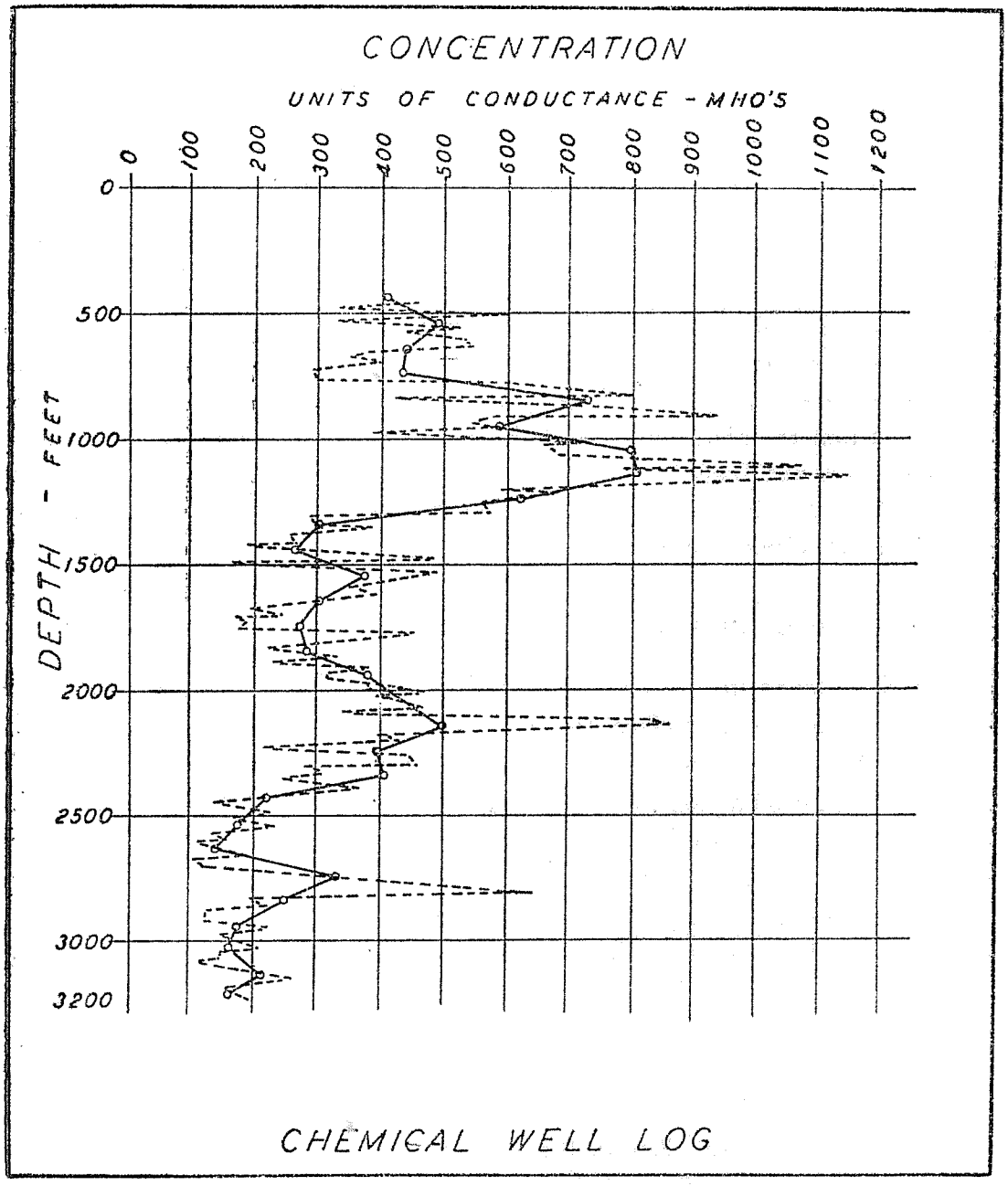


Fig. 3. Inorganic geochemical well log showing relative concentration of water soluble compounds measured by resistance method of water solution obtained by leaching. Broken line shows individual values and solid line the same smoothed by averages. Subsurface anomalies (see Fig. 1) occur at 750 to 1400, and 1750 to 2450. Two anomalies indicate two producing zones.

method as that used in the hydrocarbon methods. We also tested this theory in the three-dimensional pattern to prove its validity. Such a test will be shown in two of our illustrations (Fig. 3 and 4).

RADIATION METHODS

Long before we had worked out the laboratory procedure for inorganic geochemical surveying, in the summer of 1943 we had already determined the most satisfactory sampling pattern. We had also become painfully aware of the seasonal short-comings of surface hydrocarbon geochemistry. We believed that these seasonal short-comings would be overcome by the use of the inorganic method. This method we put into practice with our first commercial

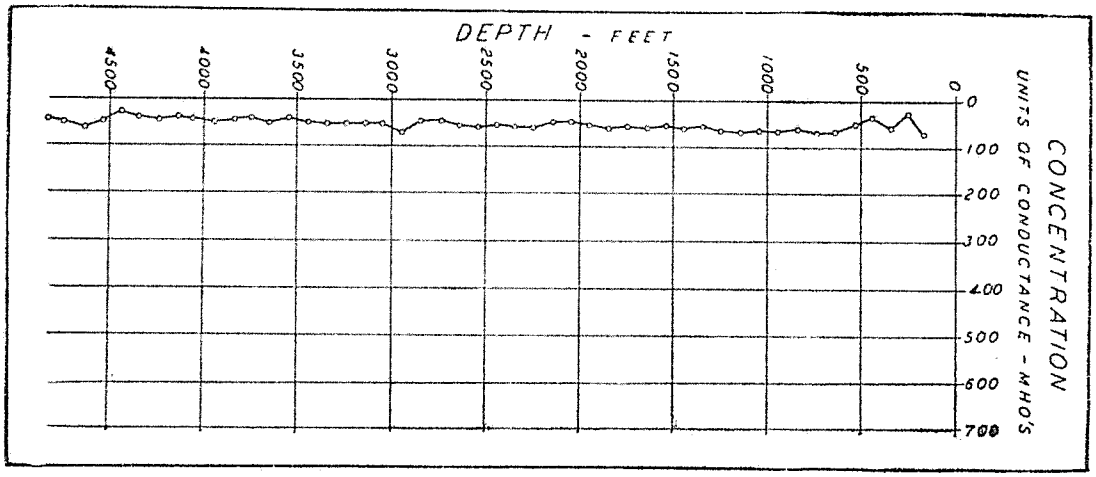


Fig. 4. Inorganic geochemical well log, showing relative concentration of water soluble compounds in well cuttings measured by resistance method of water solutions obtained by leaching. No subsurface anomalies. Dry hole.

report in November 1943, working on a stratigraphic trap. So far as we know our first survey has never been tested. We continued using this new method for four or five years.

RADON METHOD

In the meantime, I believe in 1945, an organization in Coffeyville, Kansas, known as Multiscope Incorporated began experimenting with radiation measurements. Their first experiments were made with an electroscope, measuring the relative amount of radon gas in the surface soil air. This method had already been in use for a number of years with some occasional success. The method was carried on as follows: A small hole was drilled to a depth of two or three

feet in the surface soil. A tube was inserted in this hole with a packer and the soil air extracted by means of a pump which forced this "air" into an ionization chamber containing an electroscope. The relative quantity of radon gas in the soil was determined by the time which elapsed during which the electroscope was totally collapsed. Multiscope Incorporated improved on the electroscope by using a counting device. This method was given a thorough test and was finally discarded because (1) considerable trouble was encountered in setting the packer so as to prevent the dilution of the sample with air drawn around the packer, (2) further interference was found because of the variability of the pore space and (3) variations also entered the problem because of differential quantities of moisture in the soil.

GAMMA RAY METHOD

The company then decided to use gamma ray measurements which could be made on the surface of the ground and thus eliminating problems found in the first method. After a year or two of exhaustive experiments the gamma ray method was put into commercial production. When this company began experimenting with radiation we were invited to join it as a consultant in working out field and interpretation methods. We worked for this company for a number of years before we abandoned the inorganic method and adopted the radiation method. The original reason for the use of radiation in surveying for oil and gas was twofold: (1) to get away from the requirement of collecting soil samples and running them through the laboratory and (2) to avoid the stigma of "soil analysis" and to substitute for it a "more romantic tool". In carrying the laboratory to the field it was felt that we would get away from the possible oversampling or undersampling which always occurred in the geochemical methods and could save both extra expense for the client and unnecessary time making extra trips to complete the pattern. As soon as the radiation method was put into use we began to discover irregularities in the field readings due to various natural conditions. These difficulties were found from time to time and some of them eliminated by improvements in the field methods. They will be enumerated later. Many of these problems have been discussed in an article published in *World Oil*, 1955. The new radiation method was found to yield some excellent results in the early days of gamma ray surveying, but soon history began to repeat itself (Figs. 5, 6, 7, 8, and 9). Some of our major oil companies spent vast sums of money over a period of several years trying to develop this new method as a useful tool to add to conventional screening methods in selecting oil prospects. Some of these companies then gave up the use of gamma ray suvey-

ing largely because of false patterns due to soil inequities. As a result of this, radiation surveying began to fall into disfavor. Consequently, we began to realize that something must be done to overcome this major difficulty, otherwise the method would eventually be discarded.

Instrumentation: At the beginning of gamma ray surveying an instrument was built for this purpose based upon the principle of measurement of gamma radiation by the use of a high pressure gas-filled ionization chamber which operated as follows: the instrument is placed on the ground at the customary sampling point. Gamma rays emanating from the surface of the ground penetrate the tank and ionize the gas in the chamber. The ionization sets up an electrical current which passes through an amplifying system and is then measured by a meter. The measurements were made in either of two manners: (1) by a stop watch measuring the time required to reach a certain quantitative measurement or (2) by measuring the electrical intensity. The values thus obtained were then plotted on the map and contoured in the same manner as previously done with geochemical measurements. These first instruments, many of which are still in use, were built with an ionization chamber carrying about 1000 cubic inches of argon gas with pressures ranging from 300 to 500 ps. It took some time and much ingenuity to develop an ionization chamber with electrical outlets properly insulated and capable of holding such high pressures without appreciable loss of gas content. When finally perfected they were exceedingly sensitive and relatively stable, because of the size of the chamber and the large sampling area. Sensitivity and stability are absolutely necessary because of the low grade of radiation found at the earth's surface. In recent years, following the great demand for radioactive minerals, scintillometers of high sensitivity began to appear on the market. These instruments measure radiation because certain crystals, subjected to radiation, give off flashes of light or scintillations. The degree of radiation is then measured by the degree of scintillation registered by photo-electrical equipment. It was not long before operators began to look upon the scintillometer as a useful tool for oil exploration.

We now turn to the problems connected with radiation surveying as applied to oil exploration. The following are the factors that enter into the satisfactory use of radiation surveying for oil and gas.

Either scintillometers or ionization chambers may be used providing they can meet the following conditions: (1) They must be sufficiently sensitive to record accurately the variations in the low grade radiation found in most weathered soils and to scale the values closely enough to permit the development of a suitable pattern. Normal background radiation intensity measured at various places on the earth is generally understood to be from 0.08 to 0.8

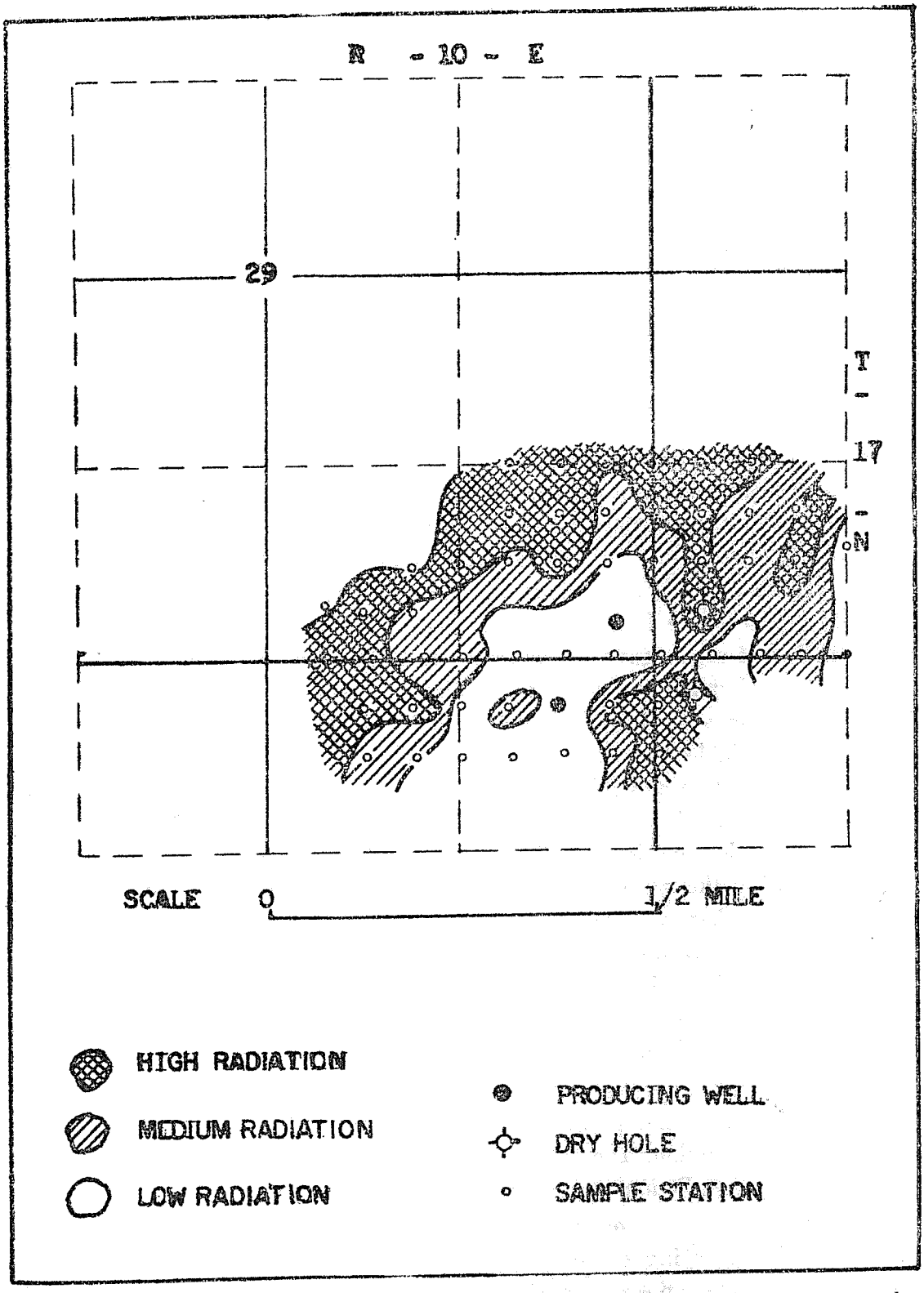


Fig. 5. Gamma radiation map of an area in Creek County, Oklahoma. When map was made the double circled dry hole (farthest northeast on map) was all the development that had been made. This well had a thin sand and was deemed non-commercial. The dark-shaded area comprises the marginal anomaly. Wells in white area came later and yielded about 300 barrels per day open hole test initially, flowing. Dry hole south of original abandoned test missed the sand. This is a stratigraphic trap. (*World Oil*, July 1, 1952.)

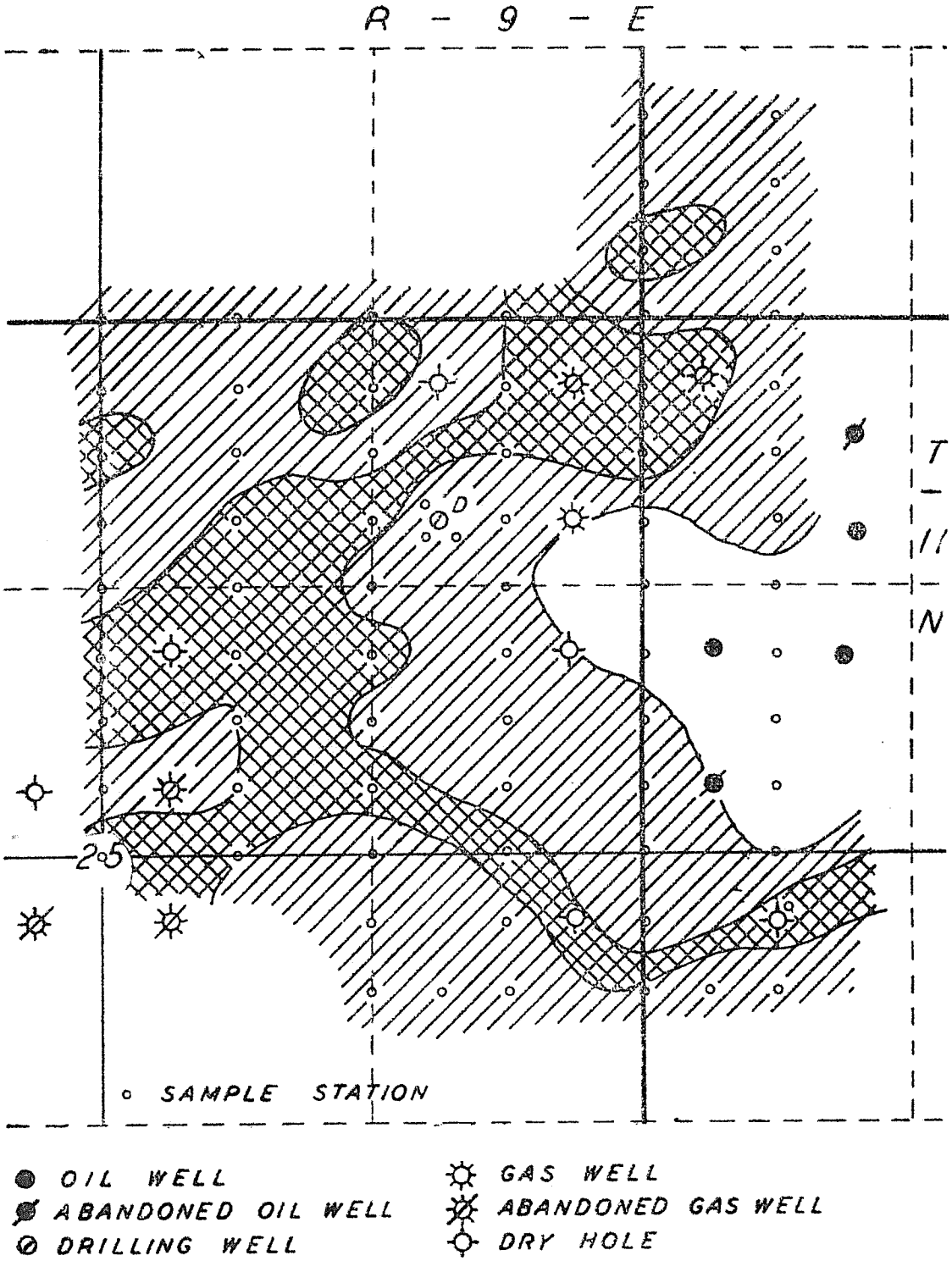


Fig. 8. Surface gamma ray map, Okfuskee County, Oklahoma. The test well marked "D" was being drilled while the survey was run. It was located on a "geophysical high". The dry holes and gas wells in the shaded area are in a very shallow gas sand with light production. These wells cover a large area and do not affect the pattern. The interpreter called the well "D" a dry hole with a light show of oil. When it was completed this interpretation was found to be correct. The well ran as high as the producing oil wells to the east, but the limestone in which the production was found (Hunton lime) was tight with very low porosity and permeability. (*World Oil*, July 1, 1953.)

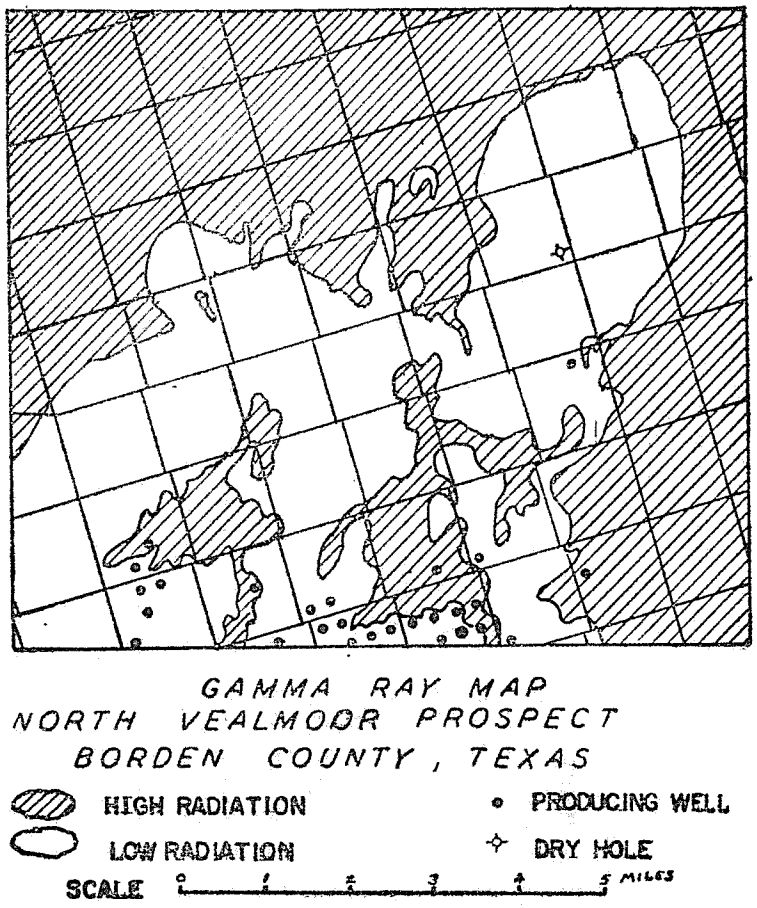
roentgens per year. In order to do satisfactory work, therefore, it will be necessary to develop a measuring device capable of reaching or approaching full scale reading on the lowest average value of radiation encountered. From the above figures the instrument should be capable of a full scale reading of 0.08 roentgens per year or 0.00913 milliroentgens per hour. (2) They must be so constructed as to have a minimum of drift due to temperature and other causes. (3) Because of the irregularity of radiation impulses, they must be so constructed as to make it easily possible to integrate the values to a minimum of variation and a maximum of repeatability. (4) They must be light enough to be easily portable in rough terrains and rugged enough to stay in good condition in handling.

Sampling technique: (1) Accurate location of sample stations is necesary. The use of transit or plane-table equipment is too slow and expensive to be practical, especially in rough country. A good compass and chain survey, tied into well established control points with all circuits closed, will be suitable. A good radiation map is no better than the accuracy of its point locations. (2) The sample pattern, both in plan and density, must be so chosen as to cover all possibilities of shape, size, and condition of the marginal and other anomalies. We find 330 feet intervals in profile lines 660 feet apart is suitable for small fields. In large features the profiles may be 1,320 feet apart. In very small fields and "shoe strings" we recommend a 330-330 grid pattern. (3) The area of the survey should be large enough to cover the potential oil or gas pool and reach well into the surrounding background.

Contamination: (1) Radiation coming from a luminous wristwatch, compass or other instrument. These should never be used by operators or be allowed near the equipment while surveying (2) Fall-out from nuclear explosions sometimes are so radioactive as to keep these sensitive instruments off-scale for days and even weeks until the radiation fades away and resumption of work is possible. These are recognized easily by watching the daily average readings. (3) Showers frequently bring down scattered radioactive particles in sufficiente quantity to materially increase the readings sometimes into the anomaly range. These particles are of such half-life that this effect rarely lasts over twenty-four hours. (4) Approaching cold fronts sometimes affects the readings. These effects, too, are short lived. (5) Cuttings, drilling mud, and well brines are usually excessively radioactive. All sample stations should be selected uphill from drilling wells, oil or gas wells, and dry holes wherever possible and should be at least 100 feet away, so as to avoid contamination.

False readings due to natural causes: (1) Diurnal variations in cosmic readigns. In instruments which do not eliminate cosmic values, account has to be taken of the diurnal cosmic curve. Usually this curve is very flat, and where

average or better anomaly contrasts are found, this curve may be ignored. But where the anomaly contrasts are weak, this curve must be figured out by frequent use of check stations and time corrections. (2) Thin soil above bedrock yields lower readings than thick soil. It has been found that values from soils less than 12 inches thick above bedrock must be adjusted to that thickness. Above 12 inches of soil, however, the values do not materially increase. (3) Rock fragments such as are mingled with soil in talus slopes also require adjustment in values. (4) Unweathered shales do not react like soil. They are frequently highly radioactive. Readings here should be avoided and such stations omitted or the instrument moved to the nearest available 12-inch weathered soil. (5) Granite wash contains solid radioactive materials, which if mixed with soil, greatly increase radiation values. These points must be avoided. (6) Marshy ground through which water seepage is in motion will be washed free of the critical radiation values that normally would be found here. Such areas must be avoided. (7) Dry lake basins. In certain areas, notably the high plains of the Texas Panhandle, there are broad, shallow depressions without drainage. Into these basins all surface waters flow and bring mineral salts with them to accumulate. Here gamma ray readings are usually exceptionally high. The only remedy is to leave these values out. (8) Work done on irrigated areas during or soon after irrigating is not dependable due to leaching, diluting, and transportation of water-soluble radioactive materials. Often such areas must be avoided or, at best, handled with care. (9) Soil interference patterns. (See Figs. 10, 11, 12, and 13). While the problems mentioned above must be overcome or avoided, they may usually be handled without too much difficulty. The one problem which has been found almost unsurmountable and which has destroyed so many patterns that it has driven many operators to give up radiation surveying entirely is the problem of soil interference patterns. It has been observed from the early day radiation surveying that heavy soils yield abnormally high values and light sandy soils abnormally low. Many unsuccessful attempts were made to apply rough corrections for this phenomenon, varying from notations of soil characteristics to a careful study of soil maps. It was soon discovered that soil maps were not sufficiently fine to be useful. The best the interpreter could do would be to try to follow his marginal "high" anomaly through changes of soil by observing points of either side. Reading such a map would be like following in a topographic map the axis of a mountain range with an irregular crest line. Failures in radiation mapping interpretations were so numerous, because of the soil interference patterns developed, that it became evident that something must be done if this promising exploration method were to be of any value.



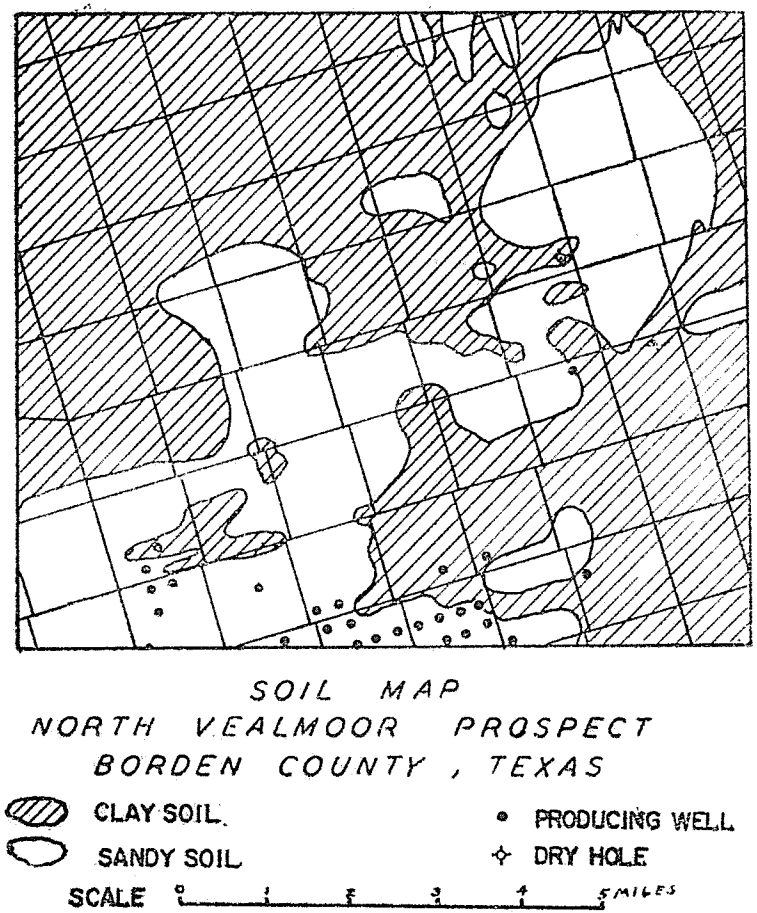


Fig. 10. Gamma ray map and soil map of North Vealmoor area, Borden County, Texas. Gamma ray map on the left shows north end of Vealmoor pool with an area to the north. Note dry hole in center of best looking low-value area. Conclusion: The sandy ground tends to yield low values. (*Petroleum Engineering*, August 1954).

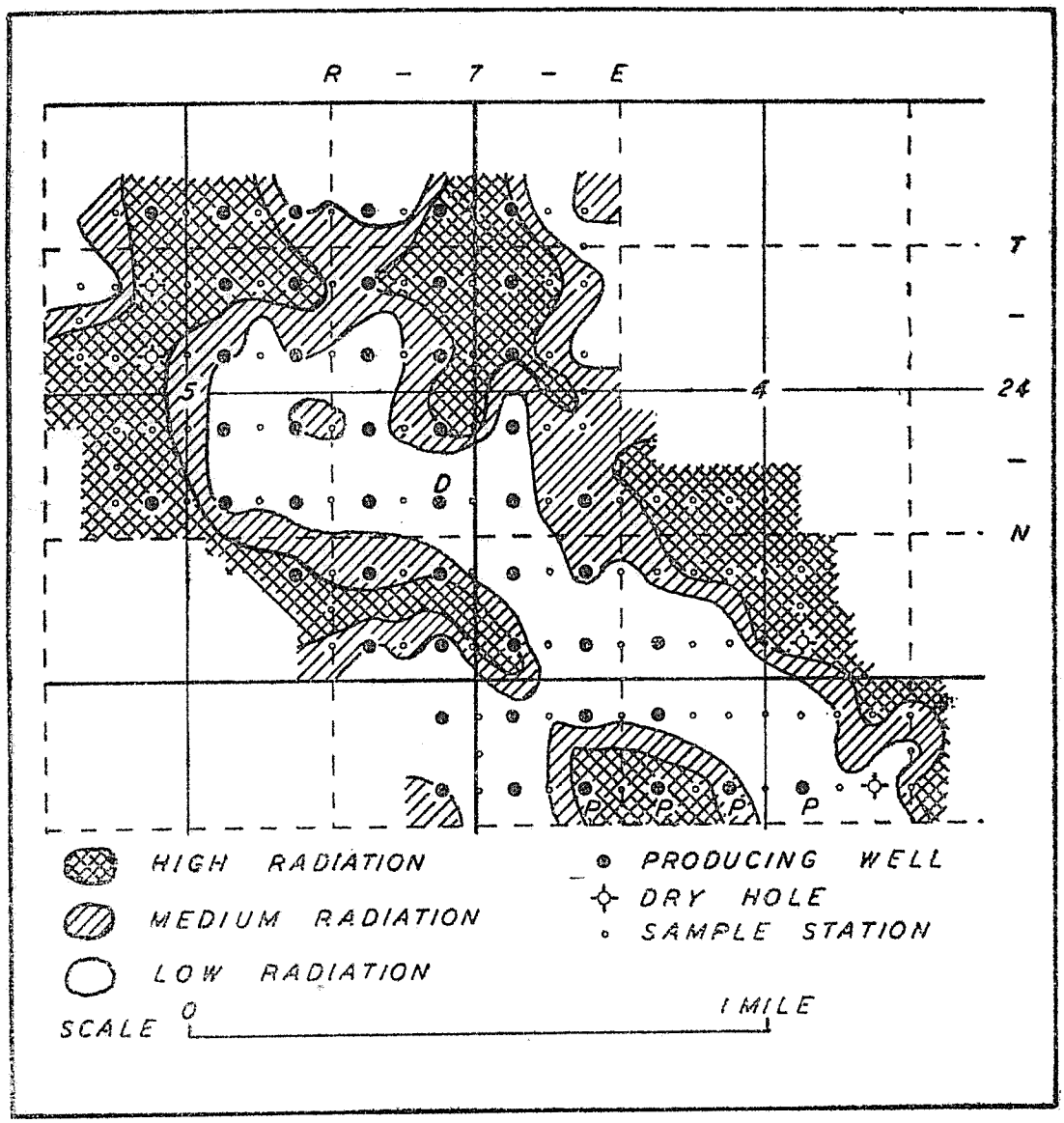


Fig. 11. Surface radiation map of extension of Naval Reserve pool in Osage County, Oklahoma. Map was made when only wells marked "P" were producing and field was under repressuring. Discovery well made upon recommendation after survey is marked "D". It started flowing at rate of 1,500 barrels per day open flow. Note that production passes through and beyond the "marginal" highs. The reason for this lies in the fact that clay soils have caused the development of false marginal highs. The original recommendation indicated the end of the field in Section 5. As a matter of fact, the field actually developed continuously northwestward and northward for several miles. Use of self-potential corrections would have found this and would have been of immeasurable value to the operator who drilled the extension well. (*World Oil*, July 1, 1952.)

Recently a soil classification method useful for this purpose has been developed. A sample of soil is collected at a six inch depth immediately beside or underneath the radiation counter and the container identified with that observation point by number. These soil samples are then brought to a laboratory and prepared for testing. A device has been developed which yields a value which we call a soil radiation self-potential. By comparing the self-potential range in any survey with the radiation range of the same area a correction

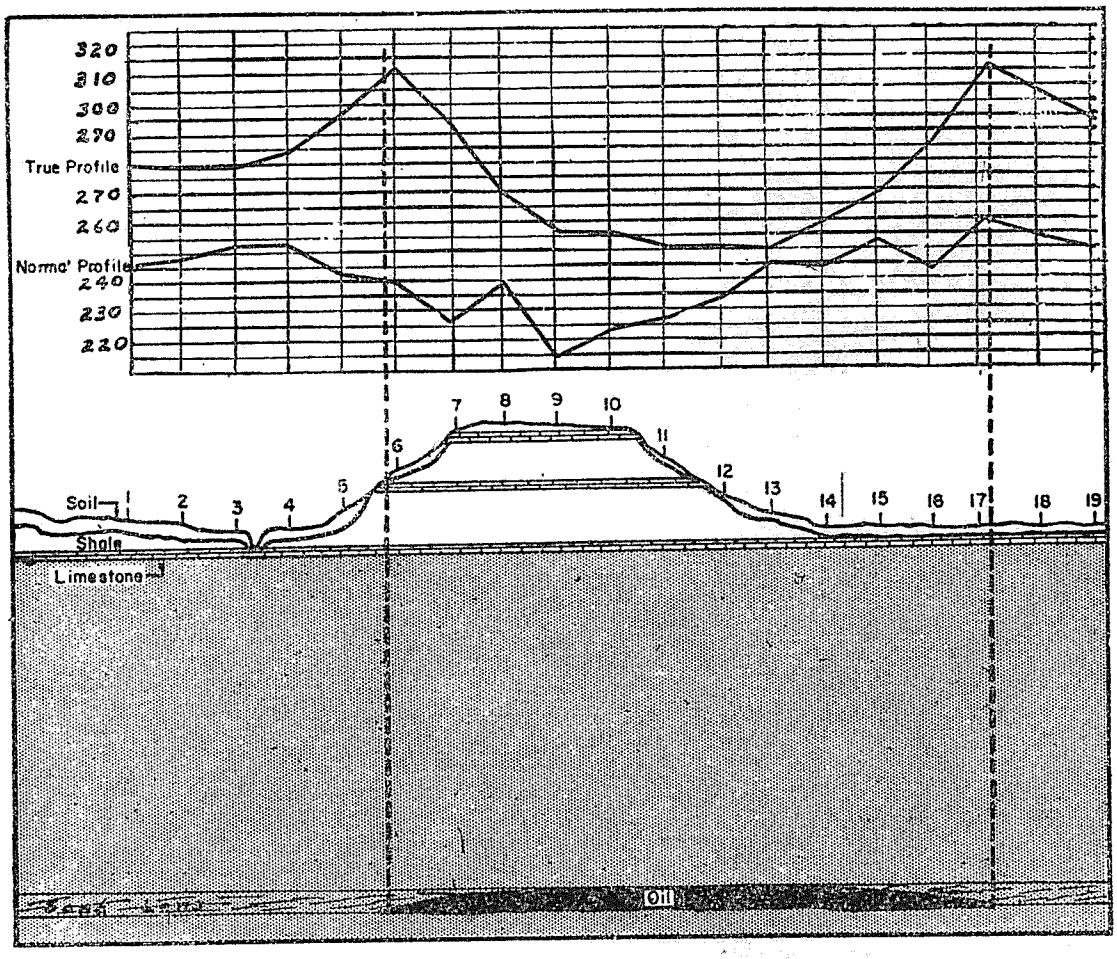


Fig. 12. Geological cross section (generalized) with superimposed radiation profiles. Radiation scale in milliamperes. Work done with ionization chamber equipment. Curves show effect of both soil corrections and also corrections for thin soil over bedrock. Lower profile is original uncorrected readings, with station points 330 feet apart. Upper profile indicates radiation reading after correcting for thin soil and for soil self-potential variations. (*World Oil*, Aug. 1, 1955.)

factor is developed for that particular project. Applying the correction factor to the original field radiation readings the resultant radiation figurse turn out to be the values that should be obtained were all points of radiation measurements taken on uniform soil. This is the same principle that is applied in

subsurface structure mapping by reducing all formation control points to a sea level basis. Several interesting observations have come out of the application of this new method of radiation surveying: (1) In the areas in which we have done this new type of work, mainly, Midcontinent, Great Plains, Gulf Coast, we have found that about 50 porcent of uncorrected surveys are undependable

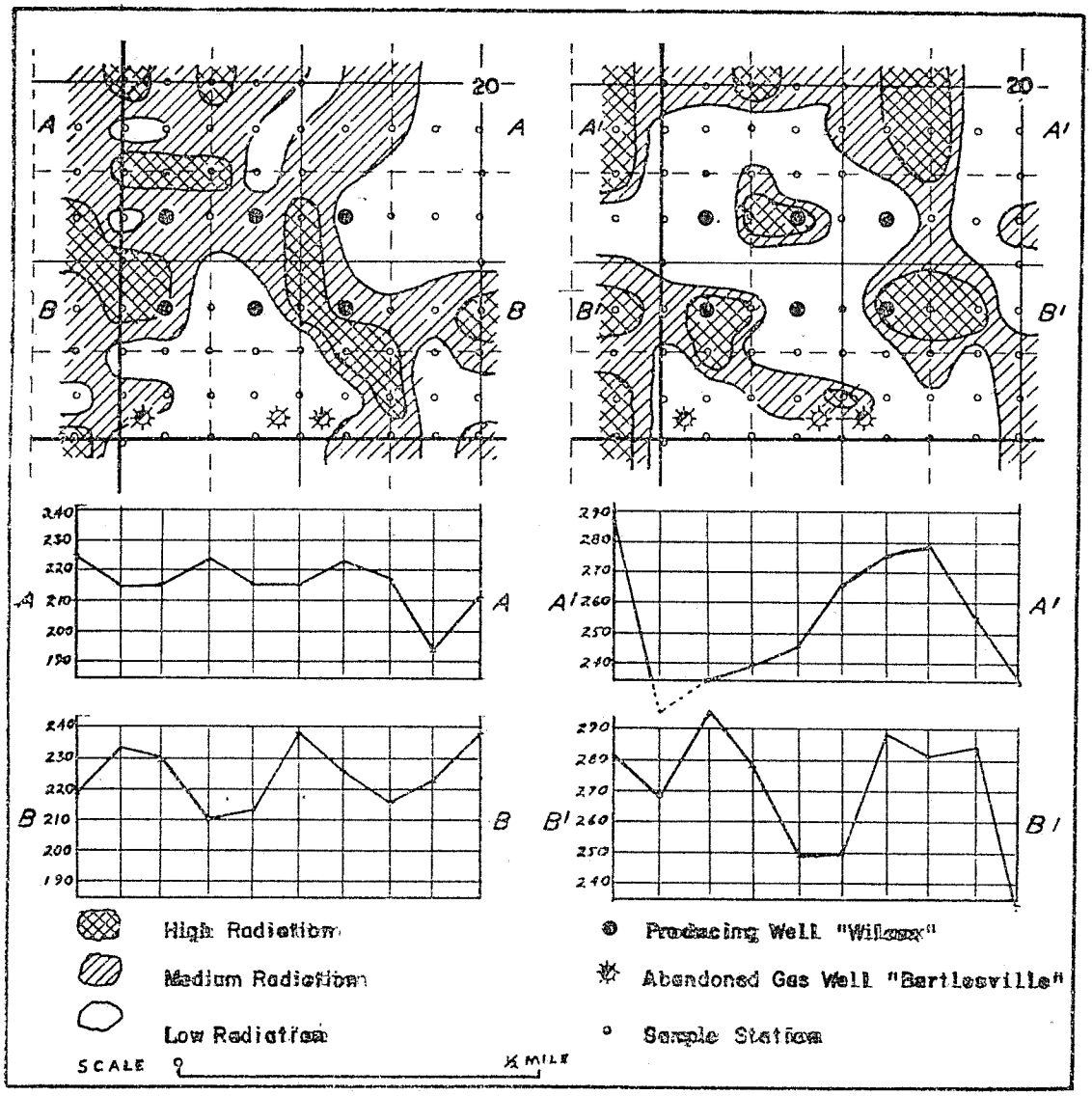


Fig. 13. Surface radiation map of a small producing anticline in Creek County, Oklahoma. The top of the anticline is at the center well in the north row of three. Map at left shows original field values. Map at right shows pattern after applying radiation self-potential corrections. Left pattern was caused by a shallow valley crossing the area from northwest to southeast with fine more or less argillaceous soil while large white areas were underlain by loose sand. Corrections bring out normal marginal high surrounding producing area. Central high is unexplained, but it happens once in a while in normal and corrected patterns. Note increase in radiation contrasts between corrected and uncorrected patterns. Radiation scale is in milliamperes,, and work was done with ionization type hand instrument.

and usually so scrambled as to be unreadable. (2) About 25 percent of our uncorrected radiation maps are approximately half correct so that the interpreter may have a fair chance of reaching a proper conclusion if he has access to good geological information and has a fair amount of good luck in his favor. (3) The remaining 25 percent of our uncorrected surveys require little or no change for satisfactory results. (4) It has been further observed that in practically all cases the application of the correction principle results in stronger contrasts between high and low values, sometimes as much as 50 percent or more increase in range. (5) We have observed that soil changes are so rapid that frequently they require a correction up to 50 percent of the radiation range in distances of 330 to 660 feet.

INTERPRETATION

Assuming that all of the interfering factors may be adjusted to a stable radiation pattern, the problem of interpreting the final results is still by no means as simple as the theoretical basis may indicate. It has been found in geochemistry as well as in radiation work that the outline of production is usually by no means simple. The only time that a simple pattern may be developed is when the entire possible productive zone contains but one producing horizon of uniform porosity and perfect continuity. This is the ideal pattern. We have observed, however, that where several oil or gas horizons occur in the same area, each producing horizon yileds its own individual pattern at the surface so that unless the margins of all producing horizons lie vertically above one another, the resultan radiation pattern will be a composite of all marginal outlines. A multiple-producing area, therefore, is apt to yield a scrambled pattern. This method of surveying is not able, at present, to segregate the zones as to depth. Under such conditions the best results the operator may expect is to outline the entire area and to segregate it from the non productive background. Sometimes the operator may distinguish between different patterns upon the basis of his knowledge of local stratigraphy, especially after some development has taken place, but he should at least be able to determine the outer limits of the total producing area.

Obviously this method is not necessarily dependent upon structre or related to it. Nevertheless, a thorough knowledge of structure and stratigraphy is necessary for the best interpretation results. Sometimes a single horizon because of lenticularity will also yield an irregular pattern with unsuspected inside "highs". The reason for this might not be discovered, except with the use of accurate core records or of electric logs.

We believe that radiation methods using corrections for the above described outside influences offer exceptional benefits to the operator exploring for oil and gas, and go beyond the presently accepted means of conventional exploration, especially in finding stratigraphic traps. We feel that there is still much to learn from future experience as the work expands into more varied fields. The road is open and invites the interested investigator.

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GEOCHEMICAL PROSPECTING FOR PETROLEUM

L. HORVITZ *

ABSTRACT

Geochemical prospecting for petroleum involves the application of chemical methods to the search for oil. Soil, or soil air, is the sample medium which is analyzed for various constituents. Liquid and wax-like organic substances are extracted from the top-soil while various inorganic constituents are found below the surface. Any relationship of these components to petroleum at depth is based on upward migration of volatile hydrocarbons from the petroleum reservoir to the surface of the earth. Because of this fundamental requirement, the gaseous hydrocarbons themselves, rather than modified by products, are considered the most significant and reliable of the diagnostic constituents of the soil. The concentrations of the hydrocarbons tend to increase with depth and, therefore, samples are collected below the surface, usually within a depth range of eight to twelve feet. Microanalytical techniques are employed to detect and measure the hydrocarbons.

Experimental data are presented which show a close relationship between methane and organic matter in the upper few feet of soil. The presence of appreciable amounts of ethane and heavier hydrocarbons, however, is more readily explained by a petroleum source.

Several hydrocarbons surveys, in different petroleum provinces, are presented. Anomalies which have been confirmed by oil discoveries are included.

INTRODUCTION

The exploratory methods that fall in the category of geochemical prospecting are those that involve the use of chemical techniques. In one such method, liquid and waxy materials (Horvitz, 1939; McDermott, 1939) extracted from the top-soil with organic solvents, are used as petroleum indicators. Another method is based on the determination in deeper samples of acid and water soluble inorganic salts (McDermatt, 1939). Others involve the determination of a fluorescent material (Campbell, 1946), carbonates, reduced iron (Horvitz, unpublished) and unidentified substances (Ransome, 1947). Actually, there are as many geochemical methods as there are constituents of the soil, and yet, all of these techniques have one fundamental requirement in common: that the lighter of the hydrocarbons which make up as and oil accumulations migrate

* *Horvitz Research Laboratories, Houston, Texas.*

from the deposit to the surface of the earth. The waxy and liquid materials may be formed through oxidation and subsequent polymerization of these hydrocarbons. The accumulation of inorganic constituents in the immediate subsurface may also be associated with hydrocarbon migration. The present paper, however, is not concerned with the evaluation of these secondary products.

The presence near the surface of volatile hydrocarbons, themselves, and their suggested relationship to petroleum accumulation at depth are phenomena that are considered of much greater interest and significance.

The first real attempt to relate near surface hydrocarbons to oil and gas deposits was made in 1929 by Laubmeyer (1933) a German, who described methods for collecting samples of soil air from systematically located bore holes and analyzing them for traces of methane. The bore holes were dug to depths of 1 to 2 meters and sealed. After allowing 24 to 48 hours for the composition of the enclosed air to reach equilibrium, a sample of this air was extracted for analysis.

Later, in 1932, a group of Russian (Sokolov, 1935) investigators became engaged in similar work. Their field procedure involved reducing the pressure in the bore holes and then collecting a sample of soil air by displacement of water in a suitable container. These samples were found to contain heavier hydrocarbon gases as well as methane. This was an important advance over Laubmeyer's method because methane might be present in the soil air as a result of decaying vegetation. The data of both Laubmeyer and the Russians indicated that the soil air over oil and gas accumulations was enriched in hydrocarbons.

Americans (Horvitz, 1939; Rosaire, 1938) became interested in this new approach to petroleum prospecting in 1936. Instead of collecting samples of the soil air in the field, a technique was developed whereby samples of the soil, itself, were collected and analyzed. Not only were much larger quantities of petroleum gases found than those reported by the Russian investigators, but heavier, saturated hydrocarbons were detected. An important advantage of this technique is that samples may be collected under practically all conditions.

FIELD AND LABORATORY PROCEDURES

In conducting a survey, sample locations are first staked over the area to be investigated. Care is taken to locate the stations at considerable distances from roads, pipelines, drilling wells, and other sources of contamination. The bore hole may be dug with a bucket-type hand auger or with mechanical drilling equipment. In either case, lubricants are avoided. When the desired depth is reached, a sample is brought to the surface, placed in a pint glass jar

or can, securely sealed, labeled and delivered to the analytical laboratory. Generally, a satisfactory sampling depth range is 8 to 12 feet. Satisfactory data are obtained in some regions from samples collected at much shallower depths. Such is the case, for example, in a large part of west Texas where the limestone and caliche near the surface occlude hydrocarbons and prevent their rapid escape to the atmosphere.

In carrying out broad reconnaissance surveys in search of large features, considerable time is saved by first taking samples one-fourth to one-half mile apart along profiles about one mile apart. If the analytical data indicate a hydrocarbon anomaly of interest, additional samples are taken to produce a more dense and uniform sampling pattern within the interesting area. This program is particularly adaptable to areas that are sectionized. In areas covered with a network of roads, sampling along these roads facilitates the reconnaissance survey. The actual sampling density that is used depends upon the areal extent of the features expected. For example, when sampling flanks of piercement-type domes, where accumulations may be only several hundred feet wide, stations are often no more than 200 feet apart.

The gases are extracted from approximately 100 grams of undried sample in a partial vacuum and at temperatures below 100 C. in order to prevent decomposition of any organic matter that may be present. A weak acid, such as phosphoric, is employed to release the hydrocarbons from the soil more efficiently.

