Determination of Mercury in a Certified Reference Sludge Material using the Agilent 710-ES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

Mercury is an element of great importance because of its toxicity. Over the last century, emissions of mercury due to human activities have resulted in a tripling of the concentration of mercury in the atmosphere and surface oceans [1]. The main present-day sources of the additional man-made burden of environmental mercury are coal combustion, municipal and medical waste incineration, and smelting [2].

Elucidation of the pathways resulting in human exposure to mercury remains a matter of great interest. According to Liebert et al., “there is now [at the time they wrote]...” scientific consensus that “...the most prevalent source of mercury exposure for the general population is from dental amalgam, and chronic inhalation or swallowing of amalgam mercury vapor is the major contributor to the total body burden of mercury in the U.S.” [3].

Additional mercury body burdens may be derived from air, water or soils. Sewage sludges and compost from solid waste and sewage sludge often have relatively high mercury concentrations. Such organic wastes are often applied in agriculture as fertilizers, and although the recycling of waste is desirable, waste contamination by mercury may lead to higher concentrations of mercury in the soil to which it is applied, compared to those found when the soil is conventionally fertilized [4, 5].

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Determination of the levels of mercury in solid wastes is therefore a matter of some interest. Concentrations of mercury in sewage sludges are typically in the region of several parts per million (by dry weight) [5]. A concentration of 5.6 µg/g has been reported in Australian urban sewage sludge [6].

Atomic spectrochemical methods such as atomic absorption spectrometry (AAS) and ICP-OES provide the required sensitivity for the measurement of mercury at the concentrations that are usually encountered in environmental analysis. Vapor generation techniques for atomic spectrochemical analysis are widely used because of the excellent sensitivities provided for several elements, including mercury. This application note describes a simple procedure for the determination of mercury in a suitable solid organic reference material (NBS 2781, Domestic Sludge) by vapor generation coupled with ICP-OES.

Experimental

An Agilent VGA-77P (Vapor Generation Accessory) was used with an Agilent 710-ES (ICP-OES) equipped with a megapixel CCD detector. The operating conditions of the ICP instrument and VGA are as shown in Tables 1 and 2. Vapor produced by the VGA was injected into the plasma through the nebulizer and spraychamber. With the VGA in operation, the plasma was run "dry"; accordingly, a lower-than-usual power was set in the method. The VGA was operated under conditions as previously described [7, 8]. Argon was used as the VGA carrier gas. The use of nitrogen as the VGA carrier gas is not recommended on ICP.

The instrument pump rate must be optimized to ensure that the gas-liquid separator of the VGA is pumped effectively and the liquid level does not rise, or fill the gas-liquid separator. A pump rate of 40–45 rpm is usually sufficient for this purpose. This rate must be maintained whenever the VGA is in operation with sample solution being pumped. This pump rate must be incorporated into the ICP method, and can be set as a default on the Ignition page of the Instrument Setup window in the ICP Expert II software, so that as soon as the plasma is turned on, the pump speed changes to the required value. An autosampler was not used in this study.

Table 1. ICP Operating Conditions

Parameter	Setting
Power	0.9 kW
Plasma gas flow	13.5 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer type	Glass concentric
Nebulizer pressure	240 kPa
Spraychamber type	Glass cyclonic (single-pass)
Torch type	Standard axial torch
Pump tubing	Spraychamber waste–blue/blue (1.65 mm ID) Gas/Liquid separator waste–purple/black (2.29 mm ID)
Instrument pump rate	45 rpm
Replicate read time (s)	5
Number of replicates	3
Sample delay time (s)	20
Stabilization delay time (s)	30
Fast pump	Off

Table 2. VGA-77P Operating Conditions

Parameter	Setting
Inert gas	Argon
Pump tubing	Sample–purple/black (2.29 mm ID) Reductant–black/black (0.76 mm ID) Acid/water–black/black (0.76 mm ID)
Solution uptake rate	Sample–8 mL/min Reductant–1 mL/min Acid/water–1 mL/min

Standard Solutions and Reagents

Working solutions for mercury determination in the micrograms-per-litre range were prepared from a mercury standard (May and Baker). All mercury solutions were stabilized with a 0.01% solution of AIR potassium dichromate, as described by Feldman [9]; this procedure resulted in the stabilization of the mercury solutions for many days. Calibration solutions were prepared at concentrations of 5, 10 and 20 µg/L. Stannous chloride was used as the reducing agent, though sodium borohydride has also been used with the VGA [7,8]. A solution of $SnCl_2$ was prepared as a 25% w/v solution in 20% HCl from AIR grade $SnCl_2$ (BDH) and AIR HCl (BDH). "Conditioning" of the VGA system was carried out according to advice by Moffett [10]. Before conditioning, the response for very low Hg concentrations may be variable. Conditioning of the active sites in the tubing carrying the solutions and reaction products, can be achieved by running the highest concentration Hg calibration standard (in this case 100 µg/L) through the system, until the response for much lower concentrations (for example, 1 µg/L) becomes stable.

Sample Preparation

The standard reference material NBS 2781 (Domestic sludge) was selected for analysis. 3 mL of mixed nitric and hydrochloric acids were added to approximately 0.1 g of the weighed SRM, in the volume ratio 2:1. This was digested on a hot plate for approximately two hours, or until fuming ceased. The solution was cooled, filtered and diluted to 50 mL. A drop of Anti-Foam B (Sigma Chemical Co.) was added to the solution after filtering.

Results and Discussion

Detection Limits

Detection limits determined for a 30-second replicate read time on the Agilent 710-ES instrument are shown in Table 3. (Detection limits (DLs) were measured on two instruments and similar values were obtained for the two.) Under the operating conditions used, it was found that the three lines used gave similar DLs, with slightly better DLs for the 253 nm line. This differs from the typical behavior for Agilent ICP-OES instruments with aqueous sample introduction, for which the 185 nm and 194 nm lines both give slightly better detection limits than does the 253 nm line [11]. This may be a result of the use of lower RF power, a condition which tends to favor the less "hard" spectral lines, as a result of the less efficient ionization and excitation at the lower power.

Table 3. Detection Limits (µg/L) for Hg in Aqueous Solution

Replicate read time (s)	184.887 (nm)	194.164 (nm)	253.652 (nm)
30	0.023	0.022	0.020

Short-term precision, determined from the RSD of replicate measurements of a 5 µg/L standard with 5 second replicate read times, was usually 1–2% RSD.

Analysis of a Certified Reference Material Containing Hg

Certified reference material NBS 2781 (Domestic sludge) was analysed by both "normal" calibration and by the method of additions. No difference was observed in the slopes of the graphs determined by the two methods, indicating no chemical interference. As can be seen from the results in Table 4 for the analysis of eight aliquots of the SRM, the recovery of mercury is within the range of values encompassed by the uncertainty in the concentration of the reference material.

Table 4. Results of Analysis of NBS 2781

	Hg Concentration, mg/kg
Measured value	3.40 ± 0.13
Certified value	3.64 ± 0.25
Recovery %	93

Conclusion

An Agilent VGA-77P has been used with an Agilent 710-ES for the analysis of a certified reference material (NBS 2781). The results obtained agree with certified values, within the combined uncertainties of the two results.

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