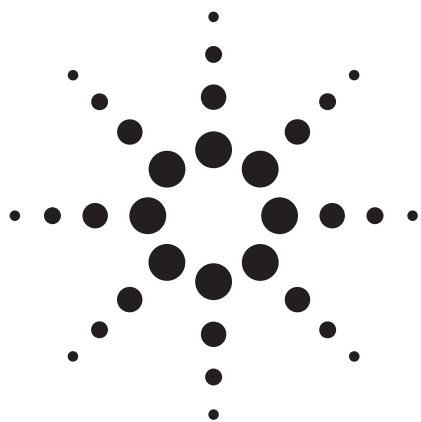




Determination of Mercury With On-line Addition of Stannous Chloride Using an Axial ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

Mercury is one of the most toxic heavy metals in the environment. It is therefore important to routinely monitor the Hg level in many types of samples. The US EPA approved methodology for the determination of Hg uses the cold vapor technique with stannous chloride as the reducing agent [1]. This methodology is applicable to Hg determinations in a range of waters (drinking, ground, surface, sea and brackish waters) plus domestic and industrial wastes. It allows mercury detection down to the sub- $\mu\text{g/L}$ range.

While Hg can be determined with direct aspiration using the ICP-OES technique, the performance achieved is not sensitive enough for many environmental applications.

Ultra-trace level determination of Hg therefore requires the use of a vapor generation accessory such as the Agilent VGA-77. The detection limit of Hg achieved with this accessory using an axially-viewing ICP-OES is $0.02 \mu\text{g/L}$ [2]. However, if the required determination level of Hg is not so low, it is feasible to use on-line addition of reductant to achieve the required signal enhancement. This work demonstrates a simple and convenient way to determine Hg in the $\mu\text{g/L}$ range using an axially-viewing ICP-OES.



Agilent Technologies

Instrumentation

All measurements were performed on an Agilent 720-ES axially-viewing ICP-OES. The Agilent 720-ES is a simultaneous ICP-OES featuring an Echelle polychromator incorporating a quartz prism and a custom-designed and patented CCD detector, which provides the benefit of simultaneous measurement and continuous wavelength coverage over the range from 167 to 785 nm. The system is available with a choice of sample introduction system; either a 3 or 4 channel peristaltic pump for sample introduction and mass flow control or manual pressure control of the nebulizer gas flow. For this application, the system was fitted with a mass flow controller and a four channel peristaltic pump. The four channel peristaltic pump allows the sample, SnCl_2 reductant and the waste to be simultaneously pumped. To enable on-line addition of the reductant to the sample, a Y-piece (Agilent p/n 1610132400) was used to combine the sample and reductant flows prior to the sample introduction system. The mixture was then nebulized into the plasma.

A conventional one piece axial torch was used. The sample introduction system consisted of a concentric glass nebulizer and a glass cyclonic chamber. Agilent ICP Expert II software was used for instrument operation. The operating parameters of the system are listed in Table 1.

Table 1. Instrument Operating Parameters

Conditions	Settings
Power	1.2 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer flow	0.65 L/min
Pump speed	12 rpm
Pump tubing	White-white (inlet) for both sample and reductant (1.02 mm id) Blue-blue (outlet) (1.65 mm id)
Sample uptake rate	1.0 mL/min
Sample uptake rate	1.0 mL/min
Replicate read time	30 s
Sample uptake delay time	80 s
Fast pump	Off
Rinse time	120 s
Sampling mode	Manual
Background correction	Fitted
Number of replicates	3 10 for detection limit measurements

The on-line addition of reductant results in an unusually large quantity of liquid being nebulized. It is recommended that the fast pump option be disabled during the sample uptake delay, to minimize droplet condensation in the injector tube of the torch.

Materials and Reagents

All chemicals and reagents used were of high-purity grade.

- HCl, Tracepur, 36%, Merck.
- HNO_3 , Ultrapure, 60%, Merck.
- 1000 mg/L Hg certified standard solution, EM Science.
- SnCl_2 , Analar, BDH.
- Milli-Q water.

Sample Preparation

Preparation of SnCl_2 Solutions

Stannous chloride (SnCl_2) can dissolve in less than its own mass of water without apparent decomposition, but as the solution is diluted, hydrolysis occurs to form an insoluble basic salt ($\text{Sn}(\text{OH})\text{Cl}$) which is readily oxidized by air. Therefore HCl must be added to suppress hydrolysis and to help prevent the oxidation of SnCl_2 by air. An insufficient amount of HCl will result in a yellow-colored solution. In this work, all SnCl_2 solutions were prepared in 20% HCl. It is recommended to dissolve SnCl_2 in concentrated HCl prior to mixing with water.

Sample Preparation for NIST 1641D Mercury in Water [3]

The certified reference material NIST 1641D mercury in water is supplied in an ampoule. After the ampoule was opened, a 0.2 mL aliquot was transferred to a 100 mL volumetric flask to make a 1 in 500 dilution with 2% v/v HNO_3 .

Calibration solutions and blank were prepared in 2% v/v HNO_3 .