The extracted gases are passed through potassium hydroxide solution, concentrated sulfuric acid and, finally, through phosphoric anhydride before they are separated into two fractions, one containing the methane and the second containing the ethane and heavier hydrocarbons. The separation is effected under a high vacuum at a temperature of - 196 C. At this temperature, methane is non-condensable while the ethane and heavier hydrocarbons are trapped. The quantity of methane present is calculated from the amount of carbon dioxide produced when the non condensable fraction is burned over a hot platinum wire in the presence of pure air or oxygen. The ethane and heavier hydrocarbon fraction is volatilized and its volume is measured with a sensitive McLeod gauge and then burned over a hot platinum wire in the presence of oxygen. The gain in volume of the carbon dioxide, produced by combustion, over the initial volume is a measure of the quantity of ethane and heavier hydrocarbons present. The analytical results are expressed in parts per billion by weight on the dry sample basis. The moisture content, required for the calculations, is determined from a portion of sample separate from that used in the analysis.

DISCUSSION

In determining if a relationship exists between near surface hydrocarbons and petroleum accumulation at depth, important producing fields such as Hastings (Horvitz, 1939, 1954), Friendswood (Horvitz, 1939) and Heidelberg (Horvitz, 1954) were sampled. The hydrocarbon distribution patterns observed in these cases are of the type which contain low hydrocarbon values over the central portions of the anomalies with relatively high concentrations at the edges, and low values again in the background areas, a pattern frequently referred to as a "halo". Because anomalies of this type alone were at first considered significant, errors in interpretation occurred. After a great deal of data were accumulated, it became apparent that commercial oil accumulation may be associated with anomalies composed entirely of intermediate and high values which are surrounded by low, background values. However, even this type of anomaly, which suggests migration to the surface from the entire deposit, frequently contains the highest values at the edges, indicating that maximum leakage occurs there.

Several different hydrocarbon distribution patterns appear in Fig. 1 which includes a portion of a large survey conducted in parts of Wharton, Matagorda, and Jackson Counties, Texas and completed in April, 1945. The portion of the survey that is presented includes 748 stations which were sampled at 10 feet over an area of 50,000 acres. Values shown on the map at the respective station locations are for ethane and heavier hydrocarbons expressed in parts per billion by weight. In this figure only the development, as of the time the data were obtained, is shown. To simplify the presentation of the data, only the contour lines enclosing values ranging from 100 to 199 and values of 200 parts per billion and above are included. The present map is very similar to the original in spite of the fact that contours enclosing values below 100 parts per billion are omitted. The reason for this is that the background values are relatively low, averaging less than 25 parts per billion, the usual range for most of the Gulf Coast. To display the variations in hydrocarbon concentrations over area sampled, those areas containing values above 100 parts per billion have been shaded. The lightly shaded areas contain values from 100 to 199 while the more heavily shaded areas include values of 200 and above. Values below 100 parts per billion are in the unshaded areas.

As pointed out previously, only halo type anomalies, the centers of which contain values of the same low order magnitude as those of the background, were first considered of importance. As a result, the first interpretation of the data presented in Fig. 1 suggested, as favorable, the elongate area of low concentrations which centers to the northeast of the intersection of the three

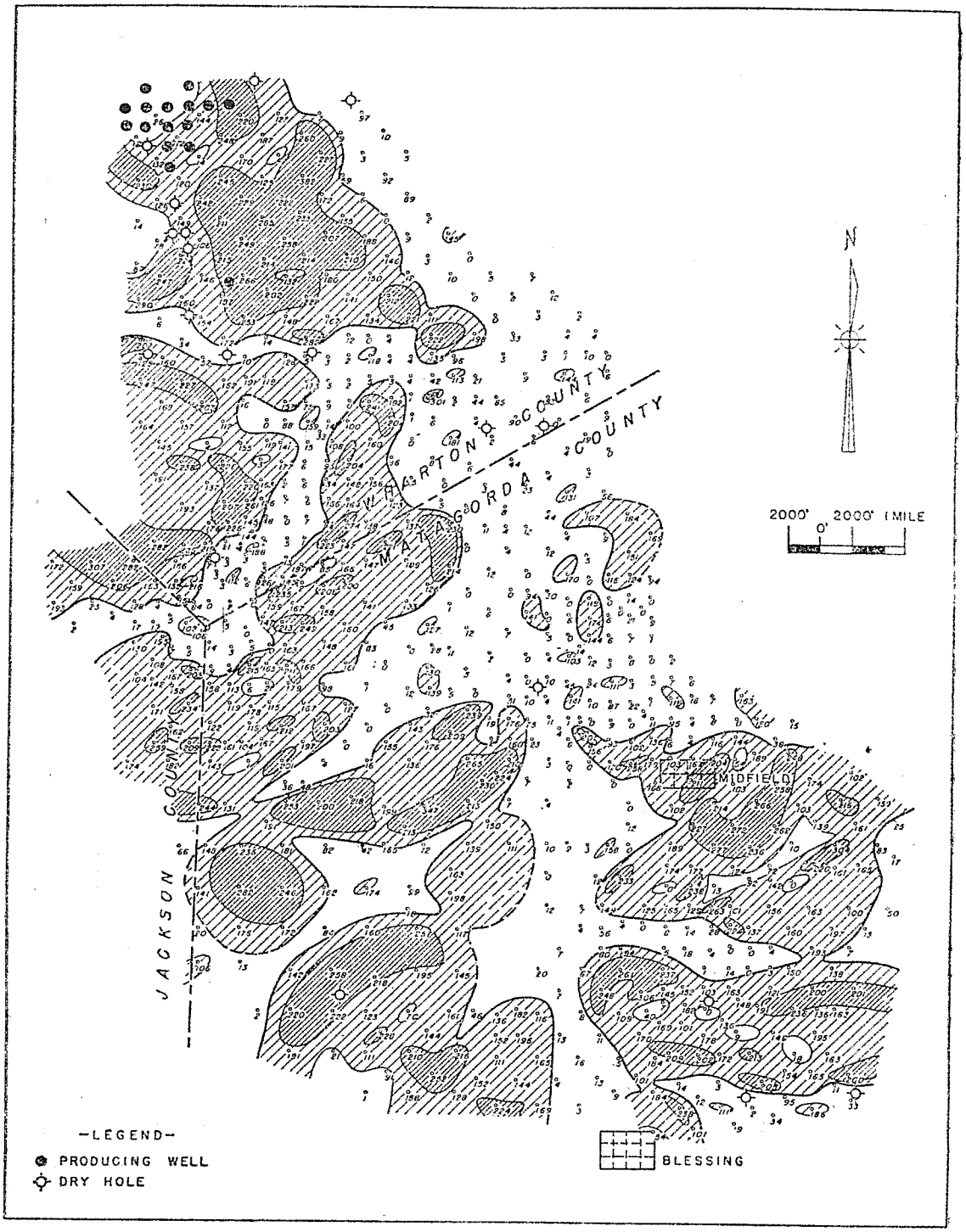

Fig. 1. Ethane and heavier hydrocarbon data obtained in 1944-1945 over an area in the Texas Gulf Coast. A number of well defined anomalies are readily recognized. Well symbols show development as time data were acquired.

counties. The failure of a test well which was drilled within this area, followed by the development of the South Hilje oil field which is associated with the area of high concentrations in the northwest part of the survey, attracted attention to the non-halo type of anomaly. The discovery of the Midfiel and Tidehaven fields, to the northwest and northeast of the town of Blessing, respectively, confirmed the importance of this type of anomaly. Because most of the area included in the survey was barren of production when sampling was completed, the possibility that the hydrocarbons are present in the soil through contamination by producing wells is eliminated.

Fig. 2 shows the development that has taken place in the area to August, 1956. In addition to the fields previously mentioned, South Hilje (A), Midfield (C), and Tidehaven (D), more recent confirmations of the data resulted by discovery of the Denman (B), North Tidehaven (E), Midfield Townsite (F) and Arch (G) fields, the last being the only one associated with an anomaly suggesting the halo type.

In addition to the anomalies which are now associated with petroleum, a number of others, also believed to be produced by subsurface hydrocarbon deposits, are apparent. The most favorable portions of these have been shaded in gray. Only one anomaly has apparently been condemned by the drill. In those parts of the survey where a reconnaissance sampling density was employed, the interpretation may be modified by additional data.

It is interesting to observe that at least 45 dry, wildcat wells were drilled in the background, or negative, areas. Thirty five of these dry holes were drilled after the data were obtained. Even some of the dry holes that fall within the anomalous areas, but close to their edges, could have been eliminated on the basis of the data. Thus far, all of the fields that are producing in the area sampled, especially the more important ones such as South Hilje (A), Midfield (C), and Tidehaven (D), are associated with well defined anomalies of high contrast. Of the untested anomalies, only a few are comparable with these, the remaining being of small areal extent. Others, such as the anomaly immediately to the northwest of the town of Midfield, are not considerad of sufficient importance to be included among those shaded.

In the lower part of Fig. 3 are shown the ethane and heavier hydrocarbon data, expressed in parts per billion by weight, that were obtained in the vicinity of the Bonney oil field of Brazoria County, Texas from samples collected at 9 to 12 feet. The following groups of values are enclosed by the various contour lines: 75-99; 100-149; and 150 and above, Several degrees of shading have been used to display the variations in hydrocarbon concentration; the heavier the shading, the higher the range of values. This area was selected as prospective on the basis of a reconnaissance survey completed in 1948, several years prior to

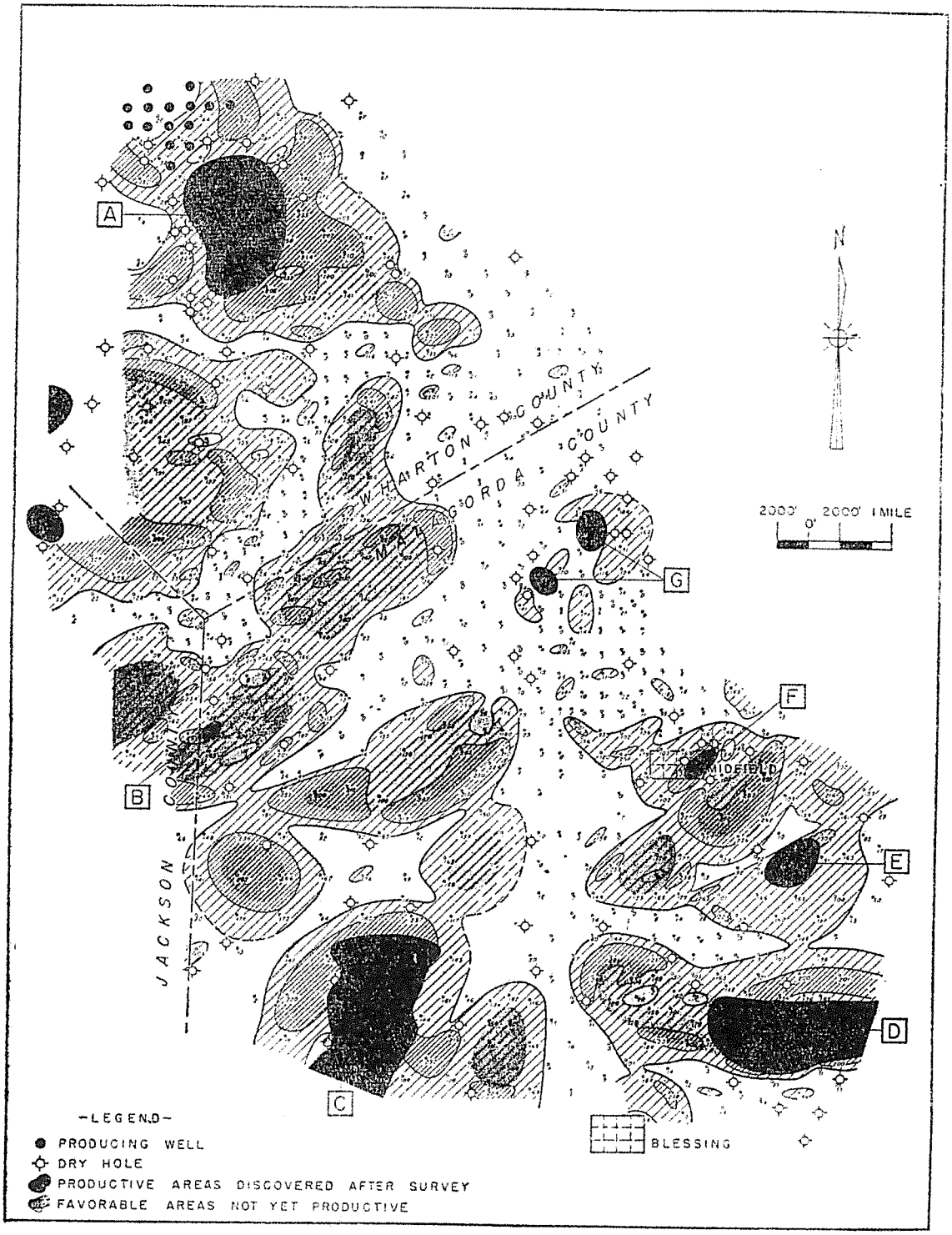

Fig. 2. Same area as that shown in Fig. 1 to which has been added results of drilling to August, 1956. The oil fields, discovered after completion of the survey, fall within anomalous areas. Numerous dry holes were drilled in the background, or negative, area. A number of anomalies have not yet been tested.

the discovery of the field. More recently, during 1955, additional experimental work was undertaken in this area in connection with a study of the relationship of hydrocarbons to organic matter in near surface soils. Those stations which were sampled in the early survey are indicated on the map by double circles. In the recent work, samples were collected along profile A-A', at the locations indicated, from the surface and at two foot intervals down to and including 12 feet. The samples were analyzed for methane, for ethane and heavier hydrocarbons and for sand content as well as for organic matter (U.S. Salinity Lab., 1954). In addition to the samples taken along the profile, a number of others were taken over the area at approximately 12 feet in order to complete the hydrocarbon survey.

In the upper part of Fig. 3, data for each of the samples taken along the profile are shown in graphic form. For the case of methane (M), and ethane and heavier hydrocarbons (E), each unit on the horizontal scale represents 100 parts per billion by weight. The distribution patterns for organic matter (O), expressed in percent, are all alike. For each station, the largest quantity occurs in the top-soil with rapidly decreasing quantities down to six feet where it practically disappears. Patterns similar to those produced by organic matter are apparent for methane for the upper part of most holes. Within this same zone, however, the ethane and heavier hydrocarbons are all present in very small amounts. The data, therefore, tend to link methane to organic matter in the upper few feet of each hole, but for the case of ethane and heavier hydrocarbons, no such relationship exists. The first two holes, located in the background area to the southwest of production, contain relatively small amounts of hydrocarbons and organic matter below four feet. Not until the third station of the profile is reached, do appreciable amounts of ethane and heavier hydrocarbons appear. Here, too, the methane begin to appear in the lower parts of the holes. Of more than passing interest is the fact that the first appearance of ethane occurs at the edge of the Bonney oil field. The change in methane patterns for the lower parts of the holes, where the organic matter is negligible, also occurs here. The conclusion seems warranted that the ethane and heavier hydrocarbons originate in the petroleum deposit itself. The same source is suggested for the methane in the lower portions of the holes. While the patterns produced by the different constituents are readily apparent, it is difficult to determine the various values from the figure; therefore, Table I is included to show the actual analytical values that were used in plotting the depth profiles. The sand contents of the samples have been included with the data for hydrocarbons and organic matter. All material retained on a 200 mesh sieve was classified as sand.

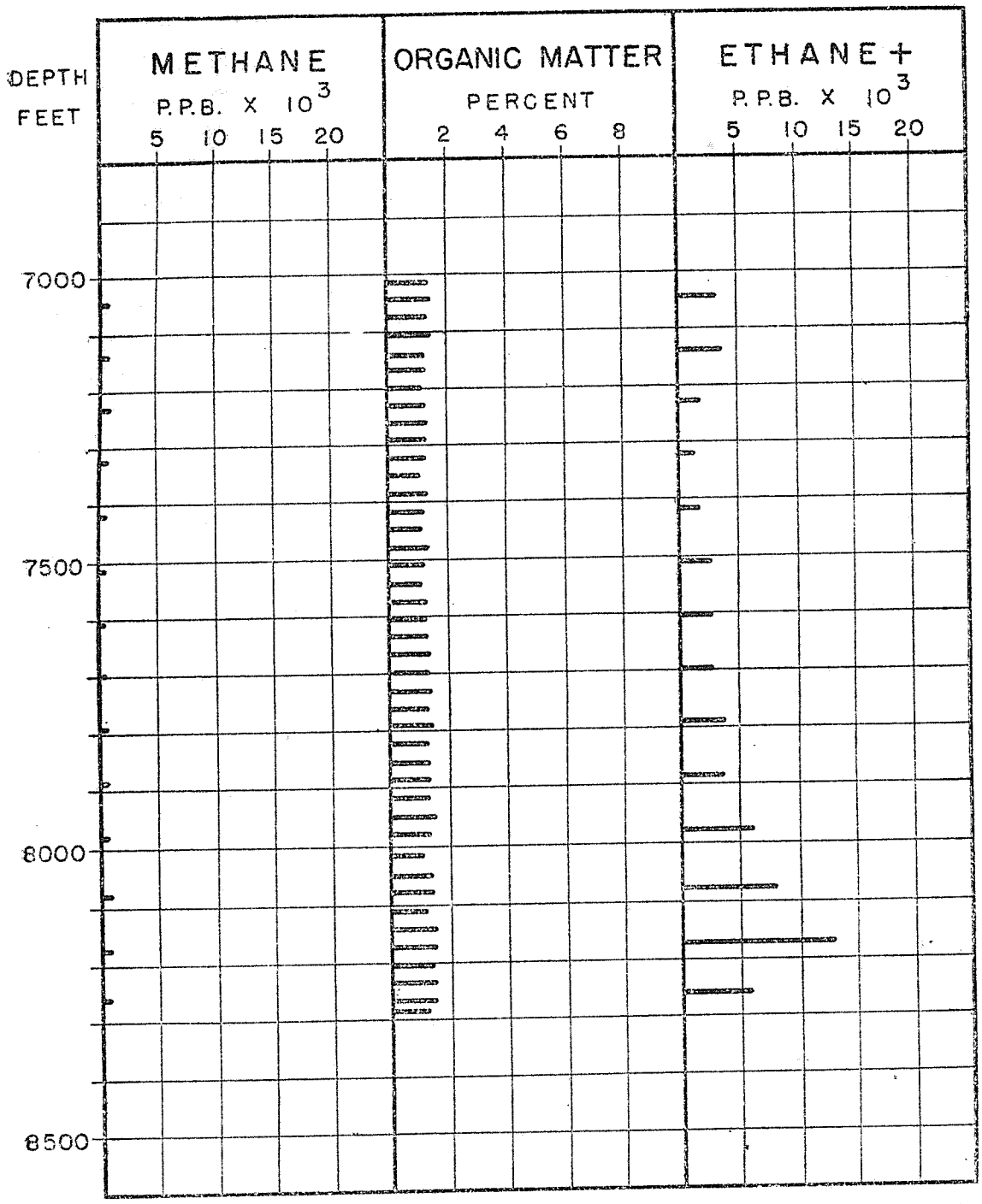

Fig. 4. Graphic representation of data yielded by cuttings from a well in the Martha oil-field, Liberty County, Texas. Well cuttings yield uniform values for organic matter while ethane and heavier hydrocarbons show distinct increase with depth. A commercial oil deposit, encountered within section which produced highest ethane and heavier hydrocarbon value, suggests source of buildup.

Returning again to the lower part of Fig. 3, it is noted that the distribution pattern produced over the Bonney oil field is an incomplete halo with relatively high hydrocarbon concentrations around all sides except the northwest. A fault, upthrown to the southeast, limits production on this side of the field. The low concentrations suggest that hydrocarbon leakage across the fault plane is restricted. This phenomenon has been noted on a number of other occasions and suggests that a zone of reduced permeability occurs at the intersection of a fault and petroleum accumulation.

In order to determine if a relationship exists between organic matter and hydrocarbons at greater depths than those included in Fig. 3, a series of cuttings, collected at 30 ft. intervals from the No. 4 Seaberg, one of the wells completed by Gulf Coast Leaseholds, Inc. in the Martha oil field of Liberty County, Texas, was analyzed for organic matter after hydrocarbon determinations were made on separate portions of composite 90 foot samples. The data are included in Table 2 and are presented graphically in Fig. 4. Only small variations in organic matter were observed for the entire section for which samples were available. Methane, as is usual for well samples, was found in reltively small amounts. The ethane and heavier hydrocarbons, however, show a distinct buildup down to 8220 ft., below which the hydrocarbon concentrations decrease. There is no apparent relationship between the organic matter and the hydrocarbons, particularly those heavier than methane. The only explanation for the hydrocarbon buildup that appears logical to the writer is the presence of a commercial petroleum accumulation at 8178 - 8193 ft. Additional data which link hydrocarbons above a deposit to the deposit itself, have previously been presented (See Horvitz, 1954). The percentage of sand for each of the cutting samples was determined and the results are included in the table.

Fig. 5 shows the ethane and heavier hydrocarbon data obtained in the vicinity of the Little Beaver oil filed of Washington County, Colorado, which was discovered in 1952. The survey, conducted in the Fall of 1954, includes 175 stations sampled at 12 feet. The contounr lines enclose values ranging 50-99, 100-149, and 150 parts per billion and above. Although the data are limited, a large anomalous area is easily recognized in the east half of the area sampled. The highest concentrations tend to be located at the edges of the anomaly with values of an intermediate range over the central portion, suggesting a halo type pattern. To the southwest of the main feature, a small anomaly is apparent and to the east a lead is developing.

Fig. 6 shows the same data as that of Fig. 5 together with the development that has taken place to August, 1956. The large producing area representing the Little Beaver oil field is seen to have a configuration very similar to that produced by the hydrocarbon data, and the small anomaly to the southwest is

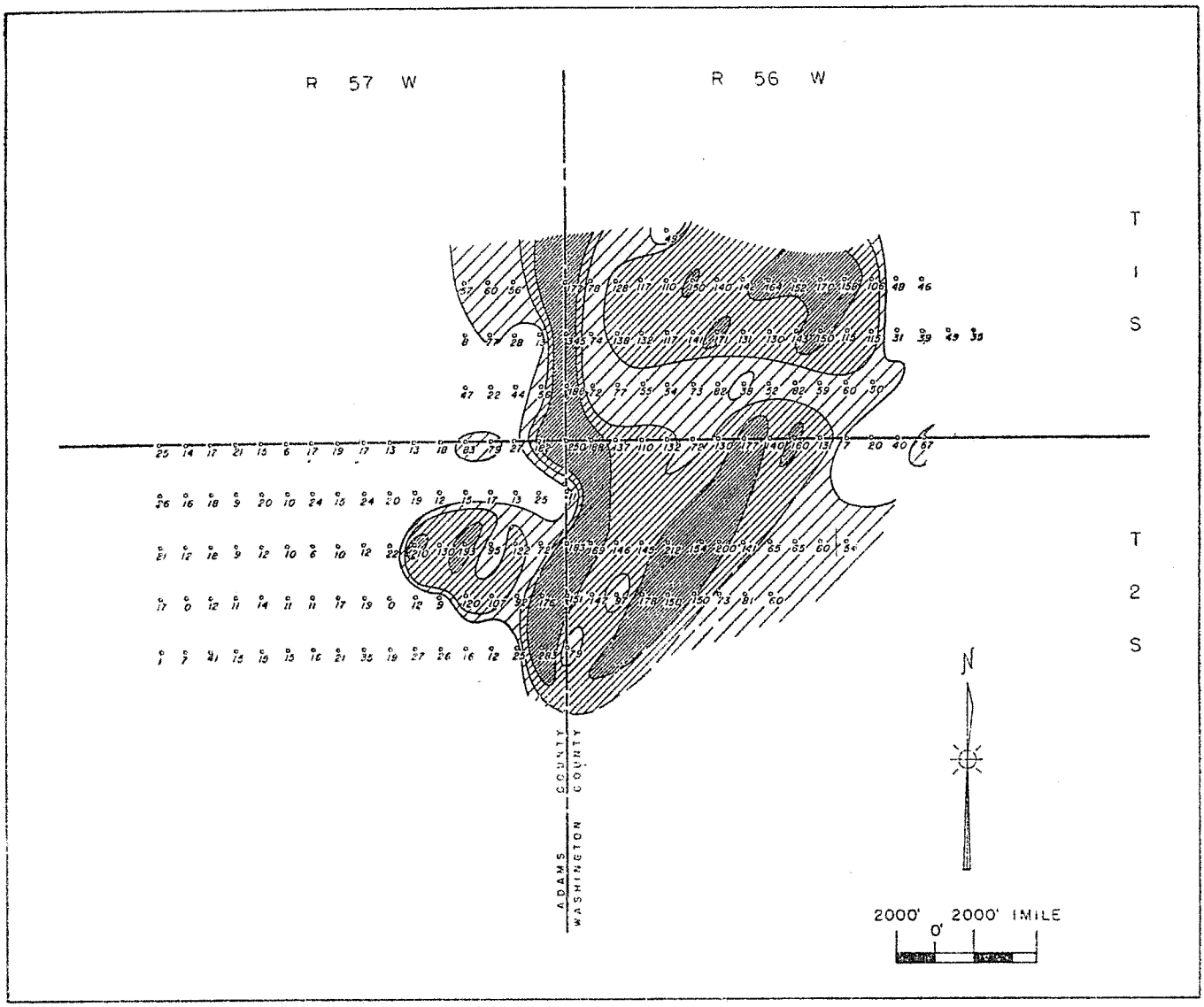

Fig. 5. Ethane and heavier hydrocarbon data in the vicinity of the Little Beaver oil field, Denver Basin, Colorado. Strong anomalous area which resembles those of other petroleum provinces is easily recognized.

associated with a very small producing area. This survey suggests two interesting observations. First, the ranges of values that are associated with both the anomalous and background areas are the same as those obtained in other petroleum provinces. For example, they are similar to those of the areas located in the Gulf coast of Texas which appear in Figs. 1 and 3 and which contain entirely different geologic sections. Another matter of interest is that the type of trap which produced the Little Beaver oil field is a permeability pinchout across a slight structural nose. This kind of trap can normally be located only by random drilling.

SUMMARY

1.—All geochemical methods of prospecting for oil and gas require that the lighter of the hydrocarbons that make up the sought deposit migrate vertically to the surface of the earth. The present paper discusses that geochemical technique which involves the determination of the hydrocarbons, themselves, in near surface soils.

2.—The data presented show a close relationship between near surface hydrocarbons, especially those heavier than methane, and the buried deposit. In general, the better oil fields produce halo type anomalies in which relatively high hydrocarbon concentrations border an area of low or intermediate values. Surrounding this type of anomaly is an area of low background values. Another pattern that has been recognized is one in which an area of uniformly high concentrations is surrouded by relatively low background values. For the case of all types, the hydrocarbon anomaly is usually larger in areal extent then the deposit that produces it.

3.—Experiments indicate that methane may be produced from organic matter, but the presence in near surface soils of appreciable amounts of ethane and heavier hydrocarbons cannot be explained away in this manner. The data presented suggest subsurface petroleum deposits as a logical source.

4.—From the hydrocarbon distribution pattern, it is not possible to predict the depth to a deposit nor the type of trap which contains it. Anomalies produced by deposits associated with structure.

5.—The data presented represents only a small part of the experience which suggests that the chance of finding a petroleum accumulation under a hydrocarbon anomaly is good, while the chance of finding an accumulation in the background (negative) area is poor.

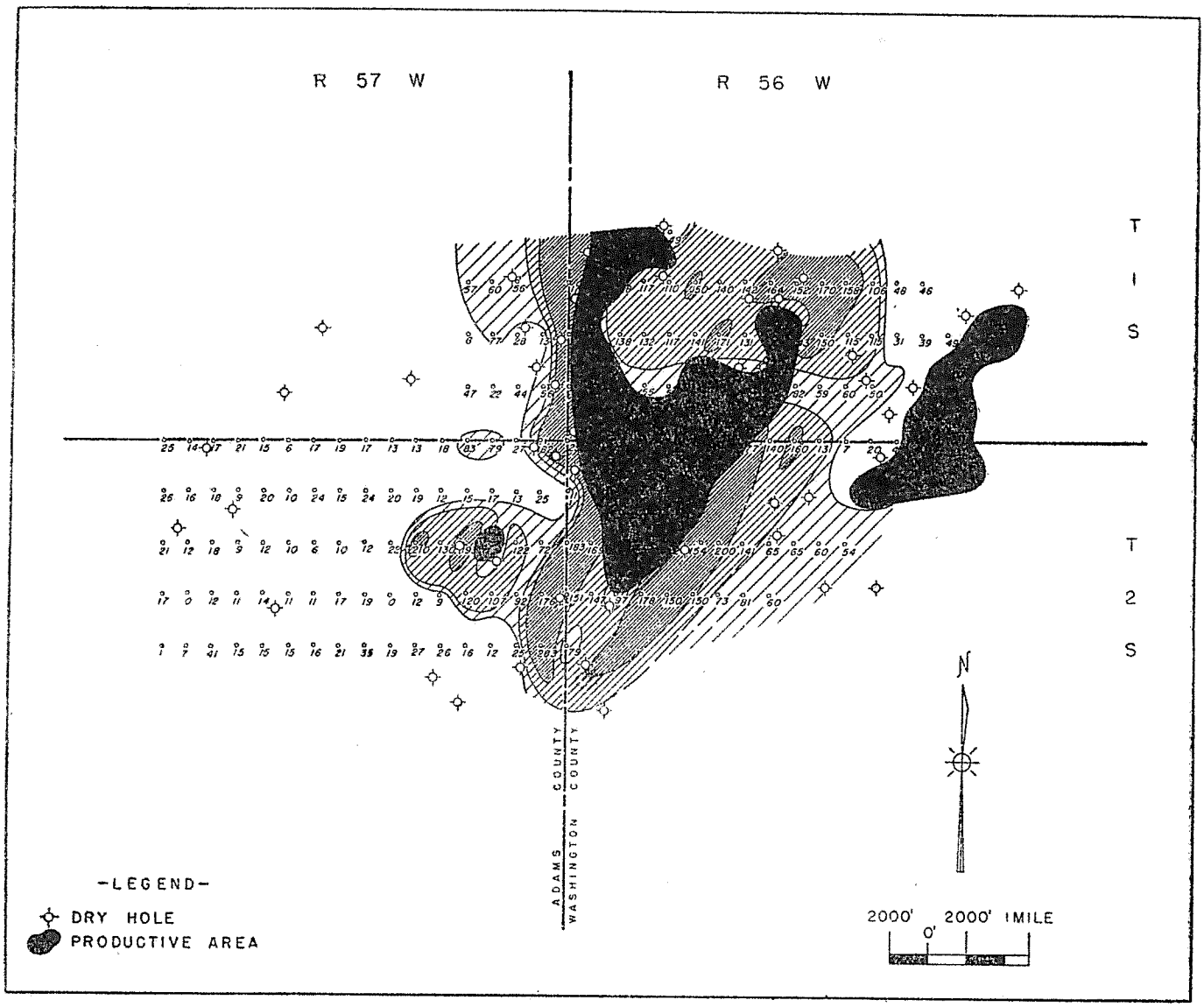

Fig. 6. Same area as that of Fig. 5 to which has been added the development to August, 1956. Configuration of the hydrocarbon anomaly is similar to that of Little Beaver oil field. Small anomaly to the southwest of main feature is associated with a minor producing area. Hydrocarbon data were acquired after discovery of Little Beaver but before discovery of field to east.

TABLE I

RELATIONSHIP OF HYDROCARBONS TO ORGANIC MATTER IN NEAR SURFACE SOIL

Station	Depth (Feet)	Methane (P.P.B. by Wt.)	Organic Matter Percent	Ethane + (P.P.B. by Wt.)	Sand Percent
1	Surface	207	2.72	11	12.0
	2′	104	1.79	6	6.4
	4′	118	1.33	10	6.0
	6′	81	0.36	18	2.4
	8′	38	0.16	2	28.4
	10′	42	0.10	1	32.8
	12′	50	0.05	3	54.0
2	Surface	214	4.89	13	18.4
	2′	161	1.48	7	8.4
	4′	72	0.69	9	8.0
	6′	92	0.26	1	12.0
	8′	66	0.10	4	16.8
	10′	56	0.08	15	71.6
	12′	49	0.06	3	62.8
3	Surface	201	3.53	6	11.2
	2′	123	1.76	11	6.8
	4′	71	0.72	9	5.2
	6′	173	0.22	6	10.4
	8′	112	0.13	4	5.6
	10′	182	0.11	105	17.2
	12′	280	0.12	167	18.0
4	Surface	83	3.99	11	6.4
	2′	64	1.62	18	4.0
	4′	91	0.69	11	8.0
	6′	63	0.21	28	5.6
	8′	301	0.22	90	4.0
	10′	164	0.13	73	9.6
	12′	76	0.20	9	12.0
5	Surface	122	2.73	12	4.8
	2′	108	2.02	17	4.0
	4′	150	0.66	8	5.2
	6′	157	0.38	11	5.2
	8′	138	0.17	6	8.0
	10′	365	0.16	109	4.4
	12′	145	0.18	81	10.0
6	Surface	203	4.14	10	2.4
	2′	141	2.54	9	3.6
	4′	72	1.50	10	2.4
	6′	52	0.34	5	2.0
	8′	56	0.18	1	2.8
	10′	89	0.12	12	4.4
	12′	49	0.13	14	11.6
7	Surface	168	2.58	8	—
	2′	129	2.23	3	2.8
	4′	78	1.27	8	2.4
	6′	59	0.30	0	1.6

TABLE I (Continued)

RELATIONSHIP OF HYDROCARBONS TO ORGANIC MATTER IN NEAR SURFACE SOIL

Station	(Feet) Depth	(P.P.B. by Wt.) Methane	Percent Organic Matter	(P.P.B. by Wt.) Ethane +	Percent Sand
	8'	193	0.17	82	1.2
	10'	157	0.09	56	6.0
	12'	222	0.16	103	1.6
8	Surface	222	2.17	10	5.2
	2'	144	1.91	10	6.0
	4'	88	1.56	5	5.6
	6'	44	0.73	3	5.2
	8'	41	0.20	5	6.8
	10'	203	0.09	105	3.6
	12'	170	0.13	101	10.8
9	Surface	179	5.12	9	4.4
	2'	107	1.62	8	3.2
	4'	82	0.72	12	2.8
	6'	52	0.20	3	3.6
	8'	190	0.12	80	1.2
	10'	67	0.09	11	1.7
	12'	396	0.21	190	1.2
10	Surface	321	3.59	4	5.6
	2'	75	1.10	15	4.4
	4'	85	0.75	8	3.6
	6'	206	0.13	65	3.6
	8'	259	0.12	170	2.0
	10'	235	0.17	91	1.2
	12'	264	0.21	154	1.2
11	Surface	228	3.10	8	6.0
	2'	70	2.26	10	7.2
	4'	85	0.69	3	4.8
	6'	116	0.14	11	4.4
	8'	149	0.19	68	1.6
	10'	358	0.15	133	1.6
	12'	374	0.19	194	0.4
12	Surface	201	3.12	9	3.2
	2'	80	1.13	11	3.6
	4'	83	1.01	13	4.0
	6'	70	0.35	3	2.8
	8'	177	0.13	93	2.0
	10'	263	0.13	131	1.2
	12'	342	0.21	138	0.4

TABLE II

RELATIONSHIP OF HYDROCARBONS TO ORGANIC MATTER IN WELL CUTTINGS

(Feet) Depth	(P.P.B. by Wt.) Methane	Percent Organic Matter	(P.P.B. by Wt.) Ethane +	Percent Sand
6994-7026		1.38		0.8
7026-7056		1.52		0.4
7056-7088	590	1.39	3240	0.8
7088-7118		1.48		0.4
7118-7150		1.21		0.4
7150-7181	495	1.26	3100	0.8
7181-7211		1.20		0.8
7211-7242		1.27		2.0
7242-7272	840	1.36	1800	0.8
7272-7303		1.34		1.2
7303-7334		1.30		0.4
7334-7366	372	1.14	1130	0.4
7366-7397		1.35		0.4
7397-7429		1.24		0.4
7429-7460	275	1.10	1460	0.4
7460-7492		1.31		0.8
7492-7523		1.27		2.0
7523-7555	320	1.12	2900	0.4
7555-7585		1.34		1.2
7585-7617		1.22		1.6
7617-7648	315	1.33	2640	1.2
7648-7678		1.36		0.8
7678-7709		1.30		0.8
7709-7742	315	1.42	2520	1.2
7742-7773		1.33		2.8
7773-7804		1.44		0.8
7804-7835	385	1.25	3650	2.8
7835-7867		1.33		8.8
7867-7898		1.30		1.8
7898-7929	325	1.27	3460	6.0
7929-7961		1.45		0.8
7961-7994		1.32		8.4
7994-8031	405	1.07	6150	2.0
8031-8064		1.35		16.8
8064-8094		1.40		2.8
8094-8125	680	1.11	7600	6.8
8125-8157		1.44		4.8
8157-8188		1.40		4.8
8188-8220	595	1.36	12600	9.6
8220-8251		1.44		6.4
8251-8283		1.41		3.6
8283-8300	435	1.28	5600	6.0

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DEVELOPMENTS IN GEOPHYSICAL-GEOCHEMICAL EXPLORATION FOR URANIUM IN THE UNITED STATES

M. E. Denson, * J. W. Pollock * and C. W. Bills *

ABSTRACT

Examples of the results or geophysical and geochemical exploration are presented to illustrate how these tools can be used in uranium exploration programs. The most satisfactory results are obtained by combining different prospecting techniques in the same program. These include surface geochemical, seismic, and resistivity techniques; subsurface electrical velocity; radiometric logging and geochemical analysis of waters and rocks. Data on the physical and chemical properties of the rocks involved aid in solving geological as well as exploration problems.

INTRODUCTION

The data which follow have been obtained in an exploration research program of the Geophysical Research and Development Branch of the Atomic Energy Commission. In this program geophysical and geochemical efforts have been integrated. Certain definite advantages are realized in an integrated program insofar as time, economy of result, and interpretability of data are concerned.

The data, which are believed to be representative of typical field problems, are discussed in relation to some of the unknowns, i.e. the limitations and the questions connected with use of the particular methods involved.

In order to arrive at more practical and economic application of geophysical and geochemical techniques in mining exploration our combined field and laboratory efforts have been keyed to three questions:

1.—What techniques of geophysics and geochemistry can be improved or developed to serve as effective and realistically economic, practical reconnaissance methods, i.e. methods applicable for surveying or evaluating areas of about 50 square miles in size?

* *U. S. Atomic Energy Commission, Geophysical Research & Development Branch, Denver, Colorado.*

2.—What types of surface data can be obtained that are more descriptive of subsurface rocks and permit increased subsurface geologic definition?

3.—What logging techniques can be developed or improved to obtain more basic information from the many bore holes drilled over known deposits?

Examples of field data are presented and discussed in relation to each of these questions.

ACKNOWLEDGEMENTS

This paper contains contributions from all of the personnel within the Geophysical Research and Development Branch of the Division of Raw Materials of the United States Atomic Energy Commission. In this connection, we wish to make particular recognition of the contributions made by R. D. Casey, C. T. Illsley, J. H. Scotte, and E. M. Wescott.

WATER GEOCHEMISTRY AS A TOOL IN RECONNAISSANCE PROSPECTING

INTRODUCTORY STATEMENT

Analysis of natural waters for uranium has been primarily to explore unfamiliar areas for dispersion halos and to trace increases in uranium concentrations along courses upstream to the source. Many controlling factors influence the results of such investigations and limit meaningful application. The following are examples from our field results.

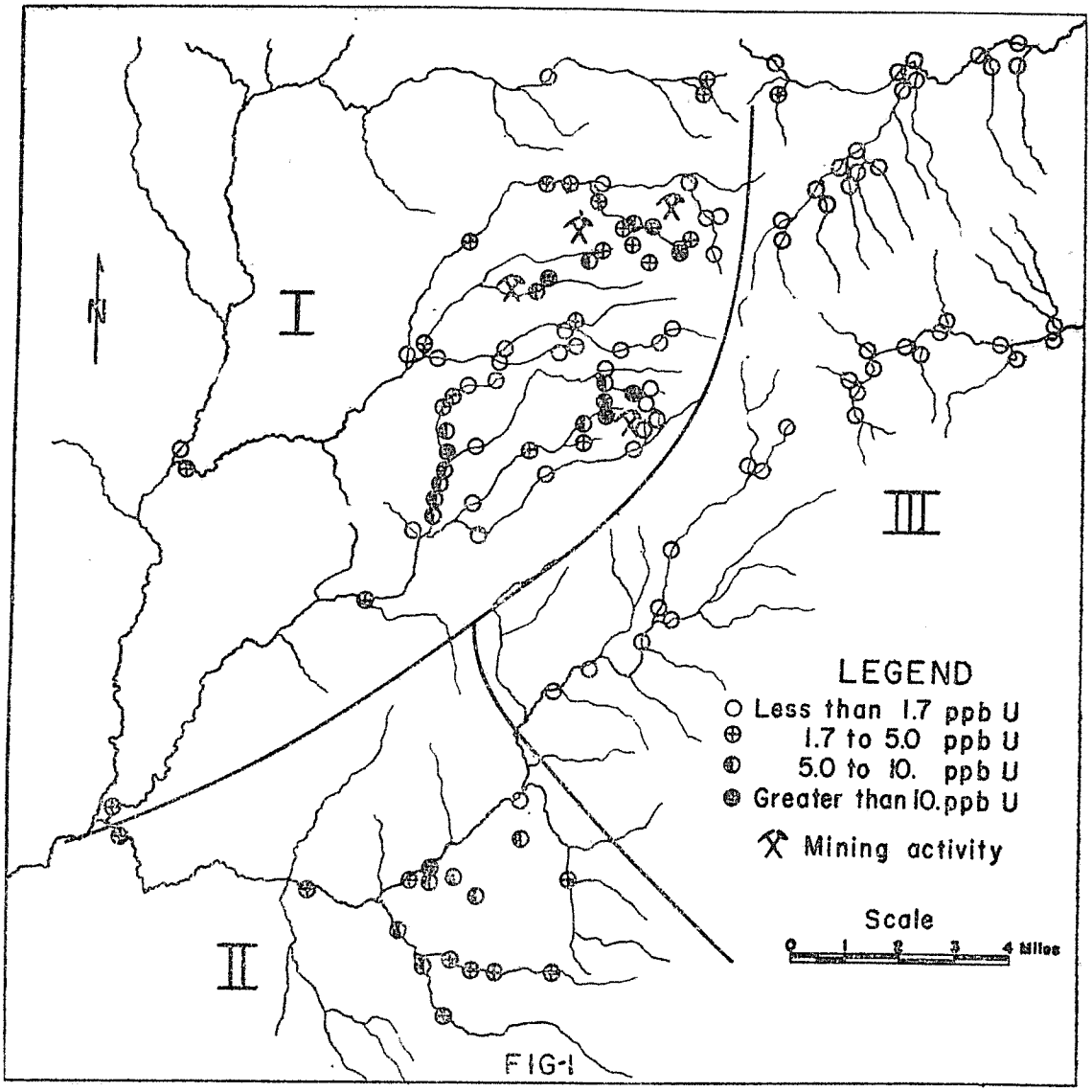
SPOKANE, WASHINGTON DATA

Figure 1 shows the distribution of the natural water system and the location of known uranium deposits in an area northwest of Spokane, Washington. Mineral concentrations are found in the contacto zone between the Noonday granite and Precambrian sediments as the phosphate, autunite. Springs in the area are both radioactive and nonradioactive. As indicated in Figure 1 we systematically sampled all waters of the major drainage ways. Our results readily confirm that the anomalies found in water coincided with locations of known uranium deposits.

From this initial information supplemented by additional laboratory analyses and the results of exploratory surface stripping by private prospectors, examples of some limitaing factors in these data were noted.

First:

Areas whose waters were consistently higher in uranium content than were waters from producing areas failed to show commercial deposits. Three of the locations of mining activity in Area I of Figure 1 are examples.



HYDROGEOCHEMICAL URANIUM RECONNAISSANCE SPOKANE AREA, WASHINGTON

Such results may be attributed to disseminations of uranium in the soil and rock with consequent concentration under physical and chemical conditions either favorable or unfavorable for leaching.

Our evaluation of such areas is made using combined geophysics, geochemistry, and geology to determine the extent of controlling geologic factors. The possibility of geologically favorable locations bearing extensive amounts of uranium below commercial grade remains as a serious limitation which does not yet appear susceptible to differentiation or quantification.

Second:

New areas of anomalous waters may or may not be significant depending upon the chemistry and kind of water as well as the background values of the country rock. Conversely, areas lacking indications of anomalous values of uranium in natural waters may be more interest than the water analyses alone would indicate. In new regions some control is needed to normalize or evaluate and weigh results. Areas II and III on Figure 1 are examples.

The pH, bicarbonate content and phosphate content in all water samples collected from this district were determined. The bicarbonate was determined since it was anticipated from previous work that it might occur as a control factor the transport of the uranyl ion $(UO_2)++$ as a carbonate complex. The phosphate content was determined because of the occurrence of uranium as autunite. On Figure 2 uranium is plotted as a function of pH. This comparison shows clearly that in this region uranium is not found in anomalous association below a pH of about 6.5; bicarbonate vs uranium shows like relationship, and below 25 ppm of bicarbonate, uranium is not found in anomalous association. The figure of 1.7 ppb uranium shown in the lowest class on Figure 2 is the background value determined for the Spokane district.

In the samples analyzed, phosphate was detected only in association with our highest uranium values. This was anticipated because the analysis for phosphate was not sensitive within the ppb range. The significance of the urannium, pH and bicarbonate relationships lies in evaluation of field data and clearly establishes the following:

a.—Area II (Figure 1), even though the waters are anomalous in uranium content, may not be significant since bicarbonate values are high by a fector of 4 or 5. If the uranium values in this area were normalized to an average value of bicarbonate, the area would not be considered anomalous in uranium. In other words the bicarbonate content is a caution sign and may indicate that the high uranium water values do not reflect subsurface mineral concentration, but rather an area of high background uranium values.

b.—Area III to the east may not be listed as lacking potential without recourse to additional information on the country rock and on the

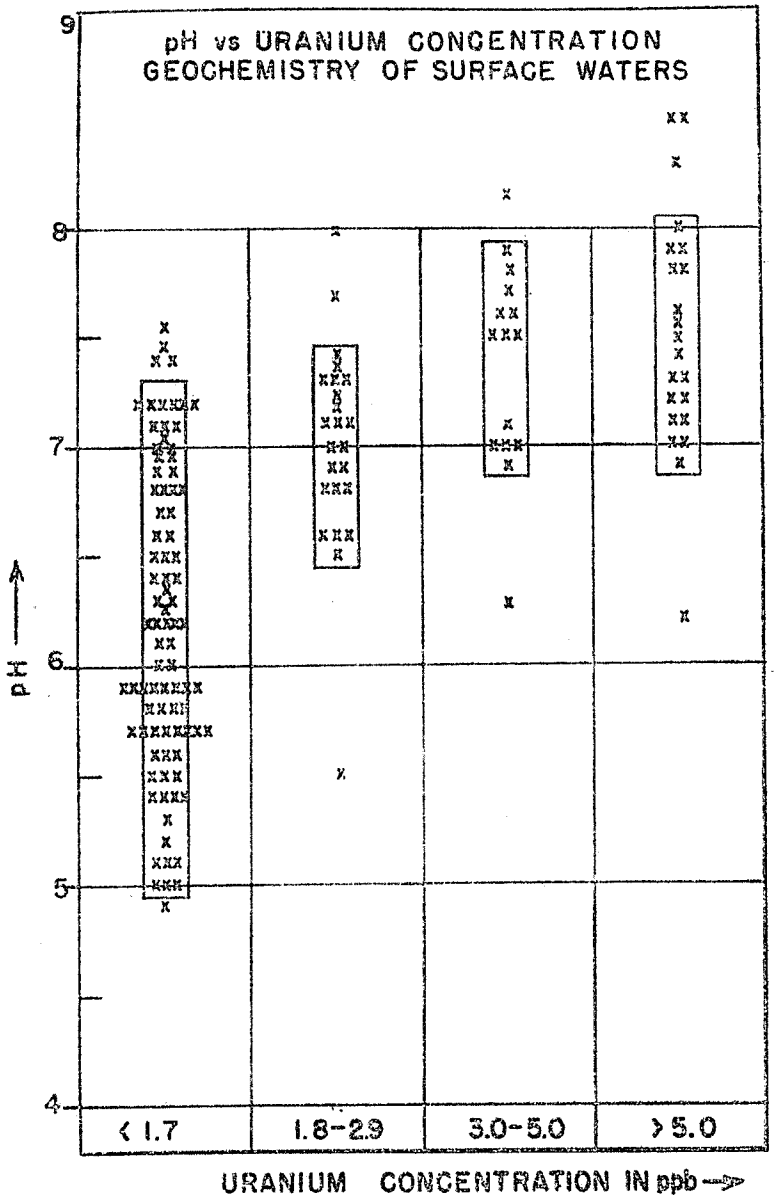

pH vs URANIUM CONCENTRATION
GEOCHEMISTRY OF SURFACE WATERS
9
8
7
6
5
4
pH
< 1.7
1.8-2.9
3.0-5.0
> 5.0
URANIUM CONCENTRATION IN ppb

FIGURE 2

geology of the area, even though the waters are not anomalous in uranium content, since pH and bicarbonate there are both low. Low pH waters are conducive to solution of uranium under suitable oxidation-reduction conditions of the water or the ore. The absence of uranium in these waters which contain normal amounts of sulphate anion may be interpreted to indicate that, other things being equal, if uranium were present in Area III, it would probably occur in a primary low valent form.

Third:

These results illustrate the need for a correlating index between stream sediments and stream waters. Locations of particular interest in this area lacked a sufficient supply of water and meaningful reconnaissance was impeded. Our work has not yet been completed on the correlation and comparison of waters and sediments. However, soil analyses are discussed further in a later section.

