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Field and Laboratory Methods used by the
Geological Survey of Canada in Geochemical Surveys

No. 12. MERCURY IN ORES, ROCKS, SOILS,
SEDIMENTS AND WATER

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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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ABSTRACT

Methods and equipment used by the Geochemistry Section, Geological Survey of Canada for the rapid, routine determination of mercury by cold vapour atomic absorption in various materials of geological interest, viz; rocks, soils, sediments, ores and waters, are described in detail. The range of mercury contents which can be covered for solid samples is 2 ng to 1000 ng Hg; i.e. 4 ng/g to 2000 ng/g for 0.500 g samples. The useful range of concentration which can be covered for water samples, including snow, is 0.01 ng/g to 2.5 ng/g. Coefficients of variation (arithmetic) for *all* samples have been calculated. In the range of Hg content: 2-25 ng, CV is 25%; 50-100 ng, CV is 15%; ≥150 ng, CV is 10% for example. Negative interferences by a number of metallic elements, in the chemical form in which they exist under the conditions of the method, have been quantitatively investigated. Au, Pd, Pt, Te at microgram levels, interfere significantly when precipitated in elemental form. Se, Cu and Ag which do not precipitate as metals, do not interfere, even at mg levels. Finely powdered sulphur, ≥15 mg, causes significant interference to the expected Hg signal. Because the levels at which most metals interfere are high relative to their natural abundances, only Te content is an important factor to be considered in routine geochemical analyses for mercury.

RÉSUMÉ

L'auteur décrit en détail des méthodes et du matériel utilisés par la Section de géochimie de la Commission géologique du Canada pour effectuer la détermination rapide et courante de mercure par absorption atomique de vapour froide dans différents matériaux intéressants au point de vue géologique comme les roches, les sols, les sédiments, les minerais et les eux. L'échelle de la teneur en mercure qu'on peut déceler dans des échantillons solides varie de 2 ng à 1,000 ng d'Hg; i.e. 4 ng/g à 2,000 ng/g par échantillon de 0.500 g. L'échelle utile de concentration qui peut être décelée dans des échantillons d'eau, y compris la neige, va de 0.01 ng/g à 2.5 ng/g. Les coeficients de variation (arithmétique) ont été calculés pour tous les échantillons. Par exemple, si on regarde l'échelle de la teneur en Hg: 2-25 ng, le CV est de 25%; 50-100 ng, le CV est de 15%; ≥ 150 ng, le CV est de 10%. L'auteur a étudié quantitativement les effets négatifs de plusieurs élements métalliques, selon la forme chimique qu'ils prennent dans les conditions de la méthode. Au, Pd, Pt, Te, à l'échelle du microgramme, ont un effet significatif lorsque précipités sous forme d'éléments. Se, Cu et Ag, qui ne se précipitent pas sous forme de métaux, n'ont aucun effet, même à l'échelle du mg. Le soufre réduit en poudre fine (≥ 15 mg) exerce un effet significatif sur le signal d'Hg attendu. Parce que la quantité nécessaire à la plupart des métaux pour avoir un effet est élevée par rapport à leur abondance dans la nature, seule la teneur en Te est facteur important à considérer lors d'une analyse géochimique régulière du mercure.

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INTRODUCTION

The Geochemistry Section of the Geological Survey of Canada receives fre-
quent requests from the public for outlines of methods of analyses suitable for geo-
chemical surveys. To meet these requests it was decided to prepare a series of
papers outlining the methods used, giving a complete list of the equipment and
reagents required, and a detailed step-by-step account of the procedures employed.

The tests described herein are based on those published in the scientific
literature, but, in some cases modified to speed production and to suit requirements
for various sample types. No attempt is made in this series of publications to dis-
cuss the principles of geochemical prospecting, sampling procedures or the inter-
pretation of the analytical data obtained.

PRELIMINARY REMARKS

The unique properties of volatility which characterize the migrational
ability of mercury are relatively familiar to exploration geochemists, geologists and
environmental scientists. However, only recently have these properties been har-
nessed to produce the reliable and sensitive techniques of analysis for this element
which are usually termed cold-vapour atomic absorption methods. One such method
has been available to geochemists of the Geological Survey of Canada for over three
years and has proved very useful for mineral exploration on both local and regional
scales. It is not within the scope of this report to assess the many different analyti-
cal techniques for mercury which have emerged in the last few years. The reader
is referred to articles by Jonasson (1970), which also cover migrational aspects of
the geochemistry of mercury; by D'Itri (1972); by Wallace et al. (1971); and to a
recent symposium publication, (Swedish Nat. Inst. Publ. Health, 1971); all of which
provide such detailed reviews.

NOTES ON THE METHOD

The basic analytical method for mercury described herein is in common use.
Apart from modifications made according to the needs of individual analysts, the
method involves a number of common sequential steps; hence the description,
"reduction-aeration-cold vapour" atomic absorption, which is usually applied to it.
Such a method aims at overcoming lack of sensitivity inherent in conventional atomic
absorption for Hg which is due to the loss of radiation-absorbing ground state atomic
mercury as a result of energetic excitation within the flame.

Acid digested samples of rock, soil vegetation, sediments or minerals are
treated with chemical reductants such as solutions of tin (II) ions to generate vola-
tile mercury (O) which is then flushed on a stream of air into a flow-through cell

placed in the light path of an atomic absorption spectrometer. Light absorption is then measured at a wavelength of 253.7 nm. One of the earliest reported uses of this method was described by Poluektov et al. (1963) who also discussed the effects on the method of various mineral and carboxylic acids, certain organic solvents and many cations, some of which induced negative interferences. The reduction-aeration procedure was subsequently modified by Hatch and Ott (1968) who brought the method into prominence in North America. Igoshin and Bogusevich (1968) applied the technique to the determination of mercury in natural water samples and numerous workers have since used similar approaches. Other workers (Vaughn and McCarthy, 1964) have used cold vapour atomic absorption techniques wherein the dry sample is heated and the evolved mercury vapour is passed into an absorption cell after being collected and subsequently released from a trap or series of traps. It is felt that solution techniques greatly reduce the magnitude of interferences which are encountered using the dry sample technique.

SAMPLE TREATMENT

Solid Samples

Rock and ore samples are powdered to about 200 ASTM mesh size ($\approx 75 \mu$m). Soil and sediment samples are sieved to less than 100 mesh size ($\approx 150 \mu$m). Samples (500 mg) are then leached in 100 ml of a solution 4M in nitric acid and M/7 in hydrochloric acid for 1.5 to 2.0 hours at 90°C in a water bath. After cooling to room temperature, 15 ml of 5% w/v tin (II) sulphate in M H_2SO_4 is added and the elemental mercury so formed is aspirated immediately from solution in the absorption cell. Glew and Hames (1971) reported that the relative volatility of mercury solute with respect to water is 15,400 at 24°C but only 8,360 at 100°C; thus the flush-out efficiency of atomic mercury at room temperature is greater than in warmer solutions. These figures account for the observed ease with which Hg is aspirated from solution. Absorbance is measured as the maximum reading on the *first* pass of the cycling vapour plug through the cell. The entire decomposition-reduction process is carried out in pyrex test tubes (38 by 200 mm). The experimental apparatus is depicted in Figures 1 and 2.

