Spectrochemical Analysis for Geochemical Purposes

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To my knowledge, it is the first time the Colloquium Spectroscopicum Internationale has a special session for geochemistry. It is natural that this happens when the Colloquium takes place in Canada, which has large territories, rich in various minerals and ores.

Geochemical analysis is an important complement to field observations, geophysical measurements, or other geological investigations. Spectrochemical analysis has always had a strong relation to geochemistry. Several elements have been discovered by spectral analysis, e.g. Cs, Rb, Tl and Ga, besides several rare earths and nobel gases. The geochemists were pioneers in applying spectroscopy for analytical purposes. V.M. Goldschmidt and his school used spectrochemical analysis to a great extent in determining the composition of different parts of the earth and the distribution of the elements in the crust. The methods, developed in the early thirties, and still used, are often variations of the same basic technique. The sample is mixed in a certain proportion with a suitable buffer or a carrier and placed in a graphite electrode against which a d.c. arc is run. Direct reading instrumentation and access to electronic computing has had a great impact on the recent developement and application of geospectrochemical analysis. These two things have made available large capacity, multi-element, low cost analysis. It should be underlined that direct reading and electronic computing also plays an important part in the developement and refinement of methods, for instance regarding sample preparation and excitation. The linear response of the photomultiplier over a wide intensity range, compared to the complicated intensity/blackening relation of the photographic emulsion, is of great importance in studying the many parameters that characterize a method. The inherent error in photographic recording very often overlaps the intensity variations which are studied. Electronic computing makes it possible to treat exhaustively all information gathered in the great number of intensity measurements.

In Sweden, the majority of geochemical analyses are performed by emission spectroscopy. Most of the analyses are made at the following three institutions: Geological Survey of Sweden, Boliden AB, a mining and refining company, and at Analytica AB, a commercial laboratory. This paper will describe methods and equipment, used at the geological survey. The conditions are similar at the other two places.

Table I reviews the types of samples and methods used. Most of the samples belong to one of the following categories: rocks, minerals, ores, soils, stream sediments, plant ashes and water.

TABLE I SAMPLES AND MOST FREQUENTLY USED METHODS

SAMPLES	METHODS
Rocks Iron ores	Tape (Borate isoformation) Tape (Powder as it is) Atomic Absorption Chemical
Sulphide ores	Tape (Sulphide isoformation) Tape (Powder as it is) Chemical
Soil samples Stream sediments	Tape (Powder as it is)
Plant ashes	Atomic Absorption Tape (Powder as it is)
Water	Atomic Absorption Em. Spectr. Vaporizer Chemical

Most of the analyses are performed with the tape machine with or without special pretreatment of the samples. The object of the pretreatment of the samples is to reduce matrix and particle size effects to an acceptable level. The word isoformation was earlier introduced as a concept for this type of pretreatment (2). Wet chemical methods are restricted to those elements that cannot be determined spectrochemically. Atomic absorption is an important complement. X-ray fluorescene is not shown in table I, as it is mainly used for special analyses.

In the following paragraphs, modifications of the tape technique are discussed, and the different isoformation methods used in geospectrochemical analyses are reviewed. Finally a simple method of preparation of water samples for emission spectroscopy is mentioned.

Tape machine

The tape machine has been previously described (1). It is a device to introduce powdered samples into the spark gap in a defined way. The machine is schematically shown in fig. 1. When running the machine the adhesive tape is unwound from the stock roll and its edges are automatically folded in and bent double so that only the central section remains adhesive. The tape is passing underneath the vibrating hopper, where the sample is fed on the adhesive central section of the tape. Leaving the hopper, the tape enters the device for removal of excess material. The sparks break through the tape and vaporize and excite the sample.

The main modifications of the tape machine are as follows:

1) the excitation occurs in a house which allows controlled atmosphere,
2) the primary optics are chosen to give an image of the spark gap on the primary slit of the spectrometer, so that the

Tape machine (continued)

image of the electrode gap is at a right angle to the slit,
3) the air blast in the gap used previously has been cancelled,
4) discharges of lower energy are now being used,
5) the mechanical strength and the purity of the spectrotape from Edaplast, Malmö, Sweden, have been improved.