Fourth:

Spring waters at their source were observed to have from 10 to 50 fold variation in uranium content following rains and with change in season. It appears possible that any combination of events may occur insofar as increase or decrease of uranium content with decreased flow and vice versa are concerned. These variations which are of importance in interpretations, are controlled by subsurface environment, drainage pattern of the spring system, and presence or absence of uranium in the soil or near surface material.

Fifth:

Not to be ignored is the effect of chemically active waters on the host or intervening rock. For example, the trace elements in a specific type of water not only characterize the rock, but may also help to explain the distribution of separation of uranium from its decay products. In this connection wide variations in the ratio of uranium to radioactivity were observed at the source of spring waters in this and other areas. A knowledge of the anions and cations associated with such waters can serve to explain by exidation-reduction or solubility considerations the presence or absence of uranium or its decay products in association with various trace element suites.

Recapitulation

In presenting these data on hydrogeochemistry we have attempted to show that a vast amount of valuable information can be obtained from waters. The

proper use and application of water data require first, an awareness of the many factors which affect and control analytical results such as type of country rock and type of water, radioactivity in water, controlling chemical constituents, rates of increase or decrease of flow, subsurface and surface drainage patterns, seasonal changes, and distance from source. Second, knowledge and information are needed to interpret variations which are observed and which can be attributed to these factors. With the combined application of principles of physics, physical chemistry, and chemistry coupled with geology, we feel solutions can be obtained to the complex problems involved. This constitutes our approach to hydrogeochemistry in our gathering of field data, in laboratory experimentation, and is statistical evaluations and study.

SOIL GEOCHEMISTRY AND SURFACE RESISTIVITY

INTRODUCTORY STATEMENT

Analysis of soils for uranium has been used primarily to explore unfamiliar areas for dispersion halos or further delineate or extend known ore bodies. Lack of ability to detect meaningful variations in content of a specific element frequently limits the extent of use of this tool. Ordinarily the geochemistry of a soil is so complex that the meaningful use of soil analyses requires recognition of many variable factors. In an attempt to minimize interpretational limitations common to soil geochemistry we have combined use with surface resistivity in the solution of the geologic problem of delineathing a buried paleostream channel. Channels are one of the common ore deposit controls in continental type sedimentary rocks of the Western United States. Primarily this work was carried out to develop a reconnaissance method which would be of value in areas where natural surface waters are absent.

Our approach to this parte of the problem has been to use water leaches from soil samples.

EDGEMONT, SOUTH DAKOTA DATA

Fig. 3, shows some results of our initial reconnaissance work in this field. The geologic setting here consists of outcrops of southerly dipping, continental-type sedimentary rocks of Lower Cretaceous Fall River-age with subjacent Fuson and Lakota rocks exposed in the canyons in the northernmost part of this area. The land surface consists of drainage patterns superimposed on a gentle dip-slope of the upper Fall River rocks and is covered chiefly by grasses in this semi-arid climate. Carnotite concentrations occur in the Fall River formation to the east and north of the area shown.

The geologic problem here was twofold: first to outline a buried Fall River paleostream channel which had been recognized in canyon outcrops and mapped by the U. S. Geological Survey, and second, to determine the presence of lithologic variations within the channel which might constitute ore controls.

Lithologically, the problem consisted of outlining predominantly sandy, locally calcite-cemented, channel-filling rocks enclosed by other continental rocks not greatly different in megascopic character. This channel is exposed at the surface in the western part of the area and lies at increasing depths eastward being buried up to 200 feet deep in the eastern part of the area. Calcite and pyrite were noted by U. S. Geological Survey personnel as being peculiar to the channel-filling rocks, and were believed by them to be related to uranium in spatial distribution and perhaps in depositional control.

The electrical surface survey was run first with the expectation that the coarser sandy channel rocks would be qualitatively differentiated by higher resistivity. Contour data shown on Figure 3 were obtained by running depth profiles along traverses using the 4 electrode Wenner arrangement and Gish-Rooney type equipment. Quantitative interpretations of resistivity data were not carried out routinely in view of the numerous vertical and lateral stratigraphic changes in lithology. The results shown are for the spread-depth of 160 feet. To the south and east decreasing resistivity contrasts from increased water saturation and increased depth prevented our being able to delineate the channel, as shown, or to detect any meaninful variations attributable to cementation differences within the channel. Over the area for which the data are shown, results from the resistivity survey were used in part to guide and control the geochemical soil sampling.

The resistivity results are particularly interesting in that they indicate changes in the subsurface geology (bends in the channel and the "waterfall" in section 35) which have influenced the migration of subsurface waters, which in turn are believed to affect the results of soil analyses.

The surface geochemistry was run with the idea that carbonate and bicarbonate determinations on the water-leach from the soils would relate to calcite cementation in the subsurface channel rocks, whereas uranium determinations might be significant for indications of subsurface mineral concentration. This work was based upon the premise that waters had migrated between the surface and the channel at depth. In this connection belief is strong that in some cases the results obtainable from the water-leach of the soil are analogous to what would be obtained from artesian spring waters if they were present.

These results demonstrate some of the problems and unknowns connected with the application of soil geochemistry.

First:

Anomalous values of uranium in the soil do not necessarily indicate subsurface commercial uranium deposits any more than a similar anomaly in natural waters does in a spring system. In the present case no commercial ore was found within one mile of the area of the anomalous uranium values shown on Figure 3. As in the case of natural-water analyses these results illustrate the need for a simple means of recognizing differences attributable to different solution and weathering phenomena which accompany those particular subsurface physical and chemical conditions which control the vertical migration of ions or elements carried by influent and effluent waters.

The resistivity data at those locations shown on Figure 3 where high bicarbonate anomalies were obtained are believed to be particularly significant, because high bicarbonate is found only where the resistivity is low. The low values of 200 ohm-feet, contrasting with the adjacent values of 1600 ohm-feet are believed to indicate saturation either from the rising of subsurface water or from water migrating from the surface downward. Lack of association of uranium anomalies with any of the bicarbonate highs would suggest that at these locations either the net migration of water was downward, that the subsurface area drained by the waters, if they were traveling upward under artesian pressure, was not uraniferous. Intensive explporation drilling has failed to locate any mineral deposits in the subsurface area to the north and west which waters would have drained if they were coming up at the locations of low resistivity.

Under such geologic and hydrologic conditions it is to be anticipated that soil geochemistry may be of the most value in suggesting the potential or possibility of surrounding areas, and may have little value as a tool for indicating locations. In this regard the limitations do not differ markedly from the results of analyses from natural-water systems as previously discussed.

Second:

The degree of significance and how to interpret the observed variations in the bicarbonate content of a water-leach of soil are not known. These variations may be comparable in significance to the bicarbonate variations noted in natural waters where the bicarbonate may be an index to the amount of uranyl ion which can be solubilized. It is apparent that here other significant control factors are involved. In this connection several puzzling features are encountered. For example: Sizeable variations were obtained from duplicate samples taken close together, even under conditions which were apparently unchanged. Further, continued rechecking has shown that the results of analyses

differ when made at different times. As an example, some samples were analyzed in the Fall of 1955 and the same sample again in the spring of 1956. Table I shows representative changes which occurred within the same samples after being stored for about six months in closed soil cartons subject only to normal variations in temperature and humidity.

TABLE I

Sample & Time of Analysis	pH	Kx10^{-6}	Ca^{++}	Mg^{++}	HCO^{-}_{3}
A — Fall 1955	6.6	7500	320	200	880
A — Spring 1956	8.3	960	900	250	2000
B — Fall 1955	6.6	2600	60	40	630
B — Spring 1956	8.2	2000	220	80	590
C — Fall 1955	7.0	5600	250	150	940
C — Spring 1956	8.4	6800	850	90	710

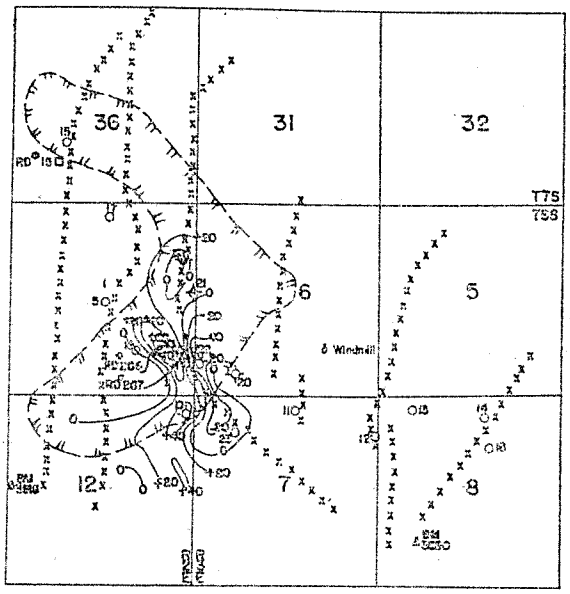
VARIATIONS IN SOIL ANALYSIS

Note that the pH increased in all cases but the conductivity, Ca^{++}, Mg^{++} and HCO^{-}_{3} show no consistent pattern of variation.

These differences are, encouragingly enough, not of the same magnitude as differences recorded in the fiel data of Figure 3. We believe that these data most importantly indicate the necessity for an understanding of soil properties and composition which bear upon their behavior in the presence of mineral-bearing or-dissolving solutions. The combined resistivity and geochemical data obtained in this case indicate that meaningful variations do exist. Their combined use was made for economic surface evaluations in this area, where results of a single technique would hace been of but limited value.

Although the resistivity and geochemical survey was extended to the south and east, as previously mentioned, the electrical results were entirely inconclusive. The diamond drill cores obtained at that time showed that no cementation was present in the channel rocks to the south and east but that abundant disseminations of pyrites were present. The sulphides were of interest because of their spatial association with uranium as shown by cores, and in accord with geologic postulation. Some holes had penetrated uranium ore at depths of about 150 feet.

In order to determine whether the sulphide areas could be outlined, variable frequency electrical resistivity was used — a technique which was pioneered by the Geophysics Department at the Massachusetts Institute of Technology. Results from this surface survey are shown on Figure 4. Drilling carried out subsequent to and concomitantly with the surface program showed that



SOIL LEACH CONDUCTIVITY AND RESISTIVITY DIFFERENCE
COAL CRAVEN AREA, EDGEMONT MINING DISTRICT
FALL RIVER COUNTY, SOUTH DAKOTA

FIGURE 4

a close association existed between locations of pyrite occurrences as seen in the cores from the area and the locations of anomalies mapped by variable frequency resistivity using d.c. and commutated d.c. in Wenner arrangements.

These electrical results are not without equivocation or difficulty, which are discussed further on page 19. However, significant results were obtained

where conventional resistivity methods failed to produce. The ability to map the subsurface metallic content or presence of electronic conductors in sedimentary rocks appears to be a long step forward in describing lithology and obtaining increased subsurface information by geophysical methods.

Analyses for calcium and sulphate which were done on the leaches of soil samples from the area of the disseminated sulphides, which were outlined, showed good correlation with conductivity of the soil leaches, i. e. high calcium and sulphate invariably correlated with high conductivity, and the soils of these leaches were observed to have high quantities of gypsum. As shown on Figure 4 a belt of predominantly gypsiferous soils was found to be associated with the pyritiferous area, while soil predominantly gypsum free, was found to characterize the areas where sulphides were absent. These results further substantiate but do not prove the premise upon which the soil leaches had been carried out — that material had been interchanged between the channel rocks (at this location about 150 to 200 feet deep) and the surface.

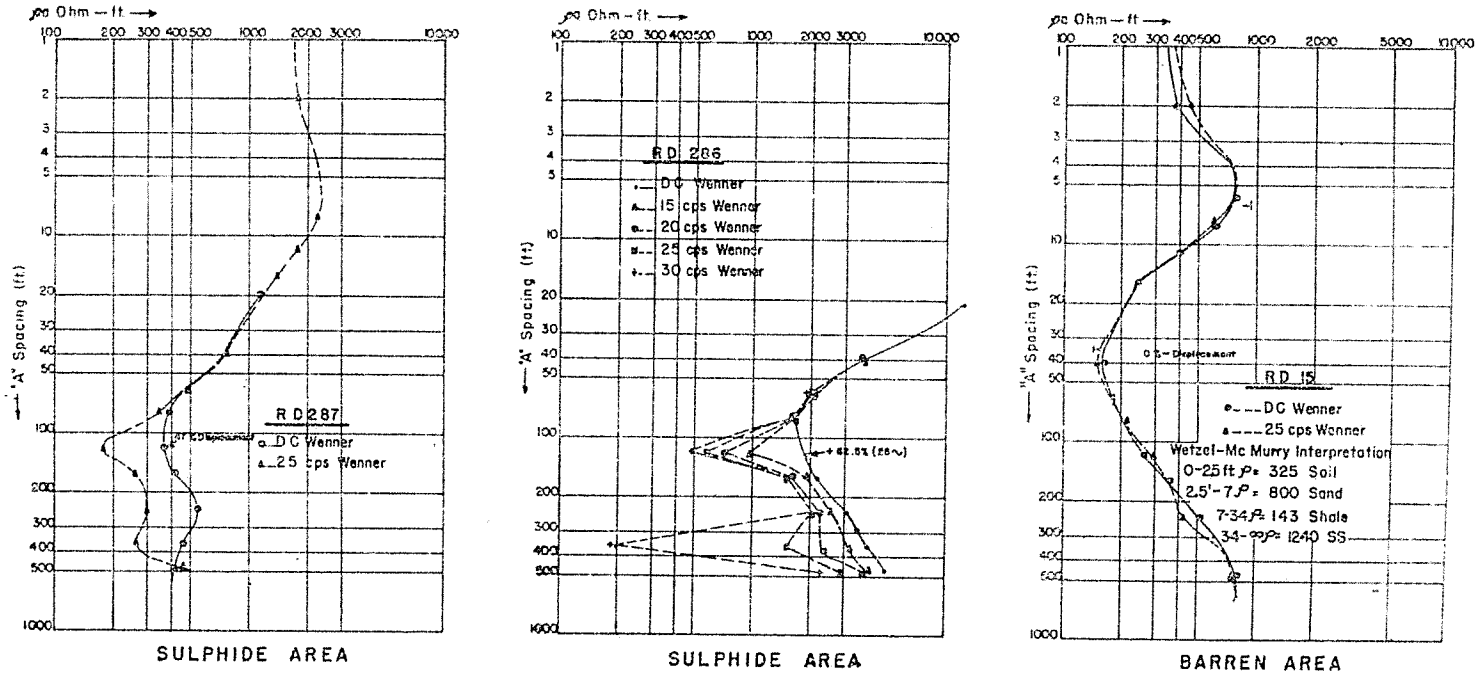
Examples of representative frequency differences from which the contour data on Figure 4 were plotted are shown on Figure 5.

At an area in the northern Black Hills where stratigraphy and mineral controls are very similar to those at the locations where the data shown on Figures 4 and 5 were taken — no encouraging results were obtained. Further, at some locations changes have been obtained which could be attributed to not known factors. The meaning of the negative displacements, which indicate an a.c. resistivity greater than d.c. resistivity, is not clear, but perhaps special geometric configurations and associated electromagnetic effects or instrumental unknowns and phase changes are atrributable to these results. Instrumentally, serious troubles have been encountered with capacitance and induction effects in current lines and instruments, which give rise to spurious readings.

In short, the authors submit that many factors affect these results which are unevaluated or unknown. For example: we do not yet know whether the amount and kind of ions in the electrolyte are more importante than the kind and amount of electronic conductors or if different effects may characterize different types of deposits, to what degree water or electrolyte saturation of the rock pore space is a critical factor, or how the degree and strength of adsorption on clays affect our measurements.

Recapitulation

These data on the combined use of geochemistry and surface resistivity are presented as an example of an unusual but extended application of soil



APPARENT RESISTIVITY CHANGES WITH FREQUENCY
COAL CRAVEN AREA, EDGEMONT MINING DISTRICT
FALL RIVER COUNTY, SOUTH DAKOTA
FIGURE 5

geochemistry. Many more data and further study are essential to establish firmly under what conditions a waterleach analyses may be meaningfull used. It seems reasonable from preliminary research that a bicarbonate leach rather than a water leach would establish an additional insight to what the composition of a natural water would have been if it existed, as well as insight into the problem of uranium distribution in the soil. The evaluation of this application may find extended meaning and economic use when combined with geophysical data in areas where natural waters are absent. In this regard, soil geochemical anomalies may well indicate only the normal surface variations expected in soils. However, where the geochemical anomalies occur in conjunction with additional geophysical anomalies, as in the present case, the suggestion is strong that subsurface geology is the controlling factor. The basic philosophy involved is not greatly diessimilar from the problem of having two equations to solve for two unknowns.

The correlation of results of variable-frequency resistivity with results of soil geochemistry, which is currently being carried out, portends to be a powerful tool for obtaining increased subsurface geologic definition and description. The experimental field and laboratory program of the Geophysical Research and Developmente Branch is concerned with consideration of physical, physical-chemical and chemical factors involved in obtaining and correlating these types of data.

BORE HOLE LOGGING

INTRODUCTORY STATEMENT

To meet the need for simple, reliable means of obtaining information on lithology and stratigraphy economically, research on logging, particularly electric, has been carried out. Two factors are of paramount importance in the electric logging of continental-type sedimentary rocks.

Firs:

The shallow sandstones in semi-arid regions where uranium is found are not fully water saturated, thus making for very high resistivities.

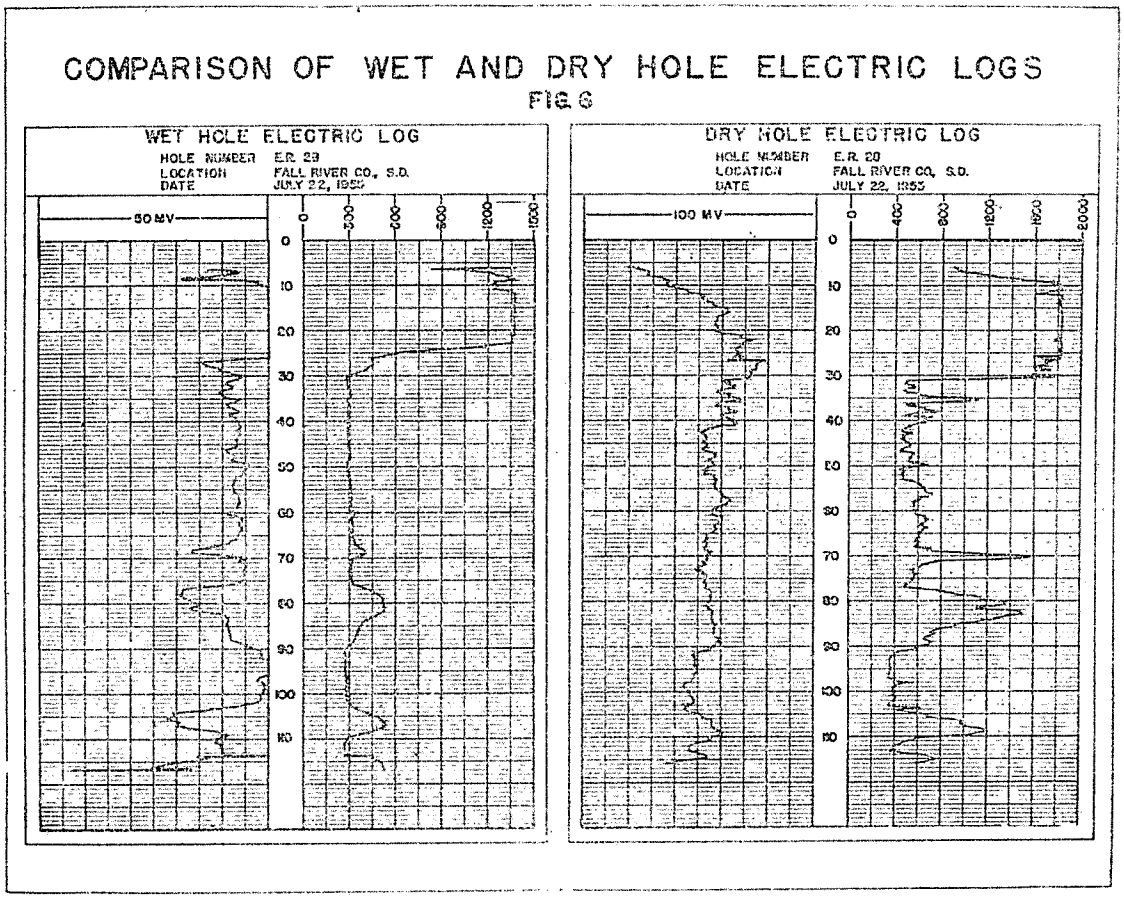
Second:

The beds and ore intervals are thin. Determination of true or relative resistivity of a thin or highly-resistant bed penetrated by a bore hole is difficult.

Not to be overlooked as a formidable factor in connection with electric logging is the importance and availability of water used for electrical contact in the bore hole. In this regard:

1. Water is scarce and expensive to obtain.
2. Frequently, it is impossible to fill a hole with water because of fracture systems or high permeability of the rocks.
3. Measurements in electric logging are directly (but not totally) related to the kind and amount of water in a rock. Water which is poured into a bore hole and imbibed by the rocks is a contaminant which precludes practical quantitative interpretation of thin resistant beds.

However, logging techniques can, if properly carried out, minimize time and cost essential for coring.



DRY HOLE LOGGING DATA

Some of the above probles were overcome by using an electric logging unit developed for dry holes as well as for holes partly dry and partly wet. An example of a log from this dry hole unit and the corresponding wet hole log obtained with the same logging instrument are shown for comparison on Figure 6. Increased detail and definition are apparent on the dry hole log.

The self-potential logs are shown to the left of the resistance logs. The profile of the wet hole log cannot be used meaningfully because of electro filtration effects accompanying the imbibition of water in the hole. Example of detection of a single and definitive electro chemical effect is included with the logs shown on Figure 7. These loge are all from the same hole. The dry hole self-potential curve on the left is obtained with the field current off. This log is reproducible. The electrical contact for drq hole logging is made with a pliable porous sponge rubber roller made conductive by saturating with a clay slurry of known electrolyte concentration. The authors believe that the surface and in-hole electrodes may complete an electro-chemical cell through the high impedance instrument circuit. Controlling factors of this cell are concentration, distribution, and kind of ions in the formations and in the rolling electrode. The magnitude of the recorded potential can be changed by changing the ion concentration in the in-hole electrode — anologous to electrochemical phenomena observed in wet hole self-potential logging in oil exploration. That this potential is real and significant is demonstrated by its effect on the resistance measurements on the log. The resistance log is reversed completely where the potential is greatest, only by reversing the polarity of the d.c. field current which the dashed line indicates. It may be of additional significance that this potential and reversal occur in coincidence with uranium concentrations determined from core analysis and substantiated by the gamma ray log on the right. A concentration of ions existing in the vicinity of an ore body can be realistically anticipated and could govern the observed phenomenon.

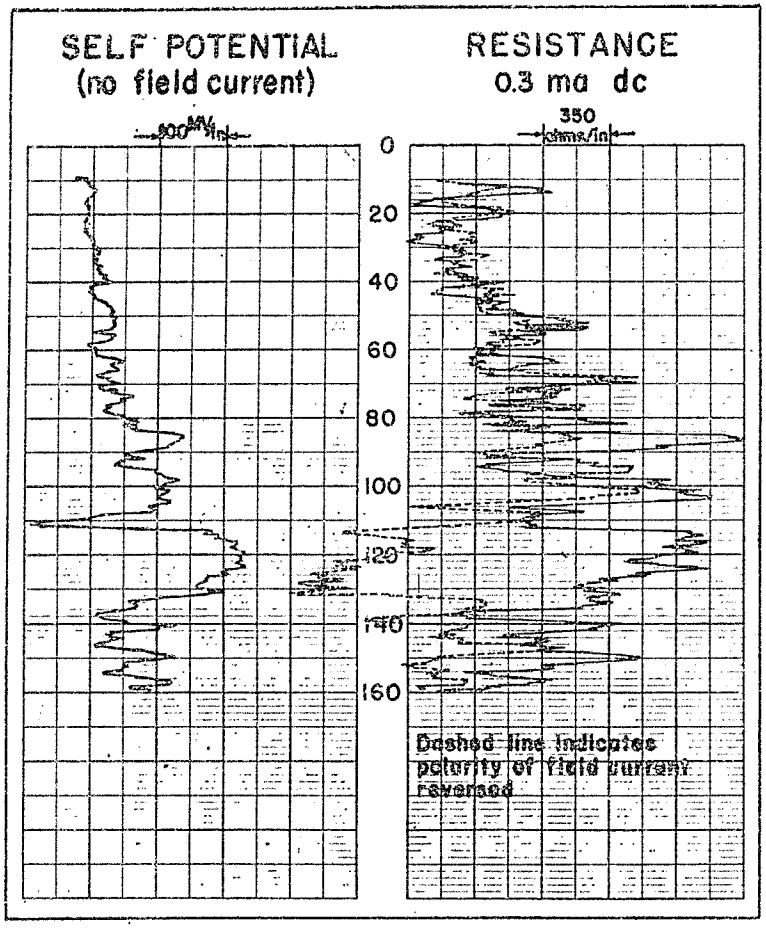
The gamma ray log and the resistance on the right are run simultaneously. While this combined application is no panacea for coring, the lithologic definition obtainable from the combined parameters is sufficient to minimize the amount of coring ordinarily carried out.

The resistance graph of the right hand log was run with a commutated field current of 17.5 cps. Variable-frequency electrical studies, which were discussed previously in connection with surface surveys on page 17 have been extended to bore hole logging. The differences which are observed between the two center solid line graphs are difference associated primarily with polarization effects accompanying current transmission in the earth. The interpretation of these differences, which is not yet clear, constitues part of our research endeavor in bore hole logging, as well as in surface exploration. The in situ properties and differences in subsurface rocks and waters can be studied most advantageously by using logging techniques.

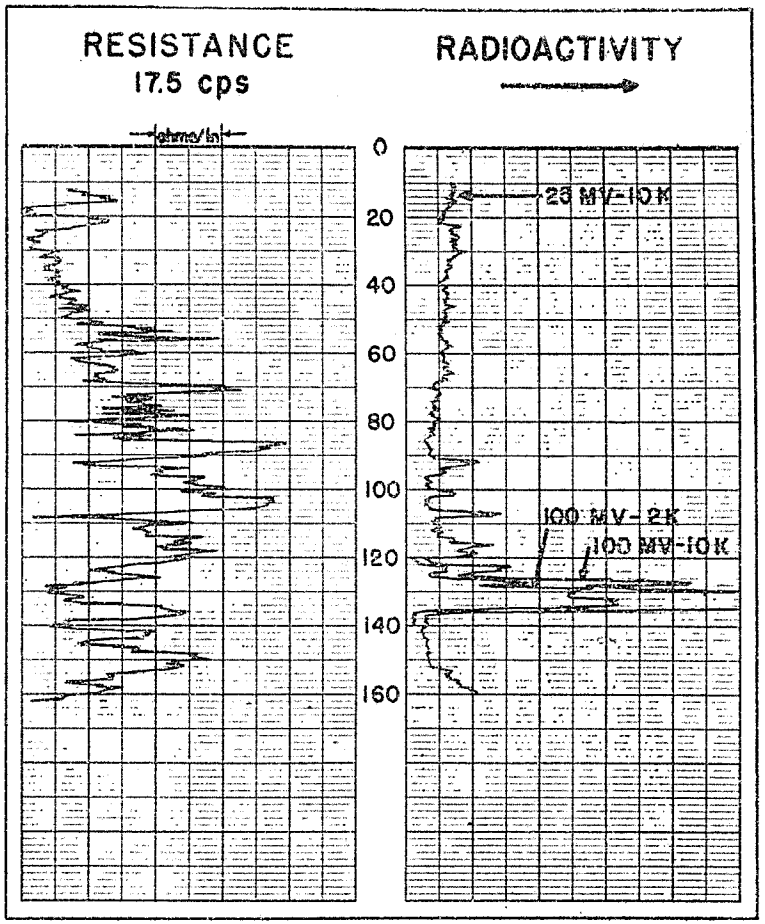
DRY HOLE LOGGING DATA

HOLE R-1, FALL RIVER COUNTY, SOUTH DAKOTA

FIG. 7



OBSERVED ELECTROCHEMICAL EFFECT



SIMULTANEOUS GAMMA RAY ELECTRIC LOG

SUMMARY AND CONCLUSIONS

The program of the U. S. Atomic Energy Commission is concerned with obtaining the maxium amount of information from mineralized and adjacent non-mineralized areas consistent with use and application of this information in geophysical and geochemical exploration. Examples have been cited of meaningful results obtained by combining geophysics and geochemistry in our field program.

Results are used to demonstrate the need for better interpretation so that conclusions can be descriptively presented in accord with geology as well as with the chemical and physical principles which give rise to the observed results. For example, much basic research needs to be carried out on the conditions under which uranium and its decay products can be carried by waters in springs and streams or from a water table to the ground surface or top soil. The factors controlling transmission of variable frequency electrical currents within the earth likewise require additional study and research.

New techniques are needed which will give more specific fundamental information concerning the physical and chemical properties of uranium-bearing formations. In order to obtain such information that its use may be projected to surface exploration, logging techniques are being applied to study the in situ properties associated with deposits which have been pentrated by bore holes. Investigations of the causes and effects of the phenomena observed in the field must be carried out in the laboratory before the maximum amount of useful information can be realized in field applications.

THE PROBLEM OF VARIATION IN GEOCHEMICAL SOIL SAMPLE FIELD TESTS

McPHAR GEOPHYSICS LIMITED *

ABSTRACT

Field geochemical tests frequently yield results that are not reproducible. Soil tests from areas with similar depths of overburden and similar bedrock mineral content may also vary greatly. These variations tend to limit the usefulness of geochemical methods in prospecting. Such discrepancies arise from improper application of methods and interpretation of results and may largely be overcome when their cause is known and allowed for while testing.

A major portion of this variability may be attributed to particle size distribution in the soil sample since the metals detectable by field methods are mainly located on the 2 micron and less clay fraction. The variation in results between samples taken at a single location is due in part to the difference in percentages of sand, silt, and clay in the separate samples. Variations in samples from otherwise similar locations may usually be traced to similar differences in soil content.

Laboratory data are presented on two sample suites to illustrate the distribution of zinc equivalents and copper in fractionated soil samples.

INTRODUCTION

Geochemical field tests have on occasion, failed to live up to expectations. Possibly the chief criticism of applied geochemistry is the frequent lack of reproducibility of results. This shortcoming may be attributed to a number of possible factors. A frequent tendency is to condemn the method in use without sufficient inquiry into the causes. Normally the chemistry of a method has been thoroughly tested and has been found to be reproducible, and therefore it is in most cases the soil sample which has yielded the erratic and non-reproducible results. Some of the factors contributing to such discrepancies will be discussed briefly.

The solid phase of soil is a heterogeneous mixture of rock and mineral fragments, and organic matter. Metallics in the soil occur in various forms,

* *Read by W.O.J. Groeneveld Meijer, geologist, McPhar Geophysics Limited, 139 Bond Ave., Mills, Ontario, Canada.*

namely as discrete particles, as neutral insoluble salts, in metal-organic compounds, on the cation exchange complex, or in the soil solution. Organic matter has a high exchange capacity and under some conditions it may contain relatively large amounts of metallics. Soil pH has a marked influence on the amount and proportion of a metallic in the soil and on the quantity that may be removed by the extractants used in rapid fields tests. Wide variations in pH can occur both horizontally and vertically over very short distances.

The minimum feasible depth of sampling will vary greatly depending to a large extent on the type of profile development exhibited by the soil under consideration. For example, podzolic soils, developed under coniferous vegetation, have an Acid A_0 or humus horizon. Underneath this horizon is the A_2, which is a leached greyish coloured siliceous layer. This is followed in depth by the B horizon which is a layer of accumulation. It is darker in colour than the A_2 and contains sesquioxides, bases, and fine clay leached from above. This horizon is usually suitable for sampling. However, it will vary in distance below the surface and thus it is often impossible to arrive at a constant sampling depth for a given area.

In order to obtained reliable results, the sample analyzed should be representative of the area sampled. A truly representative sample can only be obtained by taking a number of samples at or close to the sampling point and by properly combining these to make a composite. The number of samples required is arrived at by analyzing each sample and by applying statistical methods to determine the number of samples required for a composite. A sampling procedure as determined by statistical analysis would be time consuming and not practical. The alternative is to take a fairly large sample from what appears to be an average condition, to mix it thoroughly, and to retain a portion for analysis.

One of the most important characteristic of a soil from the geochemical point of view, is its texture or the percentage of sand, silt, and clay present. Of the different separates, the 2 micron and less clay fraction is the most important. This fraction is the seat of the major portion of the cation exchange capacity of a soil and is the location of a considerable portion of the metallics detectable by rapid field methods. Therefore, replicate soil samples that do not have approximately the same particle size distribution cannot be expected to yield reproducible results.

The purpose of this paper is to indicate the variations in the metallic content of different particle size fractions.

METHODS

Two sets of samples were taken at one hundred foot intervals across known anomalous areas. One set of six samples was collected on the property of Heath Steele Mines Limited, New Brunswick, and was evaluated for zinc equivalents. The other set, consisting of two samples, came from the Highland Valley in British Columbia and was assayed for copper.

A Beckman pH was used to determine the pH of the soil samples. They were separated into various particle size fractions by wet seiving through steel seives of mesh sizes 18, 80, and 325. The portion which passed through the 325 mesh seive, having an opening of 44μ, was treated in a No. 2 International centrifuge. This yielded one fraction of 44 to 2μ and another, the clay fraction, consisting of particles less than 2μ in diameter.

To obtain an accurate particle size distribution, the sample would normally be treated with a dispersing agent to neutralize the forces which cause soil aggregation. Effective dispersion will result in discrete mineral particles and an accurate evaluation of particle size distribution. However, dispersion involves the use of vigorous agents which would not only disperse the soil aggregates but remove metallics from the cation exchange complex. Therefore, wet seiving with demineralized water was used, and although not completely accurate, it should give comparable results within the same soil type.

The cation exchange capacity of the fractions was determined by the method of Surndale and Fields (1952). The exchange complex is hereby saturated with potassium, using normal potassium chloride, and after excess potassium chloride is removed with several washings of 95% ethanol, the exchangeable potassium is displaced with normal ammonium acetate. The latter potassium was determined with a Baird Associates flame photometer, and the exchange capacities of the fractions were calculated from the results.

The parts per million of zinc equivalents contained in the soils and their fractions from Heath Steele Mines Limited were determined with the McPhar Soil Test Kit. The total effect of zinc, lead, tin, cobalt, nickel, and silver in a soil sample is designated as zinc equivalents. The method involves the extraction of the metallics into an organic solvent phase containing dithizone, and the parts per million are estimated from the colour developed.

The copper content of the Highland Valley soils was estimated in parts per million using a McPhar Soil Test Kit specific for copper. This method involves extracting the copper from the sample, filtering, and using an indicator specific for copper to develop the colour indicative of the amount of

copper present. A comparison is made with a colour chart to estimate the parts per million present.

RESULTS AND DISCUSSION

Table I shows that both series of soils are acid and that they contain a considerable amount of finer soil fractions. In situ, the Highland Valley soil contains a varied assortment of rock particles.

TABLE 1

MECHANICAL ANALYSES AND PH OF THE SOILS FROM HEATH STEELE MINES AND HIGHLAND VALLEY

Sample	pH	% Sand	% Silt	% Clay (2 μ)	Textural Class
Heath Steele Mines	4.5	30.0	43.0	27.0	clay loan
Highland Valley	5.9	41.0	32.0	27.0	clay loan

These were removed prior to mechanical analysis by passing the sample through a 2 mm screen. Therefore, the soil would be much more open and porous than would be expected from a clay loam and it would exhibit the characteristics of a loam or sandy loam.

TABLE 2

CATION EXCHANGE CAPACITY OF WHOLE SOIL AND FRACTIONS OF SOILS FROM HEATH STEELE MINES AND HIGHLAND VALLEY

Sample	Particle Mesh	Size Microns	Cation Exchange Capacity (meq./100 gms)
Heath Steel Mines	whole	soil	12
	18—80	1000—177	2
	80—325	177—44	5
	——	44—2	10
	——	<2	21
Highland Valley	hwole	soil	10
	18—80	1000—177	2
	80—325	177—44	6
		44—2	12
		<2	16

In Table 2 the base exchange capacities of the soils and their fractions are shown. They appear to be somewhat lower than might be expected, considering the clay loam texture. This is probably due to the presence of clays with non-expanding types of lattices. These have a low exchange capacity and they are often associated with soils having low pH values. The coarser soil fractions show some exchange capacity. This may be attributed to the presence of hydrated sesquioxides or to the lack of complete dispersion of the soil aggregates.

Tables 3 and 4 show the pronounced relationship between particle size and contained zinc equivalents or contained copper. Some of the metallics apparent in the coarser fractions are due to incomplete dispersion. The partial solution of discrete metallic mineral particles is a further possibility. However, the 2 micron and less clay fraction holds a considerable proportion of the metallics detectable with the rapid field methods employed.

The comparatively large amounts of zinc equivalents in the finer fractions of samples 1,2 and 3 from the Heath Steele Mines indicate that the whole soil samples were not representative and that they contained larger amounts of the very coarse fractions. Therefore, it is possible to fail to detect an anomalous condition if the sample contains a preponderance of coarse particles. It is suggested that soil samples be passed through an 80 mesh screen prior to analysis in order to obtain a greater degree of accuracy and to expedite reproducibility.

TABLE 3

PARTS PER MILLION ZINC EQUIVALENTS OF THE WHOLE SOIL AND FRACTIONS FROM HEATH STEELE MINES, USING THE McPHAR SOIL TEST KIT

Particle Size			ppm zinc equivalents					
Hesh Size	Microns	Sample No.	1	2	3	4	5	6
whole	soil		50	50	50	150	200	250
18—80	1000—177		50	50	50	50	100	150
80—325	177—44		75	75	150	200	200	250
	44—2		200	200	300	300	450	600
	<2		450	450	600	750	900	900

TABLE 4

PARTS PER MILLION COPPER CONTENT OF THE WHOLE SOIL AND FRACTIONS FROM HIGHLAND VALLEY SAMPLES, USING THE McPHAR SOIL TEST KIT SPECIFIC FOR COPPER

Particle Size			ppm copper	
Hesh Size	Microns	Sample No.	1	2
whole	soil		20	800
18—80	1000—177		5	80
80—325	177—44		5	300
	44—2		30	550
	<2		40	1200

SUMMARY AND CONCLUSIONS

Soils from anomalous areas in New Brunswick and British Columbia were evaluated for the effect of particle size on metallic content using rapid field methods of analysis.

The following conclusions are indicated from the results obtained:

1) Particle size has a marked effect on the estimation of metallics in a soil by rapid field methods. Most of the metallics are located in the finer fractions of soils with the largest proportion in the 2 microm and less clay fraction.

2) An anomalous condition may not be apparent if the sand fraction forms a predominant portion of the sample.

3) Screening of samples through an 80 mesh screen is recommended.

ACKNOWLEDGEMENTS

The use of the laboratory facilities of the Soils Department of the Ontario Agricultural College, Guelph, Ontario, Canada are gratefully acknowledged.

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III - CHEMICAL METHODS OF TRACE ANALYSIS

ANALYTICAL METHODS FOR GEOCHEMICAL PROSPECTING

A. A. NORTH * and R. A. WELLS *

ABSTRACT

Methods of analyses for the determination of trace elements in soils that have been devised by workers at the Chemical Research Laboratory, Teddington, England are described.

The application of a chromatographic technique to the determination of copper, cobalt, nickel, niobium, tantalum, lead, uranium, and bismuth in soil extracts is explained. The method which is rapid, simple and inexpensive employs upward diffusion of a solvent in slotted sheets of filter paper for the separation of the trace element or elements from other metals present in the solution. The slotted sheets of paper enable 10 separations to be performed simultaneously. After spraying the sheets with a suitable reagent for the detection of the trace metal the amounts present can be determined by visual comparison of standards.

A method employing toluene 3:4 dithiol for the determination of tungsten and molybdenum is described. Samples are fused with a modified carbonate flux and tungsten and molybdenum extracted by leaching the melt with water. At about 100 C the blue-green tungsten dithiol complex is extracted selectively into amyl acetate from a sample solution containing stannous chloride and made at least 10 N to hydrochloric acid. At 20-25 C the yellow-green molybdenum dithiol complex is extracted selectively into amyl acetate from dilute hydrochloric acid solution. Determinations are made by visual comparison of the colour intensities of the dithiol complex with the standard.

Details are given of a field method for the determination of chromium in soils. The method is a simple adaptation of the laboratory chromate colour comparison method for the determination of small amounts of chromium.

INTRODUCTION

Field methods for the determination of numerous trace metals in soils have been developed at the Chemical Research Laboratory since 1953, when a rapid, simple and inexpensive chromatographic technique was evolved specially for geochemical prospecting purposes. The majority of the methods that have been developed utilise this technique. However, a few methods based on conventional methods of separation and colorimetric estimation have also been developed.

* *Chemical Research Laboratory, Teddington, Middlesex, England.*

A description of these methods for the determination of tungsten, molybdenum and chromium in soils is confined to the latter part of this paper.

The field methods involving the use of the paper partition chromatographic technique for the separation of trace metals are all similar in principle. They comprise the break-down of the soil samples to effect the dissolution of the trace metal to be determined, in a form suitable for chromatographic separation. This step of the method is always characterised by an endeavour to obtain the most concentrated extract possible as the volume of sample solution that can be accommodated on paper strips is very small. Despite this limitation adequate sensitivities can be achieved. Following the application of an aliquot of a soil extract close to one end of a paper strip, an organic solvent mixture is allowed to diffuse upwards through the test spot. The solvent mixture is chosen to effect the separation of the desired metal, which is then detected by spraying with a suitable reagent. The actual determination of the amount of trace metal present is then made by visual comparison with standard strips. For geochemical prospecting purposes a filter paper sheet was specially designed. The use of these sheets enables ten separations to be performed simultaneously in 15 to 60 minutes, depending on the solvent used. The only apparatus required for the separations is a 600 ml glass or polythene beaker fitted with a cover. The number of reagents and the amounts of each required is very small. Furthermore the time for manipulation is of short duration, so that the methods are rapid, as well as simple and inexpensive. Sixty or more determinations can be made per man per day.

Although the procedures used vary in detail and depend on the particular metal to be determined, the chromatographic separation is always made on a specially designed sheet of paper. This is a rectangular sheet 11 x 21.3 cm of Whatman's No. 1 filter paper. Eleven symmetrical slots 3 mm x 9 cm are cut in the paper parallel to the short side so as to leave twelve strips 1.5 x 9 cm joined together at the top and bottom. These sheets are available commercially, and are designated, sheets, type C.R.L./1. After marking above the strips the numbers of the samples being examined, the sheets are rolled to form a cylinder, and the overlapping end strips are held together at the top with a paper clip. Aliquots of ten soil extracts are applied close to the lower ends of the ten centre strips. The volume of test solution applied varies between 0.01 and 0.05 ml and is applied with the aid of a capillary pipette so that it spreads across the strip to form a rectangular patch. After suitable drying, the sheet is placed vertically, with sample spots lowermost, in a covered 600 ml beaker containing the organic solvent mixture. The depth of the solvent mixture must not exceed 1 cm. The solvent is allowed to diffuse up the sheets almost to the level of the top of the slots. The sheet is then removed from the beaker and treated with a

suitable reagent or reagents to give a colour reaction with the particular metal being determined. The intensities of the coloured bands produced are compared with standard bands. Sheets of standards are prepared by using suitable standard solutions of the trace metal in place of soil extracts.

Chromatographic methods for the determination of copper, cobalt and nickel simultaneously, of niobium and tantalum using the same soil extract, and of lead, uranium and bismuth have been developed. The accuracy of these methods, ± 30 percent or better, is considered adequate for geochemical prospecting purposes. Typical results for all metals save bismuth have been described (Hunt, et al 1955, p. 172).

Before describing the individual procedure it is necessary to stress the fact that the chromatographic separations are achieved principally by a partition process; and that the volume of the fixed aqueous phase on the paper should be controlled. Control of the water content of the paper (dependent on the relative humidity of the atmosphere) is inherent to certain of the methods, e.g., bismuth. If extreme conditions of humidity are encountered, it may be necessary to dry test spots and condition the paper in a closed vessel containing a saturated solution of potassium carbonate, such that the relative humidity inside the vessel is 44 percent.

COPPER, COBALT AND NICKEL.

The chromatographic separation of copper, cobalt, and nickel from each other, and from elements such as iron present in soil extracts, can be effected most readily when the metals are present as the chlorides. However, leaching of soils with hydrochloric acid does not result in quantitative extraction of the trace metals. It was found necessary to fuse the soils with potassium bisulphate, and then leach the melts with hydrochloric acid. A relatively large quantity of very deliquescent ferric chloride was nearly always present in the soil extracts, so thet test spots on paper could not be dried by normal methods. After the application of 0.01 ml aliquots of soil extract to the paper cylinder, the cylinder was stood inside a 600 ml beaker floating in a boiling water bath. The drying of the spots could then be accomplished in three minutes, (the temperature inside the beaker was approximately 80C). Longer drying did not effect the subsequent chromatographic separation. Prolonged drying was avoided as the paper was degraded by attack by traces of sulphuric acid present in the test solutions after a bisulphate fusion. This caused the strips to break away from the sheet in the neighbourhood of the test spots.

The best solvent mixture for the separation was found to be ethyl methyl ketone containing 15 percent of concentrated hydrochloric acid and 10 per cent

of water. Iron moved furthest to the top of the strips followed by copper, then cobalt, the nickel remained very close to the point of application of the test solution. The copper tended to give two bands. This could be prevented by adding a small amount of nitric acid to the hydrochloric acid used for leaching the bisulphate melts. The prevention of the formation of the double copper bands is most probably attributable to the affect of the nitrate ion on the partition of the copper into the organic solvent. Suphate ions did not influence the movement of the copper but cobalt was retarded. This effect was beneficial, in that the separation of copper from cobalt was improved; and the cobalt formed a slightly narrower band, thereby increasing the sensitivity.

After the applications of test spots and drying the sheets at 80C for three minutes, the paper was stood with sample spots lowermost in a covered 600 ml beaker containing 20 ml of the ketonic solvent. The solvent diffused up the paper a sufficient distance to effect a separation in 30 to 40 minutos, and satisfactory results were obtained over the temperature range 20 to 25C. It was found that about five sheets could be run before loss by evaporation changed the composition of the solvent sufficient to make it necessary to use a fresh mixture of solvent.

When the solvent had diffused almost to the top of the strips, the sheet was removed from the beaker and allowed to dry for 5 to 15 minutes. It was then placed in an atmosphere of ammonia vapour for two minutes. The atmosphere of ammonia was achieved by placing a 30 ml beaker containing ammonium hydroxide, sp. gr. 0.880, in a 600 ml beaker covered with a watch glass. The neutralised sheet was then removed from the beaker spread out flat and sprayed lightly on both sides with a solution of rubeanic acid (dithio-oxamide). Nickel appeared as a blue-purple band, cobalt as a yellow-orange band, and copper as an olive-green band, whilst iron showed as the brown hydroxide in the solvent front. Other metals that might have been present in the soil extract did not give rise to any colouration. The lower limit of detection was 0.05 μg for each trace metal, equivalent to 20 ppm in a soil. The paper contained a small amount of copper impurity which was extracted, and appeared in the normal position of the copper band. The copper impurity was not very great, but it was sufficient to make difficult an exact determination on samples at the 20 ppm level. The colour given by nickel varied in shade depending on the quality of ammonium chloride present on the paper after neutralisation. Reproducible results could be obtained by standardisation of the time and conditions used when allowing the solvent and acid to evaporate from the sheet.

Satisfactory standards, covering the range 20 to 2,000 ppm of each metal in soils, were prepared using aliquots of standard solutions containing 0.05 to 5.0 μg of each metal per 0.01 ml. To cover the whole range two sheets of paper

were required when successive standards differed by approximately 30 percent. Although the preparation of standards was time-consuming, sheets of standards could be kept for several months without showing signs of deterioration.

METHOD

Mix 0.5 g of soil (minus 80 mesh) with 1 g of powdered potassium bisulphate (minus 80 mesh) in a 18 x 150 mm hard glass test-tube, and fuse gently for 1 minute. Allow the melt to cool and add 2 ml of acid (50 ml of hydrohcloric acid, sp. gr. 1.18, 5 ml of nitric acid, sp. gr. 1.42, diluted to 100 ml with water). Immerse the bottom inch of the tube in a boiling water bath for 10 minutes and shake occasionally to help break-up the melt. Remove the tube and set it aside to cool and to allow silica to settle out. Then with the aid of a capillary pipette apply 0.01 ml of the clear supernatant liquor to the lower end of a paper strip on a sheet of Whatman No. 1 filter paper, type C.R.L./1, rolled and clipped to form a cylinder. Aliquots of ten sample solution can be applied to one sheet. Stand the cylinder of paper in a 600 ml beaker floating in a boiling water bath. After three minutes transfer the cylinder to a 600 ml beaker containing 20 ml of solvent, and covered with a Petri dish. The solvent, prepared by mixing 15 ml of pure dry ethyl methyl ketone, 3 ml of hydrochloric acid sp. gr. 1.18, and 2 ml of water, should be poured into the beaker a short time before it is required for use. Allow the solvent to diffuse to the top of the strips, then remove the cylinder of paper from the beaker, and allow the solvent and acid to evaporate. Expose the paper to ammonia vapour for two minutes, then spray both sides of the sheet with a 0.1 per cent solution of rubeanic acid (prepared by dissolving 0.1 g of the reagent in 60 ml of warm ethanol, filtering the solution, if necessary, and diluting to 100 ml with water). Allow the sheet to dry, then compare the copper, cobalt, and nickel bands with those produced on standard chromatograms. If the amount of trace metal present is greater than that of the highest standard, repeat the determination after diluting the soil extract with mixed hydrochloric and nitric acid solution. Alternatively repeat the whole of the procedure given above, but fuse only 0.1 g of soil with 0.5 g of potassium bisulphate.

