

Mercury Determination in Lichen, BCR-482, Using the QuickTrace® M-7600 CVAAS Mercury Analyzer

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INTRODUCTION

Lichen is monitored due to its ability to aid in the control of air pollution. Because it is able to absorb trace elements from the atmosphere, and its global presence is widespread, lichen possesses merits as an air pollution indicator and is more cost-effective than using air filters.

Due to its ability to absorb trace amounts of mercury, analysis of lichen is a potential model for mercury contamination in a micro-ecosystem modeling system. The purpose of this application note is to validate the capabilities of the QuickTrace® M-7600 Cold Vapor Atomic Absorbance (CVAAS) mercury analyzer in the ug/L range. This was carried out by quantitation of mercury in lichen. The QuickTrace® M-7600 mercury analyzer was validated by developing a modified custom digest. The standard reference material that was used was BCR-482, Lichen.

INSTRUMENTATION

The QuickTrace® M-7600 is an independent stand-alone mercury analyzer that uses CVAAS spectrometry to obtain reliable quantitative data from simple to complex matrices. The working range for the QuickTrace® M-7600 Mercury Analyzer is < 0.5 ng/L to > 500 µg/L. This dynamic quantitative range allows mercury concentrations to be determined in a variety of sample substrates without dilution or pre-concentration.

The QuickTrace® M-7600 is accompanied by an autosampler that allows for hands-free sample batch analysis. The four-channel peristaltic pump ensures consistent sample uptake to the analyzer, as well as online sample/reagent reduction in a closed system. The reduced sample flows to a non-foaming Gas Liquid Separator (GLS) and purged with argon, liberating the elemental mercury from the sample and carrying it into the system. The mercury is then passed through a Perma Pure® drying cartridge and to the sample cell where it is measured at 253.7 nm. Software instrument controls include argon flow, lamp, pump control, smart rinse threshold, and over-range protection, as well as other options. Optimizing these parameters allows for increased or decreased sensitivity.



EXPERIMENTAL

The M-7600 mercury analyzer is operated by QuickTrace® software that provides method specific control of the system. Parameter optimization allows for the quantitation of mercury in the µg/L range. The goal of this application note is to optimize instrument parameters to quantitate mercury at the µg/L level using the Leeman Labs QuickTrace® M-7600 Mercury Analyzer (Figure 1).

Lichen samples were digested from standard reference material BCR-482, Lichen, purchased from the Institute for Reference Materials and Measurements. The certified reference material was collected manually from pine trees located in the area of Axalp, Switzerland. The reference material was stored in a brown glass bottle with polyethylene inserts and a plastic screw cap. The reference material was shaken for approximately one minute to re-homogenize the sample prior to sample preparation. The samples were digested and analyzed in 50 mL polypropylene co-polymer centrifuge tubes. Samples were placed in the sample vials and digested with a 7:3 HNO₃/H₂SO₄ solution, followed by an additional digestion using a potassium bromide/potassium bromate solution. The samples were then diluted to 40 mL with mercury-free deionized water, placed in a dry block digestion apparatus and heated for 1 hour at 115 °C.

The samples were reduced using 12% hydroxylamine hydrochloride. Reduction of the inorganic mercury to elemental mercury was carried out by excess online addition of 10% stannous chloride, in 7% hydrochloric acid, at a rate of 4.2 mL/min, at 70% pump speed. Seven replicates were analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time was approximately 42 minutes, with each sample analysis lasting approximately 100 seconds. By optimizing conditions, this analysis was able to use only 7 mL of sample per analysis.

Calibration standards and control standards were prepared in a 7:3 HNO₃/H₂SO₄ solution, potassium bromide/potassium bromate solution, ultra-pure deionized water and 12% hydroxylamine. Appropriate aliquots of 100 µg/L working standard were used to prepare the calibration curve that consisted of one blank and six non-zero standards that ranged from 0.2 µg/L to 5.0 µg/L. Initial calibration verification and initial calibration blank were analyzed to validate the accuracy of the calibration. Mercury is detected at wavelength 253.7 nm. BCR-482 total mercury is certified at 0.48 mg/kg with an uncertainty of ± 0.02 mg/kg.

