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Spatial Distribution of Atomic Vapor of Alkaline Earth Elements around a Tantalum-filament Atomizer

Masaaki YANAGISAWA*, Seikoh YOKOYAMA**,
and Kuniyuki KITAGAWA**

* Present address: Research & Development Laboratory, Japan Fine Ceramics Center, Mutsuno, Atsuta, Nagoya 456 Japan

** Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-01 Japan

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柳沢雅明*・横山精光**・北川邦行**

* 現住所: (財)ファインセラミックスセンター試験研究所 名古屋
市熱田区六野 2-4-1 〒456

** 名古屋大学工学部応用化学科 名古屋市千種区不老町 〒464-01

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Spatial distributions of atomic vapors of alkaline earth elements around a tantalum-filament atomizer were studied in conjunction with the dissociation energy of diatomic oxide molecules. The spatial distributions of atoms in Ar atmosphere were narrower in the order which was coincident with the order of dissociation energy of oxide in magnitude. The presence of hydrogen (ca. 1%) in the purge gas expanded significantly the narrow distributions.

1. Introduction

Electrothermal atomizers (ETA's), using a non-tubular heating element such as a carbon filament¹⁾, a glassy carbon strip²⁾ or a metal boat³⁾ have an advantage in atomic absorption spectrometry (AAS); such a non-atomic species as fume which is evolved from sample matrices during a charring process is rapidly purged out of the light beam. Concurrently, background absorption caused by non-atomic species can be minimized on the subsequent atomization process. A commercially available metal-boat atomizer has been applied to practical analysis³⁾. Compared with ETA's using a

tubular heating element such as a graphite tube furnace, those using a non-tubular heating element have such a problem that more serious chemical interference can be caused by sample matrices, which may be associated with atomization process in thermal non-equilibrium. Another serious problem lies in a narrow spatial distribution of atomic vapor around a heating element. The sensitivity becomes significantly low with the wide beam diameter (4–6 mm) of a conventional hollow cathode lamp, since a large part of the source radiation undergoes no absorption. Narrowing the beam in order to gain a higher sensitivity would result in lowering the signal-to-noise ratio (S/N), particularly for the source lines of

low emission energy.

Agget and West have studied spatial distributions of atomic vapors above a carbon-filament ETA for volatile elements such as Cd, Ag, Pb and Cu¹⁾. The atomic vapors of these volatile elements were distributed over a relatively wide space above the filament. In this study, narrow spatial distributions of atomic vapors around a Ta-filament atomizer were found for alkaline earth elements, Ca, Sr and Ba. The narrow spatial distributions were studied in conjunction with the dissociation energy of diatomic molecules such as metal monoxides and monochlorides. An attempt to expand the narrow spatial distribution of atoms was also successfully made with the aid of the reductive power of hydrogen contained at a low concentration (ca. 1%) in an Ar purge gas.

2. Experimental

The ETA assembly used in this experiment was basically the same as that constructed for a previous study²⁾. In a Pylex glass dome with quartz windows for AAS measurements, a Ta-filament of 0.5 mm in diameter, as a heating element, was fitted on stainless steel electrodes. The Ta-filament had a overall length of 50 mm, and a hill of 4 mm in height and 5 mm in length. The hill top has a depression of 0.25 mm for sample holding. On both sides ca. 1 mm apart from the Ta-filament, horizontal slits of 1 mm in width were mounted in order to narrow the source light beam. The electrodes were mounted on a stage which was movable vertically at a pitch of 0.25 mm. Thus, the vertical distribution of atomic vapor around (above and below) the Ta-filament was observed through AAS measurements.

Argon or hydrogen-containing argon was used as a purge gas. The flow rates of Ar and H₂ were regulated at 2.2 l/min and 21 ml/min, respectively. An aliquot (1 μ l) of a sample solution was taken onto the filament depression, dried by passing a low current through the filament and atomized at a high current. The temperature of the Ta-filament was measured by means of an

optical pyrometer (Yokogawa Elec. Co.). A Nippon Jarrell-Ash AA-1E spectrometer equipped with a Hitachi strip chart recorder QPD-54 was used for AAS measurements. The atomic lines used for AAS measurements were Ca (I) 422.7 nm, Sr (I) 460.7 nm and Ba (I) 553.5 nm. Different salts such as chlorides, acetates and perchlorates of Ca, Sr and Ba were used for the test samples.