Controlled atmosphere - The gases O_2, N_2, CO_2, He and Cl_2 have been tried at different concentrations in a carrier of argon. It is a known fact that in steel analysis the purity of the argon is extremely important. Slight traces of oxygen, for instance, have a strong influence on the intensities. In the tape method, however, the nature of the discharge has a linear relationship to the composition of the gas mixture. The properties of the discharge in a certain mixture of argon and nitrogen, for instance, can thus be estimated from the properties of the discharges in the pure components. Slight impurities in argon have, therefore, no significant influence. In discharges against an electrode carrying the sample, a mixture of oxygen to argon is known to increase the sensitivity because of an increased electrode temperature. This does not occur in the tape machine, because there is no such electrode effect. Chlorine was also included in the investigation, as it is known that addition of certain chlorides, such as AgCl, to the sample increases the sensitivity of some elements, e.g. Mo and W in the d.c. arc methods. Varying concentrations of chlorine in argon up to 1:5 were investigated. However, no enhancement could be traced. Strong absorption bands of Cl_2 in the wavelength region 2000 - 6000 A would, never the less, make the use of high Cl_2-concentration impossible.

The relative line/background ratios for discharges in different atmospheres are illustrated in table II. The best line/background ratio is obtained in argon, independent of which discharge condition is chosen. The advantage of argon lies in high intensity, high line/background ratio and surpressed CN bands. It should be mentioned that the intensity of the CN bands in argon can be used to determine the nitrogen contents of the sample.

Primary optics - By having an image of the spark on the primary slit a gain in intensity is obtained which reduces the demand on sensitivity of the photomultipliers. The spark image must be at a right angle to the primary slit, and care must of course be taken to fully illuminate the grating or the prism.

Discharge parameters - The experiences from evaporation and excitation using the sample as an electrode, cannot directly be transfered to the tape technique. Excitation of arc-type does not increase the sensitivity in the same way in the tape technique as in conventional spectrochemical analysis. In the tape technique, there is no sample electrode, which gets heated resulting in increased evaporation. Several different discharges are being investigated as high voltage condensed a.c. discharges and low voltage condensed d.c. and a.c. discharges. The polarity has an influence, the best results being obtained with the upper electrode positive. The studies of discharge parameters are not yet finished. A result is that low energy discharges are more sensitive than those with very high energy used earlier. Moreover, the selfabsorption is reduced when low power discharges are used.

Table II

LINE/BACKGROUND RELATION FOR DIFFERENT GASES

	Ni	Mo	Zn	Ag	Sn	Bi	Mg	Co	Be	W	Sn	As	Sr	Pb	Cu	Ba	Mn	Al	Cr	Cu
	3414	3864	3345	3383	3175	3068	2795	3453	3131	4008	2840	2349	4607	4057	5218	4934	2576	3944	4254	3274
Ar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Air	0.61	0.36	0.29	0.41	0.37	0.28	1.03	0.52	0.17	0.46	0.49	0.57	0.66	0.29	1.04	0.78	0.57	0.63	0.93	1.11
N_2	0.62	-	0.28	0.47	0.82	0.86	1.18	0.59	0.22	0.51	0.63	0.70	0.60	0.26	1.00	1.10	0.64	0.71	0.89	1.23
He	0.22	0.45	0.68	0.45	0.37	0.33	0.77	0.20	0.34	0.28	1.01	0.81	0.21	0.37	1.08	0.16	0.31	0.38	0.51	0.61

Table III

SOIL SAMPLES DEVIATION OF BACKGROUND ppm

Ni	Mo	Zn	Ag	Sn	Co	As	Fe	Fe	Sr	Pb	Cu	Cu	Ba	Mn	Mn	Cr	Mg	Ti	Ca	V
3414	3864	3345	3382	3175	3453	2349	4404	4447	4607	4057	3274	5218	4934	2576	2595	4254	2790	3361	3179	4379
<1	<1	2	<1	1	<1	1	<1	250	5	<1	<1	5	5	<1	15	<1	125	250	250	2

Adhesive tape - The requirements on the cellophane tape are: high and uniform purity in respect of inorganic elements, uniform adhesive, close tolerances of dimensions, adequate strenght and availability in sufficient lenghts (500 m). Edaplast, Malmö, Sweden has in cooperation with Boliden AB and Geological Survey of Sweden developed a special cellophane tape, named 'Spectrotape" for this particular application. It should be underlined, that the properties of the tape is of extreme importance for the quality of the analyses.

The changes in the tape technique just reviewed, have resulted in improvements in light intensity, sensitivity, precision and in simpler excitation unit due to reduced demand of energy in the discharge.

Procedures

As already mentioned, most of the analyses are performed by the tape method, combined with different isoformations. The different tape methods used in geochemical analysis are summarized.

Samples run directly on tape - This is the most rapid method. In this way, sieved and dried soil samples for geochemical ore prospecting are analyzed. It should be mentioned that almost all powdered samples are run directly on the tape prior to further analysis. With this so-called direct tape method, we obtain final analyses of some trace elements, preliminary analyses of others and on the whole, a rapid and valuable guidance for further analytical work.

