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Separation of zinc compounds by sequential metal vapor elution analysis with atomic absorption detection

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Abstract

The separation of zinc compounds, containing zinc chloride, nitrate, and sulfate, at low concentrations by sequential metal vapor elution analysis (SMVEA) with argon carrier gas was reported. A molybdenum column, inserted with a tungsten wire, was developed for the separation of zinc compounds by SMVEA. The optimum separation conditions were a vaporization temperature of 1370 K, a column temperature of 1350 K, and a carrier gas flow rate of 2.5 mL min^{-1}. Under the optimized experimental conditions, the zinc compounds could be roughly separated by SMVEA, although a part of peak profiles overlapped. The number of theoretical plates was 36 for $ZnCl_2$, 62 for $Zn(NO_3)_2$, and 80 for $ZnSO_4$ in the SMVEA column. The present SMVEA system may be able to be applied widely to various analytical instruments.
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Keywords: Sequential metal vapor elution analysis (SMVEA); Zinc compounds; Speciation; Separation; Atomic absorption detection

1. Introduction

In recent years, a separation system with a high temperature column (>990 K), sequential metal vapor elution analysis (SMVEA) has been reported for the separation and analysis of trace metal elements [1–5]. The advantages of SMVEA are: (a) direct separation of metal vapors; (b) rapid analysis without a prior chemical treatment; (c) simplicity; (d) elimination of spectral and chemical interference occurring in the conventional atomic spectrometry such as atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES); and (e) possibility of a powerful accessory of analytical instruments containing mass spectrometry. However, in spite of these attractions, little information on the SMVEA has been reported, owing to the technical difficulty of instrumentation.

Zinc, the second most abundant trace element in humans, is one of the essential elements for human and animals, and is an essential cofactor for 200 important enzymes [6]. One of the functions of Zn is to provide integrity of taste perception in healthy persons [6]. Recently, it has been found that zinc group metal compounds, namely, zinc acetate, zinc chloride, zinc nitrate, cadmium acetate, and mercury chloride, showed the negative activities for human immunodeficiency virus type 1 (HIV-1) [7]. Therefore, since zinc may play a significant role in medicine and pharmacognosy in the near future, it is necessary to develop the speciation technique for zinc compounds at low levels.

Until now, as the potential of speciation technique by SMVEA, the separation of cadmium compounds, such as phosphate, nitrate, and chloride, has been demonstrated by SMVEA, and cadmium phosphate could be separated from the nitrate and the chloride [3]. However, there are few reports concerning the speciation of zinc compounds at low concentrations by SMVEA.

In the present study, the separation of zinc compounds at low levels by SMVEA was reported and the elution order

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of zinc compounds was discussed, on the basis of their chemical and physical properties.

2. Experimental

2.1. Apparatus

The SMVEA system has a high temperature column combined with three electrodes in a Pyrex glass dome. The column consisted of a molybdenum capillary tube (250 mm long, 1.43 mm i.d., 99.95% purity, NILACO Co.) and three alumina tubes (2.5 mm i.d., 8 mm long). The alumina tubes were combined with three tungsten rods in a Pyrex glass dome and supported the molybdenum column to prevent bending of the column during heating. The column consisted of a vaporization part (60 mm) and a separative part (190 mm). A tungsten wire (length 1000 mm × 0.05 mm i.d., 99.95 % purity, Goodfellow) was folded 20 times to 50 mm, and was inserted in the initial 50−100 mm position of the separating part. The vaporization part was connected to a transformer (YAMABISHI S-130-30, Cap. 3 kVA) for heating to vaporize sample. The separative part was heated with a power supply (DC generator, KIKUSUI PAD 35-60L). A 0.5 mm diameter hole was drilled at the midpoint of the vaporization portion, in which the sample was heated to vaporize, in the column to inject a sample solution. The detection portion has an 0.8 mm hole, perpendicular to the hole in the vaporization portion, for atomic absorption (AA) measurement. A monochromator (Nippon Jarrell-Ash 0.5 m Ebert-type), a lock-in amplifier (NF LI-575), a storage oscilloscope (KIKUSUI, DSS6520A), and a microcomputer (ESPON, PC-286VG) are used for AA signal detection. A zinc hollow cathode lamp (Hamamatsu Photonics Co.) was used as light source with the resonance line of 213.86 nm. The absorption signal from the amplifier was fed into the microcomputer. The temperature of the column was measured with an optical pyrometer (Minolta TR-630). Two pin-hole apertures were placed in front of and in the rear of the detection hole to provide a narrow beam of light and to remove background emission from the column surface. Molecular absorption was checked with a deuterium lamp so that the absorption was not observed.

