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Application News

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Spectrophotometric Analysis

Measurement of Metal Ion in Plating Solution by Flame Atomic Absorption

■ Introduction

To ensure that the quality of metal plating is maintained at a high level, it is important to manage the concentration of metal ions in the plating solution. Flame atomic absorption spectroscopy and ICP emission spectroscopy can be used to quickly analyze metallic ions over a wide range of concentrations, from principal component to trace constituent levels. Here, using actual examples of analysis using the Shimadzu AA-7000 Atomic Absorption Spectrophotometer, we introduce factors to be considered in the analysis of metal ions in plating solution by flame atomic absorption.

■ Sample Preparation

Preparation typically requires dilution only. If precipitation of the components occurs due to saturation, etc., steps must be taken to homogenize the sample solution adequately before collection for analysis.

As the appropriate concentration range of the instrument is on the order of mg/L for principal components at high concentrations ranging from several g/L to tens of g/L, the sample stock solution should be diluted from several hundred times to several tens of thousands of times as necessary when measuring principal components. Because the scale of this dilution factor is so large, extreme care must be taken to avoid dilution errors.

On the other hand, the concentrations of trace constituents typically range from just a few mg/L to tens of mg/L, requiring dilution from a few to several tens of times.

■ Analytical Method

The absorbance repeatability and linearity of the calibration curve are important factors for ensuring accurate results in principal component analysis.

Fig. 1 shows an example of the relationship between absorbance and repeatability (Relative Standard Deviation (RSD)).
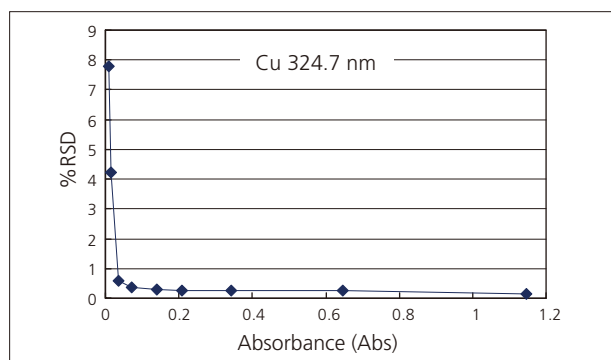
Fig. 1 Relationship Between Absorption and Repeatability

To obtain good absorbance repeatability and linearity of the calibration curve, it is best to conduct measurement in the 0.05 - 0.5 absorbance range. Therefore, when analyzing principal components, the calibration curve concentration and plating solution dilution factor must be adjusted so that the absorbance associated with the concentrations of the measurement solution and standard solution fall within this range. Another way to adjust the absorbance is to change the angle of the burner. Fig. 2 shows the relationship between the burner angle and absorbance. If the burner angle is set to 90°, the absorbance can be reduced to about 1/20 the value. The analysis wavelengths for typical analytes are shown in Table 1, along with their appropriate concentration ranges (at 0° burner angle, corresponding to 0.05 - 0.5 Abs range) and lower limits of quantitation, respectively. With a burner angle of 90°, the appropriate concentration range is about 20 times higher than the range when the burner angle is set to 0°. This method makes it possible not only to measure samples prepared at low dilutions, but also to reduce dilution error and the amount of labor required. Furthermore, the AA-7000 adopts a double-beam optical system, thereby permitting stable measurement to be conducted immediately following lamp ignition.
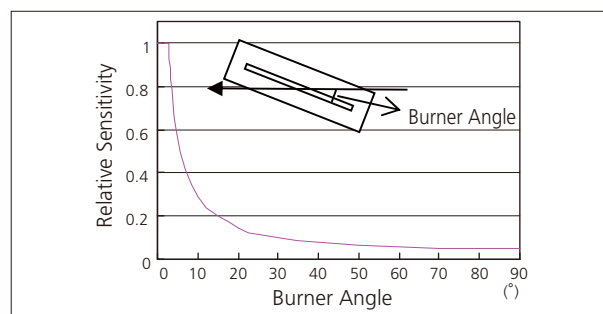
Fig. 2 Relationship Between Burner Angle and Sensitivity

Table 1 Recommended Measurement Range and Lower Limit of Quantitation for Each Element (Burner Angle 0°)

Element	Analysis Wavelength nm	Appropriate Concentration Range (0.05 - 0.5 Abs)	Lower Limit of Quantitation (0.005 Abs)
Au	242.8	1 - 10 mg/L	0.1
Bi	223.1	2 - 20 mg/L	0.2
Cd	228.8	0.07 - 0.7 mg/L	0.007
Co	240.7	0.5 - 5 mg/L	0.05
Cr	357.9	0.5 - 5 mg/L	0.05
Cu	324.7	0.3 - 3 mg/L	0.03
Fe	248.3	0.5 - 5 mg/L	0.05
Ni	232.0	0.4 - 4 mg/L	0.04
Pb	283.3	2 - 20 mg/L	0.2
Pb	217.0	0.8 - 8 mg/L	0.1
Pd	244.8	1 - 10 mg/L	0.1
Pd	247.6	1 - 10 mg/L	0.1
Rh	343.5	1 - 10 mg/L	0.1
Sn	224.6	20 - 200 mg/L	2
Sn	286.3	40 - 400 mg/L	4
Sb	217.6	2 - 20 mg/L	0.2
Zn	213.8	0.08 - 0.8 mg/L	0.008

■ Analysis of Principal Component by Changing Burner Angle

We analyzed the principal component copper in the copper plating solution using the burner angles 0 ° and 90 °. The copper plating solution was diluted so that the absorbance values would be suitable for each of the burner angles. The measurement results are shown in Table 2, and the calibration curves are shown in Fig. 3. The results indicate that approximately the same values are obtained regardless of the burner angle, and that by changing the burner angle from 0 ° to 90 °, the absorbance decreases to about 1/20 the value, thereby reducing the error due to dilution.

