

Application News

No. A479

Spectrophotometric Analysis

Flame AA Analysis of Cadmium (Cd) and Lead (Pb) in Simulated Seawater and Polished Rice Using Chelating Polymer Solid Phase Extraction

Introduction

The testing methods for industrial wastewater (JIS K 0102) as amended in 2013, newly adopt the use of solid phase extraction with a chelating resin for sample pretreatment of Cu, Zn, Pb, Cd, Fe, Ni, and Co. Using this process permits separation and concentration of the target elements from such interfering components as sodium, potassium, magnesium and calcium, etc. Solvent extraction using a chelating agent has conventionally been employed for the same purpose, but solid phase extraction using a chelating resin offers such benefits as reduced solvent consumption and pollution, and simplified processing.

Here, using the AA-7000, we introduce examples of analysis by the flame method of Cd and Pb in simulated seawater and a solution of decomposed polished rice using commercially available chelating resin cartridges for solid phase extraction.

Sample Preparation

For the simulated seawater, the sample stock solution was used as is. For the polished rice solution, 2 g of polished rice was weighed out in a beaker, nitric acid and perchloric acid were added, and decomposition was conducted using a hot plate. After cooling, the solution was filtered, and 100 mL of the filtrate was used as the sample stock solution.

The pH of the sample stock solution was then adjusted to about pH 5.6, after which the solution was passed through conditioned chelating cartridge, thereby trapping the measurement elements in the chelating cartridge. As the chelating resin in this case had a pH of about 5.6, elements such as Cd and Pb were effectively retained in the cartridge, while elements such as Na, K, Mg and Cd were not retained. After washing the chelating cartridge in distilled water, the captured elements were eluted from the cartridge using 5 mL of 3 mol/L nitric acid solution. The eluate was then adjusted to a volume of 10 mL, and this served as the measurement solution. Fig. 1 and 2 show the chelate cartridge conditioning and sample solution extraction process, respectively. As the pH dependence of the retained element and the type and concentration of the reagent used vary with the chelate cartridge that is used, it is necessary to refer to the manufacturer's instruction manual.

For validation of the extraction process, a spiked recovery test solution was prepared prior to conducting the extraction by adding standard solution to the sample solution, and then conducting the same processing as for the actual sample solution. The spiked concentrations in the simulated seawater consisted of 0.01 mg/L of cadmium and 0.1 mg/L of lead. For the rice, the prepared concentrations based on solid sample conversion were 0.2 mg/kg of cadmium and 2 mg/kg of lead.

5 mL acetone delivered
↓
10 mL of 3 mol/L nitric acid delivered
↓
20 mL distilled water delivered
↓
10 mL of 0.1 mol/L ammonium acetate delivered

Fig. 1 Conditioning of Chelating Cartridge

100 mL pH-adjusted sample solution delivered
↓
20 mL distilled water delivered (rinse)
↓
5 mL of 3 mol/L nitric acid delivered (elution)
↓
Volume adjusted to 10 mL with distilled water
↓
Analysis by flame AA

Fig. 2 Chemical Separation of Sample Solution with Chelating Cartridge

Analytical Method and Conditions

Measurement was conducting using the calibration curve method. The standard solutions were prepared by diluting commercially available standard solutions for atomic absorption measurement. The main measurement parameters of the instrument are shown in Table 1.

Table 1 Instrument Measurement Parameters

| | Cd | Pb |
|------------------------|-----------------------------------|----------|
| Measurement wavelength | 228.8 nm | 283.3 nm |
| Slit width | 0.7 nm | |
| Ignition mode | BGC-D2 | |
| Flame type | Air-C ₂ H ₂ | |

Results and Conclusion

Fig. 3 and 4 show the calibration curves for Cd and Pb, respectively. The standard solutions were spiked with nitric acid to match the concentrations of the measurement samples.

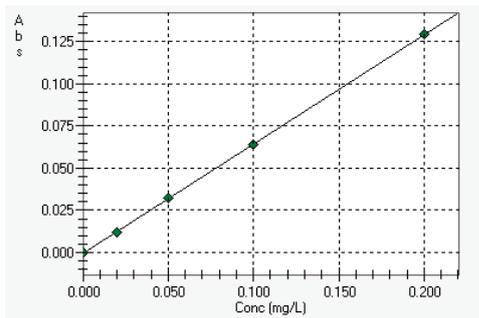


Fig. 3 Calibration Curve for Cd

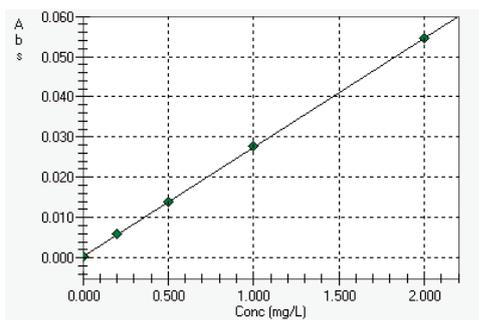


Fig. 4 Calibration Curve for Pb

(1) Measurement Results for Simulated Seawater

Table 2 shows the concentrations of Na and Mg in the original seawater and post-extraction seawater. The concentrations of both Na and Mg in the extracted seawater are less than 1/1000 those in the original simulated seawater, indicating efficient removal of interfering components.

