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Brief Report

Metal and Molecular Vapor Separation Analysis for Direct Determination of Mn and Cu by Atomic Absorption Detection, Free of Background Absorption

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Abstract: The metal and molecular vapor separation analysis (MMVSA) of solid samples with an atomic absorption detector (AA) was investigated for the direct determination of manganese and copper in biological materials. An open column made with a molybdenum tube (i.d. 1.22 mm) with three-ring supporters was developed. Pure argon as a carrier gas flowed at a flow rate of 4.0 mL min^{-1}. An ultrasonic agitation method was used for suspending NIST standard reference material powders in water. Manganese and copper in the biological powders were completely separated from Al, Ca, Fe, K, Mg, Na, and Zn elements by MMVSA under optimal experimental conditions. Several NIST biological samples were directly analyzed with satisfactory results. It was found that manganese and copper in biological materials without interferences from matrix elements could be directly determined after only an ultrasonic agitation of the biological powders. The advantages of the slurry sampling of MMVSA are simplicity, low cost, a high speed of analysis, and rapid calibration.

Keywords: metal and molecular vapor separation analysis (MMVSA); copper; manganese; atomic absorption detection; direct determination

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1. Introduction

So far, a number of direct applications of solid samples into an electrothermal atomizer for atomic absorption spectrometry (AAS) have been investigated [1,2]. The direct analysis of solid materials has many advantages, such as no contamination from added chemicals, no separation/preconcentration steps, time-saving, a lower loss of volatile elements caused by digestion steps, and fewer chemical treatments. However, the direct introduction of solids into a graphite furnace (GF) or metal tube atomizer suffers from some disadvantages, such as the notable effect of sample heterogeneity, poor precision, and the need for matrix modifiers compared with methods using a solution analysis.

On the other hand, chemical vapor generation (CVG) is a significant introduction technique for samples and is widely used in atomic and mass spectrometry for its enhanced sensitivity [3], and especially as a promising alternative to pneumatic nebulizers for inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) that utilize microplasma systems for vapor generation [3]. The analyzed sample solution contacts an electric discharge, and some volatile analyte species can form through electrochemical reactions at the solution–plasma interface (e.g., forming hydrides). Cserfalvi et al. [4] reported that a microplasma system using an electrolyte-as-cathode glow discharge (ELCAD) improved the instrumental signal. Zhu et al. [5] investigated a solution cathode glow discharge (SCGD) system. Swiderski et al. [6] described a hanging drop cathode—atmospheric pressure glow discharge (HDC-APGD) system. Liu et al. [7] studied high-efficient liquid spray dielectric barrier discharge-induced

plasma (LSDBD) vapor generation coupled with atomic fluorescence spectrometry (AFS). Moreover, Zhu et al. [8] mentioned the plasma chemical vapor generation (plasma-CVG) method with a thin film dielectric barrier discharge (TFDBD). Schwartz et al. [9] referred to the atmospheric-pressure solution-cathode glow discharge (SCGD) as an ion source for atomic, molecular, and ambient desorption/ionization mass spectrometry. Zu et al. [10] referred to the portable solution cathode glow discharger (PSCGD) with a fiber-optical spectrometer. However, in these chemical vapor generation techniques, there was little information on the separation of metal and molecular vapors.

Recently, a metal and molecular vapor separation analysis (MMVSA) has been developed for a separation method of trace elements. It was found from these studies [11–13] that the advantages of MMVSA were (a) a direct separation of the metal vapors, (b) simple analysis without prior chemical treatment, such as liquid–liquid extraction and coprecipitation, (c) the elimination of chemical and spectral interferences occurring in conventional AAS and inductively coupled plasma–optical emission spectrometry (ICP–OES), (d) no necessity for matrix modifiers and (e) the possibility to use a powerful accessory of analytical instruments (mass spectrometer, etc.). However, despite these advantages, little information on the direct slurry sampling of MMVSA has been presented.

Approximately 1/3 of all structurally characterized proteins until 2000 were metalloproteins, that is, proteins associated with a metal [14]. The function of proteins is dependent on the interaction between the proteins and the bound metals. Calcium, iron, zinc, and magnesium are the most abundant metals in proteins, followed by manganese and copper. Manganese and copper are essential components for several endogenous antioxidant enzymes as catalase and superoxide dismutases [15]. Therefore, the determination of trace metals in biological materials is very significant to metallomics and metalloproteomics, which are relevant fields for the fate, uptake, transport, and storage of trace metals essential for life. However, there are some problems, such as optical and chemical interferences, which prevent the determination of biological materials.

