Determination of Mercury in Aqueous and Geologic Materials by Continuous Flow–Cold Vapor–Atomic Fluorescence Spectrometry (CVAFS)

Techniques and Methods 5–D2

U.S. Department of the Interior
U.S. Geological Survey

Determination of Mercury in Aqueous and Geologic Materials by Continuous Flow–Cold Vapor–Atomic Fluorescence Spectrometry (CVAFS)

By Philip L. Hageman

Chapter 2
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Conversion Factors

Multiply	By	To obtain
	Length	
centimeter (cm)	3.94 x 10^{-1}	inch
millimeter (mm)	3.94 x 10^{-2}	inch
micrometer (µm)	3.94 x 10^{-5}	inch
	Mass	
gram (g)	3.53 x 10^{-2}	ounce, avoirdupois
	Volume	
liter (L)	2.64 x 10^{-1}	gallon
milliliter (mL)	2.64 x 10^{-4}	gallon
microliter (µL)	2.64 x 10^{-7}	inch
cubic centimeter (cm^3)	0.06102	inch

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\,(°C) + 32$$

Abbreviated water-quality units used in this report:

ng/g	nanogram per gram
ng/L	nanogram per liter
µg/g	microgram per gram
µg/L	microgram per liter

The following abbreviations and symbols are used in this report:

ASTM	American Society for Testing and Materials
CVAAS	cold vapor–atomic absorption spectrometry
CVAFS	cold vapor–atomic fluorescence spectrometry
DI	deionized
M	molarity (moles per liter)
MSDS	materials safety data sheet
N	normality (equivalents per liter)
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
ppb	parts per billion
ppt	parts per trillion
rpm	revolutions per minute
SRM	Standard Reference Material
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
MΩ	megohm
v/v	volume per volume
w/v	weight per volume
percent R	percent recovery
>	greater than
~	about

Determination of Mercury in Aqueous and Geologic Materials by Continuous Flow–Cold Vapor–Atomic Fluorescence Spectrometry (CVAFS)

By Philip L. Hageman

Abstract

New methods for the determination of total mercury in geologic materials and dissolved mercury in aqueous samples have been developed that will replace the methods currently (2006) in use. The new methods eliminate the use of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) as an oxidizer and preservative and significantly lower the detection limit for geologic and aqueous samples. The new methods also update instrumentation from the traditional use of cold vapor–atomic absorption spectrometry to cold vapor–atomic fluorescence spectrometry. At the same time, the new digestion procedures for geologic materials use the same size test tubes, and the same aluminum heating block and hot plate as required by the current methods. New procedures for collecting and processing of aqueous samples use the same procedures that are currently (2006) in use except that the samples are now preserved with concentrated hydrochloric acid/bromine monochloride instead of sodium dichromate/nitric acid. Both the “old” and new methods have the same analyst productivity rates. These similarities should permit easy migration to the new methods. Analysis of geologic and aqueous reference standards using the new methods show that these procedures provide mercury recoveries that are as good as or better than the previously used methods.

Principle

The digestion procedure for geologic materials is based on similar procedures that have been used for several years by the U.S. Environmental Protection Agency (USEPA) (2001).

In order to determine the total mercury concentration in geologic materials, samples are digested using a hot plate and a mixture of concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) in a ratio of 0.5 / 2.0 mL, respectively. After digestion, all mercury in the sample is oxidized to Hg (II) using bromine monochloride (BrCl). The digestate is diluted to 14.75 mL with ASTM Type I reagent water and pre-reduced with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) prior to analysis.

The methods described herein for the preservation, processing, and analysis of aqueous samples for mercury are modifications to those used for several years by the U.S. Geologic Survey (USGS) National Water Quality Laboratory (NWQL) (Garbarino and Damrau, 2001) and procedures used by the U.S. Environmental Protection Agency (2002).

