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Application Note

Mercury Determination in Industrial Sludge, SRM 2782, EPA Method 245.5, using the CETAC QuickTrace™ M-7600 CVAAS

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INTRODUCTION

Industrial sludge is the byproduct of wastewater treatment process and may contain mercury and other heavy metals. The purpose of this application note is to validate the capabilities of the CETAC QuickTrace™ M-7600 Cold Vapor Atomic Absorbance Analyzer in the µg/L range. This was carried out by quantitation of mercury in industrial sludge. The QuickTrace™ M-7600 Mercury Analyzer was validated by developing a performance-based method following US EPA Method 245.5, Mercury In Sediment (Manual Cold Vapor Technique). The standard reference material that was used was SRM-2782, Industrial Sludge.

INSTRUMENTATION

The QuickTrace™ M-7600 is an independent stand-alone analyzer that uses Cold Vapor Atomic Absorbance (CVAA) spectrometry for obtaining reliable quantitative data from simple to complex matrices. The working range for the QuickTrace™ M-7600 Mercury Analyzer is from < 0.5 ng/L to > 500 µg/L. This dynamic quantitative range allows mercury concentrations to be determined in broad range of sample substrates without dilution or pre-concentration. The QuickTrace™ M-7600 is accompanied with an autosampler that allows for hands-free sample batch analysis. The QuickTrace™ M-7600 has a four-channel peristaltic pump that ensures consistent sample uptake into the analyzer and allows for sample/reagent reduction online in a closed system. The reduced sample then flows into the non-foaming Gas-Liquid Separator (GLS), and argon is purged through the sample as elemental mercury is liberated and enters into the system. The mercury is then passed through the Perma Pure® drying cartridge and into the sample cell where it is measured at 253.7 nm. Software instrument controls include, but are not limited to, argon flow, lamp, pump control, smart rinse threshold, and over range protection. Optimizing these parameters allows for increased or decreased sensitivity.

Figure 1. CETAC QuickTrace™ M-7600 Cold Vapor Atomic Absorbance Spectrometry Mercury Analyzer

EXPERIMENTAL

The QuickTrace™ M-7600 is operated by the QuickTrace™ software and provides method specific control of the system. Parameter optimization allows for the quantitation of mercury in the sub-µg/L range. The goal of this application is to optimize instrument parameters using EPA Method 245.5 to quantitate mercury at the µg/L level using the CETAC QuickTrace™ M-7600 Mercury Analyzer. Industrial sludge samples were digested from standard reference material SRM-2782, industrial sludge, which was purchased from the National Institute of Standards and Technology. The certified reference material was collected from a site in northern New Jersey that does pharmaceu-

tical research as effluent before it was treated. The reference material was stored in an amber glass bottle and shaken for approximately one minute to re-homogenize the sample prior to sample preparation. The outside of the bottle was rinsed with mercury-free ultra-pure deionized water to remove any particles that may have adhered to the outer surface. The digestion tubes were precleaned using a detergent wash, 20% nitric acid wash, and two ultra-pure deionized water rinses. The samples were digested and analyzed in 50mL polypropylene co-polymer centrifuge tubes. Samples were treated in the sample vials with aqua regia and digested with 5% potassium permanganate solution, followed by reduction with 12% hydroxylamine. 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 4.8 mL/min at 80% pump speed. Seven replicates were analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time was approximately 33 minutes, with each sample analysis lasting approximately 90 seconds. A six-point calibration curve was analyzed, which included five non-zero standards and one blank.

Initial calibration verification and initial calibration blank were analyzed to validate the accuracy of the calibration. Calibration standards and control standards were prepared in aqua regia, potassium permanganate, ultra-pure deionized water, and hydroxylamine. Appropriate aliquots of 100 µg/L working standard were used to prepare the calibration curve that consisted of one blank and five non-zero standards that ranged from 0.2 µg/L to 10 µg/L. Mercury is detected at wavelength 253.7 nm. SRM-2782 total mercury is certified at 1.10 mg/kg with an uncertainty of ± 0.19 mg/kg.