Samples ground and run on tape - This is the way coarser material such as stream sediments are analyzed. In special cases, powdered samples are ground with a buffer containing an internal standard.

Isoformation by fusion - The samples are fused to a glass, which is ground to powder. This technique is used for the main elements in rocks and oxide ores.

Isoformation by sulphide precipitation - For accurate analysis of Cu, Pb, Zn, Ag, Bi, Sn, Mo, As, Sb and Ge, the ore samples are dissolved and the above elements are precipitated on a paper pulp. The powder obtained after filtration and drying is run on the tape.

Soils and stream sediments

Fig. 2 illustrates how the analyses for geochemical ore prospecting purposes are performed. There are two categories of material, stream sediments and soil samples. Usually the stream sediments are investigated on a regional basis to find areas of possible interest. If anomalies are found, a detailed study is made by soil sampling. As the exposure time is only seven seoonds, the speed depends entirely on the recording and evaluation system. Last year, more than 30.000 samples were analyzed with this technique, which means many hundred thousands of determinations. The accuracy is dependent upon the precision and the extent to which corrections can be made for matrix effects and interferences. Table III shows runs on pure alkali feldspar and gives an idea of the sensitivity obtained. Table IV gives a view of the disturbances. The magnitude has been determined by adding to a sample of pure alkali feldspar varying amounts of the elements that produce the disturbances. Lines without self-absorption should be chosen whenever possible, other-

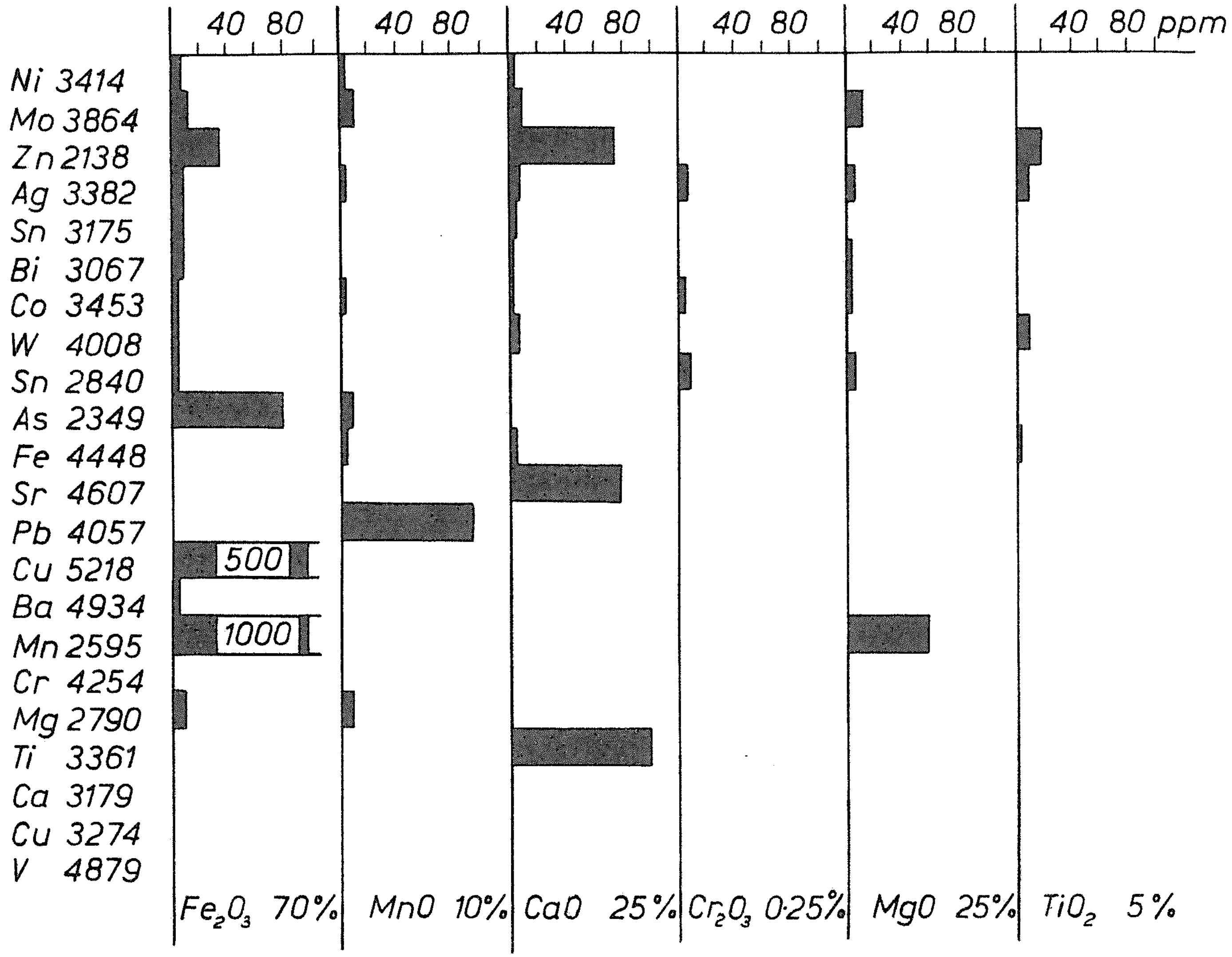
40
80
ppm
Ni 3414
Mo 3864
Zn 2138
Ag 3382
Sn 3175
Bi 3067
Co 3453
W 4008
Sn 2840
As 2349
Fe 4448
Sr 4607
Pb 4057
Cu 5218
Ba 4934
Mn 2595
Cr 4254
Mg 2790
Ti 3361
Ca 3179
Cu 3274
V 4879
500
1000
Fe_2O_3 70%
MnO 10%
CaO 25%
Cr_2O_3 0·25%
MgO 25%
TiO_2 5%