The acid mixture used in the hot leach of these samples was chosen after careful investigation of a series of similar mixtures. The basic premise for this study was that if a leach could be found which would dissolve cinnabar rapidly then this would provide the basis for a working extraction procedure. Powdered cinnabar is quite resistant to acid attack and particularly so to nitric acid of all concentrations. The addition of minimal quantities of hydrochloric acid greatly promotes the decomposition of cinnabar. Addition of excessive hydrochloric acid sometimes results in loss by volatilization of mercury chlorides. Perchloric acid mixtures were not considered because a product of perchlorate reduction is chloride ion. Many soil and sediment samples processed by the Geochemistry Section laboratories are often high in organic (up to 40% C) matter so it was further considered advantageous to avoid the use of perchloric acid leaches. As a general principle, an oxidizing leach which could be used with confidence on *all* types of geochemical samples was considered preferable.

The selected leach is capable of rapidly dissolving small amounts of most common base metal sulphides, including cinnabar, which are normally present in rock, sediment or soil samples. When ore samples of the same sulphides are presented for analysis, a mixture of concentrated nitric and hydrochloric acids in the same proportions as used in the dilute leach is allowed to react with the powdered
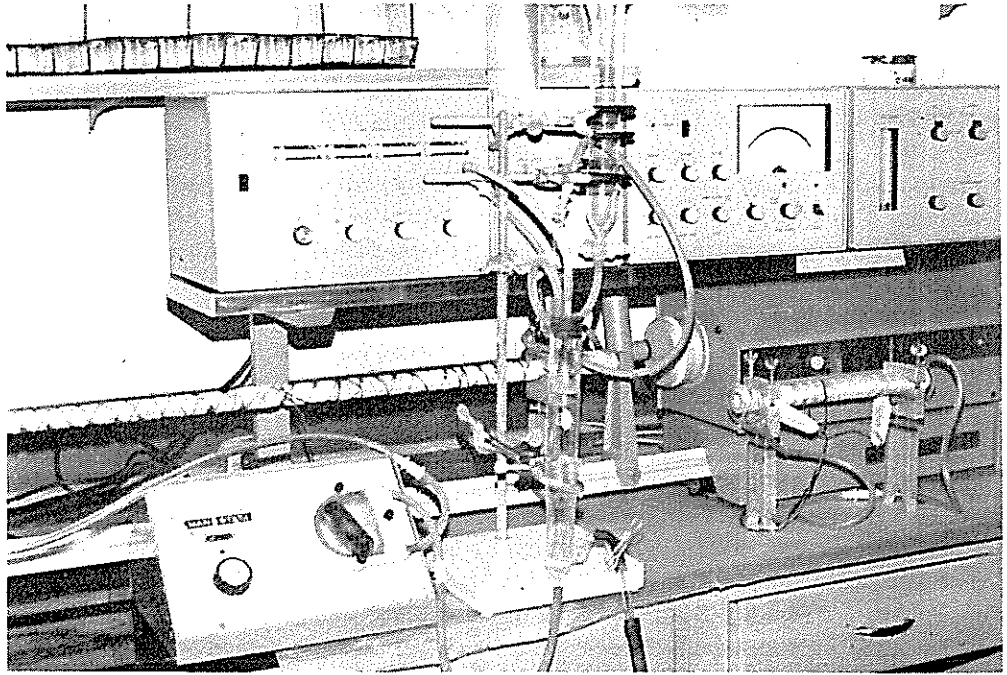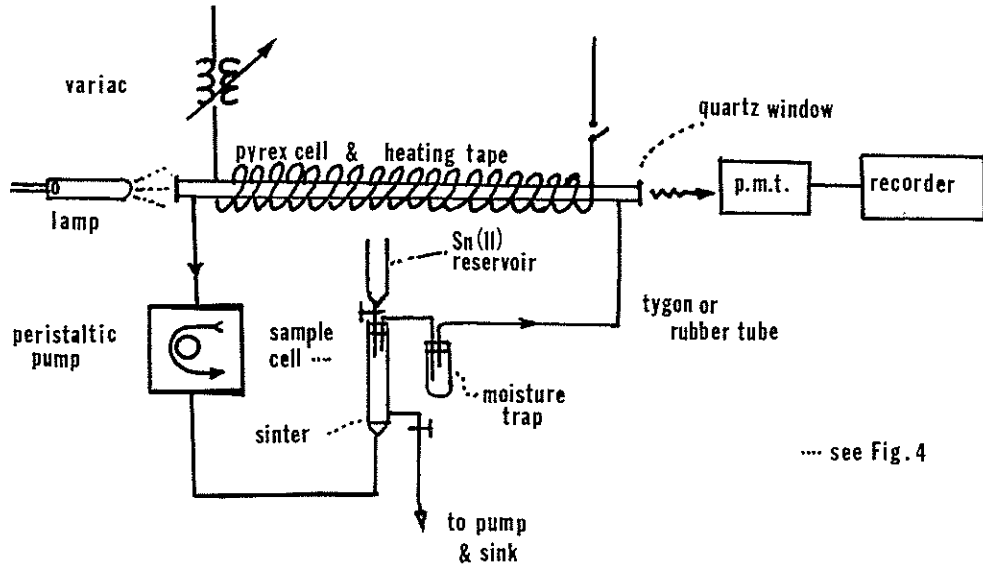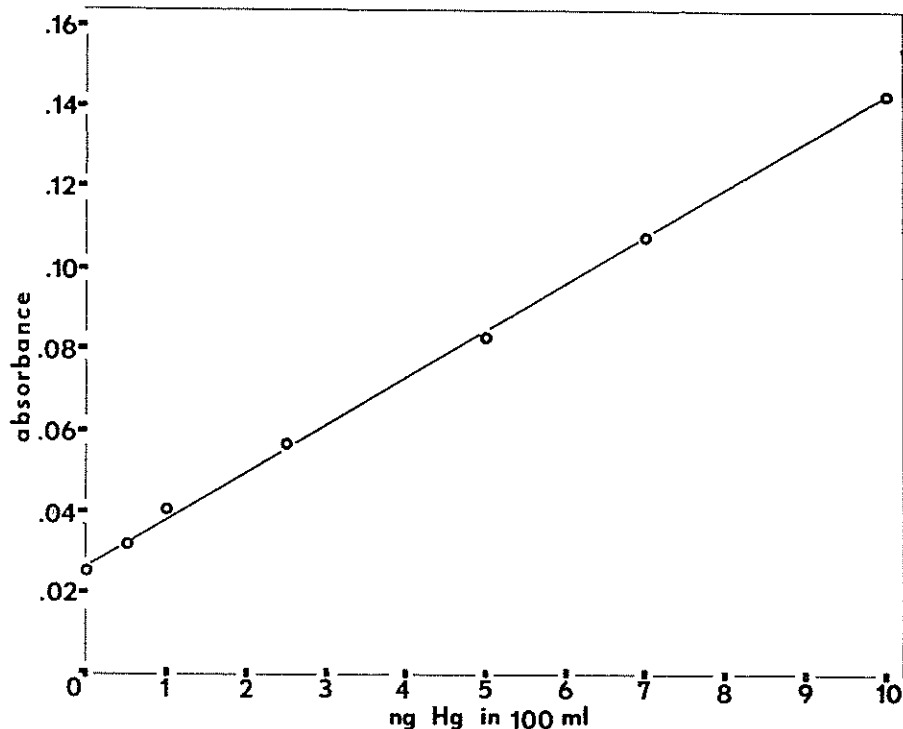
Figure 1. Instrumental apparatus: in situ.