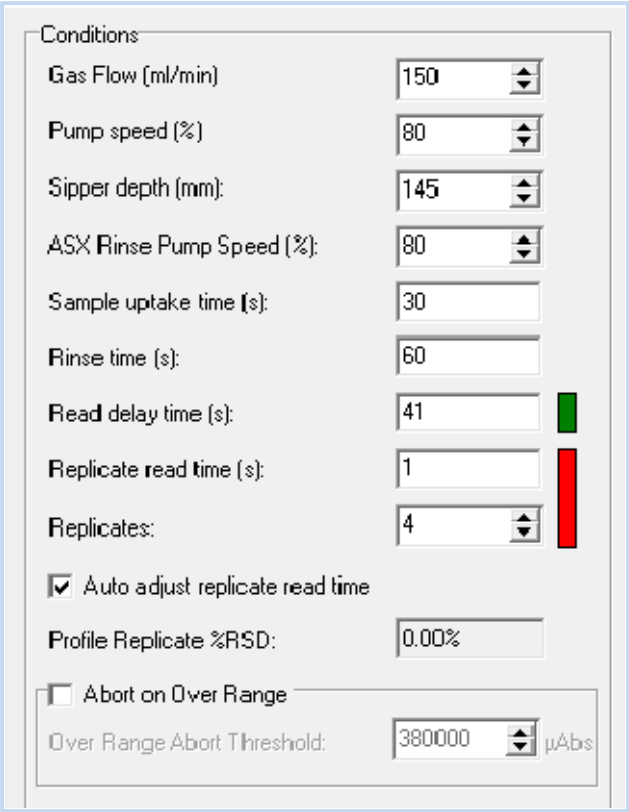

Figure 2. Method Parameters

CALIBRATION STANDARDIZATION

Calibration standards were prepared using aliquots of a 100 µg/L working standard that was prepared from serial dilutions of a 1000 mg/mL certified standard. Standards were prepared using a final volume of 50 mL. Aliquot volumes of 0.1 mL, 0.5 mL, 1.25 mL 2.5 mL, and 5.0 mL of 100 µg/L working standard were added to the ultra-pure deionized water. Calibration standard concentrations were 0.2, 1.0, 2.5, 5.0, and 10.0 µg/L. The calibration standards were matrix-matched by the addition of 1.8 mL of aqua regia prepared from trace metal grade hydrochloric acid and nitric acid in a 3:1 ratio, 5.3 mL of 5% potassium permanganate solution and 2.2 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.