Figure 1 Method Parameters

Conditions	
Gas Flow (ml/min)	150
Pump speed (%)	70
Sipper depth (mm):	150
ASX Rinse Pump Speed (%):	50
Sample uptake time (s):	40
Rinse time (s):	60
Read delay time (s):	45
Replicate read time (s):	1
Replicates:	4
<input checked="" type="checkbox"/> Auto adjust replicate read time	
Profile Replicate %RSD:	0.00%
<input type="checkbox"/> Abort on Over Range	
Over Range Abort Threshold:	380000 µAbs

CALIBRATION STANDARDIZATION

Calibration standards were prepared with aliquots of a 100 µg/L working standard that was prepared from serial dilutions of a 1000 mg/L certified standard. Standards were prepared using a final volume of 40 mL. Aliquot volumes of 0.08 mL, 0.20 mL, 0.40 mL, 0.80 mL, 1.40 mL, and 2.0 mL of 100 µg/L working standard were added to 10 mL of a 7:3 HNO₃:H₂SO₄ solution. Calibration standard concentrations were 0.2, 0.5, 1.0, 2.0, 3.5, and 5.0 µg/L. The calibration standards were matrix-matched by the addition of 1.0 mL of 0.1N potassium bromide/potassium bromate solution and 0.05 mL of 12% hydroxylamine. Calibration standards were analyzed beginning with one matrix blank and then proceeded from lowest concentration standard to the highest concentration standard. Each peak was integrated for a total of 4 seconds. The concentration and the calibration were calculated.

Figure 2 Peak Profile of 5.0 µg/L Standard

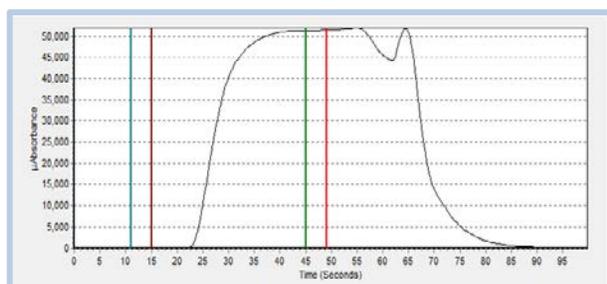
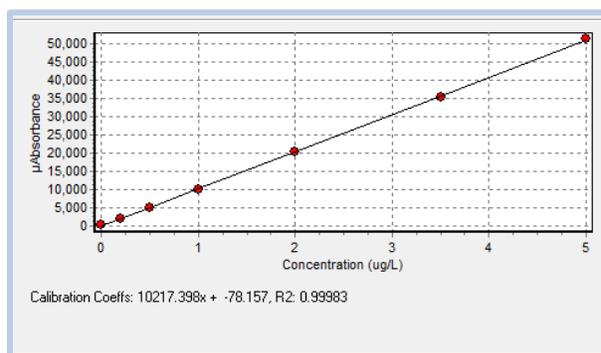


Figure 3 Calibration



PROCEDURE

After thoroughly shaking the sample bottle ~ 0.1 g of sample was added to a polypropylene digestion tube. The sample was then digested using 10 mL of 7:3 HNO₃/H₂SO₄ solution. A total of seven samples were prepared in this manner then capped and allowed to sit overnight. The samples were then placed in a block digestion apparatus for 1 hour while gradually increasing the temperature to 115 °C. The samples were then oxidized using 1.0 mL of potassium bromide/potassium bromate solution, and diluted to 40 mL using mercury-free deionized water. The samples were then heated at 115 °C for an additional hour.