Table 3 shows the measurement results for Cd and Pb. Concentration of the sample permitted measurement by the flame method even at low sample concentrations. Excellent spike and recovery results at greater than 95 % were also obtained. Fig. 5 shows the absorbance following integration.

Table 2 Na and Mg Concentrations in Original Seawater and Extracted Seawater

| Element | In Original Seawater | In Extracted Seawater |
|---------|----------------------|-----------------------|
| Na | 10000 mg/L | 2 mg/L |
| Mg | 1300 mg/L | 0.6 mg/L |

Table 3 Measurement Results for Cd and Pb in Seawater

| Element | Cd | Pb |
|---|-------------|------------|
| Simulated Seawater | 0.0017 mg/L | <0.02 mg/L |
| Spike Recovery | 98 % | 95 % |
| Quantitation lower limit ^(*) | 0.0007 mg/L | 0.02 mg/L |

(*) The lower limit of quantitation refers to the concentration in seawater corresponding to an absorbance of 0.004 when measurement is conducted using 10 mL after conducting chelating solid extraction of 100 mL of seawater.

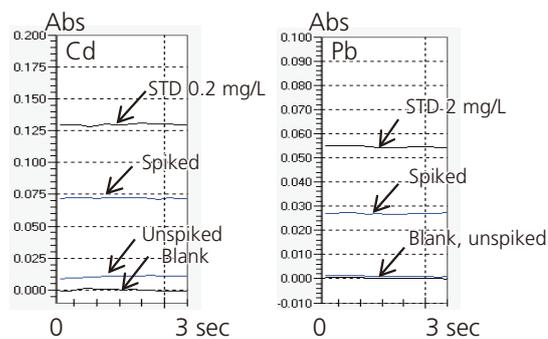


Fig. 5 Signal of Cd and Pb in Seawater and Standard

(2) Measurement Results for Polished Rice

Table 4 shows the sample measurement results in which excellent spike and recovery results were obtained. In the case of cadmium, quantitation was possible at less than one-tenth of 0.4 mg/kg, the national standard for edible rice in Japan.

Table 4 Measurements Results for Cd and Pb in Polished Rice

| Element | Cd | Pb |
|---|------------|------------|
| Polished rice | 0.03 mg/kg | <0.4 mg/kg |
| Spike Recovery | 95 % | 98 % |
| Quantitation lower limit ^(*) | 0.03 mg/kg | 0.8 mg/kg |

(*) The lower limit of quantitation refers to the concentration in polished rice corresponding to an absorbance of 0.004 when measurement is conducted after decomposition of 2 g of polished rice and subsequent solid extraction using 10 mL of chelating resin.

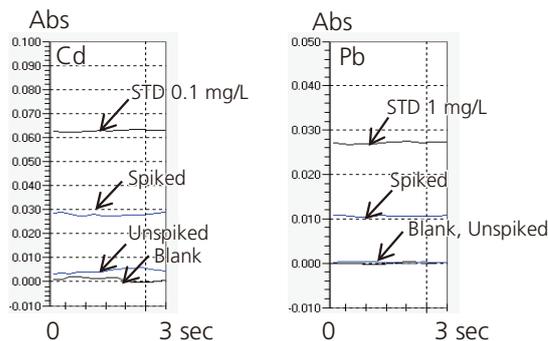


Fig. 6 Signal of Cd and Pb in Polished Rice and Standard

Application of solid phase extraction using chelating polymer for sample pretreatment permits the concentration of measurement analytes and the elimination of interfering substances using a simple operation, and can achieve the same high-sensitivity measurement results that are possible using solvent extraction pretreatment. Furthermore, since the obtained process solution consists of a nitric acid solution, it can be used not only for flame atomic absorption, but for graphite furnace atomic absorption, as well as ICP emission analysis and ICP mass spectrometric analysis.

The AA-7000 series includes models that support not only flame measurement and graphite furnace measurement, but automatic switching between the two modes as well, to accommodate a wide variety of analysis requirements.