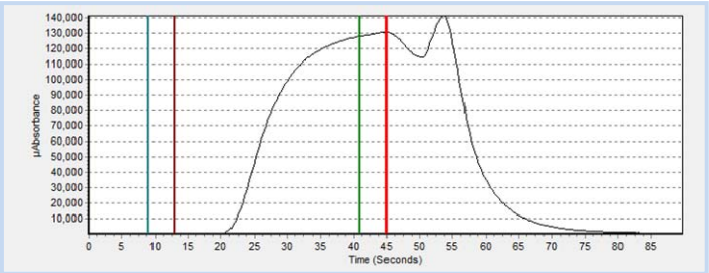

Figure 3. Peak Profile of 10 µg/L Standard

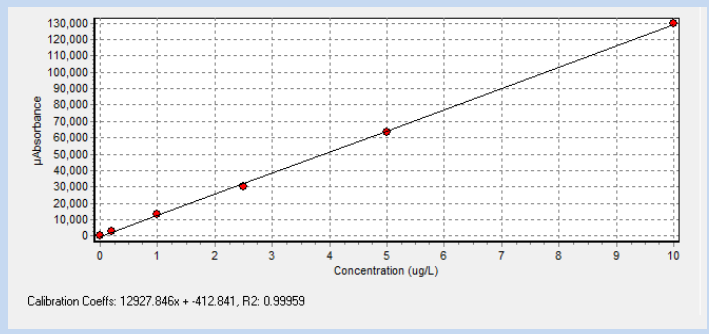

Figure 4. Calibration

PROCEDURE

After thoroughly shaking the sample bottle, ~.200 gram of SRM-2782, industrial sludge was weighed directly into a 50 mL polypropylene centrifuge tube. Then 1.8 mL of ultrapure water was added to the sample and shaken to put the sludge into solution. Then 1.8 mL of aqua regia was added to the sample vial and swirled to mix. The sample vials were then placed in a dry block digestion system set to 95 ºC for 2 min. The vials were allowed to cool and filled to 25 mL with ultra-pure DI water. Then 5.3 mL of 5% potassium permanganate was added. The vial was sealed and inverted to homogenize the sample followed by heating for approximately 30 minutes at 95 ºC in a dry block digestion system, ensuring that the solution remained purple and that all organics were oxidized. The sample was then reduced by manually adding 2.2 mL of 12% hydroxylamine, sealed and inverted, and then filled to 50 mL with ultra-pure DI water. 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 4.8 mL/min at 80% 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. Initial calibration verification was prepared with a 2.5 mL aliquot of the 100 µg/L working standard into a matrix-matched solution to give a concentration of 5.0 µg/L. The recovery was 91.4% on the initial calibration verification. Each quality control was prepared in the same manner. Continuing calibration verification had recoveries of 99.7% and 100.9%. The lab fortified blank had a recovery of 97.9%. Matrix spike and matrix spike duplicate were all prepared with 1.25 mL aliquots of 100 µg/L working standard to give a concentration of 2.5 µg/L. (Recoveries were MS = 86.8%; MSD = 90.4% with RPD at 4.1%).

RESULTS

Using the QuickTrace™ M-7600 for measurement of low-level mercury is an effective analytical technique used 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 effort along with minimizing instrument maintenance, while giving reliable, quantitative data. Total mercury in industrial sludge at the µg/L level was easily recovered by utilizing the various instrument settings of the QuickTrace™ M-7600 Mercury Analyzer. Method development using QuickTrace™ software included calibration, quality controls, and spike recovery. As a result, total mercury was accurately quantitated. Seven replicates of the digested standard reference material were analyzed and total mercury concentration was recorded and mean concentration and standard deviation were calculated. The results of 1.22 mg/kg ± 0.01 are shown in Figures 5 and 6.

SRM-2782 has a certified concentration of 1.10 mg/kg with an uncertainty of ± 0.19 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 on the QuickTrace™ M-7600 using

four peak height replicate readings for each of the 7 samples.

NIST Industrial Sludge, SRM 2782, 1.1 mg/Kg ± 0.19			
Digest	mg/Kg		
1	1.22		
2	1.22		
3	1.23		
4	1.21		
5	1.22		
6	1.22		
7	1.21		
Mean =	1.22		
Uncertainty =	0.014		
n = 7 Replicates	STDEV = 0.007	RSD% = 0.566	

Figure 5. Results

Contamination at the low-level can present many problems and can lead to inaccurate results. Therefore, 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 at the sub-µg/L level giving reliable quantitative data.

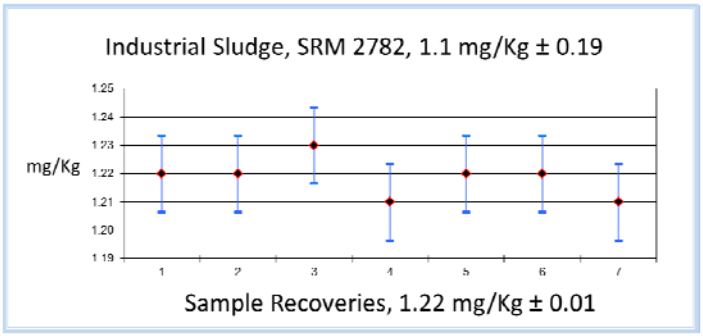

Figure 6. Results with Uncertainties

REFERENCES

US EPA. Method 245.5, Mercury in Sediment (Manual Cold Vapor Technique)