Figure 2. Instrumental apparatus: schematic.

Instrument: Techtron AA5; Cell length: 1 metre;
Slit Width: 100μ; Wavelength: 253.7 nm;
Lamp Current: 4 ma.; Scale Expansion x 5.

Figure 3. Standard curve: example.

sample until all obvious chemical action has ceased.   Upon dilution to 100 ml with
water, when the dilute leach solution would again be restored, the samples were
removed to a water-bath for 1.5 to 2 hours as already described.   It was found that
an acid solution of tin (II) sulphate was all that was necessary to completely liberate
elemental mercury.   The quantity added is more than enough to account for all other
oxidants (ferric ion, certain organics, etc.) which may be present in the leached
samples.   Sulphate was originally considered superior to the chloride salt of tin (II)
for two reasons; the first being that the sulphate salt was relatively free of mercury
impurities, although it is now routine to aerate the tin (II) solutions before use to
flush out residual mercury.   The second reason is that in the presence of significant
chloride concentrations copper (II) is reduced to copper (I) which may precipitate
and carry down mercury when samples of, say, chalcocite or chalcopyrite are under
examination.   This reaction is inoperative if tin (II) sulphate is used instead.
Recently, tin (II) chloride was used without adverse effect after dissolving in dilute
sulphuric acid.   Readings for blanks and standards were almost identical to read-
ings obtained with tin (II) sulphate.   The use of tin (II) chloride as reducing agent
gave almost identical readings to those obtained with tin (II) sulphate.

Water Samples

Water samples are subjected to a different chemical treatment.   Some men-
tion has been made previously (Hornbrook and Jonasson, 1971) of the difficulties
inherent in water analysis for mercury and of the steps taken to overcome them.   It
has been found to be judicious to analyze all water samples within two months of
collection to avoid possible laboratory contamination of the samples.

The method devised for field samples overcomes many difficulties. It is often reported that mercury is lost from aging water samples as a result of chemical or bacterial volatilization reactions, or both, even in the presence of mineral acids (pH 1 or 2), (Shimomura et al., 1969; Toribara et al., 1970; Oki and Watanabe, 1971). It may also be lost from solution upon adsorption onto the container walls. (Benes, 1969; Benes and Rajman, 1969; Coyne and Collins, 1972). The method adopted to avoid these problems permits the sample to be treated with a chemical preservative in the field after which it may be stored indefinitely in a mercury-free environment. Water samples are collected in screw-stoppered polyethylene bottles of 200 ml capacity. To each 100 ml of unfiltered sample, 1 ml of 5% w/v potassium permanganate solution and 2.5 ml of concentrated sulphuric acid are added. The effect is to destroy most active reducing bacteria and to oxidize potentially complexing or reducing organic material. All mercury, now present as mercuric ions, slowly co-precipitates with manganese dioxide as the latter is formed from decomposing permanganate. In this way, the mercury is trapped in an oxidizing, solid matrix from which no volatilization is possible. When the sample is required for analysis, 2 ml of 5% w/v oxalic acid solution is added which redissolves all manganese oxides and reduces any residual permanganate. Mercury (II) is reduced to mercury (I) in this step. The sample is then treated with 15 ml of 5% w/v tin (II) sulphate solution and analyzed for mercury as described for solid samples. It is imperative that, once the oxalic acid is added, the analyses are rapidly completed. Under no conditions can the samples be stored overnight since mercury (I) is partially reduced further to mercury (O) with the passage of time in the presence of oxalic acid.

PREPARATION OF STANDARD CURVES

Prepare one litre of 1000 μg/ml Hg standard by weighing 1.354 g of pure mercuric chloride and dissolving in 1000 ml of M H_2SO_4 in a volumetric flask. This solution, (A), represents the base standard which is stable indefinitely.

From (A) prepare a standard, (B) of concentration 1μg/ml ($\equiv$1000 ng/ml). The secondary stock solution (B) should be prepared freshly each day.

To prepare a standard curve which will cover the useful range of Hg concentrations expected in the samples, prepare 15 blank solutions which represent the dilute acid leach; i.e., add 20 ml concentrated HNO_3, 1 ml concentrated HCl and 80 ml distilled water to the test tubes (38 by 200 mm). The aim is to produce a curve made up of individual standards of 0, 5, 10, 25, 50, 75, 100, 250, 500, 750 and 1000 ng Hg, plotted against absorbance at 253.7 nm wavelength. Each standard is best prepared separately before running the next. The method used in our laboratories employs a series of Eppendorf microlitre automatic pipettes. The standard curve is constructed according to the dilutions displayed in Table 1.

A standard curve applicable to water analyses is prepared similarly but with the addition of 1 ml of 5% w/v $KMnO_4$, 5 ml of concentrated H_2SO_4 and 2 ml 5% w/v oxalic acid to each standard solution. Permanganate solutions may be prepared weekly. The concentration range of the standards should cover 1 ng up to 25 ng, as may be required. A typical example curve is displayed in Figure 3 (after Hornbrook and Jonasson, 1971).