For determination of dissolved mercury in aqueous samples, samples must be filtered (0.45-µm capsule filter) and preserved at the time of collection with 0.5 mL mercury-free concentrated hydrochloric acid per 30 mL of sample. The sample must be collected and stored in acid-washed borosilicate glass bottles with fluoropolymer lined caps. Upon return to the laboratory, samples must be further preserved and oxidized by the addition of BrCl. This procedure preserves the samples for at least 5 months (Garbarino and Damrau, 2001).

For instrumental analysis of geologic and aqueous samples, Hg (II) is reduced to elemental mercury vapor (Hg^0) by mixing the sample with stannous chloride ($SnCl_2$) in a continuous flow-cold vapor manifold. Elemental mercury vapor (Hg^0) is separated and purged from the solution with ultrapure argon, and mercury concentration is measured by atomic fluorescence spectrometry. Quality assurance is demonstrated through the analysis of blanks, replicates, and Standard Reference Materials (SRMs).

Acknowledgments

I would like to thank Sarah Stetson for help in developing these methods.

Interferences

Gold, silver, and iodide have been identified as interferences and have been shown to diminish the extraction efficiency and/or suppress the recovery of mercury from the sample when using these methods (Garbarino and Damrau, 2001; U.S. Environmental Protection Agency, 2002). Geologic samples containing >10 µg/g or aqueous samples containing > 100 µg/L of any of these constituents must be diluted prior to analysis to mitigate the potential interference.

Water vapor condensation in the fluorescence detector is a major interference if allowed to develop. To avoid this problem, the operator must periodically check for condensation during the course of analysis and make sure that fresh drying agent (soda lime) is maintained in the in-line drying cell of the instrument. An adjustable lamp with a 150-watt incandescent bulb can also be placed in front of the reaction cell (fig. 1) of the instrument. This lamp can be turned on during analysis to keep the tubing and reaction cell warm, which helps inhibit the formation of condensation.

Finally, great care must be taken when collecting samples (all matrices) for mercury analysis because contamination of either the sample or the sampling equipment is possible due to the ubiquitous nature of mercury in the environment.

Scope

For solid-phase samples, this method offers a low reporting limit of 5 ng/g mercury. Samples exceeding the working range of 5 to 500 ng/g mercury must be redigested, diluted, and reanalyzed. For all aqueous samples, this method offers a lower reporting limit of 5 ng/L. Samples exceeding the working range of 5 to 100 ng/L mercury must be diluted and reanalyzed. About 30 solid-phase samples can be analyzed per day with the digestion being the limiting factor. At least 40 aqueous samples can be analyzed per day.

Note that for the analysis of solid-phase or routine aqueous samples, the new detection limits are considerably lower than the cold vapor–atomic absorption spectrometry methods previously used. The old detection limits were 20 ng/g for solid samples and 0.10 ng/g for routine aqueous samples (Brown and others, 2002). Low-level mercury determinations in aqueous samples are currently (2006) being done using cold vapor–atomic fluorescence spectrometry and have a detection limit of 5 ng/L (Hageman, 2002). This means that for analysis of solid samples, the detection limit for the new procedure is four times lower than the method previously used, and for routine aqueous samples, the upper limit of the new procedure is equal to the lower detection limit of the old procedure. The lower detection limits will make it possible to determine mercury on a significantly higher percentage of the solid and aqueous samples submitted.

Apparatus

- Vortex mixer
- Leeman HYDRA® CVAFS Instrument with incandescent heating lamp (fig.1).
- Standard laboratory hot plate (30 by 60 cm) that must be able to maintain a temperature of 90° C.
- Drilled aluminum heating block (fig. 2) measuring 6.35 cm thick by 19.05 cm wide by 31.75 cm long that can be placed directly on top of hot plate and hold 50 16- by 100-mm disposable glass test tubes.