2. Results and discussion

Figure 1 shows the spatial distribution profiles of relative peak absorbance (as for the definition, refer to the figure caption) around the Ta-filament for Ca, Sr and Ba. The absorbance substantially reflects the number of atoms in the light beam, though

Fig. 1. Spatial distribution of relative absorbance for alkaline earth elements around the Ta-filament. The abscissa is the height above the Ta-filament, where the bottom of the source light beam passes. The ordinate is the relative absorbance with respect to the absorbance at the 0 mm height (A_0). The purge gas is Ar at 2.2 l/min, except for ■, Δ , Ba 104 ng as BaCl_2 ($A_0=0.13$, $T=2030^\circ\text{C}$); ▲, Ba 102 ng as $\text{Ba}(\text{CH}_3\text{COO})_2$ ($A_0=0.34$, $T=1950^\circ\text{C}$); ○, Ca 1 ng as CaCl_2 ($A_0=0.11$, $T=2050^\circ\text{C}$); ●, Sr 2 ng as SrCl_2 ($A_0=0.24$, $T=1840^\circ\text{C}$); ■, Ca 102 ng as $\text{Ca}(\text{ClO}_4)_2$ ($A_0=0.21$, $T=1630^\circ\text{C}$, Ar 2.2 l/min + H₂ 21 ml/min).

in order to obtain more exact results, a correction is necessary with respect to its dependence on the gas temperature, i.e. the Doppler effect.

The spatial distribution profile of Sr indicates that Sr atoms populate almost symmetrically below and above the Ta-filament. This suggests that the atomic clouds are not seriously perturbed by a purge gas flow or convection currents around the Ta-filament. Figure 1 also illustrates that the distributions of Ba, Ca and Sr atoms are narrower in that order. Among the important factors associated with the difference in the spatial distribution of atoms are the diffusion coefficient of species in Ar, and the rates of reactions such as dissociation from diatomic molecules to atoms and their recombination. The diffusion processes were theoretically estimated to affect less significantly the difference in the spatial distribution: the peak absorbance is approximately inversely proportional to the 4th root of the reduced mass of the analyte species and Ar. The following reactions are deduced to be mainly associated with the difference in the spatial distribution of atoms. In the course of the temperature rise of the Ta-filament, the analyte salts, dichlorides and oxygen-containing compounds (nitrate, perchlorates and acetate) may be rapidly decomposed into monochlorides and monoxides on the Ta-filament, respectively. Parts of them, particularly monochlorides with high vapor pressure diffuse around the Ta-filament and undergo thermal dissociation into atoms and also recombination with Cl atoms or oxygen atoms of impurities such as H_2O and CO_2 in Ar.

Most of monoxides may dissociate into atoms on the Ta-filament. The resulting atoms, during diffusing apart from the Ta-filament, also may undergo recombination. The recombined atoms can again thermally dissociate. Since the recombination reactions are very rapid, the slow dissociation reactions are most likely the rate-determining steps. For the simple thermal dissociation of diatomic molecules, the activation energy approximates to the dissociation energy. Hence, the diatomic molecules with

a higher dissociation energy are decomposed more slowly, leading to a lower population of atoms. Such a tendency may be more notable at a spatial point more distant from the Ta-filament, where the gas temperature becomes lower. Hence, the spatial distribution can be narrower for the element, the dissociation energy of the diatomic molecules of which is higher.

The dissociation energy is <2.76 eV for CaCl , 4.3 eV for SrCl , 5.0 eV for BaCl , 4.3 eV for CaO , 4.2 eV for SrO and 5.75 eV for $\text{BaO}^{4)}$ (or 5.0 eV for CaO , 4.8 eV for SrO and 5.9 eV for $\text{BaO}^{5)}$). Thus, the dissociation energies of Ba, Sr and Ca monochlorides are higher in that order. On the other hand, the dissociation energies of monoxides are higher in different order ($D_{\text{BaO}} > D_{\text{CaO}} > D_{\text{SrO}}$). As described above, the spatial distributions of Ba, Ca and Sr atoms are narrower in that order. Accordingly, monoxides are the species which exist more likely around the Ta-filament at a high temperature than monochlorides. Figure 1 also shows that the spatial distribution profile of Ba for BaCl_2 is almost the same as that for Ba $(\text{CH}_3\text{COO})_2$ from which BaO may be mostly produced on the thermal decomposition. The monochlorides, BaCl produced on the Ta-filament may be immediately converted into BaO through a reaction with oxygen atoms of impurities contained in the purge gas.

As seen from Fig. 1, the spatial distribution profile spreads over a wide space in an Ar- H_2 purge gas, in spite of a lower temperature of the Ta-filament and an oxidative salt, perchlorates used as the analyte. The reductive power of hydrogen greatly contributes to making a higher degree of atomization of the analyte on the Ta-filament and also to preventing the resulting atoms from being recombined with the oxygen atoms of the impurities in the purge gas. Thus, hydrogen at a low concentration of ca. 1% in the Ar purge gas expanded the spatial distribution notably. Such an effect would be also useful in minimizing matrix effects encountered for the electrothermal atomizers using a nontubular heating element, as well as in increasing the

sensitivity.

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