In this study, slurry sampling MMVSA with the separation column (1900 °C) was dealt mainly with for the determination of copper and manganese in biological materials, and Mn and Cu metal and molecular vapor peaks were completely separated from Al, Ca, Cd, Fe, K, Mg, Na, Pb, and Zn. From the present work, the optical and chemical interferences could be scarcely observed for the slurry sampling of MMVSA.

2. Materials and Methods

2.1. Apparatus

The apparatus for the metal and molecular vapor separation analysis (MMVSA) with atomic absorption detection are shown in Table 1. The MMVSA system was composed of a Pyrex glass dome containing a molybdenum column, and the illustration for the system was already reported in the previous work [11,12]. Argon and hydrogen purge gases were purged through the dome to prevent the oxidation of the column. Additionally, the experimental conditions for MMVSA are presented in Table 1. The metal and molecular vapor separation column consisted of a molybdenum capillary tube (99.95% purity, Goodfellow) and three alumina tubes (2.5 mm I.D., 8.0 mm O.D.). The alumina tubes were combined with three tungsten rods in a Pyrex glass dome and supported molybdenum open column to prevent the bending of the column during heating.

The column (open column) in the glass dome consisted of a vaporization part (60 mm) and a separating part (190 mm). The vaporization part had a 0.5 mm diameter hole at the midpoint (44 mm from the end) for injecting solid samples. The separating part had a penetrating 0.8 mm-hole at 35 mm from the other end, perpendicular to the hole in the vaporization part, for atomic absorption detections. Two pinhole 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. Argon carrier gas flowed through the column. The temperature of the column was measured with an optical pyrometer (Chino Works, Tokyo, Japan).

Table 1. Apparatus and experimental conditions for MMVSA measurements.

Separation
MMVSA column: molybdenum column (250 mm long, 1.22 mm i.d.)
Transformer: YAMABISHI S-130-30, Cap. 3k VA, Tokyo, Japan
Power supply: KIKUSUI PAD 35–60L, Kikusui Denki Co., Yokohama, Japan
Detector (atomic absorption spectrometry)
Monochromator: Nippon Janell–Ash 0.5 m Ebert-type, Kyoto, Japan
Lock-in amplifier: NF LI-575, NF Circuit Design Block Co. Ltd., Tokyo, Japan
Storage oscilloscope: Kikusui 5516ST, Kikusui Denki Co., Yokohama, Japan
Computer: Dell Latitude 3310, Dell Japan Inc., Kanagawa, Japan.
Experimental conditions
Column temperature: 2170 K
Drying temperature: 350 K for 40 s
Pyrolysis temperature: 480 K for 10 s
Vaporization temperature: 2220 K
Purge gas: Ar 3000 mL min^{-1} + 200 mL min^{-1} H_2
Carrier gas: Ar 4.0 mL min^{-1}
Agitating time for solid sample: 5 min
Light source: Hollow cathode lamp
(Hamamatsu photonics Co., Shizuoka, Japan)
Al 309.3 nm, Ca 422.7 nm, Cd 228.8 nm, Cu 324.8 nm, Fe 248.3 nm, K 766.5 nm
Mg 285.2 nm, Mn 279.5 nm, Na 589.0 nm, Pb 217.0 nm, Zn 213.9 nm

2.2. Reagents and Procedures

Pure water was obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan), resulting in a resistivity >18 MΩ cm.

Stock solutions of Mn and Cu (1 mg mL^{-1}, nitrate, 0.1 mol L^{-1} HNO_3) were obtained from Nakalai Tesque Inc., Kyoto, Japan. The working solution for MMVSA was prepared by mixing the stock solutions. Biological sample powders (0.025–1.0 g, average particle diameter; 2–12 μm) were accurately weighed, and water was added (5 mL). The sample powders in the water were dispersed by ultrasonic agitation for 5 min. Immediately after agitation, an aliquot of the solution (1 μL) was injected into the vaporization part of the molybdenum column after stopping the Ar carrier gas. The sample was then dried and pyrolyzed under the experimental conditions shown in Table 1. After resuming the flow of the argon carrier gas, the separating part of the column was heated to 2170 K, while the vaporization part was heated to 2220 K for 180 s. AA signals (peak area) were measured at the detection hole on the separating part of the column under the experimental conditions described in Table 1. As for the reproducibility (variability) of MMVSA, both relative standard deviations (RSDs) for Mn and Cu were less than 5% for 50 μg mL^{-1} of Mn and 10 μg mL^{-1} of Cu for 12 measurements.

