ANALYSIS OF ROCKS AND SEDIMENTS FOR MERCURY, BY WET DIGESTION AND FLAMELESS COLD VAPOR ATOMIC ABSORPTION

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CONVERSION FACTORS

For those readers who may prefer to use inch-pound units rather than the metric (SI) unit, the conversion fctors for the terms used in this report are listed below:

Multiply metric (SI)	By	To obtain inch-pound unit
	Length	
millimeter (mm)	3.937×10^{-2}	inch (in.)
nanometer (nm)	3.937×10^{-8}	inch (in.)
	Weight	
gram (g)	3.527×10^{-2}	ounce, avoirdupois (oz)
	Flow	
milliliter/minute (mL/min)	2.6417×10^{-4}	gallons/minute (gal/min)
	Volume	
milliliter (mL)	3.382×10^{-2}	ounces, fluid (oz)
liter	33.82	ounces, fluid (oz)
	Temperature	
degree Celsius (°C)	°F = 9/5°C + 32	degree Fahrenheit (°F)

ANALYSIS OF ROCKS AND SEDIMENTS FOR MERCURY, BY WET DIGESTION AND FLAMELESS COLD VAPOR ATOMIC ABSORPTION

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ABSTRACT

An accurate and precise method for the determination of mercury in rocks and sediments is presented. The method requires a minimum of 250 milligrams of sample and employs a wet digestion using a combination of nitric and hydrochloric acids. Quantitation is by cold vapor atomic absorption spectrophotomerey. Comparison of data generated by this procedure with data for U.S. Geological Survey Standard Rocks, National Bureau of Standards Sediments, and National Bureau of Standards Tissue Standards, as well as through interlaboratory comparisons on natural sediments and mineralized samples (sphalerite, pyrrhotite), indicate that precise and accurate results can be obtained.

INTRODUCTION

The chemical analysis of rocks and sediments is performed for a variety of environmental and petrological purposes. This is especially true for mercury because of its toxic nature and because of its use as an indicator in geochemical exploration. In addition, sediments generally contain significantly higher concentrations of mercury than are found in the overlying water; as such, they may be analyzed for possible contributions to the environment. Total values for mercury are only a beginning, as there are significant problems associated with the methlyated forms and their speciation would require additional analytical work. The importance of this type of analytical data is well established and has been used for decades.

Various wet digestion methods, for solubilizing the mercury in rocks and sediments prior to analysis, have been used and have been described in the literature (Hatch and Ott, 1968; Johnson and Maxwell, 1981). The method described herein represents a modification of the procedures described by Johnson and Maxwell (1981) and Bartha and Ikrenyi (1981). The upper and lower concentration limits are 50 and 0.1 micrograms per liter in solution, respectively. These values represent 5.0 and 0.01 µg/g in the original sample if no other dilutions have been made. Samples that contain mercury concentrations greater than the upper limit may be analyzed after appropriate dilution.

SUMMARY OF METHOD

A sample is ground, dried, and homogenized. It is then digested by a hot Lefort aqua regia solution (3:1 nitric to hydrochloric acids). The digestate is then preserved by the addition of potassium dichromate and diluted to a known volume with deionized water. The sample solution is made basic with potassium hydroxide, the mercury reduced to the metal with stannous chloride, purged from the liquid with nitrogen, and quantified by cold vapor atomic absorption spectrophotomerey (AAS).

INTERFERENCES

Volatile organic compounds can cause a positive interference; however, digestion with hot Lefort aqua regia will decompose organic matter (see table 2, National Bureau of Standards (NBS) oyster tissue and orchard leaves). Negative interferences exist with several easily reduced metals (Au, Ag, Cu, Pt, Se, and Te) (Bartha and Ikrenyi, 1981; Band and Wilkinson, 1972; Koirtyohann and Khalil, 1976; and Suddendorf, 1981). It is thought that these metals are reduced with the mercury and form amalgams with it, which renders the mercury nonvolatile, and thus undetectable. Addition of a 45-percent KOH solution through the pump channel prior to the addition of the $SnCl_2$ solution causes the interfering species to form oxides and(or) hydroxides which are not reduced, thereby eliminating this type of interference (Bartha and Ikrenyi, 1981).