2.2. Reagents

All chemicals used were of analytical grade purity for spectroscopic purposes. Standard stock solutions (1 mg Zn mL^{-1}) were prepared by dissolution of zinc chloride, zinc nitrate hexahydrate, and zinc sulfate heptahydrate (Nacalai Tesque Inc., Kyoto, Japan). The working solution (1 μg Zn mL^{-1}) for measurement was diluted from the stock solutions with distilled de-ionized water, immediately before use. Ultrapure water was prepared using an Advantec CW-102 ultrapure water system.

2.3. Procedure

The flow rate of purge gas in the column chamber was 3.0 L min^{-1} for argon and 200 mL min^{-1} for hydrogen. The slight hydrogen flow in the chamber was needed for the protection of metal column from oxidation by residual oxygen in argon gas. The column temperature was in the range from 1210 to 1530 K. The vaporization temperature was 1370 K.

For SMVEA measurements, after stopping the argon carrier gas (2.5 mL min^{-1}), a 1 μl of the sample solution was pipetted into a vaporization portion in the molybdenum column. The sample solution was dried at 350 K for 10 s and pyrolyzed at 450 K for 10 s. After flowing argon carrier gas again, the column was heated at 1210−1530 K and then the residue in the vaporization portion was vaporized at 1370 K for >60 s.

3. Results and discussion

In the SMVEA, with a high temperature column (>990 K), molybdenum was best as the column material since its tube is easily available. A number of parameters containing the column temperature, vaporization temperature, and carrier gas flow rate influence the retention time and separation power. From the previous works [2,5], argon was selected as a carrier gas for the separation of zinc compounds by SMVEA. The separation characteristics of zinc compounds, $ZnCl_2$, $Zn(NO_3)_2$, and $ZnSO_4$ were investigated at various experimental conditions. Hence, a variety of combinations of column temperature, vaporization temperature, and Ar carrier gas flow rate were examined. In consequence, because the separation of zinc compounds became better at the vaporization temperature of 1370 K and the carrier gas flow rate of 2.5 mL min^{-1}, the column temperature was investigated in the range of 1210−1530 K under their other conditions.

The results were shown in Table 1. The eluting order was zinc chloride, nitrate, and sulfate. At a column temperature of 1530 K, the separations of zinc nitrate and sulfate were incomplete, since these compounds were eluted with small differences in retention time (1.2 s). At lower temperature (1210 K), the SMVE peaks of zinc compounds overlapped completely because the peak widths were relatively

Table 1
Retention times of SMVE peaks at 1370 K of vaporization temperature and 2.5 mL min^{-1} of argon carrier gas flow rate

Compound	Retention time, t_r (s)		
	1530 K[a]	1350 K[a]	1210 K[a]
$ZnCl_2$	4.2 (0.8)	14.4 (0.7)	48.5 (1.0)
$Zn(NO_3)_2$	8.6 (1.3)	21.5 (2.3)	48.5 (1.6)
$ZnSO_4$	9.8 (1.6)	27.1 (1.5)	52.5 (2.3)

$n > 5$, purge gas; Ar 3.0 L min^{-1} + H_2 200 mL min^{-1}. Values in parentheses are standard deviation of t_r.

[a] Column temperature.

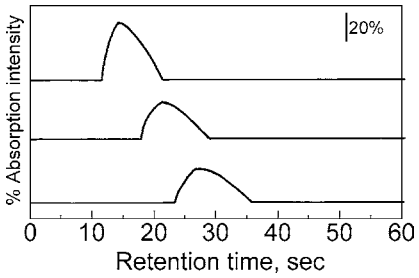

Fig. 1. SMVE peaks at 1370 K of vaporization temperature, 1350 K of column temperature and 2.5 mL min^{-1} of argon carrier gas flow rate. Purge gas; Ar 3.0 L min^{-1} + H_2 200 mL min^{-1}.