Table 1

Preparation of standard curve

Vol. Solution B (μl)	ng Hg in 100 ml
0	0
5	5
10	10
15	15
20	20
25	25
50	50
70	70
100	100

THE INSTRUMENTS AND CELL DESIGNS

The atomic absorption spectrometer used for Hg analyses is a Varian-Techtron, Model AA5 with a special 1.5 metre optical rail on which are mounted the lamp, optics and cold vapour cell (Fig. 1). The following instrumental parameters were used:

Rock, soil, sediment and ore samples:

Lamp Current:	4 mA
Gain:	3 to 4
Mode:	absorbance; auto 100
Scale Expansion:	x 5
Damping:	B
Wavelength:	253.65 nm
Cell Dimensions:	length, 30 cm; diameter, 2.5 cm
Slit:	100 microns
Chart Speed:	0.75 in/min.
Manostat Pump Speed:	5 (arbitrary)

Note: These parameters apply *only* to a Techtron AA atomic absorption spectrophotometer.

Water Samples:

As above, except for:

Gain:	5 to 6
Cell Dimensions:	length, 1 m; diameter, 2 cm

The cells are of pyrex construction with quartz end-windows cemented in place with epoxy resins. Windows may be readily removed simply by carefully heating them with the flame from a glass blower's torch. Sample inlet and outlet should be placed as near to the end-windows as practicable. Cells may be rapidly cleaned with a 1% solution of KOH. The cell used for solid samples covers a useful

range from 2 ng Hg to 1000 ng Hg in a given sample; the cell for water samples covers a range 1 ng to 500 ng. Thus for a 500 mg solid sample, the mercury contents are measured between 4 ppb and 2000 ppb; whereas for a 200 ml water sample the measured contents will cover 0.01 ppb to 2.5 ppb Hg where most natural waters would fall. Samples falling outside these ranges are treated by repeating with a larger or smaller sample, as the case may be; or if very high, by an appropriate dilution of an aliquot of the sample leachate. In this way all possible concentrations of mercury up to 0.n% levels can be analyzed. Results are quoted in ng/g, i.e., ppb, for all samples including waters, where 1 ml is considered to weigh 1 g.

Figures 1 and 2 show that each cell is bound in heating tape which allows the cell to be heated to between $90°C$ and $100°C$. The reason lies in an earlier observation made during development work that water vapour interfered (positively) by either condensing on the end-windows or by a fogging effect which scattered the light beam. The use of a magnesium perchlorate water-trap was not found to be very satisfactory for two reasons. First, it very quickly became saturated with moisture and had to be changed every three or four samples and secondly, there was some loss and dispersion of Hg on the magnesium perchlorate which reduced sensitivity and induced "memory" effects on subsequent samples. The problem was overcome by heating the cell unit to prevent condensation. The result was to minimize and to greatly stabilize background signals, especially in water samples where quite small Hg signals were to be read. Use of the heating tape also greatly reduces memory effects. Cells are held in place in the light beam by means of specially designed adjustable clamps.

ANALYTICAL PROCEDURES

Determination of mercury in rock, soil and sediment samples

1. To a clean, dry test tube (38 by 200 nm) add a weighed sample (500 or 1000 mg) of finely powdered rock (-150 mesh) soil or sediment sample. The latter two usually consist of a sieved fraction, at least -80 mesh or finer.

2. Add 20 ml concentrated nitric acid and 1 ml of concentrated hydrochloric acid. Allow to stand 10 minutes and then add 80 ml metal-free water. Heat for 1.5 to 2.0 hours in a water bath at $90°C$. Swirl occasionally.

3. Remove from water bath and cool to room temperature.
   Note: Before taking any absorption measurements the atomic absorption spectrophotometer and the peristaltic pump should be warmed up and stabilized.

4. Add 15 ml of 5% w/v $SnSO_4$ in M H_2SO_4 and immediately connect test tube to evolution apparatus. The mercury is then aspirated through the absorption cell.

5. Record the maximum absorbance reading and calculate mercury content in nanograms using a standard curve which has been prepared the same day.

$$\text{ppb Hg} = \frac{\text{ng Hg}}{\text{sample weight (g)}}$$

Rock samples which have been treated in this way in the Geochemistry Section's laboratories include granitoids, greenstones, volcanic extrusives, schists,

black shales, marbles and serpentinites. Sediment samples include both lake and stream silts, gyttjas, gels and clays. Soils from all horizons including mulls, and till samples have also been treated by this method.

Extensive studies have been made of mercury in black shales (Cameron and Jonasson, 1972) and in granitoids (R. G. Garrett, pers. comm.).

For highly organic soils (humus, etc.) or organic sediments (gyttjas, gels, sapropels, etc.), the procedure is modified slightly. Before the mercury vapour is aspirated into the cold-vapour cell, a few drops of a silicone anti-foam agent are added to both samples and standards. (Recommended is "Anti-foam": Instrumentation Laboratory Inc., Boston, Mass.)

Determination of mercury in sulphide ores

1. To a clean, dry test tube (38 by 200 mm) add a weighed sample of finely powdered ore sample (250 mg).

2. Add 20 ml concentrated nitric acid and 1ml concentrated hydrochloric acid. When the sulphide is *decomposed* ($\approx$10 min.) add 80 ml metal-free water and heat for 1.5 to 2.0 hours in a water-bath at 90°C. Swirl occasionally.

3. Remove from bath and cool to room temperature and treat as for rocks, soils and sediments, after appropriate dilutions, where necessary, are made. Different sulphides take varying times to decompose. Sometimes it may be necessary to warm the concentrated acid mixture before dilution.

Determination of mercury in waters and snows

Some developmental aspects of this method were discussed in an earlier publication by Hornbrook and Jonasson (1971) to which the reader is referred for further details. The analytical procedure is as follows:

1. 100 or 200 ml of the sample, previously treated with acidic potassium permanganate solution and then with oxalic acid solution, is placed in the specially designed aspiration vessel (Fig. 4).

2. Add 15 ml 5% w/v $SnSO_4$ in M H_2SO_4 and aspirate the mercury into the long absorption cell (1 m). Read absorbance.

3. Calculate mercury content according to the standard curve prepared previously.

   Snow meltwater is treated in precisely the same way as other water samples, except that twigs and other dead-fall debris are removed by very coarse, rapid filtering. Snow samples are usually stored in a freezer, thawed prior to treatment with acidic permanganate solution, and then left for one day.

Operation of the Atomic Absorption Spectrophotometer

1. Turn on instrument and allow 30 minutes for instrument and hollow cathode lamp to warm up as described in the instrument instruction manual.

