SHIMADZU APPLICATION NEWS

LAAN-A-AA-E002

● SPECTROPHOTOMETRIC ANALYSIS

No.A355

Cd analysis by Atomic Absorption

Cadmium is mainly produced as cadmium sulfide in the natural environment. In the industrial sphere, however, it is mostly produced as a by-product when producing zinc from zinc sulfide ore. Zinc ore normally contains about 0.01% of cadmium. Cadmium is widely used in a variety of fields. Its applications include a soldering material (due to it's low melting point), electrodes in nickel-cadmium batteries, a bearing material, a plating material with stronger anticorrosive effect than that of zinc plating, and an alloy component for neutron control rods of light-water reactors that substitutes the expensive hafnium.

However, it has been long known that cadmium is a harmful metal. Cadmium is chemically similar to zinc, which is one of essential elements for human body, and hence cadmium is easily absorbed into the body. First it accumulates in the liver, and then is sent to the kidneys. One third of the cadmium entering the body accumulates in the kidneys, and one sixth in the liver. In human body, metallothionein, a type of sulfur-containing protein, combines with cadmium to reduce its toxicity. The half-life of metallothionein is a few days, and cadmium freed from the decomposed metallothionein repeatedly combines with newly produced metallothionein. Cadmium freed during this process is toxic, and when accumulating in the kidneys, it combines with protein or enzymes those contain thiol group (-SH), and they are denatured then run into renal damage. This leads to abnormality in the metabolism of calcium and phosphorous, calcium loss from the bones, and finally symptoms such as deformation or softening of bones. Substances that render heavy metals non-toxic, like metallothionein, are also found in plants. One such substance is phytokeratin that is contained in plants resistant to cadmium and other heavy metals.

Recently there has been a strong trend towards regulating harmful heavy metals. For example, the RoHS* directive bans the use of specified harmful substances in electrical and electronic products marketed in the EU from the 1st July 2006. The harmful substances under the RoHS directive include organic halides (brominated flame retardants) and metals such as mercury, lead, hexavalent chromium, and cadmium.

Analysis of cadmium is carried out in various occasions, including the quality monitoring of tap water and wastewater, environmental analysis of groundwater and soil, as well as quality control of food, pharmaceutical, and industrial products.

Here we present examples of analyzing a nickel solution using the flame method, and plastic using the furnace method.

*RoHS: Restrictions on Hazardous Substance

■ Basic data of Cd

Atomic weight	112.4
Melting point	321˚C ($CdCl_2$ 568˚C, $CdSO_4$ 1000˚C)
Boiling point	765˚C ($CdCl_2$ 964˚C)
Oxidation number	+1 (e.g., $Cd_2(AlCl_4)_2$)etc.
	+2 (e.g., CdO, CdS, $CdCl_2$)
Solubility	$CdCl_2$ 110.6g/100g water (18˚C)
	$CdSO_4$ 76.2g/100g water (18˚C)

Reference: "The Dictionary of Physics and Chemistry", etc.

■ Wavelength of Cd

	Sensitivity ratio
228.8nm	1.0
326.1nm	0.02

Note:In these measurements the wavelength of 228.8 nm is used.

■ Flame analysis of Cd

When analyzing cadmium in a sample containing nickel, it is necessary to take care of spectral interference caused by nickel. This spectral interference occurs because the wavelength of nickel (228.84 nm) is very close to that of cadmium (228.80 nm). This is a typical example that cannot be corrected completely by the deuterium (D_2) lamp method. In such a case, accurate background correction becomes possible by employing the self-reverse (SR) method. A standard cadmium solution containing 1% nickel was analyzed using the D_2 and SR methods. The profile and calibration curve for the D_2 method are shown in Figs. 1 and 2, and for the SR method in Figs. 3 and 4 respectively. In the D_2 method, the calibration curve has a negative intercept with the y-axis due to the affect of the absorption line of nickel. In the SR method, correction is conducted properly.