Selenium is a good example of this type of interference. With acid reduction, addition of 25 µg/L Se^{+4} to a 25 µg/L Hg standard solution produced a 12 percent drop in absorbance; however, with alkaline reduction, addition of 10 mg/L Se^{+4} showed no effect.

APPARATUS

A Varian[1] model 975 atomic absorption spectrophotometer and a Varian model VGA 76 vapor generator (figs. 1, 2) with optional flow through mercury cell were used in conjunction with a Varian model PSC 55 autosampler in this study. Instrumental conditions are listed in table 1.

Hot plate (gas or electric) capable of reaching at least 150°C.

Drying tubes.

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[1] The use of brand names in this report is for identification purposes only, and does not constitute an endorsment by the U.S. Geological Survey.

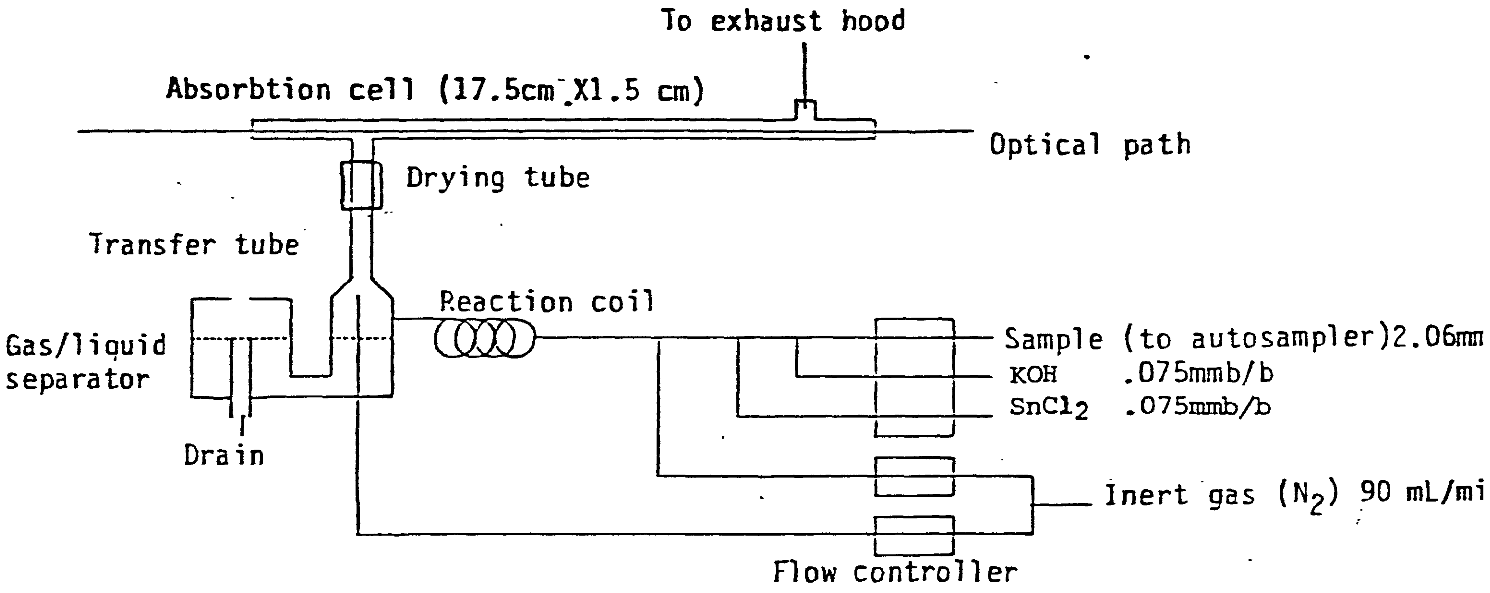

Figure 1. Schematic of the Varian VGA-76

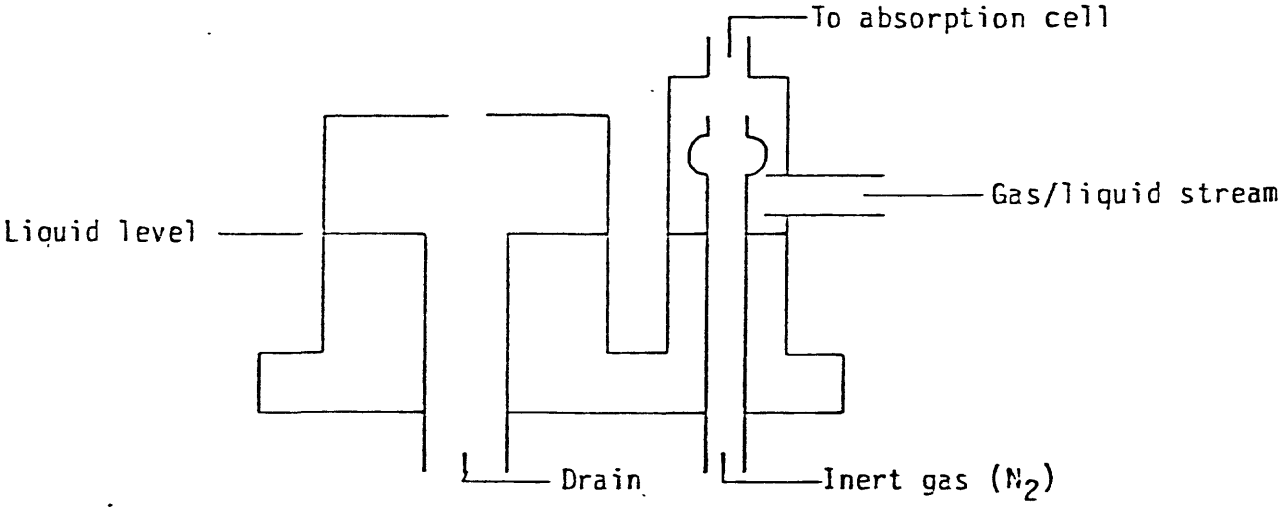

Figure 2. Gas/liquid separator

Table 1.--Instrumental settings used for this method

Instrument settings	
Wave length (nm)	253.7
Slit width (nm)	0.5
Lamp current (ma)	4.0
Integration time (s)	3.0
Background Corrector	On
Autosampler settings	
Rinse rate	1
Rinse time (s)	40
Delay time (s)	70
Multiples	3
Reslope rate	5
Vapor Generator (VGA 76)	
Base uptake tube (mL/min)	1
Reductant uptake tube (mL/min)	1
Sample uptake tube (mL/min)	7.5-8.0

REAGENTS

Hydrochloric acid, concentrated (sp gr 1.19).

Magnesium perchlorate, used as packing for drying tube[2].

Primary mercury standard used is a commercially available 1000 mg/L AA standard solution. Working standards of 2, 25, and 50 µg/L are prepared by serial dilution of the primary standard with the addition of nitric acid (10 percent v/v) and potassium dichromate (0.5 percent w/v) as preservatives.