2. Attach mounting brackets on optical rail and clamp absorption cell in place. Make vertical and horizontal adjustments to the mounting bracket so that a minimum "gain" is used on the photomultiplier tube.
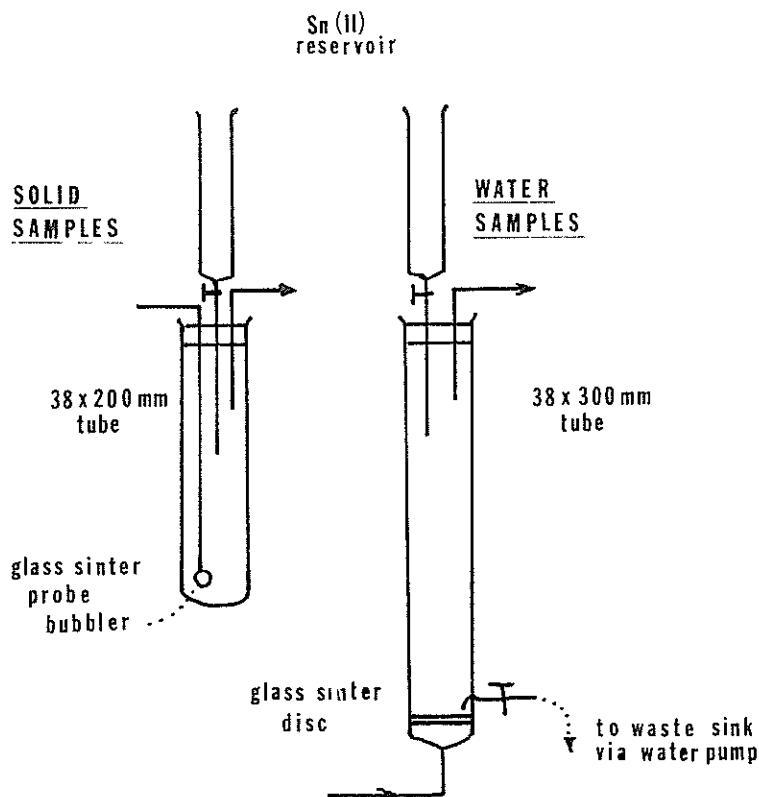
Sn (II)
reservoir

Figure 4. Designs of Aspiration Cells.

3. The speed of the peristaltic pump is somewhat arbitrary. If it is too slow
    the instrument response is sluggish and if it is too fast there is a carry-
    over of mist into the absorption cell.

PRECISION AND ACCURACY OF THE ANALYTICAL PROCEDURES

The authors are indebted to Dr. R. G. Garrett of the Geochemistry Section
for his assistance in preparing this discussion on precision and accuracy of the
analytical methods outlined above.

The data are presented in table and graphical form. Samples utilized in
this study were both field specimens and "in-house" control standards. They may
be described thus:

Q-12:   a powdered shale; used as a control standard.

SS-26-2:   a lake sediment composite, ($\leq$65 μm) less than 1% organic carbon;
            used as a control standard.

LC-11:   a stream sediment sample ($\leq$65 μm) enriched in carbonates; used as
            a control standard.

BB-2:   a podzolic soil sample, collected from the B horizon of a sequence
            ($\leq$180 μm); used as a control standard.

BG-C: a podzolic soil sample, collected from the C horizon of a sequence
            ($\leq$180 μm); used as a control standard.

The above control samples were subjected to multiple repeat analyses for mercury. Q-12, BB-2 and GB-C were used as controls over a period of two years. The analytical data for these controls and presented in Tables 2, 5 and 6 and in Figures 5 and 6, were collected from the files and therefore represent reproducibility of the analyses over that two-year period. LC-11 and SS-26-2 data represent same-day repeat analyses. "SULPH" represents a series of duplicate analyses of a suite of sphalerites and galenas collected mainly from sulphide deposits of Ontario. Samples were supplied by Dr. D.F. Sangster, Mineral Deposits Section, Geological Survey of Canada. A suite of granitoid rocks of Cretaceous age were supplied by Dr. R.G. Garrett. These too were subjected to duplicate analyses for mercury. This study of granitoids formed part of a broad survey of the granitoid plutons of the Yukon in which major and trace element content variations were investigated in detail. In this report these samples are designated G_{sd}; i.e., duplicate analyses on the same day; and G_t, i.e., duplicate analyses from several runs over a period of one month. Results presented give information on arithmetic and geometric means, standard deviations, coefficients of variation and precisions at the 95% confidence level.

Table 2. Q-12

n	$\overline{X}a$	δa	CVa	P95%a	$\overline{X}g$	log$\overline{X}g$	δg
59	136.1	13.89	10.2	20.4	135.3	2.1314	.0457

Table 3. SS-26-2

n	$\overline{X}a$	δa	CVa	P95%a	$\overline{X}g$	log$\overline{X}g$	δg
55	32.93	9.17	27.8	55.9	31.87	1.5034	.1089

Table 4. LC-11

n	$\overline{X}a$	δa	CVa	P95%a	$\overline{X}g$	log$\overline{X}g$	δg
59	40.27	6.32	15.7	31.4	39.79	1.5997	.0686

Table 5. BB-2

n	$\overline{X}a$	δa	CVa	P95%a	$\overline{X}g$	log$\overline{X}g$	δg
21	111.7	18.15	16.2	34.0	110.3	2.0427	.0685

Table 6.   BG-C

n	$\bar{X}a$	δ a	CVa	P95%a	$\bar{X}g$	log$\bar{X}g$	δ g
22	29.68	6.94	23.4	48.9	28.98	1.4621	.0954

Table 7.   Duplicate Pairs: SULPH

n pairs	$\bar{X}a$	δ a	CVa	P95%a	$\bar{X}g$	log$\bar{X}g$	δ g
62	235.6	6.78	19.5	39.0	97.13	1.9833	.1044

Table 8.   Duplicate Pairs: G. same day

n pairs	$\bar{X}a$	δ a	CVa	P95%a	$\bar{X}g$	log$\bar{X}g$	δ g
19	27.05	8.43	31.2	65.52	13.5	1.1299	.1431

Table 9.   Duplicate Pairs: G. total (all pairs)

n pairs	$\bar{X}a$	δ a	CVa	P95%a	$\bar{X}g$	log$\bar{X}g$	δ g
62	17.03	5.77	33.9	67.8	10.4	1.0170	.1649

Figure 5 presents a plot of the coefficient of variation (C.V.) against mean mercury content for *all* samples. From the plot the precision of the method, (approximately twice C.V.) may be determined at any point in a concentration range 0-250 ppb Hg. In general, C.V.a at low levels is about ±30% and improves to ±10% for mean (arithmetic) mercury contents ≥250 ppb.

Finally, a check of the method on various U.S.G.S. standard rock samples was made by Cameron and Jonasson, 1972 (Table 10). From the study it is apparent that the old standards are heterogeneous with respect to Hg, especially for G-1. The newer standards produce Hg contents systematically higher than many of the reported literature values.