To prepare solutions for standard chromatograms, add 2 ml aliquots of standard solutions containing copper, cobalt, and nickel in mixed hydrochloric and nitric acids to 0.5 g of potassium bisulphate. Warm to dissolve the bisulphate, then cool to allow potassium salts to crystallise out. Use 0.01 ml aliquots of the supernatant liquors obtained for the preparation of standard chromatograms, using the same procedure as that employed for the soil extracts.

NIOBIUM

The methods for the determination of traces of niobium and tantalum in soils are based on the fact that as the fluorides they can easily be separated chromatographically from other elements, and also from one another if the conditions are carefully controlled.

Niobium was brought into solution by treating the soils with hot concentrated hydrofluoric acid. Exceptionally a preliminary fusion with potassium bisulphate was made if the niobium was present in a refractory mineral such as ilmenorutile. Organic matter present in some soils interfered with the detection and determination of niobium, since it was not destroyed during the hydrofluoric acid breakdown and moved with the niobium during the chromatographic separation. In such cases the organic matter was destroyed by pre-heating the soil to a dull red heat for a few minutes. Prolonged heating at high temperatures was avoided, since it tended to make the niobium resistant to hydrofluoric acid attack.

The maximum volume of soil extract that could be applied to paper strips was 0.05 ml, or if a bisulphate fusion had been employed 0.02 ml. The test spots could usually be dried by allowing the oylinder of paper to stand for one hour, (or longer if potassium salts were present). However, if the relative humidity of the atmosphere exceeded 66 percent it was necessary to remove part of the water from the sheet as a whole, by drying for a further period of 30 minutes in a calcium chloride dessicator. If this was not done the niobium trailed slightly during the separation.

The chromatographic separation of the niobium was slightly temperature sensitive. Over the range 20 to 25C satisfactory separations could be achieved in 30 minutes using ethyl methyl ketone containing 15 percent of hydrofluoric acid. When the temperature was below 20C it was necessary to increase the amount of hydrofluoric acid to 20 percent, otherwise the niobium band tended to diffuse.

On completion of the separation, solvent was allowed to evaporate off, then the sheet was neutralised by exposure to ammonia vapour before spraying with a fresh solution of tannic acid. If sheets were sprayed before exposure to ammonia vapour, or re-exposed after spraying, a dark, uneven and undesirable background was formed. Niobium gave rise to an orange-yellow narrow band in the solvent front. As little as 0.1 μg of Nb_2O_5 was visible. The intensity of the coloration increased slightly on standing overnight and then was stable so that standards could be kept for several weeks.

If present tantalum moved in the solvent front, but it gave only a very pale buff coloration with tannic acid, which did not interfere with the detection

or determination of the niobium. On spraying the lower half of the strips, the original sample spots turned black owing to the presence of iron. Immediately above and still in contact with the iron band a yellow band was found when the sample contained titanium. Molybdenum, and vanadium, if present, gave brown and grey bands, respectively, just overlapping the yellow band due to titanium.

To prepare standards, Specpure niobium pentoxide was first ignited to 500 to 600C for 30 minutes. Then 0.400 g of the oxide were weighed into a platinum dish and warmed with hydrofluoric and a little nitric acid until solution was complete. The solution was evaporated to dryness on a water-bath and the evaporation repeated twice with hydrofluoric acid alone. The residue was then dissolved in the minimum volume of warm dilute hydrofluoric acid, after cooling the solution was diluted to 100 ml and transferred immediately to a polythene bottle. Portions of the solution were then diluted with water containing 2 ml of 40 percent w/w hydrofluoric acid, to give a series of standard solutions. Aliquots of these solutions were used for the preparation of standars covering the range 0.1 to 8.0μg of niobium pentoxide. These corresponded to 4 to 320 ppm of the pentoxide in soils. The use of aliquots of soil extracts smaller than 0.05 ml extended the range, but for higher-grade materials a method for the determination of niobium in low-grade ores (Hunt and Wells, 1954) was preferable.

METHOD

(1) *Procedure involving hydrofluoric acid extraction.*

Weigh 1 g of soil (minus 80 mesh) into a 10 ml polythene beaker, add 5 ml of hydrofluoric acid 40 percent w/w, and evaporate to dryness on a water-bath. To the residue add 2 ml of diluted hydrofluoric acid (1 +3) using a polythene pipette fitted with a rubber bulb. Stir the mixture with a stout polythene rod, and then stand for 30 minutes. Using a capillary pipette, fitted with a small rubber bulb, transfer 0.05 ml of supernatant liquor to the lower half of a paper strip on a sheet of filter paper, type C.R.L./1 rolled and clipped to form a cylinder. Allow the spot to dry for 1 hour. Prepare the solvent by mixing 85 ml of pure ethyl methyl ketone with 15 ml of hydrofluoric acid 40 percent w/w and pour 20 ml into a 600 ml polythene beaker 30 minutes before the drying of the paper sheet is complete. Cover the beaker with a 12 cm diameter Petri dish. Place the cylinder of paper into the beaker, allow the solvent to diffuse upwards almost to the top of the strips. Remove the sheet and allow the solvent to evaporate, then expose the sheet to ammonia vapour for 3 minutes. Spread the sheet flat and spray both sides with a 2 per cent

solution of tannic acid. Allow the sheet to dry before comparing the colour intensities of the niobium bands with standards. Standard chromatograms must be prepared daily if an immediate comparison is to be made; otherwise the sample sheet should be kept overnight before comparison with old standards.

(2) *Procedure involving potassium bisulphate fusion.*

Weigh 1 g of soil (minus 80 mesh) into a small platinum crucible, add 4 g of potassium bisulphate and fuse for 1 or 2 minutes. To the cooled melt add 5 ml of hydrofluoric acid (40 percent w/w) then evaporate to dryness on a waterbath. Add 2 ml of dilute hydrofluoric acid (1 + 3) to the crucible, stir with a polythene rod, then stand for 30 minutes. Apply 0.02 ml of the supernatant liquor to the lower end of a paper strip, on a sheet of paper type C.R.L./1. Allow the spot to dry for 1 to 2 hours, and then proceed with the chromatographic separation as given above.

TANTALUM

Hot concentrated hydrofluoric acid was used to extract tantalum from soils. Tests using numerous tantalum minerals showed that this procedure was satisfactory, although complete dissolution of tantalum was not always possible. Fusion of soils with potassium bisulphate could not be employed, since on adding hydrofluoric acid to the melts insoluble potassium tantalofluoride was formed.

No specific reagent permitting the detection of tantalum in the presence of niobium was known. Hence it was necessary to separate tantalum from niobium, before the former could be determined. Both metals moved in the solvent front using ethyl methyl ketone containing 15 percent of hydrofluoric acid. But by reducing the amount of acid in the solvent and adding water niobium could be held back. The amount of acid in the small volume of solvent actually diffusing along a 9 cm. strip of paper was then less than that in a 0.5 ml. aliquot of a soil extract. A preponderance of niobium could interfere if the amount of acid in the test spot was not reduced by prolonged drying, particularly if the separation was carried out at a low temperature (20°C). Prolonged drying of spots was not necessary when only 0.02 ml. aliquots of soil extracts were used.

Quinalizarin was found to be satisfactory for the detection of tantalum; 0.1 μg of Ta_2O_5 could be detected provided that the sheet was sprayed immediately after completing the separation. If the solvent was allowed to evaporate before spraying maximum sensitivity was not achieved. After spraying it was necessary to expose the sheet to ammonia vapour to allow the formation of the tantalum lake, then expose to acetic acid vapour to reduce the blue background,

due to unreacted reagent, to a pale pink. Tantalum gave rise to a narrow mauve-pink band in the solvent front, separated from similarly coloured niobium and titanium bands that emerged from the original spot, if these metals were present. Iron and other metals did not move from the original spot, and gave rise to a dark blue colour. All the colours were stable, so that standards could be kept for a considerable period.

To prepare standars 0.0819 g of tantalum metal were warmed with hydrofluoric acid and a little nitric acid until solution was complete. The solution was evaporated to dryness, and the evaporation repeated twice with hydrofluoric acid alone. The residue was dissolved in 5 ml of concentrated hydrofluoric acid and then the solution was diluted to 100 ml with water. This solution was diluted with water containing 5 ml of hydrofluoric acid (40 percent w/w), to give a series of standard solutions. 0.01 ml aliquots of these solutions were applied to paper strips and dried for half to one hour before developing the sheet chromatographically. A suitable range of standards covered the range 0.01 to 10.0 μg of Ta_2O_5. The lowest of these corresponded to 4 p.p.m. of Ta_2O_5 in a soil.

METHOD

Weigh 1 g of soil (minus 80 mesh) into a 10 ml polythene beaker, add 5 ml of hydrofluoric acid (40 percent w/w), and evaporate to dryness on a water-bath. To the residue add 2 ml of diluted hydrofluoric acid (1 + 3), stir with a polythene rod, then stand for 30 minutes. Using a capillary pipette transfer 0.05 ml of supernatant liquor to the lower half of a paper strip on a sheet of filter paper, type C.R.L./1 rolled and clipped to form a cylinder. Allow the sheet to dry for 1 hour. If niobium is present, dry for 1½ hours if the temperature is about 25 C. If the temperature is 20 C, or less, increase the drying time to 2 hours. Prepare the solvent by mixing 2 ml of hydrofluoric acid (40 percent w/w), 8 ml of water and 90 ml of pure ethyl methy ketone. Pour about 20 ml of the mixture into a 600 ml polythene beaker 30 minutes before the strips are dried completely. Cover with a Petri dish. Place the cylinder of paper into the beaker, allow the solvent to diffuse upwards almost to the top of the strips. Remove the sheet of paper from the beaker and spray immediately with a quinalizarin solution prepared by dissolving 0.05 g of the reagent in 10 ml of pyridine and diluting to 100 ml with acetone. Expose the sheet to ammonia vapour for a few minutes, then expose to acetic acid vapour for a further few minutes. Compare the tantalum bands with standards.

LEAD

It was found that lead could be extracted from soils by digesting them with dilute hydrochloric acid (1 + 1), or dilute nitric acid (1 + 3). The latter was adopted since it is commonly used for geochemical prospecting work using dithizone mixed or monocolour methods of analysis. After applying 0.01 ml aliquots of extracts to paper strips and drying the spots, sheets were developed chromatographically using methamol containing 5 percent of hydrochloric acid. Separations were completed in 30 minutes. All metals but lead moved to the top of the strips. The extent of the movement of the other metals was slightly greater if chloride extracts were used.

After neutralisation of the sheets by exposure to ammonia vapour, lead could be detected by spraying with a solution of dithizone. The sensitivity of the reaction was reduced if any free ammonia was present, so conditions had to be controlled carefully. After completing the chromatographic separation, sheets were allowed to dry for a least half an hour before exposing to ammonia vapour for 2 minutes. Then the sheets were allowed to stand for 15 minutes. This procedure ensured that the concentration of ammonium chloride and ammonia on the sheets was low. The sheets were sprayed with a buffered solution of dithizone; prepared by disolving a few milligrams of the reagent in 20 ml of acetone containing a drop of 2N ammonium hydroxide, and diluting to 100 ml with a 5 percent aqueous solution of ammonium acetate. When a 0.002 percent solution of dithizone was used 0.1 μg of lead could be detected. To ensure the presence of sufficient reagent for complete reaction with several micrograms of lead a 0.02 percent solution of dithizone had to be used. Under of lead bands was related to the amount of lead present on strips. This facilithese conditions the background colour of unused reagent reduced the limit of detection to 0.2 μg of lead, corresponding to 20 ppm in a soil. The width tated the determination of lead as the widths of the sample bands, as well as their colour intensities could be compared with standards.

Standards were prepared from a series of standard solutions of lead nitrate in dilute nitric acid (1 + 3), containing up to 25 μg of lead per 0.01 ml. When separations were performed at 25 C, a band width of 1.5 cm was obtained for 2.0 μg of lead, 2.5 cm for 10 μg, 3.5 cm for 25 μg of lead, whilst the band width for 0.2 μg was approximately that of the original spot. For separations carried out at 20 C, band widths were still related to concentration but approximately 4 mm wider than those obtained at 25 C. If standards were kept in the dark, save when in use, they were stable for a few days, but it was found preferable to prepare fresh standards daily.

METHOD

Weigh 1 g of soil (minus 80 mesh) into a 12 mm x 100 mm rimless test tube. Add 1 ml of dilute nitric acid (1 volume of nitric acid sp. gr. 1.42, plus 3 volumes of water) and digest on a water-bath for 1 hour, with only the bottom inch of the tube immersed. Remove the tube, cool and allow insoluble matter to settle. Using a capillary pipette transfer a 0.01 ml aliquot of the clear supernatant liquor to the lower end of a strip on a sheet of filter paper type C.R.L./1, rolled and clipped to form a cylinder. Allow spots to dry for 30 minutes. Prepare the solvent by mixing 1 ml of hydrochloric acid (sp. gr 1.18), and 19 ml of pure methanol, pour the mixture into a 600 ml beaker fitted with a cover. Place the cylinder of paper in the beaker, and allow the solvent to diffuse upwards almost to the top of the strips. Remove the cylinder of paper and allow it to dry for at least half an hour. Expose the paper to ammonia vapour for 2 minutes, and then stand in the air for 15 minutes before spraying with a buffered solution of dithizone. Compare the width and colour intensities of the lead bands with standards.

It is of interest to record that L. Marvier (Personal Communication) has found that chromatograms developed for lead can also be used for the determination of zinc, by using the Montequi reaction for the detection of the zinc, and sodium fluoride to bleach the colour due to iron. Developed chromatograms were sprayed with a solution containing copper sulphate and sodium fluoride, and then with a second containing ammonium thiocyanate and mercuric chloride, to produce a grey-violet colouration if zinc was present.

URANIUM

Uranium could be extracted from some soils by digesting them with dilute nitric acid (1 + 3). This procedure was inadequate in certain cases so that a more rigorous attack involving evaporation with concentrated hydrofluoric and nitric acids, then leaching the residues with dilute nitric acid was adopted, since it was generally applicable. Phosphates present in some samples interfered if the soils were low in iron and aluminium. But satisfactory separations could be achievd if the soil extracts were satured with aluminium nitrate (H. W. Lakin, Personal Communication).

After the application of 0.01 to 0.05 ml aliquots of soil extracts to paper strips, and drying for one hour, the separation of uranium could be accomplished in 15 minutes using ethyl acetate containing 10 percent of nitric acid and

5 percent of water. It was essential that the ethyl acetate be free from alcohol. If necessary the ester was washed with an aqueous solution of calcium chloride, the alcohol free ester was then dried over anhydrous sodium sulphate and distilled.

An aqueous solution of potassium ferrocyanide was used for the detection of the uranium. As little as 0.1 μg of uranium gave a brown band in the solvent front. Other metals giving colours with potassium ferrocyanide, iron, copper, and molybdenum moved only slightly, if at all, from the original test spot. Suitable standards, to cover the range 0.1 to 20 μg of uranium, were prepared using 0.02 ml aliquots of a series of standard solutions of uranyl nitrate in dilute nitric acid (1 + 3). On keeping sprayed sheets became discoloured owing to the oxidation of the excess of potassium ferrocyanide present. It was impossible to wash out this excess without removing part of the uranyl ferrocyanide. Hence it was necessary to prepare fresh standards daily.

METHOD

Weigh 1 g of soil (minus 80 mesh) into a small platinum dish, add 2 ml of nitric acid, sp. gr. 1.42, and 2 ml of hydrofluoric acid (40 percent w/w). Evaporate to dryness on a water-bath. Add 1 ml of dilute nitric acid (1 + 3) to the residue, stir with a glass rod, then leave to cool and settle. Transfer a 0.05 ml aliquot of the clear supernatant liquor to the lower half of a paper strip on a sheet of paper, type C.R.L./1, rolled and clipped to form a cylinder. Allow the spot to dry for 1 hour. Prepare 20 ml of solvent by mixing 2 ml of nitric acid, sp. gr. 1.42, and 1 ml of water with 17 ml of ethyl acetate, analytical reagent grade; pour the mixture into a covered 600 ml beaker. Place the cylinder of paper into the beaker, and allow the solvent to diffuse upwards almost to the top of the strips. Remove the paper from the beaker, allow the solvent to evaporate, then spray the sheet with a 5 percent aqueous solution of potassium ferrocyanide. Allow the sheet to dry, and then compare with standards.

BISMUTH

Digestion of rock or soil samples with dilute nitric acid (1 +3) was used to effect the dissolution of bismuth. A more vigorous attack employing a bisulphate fusion could not be used as sulphate ions interfered with the separation of bismuth. Organic matter present in some soils interfered with the detection and determination of bismuth. This was prevented by pre-ignition of the soils to a dull red heat for a few minutes, to burn off organic matter.

Pure dioxan containing small amounts of nitric acid and water separated bismuth from other elements present in soil extracts. Separations could be accomplished in 60 minutes. Bismuth moved in a narrow band in the solvent front. There was a tendency for the bismuth to trail if the amount of water held by the sheet as a whole was too small. In order to achieve reproducible separations, and maximum sensitivity, it was necessary to condition the paper in an atmosphere with a constant relative humidity of 81 percent. This was accomplished by completing the drying of the test spots in a desiccator containing a saturated aqueous solution of ammonium sulphate.

Dimercaptothiodiazole dissolved in N caustic soda solution was used for the detection of bismuth as a red-orange band. A 0.5 percent solution of the reagent was required for complete colour development when 10 μg of bismuth were present on a strip. However, this quantity of bismuth was only encountered when rock samples were examined, so that a 0.2 percent solution of dimercaptothiodiazole was adequate for the detection of bismuth separated from soil extracts. As little as 0.05 μg of bismuth could be detected.

Standards were prepared, using 0.01 ml aliquots of standard bismuth solutions in dilute nitric acid (1 + 3), to cover the appropriate part of the useful range 0.05 to 10 μg; depending on whether soil or rock samples were being examined. The colour of the bismuth dimercaptothiodiazole complex faded gradually, particularly when exposed to sunlight .It was necessary to prepare fresh standards every two or three days.

METHOD

Weigh 1 g of finely ground sample into a 12 x 100 mm test-tube. Add 1 ml of dilute nitric acid (1 + 3), and digest in a hot water bath for 15 minutes with only the bottom inch of the tube immersed. Remove the tube, cool, and allow insoluble matter to settle. Using a capillary pipette transfer a 0.01 ml aliquot of the clear supernatant liquor to the lower end of a strip on a sheet of paper, type C.R.L./1, rolled and clipped to form a cylinder. Allow the spots to dry in the atmosphere for at least 15 minutes, then for a further 15 minutes over a saturated aqueous solution of ammonium sulphate. Prepare the solvent by mixing 1 ml of nitric acid (1 volume of nitric acid, sp. gr. 1.42, plus 1 volume of water), and 19 ml of dry dioxan, analytical reagent grade; pour the mixture into a 600 ml beaker fitted with a cover. Place the cylinder of paper in the beaker, and allow the solvent to diffuse upwards almost to the top of the strips. Remove the cylinder, and allow the solvent to evaporate. Then spray the sheet of paper with a solution of dimercaptothiodiazole in N caustic soda. Compare the bismuth bands with standards.

TUNGSTEN AND MOLYBDENUM

Soils were fused with a mixed sodium carbonate, sodium chloride, potassium nitrate flux and the melts leached with water to extract trace amounts of tungsten and molybdenum, and to effect their separation from iron and other elements forming insoluble hydroxides. A solution of toluene-3:4-dithiol (dithiol) in amyl acetate was used for the extraction and colorimetric estimation of tungsten, or molybdenum depending on the conditions employed.

After making an aliquot of the leach liquor 10 N with respect to hydrochloric acid and adding stannous chloride, the test solution in a 16 x 150 mm test-tube was warmed to reduce any molybdenum present to a lower unreactive valency state. Then a small volume of amyl acetate containing dithiol was added. The tungsten dithiol complex was then formed and extracted concurrently by heating the tube in a boiling water bath for about 15 minutes. Most of the ester was hydrolysed, or volatilised during the heating period, so that only a globule remained. After cooling a measured volume of water white kerosene was added, so that the tungsten dithiol complex was contained in an organic solvent layer of sensibly constant volume. The tungsten present could then be determined by visual comparison of the colour intensity of the blue-green tungsten dithiol complex with standards, prepared by using aliquots of a standard tungstate solution in place of soil extracts. A set of standars could be used for about one week, as the tungsten dithiol complex was reasonably stable in the ester-kerosene layer.

Molybdenum coud be extracted selectively into amyl acetate from aliquots of soil extracts, after making them 4 N with respect to hydrochloric acid, and adding a small amount of hydroxylamine to destroy the nitrite present in the soil extract and to prevent interference from oxidation products of dithiol. Tungsten did not react with the dithiol, provided that the temperature did not exceed 30 C. The formation and concurrent extraction of the molybdenum dithiol complex was carried out in a 16 mm diameter cylindrical tap funnel. Since precipitated silicic acid frequently prevented drops of ester from coalescing, it was necessary to separate and clarify the ester phase by shaking with concentrated hydrochloric acid. The colour intensity of the yellow-green molybdenum dithiol complex was then compared with standards prepared in 16 x 150 mm test-tubes. Tubes could be used as it was not necessary to clarify the ester phase when aliquots of a standard molybdate solution were used in place of soil extracts. The ester was not hydrolysed appreciably whilst in contact with cold 4 to 5 N hydrochloric acid, so that standards could be used for several days.

The methods developed covered the ranges 4 to 400 ppm of tungsten, and

1 to 100 ppm of molybdenum in soils, but they could be extended to permit the determination of greater amounts of the trace metals. Thirty or more determinations could be made per man per day. Details of the two methods have been accepted for publication elsewhere. (North, in press).

CHROMIUM

A field method for the determination of chromium in soils was developed in order to investigate the distribution of chromium in the neighbourhood of a chromite quarry. The cromium content of the soils (up to 4 percent) was such that a simple chromate colour comparison method could be used. The method developed was capable of detecting 0.02 percent of chromium.

It was found that soils could be decomposed completely by fusing them for 5 minutes with a mixed sodium hydroxide, sodium peroxide flux; even when discrete chromite particles were present, provided that the flux to sample ratio was not less than 12:1. The mixed flux was superior to sodium peroxide alone in that decomposition of samples was more rapid, and the lower melting point of the mixed flux facilitated fusion over camping stoves used in the field. Also the attack on the crucible used for the fusion was much more severe, when the mixed flux was used, so that the life of a crucible was prolonged.

When very small amounts of chromium were to be determined, the use of chromium free iron crucibles for the fusions was desirable. Since it was found that the nickel crucibles examined contained a trace of chromium, and approximately 15 μg of chromium were removed during each fusion.

METHOD

Mix 0.1 g of soil (minus 80 mesh) with 0.6 g of sodium peroxide in a 3 x 3 cm crucible, then add six 0.1 g pellets of sodium hydroxide. Heat the base of the crucible to a dull red heat, and maintain the fusion for 5 minutes. Allow to cool, then add 5 ml of water to the melt and stir with a glass rod. Transfer the contents of the crucible to a graduated test-tube, wash out the crucible wih water, and make up to the 10 ml mark on the tube. Heat the tube in a boiling water-bath for 5 to 10 minutes, then add 0.1 ml of ethanol and maintain at just below the boil for 2 minutes to complete the reduction of any manganate present. Allow to cool, then filter through a dry 7 cm diameter Whatman Nº 540 filter paper into a dry 16 x 150 mm test-tube. Compare the colour intensity of yellow filtrate with standard chromate solutions in 12 percent w/v sodium hydroxide solution. Use a standard series of chromate solutions (prepared from potassium chromate) containing 2 to 100 ppm of chromium,

corresponding to 0.02 to 1.0 percent of chromium in soils. If samples containing more than one percent of chromium are encountered, dilute a suitable aliquot of the filtrate with 12 percent w/v sodium hydroxide solution and repeat the comparison.

The precision of the method was found to be better than ±10 percent. Fifty or more determinations could be completed per man per day.

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ACCURACY AND PRECISION OF FIELD METHODS OF TRACE ANALYSES USED IN GEOCHEMICAL EXPLORATION BY U. S. GEOLOGICAL SURVEY *

J. HOWARD MCCARTHY, Jr. * *

ABSTRACT

Data that have been compiled in the U. S. Geological Survey over a period of several years were used to determinetheprecision and accuracy of 20 rapid methods of trace analysis. The methods were evaluated for natural materials such as soil, rock, vegetation, and water. In geochemical explorations where anomalous chemical values are sought, it is apparent that the accuracy of the analyses may vary several hundred percent as ling as it is relatively uniform and that the precision may vary from ±10 percent to ±50 percent and yet allow clear definition of the anomalies sought.

The accuracy of the field tests varies fro ±20 percent to ±40 percent of the mean value obtained by careful analyses. The precision attainable by a single operator is approximately ±20 percent of his mean values. The mean value obtained by different operators varied by as much as 10 percent to 30 percent. A rapid cold field method for copper, lead, and zinc may extract less than 10 percent. The use of a scoop to obtain a measured volume of the sample in place of a balance to weigh the sample in the field results in an added error of not more than ±15 percent.

INTRODUCTION

The purpose of this study is to evaluate the precision and accuracy of some of the semi-quantitative field methods of analysis in use in the U. S. Geological Survey. A good cross section of data collected in the laboratory has been obtained, and should provide a basis for a reliable estimate of the precision and accuracy of the methods in routine use.

The field methods evaluated here include those for Cu, Pb, Zn, Co, Sb, Mo, W, Ge,P. V. Mn, Se, As, Ni, U, and for heavy metals, i.e. copper, lead, and zinc, as a group. Using field methods of analysis approximately 150,000 determinations have been made, and approximately 15,000 or (10 percent) of these

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* * *U. S. Geological Survey.*

determinations are duplicates from routine checking. The data used to evaluate the precision of the field methods were taken from these duplicate determinations. The data were selected by a random sampling of the notebooks of the analysts and include both the best and the poorest data which have resulted from routine use of the field methods. Included in the data are results of analysis of such widely different materials as limestones, dolomites, felsic and mafic igneous rocks, and soils, ranging from those collected in tropical areas of high rainfall to desert areas.

The precision and accuracy of the field methods are affected by many factors. One of the most obvious is differences in the amount of metal extracted by different methods. For example, in the "cold" heavy metals test only a small part of these metals is extracted, whereas with a method requiring a bisulphate fusion of the sample, a large part of the metals in the sample are extracted. The results obtained from the latter method should of course more nearly approach the true value. When using a routine procedure, several other factors influence the accuracy and precision of the analyses, examples of some of these are:

A dilute nitric acid digestion may be quite satisfactory for a limestone sample, yet fail to extract the metal from a silicate rock.

Some analysts may be able to estimate satisfactorily shades of pink in a standard series, but may not be able to estimate comparable differences in shades of yellow; others do equally well with either color.

The amount of sample taken for analysis; a small sample generally cannot be weighed as accurately as a larger sample.

The particle size of the sample taken for analysis; for example, we have analyzed soil samples for tungsten which contained discrete, finely disseminated particles of scheelite, which resulted in large discrepancies because several scheelite particles were in the first portion of a small sample taken for analysis and very few were in the second. This type of error may be very large if the element sought occurs as a major constituent of a minor mineral in a sample.

The use of a scoop instead of a weighed amount to obtain a small portion of the sample; this can become important when comparing analytical data for samples of varied density.

There are also factors principally of an analytical nature, which influence results obtained by the field methods. Some of these are differences in the quality of reagents from one manufacturer to another, and differences in equipment. A change in the analytical method will also alter the precision obtainable. Since the data used here were taken from analyses collected over several years' time, the effect of these factors on the results of analysis are incorporated into the estimate of precision and accuracy. The factors evaluated

for this study are: (1) the analytical method used, (2) the precision and accuracy of an analyst, and (3) the differences in precision and accuracy between analysts. The other factors mentioned are either held constant or are randomly distributed throughout the data.

I wish to acknowledge the helpful guidance provided by the members of the Statistics Committee of the U. S. Geological Survey and particularly by T. G. Lovering.

THE FIELD METHODS OF ANALYSIS EVALUATED

The field analytical methods used for geochemical prospecting are of several types, but all are colorimetric methods and are semiquantitative. These methods are listed in table 1; the range listed for each is the range of concentrations in which the methods are applied in routine analysis of samples. The figures shown in the colum listing determinations per man day are the number of determinations which can be made by an experienced analyst in an 8-hour day. All the methods are simple rapid and suitable for use in the field, and can be used by relatively inexperienced personnel. The equipment and reagents are commonly available in most laboratories with the exception of one or two special items.

All the methods require visual estimation of a colored complex by comparison with a standard series of colors. The color may be formed in a liquid, or as a precipitate collected on a restricted area of paper, or as a colored band separated by means of paper chromatography. All the field methods have been used successfully in geochemical exploration, and are widely varied in precision and accuracy.

STATISTICAL TECHNIQUES

The search for an acceptable statistical technique to evaluate the precision of the field methods presented a difficult problem because the data obtained by these methods are semi-quantitative. Most statistical procedures require more replication of analyses than was included in the available data. The technique finally utilized was that of Youden, and is one which duplicate determinations can be used in estimating precision. The precision of the methods and of the analysts is expressed as the coefficient of variation, the coefficient of variation is a measure of the relative variation about the mean, or is the standard deviation, expressed as percent. The "coeficient of variation" was calculated according to the method given by Snedecor.

TABLE 1

ELEMENTS DETERMINED BY THE FIELD METHODS, SHOWING THE RANGE AND NUMBER OF DETERMINATIONS WHICH CAN BE MADE PER MAN DAY

Element	Range* (ppm)	Determinations per man day
Cu	10—5000	60
Pb	20—5000	60
Zn	20—5000	60
Co	10—5000	50
Sb	1— 500	40
Mo	1— 500	40
W	20—1000	40
Ge	4— 500	40
P	100—50,000	80
V	50—25,000	80
Mn	50—25,000	80
Se	1—2500	30
As	10—5000	50
Ni	20—1000	60
U	2—5000	80
Heavy Metals	100—5000	100

* The range covered in routine use of the methods.

$$V = \frac{\sigma\,(100)}{X}$$

Where V = coefficient of variation
X = arithmetic mean
σ = standard deviation

The coefficient of variation is used because it expresses precision in terms that are applicable even with the large differencs in range of concentration.

The "standard deviation" was calculated using duplicate determinations according to the method presented by Youden (1950).

$$\sigma = \sqrt{\frac{\Sigma\,(d_1 - d_2)^2}{2n}}$$

Where $d_1 - d_2$ = difference between duplicates
n = number of pairs of duplicates
σ = standard deviation

"The standard deviation measures the variation or scatter about the arithmetic mean..." Arkin and Colton (1955) and is used to calculate the coefficient of variation.

The plan followed was to collect from the work of each of three analysts 10 pairs of duplicate determinations in each of 3 or 4 ranges of concentration for each of the field methods. A block diagram showing arrangement of the data is shown in Figure 1. For example, in Table 2, each pair of duplicate analyses for copper in the range 50 to 250 ppm represent the original value and the recheck for 30 different samples.

Since no individual analyst has worked with every method, it was necessary in places to substitute data from other analysts in order to have the same number of pairs of duplicates for estimating the precision in each range. An equal number of determinations were used to calculate the precision of the method in all but 4 instances. The coefficient of variation was calculated for each analyst using his 10 pairs of duplicates and provides a measure of the precision of each analyst. Then the coefficient of variation was calculated for each range using 30 pairs of duplicates. This figure gives the comparative precision between analysts and represents the precision of the method in each range of concentration. The coefficient of variation for each analyst and each method is listed by element in Table 3.

The coefficient of variation for most of the analysts is greatest at the low range of concentration, and this is reflected in the coefficient of variation of the method. This might be expected since comparison of colors in this range is less sensitive, and small differences in the result mean large differences in the coefficient of variation. There is also a general decrease in the precision in the highest range of concentration. A similar trend is noted in the coefficient of variation of each analyst from range to range in many of the methods, showing that the precision of analyst A may not be as good as that of analyst B, but this may be interpreted to mean that each analyst is using the method to the best of his ability.

Most of the methods seem to have an optimum range; in this range the precision is best between analysts, and as would be expected the precision of the individual analysts is generally best. Several of the methods, for example, nickel, germanium, phosphorus, and vanadium have essentially the same coefficient of variation in all of the ranges. This is a very desirable situation since the values obtained are of comparable precision whether those values

BLOCK DIAGRAM SHOWING THE ARRANGEMENT OF DATA USED IN CALCULATING THE PRECISION OF THE FIELD METHODS

Range (ppm)	Duplicate Results						All Analysts
	Analyst A		Analyst B		Analyst C		
10-50							
50-250							
250-1000							
1000-5000							

Fig. 1.

TABLE 2

DUPLICATE DETERMINATIONS FOR THREE ANALYSTS IN THE RANGE 50 TO 250 PPM COPPER

Range (ppm)	Duplicate determinations by three analysts using the field analytical method for copper (ppm)					
	Analyst A		Analyst B		Analyst C	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
50 to 250	60	60	60	80	50	60
	60	60	100	100	60	60
	60	60	100	130	60	80
	80	100	100	250	70	70
	100	80	130	130	90	90
	110	70	150	100	100	100
	110	110	150	150	130	130
	110	110	200	200	130	150
	150	150	200	200	130	200
	200	100	200	300	250	250

TABLE 3

THE COEFFICIENT OF VARIATION FOR EACH ANALYST AND EACH METHOD, LISTED BY ELEMENTS AND RANGES

		Coefficient of variation (percent)			
		For each analyst			For all analysts
Element	Range (ppm)	A	B	C	
Copper	10—50	25	25	37	27
	50—250	26	28	16	25
	250—1000	11	23	18	19—
	1000—5000	28	30*	10	28—
Lead	10—50	42	15	28	29—
	50—250	23	16	22	19
	250—1000	25	9	12	16—
	1000—5000	19	22	20	20
Zinc	10—50	71	38	33	43
	50—250	47	25	25	32
	250—1000	19	18	17	18
	1000—5000	18	9	14	14
Arsenic	10—50	48	12	28	50—
	50—250	59	28	17	34
	250—1000	26	10	15	19—
	1000—5000	45	20*	36*	38
Antimony	1—5	9	24	18	20—
	5—25	13	15	20	16
	25—100	10	14	9*	13
	100—500	8	10*	7*	8—
Cobalt	10—50	33	27	28	31
	50—250	16	26	18	20
	250—1000	17	22	13	18
Germanium	1—5	13	30	27*	21
	5—25	23	10	21*	17
	25—100	20	14	16*	17
Molybdenum	1—5	18	28	32	27
	5—25	13	19	26	20
	25—100	40	20	14	30
	100—500	39	16	17	23

TABLE 3 (Cont.)

THE COEFFICIENT OF VARIATIONS FOR EACH ANALYST AND EACH METHOD, LISTED BY ELEMENTS AND RANGES

		Coefficient of variation (percent)			
		For each analyst			For all analysts
Element	Range (ppm)	A	B	C	
Manganese	50—250	40	2	36	31
	250—1000	24	4	17	18
	1000—5000	5	7*	11*	8*
Nickel	10—50	29*	26	21	23
	50—250	23*	17	21	19
	250—1000	18*	13	21	16
Phosphorus	500—2500	25	27	28*	26
	2500—10,000	12	19	19*	16
Selenium	1—5	40	38	32	36
	5—25	47	15	18	23
	25—100	29	22	24	25
	100—500	20	21	23	23
Uranium	10—50	22	24	22	22
	50—250	39	16	22	31
	250—1000	19	7	6	13
Vanadium	50—250	21	27	24*	25
	250—1000	19	22	18*	21
	1000—5000	20	13	15*	17
Tungsten	10—50	34	**	**	34
	50—250	27	**	**	27

* Indicates data used to calculate coefficient of variation in this range was taken from other analysts.

* * Indicates no data available in this range.

be 20 or 200 ppm. The ideal situation is one in which the precision is the same over the entire range of concentration, and we are now experimenting with a possible means of obtaining this with all of the field methods.

ACCURACY

The accuracy of three of the methods was determined by comparing the values obtained by the field methods with those obtained by careful laboratory methods of analysis. The resultant estimate of accuracy is dependent upon the correctness of the laboratory values, which are themselves subject to error, and thus it is the relative occuracy that is actually determined. Assuming as correct the values given for the standard samples, the relative accuracy is calculated as the percentage of difference from this standard value for each of the values obtained by the field methods.

$$\text{Relative accuracy} = \frac{\text{Difference from accepted value} \times 100}{\text{Accepted value}}$$

The data used to determine accuracy of the field methods for copper, lead, and zinc were obtained by taking duplicate splits of 14 samples which had been analyzed by the most accurate methods at our disposal; all splits were given different number and then submitted for routine analysis of Cu, Pb, and Zn by the field methods. The averages of the field results as well as the results of laboratory analysis of these samples are shown in Tables 4, 5, and 6. As noted in table 4 for lead, the first three samples differ by only 30 ppm; three of the six duplicates fail to distinguish a difference in these samples, yet a relative difference is evident in the average. In the two samples with lead content of 380 and 500 ppm, one of the six duplicate results was reversed, and one failed to distinguish the high from the low sample. Despite these extremes, all duplicates distinguish samples where there is a threefold difference in lead content. The average percent deviation and the maximum percent deviation are given in Table 7.

The figure given for average deviation includes the values greater than and less than the laboratory value. These figures indicate the accuracy of the field methods; however they do not show whether a systematic bias is inherent in the field methods. To determine this, the average percent deviation was calculated separately for those values that were greater and those that were less than the laboratory value. These data are summarized in table 8 which shows the number of samples out of 100 which will be greater than, less than, and the same as the laboratory value. An example taken from this table shows that in every 100 samples analyzed by the field method for zinc, 62 of the values will

TABLE 4

RESULTS OF LABORATORY AND FIELD METHODS FOR LEAD WITH DUPLICATE ANALYSES BY THREE ANALYSTS

Replicate analyses by three analysts using the field method for copper (ppm)						Average of six replicates	Average of three determination by the laboratory method for copper (ppm)
Analyst A		Analyst B		Analyst C			
100	150	120	120	120	120	122	140
120	120	120	150	150	150	135	160
120	150	120	200	150	150	148	170
200	200	200	300	300	150	225	200
300	300	400	500	400	500	400	380
600	500	400	800	500	400	535	500
600	800	1000	1000	800	600	800	900
1000	1000	1200	1200	800	1500	1116	1200
1500	1500	1500	1500	1500	1500	1500	1800
4000	4000	4000	4000	3000	3000	3666	4500

TABLE 5

RESULTS OF FIELD AND LABORATORY METHODS FOR ZINC WITH DUPLICATE ANLYSES BY THREE ANALYSTS

Replicate analyses by three analysts using the field method for zinc (ppm)						Average of six replicates	Average of three determination by the laboratory method for copper (ppm)
Analyst A		Analyst B		Analyst C			
50	50	20	50	20	20	30	60
100	80	50	50	150	80	85	148
100	100	80	80	100	200	110	160
100	100	80	100	100	100	97	170
300	300	100	120	200	300	220	325
400	400	150	150	300	500	317	380
400	500	180	180	300	500	343	450
500	600	600	180	500	500	480	500
1500	1000	1000	700	1000	800	1000	870
1000	1500	1500	1500	1500	2000	1500	1200
1500	2000	1500	1500	2000	1500	1666	1700
4000	4000	3500	3000	4000	4000	3750	3250

TABLE 6

RESULTS OF FIELD AND LABORATORY METHODS FOR COPPER, WITH DUPLICATE ANALYSES BY THREE ANALYSTS

Replicate analyses by three analysts using the field method for copper (ppm)						Average of six replicates	Average of three determination by the laboratory method for copper (ppm)
Analyst A		Analyst B		Analyst C			
30	30	10	20	30	20	23	25
20	40	20	20	20	10	22	30
30	40	10	20	20	10	22	30
30	60	10	20	20	10	25	30
30	40	20	20	20	30	27	40
40	40	20	20	40	40	33	40
200	200	100	100	150	150	150	200
600	600	300	300	300	300	400	380
4500	4500	3000	3000	3000	3000	3500	3800

be less than the laboratory value by an average of 38 percent; and 34 of these samples will be greater than the true value by an average of 22 percent; and 4 of the values will be the same as the true value. There is then a systematic bias on the low side for each of these field methods.

The relative accuracy of the "cold" method for heavy metals is considerably less than for most of the other field procedures. Many samples analyzed by the "cold" heavy-metals test gave values which indicate that only 5 to 20 percent of the heavy metals present were extracted. The precision of this method, however, was calculated and the coefficient of variation was 30 percent. The particular merit of this "cold" method, aside from speed and simplicity, is that the ratio of background to anomaly often is greater than that obtained by the other methods. Although a less accurate procedure, it thus may be used to detect differences that would not be as evident when using a more accurate analytical technique.

TABLE 7

THE MAXIMUM DEVIATION OF SINGLE DETERMINATIONS AND OF DUPLICATE MEANS, AND THE AVERAGE DEVIATION OF DUPLICATE MEANS

Element	Maximum deviation		Average deviation of duplicate means (percent)
	of single determination (percent)	of average duplicate means (percent)	
Cu	100	71	33
Pb	60	33	15
Zn	72	66	27

TABLE 8

THE NUMBER OF RESULTS PER 100 SAMPLES ANALYZED BY THE FIELD METHODS WHICH ARE GREATER THAN, LESS THAN, AND THE SAME AS THE LABORATORY VALUE

Element	Number of samples with values less than the labortory value (per 100)	Number of samples with values greater than the labortory value (per 100)	Number of samples with values the same as the laboratory value (per 100)
Cu	65	19	16
Zn	62	34	4
Pb	70	20	10

Many of the field methods have been applied to the determination of vegetation and water as well as to soils and rocks. The data available indicate that the precision of these methods when applied to vegetation is essentially the same as for soils or rocks. The precision when analyzing water is usually better. The coefficient of variation is 20 percent for the determination of copper, lead, and zinc in water.

CONCLUSIONS

Both the precision and accuracy of these analytical methods are acceptable for geochemical prospecting, but are low when compared to accepted standards for anlytical work. Some methods are more accurate than others and some are more precise. For example, all but 4 have a coefficient of variation less than 20 percent in the optimum range, and all but one have a coefficient of variation of less than 30 percent in the optimum range. This one has a coefficient greater than 50 percent.

The data show that the differences in precision between two analysts (analyzing the same samples) may be twofold, or more. The precision of individual analysts does, however, show the same general pattern of change with increasing concentration. Therefore, the variability between analysts, particularly on a large project where several analysts may be employeed, should be ascertained, analysts should not be switched in the middle of the stream.

The field methods of analysis are quite satisfactory for the purpose for which they were developed. Despite their relatively low precision and accuracy, they have been used successfully to find ore by the U. S. Geological Survey, mining and exploration companies, and prospectors.

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FIELD PERFORMANCE OF SOME ANALYTICAL METHODS USED IN GEOCHEMICAL PROSPECTING

J. S. Tooms *

ABSTRACT

During the course of training personnel and in field operations, principally in Africa, has provided a useful volume of information on reliability, productivity and costs for a number of the analytical tests employed under a variety of field conditions. Other important variables include (a) the type of personnel engaged on routine analysis, which has ranged from qualified chemists and geologists, both male and female, to technicians and local African labour; and (b) the permissible accuracy of the analytical data, which may vary considerably according to the nature and requirements of the local problems.

On the basis of this information, which the author has compiled from a number of sources, suggestions are made concerning the training and efficiency of different classes of personnel, and the organization of fields analysis so as to obtain, in particular circumstances, the most efficient relationship between analytical reliability and operational cost.

INTRODUCTION

The analytical methods, whose performances are considered in this paper, have been developed to meet, as far as possible, the peculiar requirements of geochemical prospecting. They are semiquantitative trace element methods designed to give a sensitivity at least comparable to the normal (background) concentrations of the element sought, and to differentiate with adequate accuracy between anomalous and background metal contents. During most geochemical surveys large numbers of samples are involved, and it is essential therefore that a high productivity shall be possible, combined with low costs. If the last of these requirements is to be satisfied it is necessary for the methods to be rapid, simple and capable of operation by non-technical personnel.

In general the geochemical prospecting tests published in the literature have been produced either (a) to suit the conditions of a particular area, or (b) for general purposes. However, each area has unique problems and for any given element, no single procedure can be considered as ideally suited to the require-

* *Imperial College, London, England.*

ments of every geochemical survey. Not only do the homogeneity and intensity of anomalies, and therefore the permissible analytical accuracy, vary but so also may the form in which the element occurs. These factors control the optimum analytical technique in each particular case. Furthermore, the type of local labour and availability of various chemicals may necessitate additional modifications. Thus, just as it is essential to carry out a field orientation in any new area to decide the most efficient sampling procedure, so also is a complementary analytical orientation study required to find the most suitable analytical techniques. In particular, the number of samples required to detect an anomaly of a given form and size will depend on the analytical reliability, and this in turn must affect productivity and the cost of the survey. It is only by a consideration of all these interrelated factors that the most efficient combination of low cost and reliability can be obtained in geochemical prospecting programmes.

This paper is only concerned with the performance and operation of geochemical analytical tests under routine conditions. The data on which the present conclusions and suggestions are based have been obtained (a) in the laboratories of the Geochemical Prospecting Research Centre of the Royal School of Mines, (b) during research projects in the United Kingdom and Africa, and (c) from information supplied by mining organizations engaged on geochemical prospecting.

The writer wishes to acknowledge the co-operation he has received from the research students and staff of the Geochemical Research Centre and the Companies with whom the Centre has been associated. Especial thanks are due to Dr. Webb who suggested the subject of the paper and gave much valuable assistance in its production.

FIELD PERFORMANCE

Certain aspects of the field performance of the analytical techniques are not amenable to generalization and have not therefore been considered in detail here. Of these, the most important are the applicability of different extraction methods and sample preparation, both of which are largely controlled by the form in which the metal occurs. They are therefore very closely related to the results of the field orientation studies. However, the aspects of the field performance considered below, including the sensitivity, accuracy and productivity of the methods, are of fundamental importance in the planning of geochemical surveys.

Sensitivity:

The desirable sensitivity of a field test varies with the background fluctuations in different areas. Table 1 shows the claimed sensitivity of a number of methods and the normal range of background for different elements. It will be observed that several methods have a claimed sensitivity insufficient to detect the lower limits of background. The antimony (Rhodamine B) and cobalt (chromatography) tests fall particularly short of requirements in this respect. Lack of sensitivity in the background range is particularly serious in areas where a low background metal content is associated with anomalies of low absolute values.

Reliability:

In the detection of anomalies, the reliable determination of the relative concentration of an element is of much greater importance than estimation of the absolute value of the metal concentration. Moreover, if the dispersed metal is held more loosely than the majority of the background metal, the estimation of only the easily extractable metal will give a larger anomaly than estimation of the total metal content. This principal has been exploited by various cold extraction tests.

TABLE 1

SENSITIVITY OF SOME GEOCHEMICAL TESTS AND NORMAL RANGE OF SOIL BACKGROUND VALUES

Element	Method	Claimed Sensitivity (ppm)	Normal Range of Soil Backgrounds (ppm)
Antimony	Rhodamine B	0.5	less than 1 ppm.
Arsenic	Confiend Spot	5	1 to c50
Cobalt	2-Nitroso-1-Napthol	1	1 to 40
	Chromatography	10	1 to 40
Copper	Dithizone		2 to 100
	Chromatography	20	2 to 100
Lead	Dithizone	10	2 to 200
Molybdenum	Dithiol	1	0.2 to 5
	Potassium thiocyanate	1	0.2 to 5
Nickel	Chromographic	30	5 to 500
	Chromatography	20	5 to 500
Tin	Gallein	10	less than 5 to 25
Tungsten	Dithiol	4	
	Potassium thiocyanate	10	
Zinc	Dithizone	50	10 to 300

Confidence in the ability of a given analytical method to discriminate between anomalous and background samples can only be attained if the accuracy of the relative metal determination is known over the critical range of values. As an example it is particularly important to know the reliability of the analyses in areas, such as the Northern Rhodesian Copperbelt, where significant mineralization anomalies in near-surface soils may, in some circumstances, be less than 150 ppm compared to the background copper content of 40 ppm. Even where large anomalies are found, the detectable width of an anomaly, and thus the maximum permissible sampling interval, may be increased considerably by increasing the analytical accuracy. This applies not only to Northern Rhodesia but also to many other areas where anomalies may be relatively narrow at four times the local background but have a considerably greater lateral extent at values two or three times those of the background.

In routine prospecting it is desirable to check analytical accuracy periodically during the course of the work. The samples involved in routine check analyses should be few in number to avoid serious loss of productivity, but at the same time must be sufficient to provide adequate control of the analytical efficiency. Craven (1954) has suggested a statistical method which fulfills these conditions and has the added advantage over normal check procedures in that it gives a measure of the relative, as distinct from the absolute accuracy. His method is based on the analysis of a series of prepared mixtures containing varying known proportions of two samples, one possessing a relatively high content of the required element and the other a low content. It is not necessary to know the absolute metal content of these two samples because the calculated accuracy figure is based on the known ratios of the high and low samples. The accuracy determined by this method is the mean accuracy for the whole range of metal contents covered by the series and is not necessarily representative of the accuracy of determinations at any given level of concentration. The mean accuracy of the series of determination expressed as: 200 × standard deviation percent/mean of samples, is calculated from the following equations:

$$(1) \qquad \sigma = \sqrt{\frac{\Sigma\ (A\text{-}\hat{A})^2}{n\text{-}2}}$$

$$(2) \qquad \hat{A} = \hat{H}\theta + \hat{L}\lambda$$

$$(3) \qquad \hat{H} = \frac{\Sigma\theta.^2\ \Sigma\theta\lambda\ \Sigma\lambda^2\ \text{-}\Sigma A\lambda.}{\Sigma A\theta.\ \Sigma\lambda^2\text{-}\ (\Sigma\theta\ \lambda)^2}$$

$$(4) \quad \hat{L} = \frac{\Sigma A\lambda . \Sigma\theta^2 - \Sigma A\theta . \Sigma\theta\lambda}{\Sigma\theta^2 . \Sigma\lambda^2 - (\Sigma\theta\lambda)^2}$$

$$(5) \quad \theta = \frac{h}{(h+1)}$$

$$(6) \quad \lambda = \frac{h}{(h+1)}$$

where

h = weight of high sample in any given mixture

l = weight of low sample in any given mixture

$\hat{H}$ = Calculated concentration of required element in high sample

$\hat{L}$ = calculated concentration of required element in low sample

A = concentration of element in any mixture obtained by analysis

$\hat{A}$ = concentration of element in any mixture calculated from $\hat{H}$, $\hat{L}$, h, l

n = number of sample mixtures analysed

and σ = standard deviation.

