![SHIMADZU]

Application News

Trace Analysis of Palladium Using Electrothermal Atomization

■ Introduction

The Nobel Prize in Chemistry for "Palladium-Catalyzed Cross Couplings in Organic Synthesis" which was awarded in 2010 is a technique that is actually widely used in industry. The organic substances that are formed in this reaction must be analyzed to ascertain that there is no residual palladium (Pd) remaining in the substances. An atomic absorption spectrophotometer is used to measure precious metals such as palladium, but this requires that the sample be liquefied at the time of measurement. Usually, solid organic compounds are measured in aqueous solutions decomposed by addition of acid and heating for AAS. But the samples just diluted in organic solvents are also able to be measured directly. In this case, the standard solutions for calibration curve should be prepared with the same organic solvents.

Here we introduce examples of Pd trace analysis using the graphite furnace atomization method with the organic solvents isopropanol (IPA) and n-methylpyrrolidone (NMP), both strongly compatible with water and easy to use.

■ Pretreatment

We used commercially-available 1000 mg/L Pd as the standard stock solution. To 1 mL of this, 1 mL of concentrated nitric acid was added. Then, pure water was added to obtain 100 mL of Pd standard solution (Pd: 10 mg/L). Next, two 1 mL aliquots of this were collected, and electronics grade IPA and electronics grade NMP were added to the respective aliquots to bring the volumes to 100 mL (Pd: 100 µg/L). Finally, 10 mL was collected from each solution, and these were adjusted to 50 mL for use as the final standard solutions, each containing 20 µg/L Pd. These solutions and each of the pure solvents were placed in the autosampler, and calibration curves were generated by adjusting the injection volumes of the respective 20 µg/L Pd standard solutions.

■ Investigation of Parameters

To determine the best temperatures to be used for ashing and atomizing, we conducted an investigation in which 20 µL each of the respective Pd 20 µg/L solutions was measured within a fixed temperature range at 100 °C intervals using the "temperature search" function which looks for the best sensitivity. The results are shown in Fig. 1 to Fig. 4.

For both IPA and NMP, the absorbance was nearly constant at an atomizing temperature greater than 2200°C. Also, there was no decline in sensitivity at an ashing temperature up to 1000°C. As a result, the furnace program used for the standards was as shown Table 2.
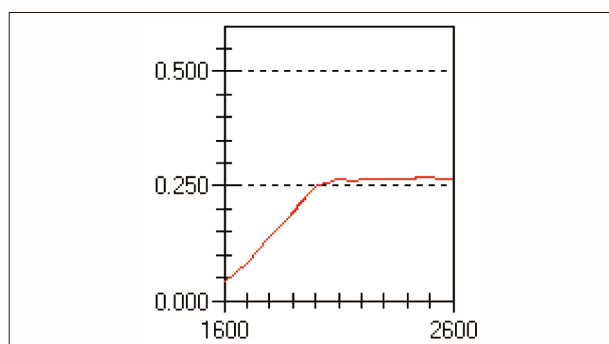
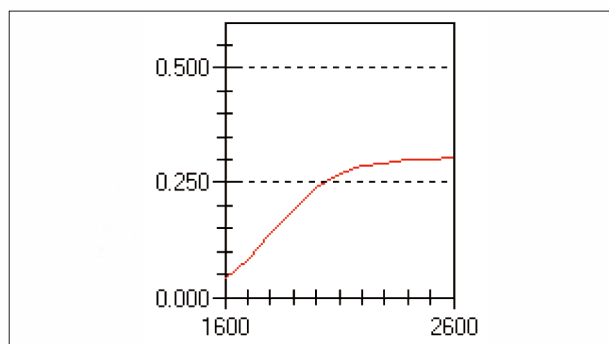

Fig. 1 Atomizing Temperature Search Results for IPA

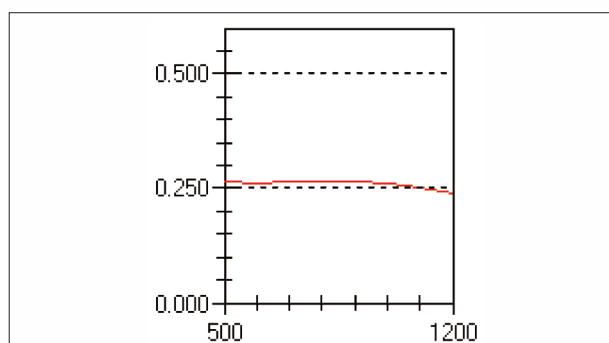

Fig. 2 Atomizing Temperature Search Results for NMP

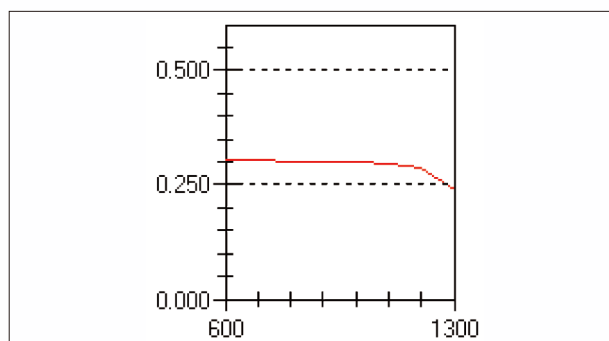**Fig. 3 Ashing Temperature Search Results for IPA**

Fig. 4 Ashing Temperature Search Results for NMP

■ Instruments and Parameters

The instruments and principal measurement parameters are shown in Tables 1 to 3.