These data are particularly interesting in view of the more recent systematic study made by McNeal et al. (1972) of the inhomogeneity of mercury in U.S.G.S. standard rocks, both old and new. Their conclusion, with which the present authors concur, is that the U.S.G.S. standard rocks ought not be used as mercury standards.

INTERFERENCE STUDIES

Preliminary remarks:

When routine analyses for mercury in geological materials were first applied to studies of different common sulphide ores, it was observed that serious interferences with the absorption signal sometimes appeared. This was especially so with some chalcopyrite samples. The nature of the interference is such that the mercury signal rises rapidly to a maximum but then just as rapidly falls off again towards zero absorbance; i.e., evolved mercury is being removed from the recycling plug of vapour. Further study revealed that elemental tellurium, formed almost simultaneously with elemental mercury upon addition of tin (II) to the sample solution, was the prime interfering agent. Later, precipitated gold metal was shown to have similar effects on mercury determinations in soil samples from certain areas around Yellowknife, N.W.T. It has long been known that tin (II) ions will reduce a number of metal ions to the zero-valent state; e.g., Au, Pt, Pd, Te, Se, Hg and Ag, under certain conditions of acidity. The presence of certain complexing anions, e.g., Cl⁻ in fair excess, suppresses or retards these reductions indicating that complex anions formed are more difficult to reduce. A few attempts have been made to investigate the effects of added metal ca'ions on the accuracy of cold vapour methods. Poluektov and his colleagues (Pol uektov et al., 1963, and Vitkun et al., 1970) found no effects by Li, Na, K, Cs, Cu, In, Zn, Cd, Pb, V, Bi, Be, Mg, Ca, Sr, Ba, Al, Zr, Mo, W, Mn, Fe, or Co, when adding quantities of these metal ions up to 5 mg/ml in the presence of 0.5 µg/ml Hg. Cu, Zn, Cd, Mg, Ca and Al were further tested up to approximately 30 mg/ml with no effect on 0.1 µg/ml Hg. However, they did find that small amounts of Te, Se, Au, Pt and Ag produced significant interferences on 0.1 µg/ml Hg; $\geq$0.1 µg/ml Te and Au, $\geq$100 µg/ml Se and $\geq$1 µg/ml Pt were the critical quantities. It would appear from Poluektov's work
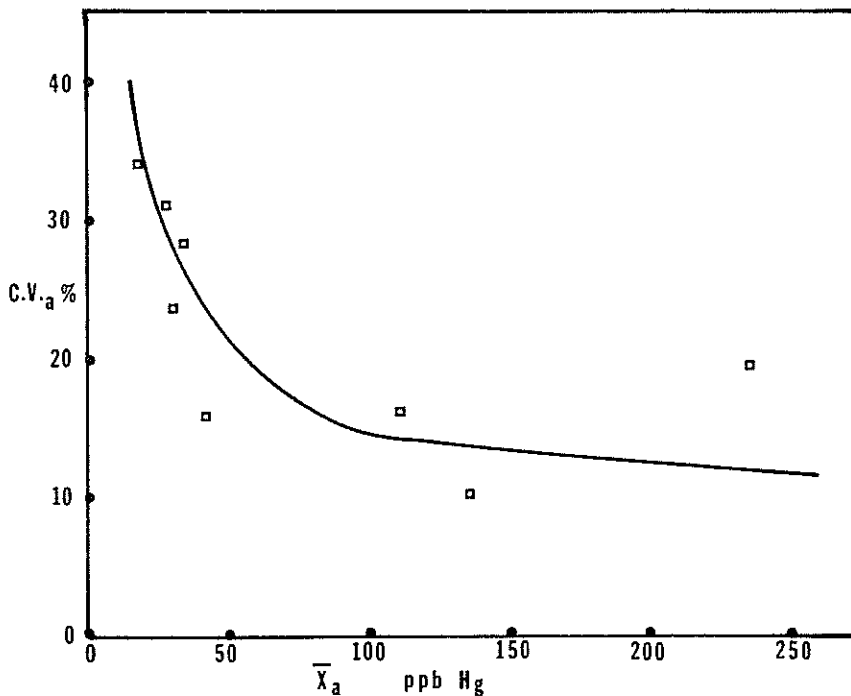

Figure 5. Arithmetic coefficient of Variation.

that interference is significantly greater in the atomic absorption mode than in the atomic fluorescence mode. Since the nature of interference is the scavenging by precipitated metals of elemental mercury to form amalgams, this observation is difficult to understand. Huffman et al. (1972) recently reported interferences by Au >4μg and Se >10μg.

This present work is a more intensive attempt to catalogue the interference effects of Se, Te, Au, Pt, Pd, Ag and S. The interference agents were all added to solutions of various mercury concentrations in the form they would be expected to take after oxidative attack by the leach solution upon a pristine sample; viz., Se as selenate, Te as tellurate, Au as a chloro-aurate, Pd as a chloro-palladate, Pt as a chloro-platinate, Ag as argentous (Ag$^+$) ion and sulphur as the polymeric, rubbery form known as plastic sulphur. In the case of sulphide oxidation by nitric acid, quantities of elemental sulphur often form, usually in lumps. Since sulphur is used to clean up Hg spills in laboratories, it was resolved to check on its potential for interfering with the evolution of mercury vapour.

Preliminary experiments indicated that a definite kinetic effect was operating on the system such that the degree of interference observed depended on the lapsed time between addition of Sn (II) to the system and when the mercury vapour was flushed out. Because the mercury is recycled through the host solution it is partially resorbed by freshly precipitating metal on each pass. In this way the rate of mercury uptake was observed qualitatively. Moreover, it was observed that mercury is released as metal *more* rap.dly than any of the interfering agents, so it was often possible to flush the mercury once around the system before interference became significant. The experiments were therefore arranged so that mercury vapour could be flushed out of the host solution within a second or two of the Sn (II) reductant being added. In this way interferences can be minimized. The procedure
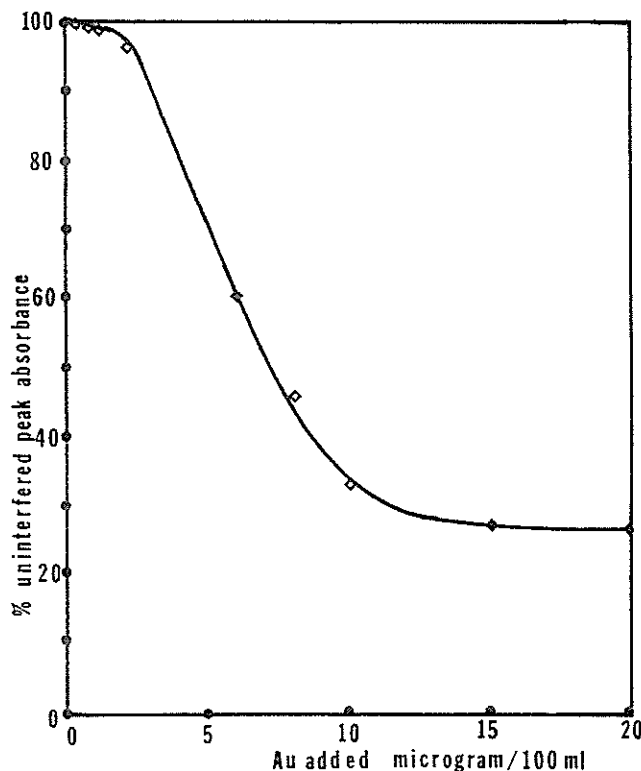