Assuming that samples are being analysed in batches, the accuracy figure obtained from the above equations is a measure of the accuracy within that particular batch. However, when the statistical series have been analysed a number of times in different batches, it is possible to calculate the accuracy of determinations on individual samples. This accuracy figure, the 'between batch' as distinct from the 'within batch' accuracy, includes the effects of changes in the conditions under which different batches are analysed. Similarly, it is

possible by calculating the accuracy of estimation of an individual sample analysed by several operators to obtain a figure which includes the error due to operator bias. This latter accuracy figure is referred to here as the 'between operator' accuracy.

The between batch and between operator accuracies have been calculated by applying the following equation:

$$\sigma = \frac{(\Sigma A^2 - (\Sigma A)^2/n)}{n - 1}$$

$$\text{accuracy} = 100 \times \frac{2\sigma}{\text{mean}} \quad \text{percent}$$

where

σ = standard deviation
A = concentration of element in sample obtained by analysis
n = number of analyses of sample

TABLE 2

NORMAL MEAN ACCURACY AND AVERAGE PRODUCTIVITY OF SOME GEOCHEMICAL TESTS

Element	Method	Range of Values (ppm)	Accuracy (±) (percent)	Average Productivity (6 hour day)
Arsenic	Confiend Spot	5 to 1000	15 to 35	75
Cobalt	Chromatography	30 to 130	15 to 30	100
Copper	Dithizone	30 to 400	15 to 30	90
Lead	Dithizone	125 to 1400	8 to 25	90
Molybdenum	Dithiol	1 to 60	10 to 40	50
Nickel	Chromatography	40 to 1100	10 to 35	100
Zinc	Dithizone	100 to 250	10 to 25	100

Table 2 gives the normal accuracies and average productivities obtained for some of the more common metals sought in geochemical prospecting, estimated by different methods. The accuracy figures given in this table are for operators ranging from local African labour to graduate chemists. In general, higher standards of accuracy have been obtained by analysts with higher

educational qualifications. The figures for both accuracy and productivity are in many cases considerably better than those claimed by their authors. However, the writer's calculated figures refer to the mean accuracy covering a relatively wide range of values and as a general rule the standard of reproducability would be less at lower concentration levels. This is illustrated by the between batch accuracies obtained by replicate arsenic determinations on a number of samples by a single analyst, as shown in Table 3, where the accuracy varies from 11% for the highest arsenic content of 700 ppm to 28% for the lowest content of 5 ppm. Furthermore, there is a similar, but greater deterioration in accuracy with decreasing contents when more than one operator is involved (see Table 4). It is these latter accuracy figures, incorporating the total error in a laboratory employing more than one analyst, that are the most important in estimating the reliability of data emanating from the laboratory.

TABLE 3

'BETWEEN BATCH' ACCURACY OF ARSENIC CONFIEND SPOT TESTS

No. of Analyses *	Mean Value	Std. Deviation	Between Batch. Acc. (percent)
4	5.3	± 0.74	27.7
4	165	±23.5	28.4
4	312	±34.4	22.0
4	544	±46.4	17.0
4	705	±39.4	11.2

* Replicate analyses in batches with a 'within batch' accuracy of 15 to 25 percent.

The reliability of analytical results depends both on the operator's appreciation of the causes of inaccuracies and on his ability to standardize his procedure, which normally improves with experiences. Variation of reliability between different operators is well illustrated by the analysis of a set of leadbearing samples by three operators, each using two different but related methods (see Table 5). In this example theer is a marked difference between the accuracies of individual operators but no significant difference between the results obtained by the two methods.

Insufficient data is available to allow general conclusions to be drawn regarding the variations in accuracy related to the qualifications of the analysts. However, taking extreme examples (Table), the accuracy of African operators on the arsenic and cold extraction copper tests compares very favourably with that of post-graduate research students working under similar conditions. The

TABLE 4

'BETWEEN OPERATOR' ACCURACY OF SOME GEOCHEMICAL TESTS

Element	Method	No. of Analysts	Minimun Accuracy of Analysts (percent)	Mean Value (ppm)	Standard Deviation (ppm)	Between Operator Accuracy (percent)
Lead	Dithizone	10	25	125	± 24	±38.7
				460	± 54	±23.6
				950	±149	±31.4
				1280	±101	±15.4
Zinc	Dithizone	10	25	90	± 24	±52.2
				130	± 24	±37.6
				195	± 31	±31.9
				255	± 26	±20.4
Arsenic	Confined Spot	4	30	9	± 2.5	±57.5
				245	± 27	±22.0
				515	± 98	±38.1
				722	±100	±27.7

TABLE 5

COMPARISON OF ACCURACY OF THREE ANALYSTS USING TWO RELATED LEAD METHODS. *

Operator	Method	Range of Values	Accuracy (percent)
A	1	140 - 1400	±24.18
A	2	140 - 1500	±24.36
B	1	150 - 1240	±17.24
B	2	150 - 1300	±17.00
C	1	130 - 1280	±10.83
C	2	110 - 1200	±11.02

Method 1. Dithizone in carbon-tetrachloride.
Method 2. Dithizone in white spirit.

available data suggest that local labour, competently trained, can be satisfactorily employed for much routine analytical work in geochemical prospecting.

TABLE 6

COMPARISON OF THE ACCURACY OF LOCAL AFRICAN LABOUR AND POST-GRADUATE STUDENTS

Analyst	Method	Range of Values	Std. Deviation	Accuracy (percent)
African operator	Cold Extraction Copper	0 – 23 mls	± 1.72 mls	±17.1
European research Student		0 – 16 mls	± 1.04 mls	±27.9
African operator	Arsenic Confined Spot	5 – 700 ppm	±55.97 ppm	±24.7
European research Student		5 – 750 ppm	±30.35 ppm	±27.1

In addition to checking analytical reliability, the use of statistical sample series can be of great advantage in reducing to absolute minimum the time and cost of training personnel. Considerable variation has been found in the time required to train individuals to the same degree of accuracy. In Table 7 are given examples of this where the average time between each statistical test is three days. Although training was terminated when a required accuracy had been attained a further gradual improvement was observed during subsequent normal routine analysis.

TABLE 7

EXAMPLES OF VARIATIONS IN THE LENGTH OF TRAINING* USING STATISTICAL SERIES

* No. of Attempts at Series		1	2	3	4	5
Metal	Operator	Mean Accuracy %				
Arsenic	A	± 45	±46	±49	±25	±26
Arsenic	B	± 36	±76	±30	±29	
Arsenic	C	± 60	±30	±21		
Lead	D	±122	±90	±18	±17	
Lead	E	± 29	±25			

* Training ceased after analysts reached an accuracy batter than ±30 percent.

* An average of three days of training elapsed between each attempt at the statistical series.

With the rapid development of new analytical techniques in geochemical prospecting it is desirable to have some method of comparing the various tests available for estimating a given element. Craven's formula for checking the accuracy of analysis is well suited to this purpose. To avoid error due to differences between analysts a given set of statistical samples should be analysed by both methods by the same operator. (Table 5). Obviously the method finally selected for any particular field problem will not necessarily be that with the highest accuracy but will depend also on (a) the productivity of the various methods at the desired accuracy level, (b) the sensitivity of the methods and (c) the availability of the chemicals required.

TABLE 8

TIME SPENT ON VARIOUS OPERATIONS IN THE ESTIMATION OF SAMPLES, FOR COPPER AND ZINC BY THE DITHIZONE METHODS, IN BATCHES OF 90 AND 100 RESPECTIVELY

OPERATION	TEST	
	Copper	Zinc
	(minutes)	
Weighing samples into test-tubes	49	54
Recording sample numbers and test-tube numbers	17	19
Addition of flux volumetrically	12	13
Mixing of soil and flux	8	9
Fusion and extraction of fused mass	73	71
Pipetting aliquot of soil extract	11	12
Addition of buffer to soil aliquot (with an automatic pipette)	9	10
Titration of buffered solution (from a wash-bottle)	14	—
Addition of Dithizone reagent (with an automatic pipette)	7	8
Shaking test-tubes in batches of ten for 30 seconds	—	6
Shaking test-tubes in batches of ten for 2 minutes	20	—
Colourimetric comparison with standards	60	70
Recording results	27	30
Preparation of standards	9	7
Cleaning apparatus	40	40
TOTAL TIME	356	359

Productivity and Cost:

Table 2 shows the average productivity, for a number of tests, obtained by personnel of the Geochemical Prospecting Research Centre. These productivities are in general higher than those claimed in the literature despite the fact

that no accuracy has been sacrificed. This high productivity has been obtained by (a) minor modifications of the published methods, (b) appropriate standardization of procedure, and (c) well balanced batch analysis of the samples. Typical examples of the amount of time spent on various operations in the zinc and copper tests is given in Table 8.

Apart from utilizing mechanical handling devices, marked increases in productivity over that shown in Table 8, can only be obtained by using coarser techniques, such as measuring the sample volumetrically, instead of weighing, or by more rapid colorimetric comparisons. Saving of time by either of these means involves a corresponding loss of reliability of results. Generally speaking, therefore, increased productivity over that shown must depend on the accuracy requirements of the current field problem.

The productivity of local African labour is in general only 80 per cent that of research students working under the same conditions. This lower productivity of African labour is probably due to complete unfamiliarity with chemical equipment and to the slower recording of results. Over a prolonged period the productivity of African analysts might well approach that of the students.

Major variations in the working costs of routine geochemical prospecting laboratories are due to differences in (a) the type of personnel employed, and (b) man-day productivity. The cost of chemicals is, in general, only a small fraction of the labour cost.

Generally speaking, if the highest standards of accuracy are required it is necessary either to employ qualified analysts, or to have a prolonged training period with unqualified personnel during which a considerable turn-over of labour is usually required before it is possible to select the most suitable individuals. However, for the majority of problems local labour can be satisfactorily employed. Local African labour is at present employed by some routine laboratories for sample preparation and weighing operations, and during our own geochemical prospecting research projects selected local African labour has been trained to carry out the complete estimation of various metals.

Mining companies have a natural reluctance to divulge detailed costs of prospecting and it is unfortunately impossible to give examples of geochemical analytical costs covering a range of conditions. An overall analytical cost of 1/6d to 2/6d a sample is probably a fair range for most operating tests under normal field conditions in Africa.

GENERAL CONCLUSIONS

1— Over normal working ranges of concentration, it is usually possible to obtain a mean accuracy of $\pm$ 15 - 30 per cent in the determinations of relative metal content obtained by geochemical prospecting methods of analysis. The

error increases with decreasing metal content, and, for many tests, an improved sensitivity is desirable for work in areas where absolute metal values are low and the anomalities relatively small.

2— For routine analysis, high productivity combined with good accuracy is more dependent on the quality of the training and the organization of standardized procedures than on the type of personnel engaged. During the course of field work in many parts of Africa, selected local labour has been competent to carry out most of the analytical tests used in geochemical prospecting.

3— The use of special statistical sample series in order to give quantitative expression to the reliability of relative metal determinations, is recommended for:

(i) controlling the development of new analytical tests, and comparing the relative reliabilities of different tests for the same metal;

(ii) checking choice of procedure and permissible modifications during the course of analytical orientation in new field areas;

(iii) determining the duration of analytical training required by the individual to attain a given level of reliability;

(iv) periodically checking the reliability of data emanating from the routine laboratories during systematic surveys.

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EXPERIMENTS AS TO THE AVAILABILITY OF BLOOM'S METHOD FOR LABORATORY USE IN THE ANDES

H. H. HELLER *

ABSTRACT

This study was undertaken to test whether Bloom's ammonium citrate dithizone-xylene method might serve to eliminate negative samples tested for traces of metals where series of several thousand samples are to be run over areas poor in metal. It was found that there are areas in which its use is impossible because of high silicification, areas in which it would serve if the loss of an occasional low anomaly is considered unimportant, and areas where it appears to function quite satisfactorily.

INTRODUCTION

Today geochemical analysis may be requested for several thousand samples from areas where no substantial metal deposit is known to exist, in the hope that a buried deposit may be found. A method that saved considerable laboratory time on such a series would provide time for a series that otherwise could not be analyzed.

At the suggestion of Dr. Peter R. Eakins this study was undertaken to investigate two points: 1. Does silicification, when observed in the rocks of an area, indicate the inadvisability of the use of Bloom's method for field or laboratory use in that area? And 2. In what type of area may the method be used to eliminate negative samples in order to save on more expensive and elaborate tests?

Because the graphs derived from our experimental material throw light on both questions, we may consider these two problems together.

Four areas were chosen for this study, three in the copper belt of the southern Peruvian desert at 7000 — 8000 feet altitude, and one in the central Peruvian puna at 14,000 feet, a zinc-lead region from which our only samples were soils and peats. Of the three southern areas, Cerro Verde, South-southwest of Arequipa, is a bald steep mountain very rich in copper with high background values in zinc; lead is negligible. Area A9, west of Arequipa, is mostly pampa

* *Cerro de Pasco Geochemical Laboratory, Arequipa, Perú.*

broken by hills, and Area A10, south of Arequipa, is similar to A9. Both these areas are far poorer in copper than is Cerro Verde. The two rich regions provide us with consecutive samples that constitute comparative material, which is far more informative than that furnished by the two poor regions. Their data will, therefore, be presented first. The two poor regions are the type of terrain in which Bloom's method might conceivably be used for elimination of negative samples; the rich copper region is not.

The rocks of Cerro Verde, in which Dr. Eakins had noted much silicification, are principally diorite, quartz monzonite, quartz porphyry and quartzite, with abundant mineralization, such as tourmaline, chlorite, limonite and hematite. The rocks of A9 and A10 are mostly granodiorite, gneiss, quartz porphyry, quartzite, diorite and andesitic porphyry, with minor deposits of schist, limestone, and old and recent volcanics; there are some aplite dykes.

A geologist, Sr. Alfonso Ballón, identified the rocks of all three areas. He was asked to be alert for silicification, and he noted it 101 times in the Cerro Verde rocks but not at all in those of A9 and A10.

COMPARISON OF BLOOM'S METHOD AND STANDARD METHODS

In Bloom's method a solution of ammonium citrate and hydroxylamine hydrochloride of pH 8.5 is used to extract soil which is placed directly in graduated cylinders. No heat is used. Dithizone (0.003% in 1 ml of xylene) is added and the whole shaken. The xylene rises to the top, away from the soil, which is an advantage except in the case of peat, which also rises. The color of the xylene is observed, and more dithizone-xylene added to the rose purple stet samples for titration back to blue. The number of ml of xylene used is the rating of the sample. Lead is determined by addition of cyanide after the first shaking. It would be hopeless to try to give the Bloom rating in parts per million of heavy metals because the three different metals affect the color of the dithizone in different degrees.

By Bloom's method a considerable but varying portion of the metal in the soil may remain undissolved. This is compensated for by using a large sample.

For Bloom's method in the southern copper region 0.25 gram of soil was used, all the soluble copper thereof being applied to the 0.003% dithizone contained in 1 ml of xylene. Titration was employed for high samples, which reduces the sample equivalent. For chromograph-rubeanic-acid determination of copper, one twenty-fifth of one half the fusion fluid from 0.25 gram of soil was used, or 1/50 of the amount of soil used for low Bloom samples.

For total heavy metal analysis in the central Peruvian zinc-lead region the amount used for the Bloom test was 0.1 gram of soil or less, the sample fre-

quently having to be weighed to 10 or even to 1 mg because of the abundant soluble zinc. The standard methods for zinc and lead employ 1/5 of the fluid from 0.25 gram of soil. Dilutions were frequently made which roughly correspond to the weighins of soil for Bloom's method. The standard zinc and lead methods therefore frequently employed 1/5 as large a sample as does Bloom's method.

Because of the large amount of soil used, any slight difference in the solubility of the metal contained in the sample used for Bloom's method is far more effective on the results obtained by that method than on those obtained by standard methods, which employ fusion or extraction and a smaller quantity of sample. This factor is probably the explanation of most of the frequent erratic highs and lows observed in the results obtained by Bloom's method.

The material used in this study was all ground and sifted through an 80-mesh screen. This somewhat invalidates direct comparison with field studies in which unground soil is used, but it was judged necessary for the type of work in hand, and it is preferable for laboratory use.

In an area where Bloom's method is found positive for all or nearly all samples designated anomalous by a standard method, there will also be quite a number of high samples by Bloom's method that are not anomalous according to standard methods. These can all be repeated by a standard method whereby they are sorted out, while the Bloom-negative samples need not be re-run. If the high Bloom samples are too many, it will not pay to run the samples twice, and changing to a standard method for all samples will be cheaper. The choice of whether to use Bloom's method on an area will depend not only on how many negative samples there are, but also on what the standard method for the sought metal costs in terms of labor.

In our laboratory a man can run 90 samples a day by Bloom's method for copper at pH2, and he can run 60 coppers in the chromograph, but another man must spend a half day fusing them, which reduces the standard method copper output to 40 per man-day. A computation of this relation indicates that there would be a saving by elimination of negative samples by the Bloom method, if up to 55% of the samples had to be re-run by the standard method. Bloom's method is not ordinarily run for lead or zinc only. The amount of lead is subtracted from the total amount to compute the zinc. If the Bloom samples from a region poor in copper were run for zinc and lead by one man at the rate of 60 per day, the saving would apply to both the zinc and the lead. With zinc at 24 samples per man-day (two men running 60 samples and one fusing), the elimination of negative samples would then pay up to 80% of positive zinc samples. In the case of lead at 12 samples per man-day (2 men

analyzing 30 samples and one extracting), the elimination of negative samples would pay up to 90% of positive lead samples.

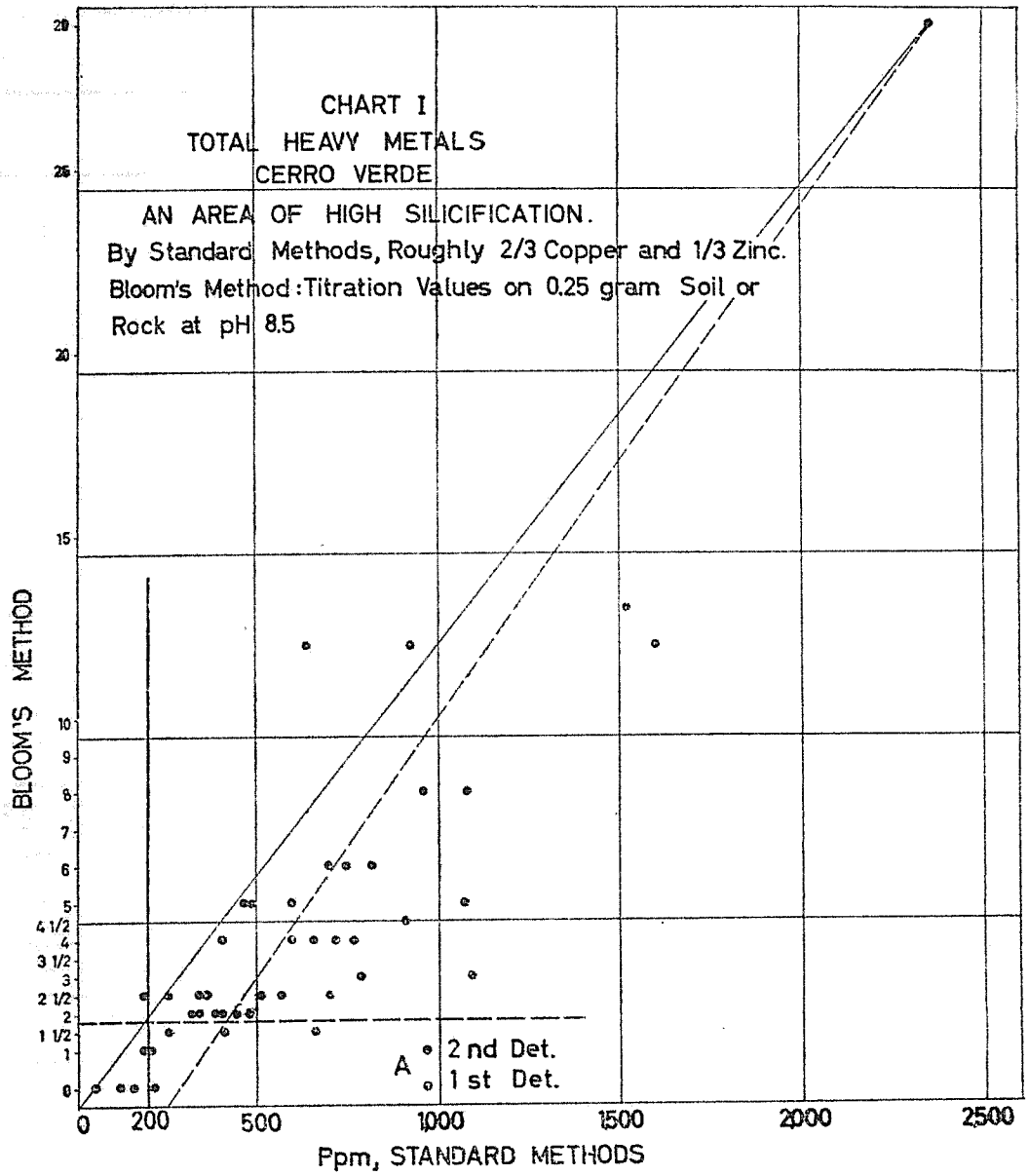
What would be the saving in man-days of time if only 20% of the samples of each metal needed to be re-run? For the copper it is .9 of a day, for the zinc 2.5 days, and for the lead 5.87 days. Thus it is obvious that the greatest saving is made in the case of lead. It is possible, however, to save on the slow lead analysis by two other methods: 1, by running for lead only the samples that have shown a certain level of zinc; 2. by not carrying low leads through the whole analytical process.

On our charts ratings in ppm for standard methods are measured to the right from the ordinate and the same samples are rated by Bloom's method as measured upward from the abscissa. Two diagonals are drawn from the highest sample to the lower left: the solid one to 0-0 and the dotted one through the center of distribution of the samples. The angle between the diagonals may be taken as a measure of the divergence of the distribution from expectation if both methods were to function equally on all samples. Height of the diagonals depends upon four principal factors: on the relation between the quantities of samples used for the two different kinds of methods, on the solubility of the metals present, on the scale of the chart relative to the two methods, and on the rating of the highest sample, which may constitute a source of error.

Experiment 1—From Cerro Verde, where silicification was frequenlty noted, where copper was high, and some zinc present, 45 consecutive soil and rock samples were chosen and run by Bloom's method for total heavy metals at pH 8.5. When the soils and rocks were sorted, there was no significant difference in the results. Bloom recommends the use of 0.1 gram of soil for total heavy metals and 1 gram for copper. Here, however, the copper was very rich; 0.25 gram of soil was chosen for this work and was found suitable for the study, as the four copper samples under 200 ppm (the arbitrary anomaly point) were rated as one or zero by the Bloom method. All but two of the samples over 200 ppm were rated as 1 or more.

The data for the standard methods were compiled as follows: Cooper: the rubeanic-acid-chromograph method was run on the samples twice, and they were analyzed once by a standard dithizone method at pH2. The three amounts were averaged. Zinc: samples fused with potassium bisulfate with no citrate added, were estimated with dithizone in cylinders that all received the same amount of sodium thiosulfate. Lead: samples extracted with acid were run at pH 8.5 with cyanide and were washed twice with dilute cyanide. Determinations for the standard dithizone methods were all made by photelometer. The zinc and lead determinations were added to the average of the three determinations to give the figures for "Ppm, Standard Methods".

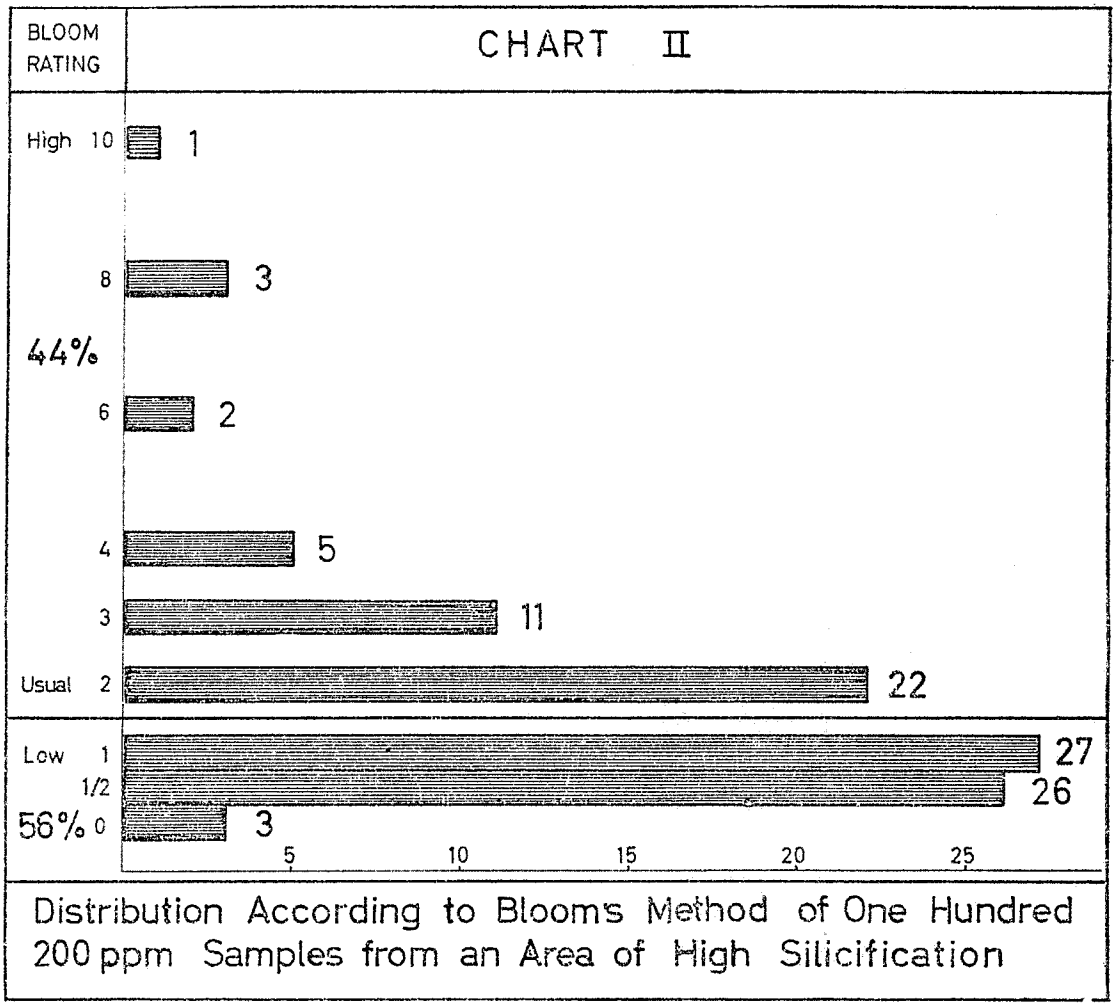
A diagonal drawn from the highest sample to zero shows a very unequal distribution: only three samples above the line indicating that Bloom's method gave proportionately higher results than the standard methods, 41 samples below



the line indicating the reverse. The dotted diagonal through the center of distribution terminates far to the right of the solid diagonal. Attention is called to the sample A at the lower right, which gave 0 by Bloom's method on the

first run and 1 on a second. It represents nearly 0.1% of heavy metal according to three closely similar standard tests —a high anomaly.

This graph should not, however, be judged by itself. It might be thought that the highest sample was an erratic freak and that even in a copper region a large sample of soil should have been used for the Bloom test. It is when this highly skewed distribution is compared with those on the following charts



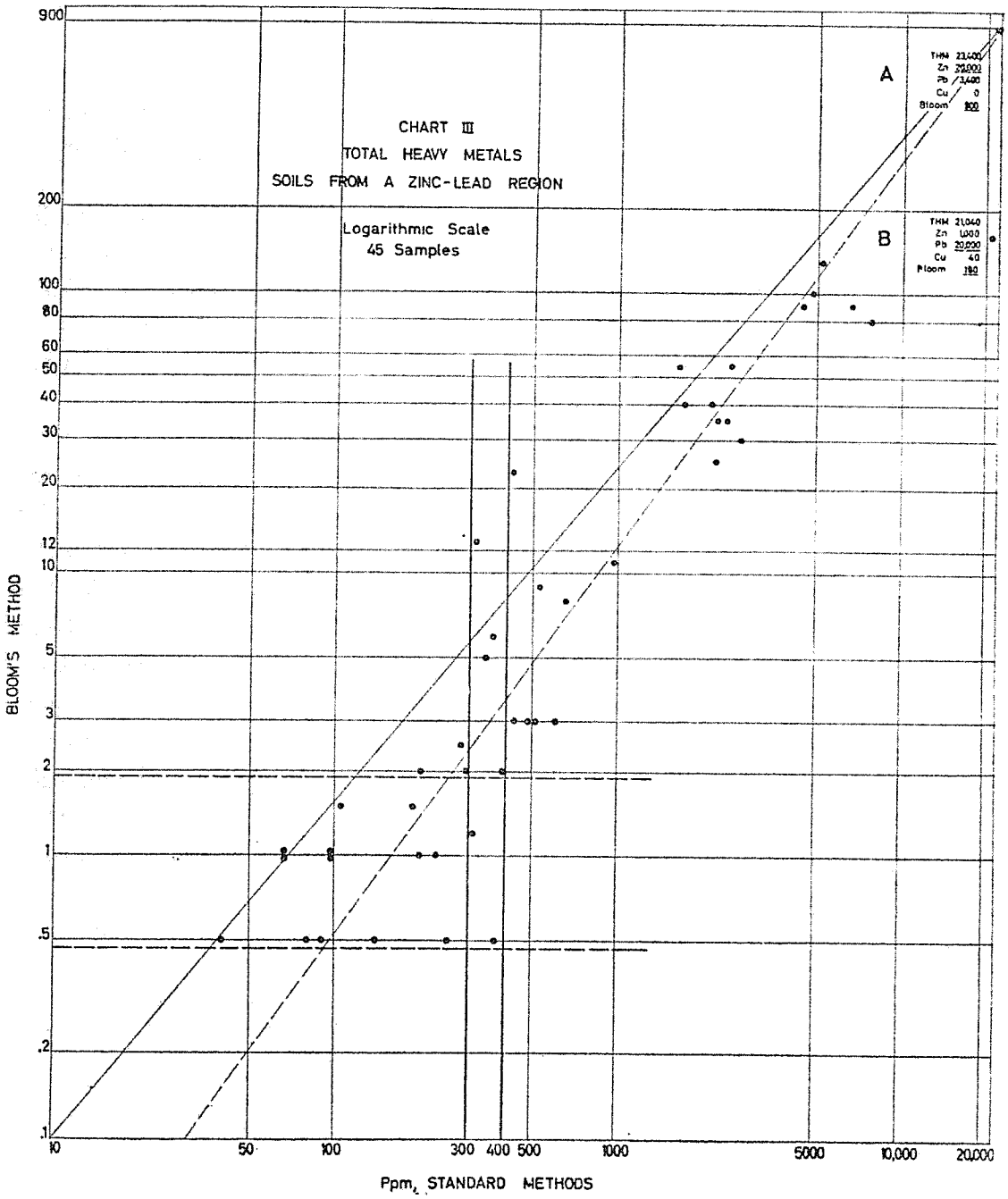
Distribution According to Bloom's Method of One Hundred 200 ppm Samples from an Area of High Silicification

from other regions that we may conclude that this distribution greatly favors the use of standard methods in the Cerro Verde area of high silicification.

Experiment 2—Another method of comparison was sought that would depend upon a different process from the preceding. From a large area of Cerro Verde 100 samples were selected that had been determined by the chromograph method to contain 200 ppm of copper. Bloom's method was run on them with 0.25 gram of soil at pH 2 instead of at pH 8.5 in order to remove the zinc and lead

from the problem. It was found in experiments in other areas that when this quantity of soils at this pH gives a reading of Bloom 2, nearly all 200 ppm copper samples are indicated by a Bloom rating of 2 or more. In the Cerro Verde area, however, 56% of the 200 ppm samples read Bloom 1 or less.

It thus appears that Bloom's method is not applicable in areas of high silicification.



Let us now turn our attention to the Bloom Total Heavy Metals test when run on the area in the high mountains of central Peru that is rich in zinc and lead.

Experiment 3—Three groups of 15 consecutive samples were chosen, the highest of which gave 23,000 ppm. of heavy metal, and the tests were run as in the case of the Cerro Verde series, except that the amount of soil used was less, as previously mentioned. Copper, zinc and lead were each determined once by standard methods and the amounts added for "Ppm, Standard Methods". The quantity of copper was too small to warrant further consideration.

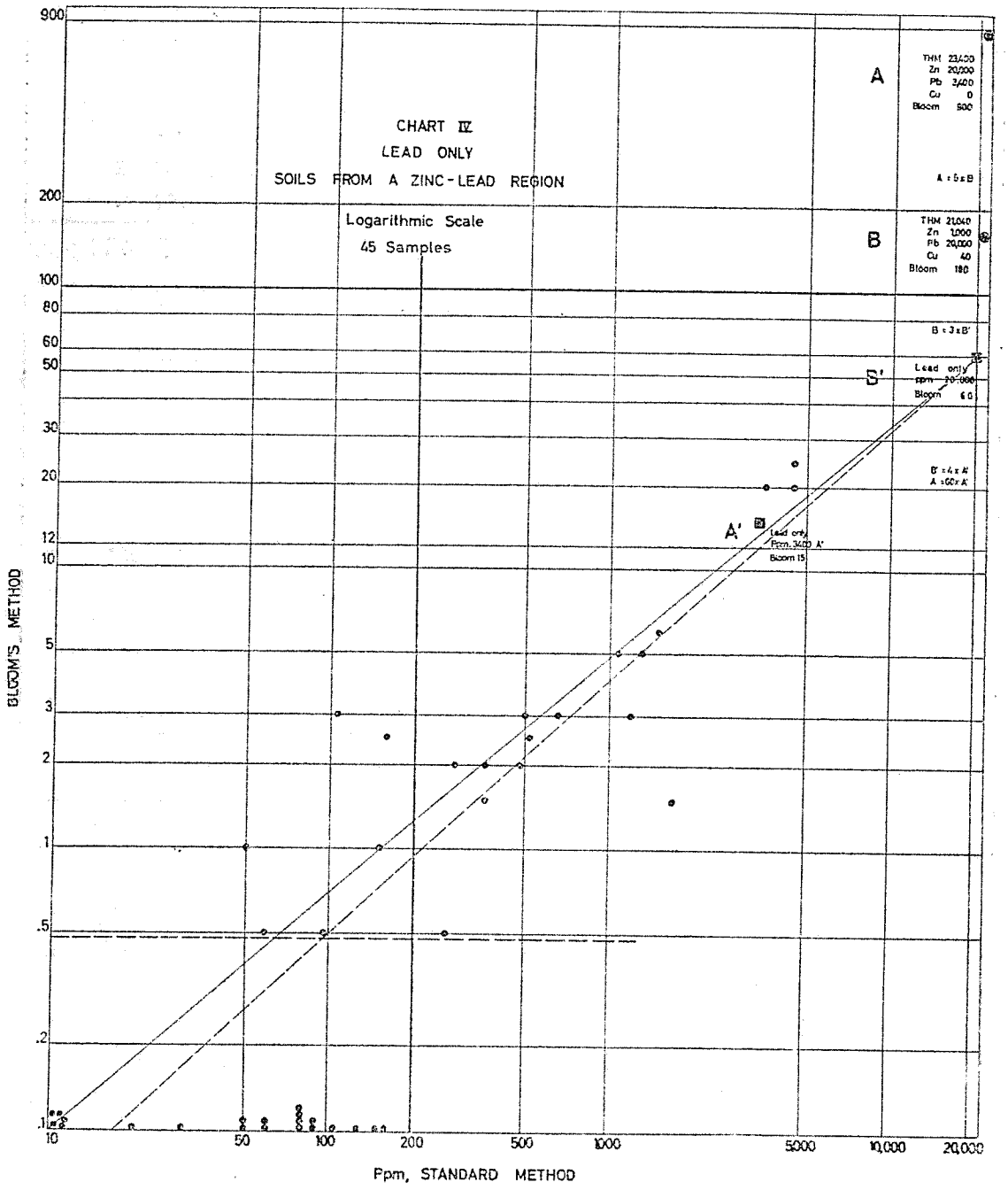
There was too much heavy metal present for representation on an ordinary scale and logarithmic paper was used for the plotting. As 1 Bloom corresponds roughly to 100 ppm of the other methods, and 2 Bloom to 200 ppm, the point chosen for terminating the diagonal in the lower left-hand corner of the logarithmic scale was at 0.1 for the Bloom test and at 10 for the standard methods. The line from this point to the highest sample is the solid diagonal. The dotted line, as before, is at the center of distribution. In this case 5 samples are above the main diagonal and 39 below it. The samples line up better than those from Cerro Verde; there are fewer wild erratics than there were in that area, indicating a more uniform solubility of the metals.

Here, much better than in Chart I., we are able to evaluate the two types of methods in regard to the lower value samples. If, because there are two metals present, an arbitrary anomaly line is drawn at 300 ppm, 29 samples would be anomalous and 16 not, and all the Bloom samples would need to be re-run in order to spot all the anomalies. However, if we were to consider the two low anomalies missed by Bloom's method as of no significance to the problem in hand, we could draw the anomaly line at 400 ppm; 23 samples would then be anomalous and 22 not, and if all the Bloom samples of rating 2 were run, all the anomalies would be spotted. We can call a line drawn below the Bloom 2 rating the "Bloom sub-anomaly line" for 400 ppm, whereas the "Bloom sub-anomaly line for 300 ppm would to be drawn below 0.5 Bloom. One can take one's choice of procedures in these matters, depending on the requirements of the geologist and the pressure of work in the laboratory.

Attention is called to the two samples, A and B, in the upper right-hand corner. Both read over 20,000 ppm, Total Heavy Metals. By Bloom's method A reads 5 times as high as B on a non-logarithmic scale. The bulk, 20,000 ppm, of the higher sample is zinc, the bulk of the lower, also 20,000 ppm, is lead. The explanation that this is due to greater color change of the dithizonate by the zinc may be inadequate, because standard zinc appears to be only about twice as penetrating as standard lead. The explanation of part of the discrepancy

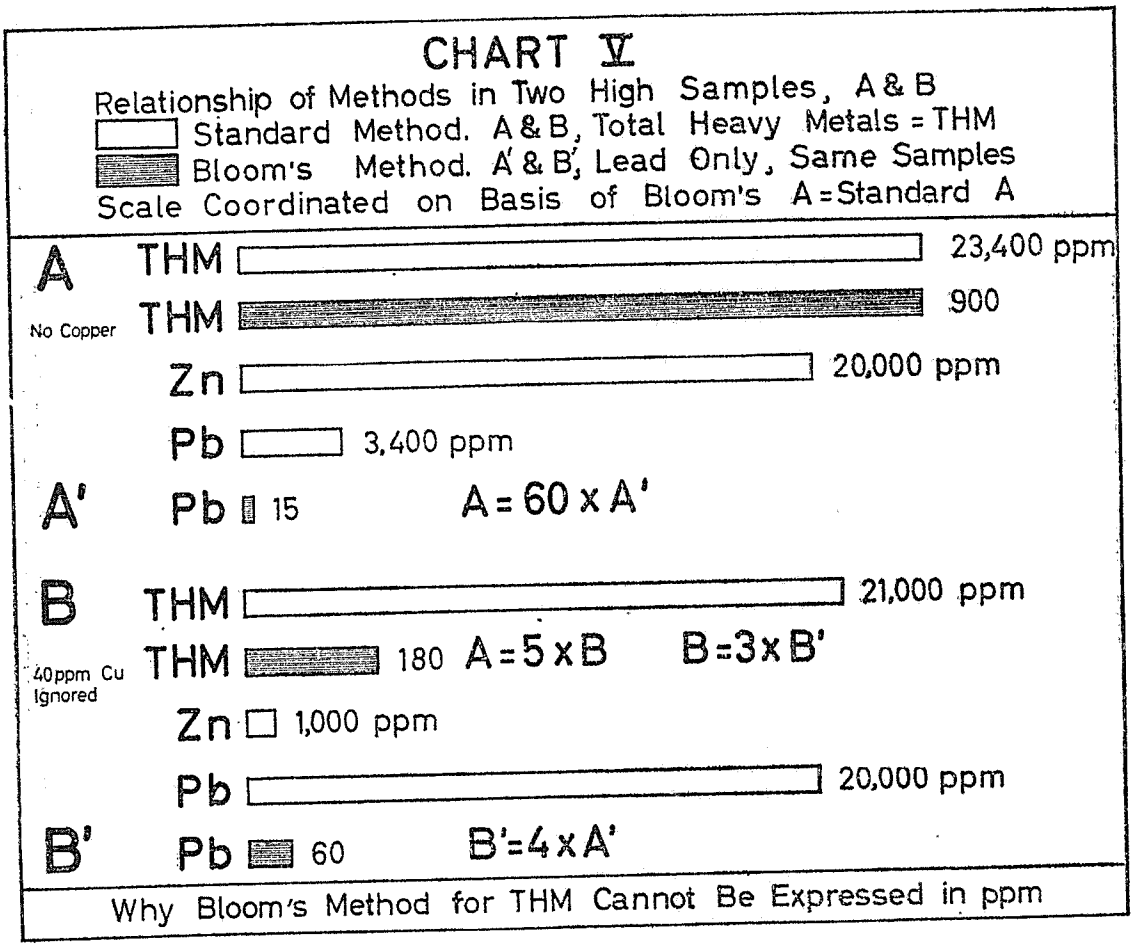
between these two samples may well be that the lead was less soluble than the zinc.

Experiment 4—The same samples that were tested for heavy metals in the previous experiment were tested by Bloom's method for lead only; the maximum quantity of soil was 0.1 gram with lower quantities weighed and computed to 0.1 gram in several cases. The plotting is logarithmic, and in the same scale



as on the previous chart. Here again we have a fairly equable distribution. The diagonal is much lower than on the previous chart because the more abundant metal, zinc, is missing; there are 21 non-reacting samples, and 18 anomalies of 200 ppm or over, estimated by the standard method.

Where should the "Bloom sub-anomaly line" be placed on this chart in order to catch all the anomalies? If the perpendicular anomaly line is placed at 200 ppm, it should be placed below Bloom 0.5, i.e., all the reacting samples should



be re--analyzed for proper mapping. There are still 21 samples, or 46%, of Bloom rating O, that would indicate a laboratory saving of 3 man-days by running preliminary Bloom tests on the lead, however.

Attention is directed to the two highest samples, A and B, placed at the upper right on Chart IV as they appeared for Total Heavy Metals, and, below them, labeled B′ and A′, as they appeared for lead only. By Bloom's rating,

$$B' = 4 \times A'$$
$$B = 3 \times B'$$
$$A = 5 \times B$$
$$\text{and} \quad A = 60 \times A'$$

This relationship illustrates the impossibility of giving a ppm rating to Bloom samples run for a total heavy metals test, not only because zinc alters the dithizone color more than does lead, but because it is more soluble than lead.

It may be concluded that if this amount of metal were distributed over a wide area of a nature similar to that of this region, Bloom's method might be chosen for the elimination of samples negative for zinc and lead, if an occasional missed low anomaly were considered to be of little import, or if larger soil samples were used.

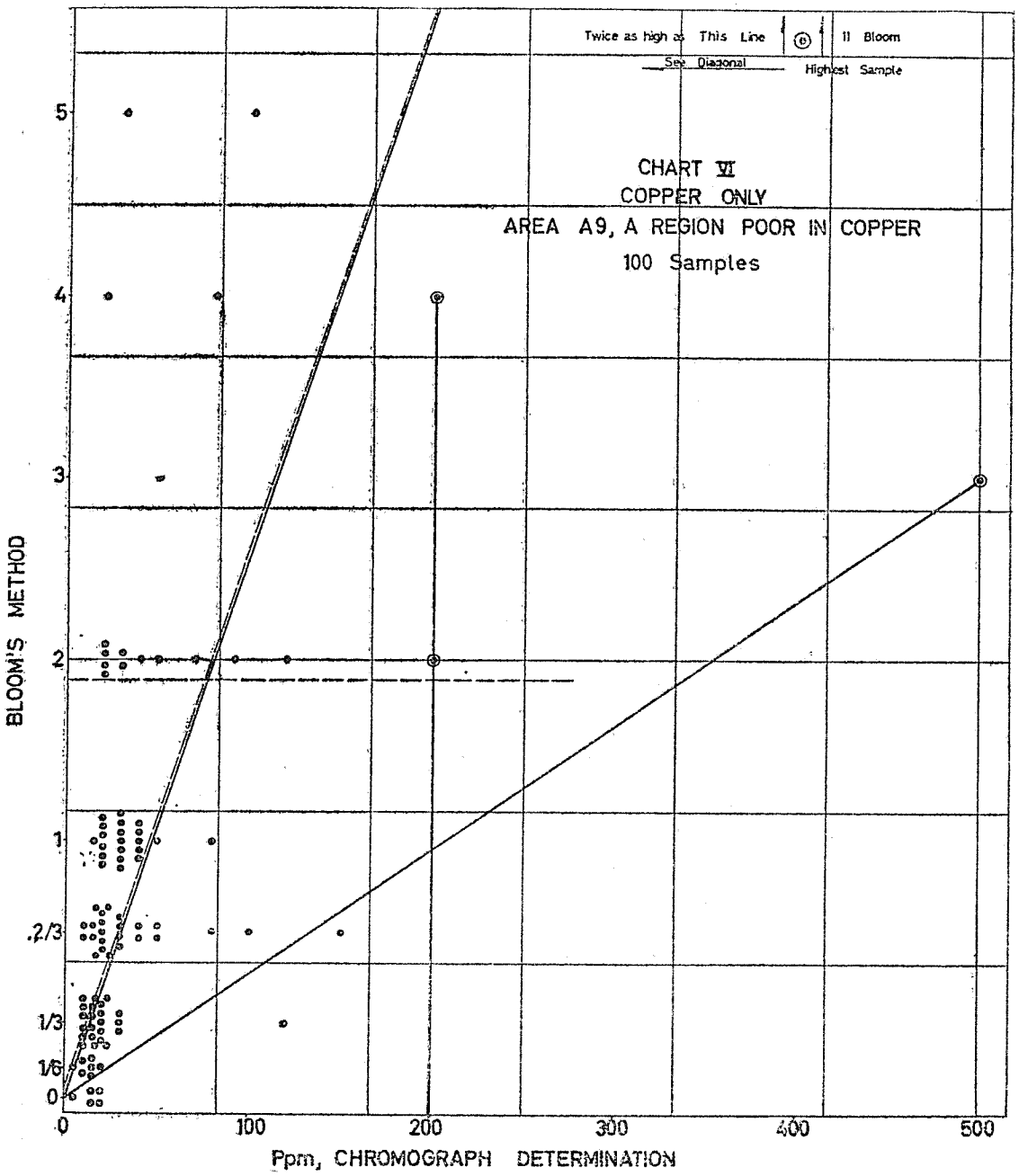
Let us now consider areas A9 and A10, the two similar regions near Arequipa, where no silicification was noted in the rocks. We shall deal only with the copper found there, running the Bloom test with 0.25 gram soil and at pH 2 in order to eliminate the zinc, and use the rubeanic-acid-chromograph test as the standard method.

Experiment 5—Chart VI shows the distribution of 100 A9 samples. There are only 4 anomalies of 200 ppm or more according to the standard method, all spotted by Bloom's method. We can place the Bloom sub-anomaly line below Bloom 2. The highest anomaly by Bloom's method is twice as high as the chart. The highest anomaly by the standard method is at the far right. The diagonal from the high Bloom sample passes almost exactly through the center of distribution, ,and that through the highest chromograph sample leaves 97 samples favoring the Bloom method —evidence that 0.25 gram of soil is an adequate amount for the Bloom test in this area.

Besides the anomalies spotted by the Bloom test, 16 samples are above the Bloom sub-anomaly line drawn under Bloom 2. They and the four anomalies, 20% of the samples, would need to be re-run by a standard method, and 80% would not. Area A9 appears, then, to be a type of area where considerable saving in money and laboratory time could be made by the use of Bloom's test, provided the rocks be checked for silicification.

Experiment 6—Area A10, somewhat more varied in its geology than A9, contained even less copper than did A9. Chart VII plots 400 samples from this area. Ten, or 2 1/2%, were anomalous, the highest, which is off the chart, reading 400 ppm and Bloom 22. To spot all the anomalies, the Bloom sub-anomaly line would have to be placed below 2/3, re-running all the green-blue

reacting samples, a procedure which would pay only a quarter man-day's time per 100 samples. If the loss of one 200 ppm anomaly be considered unimportant, the Bloom sub-anomaly line could be placed below Bloom 1 1/2, in which case 301 samples or 75% would not need to be re-run, which would constitute a saving of three quarter man-days time per 100 samples. Or one might double the amount of sample used for Bloom's test, spot all the anomalies and still make a saving.