Reagents

Acids used for solids digestion are research grade. Acids used for aqueous analysis, and for making all reagents and calibration standards, are trace metal purified (distilled) and mercury free. All other chemicals used for these procedures are reagent grade unless specified. Deionized (DI) water is ASTM Type I reagent water (18-MΩ) and is referred to in this report as reagent DI water. It is important to use the same source of reagent DI water for all processes and procedures described herein, because the use of water that has not been certified to be mercury free can be a major source of mercury contamination.

Glassware used for this method, including volumetric flasks used for making stock and calibration standards, bottles or flasks used for storage of BrCl, and sampling bottles used for collection of aqueous samples, should be allowed to sit overnight filled with 10 percent mercury free hydrochloric acid, and then rinsed three times with reagent DI water. This procedure is referred to as “acid-washed” in this publication. To remain mercury free, all 16- by 100-mm test tubes used for these methods should be kept in an oven at 90° C until needed.

Note: All reagents must be prepared in a fume hood.

Argon gas: Ultrapure (99.998 percent), with in-line dryer to dehumidify gas before it reaches instrument.

0.2N Bromine monochloride (w/v): In an acid-washed borosilicate glass or fluoropolymer bottle containing an acid-washed magnetic stir bar, dissolve 3.78 g potassium bromide (KBr) in 350 mL concentrated hydrochloric acid (HCl, 12 *M*). Mix using a magnetic stirrer until totally dissolved. **Slowly** and carefully add 5.32 g potassium bromate ($KBrO_3$) and continue stirring until dissolved.

Note: The addition of the $KBrO_3$ results in a violent reaction with the evolution of free halogens.

2 percent HCl (v/v): Dilute 20 mL concentrated HCl (12 *M*) to 1 L with reagent DI water.

10 percent HCl (v/v): Dilute 100 mL concentrated HCl (12 *M*) to 1 L with reagent DI water.

5 percent stannous chloride solution (w/v): Dissolve 50.0 g stannous chloride ($SnCl_2 \cdot 2H_2O$) suitable for mercury analysis, in 50 mL concentrated HCl. Allow to stand for 20 to 30 minutes until $SnCl_2$ is totally dissolved. Dilute to 1 L with reagent DI water, cap, and shake. Allow the solution to clarify (1/2 hour) prior to use. When not in use, this reagent must be stored in the refrigerator (~5° C) until needed. If stored in this manner, reagent shelf life is at least 10 days.

15 percent hydroxylamine hydrochloride solution (w/v): Dissolve 15.0 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 20 mL reagent DI water. After complete dissolution, bring to 100 mL with reagent DI water.

Instrument calibration standards: For solids analysis, calibration standards with Hg concentrations of 0.05, 0.100, 0.500, 1.00,

