APPLICATION NOTE

ICP-Mass Spectrometry

Authors

Jianmin Chen

PerkinElmer, Inc.
Shelton, CT 06484 USA

Determination of Mercury in Wastewater by Inductively Coupled Plasma-Mass Spectrometry

Mercury is ubiquitous in nature, and the human health consequences of mercury exposure were recognized from prehistory to the present. The first emperor of unified China who came to power in 221 B.C., Qin Shi Huang, reportedly died of ingesting mercury pills that were intended to give him eternal life. The severity of mercury's toxic effects depends on the form and concentration of mercury and the route of exposure. Although its potential for toxicity in highly contaminated areas such as Minamata Bay in Japan is well documented, research has shown that mercury can be a threat to the health of people and wildlife in many environments that are not obviously polluted. There is no safe level of mercury for humans. The main toxic effects of mercury are known to negatively affect the neurological, renal, cardiovascular and immunological systems.

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Mercury exists in three chemical forms: elemental or metallic, organic or methylmercury, and inorganic complexes. Mercury has thousands of industrial applications. Some common uses for mercury include conducting electricity, measuring temperature and pressure, acting as a biocide, preservative, and disinfectant, as well as being a catalyst for reactions. Unlike most other pollutants, mercury is highly mobile, non-biodegradable, and bio-accumulative; as a result, it must be closely monitored to ensure its harmful effects on local populations are minimized.[1] Thus, measurement of mercury in environmental samples, and in particular wastewater, is of great importance as a major tool to protect the environment from mercury released through emissions from manufacturing, use, or disposal activities. Currently, the prominent methods typically utilized by the environmental community for the determination of mercury generally require detection limits as low as 0.5 ng/L (ppt, parts-per-trillion).[2]

Traditionally, mercury is analyzed using Cold Vapor Atomic Absorption Spectroscopy (CVAAS) or Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). Both of these techniques are relatively straightforward to use and can accomplish the analytical requirements of detection limits in the low ppt range. However, they are generally specific for mercury analysis only.

In recent years, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become one of the most powerful analytical techniques for trace element analysis because of its high sensitivity, wide linear dynamic range, and simultaneous multi-element detection capability. As a result, ICP-MS has been increasingly adopted in environmental and biomonitoring laboratories for the simultaneous measurement of mercury with other toxic metals since this technique can offer the same analytical performance as CVAAS or CVAFS. This application note describes the application of ELAN® ICP-MS to the determination of mercury in wastewater.

Instrumentation

For this study, the PerkinElmer® ELAN DRC™ II ICP-MS was used for the analysis of wastewater samples under standard mode. The ELAN ICP-MS instrument conditions and general method parameters are shown in Table 1.

Table 1. **ELAN ICP-MS Instrumental Conditions and Experimental Parameters.**

RF power	1100 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	0.96 L/min
Nebulizer	MEINHARD® Concentric Type A3
Spray chamber	Baffled Quartz Cyclonic
Scanning mode	Peak Hopping
Dwell time	50 ms
Replicates	3
Integration time	1 sec/mass

Sample Preparation

The stability of mercury-containing solutions has been a topic of concern for all trace analysts performing Hg determinations. It is reported that a trace amount of gold salt added to HNO_3 preserved all forms of mercury. The gold ion acts as a strong oxidizing agent that converts or maintains mercury as mercuric ion which remains in solution.[3] Thus, a solution of 2% (v/v) HNO_3 containing 200 ug/L Au was used for preparation of all samples and standards. Two simulated wastewater certified reference materials (Trace Metals Solutions, CWW-TM-A and CWW-TM-C, High-Purity Standards, Charleston, SC, USA) were prepared according the manufacturer's description using the same diluent in this study.

Calibration

External calibration standards of mercury were at the level of 10, 20, 50, 100, 200, 500, 1000 ng/L. Figure 1 shows the calibration curve of ^{202}Hg. The correlation coefficient is 0.999973, which allowed the accurate quantitative analysis of mercury at the low ppt levels.