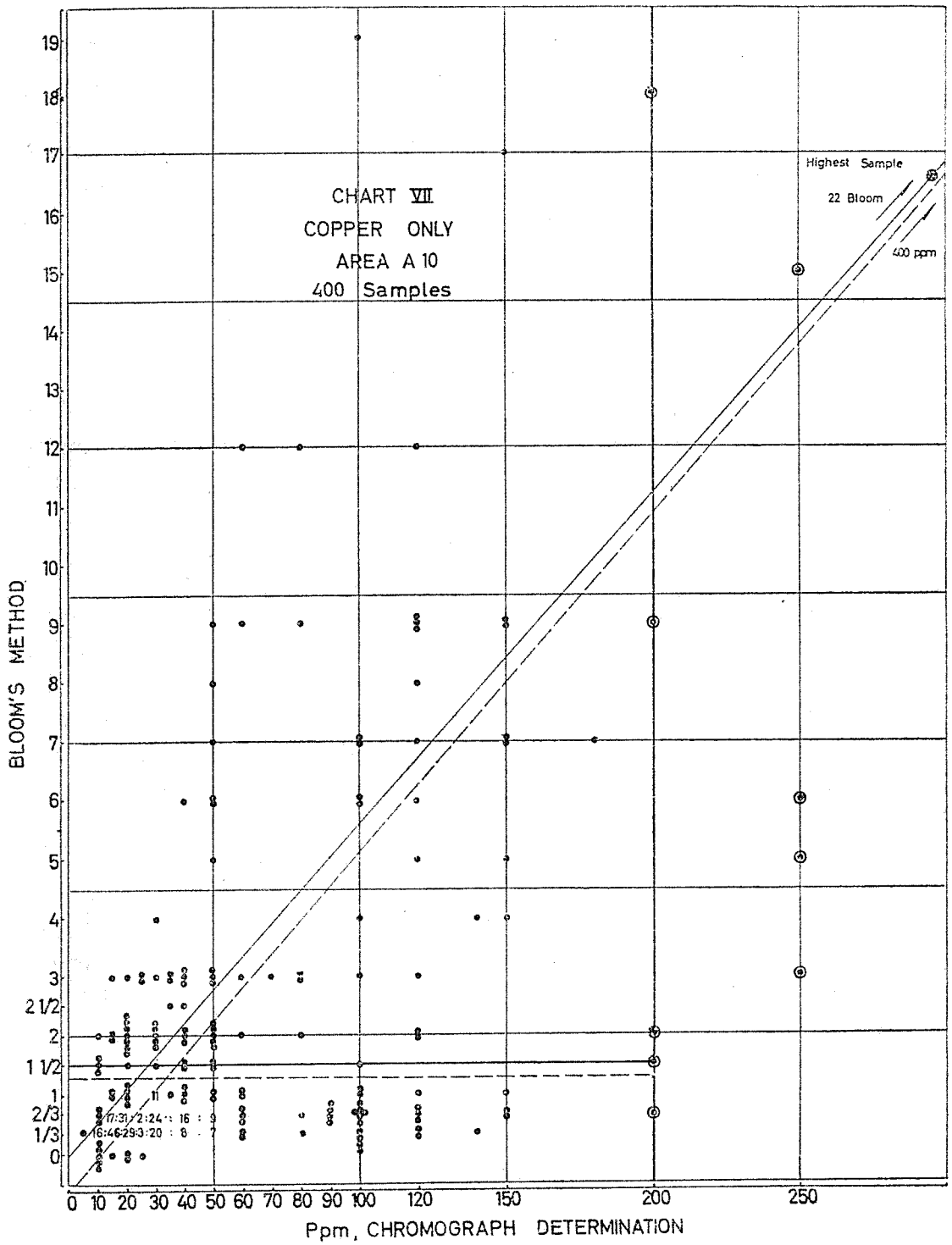


CHART VII
COPPER ONLY
AREA A 10
400 Samples
Highest Sample
22 Bloom
400 ppm
BLOOM'S METHOD
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0 10 20 30 40 50 60 70 80 90 100 120 150 200 250
Ppm, CHROMOGRAPH DETERMINATION

One notes a much wider scatter than occurred in A9, and this favors the standard method; the center of distribution is to the right of the diagonal, indicating that there is less soluble copper in area A10 than in A9. Whether this be due to silicification or to the chemical form in which the copper exists might be worth study.

A10 is thus an area which one might or might not choose for the use of Bloom's method for eliminating negative samples, depending on whether it is thought necessary to spot every low anomaly of 200 ppm.

DISCUSSION

It thus appears that in the Andes there are areas wholly unadapted to the use of Bloom's method for any but emergency field use, whereas quite close to them are areas where the method may be used to eliminate negative samples with little risk of losing any but a few low anomalies. One would, however, not choose to use it in any rich copper area, because of the large proportion of samples that would need to be re-run for serious mapping.

Several of the conclusions in this study are based on series that are too small to be of scientific value. The work should be taken as the presentation of a technique which others may adapt to their own problems as they see fit.

A routine attack on the problems presented by a new territory might be made as follows: Collect rocks corresponding to soil samples wherever possible. If they show no obvious silicification, run 200-500 soil samples by a standard method, and run all that react and a series that do not react by Bloom's method. If the percentage that need to be re-run is appropriately low, and Bloom's method spots all high anomalies and nearly all low ones, it may be used if the incoming rocks are continually checked for evidences of silicification. It would be well to check 50-100 samples by running both methods occasionally. Thus we may be able to find out if silicification is the only factor that impedes the use of Bloom's method for laboratory use, and become familiar with types of areas other than those studied here.

DOSAGES SEMI-QUANTITATIFS PAR CONFINED SPOT DE TRACES DE MÉTAUX DANS LES SOLS As – Ni – Cu – Pb – Zn – Au (avec un annexe)

R. MARTINET *

RESUMÉ

Le Bureau Minier de la France d'Outre-Mer a entrepris de nombreuses prospections géochimiques et son laboratoire de Dakar (Afrique Occidentale Française) à été conduit à mettre au point des méthodes de dosage aussi simples que possible, pouvant être utilisées par du personnel autochtone ne disposant d'aucune formation spéciale.

Les méthodes par "confined spot" ont retenu notre attention, car elles laissent des traces qui permettent aux géologues chefs de missions de contrôler, quelquefois longtemps après, le travail des aides-chimistes.

Nous avons pu mettre au point un appareil unique et des techniques similaires pour tous les modes de dosages que nous avons étudiés.

L'appareil, beaucoup plus simple que le chromographe, est un "joint" en matière plastique qui peut être construit par n'importe quel atelier possédant un tour.

Les méthodes de dosage utilisées pour l'arsenic et le cuivre sont tirées de publications antérieures; nous n'en parlerons que pour en montrer les simplifications possibles tirées de notre expérience.

Les méthodes pour le zinc et le plomb, ainsi que pour les dosages simultanés du cuivre, du plomb et du zinc dans les sols, sont originales; nous les décrirons en détail.

Enfin, dans un dernier paragraphe, nous exposerons les rapports que nous avons pu remarquer entre les teneurs en or et en arsenic de différents types de minerais aurifères, ceci pour quelques milliers d'échantillons. Nous décrirons la mise en place en forêt tropicale d'une mission de prospection géochimique de l'arsenic et nous donnerons les liaisons que nous avons obtenues entre les teneurs en arsenic des prélèvements de surface et les teneurs en or des prélèvements au bed rock sous-jacent.

GENERALITÉS

Le Bureau Minier de la France d'Outre-Mer a entrepris de nombreuses prospections géochimiques et son Laboratoire de Dakar (Afrique Occidentale Française) a été conduit à mettre au point des méthodes de dosages aussi

* *Chef du Laboratoire et de la Station d'Essai du Bureau Minier de la France d'Outre-Mer en Afrique Occidentale Française.*

simples que possible pouvant être utilisées par du personnel autochtone ne disposant d'aucune formation spéciale.

Les méthodes par "Confined Spot" ont retenu notre attention car elles laissent des "traces" qui permettent aux géologues chefs de missions de contrôler quelquefois long temps après le travail des aides chimistes.

Nous avons pu mettre au point un appareil très simple qui nous a permis avec des techniques très voisines de doser les différents métaux que nous avons été conduits à étudier.

PRINCIPE

Pour déterminer la teneur en un élément par "Confined Spot" on provoque la création d'un spot coloré sur une surface déterminée de papier filtre entre cet élément et un réactif spécifique — suivant les teintes observées on détermine par comparaison avec une échelle de standards la teneur approximative de l'élément recherché.

APPAREIL

L'appareil que nous avons construit pour réaliser les Confined Spots est extrémement simple. Il peut être utilisé aussi bien pour le dosage de l'Arsenic que pour les titrages des métaux lourds.

Il est constitué essentiellement par un joint en matière plastique (Fig. 1) permettant de serrer une rondelle de papier filtre entre deux disques parfaitement plans percés en leur centre d'un trou de 6,3 mm.

Le disque du haut est surmonté d'un petit tube de forme évasée et celui du bas se prolonge par un tube droit. Ce tube droit est relié par un joint de caoutchouc à un tube en verre de 8.10 mm de diamètre.

Cet appareil peut être utilisé pour doser l'Arsenic en reliant le tube de verre au tube dans lequel se produit la réaction libérant l'hydrogène arsènie (Fig. 2).

Il peut aussi être utilisé comme chromographe — Dans ce cas le tube en verre de longueur convenable plonge dans une éprouvette à pied remplie d'eau — On introduit la liqueur à tester dans le tube du haut du joint et on obtient la filtration en levant le "joint" le long d'un support, le tube en verre restant constamment dans l'eau — La vitesse de filtration est réglée par la hauteur à laquelle on relève le joint (Fig. 3).

Dans le cas de filtration difficile il peut être utile de remplacer l'eau de l'éprouvette par du mercure.

Joint en matière plastique
Echelle: 1/1

BUREAU MINIER F.O.M
A.O.F

APPAREIL POUR CONFINED SPOT

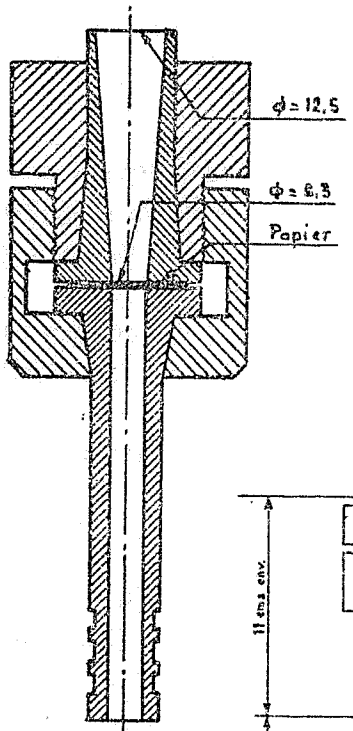


Fig. 1

Echelle: 1/3

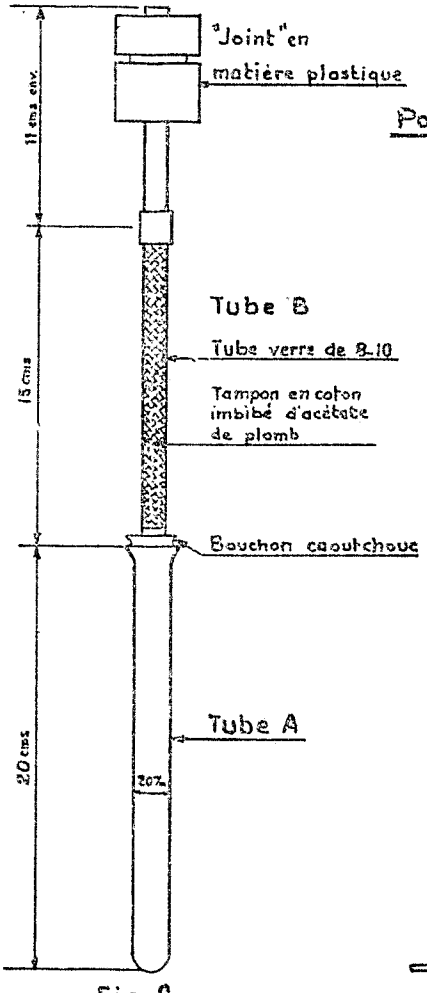
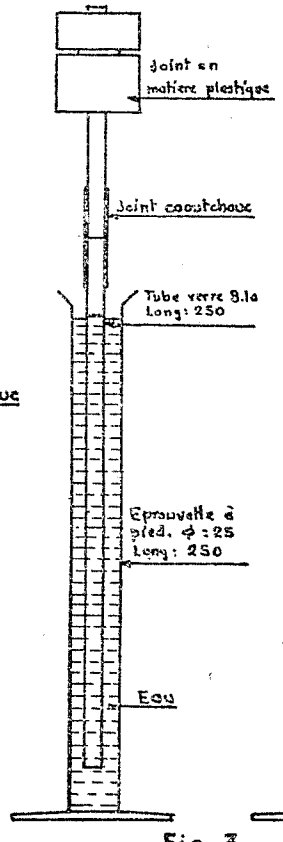


Fig. 2

Position basse



Position haute

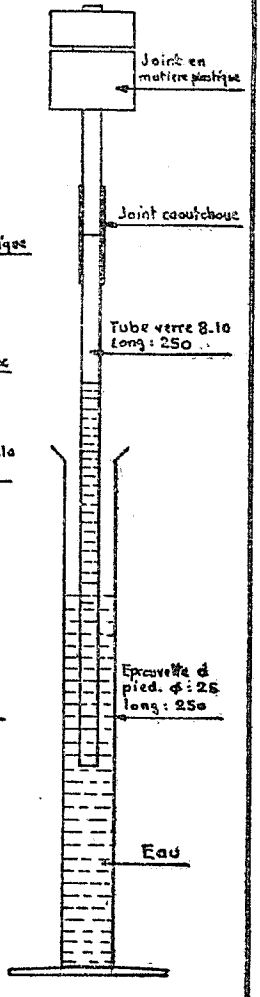


Fig. 3

DOSAGES SEMI-QUANTITATIFS DE DIFFÉRENTS MÉTAUX

Les méthodes de dosage de l'Arsenic, du Cuivre et du Nickel que nous avons utilisé sont tirées de publications antérieures.

I — ARSENIC

La méthode de dosage de l'Arsenic a été décrite par Almond sous le titre "Field Method for Determination of Traces of Arsenic in soils — Confined Spot Procedure using a modified Gutzeit apparatus", *Analytical Chemistry*, 25 (II), p. 176, 1953.

La seule modification que nous avons apportée à la technique d'analyse est d'effectuer les attaques directement dans des tubes à essai en verre pyrex, ce qui simplifie les manipulations.

Cette méthode nous a permis de doser l'Arsenic dans plusieurs milliers d'échantillons de sol avec des résultats très convenables.

II — CUIVRE ET NICKEL

Les dosages du Cuivre et Nickel par Confined Spot ont été décrites par Stevens et Lakin. On trouvera les détails de ces méthodes dans *U. S. Geological Survey Circular* 161.

Sauf l'emploi de notre appareil au lieu du chromographe nous n'avons apporté que des modifications de détail aux techniques décrites.

III — PLOMB – ZINC ET CUIVRE

Nous avons été conduits à titrer des sols à la fois pour Plomb, Zinc et Cuivre. Ceci nous a amenés à mettre au point des méthodes nouvelles pour le Plomb et le Zinc.

Nous décrirons ci-après la méthode d'ensemble que nous avons utilisée pour les titrages simultanés des trois métaux. Cette méthode pourrait être utilisée pour le dosage d'un seul des trois métaux en diminuant en conséquence les quantités d'échantillons de sol servant à la mise en solution des métaux.

A — MISE EN SOLUTION

Nous avons étudié plusieurs modes de mise en solution du Plomb, du Cuivre et du Zinc contenus dans des sols de différentes provenances.

En particulier nous avons comparé les résultats obtenus à partir d'attaque par

HCL N

NO_3 H I/3

Cl 0_4 H I/3 (20%)

C'est l'attaque à l'acide perchlorique qui nous a donné dans nos essais les meilleurs résultats tant pour la quantité de métaux solubilisés que pour la lecture des "Confined Spot". C'est donc celle que nous avons adopté.

TECHNIQUE

On pèse au trébuchet 5 gr de sol passant au tamis 100 (160 microns). On met ces 5 gr de sol dans un Erlenmeyer de 50cc et on y ajoute à la pipette à plongeur 5 cc d'acide perchlorique 20%.

On porte l'Erlenmeyer recouvert d'un petit verre de montre sur une plaque chauffante à feu doux et laisse l'attaque se poursuivre pendant 30 minutes environ à une température voisine de 90° C.

On ajoute ensuite 10 cc d'eau déminéralisée et on maintient à température encore 30 minutes. Pendant l'attaque on agite de temps en temps la fiole.

N.B — Nous avons préféré conduire l'attaque dans de petites fioles plutôt que dans des tubes à essai car les manipulations sont plus faciles et les réactions se font mieux en particulier dans le cas de sols très carbonatés.

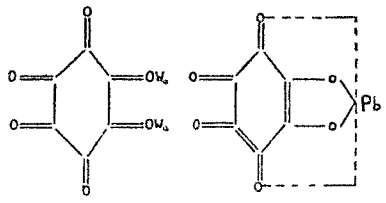
B — DOSAGE DU PLOMB

1° PRINCIPE

Une partie aliquote de la solution de sol est filtrée à travers une rondelle de Papier Durieux N° 149 vierge en présence de rhodizonate de sodium contenant des ions SO_4 et en milieu pH_5. Suivant les teintes obtenues sur les papiers on détermine par comparaison avec des Standards la teneur en plomb du sol.

2° RÉACTIF

Nous avons choisi pour réactif du plomb le rhodizonate de sodium. Feigl (1954) donne les précisions suivantes sur ce réactif: "La solution jaune de rhodizonate de sodium dans l'eau produit un précipité coloré de rhodizonate basique de plomb à partir d'une solution neutre ou légèrement acide de plomb. On obtient du violet Pb (C_6 0_6) Pb (0H) 2H20 en solution neutre et du rouge écarlate 2 Pb (C_6 O_6) Pb $(OH)_2$ $2H_2O$ en solution acide dilué. La couleur provient probablemente du fait qu'il se forme des complexes internes (chelates) avec l'acide rhodizonique



Ces réactions sont si sensibles qu'elles sont positives immédiatement même avec les minéraux peu solubles comme Pb S — Pb SO_4 — Pb Cr O_4 etc...

La limite d'identification est de 0.1 microgramme de plomb et la dilution limite 1.500,000. A pH3, les ions génants sont $TI+$, $Ag+$, Cd^2+, Ba^2+, Sn^2+ la sensibilité de ces réactions étant moindre que celle du plomb".

Difficultés d'emploi du rhodizonate de sodium - Solutions

Le rhodizonate est détruit en solution acide, dès pH3 la réaction ne se produit plus pour les faibles teneurs en plomb. Par contre le Spot est très net en milieu pH5.

Les solutions acides de sols contenant de fortes proportions de fer précipitent dès qu'on amène le pH aux environs de 4. Nous avons évité cette précipitation en ajoutant une quantité suffisante de citrate d'ammonium - Parmi les complexants usuels du fer c'est le seul qui nous ait donné des résultats convenables.

Parmi les ions réagissant sur le rhodizonate dans les mêmes conditions que le plomb seul le baryum nous a gèné dans les liqueurs d'attaque de sol.

Pour éliminer l'interférence du baryum nous avons ajouté à la solution de rhodizonate du sulfate de sodium. Dans ces conditions le spot du plomb se forme alors que celui du baryum n'a pas lieu. Ceci semble dû aux insolubilités réciproques des rhodizonates et sulfates de plomb et baryum - Le sulfate de plomb étant moins insoluble que son rhodizonate alors que c'est le contraire pour le baryum.

Couleur du Spot de rhodizonate de plomb

Le spot de rhodizonate de plomb formé en milieu très légèrement acide à pH5 et lavé avec un tampon à pH5. 6 est d'abord rouge violet, en séchant il vire au bleu noir et reste très stable.

Une échelle de standards permet d'apprécier des teneurs en plomb de 5 microgrammes centimètre cube à 500 microgrammes centimètre cube.

3º RÉALISATION DU CONFINED SPOT

a) *Produits nécessaires*

Réactif: *Solution de rhodizonate de sodium à 2.0%.*

Ce réactif doit être fraichement préparé. On dissout 10 mmgr de Rhodizonate P.U.S. dans 5 cc d'eau déminéralisée.

Solution de citrate d'ammonium: Solution de produit chimiquement pur à 10% dans de l'eau déminéralisée.

Rondelles de papier Durieux Nº 149 ϕ = 20 mm

Solution de $SO_4 Na_2$: Solution à 2% de $SO_4 Na_2 IOH_2O$ dans de l'eau déminéralisée.

Solution tampon pH5. 6: 55 cc de solution d'acide succinique à 5. 9 gr litre + 45 cc de solution de borax à 19 gr/litre.

Papier indicateur universel Merck.
Eau déminéralisée

b) *Prèparation de la solution de sol*

On prélève 2 cc de la solution de sol et on ajoute 1 cc de solution de citrate ammonium, puis 2 à 3 gouttes de Am OH concentré de façon à amener à pH5. On vérifie l'acidité à la touche sur papier indicateur Merck – Si on dépasse le pH on revient en arrière par une goutte d'acide.

c) *Confined Spot*

L'appareil étant à la position basse on place une rondelle de papier dans le joint et on serre celui-ci. On met 2 gouttes de solution de SO_4 Na_2 puis O.2 cc de la liqueur à tester, deux gouttes de solution de SO_4 Na_2 et 3 gouttes de rhodizonate.

On attend 2 minutes, relève l'appareil de 10 cm environ, on laisse filtrer puis on lave avec 3 gouttes de solution tampon. [1]

On retire la rondelle de papier et on compare le Spot lorsqu'il est sec avec les standards.

Avant de recommencer le nouveau spot il est nécessaire de bien nettoyer l'interior du joint avec un moreau de papier filtre.

4º PRÉPARATION des STANDARDS

L'échelle de Standards que nous utilisons habituellement varie de 0 à 1000 ppm avec les valeurs intermédiaires suivantes 0 — 20 — 50 — 100 — 200 — 500 — 1000.

Nous préparons ces standards suivant la méthode habituelle en Confined Spot en partant d'un échantillon de sol (de la région à prospecter) ne contenant pas de plomb. Cet échantillon sert à faire une liqueur de sol à partir de laquelle on réalisera les Spots standards en y ajoutant des quantités connues de plomb –

Les standards sont collés sur un carton. Ils sont très stables.

5º RAPIDITE de la MÉTHODE

Un chimiste entrainé peut faire 80 titrages jours en menant les attaques par 40 à la fois – Les résultats sont suffisamment précis pour des titrages de géochimie.

C—DOSAGE DU ZINC

1º PRINCIPE

Une partie aliquote de solution de sol acide est filtrée à travers une surface

[1] Il est possible de simplifier cette technique en mélangeant les solutions de rhodizonate et de sulfate de sodium, mais il arrive alors parfois que les spots aient des couleurs inhabituelles.

déterminée de papier Durieux Nº 149 imprégné de nitrate de cuivre en présence de sulfocyanure d'ammonium mercurique, suivant les teintes obtenues on détermine les teneurs en zinc par comparaison avec des standards.

2º RÉACTIF

Pour former le spot de zinc nous avons choisi le réactif de Montequi.

Ce réactif est une solution dans l'eau de chlorure mercurique et de sulfocyanure d'ammonium.

En présence d'ions cuivre et zinc et en milieu acide 10% il se forme un précipité violet –

Feigl (1954) qui a décrit cette réaction pour la détection du zinc dans les revêtements métalliques pense que la coloration est due à la coprécipitation de Zn (Hg (CNS)$_4$) et Cu (Hg(CNS)$_4$). Il signale en cutre que la coloration due au fer peut ètre eliminés par une solution de fluorure d'ammonium et que le cobalt et le nickel génent –

Wenger (1946) donne la réaction remarque que l'emploi du Fluorure est tojours nécessaire car le cuivre donne des teintes vert-olive qui sont éliminées par le fluorure.

La réaction a encore lieu pour une dilution de $1/10^5$. Le nickel ne devient génant qu'en proportion importante et le cobalt donne des spots bleus différents de ceux du zinc. Pour être génant le cobalt doit être dans une proportion voisine de celle du zinc.

3º RÉALISATION DU "CONFINED SPOT" DE ZINC

a) *Produits nécessaires*

Réactif de Montequi 8 gr de chlorure mercurique et 9 gr de sulfocyanure d'ammonium sont dissous dans 50 cc d'eau déminéralisée, on laisse reposer plusieurs jours –

Rondelles de papier Durieux Nº 149 imprégnées de nitrate de cuivre à 0.1%

On prépare ces rondelles de la façon suivante. On découpe à l'emporte pièce en acier dands les feuilles de papier Durieux Nº 149 des rondelles de 20 mm de diamètre — Ces rondelles sont trempées dans du nitrate de cuivre à 0.1% puis séchées à l'air. Une fois sèches elles sont à nouveau trempées dans la solution de nitrate de cuivre puis séchées définitivement.

Eau déminéralisée

Fluorure d'ammonium solution à 5% dans l'eau.

b) *Préparation de la solution de sol*

La solution de sol doit être acide — L'acidité la plus convenable est aux environs de 10% (une acidité plus forte de l'ordre de 20% en NO_3 H par exemple détruit les réactifs)

c) *"Confined Spot"*

L'appareil étant à la position basse on place une rondelle de papier imprégnée de nitrate de cuivre dans le joint -

Après serrage on introduit dans le tube du haut 1 goutte de fluorure d'ammonium à 5%, 3 gouttes de réactif de Montequi et 0.5 cc de liqueur de sol à essayer. On laisse au repos 2 minutes puis on filtre en relevant l'appareil et on lave une fois à l'eau.

L'appareil est ensuite démonté et on compare le spot violet obtenu à une échelle de standards varient de 0 à 2000 ppm.

Avant de faire un nouveau Spot il faut nettoyer soigneusement l'intérieur du joint avec un papier filtre.

4º PRÉPARATION DES STANDARDS

Ils se préparent de la façon habituelle en partant d'un échantillon de sol (de la région à prospecter) ne contenant pas de Zinc.

Nous utilisons habituellement l'échelle suivante

0 — 40 — 100 — 200 — 500 — 1000 — 2000

Ces Spots standards sont collés sur un carton et recouverts d'une bande de papier collant transparent - La bande protectrice est nécessaire car les Spots très épais pour les hautes teneurs ont tendance à être effacés par frottement.

5º VALEUR ET RAPIDITÉ DE LA MÉTHODE

La méthode que nous venons d'exposer nous a toujours donné de bons résultats.

Un géochimiste entrainé peut avec 6 appareils effectuer le titrage de 80 échantillons jours en conduisant les attaques par 40 à la fois.

D—DOSAGE DU CUIVRE

Le dosage du Cuivre sur les mêmes liqueurs d'attaques de sol que pour le plomb et le Zinc peut être effectué comme suit.

a) *Préparation de la solution de sol*

On prélève 1 cc de la solution acide de sol et on y ajoute 1 cc de citrate d'ammonium à 10% on neutralise à l'ammoniaque jusqu à virage bleu d'un papier de tournesol. On amène à 5 cc avec de l'eau et on ajoute 1 cc acide acétique au demi.

b) *"Confined Spot"*

L'appareil étant à la position basse on place une rondelle de papier à l'acide rubéanique dans le joint et serre celui-ci.

On introduit 0.2 cc de la solution à tester dans le tube du haut on rélève

l'appareil de 10 cm environ et on laisse filtrer puis on lave avec un jet de pissette d'eau déminéralisée.

On retire la rondelle de papier et on compare le spot sec avec les standards.

d) *Préparation des Standards*

On les prépare de la façon habituelle en choisissant un échantillon de sol ne contenant pas de Cuivre -

Nous utilisons habituellement l'échelle suivante:

0 — 10 —20 — 50 — 100 — 200 — 500 — 1000 — 1500

E—MATERIEL, ET PRODUITS NECESSAIRES POUR 3000 DOSAGES SOIT 1000 DE CHAQUE METAL

MATÉRIEL

A—*Préparation des échantillons*

Tamis 100 (ϕ 150)	2
Mortier fonte de 1 litre avec pilon	1
Pinceaux pochoirs	2
Spatule Prolabo à cuiller	2
Petits sacs de papier pour échantillons	1100
Cuvettes en carton de 50 x 70 mm	100

B—*Attaque des sols*

Balance de prospection	1
Plaque chauffante 40 x 50 cm avec brûleur à essence ou butane	1
Fioles Erlenmeyer de 50 cc	50
Entonnoirs de ϕ 50 mm	25
Tubes à essais de ϕ 20 mm	50
Filtres Durieux N° III - ruban bleu	1200
Pinceaux pour balance	2
Verres de montre ϕ = 40 mm	50

C—*Analyse Plomb - Cuivre - Zinc*

Pipette de 2 cc	3
Appareils pour Confined Spot	18
Pipettes de 5 cc	3
Pipettes droites de précision de 1 cc au 1/10	6
Flacons compte goutte	6
Tube à essai de 16 x 160 mm	100
Tube à essai de 16 x 160 mm marqués à 5 cc	50

Pissette en matière plastique de 500 cc	4
Burettes au 1/10 de cc de 50 cc	2
Papier filtre ordinaire	25 Flles
Chronomètre montre	1
Tube compte gouttes fins	6

PRODUITS

Acide perchlorique 20% (⅓)	6 litres
Ammoniaque concentré	1,5 „
Acide acétique glacial a 50%	1,5 „

Cuivre

Solution de citrate d'ammonium à 10%	4 „
Rondelles de papier à l'acide rubéanique	1200
Papier tournesol (rouge)	1 carnet
„ „ (bleu)	2 „
Liqueur Standard de Cuivre à 100 microgr/cc	250 cc
„ „ „ 1000 „	250 cc

Plomb

Rhodizonate de sodium (capsule de 10 mmgr)	50
Sulfate de sodium à 25%	1 litre
Borax pour solution tampon	20 gr
Acide succénique pour solution tampon	10 „
Citrate d'ammonium à 10%	1 litres 5
Papier indicateur universal Merck	1 carnet
Liqueur standard de Pb à 100 microgr/cc	250 cc
„ „ „ „ 1000 „	250 cc

Zinc

Réactif de Montequi	500 cc
Fluorure d'ammonium	250 cc
Rondelles de papier Durieux imprégnées de nitrate de Cuivre	1200
Papier tournesol bleu	1 carnet
Liqueur de Zn à 100 microgr/cc	250
„ 1000 „	250
„ 2000 „	250
Eau éminéralisée si le géochimiste ne dispose pas d'un appareil spécial	25 litres

IV — OR

Le dosage rapide de l'or dans les sols que nous décrivons ci-dessous permet d'effectuer 24 analyses par jour. Cette méthode est plus compliquée que les méthodes habituelles de géochimie mais n'exige cependant qu'un matériel réduit.

Elle permet de doser jusqu' à 0.05 gr d'or à la tonne.

Nous l'avons vérifiée sur plusieurs centaines d'échantillons et elle nous a donné des résultats très comparables à ceux obtenus par fusion et coupellaiton sauf pour quelques minerais très graphiteux où la mise en solution de l'or semble particulièrement difficile.

On verra plus loin les résultats obtenus par cette méthode dans une prospection géochimique à l'AFEMA en Côte d'Ivoire.

I — PRINCIPE

Notre méthode comprend:

a) Mise en solution de l'or par attaque du mineral à l'eau régale puis filtration des liqueurs d'attaque et prélèvement d'une aliquote de 5 ou 10 cc

b) Elimination de l'acide nitrique par évaporation à sec de l'aliquote puis reprise par HCl dilué.

c) Précipitation de l'or par réduction au chlorure stanneux en présence de chlorure mercurique comme entraineur puis centrifugation du précipité et distillation du mercure.

d) Reprise du résidu par 1 goutte d'eau regale et 1 cc d'HCl O, I N.

c) Réalisation du "Confined Spot" par précipitation de l'or à l'aide de la rhodanine.

Ces différentes opérations sont suffisamment rapides pour qu'un opérateur effectue 24 titrages jour -

II — MISE EN SOLUTION

La mise en solution de l'or contenu dans un mineral est assez difficile. M. Shima (1953) emploi un mélange de brome et d'éther. Cette méthode donne de bons résultats mais nous l'avons rejetée étant donné ses difficultés d'emploi en pays tropical -

Après différents essais nous avons adopté la technique suivante.

On prélève 20 gr de sol passant à 160 microns que l'on attaque à chaud au bain de sable avec 20 cc d'eau régale pure. L'attaque est conduite dans une fiole Erlenmeyer de 150 cc recouverte d'un verre de montre. La température d'attaque est maintenue à ébullition commençante vers 90 º pendant une heure.

On ajoute ensuite 20 cc d'eau et on continue l'attaque ½ heure.

On filtre sur filtre Durieux Nº III ruban rouge et on prélève 10 cc de filtrat clair correspondant à 5 gr de sol.

Remarque—Il arrive asses rarement que sur des terres très argileuses une attaque par 20 cc d'eau régale soit insuffisante, le sol et l'acide formant une pâte épaise - Dans ce cas nous attaques par 30 cc d'eau régale puis 30 cc d'eau et reprenons 15 cc de filtrat clair.

III — ELIMINATION DE L'ACIDE NITRIQUE

Comme dans les opérations suivantes nous précipitons l'or par réduction il est nécessaire d'éliminer l'acide nitrique - Pour ce faire, les 10 cc de filtrat sont versés dans de petits bechers de 50 cc puis menés à sec au bain de sable. On évitera autant que possible les surchauffes qui rendent l'oxyde de fer difficilement soluble.

Le résidu sec est repris par 2 cc d'acide chlorydrique au demi puis par 3 cc d'eau. Si l'oxyde de fer se dissout mal en double la quantité d'acide au demi.

On doit obtenir une solution claire.

IV — PRECIPITATION DE L'OR

Les liqueurs d'attaque ainsi préparées contiennent de grandes quantités d'impuretés en particulier du fer très génant pour la colorimétrie - Noun avons done été conduits à isoler l'or.

La solution chlorhydrique est réduite par du chlorure stanneux (10 cc environ de Sn Cl_2 à 20%) puis on ajoute à froid 1 cc de chlorure mercurique (1%) comme entraineur - Il se forme un voile gris puis noir -

On agite puis laisse au repos 15 minutos et on transvase le contenu du becher dans un tube d'une petite centrifugeuse à main Prolabo à 4 tubes.

On tourne 15 secondes environ et on décante le jus clair. La poussière de mercure se colle au fond du tube et la décantation est très facile. On lave par centrifugation une fois à l'acide HCl 20% et deux fois à l'eau.

Le tube de la centrifugeuse est séché au bain de sable puis chauffé à feu vif pour distiller le mercure.

V—REALISATION DE LA SOLUTION POUR COLORIMÉTRIE

Après refroidissement on laisse tomber au fond du tube une goutte (1/100 de cc) d'eau régale pure et on laisse digérer 15 minutes environ. On ajoute ensuite 1 cc d'acide HCl O, I N et on agite.

VI—REALISATION DU CONFINED SPOT

Réactif

Le réactif que nous employons est une solution de rhodanine à 0.03% dans l'acide acétique pur.

La rhodanine ou P. Diméthylaminobenzylidénerhodanine (Sandell, G., s. f.) donne des solutions stables dans l'alcool et les acides forts et réagit en donnant des composés insolubles rouges ou violets en solution acide avec l'argent, le mercure I et II, le cuivre, l'or et le palladium. Le platine réagit aussi mais la réaction est moins sensible. En solution alcaline beaucoup de corps précipitent.

Remarque — Notre mode d'attaque et la préparation des liqueurs pour Confined Spot éliminent pratiquement tous les métaux qui interférent dans la réaction de l'or sur la rhodanine.

Confined Spot

Réalisation—L'appareil étant à la position basse placer dans le joint une rondelle de papier Durieux Nº 149 vierge. Introduire dans le tube du haut une goutte de solution de rhodanine, 0.2 cc de la solution à essayer et enfin 3 gouttes de rhodanine, attendre 2 minutes, puis relever l'appareil et laisser filtrer.

On démonte ensuite le joint et retire le Spot.

Examen

Le Confined Spot obtenu est violet rouge. En séchant il vire au brun rouge et reste très stable. Son intensité dépend le quantité d'or contenue dans la liqueur de sol.

Par comparaison avec une échelle de standards on détermine la teneur en or du sol.

VII — STANDARDS

Pour faire les standards il suffira de partir d'un sol de la région prospectée de teneur nulle en or et d'opérer comme suit.

Attaquer 100 gr de sol par 100 cc d'eau régale pure puis ajouter 100 cc d'eau filtrer.

Dans II bechers de 50 cc marqués de I à II mettre 10 cc de liqueur de sol et ajouter des quantités d'or connues à partir de liqueurs à 10 et 100 microgramme/cc.

Aller à sec, précipiter l'or au chlorure mercurique, laver par centrifugation distiller le mercure et reprendre par I goutte d'eau régale et I cc d'HCl O, I N.

Effectuer ensuite les spots selon la méthode indiquée précédemment.

Dans le tableau ci-dessous nous indiquons les quantités d'or à ajouter à chacun des bechers pour avoir des échelles bien lisibles et les correspondances en ppm suivant l'attaque employée.

Bechers	1	2	3	4	5	6	7	3	9	10	11
Liqueur de sol cc	10	10	10	10	10	10	10	10	10	10	10
Au microg.	0	0.5	1.25	2.5	5	10	15	20	25	37.5	50
Correspondance en gr/T pour ne attaque de 20 gr de sol	0	0.1	0.25	0.5	1	2	3	4	5	7.5	10

MATÉRIEL ET PRODUITS NÉCESSAIRES POUR 1000 ANALYSES

MATÉRIEL

Balance de prospection	1
Fioles Erlenmeyer pyrex de 150 cc	40
Entonnoirs à filtration 70 mm pyrex	25
Filtres Durieux Nº III bande rouge de 120 mm	1200
Tubes à essai de 20 x 200 mm	40
Bechers de 50 cc	40
Pipettes de 5 cc	3
Pipettes de 10 cc	3
Pipettes de 1 cc au 1/10	4
Pipettes de 1 cc au 1/100	2
Eprouvettes à pied de 20 cc	3
Eprouvettes à pied de 500 cc	2
Pipettes droites de 10 cc en 1 cc	2
Centrifugeuses à main à 4 tubes	1
Compte-gouttes	4
Appareil à Confined Spot complet	6
Rondelles de papier Durieux Nº 149 de 20 mm	2000
Bain de sable de 40 x 50 cm avec brûleur à essence ou butane	1
Tubes de centrifugeuse	50
Bec butane ou essence	2
Pinces pour tubes à essai	6
Montre chronomètre	1
Verres de montre = 40 mm	40

Supports pour tubes à essai	4
Agitateurs verres avec bouts caoutchouc	30
Papier filtre ordinaire	25 feuil.
Bechers de 250 cc	2

PRODUITS

Acide nitrique pur pour analyse	6 Kgs
Acide chlorhydrique pur pour analyse	20 Kgs
Chlorure mercurique	50 grs
Chlorure stanneux pur pour analyse	2 kgs
Acide acétique	1 lit.
Rhodanine	100 ampoules de 3 mm gr
Acide acétique pur	1 lit.
Solution Standard d'or à 1000 microgr/cc	100 cc.

On prépare sur place au fur et à mesure des besoins par 1 litre à la fois

— L'eau régale pure en ajoutant à 750 d'HCl pur 250 cc d'acide nitrique

— L'acide HCl au demi

— L'acide HCl O, IN en diluant à 1 litre 10 cc d'HCl pur

— Le chlorure stanneux en dissolvant 200 gr/ de chlorure stanneux dans 200 cc d'HCl pur et diluant à 1 litre.

La solution de chlorure mercurique sera préparée par 100 cc à la fois en dissolvant 1 gr de chlorure mercurique dans 100 cc d'eau.

La solution de rhodanine est faite chaque jour en dissolvant le contenu d'une ampoule dans 10 cc d'acide acétique pur puis en filtrant.

Matériel de préparation des échantillons

— Tamis 100 (ϕ 150 mm)	3
— Mortier fonte avec pilon	1
— Pinceaux pochoirs	1
— Spatule Prolabo à cuiller	2
— Sacs à échantillon	1100
— Cuvettes en carton de 50 x 70 mm	100

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MÉTHODE DE TERRAIN POUR LE DOSAGE SEMI-QUANTITATIF PAR CHROMATOGRAPHIE SUR PAPIER, DU CUIVRE, DU PLOMB ET DU ZINC DANS LES SOLS

A. BLANCHOT * et B. MARTINET * *

RÉSUMÉ

Une méthode simple pour la prospection géochimique du cuivre, du plomb et du zinc dans les sols, inspirée des travaux de Hunt, North et Wells est décrite.

Après attaque des échantillons de sol à l'acide nitrique, les traces de métaux sont separées, par chromatographie ascendante, par diffusion d'alcoool méthylique acidifié à 5% d'acide chlorhydrique sur des bandelettes de papier filtre Arches 302. Ce papier est découpé de telle façon que dix analyses puissent ètre conduites simultanément. Les métaux des décelés par pulvérisation avec un réactif approprié-réactif de Montequi pour le zinc, rhodizonate de sodium pour le plomb, acide rubéanique pour le cuivre. Les analyses pour plamb et cuivre peuvent être faites sur la même fauille. Le teneur en chacun de ces métaux est déterminée par comparaison avec des chromatogrammes étalons préalablement préparés. L'élimination d'interferences possibles est étudiée. Le caractère original de la méthode réside dans l'emploi du réactif de Montequi et du rhodizonate.

INTRODUCTION

En zone tropicale, la dithizone a donné satisfaction pour la prospection géochimique du cuivre; par contre, ce reactif s'est montré d'un emploi trop délicat pour la recherche du zinc. Par ailleurs, le chromographe utilisé par l'U.S. Geological Survey est un appareil trop délicat pour les missions "en brousse": les joints de caoutchouc se détériorent sous le climat tropical, les capillaires se bouchent par vent de sable.

Nous avons déja expérimenté, avec entière satisfaction, la méthode de séparation chromatographique du cuivre, du nickel et du cobalt décrite et discutée par Hunt, North et Wells *(The Analyst*, vol. 80, mars 1955, p. 172 *sq)*. Ces métaux sont révélés par pulvérisation à l'acide rubéanique. Dans ce même article, ces auteurs décrivent également une méthode analogue pour la détermina-

* *Ingénieur Géologue, I.G.N.*

* * *Ingénieur Chimiste, E.N.S.I.C.N.*

tion chromatographique du plomb à la dithizone. Nous avons pensé que cette méthode pouvait être utilisée, avec d'autres réactifs, pour le zinc et le plomb. Nous nous sommes efforcés de trouver des réactifs donnant des taches colorées assez stables pour que demeure un résultat de la prospection géochimique permettant le contrôle de l'opération à distance et la discussion des résultats obtenus. Un avantage supplémentaire de cette méthode est de n'utiliser que de faibles quantités d'eau déminéralisée.

A la suite de divers essais de laboratoire, nous avons mis au point une méthode qui va être utilisée sur le terrain dès le début de 1956.

II — ATTAQUE DE L'ECHANTILLON DE SOL

Hunt, North et Wells font digérer 1 g de sol dans 1 cm^3 d'acide nitrique dilué à 1/3. Dans le cas de sol très argileux, le liquide est practiquement entièrement absorbé par le sol et, par la suite, il est impossible de pipeter une aliquote, même faible, dans cette boue. Aussi avons nous préféré la méthode d'attaque suivante:

2 g de sol sont attaqués à douce ébullition, pendant 10 minutes, par de l'acide nitrique 1/1, dans un tube à essai de 20 x 200. Dans ces conditions, la perte par évaporation est faible, inférieure à 10% du volume initial. Pour une évaluation semiquantitative des métaux lourds, il est donc inutile de réajuster le volume de la liqueur d'attaque. 5 cm3 de celle-ci sont pipetés et évaporés à sec dans un petit creuset ou un petit cristallisoir, sur un bain d'air facilement utilisable en campagne. Le résidu sec est repris par 1cm3 d'acide nitrique 1/3.

Cette méthode d'attaque s'est montrée satisfaisante.

III — CHOIX DU SOLVANT

Hunt, North et Wells préconisent, pour la séparation chromatographique du plomb, l'alcool méthylique acidulé à 5% d'acide chlorhydrique.

D'autres auteurs (par ex. C. G Lamm, *Act. Chem. Scand.*, vol. 7, 1953, nº 10, p. 1420-22) emploient, pour la separation chromatographique du zinc, de l'alcool butylique normal plus ou moins chargé d'acide chlorhydrique.

Aprés divers essais, nous avons préféré le premier solvant car son ascension dans le papier est plus rapide.

Avec l'alcool méthylique à 5% d'HCl, le fer est au front du solvant, suivi par le zinc et le cuivre (rf respectivement d'environ 0,9 et 0,8) ; le plomb s'élève moins : son rf est à peu près de 0,45 dans les conditions d'humidité et de température de Dakar, au mois de novembre.

IV — CHOIX DU PAPIER

Les auteurs anglais utilisent du papier Whatman CRL/1. Il se présente en feuille de 21,3 cm x 11 cm où, parallèlement au petit côté, sont découpées 11 fentes de 0,3 cm x 9 cm qui ménagent 12 bandes de 1,5 cm jointes aux deux extrémites.

Nous n'avons pu, jusqu'ici, nous procurer ce papier. Nous l'avons remplacé, après l'essai de divers papiers, par du papier Arches 302 découpé à la main à l'aide d'une matrice. C'est à ce papier qu'est allée notre préférence car:

— son grain serré permet une bonne séparation chromatographique avec, cependant, une ascension suffisamment rapide du solvant.

— il est pratiquement dépourvu de Zinc et trés pauvre en cuivre, de sorte qu'un lavage préalable est inutile.

V — CHOIX DES REACTIFS

Nous avons conservé, pour révéler le cuivre, l'acide rubéanique qui donne, en milieu neutre, une belle coloration vert olive, très stable.

Pour le zinc, le ferrocyanure, d'uranyl l'oxine et le réactif de Montéqui ont été expérimentés. Ce dernier réactif a donné les meilleurs résultats. Rappelons en quoi consiste la réaction: un sel de zinc, en présence d'un sel de cuivre, donne, avec un mélange de sulfocyanure d'ammonium et de chlorure mercurique, un précipité cristallin gris-violacé de mercuro-sulfocyanure mixte de zinc et de cuivre. La réaction faite sur papier, est encore bien sensible pour 5 γ de zinc. Cette réaction a lieu en milieu acide.

La coloration intense rouge sang que donne le fer avec le sulfocyanure masquerait la réaction de Montéqui, si l'on n'additionnait la solution cuivrique, de fluorure d'ammonium qui complexe le fer.

La coloration obtenue est très stable mais les taches risquent de s'effacer au frottement aussi faut-il conserver les chromatogrammes avec quelques précautions.

Différents réactifs ont été essayés pour révéler le plomb sous forme de taches colorées: gallocyanine, thionalide, sulfure d'ammonium, viscose, tétrahydroxyquinone, chromate de potassium, rhodizonate de sodium. Ce dernier réactif produit avec le plomb des taches mauves donnant des chromatogrammes très lisibles.

Ces taches fanent à la longue mais peuvent être ravivées par une nouvelle pulvérisation avec une solution de rhodizonate. Cette réaction, qui se produit en milieu neutre ou légèrement acide, est sensible, sur papier, à moins de 1 γ

de plomb. Nous verrons par la suite que, dans certains cas, le barym peut gêner mais qu'il est possible d'éliminer cette interférence.

Le fait que la réaction de Montéqui a lieu en milieu acide, tandis que l'acide rubéanique et le rhodizonate réagissent en milieu neutre, empêche l'emploi d'un même chromatogramme pour déceler simultanément ces trois métaux. Deux chromatogrammes sont donc préparés simultanément, l'un pour le zinc, l'autre pour le cuivre et le plomb. On peut ainsi, grâce au déccupage du papier, traiter à la fois dix échantillons de sol.

VI — ELIMINATION DES INTERFERENCES POUVANT GENER LA DETERMINATION DU CUIVRE ET DU PLOMB

Dans la séparation chromatographique employée, le cuivre suit de très près le fer. Dans le cas d'un sol très riche en fer, il se peut que les taches colorées du fer (ocre) et du rubéanate de cuivre (vert olive) se chevauchent, ce qui peut rendre difficile la détermination du cuivre. Toutefois, en général, la coloration vert foncé du cuivre prédomine. Dans le cas où le fer serait gênant, il y aurait lieu d'additionner de 10% (poids/volume) de fluorure d'ammonium ou de sodium, la solution d'acide rubéanique. L'ion fluorure complexe le fer qui est décoloré; par contre, ce produit n'inhibe nullement les autres réactions.

Dans l'élution avec le solvant employé, le cobalt et le nickel accompagnent le cuivre. Ces deux métaux donnent avec l'acide rubéanique des colorations intenses: bleu avec le nickel, jaune ocre avec le cobalt, qui rendent difficile l'appréciation de la teneur en cuivre des échantillons. Dans ce cas, la méthode employée donne une indication qualitative en signalant la présence de nickel ou de cobalt dans le sol étudié, ce qui peut être intéressant. D'autre part, l'association Zn — Pb — Cu — Ni — Co est rare; si on avait à l'étudier, il faudrait le faire sur 3 chromatogrammes: un pour le zinc, un pour le plomb au rhodizonate, le dernier pour l'ensemble Cu — Co — i que l'on traiterait suivant la méthode de Hunt — North et Wells (op. cit.)

Plus gênante est la présence de baryum dans le sol à étudier. L'indice minéralisé que nous nous proposons d'étudier prochainement sur le terrain contient en abondance de la barytine. Ce minéral résiste à l'acide nitrique 1/1 employé dans notre attaque de l'échantillon du sol mais il est presque constamment associé à de la withérite (carbonate de baryum), minéral facilement mis en solution par les acides.

