SHIMADZU APPLICATION NEWS

LAAN-A-AA-E016

● SPECTROPHOTOMETRIC ANALYSIS

No.A392

Mercury (Hg) Analysis by the Electrothermal Atomization Method

■ Introduction

Cold vapor atomic absorption is often used for the microanalysis of mercury. Electrothermal atomization is hardly ever used for mercury analysis, although it is used for the microanalysis of other elements. The main reason for this is the propensity of mercury to vaporize at low temperatures makes it impossible to attain sufficient sensitivity with this method. Here, it is shown how using palladium (Pd) as a matrix modifier makes it possible to quantify mercury at concentrations of around 10 ng/mL with electrothermal atomization, and an example in which this method is used to analyze the mercury in resin is described. The AA-6300 and GFA-EX7i were used for this analysis.

■ Study of Matrix Modifiers for Mercury

In electrothermal atomization, measurement is performed using a furnace (heating) program that consists of drying, ashing, and atomization stages. Mercury vaporizes very easily, as illustrated by the fact that it is a liquid at room temperature, and in a standard furnace program, most of it has vaporized by the time it reaches the atomization stage, making measurement almost impossible. The effects of adding palladium (Pd), which is widely used as a matrix modifier, and gold (Au), which readily forms an amalgam with mercury, with the objective of preventing vaporization of the analyte during heating were compared. With a sample injection volume of 20 µL and a modifier concentration of 1,000 mg/mL (injection volume: 10 µL), an absorbance of approx. 0.200 was measured for gold at a mercury concentration of 1,000 ng/mL, whereas an absorbance of approx. 0.230 was measured for palladium at a mercury concentration of 200 ng/mL. In other words, using palladium as a matrix modifier gave a sensitivity approximately five times that attained with gold (Fig.1 and Fig.2).

■ Study of Furnace Program and Modifier Concentration

Next, the ashing temperature and atomization temperature in cases where palladium is used as the modifier were considered. Sensitivity was nearly constant for ashing temperatures less than 500 ˚C, and was constant for atomization temperatures greater than 900 ˚C (Fig.3). In the standard measurement, an ashing temperature of 300 ˚C and an atomization temperature of 1,000 ˚C were used. Regarding the additive concentration, with a sample injection volume of 20 µL and a modifier injection volume of 10 µL, the sensitivity was constant for palladium concentrations greater than 500 µg/mL (Fig.4). In the standard measurement, a palladium concentration of 1,000 µg/mL was used. The measurement conditions that were ultimately used are given in Table 1 and Table 2. With these conditions and an injection volume of 40 µL (and 10 µL of modifier), an absorbance of approx. 0.400 was measured for a mercury concentration of 200 ng/mL, and an absorbance of approx. 0.020 was measured for a mercury concentration of 10 ng/mL. So, quantification around 10 ng/mL-Hg was possible by this method (Fig.5).

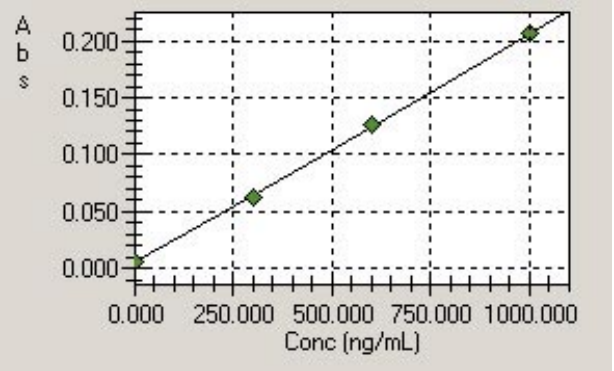

Fig.1 Hg Calibration Curve with Au

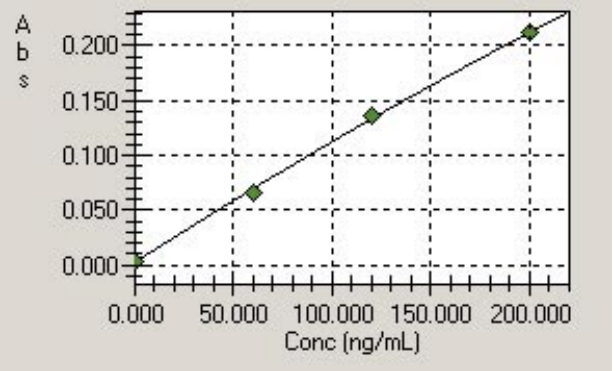

Fig.2 Hg Calibration Curve with Pd

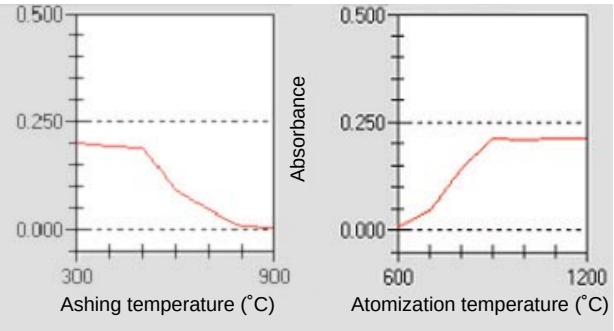

Fig.3 Study of Ashing Temperature and Atomization Temperature (Hg: 200 ng/mL, 20 µL + Pd: 1,000 mg/mL, 10 µL)