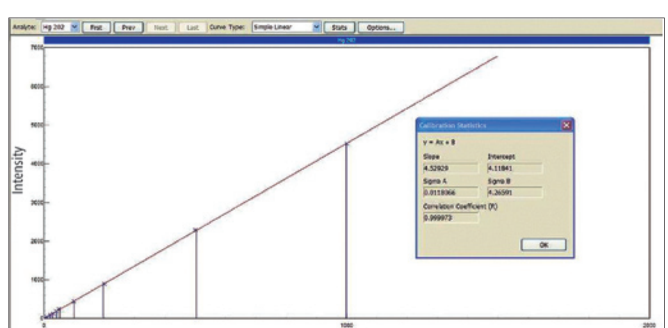

Figure 1. External calibration curve of ^{202}Hg. Standard solutions were prepared in 2% HNO_3 containing 200 ug/L Au with concentrations ranging from 10 to 1000 ng/L.

Spike recovery

The spike recovery test was performed using two simulated wastewater certified reference materials (HPS CWW-TM-A and CWW-TM-C). The results are presented in Table 2.

Table 2. **Spike recovery test results from two simulated wastewater certified reference materials (HPS CWW-TM-A and CWW-TM-C).**

Wastewater Sample	Found (ng/L)	Spike Level (ng/L)	Measured (ng/L)	Recovery %
CWW-TM-A	49	200	238	95
CWW-TM-C	375	1000	1370	99

Memory effect

It is generally viewed that routine determination of mercury by ICP-MS is affected by a pronounced memory effect in the sample introduction system. This results in long washout times for the analyte, which affects the accuracy and reliability of the analytical procedure. To minimize the memory effect, the system was washed using 2% (v/v) HNO_3 containing 200 ug/L Au between samples. Figure 2 shows the uptake and wash out profile of Hg. The signal of four mercury isotopes returns to the background level in around 60 seconds, which is equivalent to the typical rinse time used for many other analytes. Thus, the results indicated application of gold salt is effective in preventing mercury sorption and vapor buildup within the sample introduction system.

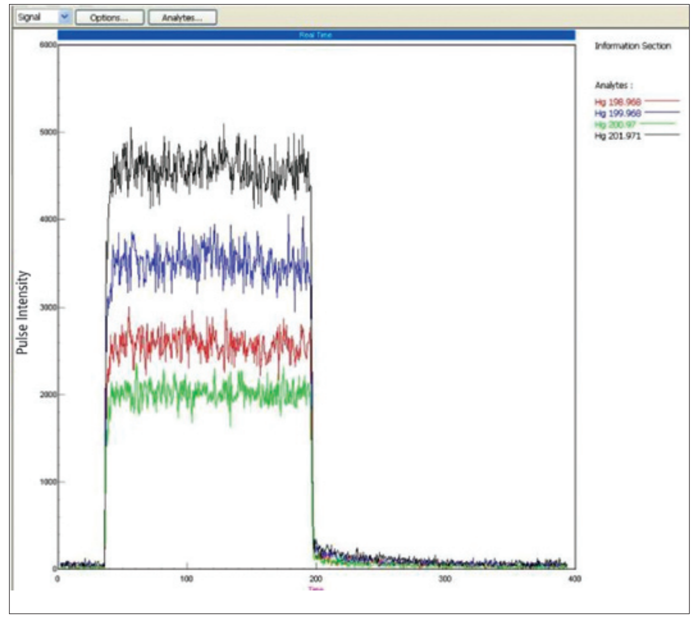

Figure 2. Uptake and wash out profile for Hg at 1000 ng/L level. The signal of four mercury isotopes returns to the background level in around 60 seconds, which is equivalent to the typical rinse time used for many other analytes.

Conclusion

The ELAN ICP-MS combines high sensitivities and superior detection limits with ease of use and high sample throughput. This allows it to be an excellent tool for trace mercury determination in wastewater samples. Mercury can be detected simultaneously with the other trace elements of interest within a single sample run.

References

1. J.O. Nriagu, Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, Nature 279 (1979) 409–411.

2. EPA Method 1631. Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

3. www.epa.gov/nerlesd1/factsheets/mpt.pdf. Mercury Preservation Techniques.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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