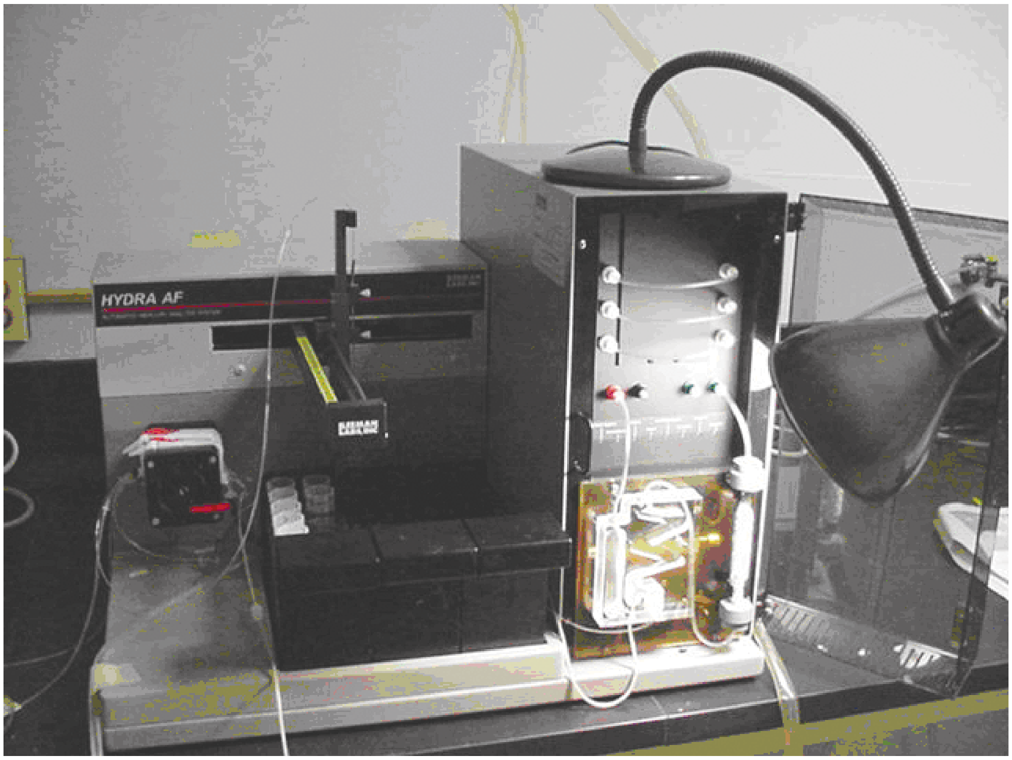

Figure 1. Leeman HYDRA® mercury analyzer with added incandescent heat lamp.

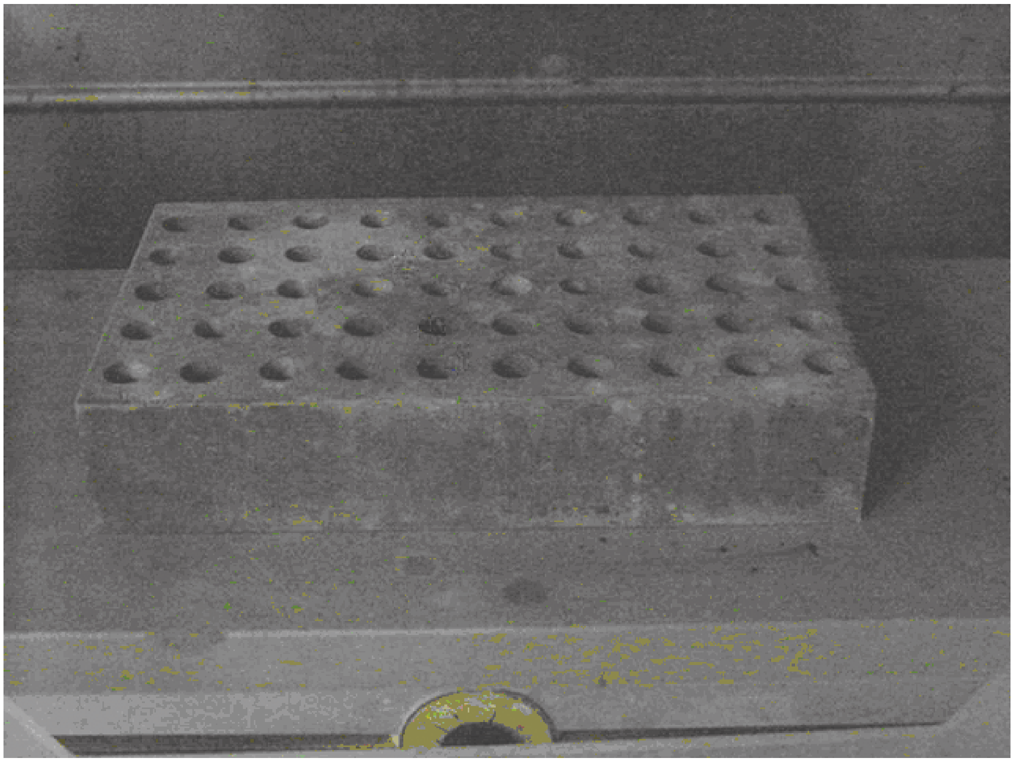

Figure 2. Drilled aluminum heating block used for digestion of geologic matrices.