Table 2 Results of Cu in Cu Plating Solution with Burner Angles 0 ° and 90 °

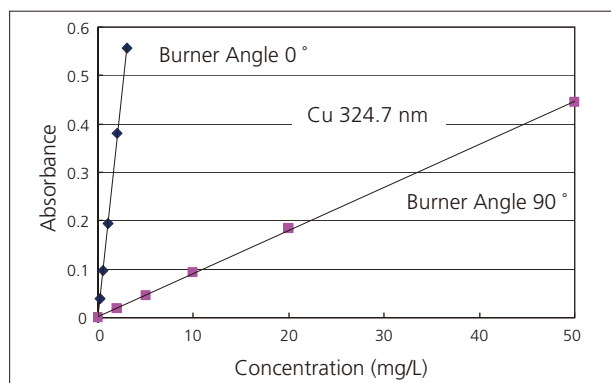| Burner Angle (°)	0 °	90 °
Recommended Concentration Range (mg/L)	0.3 - 3	6 - 60
Dilution Factor	2500	100
Cu Concentration in Measurement Solution (mg/L)	1.62	40.0
Cu Concentration in Stock Solution (g/L)	4.05	4.00

Fig. 3 Calibration Curves of Cu at Burner Angles 0 ° and 90 °

■ Analysis of Trace Element

We analyzed 1 mg/L palladium added to copper plating solution. Because measurement was conducted using a small dilution factor in the single- to double-digit range, a change in measurement sensitivity and background absorption (BG) occurred due to the influence of the principal component metal ions and additives. These effects can be offset to some degree by using the standard addition method in conjunction with background correction. The AA-7000 is equipped as standard with two types of background correction methods, including the high-sensitivity deuterium lamp method (D_2 method) and the self-reversal method (SR method), the latter of which extends coverage up to the long wavelength region.

A two-fold dilution of copper plating solution was prepared, and after palladium standard solution was added stepwise to prepare two standard-added samples, measurement was conducted by the standard addition method. The standard-added samples were prepared as shown in Table 3. Background correction was conducted by the D_2 method. The integrated signals are shown in Fig. 4, and the standard addition calibration curve and measurement results are shown in Fig. 5. Background absorption due to the principal component does occur, but it is clear that accurate values can be obtained by using background correction.

Table 3 Standard Solutions for Standard Addition Method

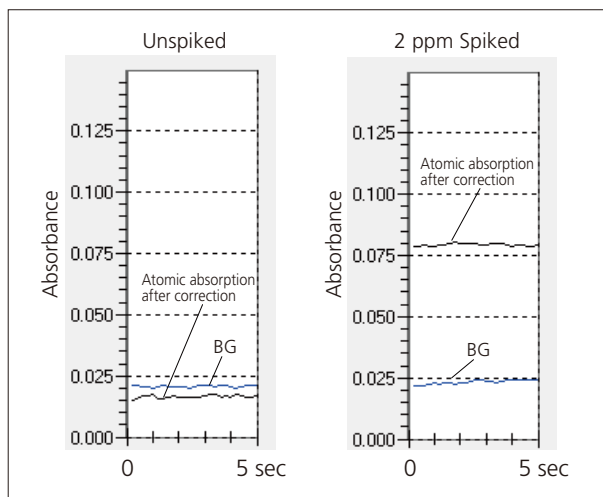|	Collected Plating Solution Volume	Spiked Volume of Pd 10 ppm Std. Solution	Spiked Volume of Distilled Water	Total Volume
Unspiked	5 mL	0 mL	5 mL	10 mL
Spiked at 1 ppm	5 mL	1 mL	4 mL	10 mL
Spiked at 2 ppm	5 mL	2 mL	3 mL	10 mL

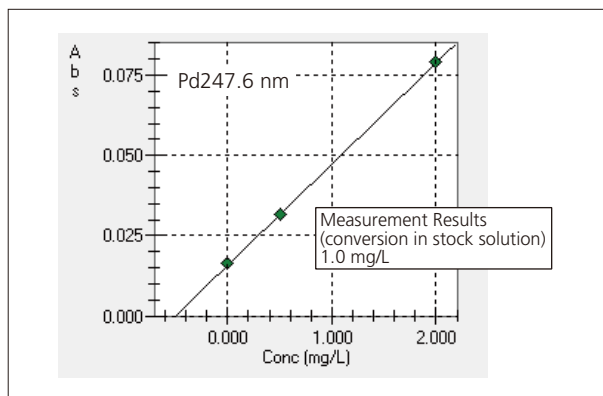**Fig. 4 Integrated Signal of Pd**

Fig. 5 Calibration Curve and Result of Pd in Cu Plating Solution Using Standard Addition Method

■ Conclusion

In the measurement of principal component elements in plating solution, changing the burner angle permits the reduction of error due to dilution. Furthermore, use of an appropriate background correction method allows accurate measurement of trace-level elements.

Thus, the AA-7000 is capable of measuring metal ions present in a wide range of concentrations in plating solution, from principal components to trace-level elements.

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