Figure 6. Effect of Gold on 25 ng Hg.
(Similar profiles for 5, 10, 100, 500 ng)

Table 10

Mercury determinations on standard rock samples as ppb Hg*

Standard rock	Fleischer (1965) neutron activation	Fleischer (1969) neutron activation	Ehmann and Lovering (1967) neutron activation	Laul et al. (1970) neutron activation	Ishida et al. (1970) neutron activation	This study
W1	170	110		94		212, 212, 241, 292
AGV-1			4	16		55, 57
PCC-1			4	3.6		20, 22
G-1	340	245		70	120	118, 142, 156, 225
G-2			39	29		64, 78
GSP-1			21	41		36, 36
BCR-1			7	4		34, 36
DTS-1			4			30, 34

* after Cameron and Jonasson (1972).

Standard rock	McCarthy (see Fleischer, 1965; and Flanagan, 1969) atomic absorption	Hatch and Ott (1968) atomic absorption	Omang and Paus (1971) atomic absorption	Weissberg (1971) atomic absorption	Muscat and Vickers (1971) atomic fluorescence	This study
W1	340	180	260	280	180	212, 212, 242, 292
AGV-1	15		27	25		55, 57
PCC-1	10			5		20, 22
G-1	130	95		97		118, 142, 156, 225
G-2	50			40		64, 78
GSP-1	15			15		36, 36
BCR-1	5			18		34, 36
DTS-1	8			12		30, 34

Note: Our data for W1 and G1 are single determinations on four separate bottles of each standard. Data for other standards are duplicate determinations on one bottle of each standard.

developed is now used routinely in our laboratories so that potential interferences in all samples can be detected and roughly estimated. The mercury contents recorded in this section are those derived from absorbance measurements of the first pass of the vapour plug through the absorption cell.

Effect of gold:

Figure 6 indicates the effect of added gold on the analytical procedure. Interferences are expressed as percentage decrease from the expected mercury signal if no gold were present. For mercury concentrations between 5 and 500 ng/100 ml, it is clear that gold concentrations must exceed 3 µg/100 ml before significant interference occurs, i.e., when the expected Hg signal is reduced by more than 10 per cent. For a sample weight of say, 500 mg, this last figure would be equivalent to a gold content of 6 ppm; which would be very unusual in most soils or rocks likely to be encountered in routine geochemical surveys.

Effect of palladium:

Figure 7 indicates the effect of added palladium on the analytical procedure. For mercury concentrations between 5 and 100 ng/100 ml, the level of palladium must reach 15 µg/100 ml before interference becomes significant. This would be equivalent to a palladium content of 30 ppm in a 500 mg geological sample.

Effect of platinum:

Figure 8 illustrates the effect of added platinum on the analytical procedure. For mercury concentrations between 5 and 100 ng/100 ml, the platinum content must exceed 1 µg/100 ml before interference occurs. This content would be equivalent to a platinum content of 2 ppm in a 500 mg geological sample. Such levels might occur occasionally in certain ultramafic rocks or nickel ores.

Effect of tellurium:

Figure 9 presents data on the interference of tellurium on the analytical procedure. For mercury concentrations between 5 and 500 ng/100 ml, the interference by tellurium does not become significant until a content of 4 µg/100 ml is present. This would be equivalent to a tellurium content of 16 ppm in a 500 mg geological sample. Because tellurium is reasonably abundant in certain types of base metal sulphide deposits and in some gold ores, it might be anticipated that interferences would be manifest in Hg analyses of ore materials.

Effect of selenium:

No deleterious effects on the analytical procedure were observed even when 1000 µg Se were added. It is probable that $SeO_4^=$ is not reduced by tin (II) ions under the conditions of test.

Effect of silver:

No effects were observed on the addition of up to 10,000 µg Ag^+ to the test solutions containing 100 ng Hg/100 ml. Silver (I) does not reduce to silver (O) under the conditions of the routine analytical procedure.
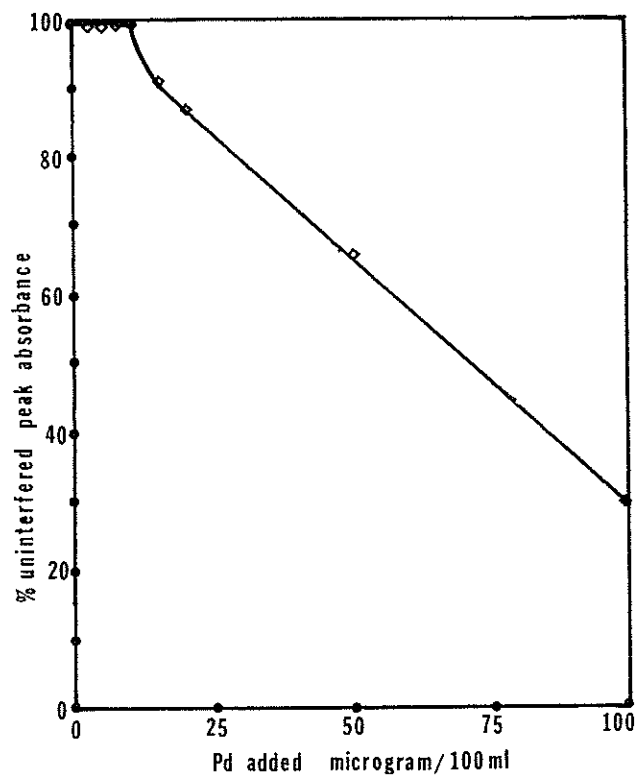
Figure 7. Effect of Palladium on 25 ng Hg.
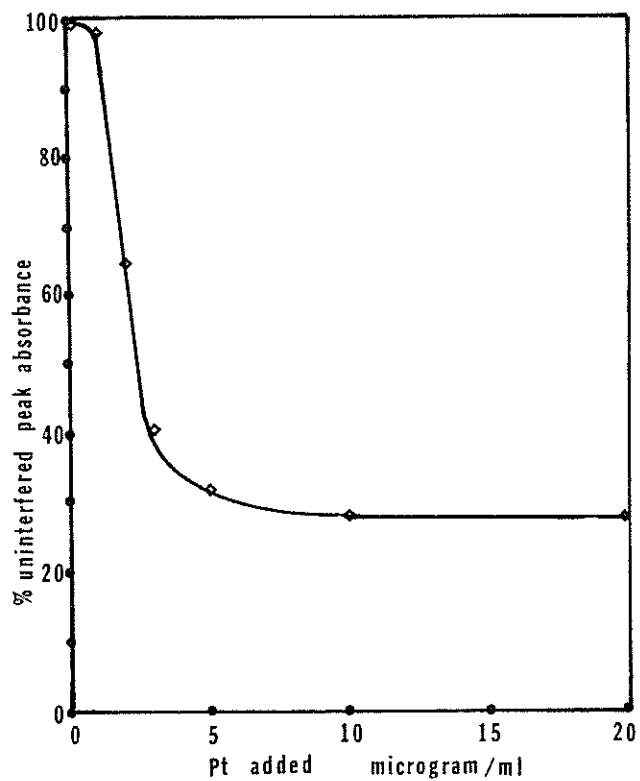(Similar profiles for 5, 100 ng)