Table IV

Soils and stream sediments (continued)
wise the relationship is nonlinear and less accurate between the measured intensity of the disturbing elements and the correction that has to be made.

How good are these analyses of soils and stream sediments? In this particular case, nature helps to make the judgement. The soils for instance, are sampled along straight lines and analyzed in the same order. In plotting on a map, a squared net of figures is obtained. The equi-concentration curves of different elements on this map do not only tell something about anomalies, but also a great deal of the quality of the analyses as well. Smooth curves and distribution of the elements in conformaty with geological facts are examples of what must be expected. The simultaneous multi-element analysis gives a good statistical base as there are many elements that must fit into the picture.

Rocks

The demand on the number of complete rock analyses has varried. Previously, the geologists had to adjust themselves to a rather limited number of analyses due to high cost and low output of classical methods of silicate analysis. The application of spectrochemistry and X-ray fluorescenceto the analysis of main elements has changed the situation.

Fig. 3 shows the procedure of the analysis of the main elements in rocks. The same fusion is used for analysis of Na_2O, K_2O by atmic absorption, and SiO_2, Al_2O_3, CaO, MgO, Fe_{tot}, MnO, TiO_2, BaO by the tape method. Most of the scheme is known and needs no comment. The application of prefused buffer was introduced by Danielsson et al (3) and seems to be generally accepted. At this occasion, I would like to emphasize the importance of using prefabricated fused standards. The advantage is that possible errors in weighing of standard samples and buffers are completely eliminated and besides the homogeneity in standard samples is no longer a problem. In order to perform rock analyses efficiently, it is important to have everything well standardized for a rather long time. The buffer must therefore be made in sufficiently large quantities, in our case 50 kg. The standard samples are prepared in units of 5 kg. One sample corresponds to granite and the other to gabbro in composition. These standards are made in the same way as the prefused buffer. Chemicals, SiO_2, Al_2O_3 etc. and buffer are mixed in desired proportion. The mixture is fused and quenched in destilled water. The granules are dried and ground. The large amounts of prefused buffer and prefabricated standards make it possible to keep the same condition, at least over a couple of years. The prefabricated standards guarantee that there can be no errors due to mistakes in weighing standard samples or errors from possible nonhomogeneity of reference samples. Having homogenous standard samples with an unchanged composition over a long period of time, makes it easier to check on the operator and on instrumentation factors. Table V shows the precision of the analyses. The sensitivity may be estimated from variation in background, table VI. The normal dilution factor which these two tables refer to, is 1:20. In particular cases, when higher sensitivity is required, less dilution is used. It is possible to go as far as 1:4 with this buffer and still get a glass. The accuracy comes very close to the precision, as there is no matrix effects in the range of ordinary composition of rocks, except the effect of silicon on aluminium which can be corrected. Generally the mean of four runs is taken.