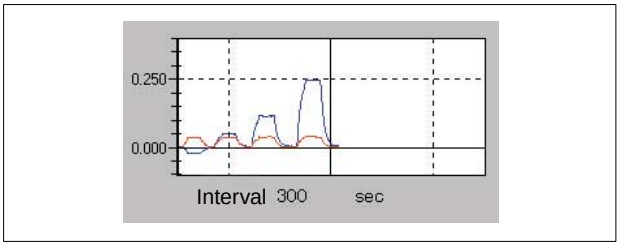

Fig.1 Profile of D_2 method

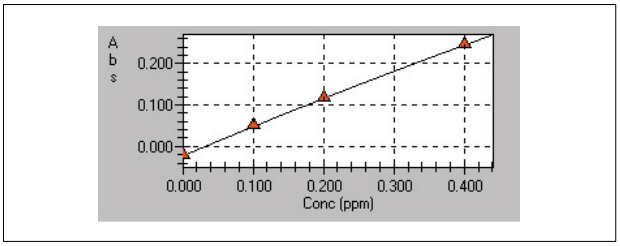

Fig.2 Calibration Curve of D_2 method

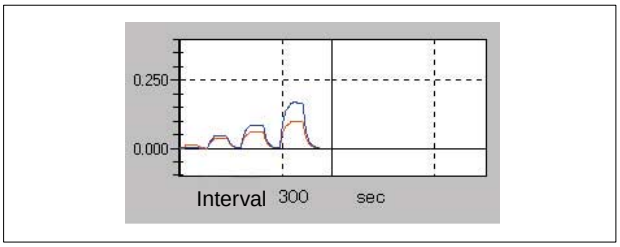

Fig.3 Profile of SR method

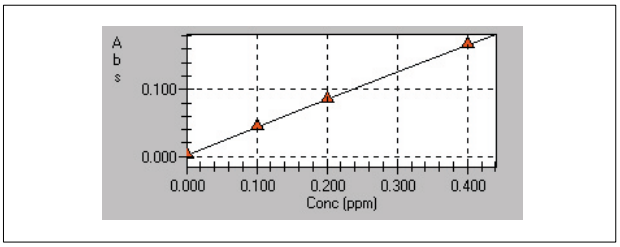

Fig.4 Calibration Curve of SR method

■ Furnace Analysis of Cd

In this analysis, 0.1g of polyethylene standard BCR-681 (see Table 1 below) was weighed out, decomposed with nitric acid on a hot plate, let cool, and measured up to 100mL with distilled water. This solution was analyzed using the furnace (calibration curve) method. The sample injection volume was 2µL. The sample peak is shown in Fig. 5, and the calibration curve in Fig. 6. The test result was 21.2 mg/kg, which agrees with the guaranteed value. In this analysis, a platform tube was used for the graphite tube, and the heating conditions shown in Table 2were used. A 100-ppm mixture of Pd and magnesium nitrate was used to suppress interference.

Table 1 Element of BCR-681

	As	Br	Cd	Cl	Cr	Hg	Pb	S
mg/kg	3.93	98	21.7	92.9	17.7	4.50	13.8	78

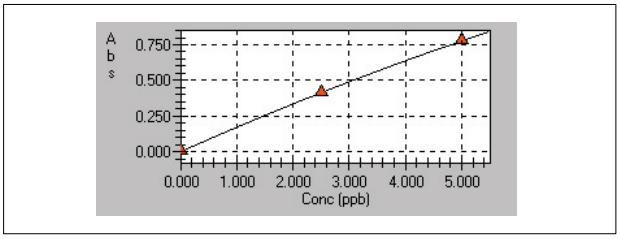

Fig.6 Calibration Curve of Cd

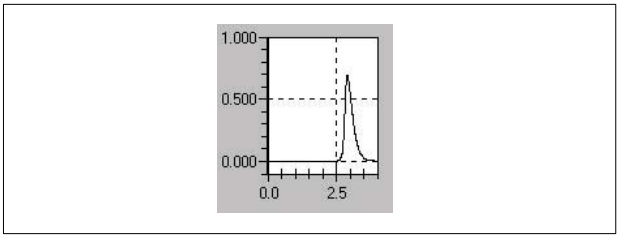

Fig.5 Profile of furnace method

Table 2 Heat condition

	Temp.	Heating time	Heating method	Ar flow
1	250	20	RAMP	0.1
2	250	10	RAMP	0.1
3	800	10	RAMP	1.0
4	800	10	STEP	1.0
5	2200	2	STEP	0.0
6	2400	2	STEP	1.0

■ Conclusion

In atomic absorption analysis, it is always necessary to be careful of interference due to substances existing in the sample, regardless of the target element. Cadmium is not significantly subject to interference with the flame method. However, with the furnace method, cadmium is easily affected by interference due to the formation of cadmium chlorides caused by the presence of chloride ions. Chlorides normally have low boiling points and easily sublimate on charring stage, and it causes deterioration in sensitivity and reproducibility. To prevent this, palladium nitrate is often added to the sample.

Palladium (Pd) is a platinum group element that is often used as a catalyst. It forms thermally stable compounds with cadmium and thus suppresses the sublimation of cadmium. The addition of Pd is adopted in official test methods, including JIS K 0101 (Testing methods for industrial water) and JIS K 0102 (Testing methods for industrial wastewater).

It is expected that high-sensitivity analysis of cadmium will be increasingly important with the tightening of regulations. Cadmium is said to be comparatively free from contamination during analysis. However, when analyzing trace amounts of cadmium, care is required for contamination from the environment, equipment, and reagents.

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