and 5.00 µg/L are made from serial dilution of a 100-µg/L stock solution [stock made from dilution of National Institute of Standards and Technology (NIST) 3133] in the following manner: In acid-washed 100-mL volumetric flasks, 0.05, 0.10, 0.50, 1.0, and 5.0 mL of the stock solution is added to separate flasks containing 0.5 mL 0.2 N BrCl. All flasks are diluted with reagent DI water to final volume (100 mL), stoppered, and mixed.

For aqueous calibration standards, 5-, 10-, 50-, and 100-ng/L standards are prepared from serial dilution of a 1.0-µg/L stock solution (stock solution made from dilution of NIST 3133) as follows: In acid-washed 100-mL glass volumetric flasks, 0.5, 1.0, 5.0, and 10.0 mL of the stock solution is added to separate flasks containing 0.5 mL 0.2 N BrCl. All flasks are diluted with reagent DI water to final volume (100 mL), stoppered, and mixed.

The blank solution for solid and aqueous analyses is made by adding 0.5 mL 0.2 N BrCl solution to an acid-washed 100-mL volumetric flask and diluting to volume with reagent DI water. Stock and calibration standards preserved with BrCl should be replaced every 3 months.

Safety Precautions

Observe normal laboratory safety procedures, including the use of protective eyewear, laboratory coat, and gloves. Perform all reagent mixing and chemical digestion activities in a chemical hood. See the Chemical Hygiene Plan (CHP) and Material Safety Data Sheet (MSDS) for further information concerning first-aid treatment and disposal procedures for chemical products used in this method. The atomic fluorescence spectrometer needs to be located under a vented exhaust hood so as to evacuate the acid gases and mercury vapors that are produced by the continuous flow–cold vapor system.

Procedure for Digestion of Geologic Samples

1. Weigh 0.100 g of sample into 16- by100-mm disposable borosilicate glass test tube.
2. Add 0.5 mL concentrated HNO_3 (16 *M*) to test tube and mix with vortex to wet sample.
3. Add 2.0 mL concentrated HCl (12 *M*) (Add HCl in 0.5-mL aliquots to carbonate rich samples.)
4. Vortex and let samples react overnight.
5. Vortex samples and place into a room temperature aluminum heating block.
6. Turn hot plate on and heat samples (uncovered) for 2 hours at 90° C.
7. Remove samples from hot plate and cool to room temperature.
8. Add 30 µL 0.2 N BrCl to all samples and vortex.
9. Dilute all samples to 15 mL (0.6 cm below top of test tube) with reagent DI water.
10. In order to analyze samples at a later time, cap, shake, and store samples (samples processed in this manner can be stored for at least 1 month before being analyzed).
11. Prior to analysis, add 60 µL 15 percent $NH_2OH{\cdot}HCl$ to each tube. Cap and shake samples. Let samples stand until the particulate matter has settled. This can also be achieved by centrifuging the samples at 3,000 rpm for 10 minutes.
12. Remove cap and place samples into the instrument's autosampler for analysis.
13. Any sample with mercury concentration exceeding the highest calibration standard (500 ng/g in sample) must be redigested, diluted, and reanalyzed. After the sample has been redigested and processed using the procedures described above, dilute the digestate by taking a 1.5-mL aliquot and adding it to a new 16- by 100-mm test tube containing 60 µL $NH_2OH{\cdot}HCl$. Bring to volume (14.75 mL) with reagent DI water. Cap and shake the sample, and reanalyze using the procedures described above.