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[2] A drying tube is used to prevent moisture carryover into the absorption cell where it can condense and cause erratic readings. The drying tube should be repacked or replaced daily, or more often, if caking (over 2/3 or more of the drying tube) or blockage occurs.

Nitric acid, concentrated (sp gr 1.41).

Potassium hydroxide solution, 45 percent w/v, commercially available.

Potassium dichromate solution, 5 percent w/v, dissolve 50 g $K_2Cr_2O_7$ in deionized water. Dilute to 1 L with deionized water.

Stannous chloride solution, 12.5 percent w/v, dissolve 125 g $SnCl_2 \cdot 2H_2O$ in 150 mL HCl (sp gr 1.19) and dilute to 250 mL with HCl (sp gr 1.19). Do not heat this solution to dissolve the $SnCl_2 \cdot 2H_2O$ as this will cause loss of reductive capacity. Dilute to 1 L with deionized water.

PROCEDURE

Immediately before each use, clean all glassware by rinsing first with (1+1) HNO_3 and then with deionized water. As an alternative, the glassware can be heated to 800°C for 1 hour to remove all traces of Hg. Dry the sample by freeze drying, oven drying at 105°C or 40°C, or air drying at room temperature[3]. If the sample weight is greater than 100 g, split it down to less than 100 g with a nonmetalic sample splitter (riffle splitter), or by coning and quartering. Grind the sample with a mixer mill or an agate mortar and pestle until all material is finer than 100 mesh. Weigh and transfer 0.5000 g of finely ground sample to a 125 mL Erlenmeyer flask; weigh out appropriate reference standard materials as well [NBS standard reference materials or U.S. Geological Survey (USGS) rock standards], and use several empty beakers as blanks[4].