3. Results

3.1. Separation of Cu and Mn by MMVSA

It has been reported that some elements were separated by similar MMVSA with an open column. In a previous study with the open molybdenum column [11], it was reported by Ohta et al. that the suitable vaporization and separating temperatures were 2220 K and 2170 K for manganese and copper separation in Ar carrier gas, respectively. Since the metal chloride standard solutions were used in the study by Ohta et al. [11], manganese and copper chlorides may be formed in the pyrolyzing step. In the study, the order of the appearance of the metals was Cd, Zn, Pb, Cu, Na, and Mn, and this was reasonable considering the boiling points of these metals or chlorides.

In MMVSA, with a high-temperature column (>2170 K), molybdenum was best as the column material because its tube was easily accessed. However, the molybdenum metal was oxidized at >970 K in rge air, so Ar gas was used as a purge gas in the chamber. In addition, some hydrogen was needed to protect the metal column in the chamber from

oxidation by residual oxygen in the Ar gas. Hence, Ar gas as a carrier gas was selected for direct determination by MMVSA.

Some parameters containing the column temperature, vaporization temperature, and carrier gas flow rate affected the retention time and separation power. With reference to these results, some vaporization and separating temperatures were investigated for the separation of manganese and copper from Al, Ca, Fe, K, Mg, Na, and Zn in solid samples of MMVSA with an open molybdenum column. The elements selected here were major elements contained in biological materials (the elemental content in NIST apple leaves: Al 284.5 mg kg^{-1}, Ca 1.525%, Fe 82.7 mg kg^{-1}, K 1.609%, Mg 0.271%, Na 24.4%, and Zn 12.45 mg kg^{-1}). In the case of the solid sample of MMVSA, organic compounds could not be completely removed during the normal drying and pyrolyzing steps, but there was a possibility for their release during the vaporizing step and in the separating column. In order to minimize and eliminate the molecular absorption caused by organic compounds, an MMVSA study was performed at some separating and vaporization temperatures by injecting the solid suspension for the biological standard materials. The optimal separating (column) and vaporization temperatures were 2170 K and 2220 K for the solid NIST apple leaves, as shown in Figure 1. It was ensured with a deuterium lamp that the peak could not be originated by molecular absorption due to organic compounds formed by pyrolyzing the solid biological samples. Consequently, Mn and Cu could be completely separated under the same conditions as those performed by Ohta et al. [11].