Table 1 Instruments and Optical Parameters

Instruments	Main unit: AA-7000 Graphite furnace: GFA-7000
Analysis wavelength	247.6 nm
Slit width	0.7 nm
Current	10 mA
Lamp mode	BGC-D2

Table 2 Furnace Program

	Temperature (°C)	Time (sec)	Heating Mode	Sensitivity	Gas Flowrate (L/min)
1	60	3	RAMP	REGULAR	0.10
2	120	20	RAMP	REGULAR	0.10
3	250	10	RAMP	REGULAR	0.10
4	600	10	RAMP	REGULAR	1.00
5	600	10	STEP	REGULAR	1.00
6	600	3	STEP	HIGH	0.00
7*	2500	3	STEP	HIGH	0.00
8	2600	2	STEP	REGULAR	1.00

7*: Atomizing stage
Graphite tube used: Pyrolytic graphite tube

Table 3 Autosampler Parameter Settings for Calibration

Concentration	Pd; 20 µg/L	Each Solvent	Total
0 µg/L	0 µL	30 µL	30 µL
4 µg/L	6 µL	24 µL	30 µL
12 µg/L	18 µL	12 µL	30 µL
20 µg/L	30 µL	0 µL	30 µL

■ Results

The calibration curves generated using the standard parameters are shown in Fig. 5 and 6. The detection limit (3 σ) and lower limit of quantitation (10 σ) calculated from the standard deviation of absorbance obtained from 10 repeat blank measurements are shown in Table 4. These refer to the concentrations in solution. For example, if measurement is conducted on a solution of IPA or NMP in which 1 g of solid organic material is dissolved in 100 mL of the organic solvent, the lower limit of quantitation in the solid would be about 30 ng/g.
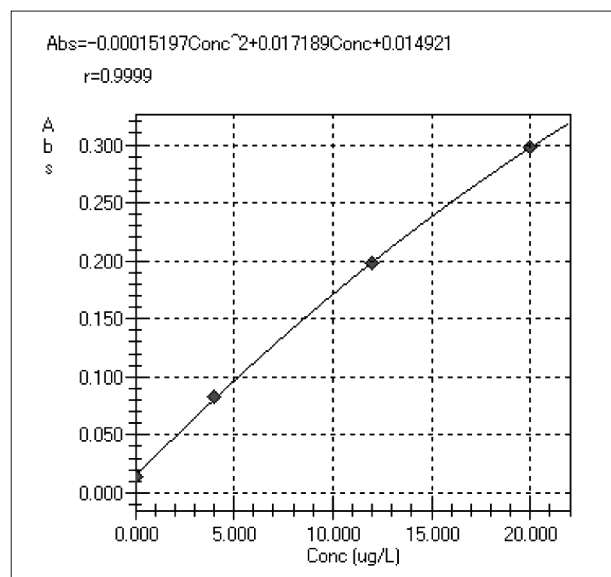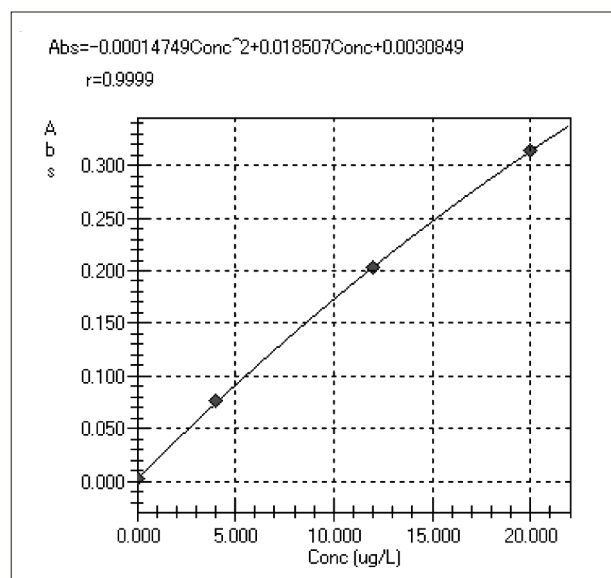

$$Abs = -0.00015197 Conc^2 + 0.017189 Conc + 0.014921$$
$$r = 0.9999$$

Fig. 5 Calibration Curve Using IPA

$$Abs = -0.00014749 Conc^2 + 0.018507 Conc + 0.0030849$$
$$r = 0.9999$$

Fig. 6 Calibration Curve Using NMP

Table 4 Summary of Sensitivity

Solvent	Calibration Curve Slope (k)	SD	LOD (µg/L)	LOQ (µg/L)
IPA	0.0148	0.0005	0.1	0.3
NMP	0.0155	0.0005	0.1	0.3

Calibration curve slope : Absorbance / Concentration (µg/L)
SD : Standard deviation of absorbance obtained in 10 repeat measurements of blank solution
LOD : Lower limit of detection ($3 \times SD \times 1/k$)
LOQ : Lower limit of quantitation ($10 \times SD \times 1/k$)