Cleaning of the Torch After Analysis

After the analysis, it was observed that the end of the outer tube of the torch was covered by a layer of white powder, which is presumably SnO_2 . This can be removed by simply soaking the torch directly in concentrated HCl to dissolve the white deposit. After soaking, rinse the torch with de-ionized water and allow to dry.

Results and Discussion

Effect of SnCl₂ on Hg Signal Intensity

The effect of different SnCl₂ concentrations on the signal intensity of a 50 µg/L mercury solution was studied. As illustrated in Figure 1, on-line addition of SnCl₂ has enhanced the Hg signal over 30 times.

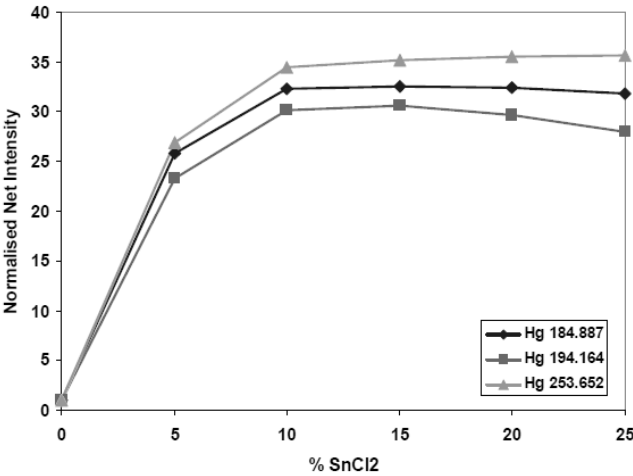


Figure 1. Effect of different SnCl₂ concentrations on the signal intensity of 50 µg/L Hg.

As the concentration of SnCl₂ increases, the Hg signal intensity increases, and then plateaus out at about 10–15% SnCl₂. Therefore, the concentration of SnCl₂ used in this work was 15%.

It is noted that for both the Hg 184 nm and Hg 194 nm lines, the Hg signal increases up to 15% SnCl₂, then slowly decreases as the concentration of SnCl₂ increases. This is caused by the spectral interference of Sn on both the Hg 184 nm and Hg 194 nm lines, respectively. The potential spectral interferences on various Hg lines are listed in Table 2.

Table 2. Potential Spectral Interferences on Hg Emission Lines

Wavelength (nm)	Potential interferences
184.887	Sn 184.821 nm
194.164	Sn 194.205 nm
253.652	Cr 253.634 nm Cr 257.692 nm

Figures 2 to 4 show the signal graphics for Hg at the 184, 194 and 253 nm lines with various SnCl₂ concentrations. The sloping background at the Hg 184 nm and Hg 194 nm lines is caused by the presence of high levels of Sn. The Hg 253 line is free of interference from Sn, but there is the potential for interference

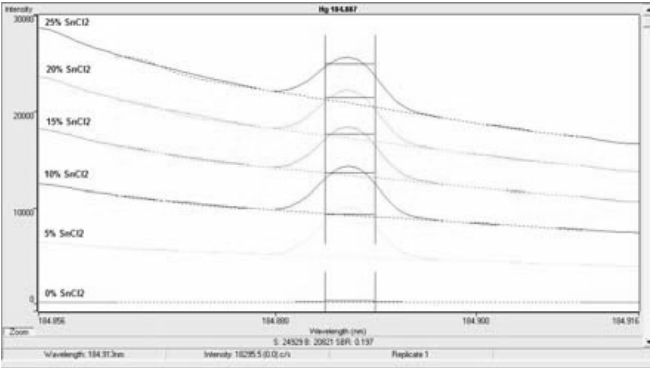


Figure 2. Signal traces of 50 µg/L Hg 184 nm at various SnCl₂ concentrations.

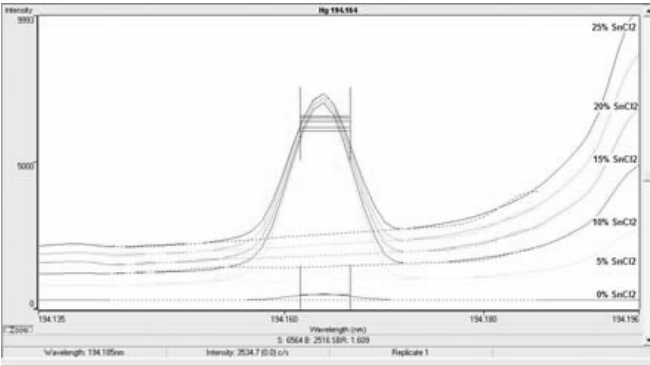


Figure 3. Signal traces of 50 µg/L Hg 194 nm at various SnCl₂ concentrations

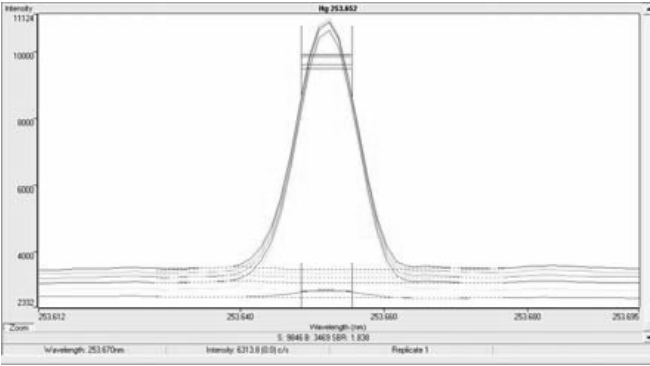


Figure 4. Signal traces of 50 µg/L Hg 253 nm at various SnCl₂ concentrations.

from Cr if the sample has been prepared in K₂Cr₂O₇.