The samples were reduced by manually adding 0.05 mL of 12% hydroxylamine. They were then sealed, inverted, and allowed to sit for five minutes. The sample vials were then placed on the autosampler tray and analyzed. Inorganic mercury was reduced to elemental mercury with online excess addition of 10% stannous chloride in 7% hydrochloric acid at 4.2 mL/min, at 70% pump speed. Peak height of each sample was integrated for 4 seconds. Initial calibration verification, initial calibration blank, continuing calibration verification, lab fortified blank, lab reagent blank, matrix spike and matrix spike duplicate were analyzed to validate the instrument stability and to identify any method inconsistencies. Initial calibration verification was prepared with a 0.8 mL aliquot of the 100 µg/L working standard into a matrix-matched solution to give a concentration of 2.0 µg/L. Each quality control was prepared in the same manor. Matrix spike and matrix spike duplicate were all prepared with 0.4 mL aliquots of 100 µg/L working standard to give a concentration of 1.0 µg/L (recoveries were MS = 90%; MSD = 95% with RPD at 5.4%).

RESULTS

Using the QuickTrace® M-7600 mercury analyzer for measurement of mercury at trace levels is an effective analytical technique for obtaining reliable quantitative data. Optimizing carrier gas flow, pump speed, sample uptake and rinse time allows for analysis of a calibration, quality controls, and samples over a broad dynamic range. Minimal sample analysis time reduces laboratory costs, analyst time and instrument maintenance, without loss of data quality. Total mercury in lichen at the µg/L level was easily recovered by utilizing the various instrument settings of the QuickTrace® M-7600 Mercury Analyzer. Method development using the QuickTrace® Software included calibration, quality controls, and spike recovery. A separate MDL study was performed in accordance to CFR 40 Part 136 Appendix B resulting in an ultra-trace MDL of 0.034 µg/L for the instrument settings associated with this application note. As a result, total mercury can be determined as accurately quantitated. Seven replicates of the digested standard reference material were analyzed, corrected for moisture content, total mercury concentration recorded; and mean concentration and standard deviation calculated. The results of 0.471 mg/kg ± 0.015 dry mass are shown in Figure 4 and Figure 5.

BCR-482 has a certified concentration of 0.48 mg/kg with an uncertainty of ±0.02 mg/kg. Uncertainty values correspond to a level of confidence at 95%, and was calculated for seven replicates of the standard reference material that were analyzed using four one second peak height replicate readings for each of the seven samples.

Figure 4 Results

IRMM Lichen, BCR 482, 0.48 mg/Kg ± 0.02		
Digest	mg/Kg	
1	0.478	
2	0.471	
3	0.482	
4	0.469	
5	0.458	
6	0.471	
7	0.469	
	Mean = 0.471	
	Uncertainty = 0.015	
n = 7 Replicates	STDEV = 0.008	RSD% = 1.614

Figure 5 Results with Uncertainties

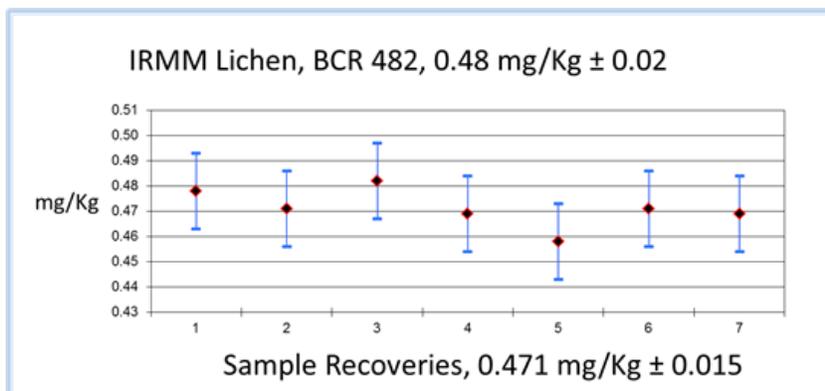


Figure 6 Quality Control Chart

Mercury Determination in Lichen Quality Control		
Quality Control (µg/L)	% recovery	RPD%
CCV (2.0)	100.5-100.2	
ICV (2.0)	101.6	
LFB (1.0)	101.0	
MS (1.0)	89.8	
MSD (1.0)	95.0	5.6

Contamination can present many problems and lead to inaccurate results. Consequently, careful attention was given to minimize contamination in reagents, acids, and deionized water. Through method development, parameter optimization, and sample preparation, the QuickTrace® M-7600 mercury analyzer quantitates total mercury and produces reliable quantitative data.

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