Separation of $Cd_3(PO_4)_2$, $Cd(NO_3)_2$ and $CdCl_2$ by Sequential Metal Vapor Elution Analysis

Kiyohisa Ohta,* Hajime Kawai, and Takayuki Mizuno
Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514

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The separation of cadmium compounds, ($Cd_3(PO_4)_2$, $Cd(NO_3)_2$ and $CdCl_2$), by sequential metal vapor elution analysis (column temperature; >1050 K) with helium carrier gas is described. The column consists of a molybdenum capillary tube inserted tungsten coil. Each cadmium vapor was separated at a column temperature of 1050 K and an vaporization temperature of 1050 K. Under the experimental conditions, the retention times of $Cd_3(PO_4)_2$, $Cd(NO_3)_2$ and $CdCl_2$ were 20.4, 32.0 and 35.0 s, respectively. The relative standard deviation for the retention times was better than 2.5%.

Cadmium is highly toxic to a wide variety of organisms and often causes the quality of raw materials to change poor. Brief exposure leads to a persistent cough and chest pains. The low-concentration and long-time ingestion of cadmium leads to a "rheumatic" disease well known as "itai-itai (ouch-ouch)" disease, which cause painful skeletal deformities (bone disease), severe pain and discomfort.[1] The virulence for organisms and the degradation (contamination) of raw materials differs with cadmium compounds. Therefore, the speciation of cadmium compounds is important. Recently, we have demonstrated a new separation system for high temperature gaseous metals, sequential metal vapor elution analysis (SMVEA) with a separative open-tubular column (1300-2400 K) or a tungsten powder-packed column.[2-8] The advantage of SMVEA is a direct separation of metals with relatively high melting and boiling points, without a prior chemical treatment, e.g. liquid-liquid extraction, coprecipitation, ion exchange, bubble separation, chemical modification and standard addition method. Despite the advantages, few SMVEA studies for various elements have been reported. In this study, the separation of cadmium compounds, $Cd_3(PO_4)_2$, $Cd(NO_3)_2$ and $CdCl_2$, by SMVEA-atomic absorption (AA) detection using a high temperature column (>1050 K) inserted a tungsten coil with helium carrier gas is evaluated.

The separation mechanism of gaseous metals in SMVEA is due to gas chromatographic and thermal separative principles. The retention volume for the separation by SMVEA, V(t,T), is defined as follows;

$V(t,T) = V_g(t,T) + V_h(t,T)$ t: time, T: temperature

where $V_g(t,T)$ is related to a gas chromatographic separation. $V_h(t,T)$ is the thermal separative principle and refers to the pyrolytic property of compounds and a difference in vapor pressure of gaseous metals at a temperature. The time, t, it takes after sample vaporization for analyte peak to reach the AA detector, is conventionally called the retention time and is given the symbol t_r. Since the void volume of the column is 0.175 ml, the time for the unretained species, called as dead time, was 1.5 s. In general, it is presumed that elements and compounds having relatively low boiling point (T_b) and high vapor pressure (T) tend to be eluted more rapidly. Therefore,

$V_h(t,T) = f(t,T_b) + f(t,T)$

As well known, the principle of partition and adsorption gas chromatography is as follows:

$V_g(t,T) = jtF = (KV_s/W) \cdot (273/T)$

where T is column temperature (constant) and F is carrier gas flow rate. j is a quantity relating the carrier gas pressure at the beginning and end of the column. K is partition coefficient and W is the weight of the stationary phase. V_s is the volume of the coil (stationary phase) in the column.

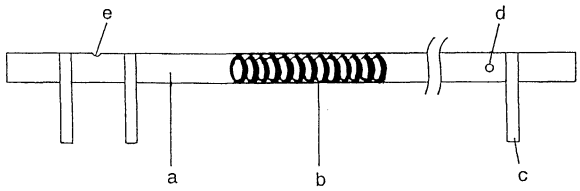

Figure 1. SMVEA column.
a: molybdenum column (250 mm long, 1.22 mm i.d.),
b: tungsten coil, c: column supporter, d: hole for AA measurement,
e: hole for sample injection.

Table 1. Experimental conditions

Purge gas	3 l/min Ar and 0.2 l/min H_2
Carrier gas	2.0 ml/min He
Column temperature	1050-1550 K
Vaporization temperature	1050-1650 K
Detector	atomic absorption spectrometer
	analytical line Cd 228.9 nm

A column for SMVEA consisted of a molybdenum capillary tube (i.d. 1.22 mm, length 250 mm, 99.95% purity, Goodfellow) inserted tungsten coil (wire: ϕ0.05 mm x 250 mm, coil: ϕ1.1 mm x 70 mm), as shown in Figure 1. The column has a 0.5 mm diameter hole, drilled at the midpoint of the vaporizing portion in the column to inject a sample solution, and another penetrating hole (0.8 mm), in the detection portion for AA measurements, perpendicular to the hole in the vaporizing portion. The column was set in a SMVEA chamber, which was reported in detail in a previous paper.[2] A monochromator (Nippon Jarrell-Ash 0.5 m Ebert-type), a lock-in amplifier (NF LI-575), a storage oscilloscope (KIKUSUI 5516ST), and a microcomputer (EPSON, PC-286VG) are used for AA signal detection. A hollow-cathode lamp (Hamamatsu Photonics Co.) was used as a light source. The temperature of column was measured with an optical pyrometer (Chino Works). The working solutions for the measurement were mixed and diluted from stock solutions (1 mg Cd/ml) with distilled-deionized water just before use. The experimental conditions are shown in Table 1. Some hydrogen in the purge gas was needed to protect the metal column from oxidization by residual oxygen in argon gas. After stopping the carrier gas, a 1 μl of cadmium sample solution was injected into the vaporizing portion.