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[3] A search of the literature has indicated that sample drying procedures can have a significant effect on Hg quantitation. Various procedures for drying samples prior to digestion and analysis have been recommended; these include air-drying, freeze-drying, or oven-drying at either 105°C or 40°C. Additionally, some procedures recommend that digestion and analysis be performed on a wet sample with subsequent moisture determination(s) done on separate sample aliquots. Corrections for moisture content are then made on the analytical results. An investigation of various drying procedures was made on several sediment and soil samples from various locations to determine the best procedure for drying (table 5). Statistical analysis of the data (a paired-t test and correlation coefficient) show no statistically significant difference ($t = 0.1562$) at a probability of 95 percent and the correlation coefficient (r) is 0.9953. The varibility seen would seem to be due to inhomogeneity in the samples. However, as previously noted, others have found significant differences in the analytical results based on drying procedures. Comparisons should be made to determine which procedure is most suitable to specific types of samples.

[4] This procedure can be used with sample weights between 0.2500 and 1.000 g. Sample weights greater than 1.000 g may cause erroneous readings due to unoxidized organic matter.

Place the hotplate in the hood and adjust it to produce a temperature of 150°C. Add 9 mL HNO_3 (sp gr 1.41) and 3 mL HCl (sp gr 1.19) to each flask and swirl to mix well. Allow to stand in the hood for approximately 20 minutes, or until excessive foaming stops, before placing on hotplate. Heat flasks on the hotplate for approximately 30 minutes or until the blanks become colorless.

Remove the flasks from the hotplate and allow to cool for 10 minutes. Add 5 mL $K_2Cr_2O_7$ solution to each flask[5] and quantitatively transfer the solutions to 50 mL graduated centifuge tubes. Dilute to 50 mL with deionized water and shake to insure thorough mixing. Centifuge the samples to settle the undissovled sediment. Alternatively allow the samples to stand overnight to settle. This solution represents a dilution factor of 100X.

Set up the atomic absorption spectophotometer, vapor generator, and autosampler according to conditions outlined in table 1 and figure 1. Allow the system to stabilize for at least 20 minutes using a rinse solution of 10 percent (v/v) HNO_3 in the sample line. Analyze the high (50 µg/L) standard and the blank solution alternately until stable readings are obtained for each. Analyze the samples, and any standard reference materials used, for Hg using the working standards (2, 25, and 50 µg/L. Dilute samples with deionized water, if required.

CALCULATIONS AND REPORTING LIMITS

Determine the concentration of Hg in the 100X solutions from the digital display, printer, or chart recorder, and record the results. The actual concentration of Hg in the sample, in µg/Kg, is obtained by multiplying the concentration in each sample by 100, if no other dilutions are made. To obtain a concentration in µg/g, divide the concentration of each sample solution by 10, if no other dilutions are made.

The reporting limit for Hg in solution is to the nearest 0.1 µg/L; i.e., the nearest 10 µg/Kg (or 0.01 µg/g) in the sample.

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[5] If there is an excess of unoxidized organic material remaining in the sample, it may be necessary to add additional 5 mL aliquots of the $K_2Cr_2O_7$ solution. This is evidenced by the orange color of dichromate changing to green.

PRECISION AND ACCURACY

The precision and accuracy of this method were determined by replicate analyses (actual separate digestions and subsequent quantitation) on four NBS standard reference materials and three USGS rock standards. The results are presented in table 2. As can be seen from the data, the method is capable of providing both precise and accurate analytical results.

Table 2.--Comparison of reported concentrations with those found by this method

[Concentrations in mg/kg]

		Concentration of mercury	
Standard	Number of replicates	Determined	Reported value
NBS Esturine Sediment	15	0.06 ± .016	0.063 ± 0.013
NBS River Sediment	12	.92 ± .09	1.1 ± .5
NBS Oyster Tissue	4	.04 ± .005	.057 ± .015
NBS Orchard Leaves	7	.12 ± .01	.155 ± .015
USGS G-2	8	.04 ± .01	.049 ± .013
USGS SCO	9	.07 ± .01	.052 ± [1].002
USGS MAG-1	5	.05 ± .008	.043 ±

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[1] Values reported by Flanagan et al (1982).