Procedure for Aqueous Samples

Aqueous samples are filtered into acid-washed borosilicate glass bottles using a 60-cm^3 (cubic centimeter) syringe and a 0.45-µm pore-size nitrocellulose filter. If filtration is difficult, a 0.70-µm glass fiber pre-filter can be used in conjunction with the 0.45-µm filter in a serial manner. Preserve the filtrate in the field or the laboratory by adding 0.5 mL concentrated, mercury free HCl (12 *M*) per 30 mL filtered sample. After preservation, store the bottles with caps that have fluoropolymer liners.

1. Upon arrival at the laboratory, add 60 µL 0.2 N BrCl to all samples. Following this, recap and shake all bottles. Samples preserved in this manner can be stored for up to 5 months.
2. Just prior to analysis, add 60 µL 15 percent $NH_2OH{\cdot}HCl$ to all 16- by 100-mm test tubes that will go into the autosampler, and bring the test tubes to volume (14.75 mL) with sample. Cap, shake, and let samples stand 5 minutes.
3. Use aqueous calibration standards of 0, 5, 10, 50, and 100 ng/L Hg for analysis. Analyze samples

using the same reagents and apparatus used for solids analysis.

4. Dilute and reanalyze any sample with mercury concentration exceeding the highest calibration standard (100 ng/L). To dilute the sample, take a 1.5-mL aliquot from the original sample and add it to a new 16- by 100-mm test tube containing 60 µL $NH_2OH{\cdot}HCl$. Bring to volume (14.75 mL) with reagent DI water. Cap, shake, and let stand for 5 minutes.

Analytical Procedure for Analysis of Samples for Mercury Using Continuous Flow–Cold Vapor–Atomic Fluorescence Spectrometry (CVAFS)

Mercury determination is fully automated using a Leeman HYDRA AF® CVAFS mercury analyzer (fig. 1). Prepared or digested samples are uncapped and loaded into the instrument autosampler. The instrument is calibrated using matrix appropriate calibration standards, as explained in the previous section. For sample analysis, the instrument takes up a set volume of sample and mixes it with 5 percent $SnCl_2$. This procedure results in any Hg (II) in the sample being reduced to Hg^0. The solution is purged into the in-line phase separator of the instrument, and the liquid is separated from the mercury vapor. Ultrapure argon gas carries the vapor through a drying cell and introduces it into the fluorescence cell of the instrument. Mercury concentration is calculated by the instrument using the calibration curve and linear regression. Mercury concentration is reported in micrograms per kilogram for solids, and in nanograms per liter for aqueous samples.

Discussion of Results

As part of the validation process for the new methods, a series of reference standards and blanks were digested and analyzed using the described procedures. The results for analysis of the reference standards are listed in table 1.

Table 1. Analytical performance summary for determination of mercury by continuous flow–cold vapor–atomic fluorescence spectrometry (CVAFS)

[Mercury concentration for aqueous samples in nanograms per liter, solid-phase samples given in micrograms per kilogram; n, number of samples analyzed; s, standard deviation; pv, preferred value for the reference materials; Ref., Reference (footnote number); % RSD, percent relative standard deviation; %R, percent recovery; %R (new), percent recovery achieved using CVAFS and the new methods described in this paper; %R (old), percent recoveries achieved using CVAAS and the old dichromate method; ±, plus or minus; - -, not applicable]

Aqueous reference standard	Type	n	Mean	s	pv	Ref.	%RSD	%R
Hg 40	Water	9	62	- -	66(±2)	-[2]	- -	94
Hg 41	Water	9	46	- -	51(±7)	-[2]	- -	90