Table IV

Table V

BORATE ISOFORMATION

PRECISION IN SINGLE DETERMINATION ESTIMATED FROM 20 FUSIONS 4 RUNS ON EACH FUSION TOT 80 RUNS

ELEMENT	Co	Si	Fe	Al	Be	Ca	Mg	Mg	Mn	Ba	Ti	Bg (background)
WAVELENGTH	I 3453	I 3905	I 4405	I 3944	II 3131	II 3179	II 2790	II 2795	II 2576	II 4934	II 3361	3901
CONTENTS %	Int.st	68.9	3.84	14.1	Int.st	1.50	0.60	0.60	0.08	0.29	0.37	
SD		0.57	0.12	0.14		0.059	0.040	0.011	0.0033	0.0064	0.011	
CV		0.83	3.1	1.0		3.9	6.7	1.8	4.1	2.2	2.9	

Table VI

BORATE ISOFORMATION

PRECISION IN SINGLE DETERMINATION - "ZERO SAMPLE" ESTIMATED FROM 20 FUSIONS 4 RUNS ON EACH FUSION TOT 80 RUNS

ELEMENT	Co	Si	Fe	Al	Be	Ca	Mg	Mg	Mn	Ba	Ti	Bg
SD		0.13	0.10	0.019		0.05	0.043	0.0018	0.0021	0.0186	0.0086	

Table VII

SULPHIDE ISOFORMATION

PRECISION IN SINGLE DETERMINATION ESTIMATED FROM 12 PRECIPITATIONS 4 RUNS ON EACH TOT 48 RUNS

ELEMENT	Cd	Zn	Cu	Cu	Pb	Ag	As	Bi	Mo	Sn
WAVELENGTH	4800	3345	5218	3274	4058	3384	2349	3063	3864	3175
CONTENTS %	Int.st	0.40	0.40	0.40	0.080	0.0050	0.10	0.025	0.025	0.025
SD		0.0081	0.012	-	0.0017	0.00018	0.0044	0.00048	0.00064	0.00083
CV		2.0	3.0	-	2.1	3.6	4.4	1.9	3.4	2.6

Table VIII

SULPHIDE ISOFORMATION

PRECISION IN SINGLE DETERMINATION - "ZERO SAMPLE" ESTIMATED FROM 12 PRECIPITATIONS 4 RUNS ON EACH TOT 48 RUNS

ELEMENT	Cd	Zn	Cu	Cu	Pb	Ag	As	Bi	Mo	Sn
SD		0.0056	0.0057	0.00086	0.0017	0.00012	0.0022	0.00031	0.00036	0.005

Rocks (continued)
The silicon is the most critical one to determine as it is of the highest concentration. The coefficient of variation in the mean of four is less than 0.5%. The line Si 3905 is used instead of, for instance, Si 2881, in order to avoid selfabsorption. The background is comparatively high, but as can be seen, the variation in background is small. When complete analysis is performed, the analysis sum lies between 99.5 - 100.5%.

Ores

In the sulphide isoformation, developed by G. Sundkvist (4) the ore minerals are dissolved by treatment with nitric and hydrochloric acids. The procedure is schematically shown in fig. 4. A strong solution of magnesium chloride, buffer and internal standard (Cd) solutions are added. The sample solutions are decanted to plastic vessels where a precipitation is achieved on paper pulp by adding H_2S-saturated water. The dried and filtered powder is run on the tape machine. Precision and sensitivity determined on synthetic samples are shown in table VII and VIII and refer to the normally used amounts of sample and cadmium sulphide. The amount of sample can be varied according to the required sensitivity. In our routine operation a rapid estimation of concentration of the element of interest is made by analyzing the sample directly on tape prior to the sulphide isoformation. The information, obtained by this analysis, is used to select the sample weight for the sulphide isoformation and to estimate the concentration of trace elements as Ni, Co, Cr which cannot be determined by sulphide precipitation. It should be mentioned that sulphide isoformation is also used as an enrichment method for trace elements in rocks. As the method is identical for a great variety of samples, it has been worth while to design and build a special sulphide isoformation equipment.

Water analyses

The anions are analyzed by ordinary chemical methods. The metal contents are analyzedby atomic absorption and by emission spectroscopy. Only the emission method will be discussed. The technique is a new version of a very old method of dropping and vaporizing solutions on graphite electrodes. The equipment, shown in fig. 5 consists of an electric plate heated to 120°C, where a number of graphite electrodes are positioned. Compressed filtered air blown on to the tips of the electrodes increases the vaporization rate and eliminate the contamination from the surrounding air. The sample is pumped at a rate of 5 ml/h through plastic tubes and platinum nozzles and falls as droplets on to the electrode tips. In analyzing naturally occurring water, the normal size of samples is 10 - 30 ml, depending upon the required sensitivity. The prepared electrodes are at present analyzed by d.c. arc and photographic recording. Other excitation conditions and direct reading is being investigated. Prior to use, the graphite electrodes are purified by ignition in an induction coil. In this equipment, 15 samples are prepared simultaneously and the only manual operation is to change samples and electrodes. The advantages of this method are high sensitivity and low risk of contamination. The use of emission spectroscopy for trace elements in water is a question of enrichment through evaporation, precipitation, extraction or ion exchange. In routine work, it is very important to keep the risks of contamination low. That means as little handling and as few added chemicals as possible.