Figure 8. Effect of Platinum on 25 ng Hg.
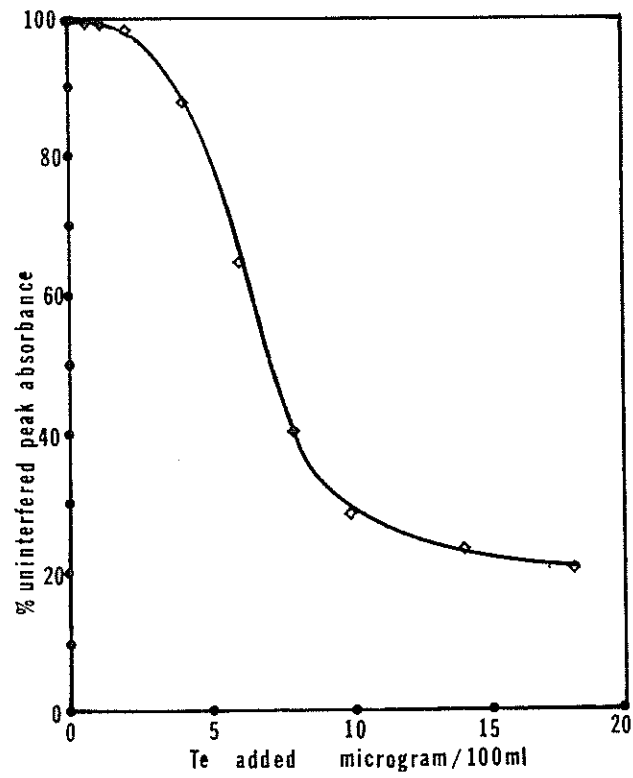(Similar profiles for 5, 10, 100 ng)

Figure 9. Effect of Tellurium on 500 ng Hg.
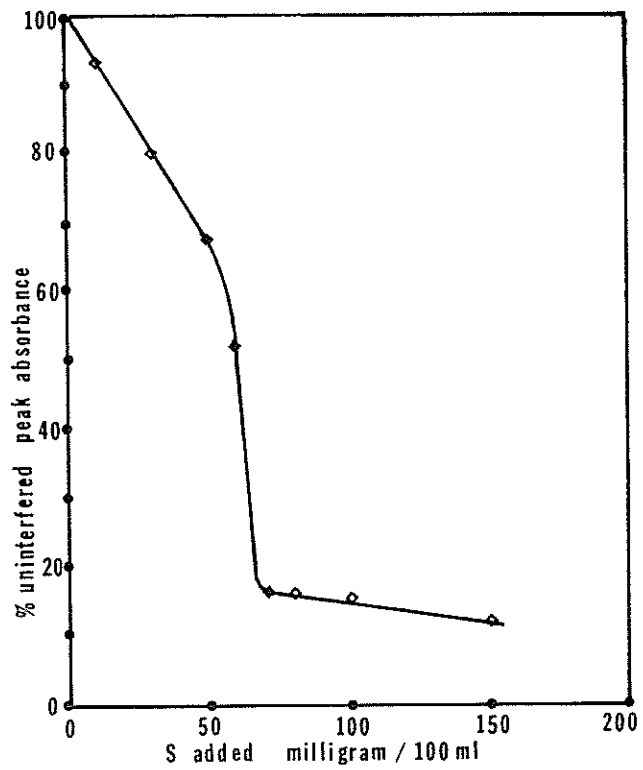(Similar profiles for 5, 50 ng)

Figure 10. Effect of Sulphur (flowers) on 100 ng Hg.

Effect of sulphur:

No effects were observed on the addition of up to 1g of small particles of plastic sulphur. Consequently no interferences are anticipated in sulphide analyses where this material may be formed in the sample solution.

To further test the effects of sulphur, small quantities of finely powdered "flowers" of sulphur were added with stirring to test solutions containing 100 ng Hg/100 ml. Figure 10 shows the results.

The addition of 15 mg of sulphur dust induces significant interference in the mercury procedure. Sulphur dust undoubtedly is very efficient in scavenging dissolved or free mercury vapour, but it should not cause a problem unless uncontrolled decomposition procedures permit the formation of such very finely divided sulphur.

Effect of copper:

It has sometimes been reported that copper present in high concentrations interferes with mercury evolution from a sample solution. Tests with 0.500 g of chalcocite samples and 0.500 g of chalcopyrite samples reveal no such interference. In nitric acid solutions low in chloride, Cu(II) is not readily reduced to Cu(I) (Nunes, 1970) which would form large flocculent precipitates of CuCl causing Hg to be coprecipitated. In hydrochloric acid solutions or nitric acid solutions enriched with HCl, this reduction step *does* occur. Interferences with copper can therefore be easily circumvented by keeping chloride concentrations to a minimum. It is worth noting that copper was present in the test solutions at a maximum concentration of 4 mg/ml in the case of chalcocite samples, and at 1.7 mg/ml in the case of chalcopyrite samples. Several hundred reliable mercury determinations have been made on chalcopyrite samples using the method described for ores.

Summary:

The effects of various reducible metal ions have been investigated. Of these only tellurium and perhaps platinum should be regarded as common hazards. Certain gold ores may also cause problems. In the case of significant interference by gold in rock samples, a technique was developed whereby Hg could be easily removed from the gold before analysis. For example, Hg was determined in gold nuggets after the Hg was distilled from the molten sample and resorbed into a plug of wet manganese dioxide-coated glass wool which was then measured for Hg content in the usual manner.

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