large ($W_{1/2}$ = 10–17 s). However, at 1350 K the zinc compounds containing zinc chloride, nitrate, and sulfate, could be roughly separated, as illustrated in Fig. 1. The difference of the retention time between zinc chloride and nitrate was 7.1 s and 12.7 s between chloride and sulfate. The resolution factor and separation factor were 1.5 and 0.70, 1.9 and 1.2, between chloride and nitrate, respectively. The mixed sample of zinc chloride, nitrate, and sulfate was investigated at the column temperature of 1350 K. The peaks overlapped in part, but by calculating the retention time of each zinc compound with Gaussian distribution method, these compounds could be identified. From these results, it was found that the optimal separation condition of zinc compounds was a combination of the vaporization temperature of 1370 K, the column temperature of 1350 K, and the carrier gas flow rate of 2.5 mL min^{-1}.

3.1. Separation mechanism

If the elution phenomena are caused only by the boiling point of compounds, the signals for all zinc compounds must appear within 2.2 s at the column temperature of 1350 K and the carrier gas flow rate of 2.5 mL min^{-1}. However, in fact the signal appeared at the retention time of >12 s. The 2.2 s is a dead time, which means the time of carrier gas elution in the column (1.2 s; 0.239 × 273 × 60/(2.5 × 1350), 0.239 mL; void volume of 150 mm column), plus a maximum vaporization time (<1.0 s). This delay means an appreciable interaction between the compound vapors and the surface of the column and tungsten wire.

The retention volume for the separation by SMVEA, $V(t, T)$, is defined as follows:

$$V(t, T) = V_g(t, T_c) + V_h(t, T_v)$$

where $V_g(t, T_c)$ is related to gas chromatographic separation at a column temperature of T_c in kelvin. Vaporized gaseous metals and molecular species are governed by gas chromatographic principle in the SMVE column. $V_h(t, T_v)$ is the term concerning a thermal separative principle at a vaporization temperature of T_v, which refers to physical properties (bond energy, melting point, boiling point, and vapor pressure) of compounds and metals. t, conventionally called as retention time (t_r), is the time required for analyte peak to reach an AA detector.

The number of theoretical plates N is given by

$$N = \frac{L}{H} = \frac{L^2}{\sigma^2} = 5.54\left(\frac{t_r}{W_{1/2}}\right)^2$$

where L is the length of the column, H the height equivalent to a theoretical plate, σ the standard deviation of a measurement, and $W_{1/2}$ is the width of SMVE peak at half its maximum height. Under optimum experimental conditions, the number of theoretical plates were 36 for $ZnCl_2$, 62 for $Zn(NO_3)_2$, and 80 for $ZnSO_4$ in the SMVE column.

Generally, in the SMVEA the element and molecular species having relatively low melting and boiling points have the tendency to be eluted more rapidly [1–5]. Therefore, we tried to discuss the elution phenomena with regard to chemical and physical properties of the zinc compounds. Since the neutral atoms were detected in the detection portion by atomic absorption spectrometry, the zinc compounds should become zinc neutral atoms in the detection hole. The zinc compounds may be atomized gradually in the separative part of the column. Zinc nitrate seems to become zinc atoms through oxide, and zinc sulfate through oxide and/or sulfide. The melting and boiling points of zinc metal are 693 and 1180 K, respectively [8]. The melting points of $ZnCl_2$, ZnO, and ZnS are 556, 2248, and 1322 K, respectively [8]. The boiling point of zinc chloride is 1005 K [8]. Zinc sulfate converts to oxide at >1103 K [9]. The chemical bond strengths of Zn–Cl, Zn–O, and Zn–S are 228.9, <270.7, and 205 kJ mol^{-1}, respectively [8]. Although the elution order in the SMVE-curves could not be clearly explained from these values cited, it may be reasonable that the first appearance of zinc compound was chloride.

Consequently, the zinc compounds containing zinc chloride, zinc nitrate, and zinc sulfate, could be roughly separated by SMVEA at the vaporization temperature of 1370 K, the column temperature of 1350 K, and the carrier gas flow rate of 2.5 mL min^{-1}. Though the complete separation conditions should be precisely optimized, the present SMVEA system will become a powerful speciation technique for zinc compounds. Further investigation is in progress.

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