Water analyses (continued)
The old method of dropping the sample on carbon or graphite electrodes seems to fulfill these requirements well. The sensitivity is in the ppb range.

Regarding future developments in geospectrochemistry, almost any element with suitable spectral lines is of interest. For several elements, there is a need for more than one line due to a large concentration range. The direct reading spectrometer should therefore, have as few geometrical or other restrictions as possible in choice of lines. This requires a large wavelength range including the second order of lines of interest. To reduce interferences, high dispersion and narrow secondary slits are desirable. The last condition requires high mechanical and thermal stability of the instrument. As high dispersion and large wavelength range in available spectrometers are contradictory to each other, the choice has, at present, to be a compromize between wavelength range, dispersion and blaze. Simultaneous use of more than one grating with different blaze is an advantage.

Interferences and certain matrix effects can be corrected by using intensity measurements of suitable spectral lines. Disturbances due to particle size and structural effects, however, can be eliminated only by pretreatment, isoformation of the samples. Fusion and dissolving are the most efficient ways. In some cases, grinding is sufficient. The uniformity of a particular isoformation procedure, independent of the variety of the samples treated, has made it possible to design special isoformation equipment. The economic justification lies in the great number of samples treated. Further development along these lines, with more automation, can be expected. Sample preparation machines, isoformation robots will come, which, from a variety of samples, produce new samples suitable for the instruments.

In my paper, I have particularly underlined the usefulness of spectrochemical analysis. The inherent sensitivity of spectroscopy and the possibilities to make simultaneously multi-element analysis are the most attractive features. In further presentations and discussions in the geochemical session of this colloquium, we will hear about a broad spectrum of methods, emission, absorption, X-ray and so on. There are always many ways of reaching a certain goal in analytical chemistry. From a practical point of view, we are all aiming at the best compromize between sensitivity, accuracy, speed and cost for a certain analytical task.

References

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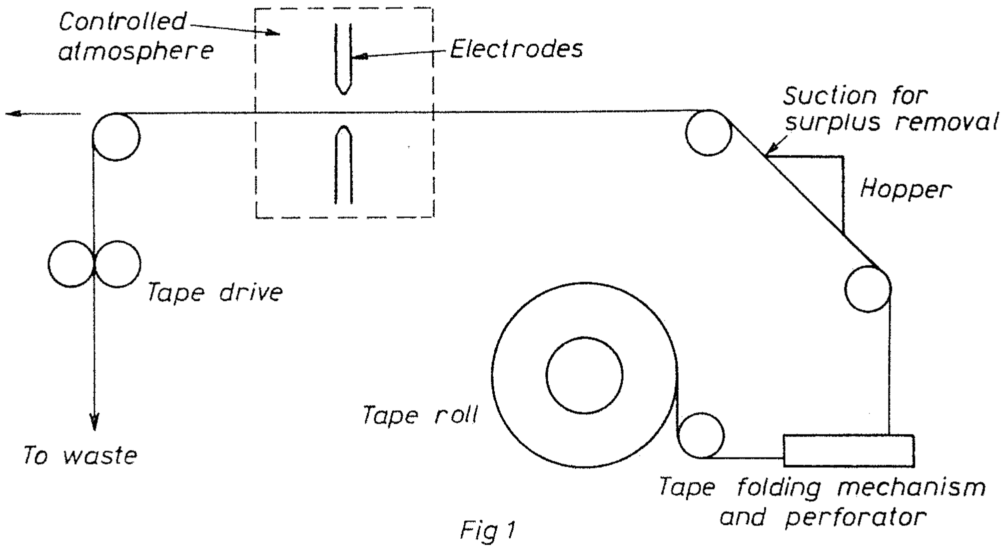

Controlled atmosphere
Electrodes
Suction for surplus removal
Hopper
Tape drive
Tape roll
To waste
Tape folding mechanism and perforator