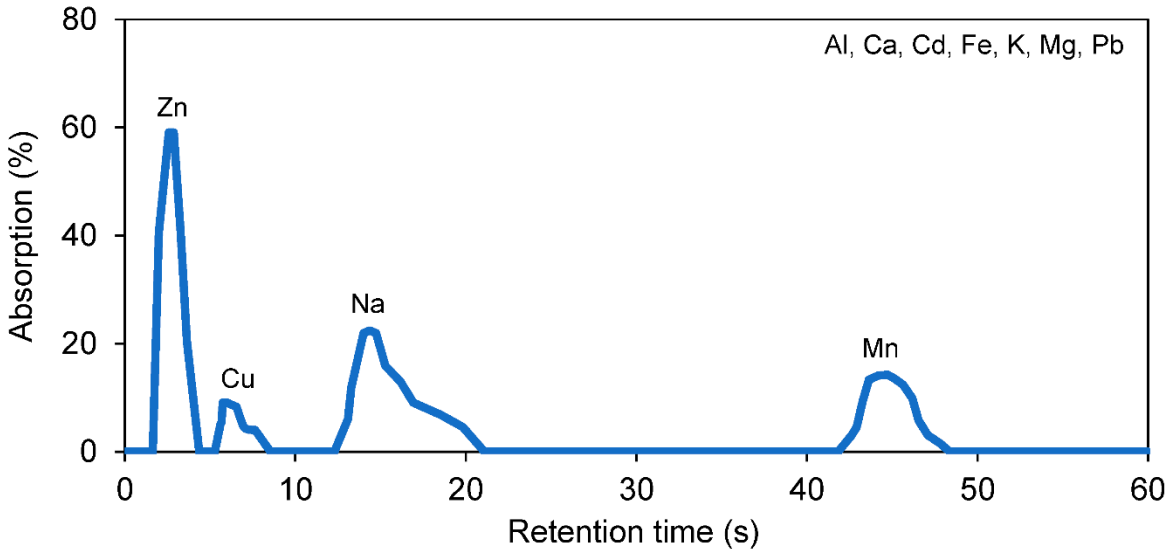

Figure 1. MMVSA peaks with a column at 2170 K of column temperature, 2220 K of vaporization temperature, and Ar 4.0 mL min^{-1} carrier gas. Purge gas: Ar 3000 mL min^{-1} + 200 mL min^{-1}.

If it is assumed that the elution phenomena are caused only by the boiling point of metals and compounds, the signals for all the metal elements must appear at the same time. The dead time seems to be estimated as 1.36 s, which means that the time of the carrier gas elution in the column (0.36 s; 0.175 × 300 × 60/(4 × 2170), 0.175 mL; a void volume of 150 mm column) would be 4.0 mL min^{-1} flow rate, plus a maximum vaporization time (<1.0 s). This delay means an appreciable interaction between the metal and compound vapors and the inside surface of the molybdenum separation column.

The sequence of the elution of metal elements was Zn, Cu, Na, and Mn. Cadmium and lead could not be detected by the present MMVSA because both the elemental contents were very low in the biological materials. In the previous study [11], the chlorides were formed in the pyrolyzing step, and the order of appearance in the metals was Cd, Zn, Pb, Cu, Na, and Mn. On the other hand, in the present work, the sequence of the elution of metal elements was roughly reasonable by considering the thermal characteristics (melting point Zn 693 K; CuO can be reduced to Cu metal at 523 K under H_2 atmosphere; melting

point Cu 1358 K; Na_2O 673 K decomposition to Na metal and Na_2O_2; boiling point Na 1156 K; boiling point Mn 2334 K [16]).

Probably, Al, Ca, Fe, K, and Mg elements may be condensed and were trapped at an entrance surface of the separating part at the column temperature. After heating to 2070 °C in the H_2 carrier gas with >30 mL min^{-1} in order to clean up the column, there was no memory effect resulting from the matrix elements (Al, Ca, Fe, K, Mg, Na, and Zn).

3.2. Effect of Ultrasonic Agitation

Kulek de Andrade et al. [17] reported that an ultrasonic agitation method was very useful for the suspensions of powder samples in the determination of trace elements by the graphite furnace (GF) AAS. Therefore, the agitation method was applied to the suspension of the biological sample powders in the water. A stabilizing agent of the suspension, such as glycerin, was not necessarily used. The average particle diameters of the samples were 2–12 μm. The effect of the ultrasonic agitating time on the Cu peak area was investigated for a biological sample (Oyster tissue NIST SRM1566). At over 30 s, the curve of the Cu peak area rose sharply, and at >5 min was the plateau. The relative standard deviation calculated from four repeated measurements was steadily 3% at 5 min agitating time. From the results, it was found that the suitable agitating time was 5 min for the determination of trace elements in the biological sample powders with particle diameters of 2–12 μm.

3.3. Direct Determination of Mn and Cu

A solid sample MMVSA was evaluated by application to the analysis of NIST standard biological materials. The calibration curves for the determination of manganese and copper were prepared by measuring the integrated absorbance obtained from manganese and copper standard solutions. The linear ranges of the calibration curves were up to 100 ng (corresponding to 100 μg g^{-1}) for manganese and up to 20 ng (corresponding to 200 μg g^{-1}) for copper. Table 2 shows the analytical results obtained by MMVSA. The accuracy for the certified values of Mn and Cu was less than 13%. The analytical results by direct determination with MMVSA were satisfactory. Precision was estimated by the cadmium and zinc contents of six replicates for each standard material. The relative standard deviations (RSDs) were in the range of 8.2 to 15.7%. Precision was relatively good, notwithstanding the direct introduction method of solid samples. Therefore, MMVSA was useful as a method to determine the manganese and copper in complex matrix samples such as biological materials. The advantages of the present method are freedom from spectral, chemical, and molecular interferences, less contamination from reagents, and a high speed of analysis. However, sensitivity was relatively poor compared with the ICP methods because the detection method was atomic absorption spectrometry.

