SHIMADZU APPLICATION NEWS

LAAN-A-AA-E003

● SPECTROPHOTOMETRIC ANALYSIS

No.A359

Zn Analysis by Atomic Absorption

Zinc is obtained mainly from mineral ores such as smithsonite ($ZnCO_3$), sphalerite, or wurtzite (ZnS). Zinc is refined by calcinating the ore to form zinc oxide, which is then reduced with carbon (dry reduction method) or dissolved in sulfuric acid and subjected to electrolytic reduction (wet reduction method). Zinc is used primarily as corrosion-resistant plating. Corrugated iron is steel sheet plated in zinc, which has a higher ionization tendency than steel. Zinc-plated corrugated iron, as well as tin-plated sheet iron, is a commonly used material. Zinc is also widely used in alloys, such as brass, which is a zinc-copper alloy.

The oxidation number of zinc compounds is normally limited to +2. Zinc oxides and hydroxides are amphoteric compounds that dissolve in both acids and alkalis. The applications of zinc compounds include the use of zinc oxide (ZnO) as a dye, pigment, and ink; and zinc in pharmaceuticals, such as zinc ointments with bactericidal properties. Zinc sulfide (ZnS) is used with copper as a fluorescent material in cathode-ray tubes that fluoresces yellow/green when irradiated by the electron beam.

Zinc is an essential element that participates in various functions in organisms, including immunological actions, alcohol metabolism, and stabilizing biomembranes. Many enzymes and proteins containing zinc have been discovered, and their roles include 1) maintaining the protein structure, 2) fixing enzymes to the matrix during enzyme reactions, and 3) catalytic actions. Whereas iron and copper often participate in reduction reactions in organisms, zinc is often related to hydrolysis. Of the transition metals, the zinc content in the human body is second only to the iron content. The zinc content in a 70kg person is approximately 2g. About 50% of the zinc in the body is contained in the blood, 25% to 30% in the skin and bones, and the remainder in the pancreas, eyes, and sperm. The required daily intake of zinc is approximately 15mg and zinc deficiency leads to loss of sense of taste (ageusia) and skin diseases. As zinc tends to be deficient in the body, supplements and natural foods are now available in more and more stores.

While excessive zinc consumption rarely causes problems, poisoning by zinc eluted from food cans is known to cause abdominal pains and nausea and the inhalation of zinc vapor from overheated zinc metal is known to cause fever and trembling.

The analysis of zinc was originally conducted in the environmental field, including mains water and sewage, and is now widely used in the electroplating and metals, food, and pharmaceutical industries.

This Application News introduces AA flame analysis of zinc in copper and AA furnace analysis of zinc in river water.

■ Basic Data for Zinc

Atomic number :65.4
Melting point :419.6˚C (365˚C for $ZnCl_2$)
Boiling point :907˚C (730˚C for $ZnCl_2$)
Oxidation number:+1 For example, Zn_2^{2+} (in glass)
+2 For example, ZnO, ZnS, $ZnCl_2$, $Zn(OH)_2$, etc.
Solubility :$ZnCl_2$ 420 g/100 g water (25˚C)
$ZnSO_4$ 52.7 g/100 g water (18˚C)

Source: Rikagaku Dictionary etc.

■ Measurement Wavelengths for Zinc

Wavelength	Sensitivity Ratio
213.9nm	1.0
307.6nm	0.002

Note: 213.9 nm was used for these measurements.

■ Flame Analysis of Zn

When measuring zinc in samples containing significant copper and iron, care is required with the spectroscopic interference from the copper and iron. This spectroscopic interference arises due to neighboring lines. Spectroscopic interference occurs because the 213.856nm measurement wavelength for zinc is extremely close to the measurement wavelengths of 213.8507nm and 213.8589 nm for copper and iron, respectively. This can often not be adequately corrected by the deuterium (D_2) lamp method. In such cases, the background correction by the SR (self-reversal) method offers accurate correction. For these tests, zinc impurities in a 1% copper solution were analyzed by the standard addition method using both D_2 and SR correction. Figs. 1 and 2 show the profile and calibration curve with the D_2 method; Figs. 3 and 4 show the profile and calibration curve with the SR method. The 0.05 ppm measured value with the SR method appears higher, at 0.08ppm, with the D_2 method, due to the effects of the neighboring lines.

While the standard addition method can effectively correct for physical interference due to differences in sample viscosity, for example, and chemical interference due to bonding between coexisting substances, correction for spectroscopic interference may not be possible, as in this test. Due care is required.