Fig 1

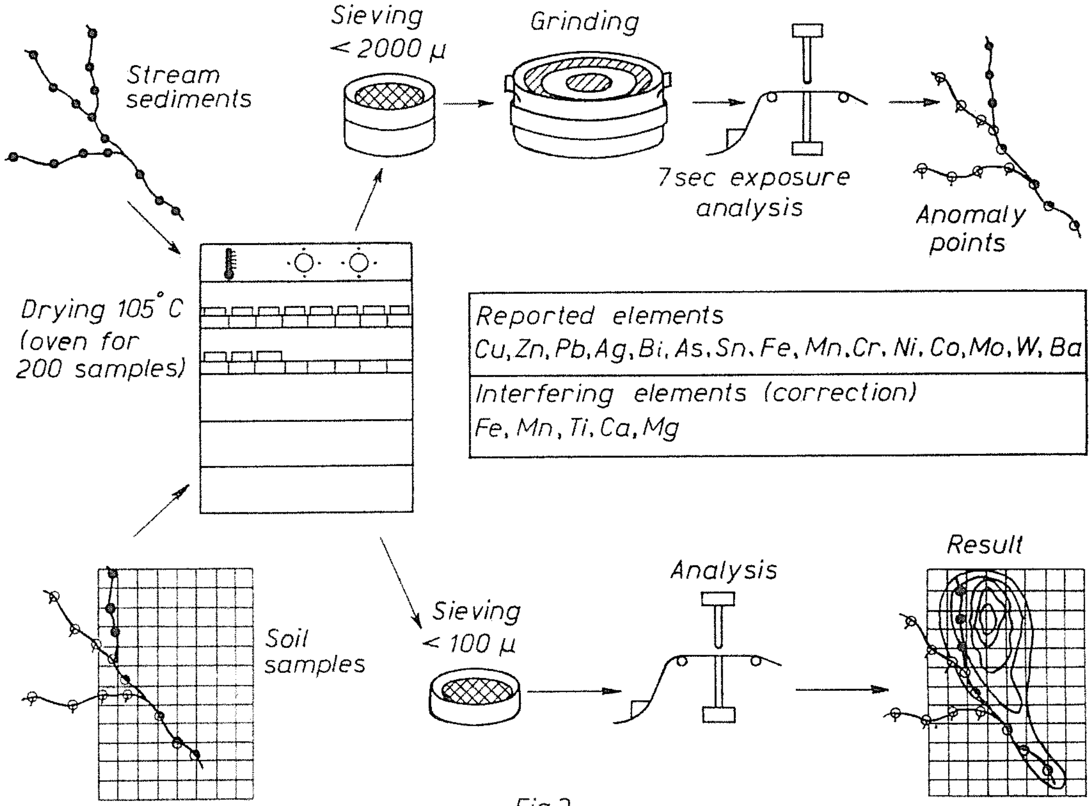
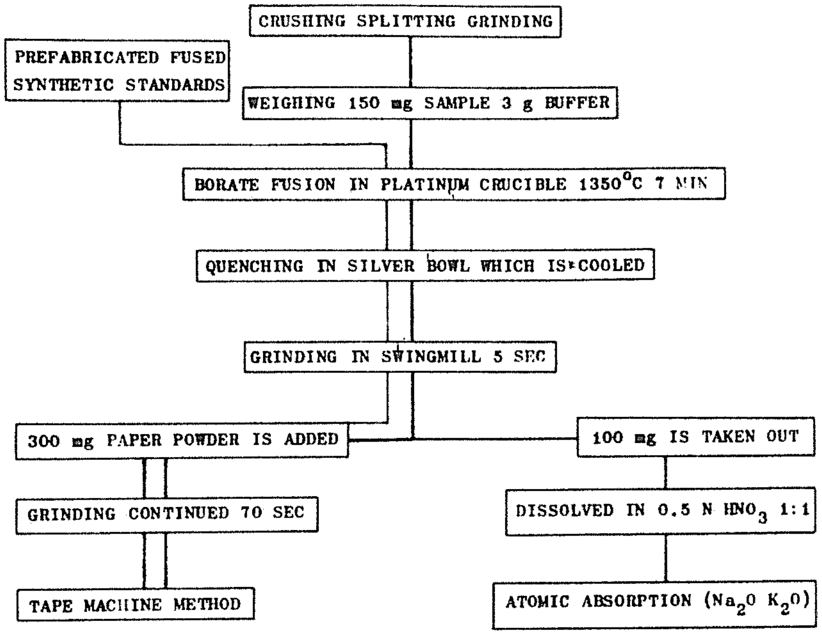

Stream sediments
Sieving < 2000 μ
Grinding
7sec exposure analysis
Anomaly points
Drying 105° C (oven for 200 samples)
Reported elements
Cu, Zn, Pb, Ag, Bi, As, Sn, Fe, Mn, Cr, Ni, Co, Mo, W, Ba
Interfering elements (correction)
Fe, Mn, Ti, Ca, Mg
Soil samples
Sieving < 100 μ
Analysis
Result