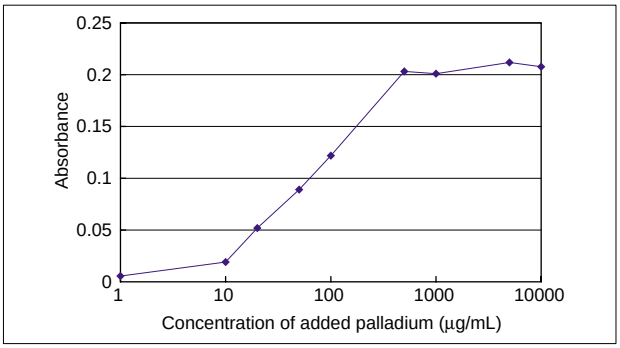

Fig.4 Hg Sensitivity vs. Pd Concentration

Table 1 Optics Parameters for Hg

Analysis wavelength	253.7 nm
Slit width	0.7 nm
Current	4 mA
Ignition mode	BGC-D2

Table 2 Furnace Program

	Temperature (°C)	Time (s)	Mode	Ar Gas
1	60	3	RAMP	0.10
2	120	15	RAMP	0.10
3	300	10	RAMP	1.00
4	300	5	STEP	1.00
5	300	3	STEP	0.00H
6	*1000*	*4*	*STEP*	*0.00H*
7	2500	5	RAMP	1.00
8	2500	4	STEP	1.00

Note : Atomization corresponds to stage 6.

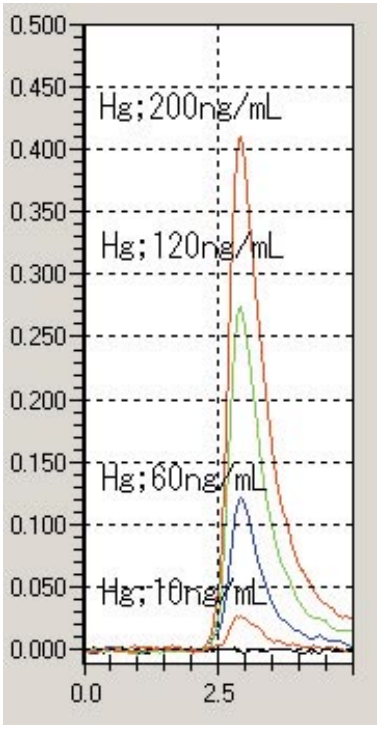

Fig.5 Peak Profiles of Hg (40 μL injection)

■ Application to Digested Polymer Solutions

The method obtained from the above results was applied to the analysis of mercury in polymers. The polymers used were ABS and PVC. Nitric acid and hydrogen peroxide were added to masses of between 0.10 g and 0.12 g of each. The resulting mixtures were then processed using a microwave decomposition system, and the volume was standardized to 50 mL using pure water. Both solutions were analyzed using the standard addition method. The ABS solution was analyzed without further dilution whereas the PVC solution was analyzed after being diluted first by a factor of 10 and then, in an autosampler, by a factor of 8. The results corresponded almost exactly to those obtained with the cold vapor atomic absorption method (MVU) (Table 3).

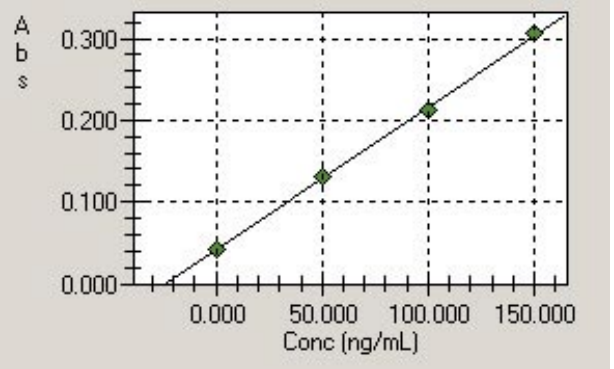

Fig.6 Calibration Curve for ABS

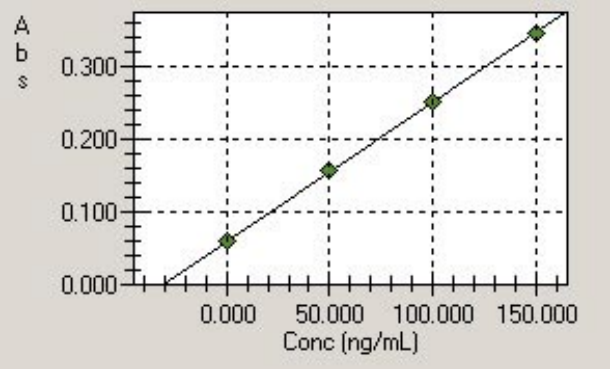

Fig.7 Calibration Curve for PVC

Table 3 Results of Polymer Analysis

Sample	Electrothermal Atomization		MVU
	Concentration in Undiluted Solution	Concentration in Solid	Concentration in Solid
ABS	193 ng/mL	96.5 mg/kg	91.5 mg/kg
PVC	2400 ng/mL	1020 mg/kg	1050 mg/kg

NOTES:
✻This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.

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Printed in Japan 3100-08702-10A-IK