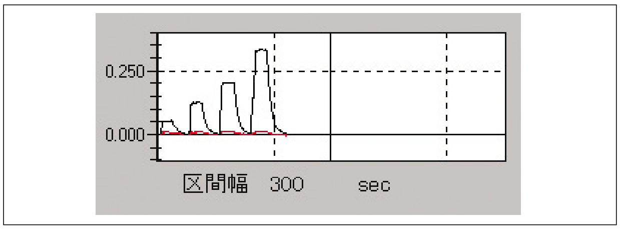

Fig.1 Profile with the D2 method

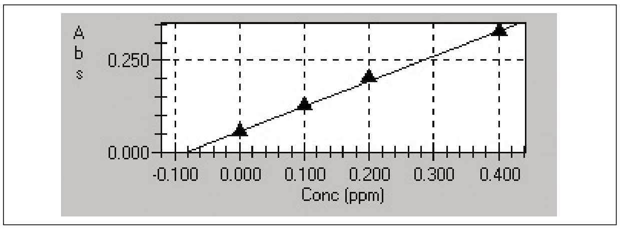

Fig.2 Calibration Curve with the D2 method

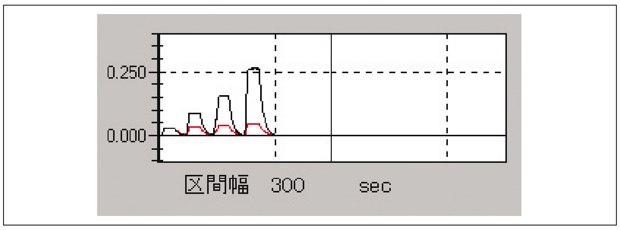

Fig.3 Profile with the SR method

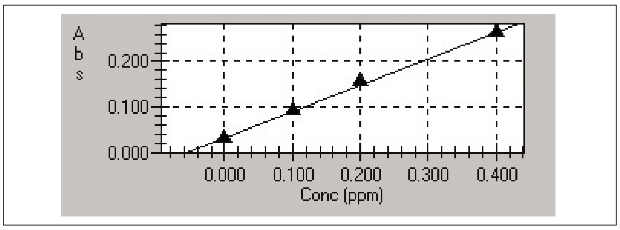

Fig.4 Calibration Curve with the SR method

■ Furnace Analysis of Zn

Furnace measurements (calibration curve method) were conducted on the JAC0032 river water standard sample (spiked) with the composition shown in Table 1. As zinc is an extremely sensitive element, measurements at maximum sensitivity conditions can detect zinc from some blank samples, depending on the degree of contamination, and this can cause problems during analysis.

An argon (Ar) gas flow during atomization solves this problem by reducing the analysis sensitivity. Other methods to reduce sensitivity include changing the measurement wavelength and reducing the injected sample volume. For these tests, 4µL sample was injected. Fig. 5 shows the sample peak and Fig. 6 the calibration curve. The result of 10.8µg/L matches the certified value.

A platform tube was used as the graphite cuvette for this test. Measurements were conducted at the heating conditions shown in Table 2.

Table 1 Composition of JAC0032

	Al	As	B	Cd	Cr	Cu
µg/L	61	5.5	59	1.00	10.1	10.5
	Fe	Mn	Ni	Pb	Se	Zn
µg/L	57	5.4	10.2	9.9	5.2	11.3

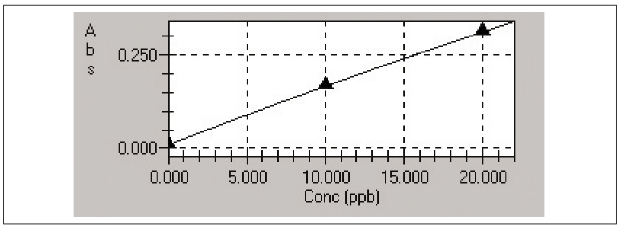

Fig.6 Calibration Curve for Zn

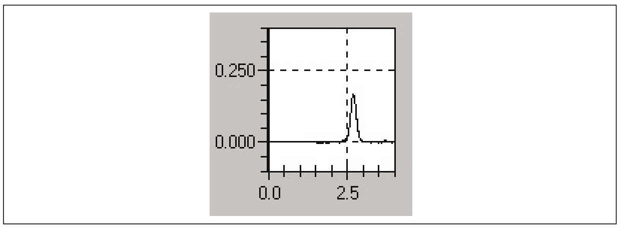

Fig.5 Profile with the Furnace Method

Table 2 Heating conditions

	Temperature	Heating time	Heating method	Ar flowrate
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	0.1
6	2400	2	STEP	1.0

■ Conclusions

Great care must be taken with interference due to coexisting substances during atomic absorption spectrophotometry, regardless of the element measured. Zinc is said to be an element relatively resistant to interference during flame measurements. However, interference does occur with the furnace method, due to the existence of chloride ions that form zinc chlorides. As chlorides generally have a low boiling point, they are readily vaporized during incineration, causing decreased sensitivity and repeatability. Consequently, appropriate setting of the incineration temperature is important for furnace measurements of zinc.

Zinc contamination from the environment occurs easily, as the Earth's crust contains about 0.044% zinc and soil about 0.005%. In the electronics and semiconductor industries, zinc is used as a pollution indicator, along with sodium and calcium. Consequently, precautions against contamination of the environment, equipment, and reagents are required during the analysis of trace levels of zinc.

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Printed in Japan 3100-07405-10A-IK