CONCLUSIONS

To further evaluate the precision and accuracy of this method, six field-collected samples were dried, digested, and analyzed. The samples came from different geological settings (Belle Fourche River, South Dakota; Mine Tailings from the Homestake mine, South Dakota; soil samples from the flood-plain of the Shenandoah River, Virginia; Colombia Slough, Oregon; and Ned Wilson Lake, Colorado). These samples were dried, ground, and analyzed, and then sent to another laboratory for dissolution and subsequent quantitation. Results of the two sets of data are presented in table 3. As an evaluation of the effectiveness of the Lefort aqua regia digestion on mineralized sulfide samples, sulfide ore samples were obtained from the U.S. Geological Survey, Branch of Analytical Services, Reston, Va. These were digested and analyzed and the results are presented in table 4. The data cited above indicate that this method can be used with good precision and accuracy on a wide variety of sediment, soil, and rock samples.

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Table 3.--Interlaboratory comparison of data for selected sediment samples

[Concentration in mg/kg]

Sample	Concentration of mercury	
	This method	USGS, Reston, Va.[1],[2]
NBS Esturine Sediment	0.06	0.07
Belle Fourche River near Sturgis, S.D.	2.64	2.4
Oxidized Mine Tailings	.57	.53
Shenandoah Valley site M-1-5 FP	5.5	5.1
NBS River Sediment	.95	.75
Shenandoah Valley site 20-1-FP	22	23
Columbia Slough	.09	.083
Ned Wilson Lake	.06	.038

[1] U.S. Geological Survey, Branch of Analytical Services, Reston, Va.

[2] Sample is digested with a combination of HNO_3, $HClO_4$, and HF in a sealed Teflon bomb, the mercury is reduced with stannous chloride solution and collected on gold chips. The mercury is then thermally desorbed from the gold chips and swept into an analytical cell for quantitation. Conversations with Phil Aruscavage, U.S. Geological Survey, Branch of Analytical Services, Reston, Va. (oral commun., 1985), indicate that this procedure may be subject to the same selenium interferences (suppression) as the acidic reduction method.

Table 4.--Effectiveness of Lefort aqua regia digestion on mineralized sulfide samples

[Concentration in mg/kg]

Sample[1]	Concentration of mercury	
	This method	USGS, Reston, Va. [2], [3]
365	48	40
377	1.7	1.2
379	0.66	.60
389	.63	.30
392	.26	.17
399	.11	.06

[1] Samples are all sulfide-ore samples, and were supplied by U.S. Geological Survey, Branch of Analytical Services, Reston, Va. Sample 365 is sphalerite rich, and sample 399 is pyrrhotite rich.

[2] U.S. Geological Survey, Branch of Analytical Services, Reston, Va.

[3] Sample is digested with a combination of HNO_3, $HClO_4$, and HF in a sealed Teflon bomb, the mercury is reduced with stannous chloride solution and collected on gold chips. The mercury is then thermally desorbed from the gold chips and swept into an analytical cell for quantitation. Conversations with Phil Aruscavage, U.S. Geological Survey, Branch of Analytical Services, Reston, Va. (oral commun., 1985), indicate that this procedure may be subject to the same selenium interferences (suppression) as the acidic reduction method.

Table 5.--Effects of methods of drying on the recovery of mercury from sediment samples

[Concentration in mg/kg; numbers separated by a slash represent two different digestions done on different days]

Sample no.	Method of drying				
	Wet	Air dried	Freeze dried	Oven dried--105°C	Oven dired--40°C
1	1.5/1.4	1.5/1.5	1.6/1.6	1.4/1.4	1.4/1.4
2	2.0/2.1	2.1/2.1	2.0/1.9	2.0/2.0	2.0/2.0
3	.26/.27	.33/.35	.25/.26	.20/.19	.23/.22
4	6.6/9.6	7.4/7.1	7.8/6.8	7.3/7.1	6.4/6.6
5	8.7/11	13/13	13/11	9.7/9.6	11/11
6	23/27	27/27	24/23	25/26	26/26