Table 2. Retention times of peaks by SMVEA

Compound	Retention time t_r, s		
Vapor.temp.	1650 K	1410 K	1050 K
Column temp.	1550 K	1550 K	1050 K
$Cd_3(PO_4)_2$	8.4(3.1)[a]	8.7(2.3)	20.4(2.5)
$Cd(NO_3)_2$	9.0(3.3)	11.3(1.5)	32.0(1.1)
$CdCl_2$	8.9(6.9)	13.6(2.4)	35.0(0.7)

Number of measurements; 4–6
a; Values in blanket are r.s.d. of t_r, %.

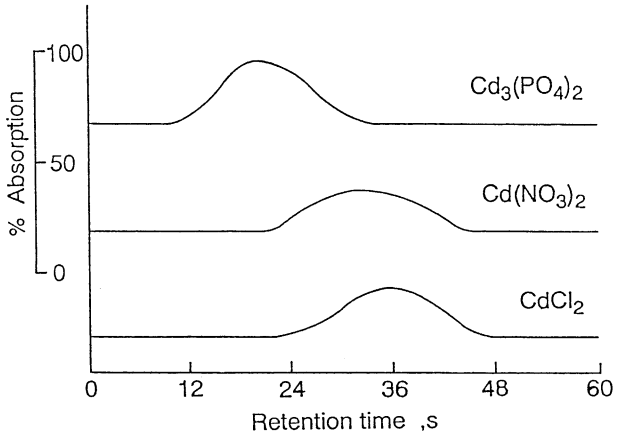

Figure 2. SMVEA peaks at a column temperature of 1050 K and an vaporization temperature of 1050 K.

The sample was dried at 350 K for 10 s and pyrolyzed at 450 K for 10 S. After continuing the carrier gas, the column was heated at 1050–1550 K and then the residue in the vaporizing portion was vaporized at 1050–1650 K. Molecular absorption was checked with a deuterium lamp so that the absorption was not observed. Column and vaporization temperatures significantly influenced the retention time and resolution for gaseous metals in previous papers.[2-8] The separation study of cadmium compounds, $Cd_3(PO_4)_2$, $Cd(NO_3)_2$ and $CdCl_2$, in the SMVEA was performed at a column temperature of 1050–1550 K and an vaporization temperature of 1050–1650 K. The amounts of the phosphate, nitrate and chloride introduced into the column were 2 ng as cadmium metal. The results are shown in Table 2. The cadmium compounds were not separated at a column temperature of 1550 K and an vaporization temperature of 1650 K. At the temperatures the SMVEA–signals of phosphate, nitrate and chloride exhibited similar retention times (Table 2). At a column temperature of 1550 K and an vaporization temperature of 1410 K, these compounds were eluted with small differences in retention time, and the separation was not complete. However, at lower temperature (column and vaporization temperature; 1050 K), cadmium vapor from phosphate was distinguished away from those from nitrate and chloride, as shown in Figure 2. The retention time of the phosphate was 20.4 s and the r.s.d. of the t_r was 2.5%. The eluting order was phosphate, nitrate and chloride. The difference of the retention times between cadmium phosphate and the nitrate was 11.6 s and that between the nitrate and the chloride was 3.0 s. The mixed sample of cadmium phosphate, nitrate and chloride was investigated at a column temperature of 1050 K and an vaporization temperature of 1050 K. The peaks overlapped in part, but by calculating the retention time of each cadmium compound with Gaussian distribution method these compounds could be identified. From these results, it was found that the separation of cadmium compounds at relatively low column temperature is preferable to high column and vaporization temperatures.

In general, for cadmium the element and molecular species having relatively low melting and boiling points tend to be eluted more rapidly.[7-8] Therefore, we discuss the elution phenomena with regard to melting and boiling points. Melting and boiling points of cadmium metal are 593.9 and 1038K.[9] Melting point of $Cd_3(PO_4)_2$ is 1773K.[9] Melting point of $Cd(NO_3)_2$ is 623K.[8] The nitrate converts to cadmium oxide, CdO, during pyrolyzing at 450K.[10] Melting point of the oxide is >1773K but the compound decomposes at 1173–1273K.[9] Melting and boiling points of $CdCl_2$ are 841K and 1233K.[9] The chemical bond strengths of Cd–O and Cd–Cl are 235.6 and 208.4 kJ/mol, respectively.[9] From these values cited, the elution order in the SMVEA–curves can not be explained. After vaporizing from the compounds, the gaseous cadmium, of course, has the same adsorptivity on the tungsten coil and on the inside surface of the column. However, the behavior was very specific. One of the reasonable reasons may be a difference of the adsorption characteristics for gaseous molecular species from the cadmium compounds, because, if there is no appreciable interaction between the molecular vapors and on surface of the column and coil, the signals of the phosphate, the nitrate and the chloride must appear at same time, that is in <2.5 s (1.5+1.0 s) under the experimental conditions. The retention times for the elements, even by considering the vaporization rate (< 1 s till 1650 K), are much longer time.

Consequently, as described above, cadmium phosphate was separated from the nitrate and the chloride at the column temperature of 1050 K and the vaporization temperature of 1050 K and a feasibility of chemical speciation by SMVEA system was proved without a prior chemical treatment.

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