Table 2. Direct determination of Mn and Cu in biological materials by MMVSA.

Sample	Element	Concentration (μg g^{-1})	
		Found	Certified Value
Apple leaves (SRM 1515)	Mn	48.9 ± 6.0	53 ± 3
Bovine liver (SRM 1577a)	Cu	140 ± 22	158 ± 7
Oyster tissue	Mn	17.1 ± 1.4	17.5 ± 1.2
(SRM 1566)	Cu	60.9 ± 8.7	63.0 ± 3.5

Number of measurements >5.

4. Discussion

During the drying step at 350 K, the main reaction was the removal of water. During the pyrolyzing step at 480 K, volatile organic compounds were removed, and a part of some metal compounds may have converted to oxide by the small amounts of residual

oxygen in the Ar cylinder and from the oxygen contained in the biological samples. The organic compounds are washed with the residual oxygen and/or were released during the vaporizing step (2220 K) and in the separation column.

The retention volume for MMVSA, V_R, is defined as follows:

$$V_R = \sum k_{GC}(T_c) \cdot C + k_{TS}(T_v) \quad (1)$$

where $k_{GC}(T_c)$ is related to the gas chromatographic separation at a column temperature of T_c in kelvin. Vaporized gaseous metals and molecules are governed by a gas chromatographic principle in an open MMVSA column. C is the carrier gas flow rate. $K_{TS}(T_v)$ is the term concerning a thermal separating principle at a vaporization temperature of T_v, which refers to the physical properties (bond energy, melting point, boiling point, vapor pressure, and diffusion coefficient) of compounds and metals. In the initial part of the separation column, the chemical species for manganese and copper seem to be the oxide. Since the neutral atoms were detected in the detection potion by atomic absorption spectrometry, the oxide compounds should have neutralized the atoms in the detection hole. Therefore, the sum ($\sum$) of $k_{GC}(T_c) \cdot C$ for each chemical species in the separation column should be necessary since their chemical species (oxide and metal vapers) have different k_{GC} values.

In general, it is presumed that elements and compounds with a relatively low boiling point (T_b) and high vapor pressure (T_p) tend to be eluted more rapidly. Therefore,

$$k_{TS}(T_v) = f(T_b) + f(T_p) + f(T_v) \quad (2)$$

where $f(T_v)$ is related to the diffusion coefficient for the chemical species at a vaporization part at a temperature of T_v.

If the well-known principle of partition and adsorption gas chromatography is applied to MMVSA [11–13,18], $k_{GC}(T_c)$ is as follows:

$$k_{GC}(T_c) = f(CGP) + f(I) \quad (3)$$

where f(CGP) is associated with a quantity relative to the carrier gas pressure at the beginning and end of the column and f(I) is connected to the interaction between the compound and metal vapors and the surface of the Mo separation column.

The number of theoretical plates N is given by:

$$N = L/H = (L/\sigma)^2 = 16(V_R/W)^2 = 5.54(V_R/W_{1/2})^2 \quad (4)$$

where L is the length of the column, H is the height equivalent to a theoretical plate, σ is the standard deviation of a measurement, W is the bottom width of the MMVSA peak, and $W_{1/2}$ is the width of the MMVSA peak at half its maximum height. The numbers of the theoretical plates were 14 for Zn, 81 for Cu, 120 for Na, and 856 for Mn in the open column.

5. Conclusions

As described above, manganese, copper, and vapors were separated from Al, Ca, Fe, K, Mg, Na, and Zn elements by MMVSA with an open column, so that interferences by the matrix elements observed by GFAAS could be eliminated. Consequently, under the experimental conditions, an accurate determination of manganese and copper in biological materials was possible after a simple injection of the solid sample agitated by an ultrasonic. Thus, the slurry sampling of MMVSA could become a promising tool for analyzing traces of manganese and copper in biological materials. This method is expected to be widely applied to AAS, ICP-OES, and ICP-mass spectrometry (MS).

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