Or le baryum donne une coloration rouge groseille intense avec le rhodizonate de sodium.

Dans la séparation chromatographique que nous employons, le baryum ne migre presque pas, mais malgré cela, la tache rouge qu'il produit risque, s'il

est abondant, de chevaucher partiellement la tache mauve du plomb et de rendre sujette à caution l'estimation de ce métal. Dans les cas de sols riches en baryum soluble, il y aura lieu d'additionner la solution de rhodizonate de 1% (poids/volume), —ou même plus—, de sulfate de soude. En effet, l'ion sulfate décolore le rhodizonate de baryum alors qu'il n'a aucune action sur le rhodizonate de plomb, ce réactif supplémentaire ne géne nullement l'action de l'acide rubéanique sur le cuivre.

VII — MATERIEL ET REACTIFS NECESSAIRES

Matériel:

Mortier et pilon [1]
Tamis à 80 mesh
Trébuchet
Tubes à essais en pyrex de 20 x 200 mm
Support métallique de tubes à essais modèle U.S. Geological Survey
Réchaud à essence ou butagaz
Petits creusets ou petits cristallisoirs
Bain d'air
Feuilles de papier Arches 302 découpées comme il a été dit plus haut.
Pupitres en bois pour ces feuilles
Pipettes de 1 cm^3
Pipettes de 5 cm^3
Micropipettes graduées en 0,01 cm^3
Eprouvette de 20 cm^3 graduées en cm^3
Béchers forme basse de 600 cm^3
Boîtes de Pétri formant couvercle pour ces béchers
Pulvérisateurs en verre
Papier collant
Ciseaux.

Réactifs: Tous, sauf l'ammoniaque, doivent être de la qualité "chimiquement pur pour analyse".

Acide nitrique concentré
Acide chlorhydrique concentré
Alcool méthylique
Ammoniaque concentré
Réactif de Montéqui:

[1] Au début de chaque prospection, il y a lieu de s'assurer par quelques essais, de la nécessité d'un broyage préalable du sol; dans sertains cas, un simple tamisage est suffisant.

Solution A: sulfate de cuivre 0,2%
fluorure d'ammonium 5% — dans l'eau

Solution B: 16% de chlorure mercurique
18% de sulfocyanure d'ammonium
dans l'eau.

rhodizonate de sodium, pesé à l'avance en tubes de 0,02g. Dissoudre cette quantité, au moment de l'empleoi, dans 10 cm3 d'eau. La solution ne se conserve pas plus de 24 h.
acide rubéanique — pesé à l'avance en tubes de 0,1g; dissoudre 0,1g d'acide rubéanique dans 60 cm^3 d'alcool méthylique et diluer à 100 cm^3 avec de l'eau. Cette solution est stable.
fluorure d'ammonium
sulfate de sodium
solutions étalons de zinc, cuivre, plomb ou chromatogrammes étalons préparés au laboratorie.

VIII — MODE OPERATOIRE

A — *Préparation des chromatogrammes étalons:*

Des solutions étalons à : 50 — 100 — 200 — 500 — 1000 et 2000 ppm de zinc, de cuivre et de plomb dans de l'acide nitrique 1/3 sont préparées au laboratoire.

Une échelle plus nuancée ne nous a pas paru nécessaire pour le travail sur le terrain; très rapidement, l'opérateur arrive à estimer les valeurs intermédiaires entre celles des étalons.

Prélever à la micropipette 0,02 cm^3 pour le plomb et le cuivre, 0,5 cm^3 pour le zinc, de la liqueur étalon; appliquer cette aliquote à la base d'une bande du papier Arches fixée sur un pupitre. Chaque feuille de papier filtre permet dix essais simultanés. Prévoir un essai à blanc.

Laisser sécher à l'air.

Préparer le solvant en mélangeant 1 cm^3 d'alcool méthylique et 1 cm^3 d'acide chlorhydrique. Ne préparer ce solvant qu'au moment de l'emploi. Il peut servir à deux élutions successives. Verser ce solvant dans un bécher de 600 cm3 couvert d'une boîte de Pétri.

Enrouler la feuille en cylindre en la maintenant dans cette forme par un bout de papier collant.

La placer dans le bécher à solvant, les taches en bas.

Laisser diffuser le solvant presque jusqu'en haut des bandelettes. Laisser sécher à l'air.

Pour le zinc: pulvériser la feuille déroulée et placée sur un pupitre avec la solution A, puis la solution B du réactif de Montéqui. Les taches gris violacé caractéristiques du zinc apparaissent au bout de quelques secondes.
Pour le cuivre et le plomb: Placer la feuille enroulée en cylindre dans un bécher contenant une coupelle d'ammoniaque. Laisser neutraliser l'excès d'acide retenu dans le papier filtre.

Etaler la feuille sur un pupitre et pulvériser avec la solution d'acide rubéanique (cuivre) ou de rhodizonate (plomb).

B—*Attaque des sols:*

Peser 2 g de sol, éventuellement broyé passé au tamis 80.
Placer cet échantillon dans un tube à essai de 20 × 200
Ajouter 10 cm^3 d'acide nitrique 1/1
Attaquer 15 minutes à douce ébullition
Laisser décanter
Prélever, à la pipette, 5 cm^3 du liquide surnageant, les placer dans un petit creuset
Evaporer à sec au bain d'air
Reprende le résidu sec par 1 cm^3 d'acide nitrique 1/3

C—*Préparation des chromatogrammes*

Travailler simultanément sur deux feuilles fixées sur des pupitres;
sur la première, destinée à la détermination du zinc, déposer à la base de chaque bandelette 0,05 cm^3 de chacune des solutions à étudier;
sur la seconde, déposer de même, 0,02 cm^3 de solution; cette feuille sera destinée à l'évaluation simultanée du cuivre et du plomb.

Il est bien évident que l'opérateur profitera du même "coup de micropipette" pour préparer chacun des 2 chromatogrammes.

Procéder ensuite comme pour la préparation des chromatogrammes étalons.

Pour le deuxième chromatogramme, il est prérérable de pulvériser le rhodizonate avant l'acide rubéanique : on obtient ainsi de plus belles colorations.

Si le fer ou le baryum gênent, additionner l'acide rubéanique de fluorure d'ammonium et le rhodizonate de sulfate de soude ainsi que cela a été précédemment indiqué.

Comparer les tache colorées ainsi obtenues avec celles des chromatogrammes étalons en tenant compte de la largeur de la bande et de l'intensité de la couleur.

IX—CONCLUSIONS

Cette méthode a été appliquée avec satisfaction; au laboratoire, sur des sols africains. Dans quelques jours, elle será employée sur le terrain, pour l'étude géochimique d'indices situés en zone désertique, dans le nord du Soudan.

Cette méthode demande un appareillage réduit et de faibles quantités de réactifs. Son emploi est simple et voici, à titre d'indication, les résultats obtenus par un opérateur au bout de cinq jours d'entrainement:

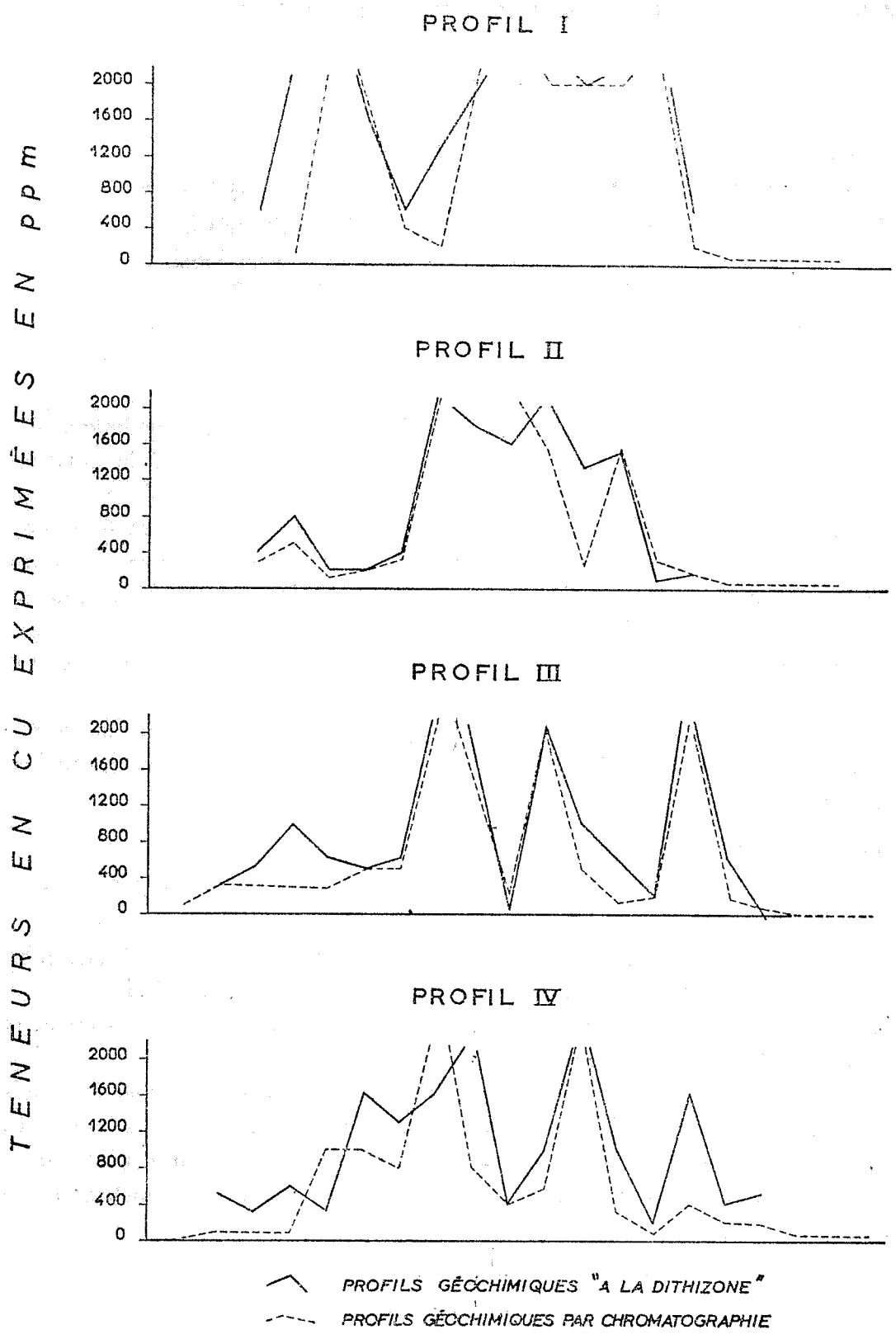
N° Echant.	Zn		Cu		Pb	
	Teneur réelle	Teneur estimée	Teneur réelle	Teneur estimée	Teneur réelle	Teneur estimée
1	70	50	20	25	50	50
2	140	150	10	25	100	50
3	250	180	30	50	200	200
4	500	500	40	50	350	400
5	700	750	40	50	400	350
6	1400	1500	40	50	1000	1500
7	2700	plus de 2000	80	75	2000	1500
8	20	0	85	50	10	0
9	40	50	100	100	25	25
10	70	50	200	275	48	50
11	130	150	350	300	100	150
12	180	150	500	400	120	150
13	360	300	1000	750	240	300
14	650	500	1500	750	360	400
15	720	350	1800	1500	480	500

Les lectures non satisfaisantes, pouvant d'ailleurs provenir de l'hétérogénéité de l'échantillon, ont été soulignées. On voit donc que l'emploi de cette méthode est, dans l'ensemble, simple et sûre.

Il semble qu'un opérateur puisse aisément étudier ainsi 60 échantillons de sol chaque jour.

Les réactifs employés sont peu coûteux. C'est donc une méthode rapide et économique.

La prospection que nous allons entreprendre au Soudan devrait permettre éventuellement de perfectionner cette méthode. Nous pensons procéder après cette prospection, à une discussion plus serrée de son emploi et de son efficacite.



Dosage chromatographique de Cu·Zn·Pb· (Blanchot)

APPENDICES

I—EMPLOI DE LA MÉTHODE SUR LE TERRAIN

La méthode décrite dans cet article a été employée sur le terrain au début de l'année 1956 et les résultats obtenus ont pu être critiqués lors de la présentation de cette note au XX° Congrès Géologique International.

La prospection géochimique menée dans la région de Tessalit (Soudan septentrional) a montré que cette méthode est trés satisfaisante. Le rendement est de 70 échantillons par jour de travail analysés pour Zn — Pb — Cu par un manipulateur expérimenté (temps de prélévement inclus).

A titre de vérification, les échantillons de plusieurs profils géochimiques ont été analysés pour cuivre par cette méthode et par une méthode à la ditrizonc. L'allure des courbes (cf fig.) traduisant ces deux groupes de résultats est identique. Cependant les courbes correspondant à l'emploi de la dithizone enveloppent généralement celles traduisant les analyses chromatographiques. Ceci traduit un fait que nous avons déjà noté à savoir que la chromatographie a tendance à donner des résultats légérement plus faibles que la réalité alors que l'emploi de la dithizone conduit à évaluer des teneurs fréquemment supérieures aux teneurs réelles.

La campagne de prospection géochimique conduite à Tessalit a montré que nous avions là une méthode rapide, peu onéreuse et satisfaisante pour les régions d'abord difficiles.

II—EMPLOI DU "ZINCON"

Nous avons signalé plus haut la difficulté de trouver un produit donnant des réactions colorées avec le zinc.

Le "zincon" (cf *Analytical Chemistry* – vol 26 – 1954 p. 1345 frs. R.M. Rush et J.H. Yoe), nom commercial du 2 carboxy 2'hydroxy 5'sulfoformazylbenzène, fabriqué par Lamotte Chemical Produits Baltimore et par Hopkin et Williams (Angleterre) semble répondre à ce besoin.

Le zincon n'est pas un réactif spécifique: il donne des complexes colorés avec un grand nombre de métaux. La solution à 0,002 N dans la soude N/10 est rouge orangé. Les complexes métalliques obtenus sont en général roses, mauves ou violacés mais certains éléments donnent des teintes tranchant nettement sur le fond, ainsi:

Cobalt	:	vert amande
Nickel	:	gris mauve
Fer	:	jaune paille
Argent	:	marron

et surtout *Cuivre* : bleu vif (stable de p. H 5 à 9,5)
Zinc : bleu vif (stable de p. H 8,5 à 9.5)

Cette derniére remarque suggére l'emploi de ce réactif en chromatographie, en milieu légérement alcalin, ce qui permet de révéler le Pb au rhodizonate sur la même feuille. On peut donc espérer une simplication de la méthode précédemment décrite.

Les premiers essais faits au laboratoire de la Direction Fédérale des Mines et de la Géologie sont encourageants. L'inconvénient majeur est la faible stabilité du complexe avec le zinc. Les taches bleues obtenues sont encore visibles pour 0,05 de zinc et très nettes pour la même teneur de cuivre. Les taches du complexe cuivrique sont très stables; celles obtenues avec le zinc disparaissent en quelques heures mais peuvent être ravivées par le réactif.

Il est à présumer que l'instabilité des colorations correspondant au zinc est due au faible intervalle de p. H (8,5 à 9,5) où le complexe du zinc est stable. Il est probable qu'un tampon à base de borate de sodium ou de phosphate de sodium améliorerait les résultats.

Nous avons donc là les bases d'une nouvelle méthode de prospection géochimique de Zn, Cu, Pb, par chromatographie qui peut être encore plus pratique que celle décrite au début de cette note. Les essais seront poursuivis au laboratoire de la Direction Fédérale des Mines et de la Géologie et la méthode expérimentée sur le terrain.

EQUIPEMENT ET MÉTHODE DE TERRAIN POUR LE DOSAGE SEMI-QUANTITATIF DU ZINC ET DU PLOMB PAR LA DITHIZONE

J. BEGUINOT *

RESUMÉ

Le Départment de Géochimie du B. R. G. G. M. est équipé d'une camionette et d'une remorque laboratoire:

La camionette est aménagée pour la préparation des échantillons stockés. Son installation comprend:

a) un compartiment pour le rangement de mille échantillons stockés dans des boîtes en matière plastique,
b) une étuve permettant le séchage de 150 échantillons en quelques heures.
c) deux paillasses pour les opérations de broyage et tamisage.
d) un réservoir de 150 litres assurant une distribution d'eau.

La remorque sert uniquement aux opérations chimiques, son équipement est constitué par:

a) deux paillasses,
b) une hotte avec ventilation,
c) un bain-marie,
d) plusieurs placards et tiroirs pour le rangement de la verrerie et des réactifs,
e) un appareil à lecture colorimétrique,
f) un réservoir d'eau de 150 litres, placé sur le toit du vehicule, qui assure une distribution d'eau déminéralisée.

Determination des teneurs (par la dithizone).

0.5 g. de sol sont attaqués pendant una 1/2 heure au bainmarie (95-100°) par un mélange d'acide chlorhydrique et nitrique dans des tubes de pyrex jaugé à 50 cc.

Le Zinc et le Plomb sont extraits d'une partie aliquote (0.1 à 5 cc selon les teneurs présumées) par agitation avec une soluton diluée de dithizone dans CCl^4 pour le Zinc, dans $CHCl^3$ pour le Plomb.

Le pH es estabilisé à 5,5 par adjonction de 5 cc. d'une tampon complexant pour le Zinc et à 9,5 pour le Plomb.

Les colorations sont comparées visuellement à une gamme d'étalons (0 à 56 pour le Zinc 0 à 98 pour le Plomb); ces étalons sont préparés journellement.

* *Ingénieur au Bureau de Recherches Géologiques, Géophysiques et Minières, France.*

INTRODUCTION

Le Bureau de Recherches Géologiques, Géophysiques et Minières a mis sur pied deux équipes de prospection géochimique, dont l'une travaille depuis un an, sur des problèmes de recherches d'extension de gîtes déjà connus de Plomb et de Zinc, au moyen de l'analyse des sols.

Les méthodes de travail employées ont été modifiées peu à peu à la lumiére des essais effectués et des résultats obtenus.

Le but de cette note est de décrire les méthodes et le matériel actuellement utilisés.

MÉTHODES DE TRAVAIL

I — ECHANTILLONNAGE

Les prélèvements de sols sont généralement effectués à la pelle, à la limite de la couche d'humus (20 à 30 cm. de profondeur). Des tests ont montré que cette profondeur était, dans la majorité des cas, favorable.

Signalons, à ce sujet, que des prélèvements effectués à différents niveaux sur le front de tranchées implatées dans des terrains de recouvrement, ont montré que la partie superficielle (40 premiers centimètres) était beaucoup plus riche en Plomb, les teneurs de cet élément diminuant rapidement avec la profondeur. Ce phénomène est beaucoup moins sensible pour le Zinc.

Dans certains cas particuliers, les prélèvements sont faits à la tarière, à profondeur variable, selon les renseignements cherchés.

Chaque échantillon est constitué par une prise de 200 g. de sol environ, et est recueilli dans une boîte en plastique (9 cm x 6 cm x 5 cm) portant un numéro.

La localisation des points de prélèvements faite sur fond topographique, carte ou photo aérienne, selon les cas.

La maille de l'échantillonnage varie avec le probléme à étudier.

II — PREPARATION DES ECHANTILLONS

Les prélèvements sont amenés au camion-laboratoire. Les boîtes, une fois ouvertes, sont rangées sur les étagères d'une étuve électrique qui assure le séchage.

Les échantillons séchés sont alors broyés sommairement dans un mortier de porcelaine (les cailloux sont rejetés) et tamisés à 80 mesh. Seul le tamisat est conservé dans la boîte numérotée, en vue des opérations chimiques, le refus étant rejeté; ce dernier représente, généralement, le tiers de l'échantillon prélevé.

III — MISE EN SOLUTION

Les deux éléments Plomb et Zinc se dosent sur la même liqueur d'attaque.

Il est pesé 0.5 g. de chacun des échantillons broyés et tamisés. Ces quantités sont introduites dans des tubes à attaque 24 x 280 jaugés à 50 cc. par un trait circulaire.

L'attaque de ces sols s'effectue au bain-marie pendant 20 minutes en milieu acide concentré (1 cc. ClH + 1 cc. NO_3H), puis 30 minutes en milieu acide dilué, en ajustant le volume de la liqueur acide au trait de jauge avec de l'eau déminéralisée.

La mise en solution terminée, les tubes sont sortis du bain-marie. Aprés refroidissement, le volume est ajusté exactement au trait de jauge (50 cc.) avec de l'eau déminéralisée. La liqueur d'attaque est alors homogénéisée par une rapide agitation.

IV — MODE OPERATOIRE POUR LE DOSAGE DU ZINC

Selon la teneur présumée en Zinc, il est pipeté de 0.1 à 5 cc. de la liqueur d'attaque homogénéisée.

Ces parties aliquotes sont introduites dans un tube colorimétrique 18 x 180.

Le pH est stabilisé à 5,5 par 5 cc. de tampon, auquel il a éte ajouté de l'hyposulfite de sodium, afin d'éliminer les interférences du Cuivre et du Plomb, qui pourraient perturber le dosage du Zinc à ce pH. L'extraction du Zinc contenu dans la prise d'essai est obtenue par agitation pendant 30 secondes avec 5 cc. d'une solution de dithizone (0.02 g. par litre) dans le tétrachlorure de carbone. La coloration rouge du dithizonate de Zinc formé se superpose à la coloration verte de l'excés de dithizone, et donne, selon les teneurs en Zinc, une gamme de teintes échelonnée du vert au rouge; la détermination de ces teneurs se fait en comparant les teintes obtenues à une série de témoins contenant de 0 à 5γ de Zinc.

Entre 0 et 4 γ, il est possible, avec une certaine habitude, d'évaluer le 1/10e de γ. La sensibilité maximum avec la concentration de la solution de dithizone employée est de 10 p.p.m. Il est possible de descendre beaucoup plus bas, en diminuant la concentration de la solution de dithizone.

Gamme d'étalons

Dix témoins contenant 0 - 0,5 - 1 - 1,5 - 2 - 2,5 - 3 - 3,5 - 4 - 5γ de Zinc sont préparés selon le mode opératoire ci-dessus, à partir d'une solution de Cl_2Zn contenant 1γ de Zinc par cc.

Les témoins sont stables 12 heures, si l'on prend soin de ne pas les exposer directement à lalumière solaire.

Solution tampon

Ce réactif est préparé dans des tonnelets de 10 litres par dissolution de:
— 2750 g, d'acétate de sodium
— 600 g. d'hyposulfite de sodium
— 40 g. de chlorhydrate d'hydroxylamine

dans 8 litres d'eau déminéralisée, puis purifié par agitation mécanique avec une solution tétrachlorée de dithizone, concentraée d'abord, diluée ensuite. Ce réactif, préparé en laboratoroire avant chaque prospection, est stocké et transporté dans des flacons de polythène de 10 litres.

Solution de dithizone

La solution de dithizone (0.02 g./litre) employée pour les analyses doit être préparée journellement par dilution d'une solution mère à 0.1 g./litre. Cette solution mère est stable 3 à 4 jours, si l'on prend la précaution de la maintenir à l'abri de la lumière.

V — MODE OPERATOIRE POUR LE DOSAGE DU PLOMB (méthode bicolore)

Selon la teneur présumée en Plomb, il est introduit de 0.1 à 5 cc. de la liqueur d'attaque homogénéisée dans un tube colorimétrique 18 x 180.

Le pH est stabilisé à 9,5, par addition de 5 à 7 cc. d'une solution tampon à laquelle il a été ajouté du cyanure de potassium afin d'eviter les interférences du Zinc. L'extration et la détermination des teneurs en Plomb se font par agitation pendant 30 secondes avec 5 cc d'une solution de dithizone dans le chloroforme (0.01 g/litre) et comparaison des colorations obtenues avec une gamme de témoins échelonnés de 0 à 9 γ.

Entre 0 et 6γ il est possible d'évaluer 1/10 de γ. La sensibilité maximum avec la concentration de dithizone employée est de 10 p.p.m. Il est possible de descendre beaucoup plus bas en employant une solution de dithizone plus diluée.

Gamme d'étalons

Dix témoins de 0 à 9 γ sont préparés selon le mode epératoire ci-dessus, à partir d'une solution de $(NO_3)_2Pb$ contenant 2γ de Plomb par cc. Ces témoins sont stables 12 heures si l'on prend soin de ne pas les exposer directement à la lumière solaire.

Solution tampon

Ce réactif est préparé dans un tonnelet de 10 litres, par dissolution de:
— 2750 g. de citrate trisodique
— 160 g. de chlorhydrate d'hydroxylamine

dans 8 litres d'eau déminéralisée. Le pH est ajusté à 9.5 par NH_4OH.

Le réactif est ensuite épuré par agitation mécanique avec une solution con-

centrée, puis diluée, de dithizone dans le chloroforme, puis deux fois avec du chloroforme pur, afin de récupérer la dithizone passée dans la phase aqueuse sous forme de dithizonate d'ammonium.

Ce réactif, préparé en laboratoire avant chaque prospection, est stocké et transporté dans des flacons de polythène de 10 litres. Au moment de l'emploi, on ajoute 18 g. de cyanure de potassioum et 20 cc. NH_4OH par litre de réactif.

Solution de Dithizone

La solution de dithizone (0.01 g./litre) est préparée journallement par dilution d'une solution mère à 0.1 g. par litre. Cette solution mè est stable 3 à 4 jours, si l'on prend la précaution de la garder à l'abri de la lumière.

VI — PRECISION DE CES DEUX METHODES DE DOSAGE

Deux cents tests de reproductibilité ont été faits, tant en Plomb qu'en Zinc, sur 5 prèlèvements de 200 g. chacun, longuement broyés et homogénéisés.

Ces déterminations, réparties sur une période de 4 mois, ont été faites dans les conditions de travail de terrain, par des opérateurs différents avec des réactifs de fabrications différentes.

L'écart-type moyen calculé est de $\pm$ 5,6% pour le Zinc

$\pm$ 7 % pour le Plomb

REMARQUES

Les acides nitrique et chlorhydrique doivent être d'excellente qualité. Les qualités "pur pour analyse" doivent être redistillées.

L'eau utilisée, pour la préparation des réactifs et pour les dosages, est de l'eau déminéralisée d'une résistivité movenne de 1 000 000 ohms/cm. Elle est obtenue avec un appareil très simple à echange d'ions, d'un débit moyen de 10 litres/heure.

ORGANISATION DU TRAVAIL

I — PERSONNEL

Les équipes du B.R.G.G.M. sont composées de 3 personnes:

— 1 chef d'équipe
— 1 aide de terrain
— 1 ouvrier chimiste

D'autre part, 3 à 4 maœuvres, selon les besoins, sont engagés sur place. L'implantation du système d'échantillonnage est faite généralment par le

chef de l'équipe, avec l'aide d'un ou de deux manoeuvres, de mêmé que l'échantillonnage.

L'aide de terrain, selon l'urgence, est utilisé soit à l'échantillonnage, soit au laboratoire; un ou deux manoeuvres s'occupent, sous la responsabilité du chimiste, de la préparation des échantillons (séchage, broyage, classement) et, dans certains cas, des pesées et des attaques.

Les résultats des analyses sont consignés au fur et à mesure de leur obtention sur des feuilles spéciales, et reportés, chaque soir, sur cartes ou fonds topographiques, ce qui permet de tracer les courbes d'isoteneurs. Le chef d'équipe a ainsi la possibilité de modifier, si besoin est, son programme de travail.

Les géochimistes et géologues responsables du Siège sont tenus, journellement, au courant des travaux par l'envoi des doubles des feuilles où sont consignés les résultats des analyses.

II — CADENCES DE TRAVAIL EN COURS DE MISSION

Les chiffres donnés ci-dessous ont trait à une prospection effectuée au mois de Mai 1955.

Depuis cette époque les cadences ont été sensiblement améliorées.

La zone à prospecter, lors de cette campagne, était accidentée et le passage de bois a obligé de procéder à un élagage important.

Le nombre total d'échantillons prélevés fut de 2071. La localisation et le repérage de ces échantillons furent assurés, soit par opérations topographiques (au théodolite, pour 1585 d'entre eux), soit à l'aide de photos aériennes (pour les autres, soit 486, prélevés lors de tests préliminaires) ; étant donné l'expérience acquise, cette prospection, si elle était à faire actuellement, ne nécessiterait pas un aussi grand nombre de tests.

Soit un total d'échantillons prélevés de: 2071

Tous ces échantillons ont été préparés aux fins d'analyse; ils ont tous été analysés en Plomb, et un certain nombre seulement en Zinc:

— détermination en Plomb	2071
— détermination en Zinc	1059
soit un total de déterminations de	3130

Opérations de terrain

La topographie (y compris l'elegage) a permis de localiser les 1585 points de prélèvements en 47 journées ½ de travail,

soit à une cadence de ..... *34 points/homme-jour*

45 journées de travail ont été nécessaires pour effectuer les 2071 prélèvements

soit à une cadence de ..... *46 échantillons/homme-jour*

En regroupant ces deux opérations, on obtient la cadence des opérations qui précèdent l'arrivée, au laboratoire, des

échantillons, soit ..... *20 échantillons/homme-jour*

Opérations de laboratoire

2071 échantillons ont été préparés en 37 journées de travail

soit ..... *56 échantillons/homme-jour*

3130 déterminations en Plomb et Zinc ont demandé 46 journées de travail

soit ..... 68 déterminations/homme-jour

Le regroupement de deux cadences précédentes conduit à celle des opérations de laboratoire intermédiaires entre l'arrivée au laboratoire des échantillons et l'obtention du résultat brut.

1) Cas d'une *simple* détermination:

on obtient ..... 31 déterminations/homme-jour

2) Cas d'une *double* détermination:

on obtient ..... *21 échantillons/homme-jour*

ou ..... 42 détermination/homme-jour

Cadence moyenne

1) pour les échantillons analysés en *simple* détermination:

terrain ..... *20 échantillons/homme-jour*

laboratoire ..... 31 déterminations/homme-jour

soit une cadence globale de ..... *12 échantillons-/homme-jour*

2) pour les échantillons analysés en *double* déterminations:

terrain ..... *20 échantillons/homme-jour*

laboratoire ..... *21 échantillons/homme-jour*

soit une cadence globale de ..... *10 échantillons/homme-jour*

ou ..... 20 déterminations/homme-jour

Pour cette prospection, les cadences globales de travail étaient donc de soit 12, soit de 20 déterminations par homme-jour selon que l'on recherchait le Plomb seul, ou le Plomb et le Zinc.

III — EQUIPMENT ET MATERIEL

Equipment automobile

L'équipe du B.R.G.G.M. qui travaille sur des problèmes de Plomb et de Zinc dispose:

1 — d'une camionnette 850 kg aménagée en atelier de préparation des échantillons. Deux paillasses offrent une surface suffisante pour le broyage et le classement des échantillons. 9 tiroirs permettent le rangement du matériel nécessaire (boîtes, mortiers, tamis).
Un réservoir, au toit du véhicule, assure une distribution d'eau.

2 — d'une remorque aménagée en laboratoire. Deux paillasses assurent une surface de travail suffisante, un certain nombre de tiroirs permettent le rangement des produits chimiques et verrerie nécessaires. Au toit du véhicule un réservoir de 150 litres assure la distribution d'eau.

3 — d'un véhicule de servitude, fourgonnette Citroën 2 CV, permettant le transport du personnel sur le terrain, le ramassage des échantillons etc....

Camionnette-atelier et remorque-laboratoire sont équipées d'une installation électrique permettant de se brancher sur les lignes de l'Electricité de France. Cette installation permet de disposer de 50 ampères sous 220 volts.

Matériel utilisé par cette équipe

a) *Echantillonnage:* — un omnimètre et son pied,
— deux boussoles avec système de visée,
— deux chaînes d'arpenteur,
— cinquante jalons,
— cinq bêches pliantes,
— deux pics,
— une tarière,
— 2000 boîtes en plastique (9 x 6 x 5 cm),
— trois caisses métalliques légères, permettant chacune le transport de 60 boîtes d'échantillons entre le lieu de prélèvement et le laboratoire.

b) *Préparation des échantillons:* — une étuve électrique d'une puissance de 3 KW, munie d'un ventilateur débitant 400 m3/heure, contenant 150 échantillons et permettant leur séchage en quelques heures.
— 4 mortiers et pilons de porcelaine.
— 4 tamis (80 mesh, en nylon) avec fond et couvercle,
— 3 spatules de nickel
— 1 balance de diamantaire (portée maximum 20 g. sensible au milligramme).

c) *Laboratoire:* — 1 appareil à déminéraliser, branché sur la canalisation de sortie du réservoir,
— 1 bain-marie (au gaz butane) en acier inoxydable,
— 6 portoirs de tubes à attaques (chaque portoir comporte 4 rangées

de 8 tubes). Le bain-marie peut contenir deux de ces portoirs. Ils sont en acier inoxydable.
— 200 tubes à attaque en pyrex 24 x 280, avec trait de jauge circulaire à 50 cc.,
— 200 tubes colorimétriques 18 x 180 en pyrex,
— 20 porte-tubes en aluminium contenant chacun 8 tubes colorimétriques,
— 1 porte-tubes colorimétriques avec échelle de lecture,
— 10 burettes 50 cc. au 1/10e,
— 6 microburettes 5 cc. au 1/50e,
— 2 pipettes de 1 cc. au 1/10e,
— 6 pipettes de 1 cc. à écoulement total,
— 6 pipettes de 5 cc. à écoulement total,
— 2 porte-pipettes muraux,
— 2 bonbonnes de polythène de 30 litres.
— divers bouchons de polythène de différents diamètres.
— 1 agitateur mécanique.

d) *Consommation:* Il faut compter *pour 100 déterminations de Zinc:*

1,5 kg de tétrachlorure de carbone
1 litre de réactif, c'est-à-dire
— 275 g. d'acétate de sodium
— 60 g. d'hyposulfite de sodium
— 4 g. de chlorhydrate d'hydroxylamine

pour 100 déterminations de Plomb:

1,5 kg de chloroforme
1 litre de réactif, c'est-à-dire
— 275 g. de citrate trisodique
— 16 g. de cholorhydrate d'hydroxylamine
— 18 g. de cyanure de potassium

De plus, il faut compter *pour* 100*attaquess*
— 100 cc d' acide clorhydrique concentré
— 100 cc d'acid nitrique concentré.

e) *Coût total de l'équipement:* Le montant des dépenses occasionnées par l'achat des véhicules utilisés par l'équipe de terrain du B.R.G.G.M. ainsi que par leur aménagement revien à 2 500 000 Fr. environ.

Le matériel nécessaire, tant pour la partie échantillonnage, que pour la partie chimie, représente une dépense de 300 000 Fr.

Soit une dépense totale de 2 800 000 Fr.

IV — PRIX DE REVIENT

L'étude du coût des différentes opérations de terrain de la prospection, dont il a déjà été mention, a conduit aux évaluations suivantes:

Localisation d'un point de prélèvement:

coût approximatif	107 Fr.
Prélèvement	89 Fr.
Préparation d'un échantillon	66 Fr.
Détermination d'un élément	101 Fr.
Soit pour l'analyse d'un échantillon comportant une détermination	*360 Fr environ*
Pour l'analyse d'un échantillon comportant deux déterminations	*460 Fr environ*

Ces prix de revient ne tiennent compte que des dépenses directes de prospection.

Il conviendrait d'y ajouter les dépenses du travail d'organisation: tirages de plans voyages, examents des résultats, rapport final, pour obtenir le prix de revient prospection.

La décomposition du prix de revient de cette prospection a montré l'énorme importance des salaires par rapport aux autres postes de dépenses:

Salaires (charges comprises)	68,6% (	
(frais de mission)	16,6%)	85,2%
Produits consommables	7 %	
Transports	4,2%	
Matériel (amortissement)	3,6%	

RAPID FIELD METHODS FOR THE COLORIMETRIC DETERMINATION OF NICKEL IN GEOCHEMICAL PROSPECTING

H. BLOOM *

ABSTRACT

Dimethylglyoxime reacts with nickel in a buffered ammoniacal-citrate solution containing the detergent "Aquet" and hydroxylamine-hydrochloride. The resulting nickelous dimethylglyoxime in extracted with xylene. Visual comparison to standards permits the estimation of from 50 to 10,000 ppm of nickel. Soil, rock, or sediment may be decomposed by digestion with (1+3) nitric acid. This method permits about 70 determinations per man-day.

With minor modifications to the above procedure, sediment and soil may be semi-quantitatively analyzed for nickel at the sample site. The chemical equipment is easily portable and the analysis extremely rapid because the buffer, dimethylglyoxime and xylene are added simultaneously to the sample and no heating is required. The sensitivity varies with the "availability" of the nickel ions; under favorable conditions, one may obtain a positive test for as little as 10 micrograms in soils and sediments. This procedure is similar to one for the field determination of heavy metals described elsewhere by the author.

INTRODUCTION

Much of the recent progress in geochemical propecting may be attributed to the development of simple and rapid analytical techniques known as "field tests". Colorimetric methods of analysis for traces of metals have been found satisfactory and are the basis of many of the methods that have appeared in the literature. A sensitive organic reagent reacting with a specific metal, yields a colored solution whose intensity is a measure of the metal content. A colorimetric method of analysis for nickel would be desirable in geochemical prospecting.

Of the two important methods that have been published for the rapid determination of nickel, neither is colorimetric.

Stevens and Lakin (1949) designed a chromograph from which they obtain "total" nickel as a confined spot on filter paper. The intensity of the spot is

* *Colorado School of Mines, Golden, Colorado.*

proportional to the amount of metal present. The chromograph is of special design, and is neither inexpensive nor easily obtained. Many units are required for the rapid production of even small numbers of samples. Almond (1955) found that the equipment is difficult to keep in good working order under field conditions.

Hunt, North and Wells (1955) use paper chromatography to obtain "total" nickel values as follows: After the sample is decomposed, an aliquot is applied to one end of a filter-paper strip through which an organic solvent mixture diffuses. The amount of metal present is then determined by spraying the strip with a suitable reagent and measuring the band of color that results. This method is quite new and shows much promise. Early attempts to use the technique in the field (private communication) suggests that it is difficult to control the rate of evaporation of the aliquot and organic solvent since they are dependent upon the relative humidity of the atmosphere. Neither of these tests easily lend themselves for the determination of the "available" metal content of a sample in the field.

Lovering, Sokoloff and Morris (1948), Debnam (1954) and more recently Bloom (1955) and Hawkes and Bloom (1955, 1956), have shown how the available metal content of rock, soil and sediment may be related to abnormal metallization. Cold solutions of acetate, dilute hydrochloric acid, or citrate are used to bring the metal into solution.

Presented here, are two field procedures: one to measure "total" nickel in soil, rock, and sediment, and the other to measure "available" nickel in soil and sediment. As used in this paper, the term "total" is defined as the amount of metal extracted from the sample by hot (1+3) nitric acid after digestion for 1 hour. "Available" metal refers to that metal which is extracted by ammonium citrate at ambient temperature.

The total nickel field method has the following features: (1) equipment is inexpensive and readily available from chemical supply houses; (2) more than 70 determinations per man day may be carried out; (3) the wide range of standards allows from 50 to 10,000 ppm to be determined. Higher values may be obtained by making appropriate dilutions.

The available nickel method is easily portable, making immediate semi-quantitative determinations at the sample site possible. Nonbreakable polyethylene wash bottles are suitable containers for these solutions and are easily carred in a kit or vest. A sample is placed in a calibrated cultura tube, appropriate amounts of reagents are added by squeezing the polyethylene reagent bottles, the tube is vigorously shaken and the intensities of the resulting colors estimated. About two minutes are required for a determination. The method is particularly suited for the analysis of stream sediments.

These methods closely follow procedures already described by the author for the determination of "total" copper, lead and zinc (Bloom, H. and H. E. Crowe, 1953) and "available" heavy metals (Bloom, H., 1955). With minor modifications, the nickel methods can be made a part of these schemes of analysis.

ACKNOWLEDGEMENTS

The cooperation of the Geochemicl Exploration Branch of the U. S. Geological Survey is gratefully acknowledged, particularly that of F. C. Canney who offered valuable suggestions in the preparation of this paper. Financial assistance for this work was provided in part by the Selco Exploration Co. Ltd., of Toronto, Canada.

EXPERIMENTAL

Nickelous dimethyglyoxime may be extracted from a slightly basic solution into 1 ml of xylene, where it forms a yellow color. When more than 6 micrograms of nickel are present, a pink precipitate forms and collects at the aqueous-organic interface, from which position it is difficult to estimate the amount present. It was found that the amount of precipitate can be easily judged if it is dispersed in the xylene by shaking with butyl phenoxy polyoxyethylene ethanol (sold commercially under the trade name "Aquet"). More than 15 micrograms of the nickel precipitate can be kept in suspension this way. Colors are obtained that vary from faint yellow through orange to bright pink, reflecting increasing amounts of nickel. The precipitate settles out after about one-half hour but is easily restored by gentle agitation for a second or two.

More than 500 micrograms of either copper or cobalt do not interfere. When 200 micrograms of each metal plus 12 micrograms of nickel were extracted together, an intense yellow color, foreign to the standards, resulted. When about 25 mg of hydroxylamine-hydrochloride were added to the buffer solution, and a repeat extraction made, approximately 12 micrograms were recovered. This is shown in Table 1.

As much as 1,000 micrograms of ferrous iron forms a deep pink color in the aqueous layer, but does not extract into the xylene. Chromium has been reported to interfere when in appreciable amounts, but manganese in its reduced form does not (Sandall, 1950).

In the section on the preparation of buffer solutions, it will be found that the hydroxylamine-hydrochloride is omitted from Buffer Solution "B", but is added later on in the analysis as a crystal. This is done to ensure reliable yellow colors in the low range of 1 to 6 micrograms. Hydroxylamine-hydro-

chloride is added directly to Buffer Solution "A" for two reasons: (1) to keep the number of operations in the field method to a minimum; (2) to prevent the interference of copper and cobalt. It should be noted that hydroxylamine-hydrochloride slowly loses its effectiveness as a reducing agent when once it is added to the buffer solution. No study has been made to determine the period of its effectiveness.

TABLE 1

EFFECT OF COBALT AND COPPER UPON NICKEL DETERMINATION

Nickel Added micrograms	Cobalt Added micrograms	Copper Added micrograms	Nickel Found micrograms
* 7	500	—	8
* 7	—	500	9
* 0	200	200	0
12	200	200	intense yellow
*12	200	200	12
*12	300	300	10

* 25 mg of hydroxylamine-hydrochloride added.

It is sometimes difficult to visually estimate the intensity of yellow colors under field conditions and for this reason orange, (which is equivalent to about 10 micrograms of nickel,) or pink colors are used in the available nickel procedure. A further advantage in the use of these colors is that neither copper nor cobalt forms a pink precipitate, so their interference tends to be minimized. The use of these colors also provides a simple means for estimating semi-quantitatively the amount of nickel; it can be shown that the volume of xylene required to discharge the orange or pink colors is proportional to the amount of nickel that is present as the precipitate. The nickel present may then be converted to "parts per million" in the manner described under "Available Nickel Procedure".

The detergent action of the Aquet causes many soils and sediments rich in organic matter to form a thick emulsion after shaking, which prevents the xylene layer from readily separating. A rapid partition can be affected, however, by holding the tube in a horizontal position and revolving it slowly for about 1 minute.

REAGENTS AND APPARATUS

Standard Nickel Solution, 0.01 percent. Dissolve 0.0448 g of $NiSO_4.6H_2O$ in water and dilute to 100 ml with water. One ml contains 100 micrograms of nickel. Make dilutions of 10 micrograms per ml from this solution.

Water—All references to "water" refer to metal-free water usually obtained by passing it through a resin demineralizer.

Dimethylglyoxine—1 percent. Dissolve 1 g dimethylgyoxime in 10 ml of ethyl alcohol.

Aquet—50 percent solution in water. Add 1 part of Aquet to 1 part water and mix. (Aquet is a 25 percent solution of non-ionic butyl phenoxy polyoxyethylene ethanol and is sold a detergent by the Emil Greiner Co., 20 N. Moore St., New York 13, N. Y.)

Thymol Blue—0.04 percent solution.

Hydroxylamine-hydrochloride— Grind coarse crystals down to about minus 2 mm to obtain rapid solution.

Nitric Acid (1+3)—Mix 25 ml of concentrated nitric acid with 75 ml water.

Xylene—ACA GRADE.

Buffer Solution A (for use with available nickel test). Dissolve 25 f of ammonium citrate, 4 g hydroxylamine-hydrochloride in about 300 ml of water and add 5 ml of thymol blue. Add concentrated ammonium hydroxyde until a strong blue color is obtained (pH8.5). Remove heavy metals by extracting with 15 ml portions of 0.01 percent dithizone in carbon tetrachloride, until dithizone is purple. Remove dithizone with several washings of chloroform until the latter is colorless. Dilute to 500 ml with water and add 3 mls of Aquet and mix. If resulting solution is not blue, add more ammonium hydroxide. (It may be unnecessary to clean the buffer if reagents are nickel free and not too high in copper and cobalt. This may be determined by running a blank).

Buffer Solution B (for use with total nickel test). Proceed as with the preparation of Buffer Solution A, above, but omit the addition of hydroxylamine-hydrochloride.

2 100 ml volumetric flasks, glass stoppered.

50 culture tubes, borosilicate, 18 x 150 mm.
Calibrate at 10 ml volume.

10 Culture tubes borosilicate 18 x 150 (for use with available nickel test).
Calibrate as follows: Mark 5½ ml volume with a zero. Graduate rest of tube at 2 ml intervals; marks at 2, 4, 6, ... 14.

4 test-tube racks to hold about 20 tubes each.

2 dropping bottles, 125 ml capacity, stoppered.

6 polyethylene wash bottles, 8 oz. capacity.

2 pipettes 1 ml capacity, 0.1 ml graduations.

2 pipettes 10 ml capicity, 0.5 ml graduations.

50 corks to fit culture tubes (polyethylene stoppers are available from the Kimbell Glass Co., Toledo 1, Ohio, catalgue No. 60975, size 3).

TOTAL NICKEL PROCEDURE

Weight 0.2 g sample, minus 80 mesh fraction, into a culture tube, and add 3 ml (1+3) nitric acid. Digest sample for about 1 hour at low heat on a hot plate. If this volume approaches dryness, add water. Dilute with water to 10 ml mark and mix. Transfer a 2 ml aliquot to a tube containing 5 ml Buffer Solution "B". Scoop about 25 mg of hydroxylamine-hydrochloride into tube, add ½ ml dimethylglyoxime solution and mix. Solution should be blue; if not, add dilute ammonium hydroxide until blue. Add 1 ml xylene and shake vigorously for about 20 seconds. Let phases separate for 5 minutes and read colors. Compare with standards. If nickel content of aliquot used is greater than the end standard, repeat using a smaller aliquot.

Preparation of Standards: To eight tubes, add 0, 2, 4, 6, 9, 12, 15 and 20 micrograms of nickel, respectively. Add 5 ml of Buffer Solution "B". Scoop 25 mg of hydroxylamine-hydrochloride into the tube, add ½ ml dimethylglyoxime solution and mix. Add 1 ml xylene shake vigorously for 20 seconds. Let phases separate for 5 minutes and use. These standards are usually good 48 hours. As the precipitate settles out after about ½ hour, shake tube gently from side to side for a second or two before using.

Calculate parts per million as follows: Micrograms in standard

$$\times \frac{10}{\text{ml aliquot}} \times 5 = \text{parts per million.}$$

AVAILABLE NICKEL PROCEDURE

Scoop about 0.5 or 1 g of minus 80 mesh sample into a calibrated tube. Add ½ ml dimethyglyoxime solution and then add Buffer Solution "A" up to the zero mark. Add 1 ml xylene and shake vigorously for about 20 seconds. Revolve the tube for about 1 minute in a horizontal position. Hold upright and look for orange or pink colors in the upper layer. If 0.5 g sample does not yield orange color, try 1 g sample.

Semi-quantitative estimations are made as follows: Add 1 or 2 ml increments of xylene and shake vigorously for about 3 seconds between additions and continue until the orange or pink color is discharged. Record the volume of xylene used. This volume may then be converted to parts per million of nickel as follows:

Multiply "ml of xylene" by 7 if 0.5 g sample is used, of by 3.5 if 1 g sample is used.

FIELD TRIALS

Soil Results: Field trials of both methods were made on samples collected during April and May, 1956, at a nickel deposit near Gold Hill in Boulder County, Colorado, known as the Copper King Mine. The following is taken from Goddard and Lovering's report on this mine (Goddard and Lovering, 1942): discovered in 1930, development in following years has exposed some 25,000 tons of ore containing 2 to 3 percent nickel. The ore occurs in the coarser-grained and more calcic layers of the amphibolite. Phyrrhotite, pyrite, chalcopyrite and several nickel minerals are irregularly disseminated through or form a network replace various minerals of the amphibolite. Among the nickel minerals present are niccolite (NiAs), pentlandite (NiFe)S and millerite (NiS). The ore is completely oxidized to a depth of 15-20 feet below the surface, and partial oxidation extends to a depth of about 50 feet.