Fig 2

SiO_2 Al_2O_3 CaO MgO Fe_{tot} MnO TiO_2 BaO Na_2O K_2O IN ROCKS



BUFFER

A MIXTURE OF THE FOLLOWING IS PRE-FUSED

73.00 %	$Li_2B_4O_7$	3.47	Co_3O_4
2.50	$LiCO_3$	0.03	BeO
21.00	$SrCO_3$		

Fig. 3

SULPHIDE ISOFORMATION

Zn Cu Pb Ag Bi As Sn Mo

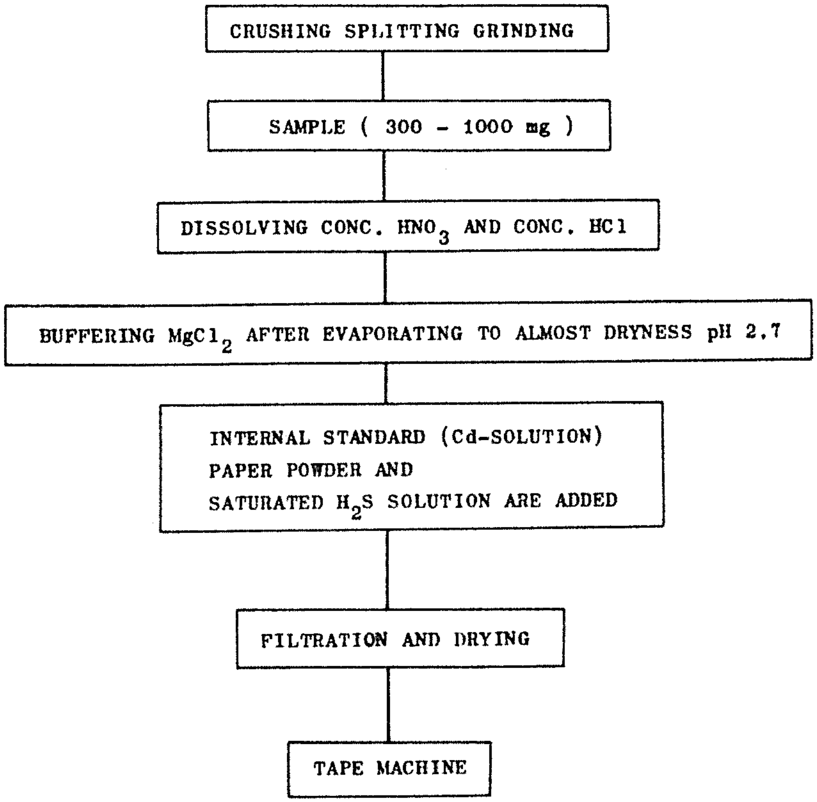


Fig. 4

Fig. 4

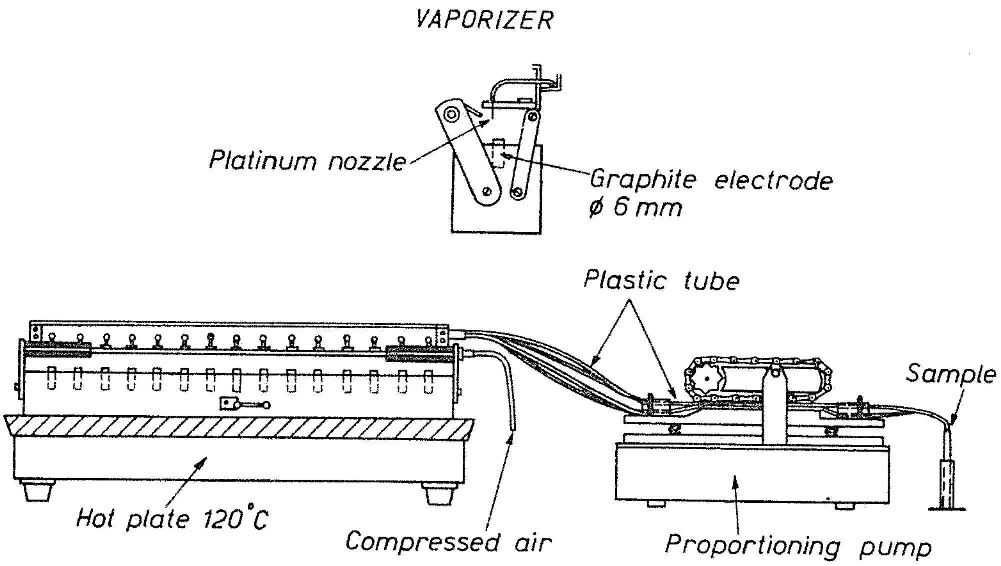


Fig 5

Fig. 3