Geologic reference standard	Type	n	Mean	s	pv	Ref.	%RSD	%R (new)	%R (old)
GXR-1	Jasperoid	9	4,100	117	3,900	-[1]	2.8	105	103
GXR-2	Soil	9	2,900	148	2,900	-[1]	5.1	99	107
GXR-3	Hot springs deposit	9	326	26	330	-[1]	8.0	99	97
GXR-5	Soil	9	181	15	167	-[1]	8.5	108	112
SGR-1	Shale	9	214	25	254	-[1]	11.6	84	69
G-2	Granite	9	51	5.0	49	-[1]	9.01	104	135
MESS 2	Marine sediment	9	79	9.3	92	-[4]	11.8	86	- -
GDS 6	Steam sediment	9	47	10	45	-[3]	21.4	104	- -
SRM 2709	Soil	9	1,500	37	1,400	-[1]	2.5	105	99
SRM 2711	Soil	9	6,200	180	6,250	-[1]	2.9	100	94

Method blank results

Method blank	n	Mean	s	3s	5s
Aqueous method	9	1.63	0.56	1.68	2.80
Geologic method	9	.071	.013	.039	.065

[1] Brown, and others (2002).

[2] U.S. Geological Survey (2006).

[3] Govandaraju (1994).

[4] Govandaraju (1989).

Ten geologic reference standards were processed, digested, and analyzed using the methods described in this report. These standards represent a wide variety of geologic matrices. Percent recoveries for the six reference standards ranged from 84 to 108 percent. Also listed in table 1 are the percent recoveries for the same reference materials that were digested and analyzed by the old procedures, which included the use of sodium dichromate (Brown and others, 2002). Two samples, MESS 2 and GSD 6, were not reported using the old procedure and thus no percent recoveries are listed for these materials.

Two aqueous reference standards were analyzed using the new procedures, and percent recoveries for the two samples were 94 and 90 percent, respectively. These reference samples were not preserved with dichromate so that no comparison can be made with the method that was previously used.

Overall, the new methods (geologic and aqueous) produce recoveries as good as, or better than, the dichromate methods that were previously used.

Blanks were digested and analyzed as part of the validation of the new procedures. Blanks for aqueous samples and solid-phase samples were taken through all the procedures described herein and analyzed using CVAFS. Data for the blanks are listed in table 1. The value represented by three standard deviations is considered to be the lower limit of detection, and the value represented by five standard deviations is considered to be the lower limit of determination for the new methods.

Conclusion

New digestion and analytical methodology have been designed and tested for the determination of total mercury in geologic materials, and dissolved mercury in aqueous samples. These methods have been designed to replace the methods and procedures that are currently in use (2006) for these matrices. This study indicates that the new methods offer significant improvements over the procedures currently in use. The new methods eliminate the use of sodium dichromate as an oxidant and preservative, replacing it with concentrated hydrochloric acid and bromine monochloride. Eliminating the dichromate will result in a substantial cost savings because it will not have to be collected, stored, and disposed of as hazardous waste. The use of hydrochloric acid is also safer, less restrictive, and less expensive to ship to or from the field.

The new methods offer lower detection limits for solids and aqueous samples and update the instrumentation used for analysis. These improvements are achieved by replacing the traditional use of cold vapor–atomic absorption spectrometry (CVAAS) with cold vapor–atomic fluorescence spectrometry (CVAFS) for geologic and all aqueous samples, thus eliminating the two-tier system of analysis for aqueous samples, which previously required analysis by CVAAS and CVAFS.

The new methods will result in an increase in laboratory capacity and promote efficiency of the operator/analyst because a higher percentage of the submitted samples will be quantified for mercury. Benefit and production increases also will be seen by the submitter/investigator due to the generation of more geochemical data and increased sampling efficiency.

Finally, the new digestion procedures for geologic materials have been designed to use the same size test tubes, aluminum heating block, and hot plate as the current methods (2006) require. For aqueous samples, the new method for collection and processing require the use of the same collection procedures and equipment as have been used traditionally except that the samples are preserved with concentrated hydrochloric acid instead of sodium dichromate. Ultimately, for geologic and aqueous samples, these similarities will allow for relatively simple changeover to the new methods, and once implemented, the new methods will enhance, simplify, and provide substantial cost savings over the old methods.

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