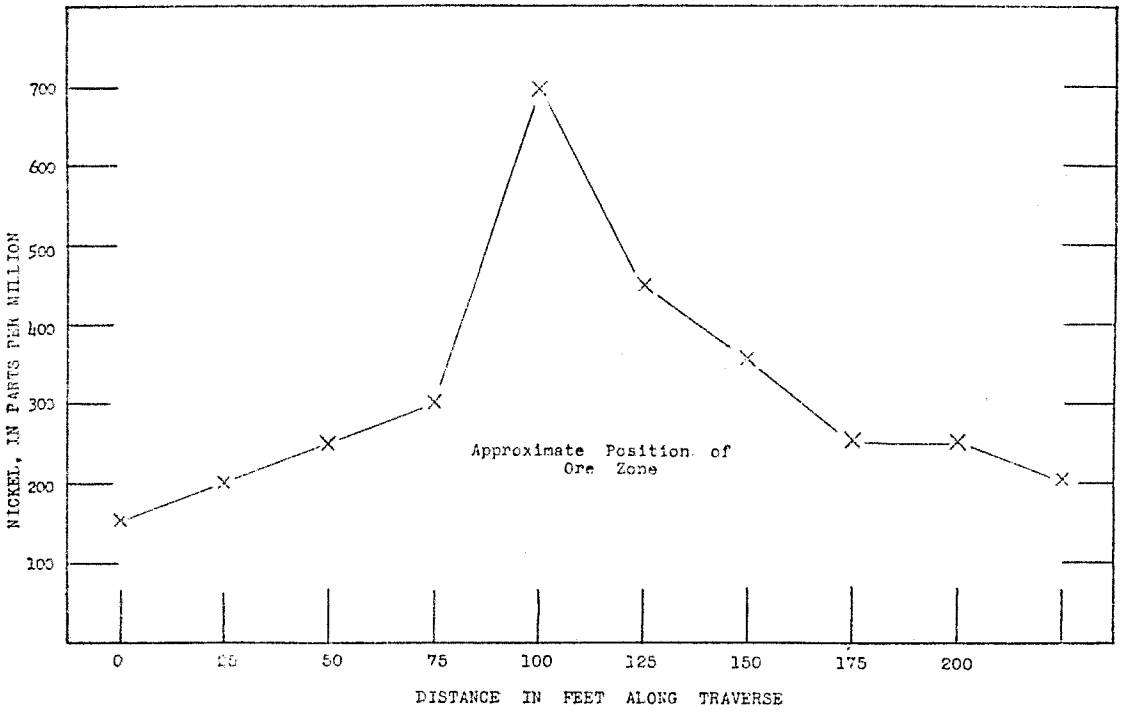


Fig. 1. Total nickel in soils over nickeliferous amphibolite zone at Copper King Mine, Gold Hill, Colorado.

The soil mantle in the mine area is composed of angular fragments of bedrock in a matrix of sand, silt and clay covered by a thin layer of humus and pine needles. Because there has been little development of the genetic horizons, the soils can be classified as a thin stony lithosol. The topography is steep, falling off about 1,000 feet in 1½ miles.

A traverse across a nickeliferous amphibolite zone is plotted in Figure 1. Soil samples were collected 6 inches below the land surface, sieved to minus 80 mesh and analysed by the total nickel procedure. The total nickel content of these samples very clearly indicates the approximate position of the ore zone. The same samples, when analysed by the available nickel method, failed to reveal a well-defined anomaly. These inconclusive results are probably due to the lack of good soil development at this depth. They would be expected if the nickel sampled occurred in a form such as garnierite, which would be little affected by the cold ammoniacal-citrate solution. The garnierite listed in Table 3 for example, was negative. Further work in areas providing better soil development will have to be carried out before the cold extraction technique may be fully assessed.

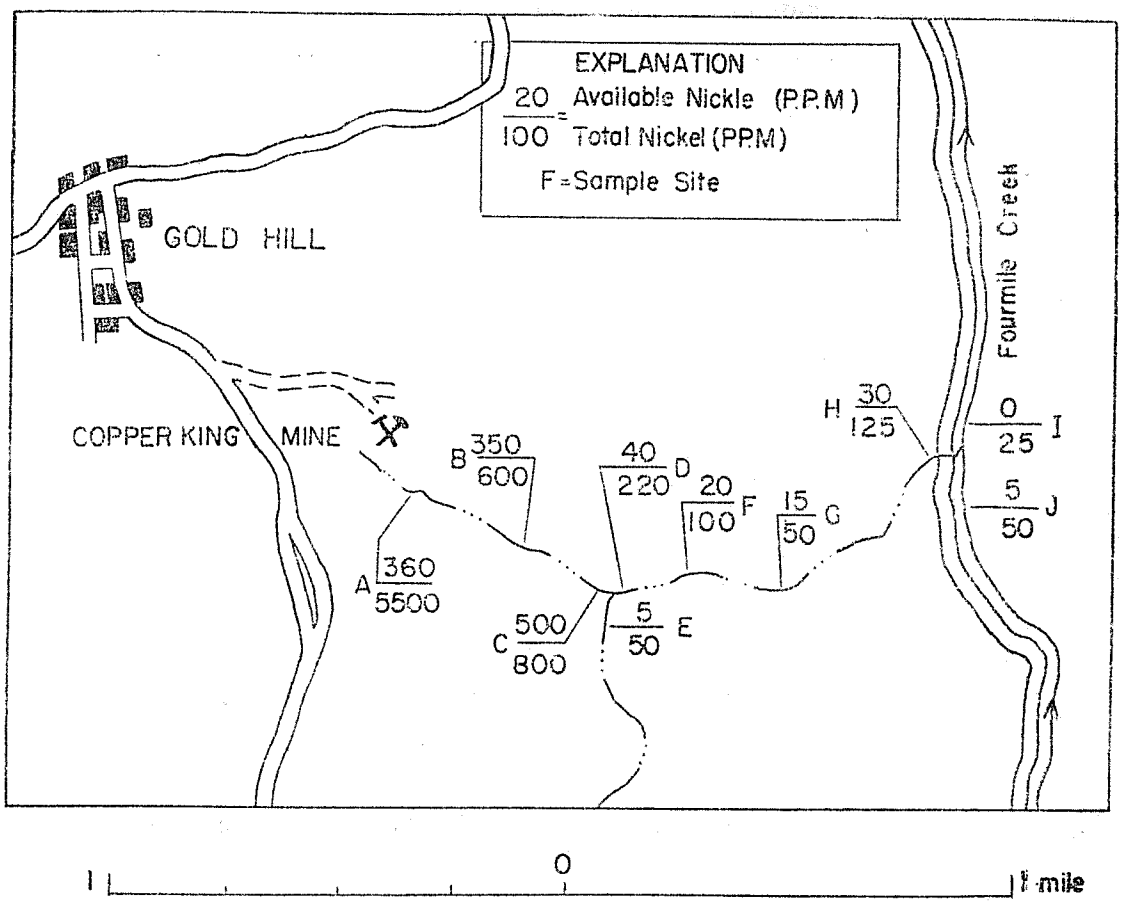


Fig. 2. Plan showing ratio of available nickel to total nickel in sediment from stream draining the Copper King Mine area, Gold Hill, Colorado.

A set of soil samples were obtained from another laboratory to compare their nickel values obtained by the chromograph with those by the total nickel procedure. This comparison is shown in Table 2. These samples originated from

the Copper King Mine, but their exact location or details of collection are not known. Yet, it was interesting to note that significant available nickel which is listed in colum 6 was obtained from most of these samples. It may be that these samples were collected from a shallower depth where the soil-forming processes, presumably acting with greater intensity, have broken down some of the oxidized nickel minerals to a more available form.

Sediment Results: Even though the drainage from the Copper King Mine is contaminated with much nickel, a study of the stream sediment can serve to further illustrate the applicability of the two colorimetric methods. The ratios of available to total metal of samples taken along the streams are shown in Figure 2. These samples consist of fine-grained sand and silt and were collected from the activite stream channel. Sample Site A, which is about 200 feet from the adit is high in total nickel. Deposition of the metal here could be explained by several mechanisms, all of which may play a part: 1) When the pH of the mine water rises above 6.7, nickel will begin to precipitate. 2) Precipitation of iron would carry down ionic nickel with it. 3) Because this sample site is close to the adit, minute particles of sulfides would settle out here. A sharp reduction of detrital sulfides is indicated at Sample Sites B and C as the available to total nickel ratio is less than 1:2. The stream bed at Sample Site C was dry at the time of sampling, and it is quite possible that if waters were being tested instead of sediments, the metal train could have been lost at this important junction.

TABLE 2

COMPARISON OF NICKEL VALUES IN SOIL FROM THE COPPER KING MINE, GOLD HILL, COLORADO

Sample No.	Chromograph PPM Nickel (1)	Replicate Analyses Total Nickel PPM (2)	(3)	(4)	Average Total Nickel PPM (5)	Available Nickel PPM (6)
1	200	200	200	200	200	0
2	200	400	300	400	370	6
3	300	500	600	600	570	10
4	900	1100	1400	1400	1300	30
5	1200	900	1100	1800	1270	9
6	900	700	600	—	650	7
7	400	400	400	—	400	0

The dilution effect of the side stream is evident from the values at Sample Sit D, F and G. Station H shows an increase in values that is probably due to a higher percentage of the minus 200 mesh size fraction present in the sieved

minus 80 mesh sample. Hawkes and Bloom (1956) report that variations in sediment sizes have a pronounced effect upon available metal values, and that more metal is carried in the finer fractions. The nickel train, 1.5 miles long, is no longer detectable below the confluence with the Fourmile Creek. The values at Stations I and J are essentially the same, approximating background.

Rock Results: In Table 3 results of total metal analysis of a serpentine, garnierite and five other rocks of unknown origin, are shown. The values in column (1) were provided by outside laboratories. These samples were given a preliminary treatment of hydrofluoric acid, colum (2), to release any nickel enclosed in the silicate lattice. Columns (3) and (4) show duplicate determinations of nickel using (1 + 3) nitric acid digestion. The favorable agreement of these duplicates, permits a reliable comparison with column (2) and helps determine whether nickel was withheld as a silicate. The serpentine yielded about 33% more nickel and Sample 903 showed a 36% increase. The differences shown by the other samples are probably due to the experimental error inherent in the analysis. Precision at these high ranges depends largely on good dilution techniques, and except for the garnierite, no special dilutions were made in obtaining these results, although the sample size was reduced to o.l g.

TABLE 3

COMPARISON OF TOTAL NICKEL CONTENT OF ROCK FROM UNKNOWN AREAS

Sample No.	Reported Values	$HF - HNO_3$	Duplicate HNO_3	HNO_3
	Percent Nickel (1)	Percent Nickel (2)	Percent Ni (3)	Percent Ni (4)
Serpentine	0.26	0.24	0.16	0.16
Garnierite	—	2.4	2.4	2.6
900	0.977	0.9	0.6	0.7
901	1.180	1.0	0.9	1.0
903	1.725	1.5	1.0	0.9
131	0.62	—	0.5	0.4
961	1.51	—	1.2	1.4

CONCLUSIONS

Two colorimetric field methods for the determination of nickel are presented for use in geochemical prospecting. These methods are rapid, inexpensive and simple to operate. As little as 50 ppm of total nickel can be obtained from

soil, rock or sediment, after digestion with hot nitric acid. The available nickel content may be semi-quantitatively determined from sediments and probably soils, at the sample site, after extraction with ammoniacal citrate solution at ambient temperature. Further work on soils from other nickel areas is necessary, however, before this approach may be fully assessed.

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A FIELD TEST FOR SELENIUM *

H. W. LAKIN * *

ABSTRACT

A small, simple, one-piece still has been devised for use in a rapid field determination for selenium. One fram of material is placed in the still followed by 2 ml of concentrated sulfuric acid and 5 ml of hydrobromic acid and bromine. A plug of glass wool is inserted to prevent any portion of the sample being mechanically carried over into the distillate. The still is placed on a simple rack and heated with an alcohol lamp. Three to 4 ml are distilled into a 15-ml Erlenmeyer flask and small crystals of sodium sulfite and hydroxylamine hydrochloride are added to the hot distillate. A pink precipitate develops immediately for samples containing as little as 50 ppm. On standing overnight as little as 10 ppm in the sample is revealed. The amount present can be estimated to within —50 to +100 percent of the actual value by comparison with standards.

INTRODUCTION

Selenium cannot be visually recognized in minerals in which it is usually concentrated; therefore a simple field test for selenium is a very desirable tool for the prospector and geologist who are evaluating prospects or mines. On the Colorado Plateau, selenium may be present in sulfides, especially in the pyrite and galena associated with uranium ores or adjacent to these ores (Coleman, 1956). Oxidation of the sulfides results in a red elemental selenium halo about the ore. The selenium content of the sulfide ores and the elemental selenium halos may be as high as 2 to 2.5 percent.

Many efforts have been made to determine selenium quantitatively in soils and rocks, and none of them have been wholly satisfactory. Gooch and Peirce (1896) observed that selenium can be separated from tellurium by distillation as selenium tetrabromide. Noyes and Bray (1927) used this property in their systematic qualitative analysis of the rarer elements. Robinson and co-workers (1934) developed methods for the determination of selenium in pyrite, soils, and plant material, using the distillation of selenium tetrabromide.

* *Publication authorized by the Director, U. S. Geological Survey.*

* * *U. S. Geological Survey.*

In Robinson's method the selenium tetrabromide is distilled from a constant-boiling solution of hydrobromic acid and may be accompanied by arsenic, some germanium, tin, and antimony. The distillate, diluted with water to 4 N acid, is treated with sulfur dioxide, hydroxylamine hydrochloride, or sodium sulfite to reduce the selenium to the element, thus giving a specific test for selenium. With dilute solutions of selenium, the colloidal precipitate of elemental selenium obtained by the action of a reducing agent is a light pink to orange-red. As the amount of selenium per milliliter of solution increases, the precipitated selenium becomes darker red, eventually taking on a purple tinge and ultimately changing to a dark red or black amorphous from which settles to the bottom of the beaker.

The proposed rapid field test for selenium differs from the well-established laboratory methods of analyses outlined above in two respects: first, the simplicity of the still designed for field use; second, the elimination of the transportation of liquid bromine by preparation of the reagent in the field through the use of the well-known reaction between sodium bromate and hydrobromic acid. The transportation of bromine is hazardous and has heretofore prevented the field distillation of selenium. With oxidized materials the practical range of the proposed rapid field test is 50 to 1000 ppm; the range can be extended downward to 10 ppm by allowing the precipitated selenium to stand overnight. A somewhat more tedious method is necessary for sulfide ores and materials containing organic matter, such as carbonaceous shales. The sensitivity for the sulfide ores and carbonaceous shales is approximately 50 ppm; the upper limit is determined by how small a sample one wishes to take.

APPARATUS AND REAGENTS

All reagents must be "reagent" grade.

Pipette, 1 ml graduated to 0.1 ml.
Large scoop. A lucite bar with a cavity of 1 ml drilled near one end.
Small scop. A lucite bar with a cavity of 0.2 ml drilled near one end.
Glass wool.
Alcohol lamp.
Selenium still (see Fig. 1)
Erlenmeyer flasks, 15-ml.
Beakers, 30-ml
Selenium still rack (see Fig. 2)
Metal dish, 8 cm in diameter and 4 cm high.

Hydrobromic acid-bromine reagent; in a 250-ml beaker dissolve 1.5 large scoops (1.5 grams) of sodium bromate in 10 ml of water. In one continuous operation rapidly pour 90 ml of concentrated hydrobromic acid (48 percent) into the bromate solution. The rapid addition of hydrobromic acid is necessary to provide sufficient volume to dissolve the bromine produced during the initial violent reaction and prevent its loss. Transfer to a glass-stoppered bottle and keep cool. The reagent contains approximately 1.5 percent bromine.

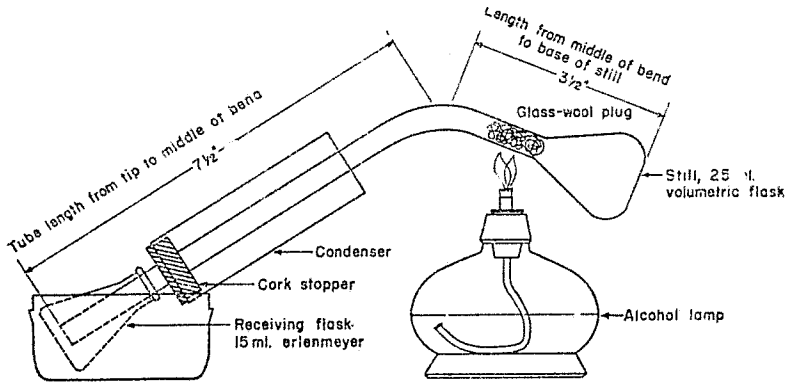

Fig. 1. Dimensional drawing of a field selenium still, showing position of still in use.

Nitric acid-mercuric nitrate reagent. Dissolve 1 large scoop (1.0 gram) of mercuric oxide in 100 ml of concentrated nitric acid.

Standard selenium solution (500 ppm.). Dissolve 500 mg of reagent grade selenium in 200 ml of the hydrobromic acid-bromine reagent. Warm on water bath to insure solution of the selenium and dilute to 500 ml with water.. The final solution must be colored red with an excess of bromine.

Sulfuric acid - Sp. Gr. 1.84.

Sodium sulfite.

Hydroxilamine hydrochloride.

Standard selenium series

Prepare a series of selenium standards as follows: Transfer 0.1, 0.2, 0.4, 0.8, and 2.0 ml of the selenium standard solution to each of five 15-ml Erlenmeyer flasks. Add 2 ml of hydrobromic acid-bromine reagent and dilute each standard to 6 ml water. Add an excess of sodium sulfite and warm each flask until the red color of the bromine disappears, then add a small scoop of hydroxylamine hydrochloride and set aside. Fresh standards must be prepared daily.

PROCEDURES FOR THE DETERMINATION OF SELENIUM

Procedure for oxidized materials

Add a large scoop of finely ground material (approximately 1 gm) to the dry still through the condenser tube and tap gently. Wash the condenser tube down with 1 ml of water, followed by 2 ml of sulfuric acid. If the material is limestone or contains large amounts of carbonate, add the sulfuric acid slowly, to allow the reaction to proceed without undue violence. Cool the contents of the still by immersing it in cold water. When cool, add 5 ml of hydrobromic acid-bromine reagent. Push a small plug of glass wool with a pliable plastic tube down the condenser about one inch past the bend in the condenser

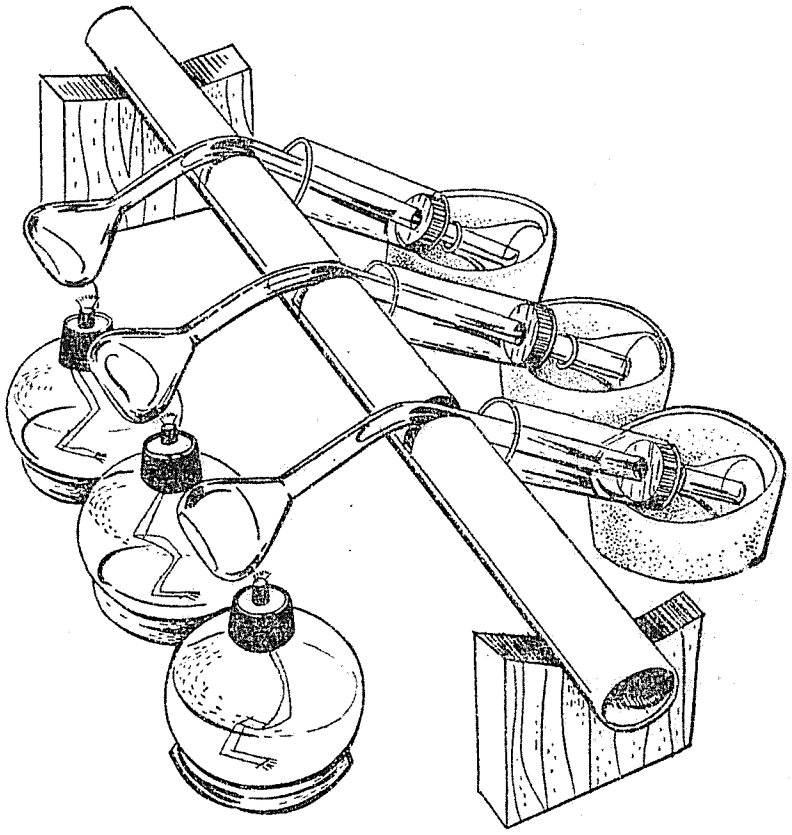

Fig. 2. Simple distillation rack supporting three stills.

so that the glass wool is well below the uppermost part of the still when the latter is placed in the distillation rack (see Fig. 2). Push the condenser tube through the cork in the condenser sleeve, place the still in the distillation rack and fill the condenser sleeve with cold water. Add about 10 drops of water to the receiving flask (15-ml Erlenmeyer flask), place the flask in a metal dish containing 50 ml of cold water and insert the condenser tip of the still in

the receiving flask until the condenser tip dips below the surface of the water. Light the alcohol lamp and place it under the still adjacent to the condenser so that the flame heats the glass wool plug and just touches the liquid. During this stage of heating, red fumes of bromine distill over and condense in the receiving flask. After a few moments, gradually push the flame under the liquid charge in the still to increase the heat and cause the hydrobromic acid to distill. The first small portion of the distilled hydrobromic acid contains the selenium. Further distillation guarantees that the selenium has been swept out of the still and condenser, and is in the receiving flask. When about 3- or 4-ml have distilled, extinguish the alcohol lamp and remove the receiving flask. Add water to the distillate to adjust the volume to 6 ml, the volume of the standards. Add sodium sulfite and heat the flask to destroy the excess bromine —which is indicated by the disappearance of the red color— and continue heating until the flask is distinctly warm. It is essential that an excess of sodium sulfite be present throughout this heating step. Add one small scoop of hydroxylamine hydrochloride and set the flask down adjacent to the standards for later comparisons. After 15 minutes, compare the sample solution with standard series and record the result.

Procedure for sulfides

Place a small scoop (approximately 0.2 gm) of the finely ground sample in a 30-ml beaker. Add 2 ml of nitric acid-mercuric nitrate reagent and heat the mixture over an alcohol lamp until the brown oxides of nitrogen are evolved copiously. Set aside until the reaction subsides and then heat again. Repeat this cycle until the evolution of oxides ceases. One can conveniently handle 5 to 10 samples by intermittently heating them. If the sample is largely sulfide it may be necessary to add one more milliliter of nitric acid-mercuric nitrate reagent to bring it into solution. When the sulfide appears to be in solution, usually in about 20 minutes, evaporate almost to dryness, then add 2 ml of sulfuric acid and heat to white fumes. Cool and transfer the sample solution to a still, wash down with 1 ml of water, cool again, and then add 5 ml of hydrobromic acid-bromine reagent, rinsing first the beaker and then the condenser with each reagent. Place the glass plug in the condenser and proceed with the distillation previously described.

Procedure for materials containing large quantities of organic matter.

For the determination of selenium in materials containing organic matter such as carbonaceous shales, the procedure is the same as that followed for sulfides. Howeyer, a gram sample can be used if the material is low in organic matter.

TABLE 1

COMPARISON OF SEMIQUANTITATIVE FIELD TEST FOR SELENIUM WITH RAPID LABORATORY METHOD

Sample no.	Location	Description	Rapid lab method (ppm)	Field test (ppm)
55-287	Cullowhee mine	Pyrrhotite, pyrite, chalcopyrite (magnetite?)	40	80
55-2818	Cleburn Co., Ala.	Pyrrhotite, pyrite, chalcopyrite	50	40
55-2831	Madera Co., Calif.	Unsorted specimens from the 200 level (estimated to be 90 percent chalcopyrite)	50	80
55-2461	Lucky Mc mine Fremont Co., Wyo.	Grab sample — pyritic, uraniferous sandstone from stockpile, 115 to 150 mesh	50	80
55-1271	Near Tordillo Hill, Karnes Co., Texas	Soil over sandstone of the Jackson Formation (Eocene) in shallow prospect pit	50	40
55-5503	Marding Co., S. Dakota	Carbonaceous mudstone and sandstone	50	40
55-5511	Harding Co., S. Dakota	Carbonaceous mudstone from bottom of bed	70	80
240056	Henry Mts., Utah	Mineralized sandstone	70	150
240086	Henry Mts, Utah	Mineralized sandstone	70	80
240105	Henry Mts., Utah	Mineralized sandstone	100	150
240112	Henry Mts., Utah	Mineralized sandstone	150	150
55-5503	Harding Co., S. Dakota	Carbonaceous mudstone and sandstone	150	150
D-67878	Jefferson Co., Colorado	Pulp and fines from a radioactive coal bed	200	150
55-5718	Lucky Mc mine Fremont Co., Wyo.	Composite selenium stockpile representing approximately 100 tons	250	300
240046	Henry Mts., Utah	Mineralized sandstone	400	500
240126	Henry Mts., Utah	Unmineralized sandstone	500	500
55-2822	Paulding Co, Georgia	Pyrrhotite and pyrite (also chalcopyrite)	1000	1000
D-67877	Jefferson Co., Colorado	Composite from a radioactive coal bed	5000	5000

RESULTS

The realibility of the field procedure was tested by comparing the results obtained on sulfides, sandstones, and carbonaceous shales with those obtained by more drastic treatment of the sample and a more careful measurement of selenium in a rapid laboratory method (Lovering, and others, 1956). The comparison is shown in table 1. The results from the proposed field test compare favorably with those obtained by the rapid laboratory method, especially in the range of 100 ppm or more. A single determination of selenium requires 15 minutes for oxidized material, and 40 minutes for sulfides or carbonaceous material. The procedure was found useful for reconnaissance evaluation of prospects and mines in Wyoming.

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A RAPID METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF TIN IN SOILS

G. A. Wood *

ABSTRACT

A rapid field procedure is described for the colorimetric determination of tin in soils by means of gallein after attacking the sample by heating it with ammonium iodide. About 30 determinations can be carried out in a normal working day and the method is well suited for geochemical prospecting purposes.

INTRODUCTION

The determination of small amounts of tin in soils is a matter of considerable difficulty for two main reasons: firstly, the fact that the tin is frequently present in the form of the refractory mineral, cassiterite, and secondly, the lack of a sensitive and specific colorimetric reagent for tin. The methods hitherto described in the literature for such determinations have all required prolonged fusions for attacking the sample and have involved lengthy separation procedures for the isolation of the tin, and are therefore unsuitable for the rapid analysis of large numbers of samples such as is required in geochemical prospecting.

The most common method of attack for tin-bearing minerals is by prolonged fusion with sodium hydroxide and/or peroxide. A mixture of sodium carbonate and sulphur has also been recommended (Sarudi, 1950). The latter has the advantage that the majority of heavy metals are precipitated as insoluble sulphides on leaching but suffers from the defect that the crucible is always severely attacked whether it is made of porcelain, silica, iron or nickel, and it can only be used for one determination. Neither of these procedures is well adapted, therefore, to a rapid routine method and an alternative was sought. It has been found by Caley and Burford (1936) that tin can be completely volatilised from precipitated and ignited stannic oxide by heating it at 450°C with an excess of ammonium iodide. This reaction was used by Chatterjee (1941) and by Besson (1952-1953), for the determination of tin in impure

* *Senior Analytical Research Fellow, Geochemical Prospecting Research Centre, Imperial College, London.*

stannic oxide precipitates obtained in metallurgical analysis, but very little work appears to have been carried out on the possibility of using it to break down tin-bearing minerals, although Harvey (1944) states, without giving any results or references, that such an attack when applied to low-grade ores may leave a residue requiring fusion for complete recovery of the tin.

Some experiments, described in the next section, have therefore been carried out and have shown that tin in the form of cassiterite is rapidly and completely volatilised by this treatment. The ammonium iodide attack has accordingly been adopted as the basis of the present method.

It was originally hoped to separate the tin by paper chromatography and estimate the metal concentration by visual comparison of the stain produced on the paper by a suitable spraying reagent, in a manner similar to that recommended for several other metals by North, Hunt and Wells (1955).

The $SnCl_6^{2-}$ ion is readily mobile in a number of solvents and can be separated relatively easily from most other elements by using ethyl acetate, dioxan or various alcohols as the basis of the solvent mixture. By spraying the chromatogram with a suitable lakeforming reagent such as purpurin, anthra-purpurin or gallein, excellent standard chromatograms were obtained from pure tin solutions.

When the solution obtained from ammonium iodide attack of a soil was used, however, difficulties were encountered due to the large amount of free iodine present in the solution. This moved in the solvent front, obscuring the chromatogram with a dark brown stain which trailed back a considerable distance down the paper. The iodine could be reduced with some difficulty by exposing the developed paper to an atmosphere of sulphur dioxide, but the tin bands were usually found to be diffuse and erratic in shape and were sometimes not observed at all. Reduction of the iodine in the solution before running the chromatogram proved to be ineffective as reoxidation always occurred during the run. This could not be prevented even by the addition of reducing agents to the solvent mixture or by running in an atmosphere of sulphur dioxide. The trouble could be minimised by reducing the solution, running the chromatogram in an atmosphere of sulphur dioxide and reducing again after development. Even then erratic results were obtained and only a small proportion of the chromatograms were satisfactory.

Attempts were also made to remove the iodine from the solution by volatilisation and by solvent extraction, but it was found impossible to do so without loss of tin.

No way of overcoming this difficulty has yet been found, and the chromatographic method has therefore been abandoned for the time being.

Attention was then turned to a direct colorimetric method. Colorimetric reagents for tin fall into three groups: (a) sulphur containing compounds such as toluene —3:4— dithiol, thiourea and dithizone, (b) substances which are reduced by stannous tin to give highly coloured compounds e.g. iodo-methylene blue, phosphomolybdic acid, cacotheline and (c) lake-forming dyes.

All these groups have disadvantages. The reagents of group (a) are rather insensitive. Toluene —3:4— dithiol has been used by many workers for the determination of quantities of tin in the range 20 - 100 μg (micrograms), but ten times this sensitivity is desirable for soil analysis. Also the reagent reacts with other metals of the hydrogen sulphide group and some separation procedure would be necessary. The group (b) reagents are sensitive but react with any strong reducing agent; they also necessitate the quantitative reduction of tin to the stannous state which is not easily achieved. P. Jeffery (pers. comm) has developed a method based on phosphomolybdic acid; this can give good results in the hands of a skilled operator, but is not so satisfactory for multiple routine determinations.

There remain the lake-forming reagents, which give highly sensitive reactions with stannic tin but are, for the most part, unselective. A study has been made of a large number of these reagents and the most satisfactory found to be gallein. Although this substances gives coloured lakes under suitable conditions with many metals, interference can be limited by pH control, and the reaction with several metals is suppressed in the presence of iodide.

It has been found possible to determine tin in soils by heating the sample with ammonium iodide, leaching with dilute acid an after reducing free iodine and adjusting the pH by addition of a suitable buffer, developing a colour by addition of gallein and comparing it with standards.

EXPERIMENTAL

Sample attack:

In order to determine whether the ammonium iodide treatment would attack cassiterite, a mineral sample known to contain 77.0% SnO_2 was ground to pass through an 80 mesh sieve and dried. 0.2346g was then mixed intimately with 1g of ammonium iodide and heated at 500°C until all the ammonium iodide had volatilised. The residue was evaporated with a few drops of nitric acid and ignited to reconvert the remaining material to oxide and weighed. The loss in weight was 66.6%. The treatment was repeated with another gram of ammonium iodide, and the loss in weight increased to 77.0%. Further treatment caused only a fractional percentage loss in weight, indicating that the tin was virtually completely volatilised by the double treatment.

The attack on tin-bearing soil samples was next investigated. The soil (0.25 or 0.5g.) was well mixed with 1g of ammonium iodide in a 10" x ½" Pyrex test-tube and heated to dull redness in a Bunsen flame until all the ammonium iodide had volatilised. A mixture of ammonium iodide and iodine was seen to sublime on the walls of the tube; no fumes escaped from the open end.

The ignited residue was examined spectrographically for tin. The sublimate was dissolved in 2N-hydrochloric acid and filtered. 10mg of "Specpure" ferric oxide dissolved in a little hydrochloric acid was then added as a carrier and precipitated with ammonium hydroxide. The precipitate was ignited and also examined spectro-graphically for tin. The results are shown in Table I below.

TABLE 1

Sn in sample (spectrographic)	Sn in residue	Sn in sublimate
6 ppm	Not detected	> 2 μg
40 „	„ „	(strong lines)
80 „	„ „	>10 μg

These results indicate that the tin was completely volatilised.

Colorimetric determination of tin:

Among the reagents examined were toluene —3:4— dithiol, thiourea, dithiozone and a number of lake forming reagents including purpurin, anthrapurpurin, quinalizarin, anthraquinone —1—azo—4—dimethylaniline, cerulein, thiogallein, hematoxylin, hematein and gallein. Most of these were unsatisfactory owing to either lack of sensitivity or selectivity, or to both. The last three showed the most promise and were studied in some detail; gallein was found to be the most satisfactory of the three.

The reagent is stable and sensitive and gives a pinkish colour with stannic ions which contrasts well with the pale yellow of the reagent. In the pH range 2-3, pH variation has little effect on the colour intensity. The optimum wavelength for absorptiometric determination is 520 mμ; at this wavelength the difference between the absorption of the reagent blank and that of the sample is at a maximum. Beer's law is obeyed up to a concentration of 0.5 μg Sn/ml; (Fig. 1) at higher concentrations there is a marked falling off in linearity as the colour of the complex tends to become purplish instead of pink. A calibration curve obtained with a Unicam model SP600 spectrophotometer at 520 mμ

is shown in Fig. 1. The solutions were held at a pH within the range 2.4-2.7 by means of a phthalate buffer.

The reagent is equally suitable for visual colorimetric determinations in the same range. A set of standards containing 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and

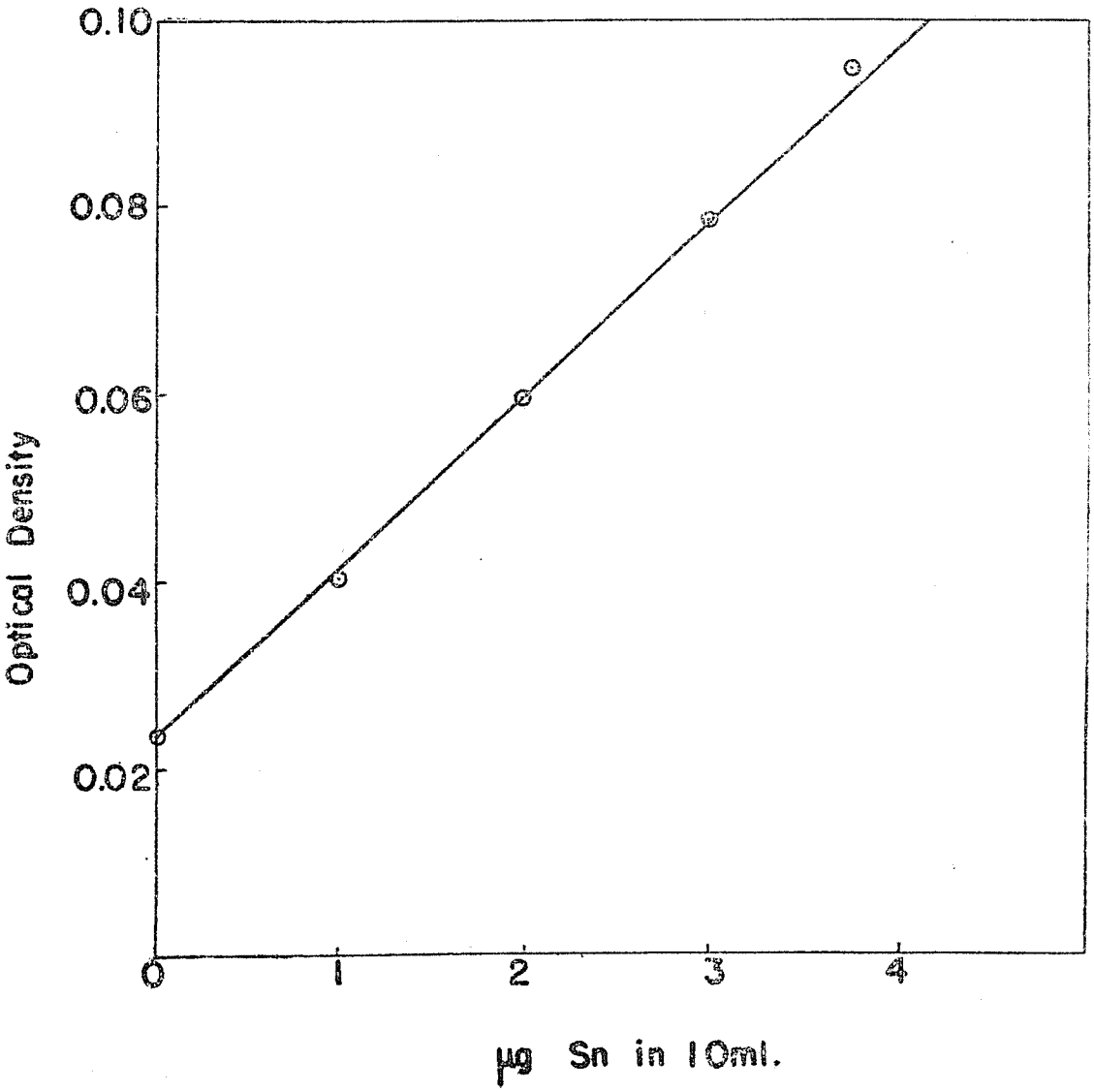

Fig. 1. Extinction of tin-gallein complex at 250 mμ.

5.0 μg of tin in 10 ml has been found to provide good discrimination between adjacent standards and easy comparisons.

Although the reagent is capable of giving coloured lakes with a great many metals, relatively few react below pH3, and of these, the reaction of several is

partially or completely suppressed in the presence of iodide. The table below indicates the reaction at pH 2.5 between gallein and the most important elements likely to be encountered in soil analysis.

TABLE 2

Interfering metal	Weight taken	Reaction and remarks
Cu^{2+}	10 mg.	Pink colour, totally suppressed by iodide.
Pb^{2+}	"	" " "
Zn^{2+}	"	No reaction.
Al^{3+}	100 mg.	" "
Cr^{3+}	10 mg.	" "
Fe^{2+}	100 mg.	" "
Fe^{3+}	—	Strong purple colour. See below.
Mn^{2+}	10 mg.	Purplish colour, totally suppressed by iodide.
Ti^{4+}	20 μg.	Purple colour; intensity reduced by iodide. See below.
As^{3+}	10 mg.	No reaction.
As^{5+}	"	" "
Sb^{3+}, Sb^{5+}	10 μg.	Pink colour; equivalent to 1 μg tin.
V	10 mg.	No reaction.
Mo, W	—	Purplish colours. See below.
Alkalis and alkaline earths	1 g.	No reaction.

The potentially interfering metals are, therefore antimony, ferric iron, titanium, molybenum and tungsten. The interference by antimony is unlikely to be serious as the reaction is not very sensitive and tin-bearing soils are not likely to have a high antimony content, Ferric iron should not be present in the solution, as it is reduced by iodide to the ferrous state. It was found, however, that at pH of 2.5 or over in the presence of gallein, it was impossible to maintain the iron completely reduced, and considerable difficulty was caused by this effect in the early stages of the work. The difficulty was overcome by maintain-

TABLE 3

APPARENT Sn PRESENT

Sn present	+5 μg Ti	+10 μg Ti	+20 μg Ti	+50 μg Ti	+5 μg Mo	+10 μg Mo	+5 μg W	+10 μg W
0	0	0.5	1?–discoloured		1.5?–discoloured		0	0.5
0.5	0.5	0.75	1– „		2.5?– „		0.5	0.75
1.0	1.0	1.25	1.5– „		3?– „		1.0	1.25
1.5	1.75	1.5	1.75	Unreadable	4?– „	Unreadable	1.5	1.75
	Rpt. 1.5							
2.0	2.0	2.0	2+	–purple	4?– „	–discoloured	2.0	2.5
3.0	3.0	3.0	3.0	Colours	5–slightly „	solutions	3.0	3.0
4.0	4.0	4.0	4.0		5		4.0	4.0
5.0	5.0	5.0	5.0		5		5.0	5.0

ing the pH between 2.0 and 2.5 and ensuring that at no stage was it allowed to rise above this value. No interference was then encountered, even by 100 mg of iron. The pH control was achieved by the use of a sodium chloroacetate-chloroacetic acid buffer (pH 2.4-2.5) which was added directly to the acid leach solution obtained from the ammonium iodide treatment.

In the cases of titanium, molybdenum and tungsten, attempts were made to suppress the interference by the addition of complexing agents such as fluoride, phosphate, arsenate, citrate and oxalate. It was found impossible to suppress the reactions of these elements without serious error in the tin determination. Sets of standards were, therefore, prepared with addition of varying amounts of the interfering elements and the apparent tin concentrations were read. The results are shown in Table III below.

Interference by tungsten is thus not likely to be serious, as at least a tenfold excess of tungsten over tin would be necessary to introduce serious error. In the case of titanium, a twentyfold excess could lead to results appearing about 50% too high while a tenfold excess would not lead to serious error. Serious interference by titanium would be noticed immediately, as the colours of the solution would be quite different from the standards and would be unreadable; spurious results could not, therefore, be obtained.

The most serious potential interference is that due to molybdenum, a concentration of the metal equal to that of the tin leading to high results. Again however, the solution would be discoloured, so that the interference would be immediately noticeable.

The figures quoted above all refer to concentrations in the final solutions. The interfering elements, even if present in the soil, are not necessarily extracted, however, by the ammonium iodide procedure. In fact, Caley and Burford (loc. cit.) state that titanium dioxide is not appreciably attacked by the treatment. The loss in weight of molybdic and tungstic oxides on heating with ammonium iodide has been determined in several experiments and found to vary between 2 and 2.5%. In another experiment 0.1g sample of the two oxides were heated with ammonium iodide and treated as for tin determination. The apparent tin concentrations found were 0.5 μg in the case of molybdenum and zero in the case of tungsten. In addition, a soil containing 1,000 ppm of molybdenum was analysed for tin by the procedure given in the next section; no tin was found, the colour of the final solution being the same as that of the blank. When equal weights of this soil and one containing 75 ppm of tin were mixed and the tin content of the mixture was determined, a value of 45 ppm was obtained.

Thus, although it cannot be stated categorically that the interfering elements if present in the soil will not be extracted to some extent by the ammonium iodide treatment, the available evidence indicates that they are not readily

extracted and the concentration in the final solution is likely to be too low to cause interference.

In fact, in a considerable number of determinations carried out on Cornish soils, no colours due to interfering elements have been observed, although the soils are known to contain appreciable quantities of titanium and probably also contain tungsten.

Leaching of the ammonium iodide sublimate:

In the early experiments on this work, the ammonium iodide sublimate was leached with 2N - hydrochloric acid in order to prevent hydrolysis of tin. This necessitated the use of a large amount of buffer solution; experiments were therefore carried out to determine whether the acid concentration could be reduced without affecting tin recovery.

Two soil samples containing different amounts of tin were leached with 2N, N, and 0.5N-hydrochloric acid, with water and with pH 2.5 buffer solution. The tin recovery is shown in Table IV.

TABLE 4

	Sample A	Sample B
2 N–HCl	400 ppm	1,125 ppm
N–HCl	350 „	1,250 „
0.5 N–HCl	400 „	750 „
Water	Nil	Nil
Buffer	Nil	Nil

From this it appears that N - hydrochloric acid is satisfactory, but that it is unsafe to reduce the acid concentration further.

With samples containing much organic material, a black carbonaceous deposit is frequently formed on the walls of the tube. It has been found in some cases that this material forms a protective coating over part of the sublimed ammonium iodide and can lead to low results through incomplete leaching. Addition of alcohol to the acid used for leaching assists in breaking up the deposit, but when it is heavy, it has been found necessary to break it up mechanically by rubbing with a polythene rod or a glass rod covered with rubber tubing. The presence of alcohol has the additional advantage of considerably improving the rate of settling of the suspended solid matter.

PROCEDURE

1—Weigh 0.2 g of soil into an 18 x 180 mm test-tube, add 0.5 g of ammonium iodide and mix throughly. (a)

2—Heat the end of the test-tube in a Bunsen or Primus flame until the ammonium iodide ceases to sublime and the residue reaches a dull red heat. (b)

3—Allow to cool and add 5 ml of N — hydrochloric acid. (c)

4—Heat the solution gently and shake to dissolve the sublimed ammonium iodide and iodine.

5—Allow to stand at least 15 minutes.

6—Pipette an aliquot into a 15 x 150 mm test-tube calibrated at 10 ml taking care not to disturb the residue.

7—Add a volume (e) of buffer solution equal to four times the aliquot taken.

8—Warm the solution until the iodine colour disappears, leaving a colourless solution.

9—Dilute with water to 10 ml.

10—Add 1 ml of 0.005% gallein solution (f) and mix throughly.

11—Allow to stand 10 minutes and compare the colours with standards.

(a) Use a nickel or polythene spoon for the ammonium iodide.

(b) Keep the upper part of the test-tube as cool as possible, and adjust the flame so that loss of fume is minimised.

(c) Use an automatic pipette.

(d) If a black ring remains on the walls of the tube, break it up by means of a polythene rod.

(e) Use an automatic pipette.

(f) Use an automatic pipette.

STANDARDS

1—Dissolve 0.100 g of tin metal in 10 ml of hydrochloric acid (S.G. 1.18).

2—Dilute to about 20 ml, add 0.5 g of potassium bromate and boil gently until the solution is colourless.

3—Transfer to a 100 ml standard flask and dilute to the mark. (a)

4—Pipette 1 ml of the above solution into a 100 ml standard flask, add 10 ml of hydrochloric acid (S.G. 1.18) and make up to the mark. (b)

5—Pipette 5 ml of the 10 μ g/ml solution into a 50 ml flask, add 5 ml of hydrochloric acid (S.G. 1.18) and make up to the mark. (c) (d)

6—Pipette aliquots containing 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 μ g of tin into series of 15 x 150 mm test-tubes.

7—Add buffer solution equal to four times the volume of the aliquot taken.

8—Dilute to 10 ml with water.

9—Add 1 ml of 0.005% gallein solution (e) and mix thoroughly.

10—Allow the standards to stand at least 10 minutes before use. (f)

(a) This solution contains 1 mg. of tin per ml

(b) This solution contains 10 μg of tin per ml

(c) This solution contains 1 μg of tin per ml

(d) This solution should be prepared fresh every day.

(e) Use an automatic pipette.

(f) The standards are normally stable for one day, but must be discarded if any precipitate appears.

RESULTS

The method was tested using a series of soil samples collected at a depth of 6-12" along a traverse on Carn Brea, Camborne, Cornwall across an area where the presence of a tin-bearing lode was suspected. Semi-quantitative spectrographic analyses [1] were also carried out on some of the samples as a check on the method.

The results, given in Table V, show a marked anomaly close to the expected position of the vein. The table also gives the results on two "background" soil samples collected well away from known mineralization.

The reproducibility of the method was checked using a statistical series made up from nine samples selected from the above. These were analysed independently by two operators who obtained standard deviation of 29.9% and 34.5%.

[1] Spectographic analyses by Mr. J. Martin and Miss R. A. Hall, Geochemical Laboratories, Imperial College, London.

TABLE 5

Sample no	Distance from suspected mineralization (ft.)	Sn found (ppm)	Spectrographic results
1,363	35	75	
1,364	30	100	
1,365	25	150	
1,366	20	75	60
1,367	15	75	80
1,368	10	625	1,000
1,369	0	1,250	700
1,370	5	1,000	1,000
1,371	15	350	200
1,372	25	250	500
1,373	30	100	
1,374	35	250	
1,375	40	100	
1,318	("Background samples from unmineralised)	75	80
1,319	(area.)	75	100

Working with batches of 40 samples at a time, it is possible to carry out 80 analyses per 8 hours day.

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APPENDIX

Equipment:

1—Torsion balance, 500 mg capacity.
2—Water still or mixedbed deionisation unit. (a)
3—3 racks to hold 40 test-tubes each.
4—1 rack to hold 10 test-tubes.
5—1 glass-writing diamond.
6—100 Pyrex rimless test-tubes — 18 x 180 mm.
7—60 Pyrex rimless test-tubes — 15 x 150 mm. (b)
8—50 corks, ½ in diameter at the narrow end.
9—1 gas burner or Primus stove.
10—Rubber tubing for burner.
11—1 water bath.
12—1 polythene rod 12 in x ¼ in.
13—1 nickel or polythene spoon to measure 1 g.
14—1 1 ml pipette graduated in divisions of 0.1 ml.
15—2 5 ml automatic pipettes, graduated in divisions of 0.1 ml.
16—1 1 ml automatic pipette.
17—1 100 ml standard volumetric flask.
18—1 50 ml standard volumetric flask.
19—2 polythene reagent bottles, 500 ml.
20—3 polythene reagent bottles, 200 ml.
21—1 polythene wash-bottle, 500 ml.
22—1 Pyrex measuring cylinder, 500 ml.
23—1 Pyrex beaker, 250 ml.

(a) A simple unit may be made from 1 in diameter polythene tubing with about 1 lb of ion exchange resin.

(b) Calibrate these tubes at 10 ml.

24—1 Pyrex of polythene funnel, 2½ in diameter.
25—1 box of Whatman No. 1 filter papers, 11 cm diameter.

Reagents for 1,000 determinations:

1—Water, distilled or deionised.
2—1,200 g of ammonium iodide.
3—600 ml of hydrochloric acid A. R. (S. G. 1.18) (a)
4—3,000 ml of ethyl alcohol. (a)

5—500 g of chloroacetic acid. (b)
6—500 g of sodium chloroacetate. (b)
7—250 g of hydroxylamine hydrochloride. (b)

8—1 g of gallein. (c)
9—1 g of tin metal (A. R.)
10—5 g of potassium bromate.

(a) *N-hydrochloric acid:* add 45 ml of hydrochloric acid (S. G. 1.18) to 250 ml of ethyl alcohol and dilute to 500 ml with water.

(b) *Buffer solution:* dissolve 50 g of chloroacetic acid, 50 g of sodium chloroacetate and 25 g of hydroxylamine hydrochloride in 500 ml of water.

(c) *0.005% gallein solution:* warm 10 mg of gallein with 100 ml of ethyl alcohol until no more dissolves. Filter through an 11 cm Whatman No. 1 paper and dilute to 200 ml with ethyl alcohol.

XX
Congreso
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