Detection Limit

Detection limit (DL) is expressed as three times the standard deviation of the blank intensity in concentration units. The detection limits for Hg with and without the addition of SnCl₂ are listed in Table 2. Generally speaking, an order of magnitude improvement in detection limit is achieved with the addition of SnCl₂ as a reductant.

However it is also noted that these detection limits are around a factor of 10 higher than those that can be achieved

with the use of the cold vapor technique using the VGA-77 ($0.02 \mu\text{g}/\text{L}^2$).

Table 2. Detection Limits for Hg Achieved with On-line Addition of SnCl_2

Wavelength (nm)	DL ($\mu\text{g}/\text{L}$) with 15% SnCl_2	Without SnCl_2
184.887	0.4	2.0
194.164	0.2	2.0
253.652	0.2	3.0

Analysis of NIST 1641D Mercury in Water

Conventional aqueous Hg standards of 1, 5 and 10 $\mu\text{g}/\text{L}$ were used to calibrate the instrument at each of the respective Hg wavelengths. The calibration graphs obtained for each Hg emission line are shown in Figure 5. The NIST 1641d mercury in water certified reference material was

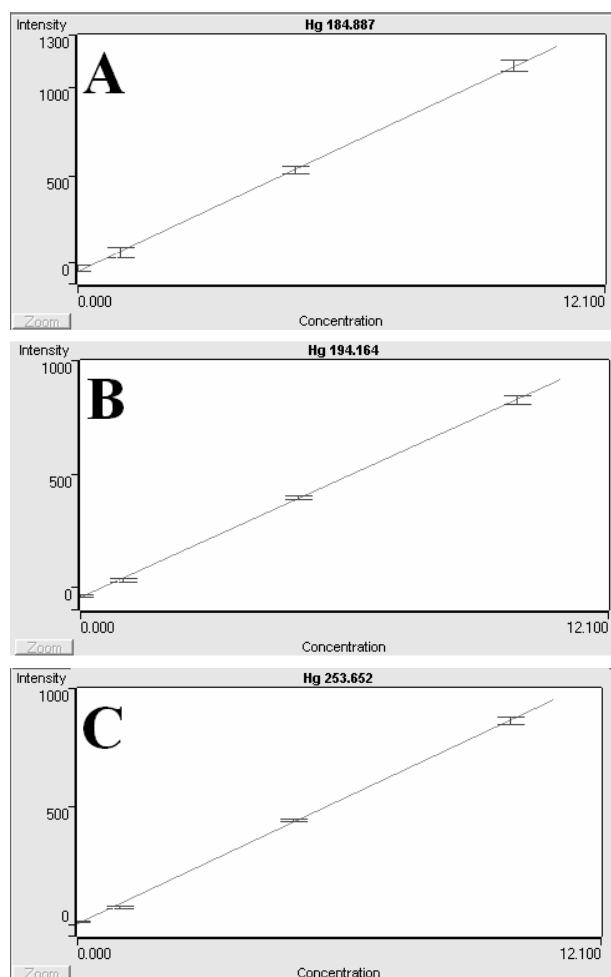


Figure 5. Calibration curves for Hg at (A) the 184 nm emission line, (B) the 194 nm emission line and (C) the 253 nm emission line.

measured against these calibrations. The results are listed in Table 3. The measured values are in good agreement with the certified values.

Table 3. Results for Analysis of the NIST 1641D Mercury in Water Certified Reference Material

Wavelength (nm)	Concentration (mg/kg) measured	Certified
184.887	1.592 ± 0.010	1.590 ± 0.018
194.164	1.585 ± 0.010	1.590 ± 0.018
253.652	1.596 ± 0.012	1.590 ± 0.018

Conclusion

The determination of Hg by on-line addition of SnCl_2 using the Agilent 720-ES axial ICP-OES instrument has been described. The on-line addition of SnCl_2 reductant for Hg determination can provide a tenfold improvement in detection limit compared with routine determination. This on-line reduction method allows Hg determinations at $\mu\text{g}/\text{L}$ levels without the use of a cold vapor generation technique. It is also simple and easy to implement.

References

1. US EPA Publication No. EPA-600/4-79-020, "Method for chemical analysis of water & wastes", (1979), Method 245.1.
2. P. Doidge, "Determination of mercury in a certified reference sludge material using the Varian 710-ES",

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Printed in the USA
November 1, 2010
SI-01319



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