

Original Paper

Some Observations on the Interferences in Atomic Emission Spectrometry of Lithium with Metal Tube Atomizer

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Chemical interference effects on lithium atomic emission signal in a tungsten tube atomizer have been investigated. The matrix elements are Ca, Cs, Cu, K, Mg and Na. The depression effects on the lithium emission signal were observed when 100 pg - 100 ng (10 - 10000 fold) of the interferents were added. The relationship between the intensity of lithium emission ($I_{\text{Li}} - I_{\text{I}}$) and \log (multiple of the interferent for the amount of lithium) was linear.

Key Words: lithium, interference effects, atomic emission spectrometry, tungsten tube atomizer

1. Introduction

Recently, some workers have studied the analytical characteristics of atomic emission spectrometry with electrothermal graphite furnaces and metal tubes¹⁻¹⁷). These excitation sources were found very useful for alkali metal analyses because of the lower excitation temperature, better sensitivity and simplicity than conventional sources (flame, arc and spark, DC plasma, and inductively coupled plasma)^{10,11,15,17,18}). In previous publications¹²⁻¹⁷), we have discussed the development and usefulness of a simple, sensitive atomic emission spectrometry with a metal tube atomizer.

Lithium is one of the essential elements in life processes of organisms and one of the impurities in highly pure industrial materials. It is important to accurately determine lithium in various materials. Many workers have reported the trace determination of lithium in food, metal, somatic, biological and environmental samples with matrix interferences by atomic emission spectrometry with graphite furnaces^{2,11,19}). However, little information on the systematic chemical interference on atomic emission spectrometry of lithium has been reported.

In this paper we examine interference effects of matrix elements on lithium emission signal in a metal tube atomizer.

2. Experimental

2. 1 Instrumentation

A thin-wall tungsten tube (2 mm inside diameter, 35 mm long and 0.05 mm wall) used as an excitation source was made from a high purity tungsten sheet (99.95 %, Goodfellow Metals Ltd.). Two legs for supporting the tube at both ends were made from molybdenum sheets (0.1 mm thickness, 99.95 % purity, Rembar Co.). The tube atomizer was mounted in a Pyrex glass chamber²⁰⁾. Signal measurements were achieved by a system consisting of a Nippon-Jarrell Ash Ebert type monochromator, an R943 photomultiplier (Hamamatsu Photonics Co.), a dc amplifier, a memoriscope (Iwatsu MS-5021), and a microcomputer (Sord M223) coupled with a plotter (Graphtec WX4675). A lithium hollow-cathode lamp (Hamamatsu Photonics Co.) was used for alignment of atomic emission line at 670.78 nm. Lithium emission signals passed through two light apertures (0.5 mm and 2 mm diameter) which were placed between the tube and a condensing lens. The apertures greatly reduced the amount of tube-wall radiation reaching the monochromator. The temperature signal of the tube wall from a photo diode (S641, Hamamatsu Photonics Co.) was preliminarily calibrated with an optical pyrometer (Chino Works) and was fed simultaneously with emission signals to the microcomputer. A glass micropipette (1 μ l) with a Teflon tip at the end was calibrated with a microbalance (Mettlar H20) and used for sample introduction.

Water used in the study was purified four times by deionization and distillation through an autodistiller (Isuzu Works), a deionizer (Monopet type, Organo Co.) and a super purifier (PS-1 type, Fujiwara Works).

2. 2 Reagents

A lithium standard stock solution of 0.5 mg/ml was prepared as chloride by dissolving an appropriate amount of lithium carbonate in 0.1 M hydrochloric acid. All working solutions were prepared from the stock solution just before use. Matrix solutions were also prepared as chloride.

Analytical reagent grade chemicals were used throughout the study. Lithium contents in these chemicals were checked.

2. 3 Procedure

A voltage of 680 V was supplied to the photomultiplier.

Hydrogen was added to the argon purge gas in order to protect the metal tube from oxidation by traces of oxygen in the Pyrex chamber and the gas cylinder. The purge gases flew through the chamber at 480 ml/min for Ar and 20 ml/min for H₂. Since trace lithium may exist in glasswares, laboratory apparatus, Teflon wares and plastics, they were cleaned with nitric acid and water.

A 1 μ l aliquot solution which amounts 10 pg Li was introduced into the

metal tube with the micropipette. The sample was dried at 360 K for 10 s and atomized by heating to a final temperature of 2620 K. Atomic emission and background profiles were measured alternatively. After smoothing, the data were stored on a disk and hard copies were obtained by the plotter, if desirable.

3. Results and Discussion

It has been found from our previous studies^{12-16,21)} that the mixing ratio of argon and hydrogen and the heating rate of the tube atomizer influenced the atomization and excitation of analytes in the electrothermal metal tube. In this study, a purge gas of 480 ml/min Ar and 20 ml/min H₂ and a heating rate of 6.5 K/ms were selected because of the better sensitivity and reproducibility of the lithium emission signal and the lower background emission over wide wavelength ranges.

Some workers²²⁾ have reported observations of severe problems of ionization and self-absorption for lithium emission in most excitation sources and atomizers. The ionization of lithium atoms is remarkable in an inductively coupled plasma (ICP) with a gas temperature of 9000-10000 K²³⁾. Therefore, the detection limit (0.0002 µg/ml, S/N=2) of lithium in the plasma is worse than that in a flame (0.0001 µg/ml, S/N=2)¹⁸⁾. Ionization of lithium in conventional excitation sources is one of the largest problems for accurate trace determinations. In a graphite furnace, Sturgeon *et al*²³⁾ described that ionization of alkalis is not significant in atomic absorption, but ionization interference should be taken into account for atomic emission. In the electrothermal metal tube, the emission signal of lithium (10 pg) in the presence of cesium (100 pg) was similar to that without cesium. Therefore, in the case of the metal tube, ionization interference was not significant for lithium determination, because if the ionization of lithium was large, the lithium signal would be larger by the addition of cesium, which has lower ionization energy (3.89 eV) than lithium (5.39 eV).

Biological materials, in general, contain large amounts of Ca, Cu, K, Mg and Na. The effects of the elements and cesium (100 pg - 100 ng) on a lithium (10 pg) emission profile were investigated with the metal tube atomizer. The relative standard deviations calculated from 4-10 repeated measurements of 10 pg lithium in the presence of these elements (10 ng) were better than 7.3

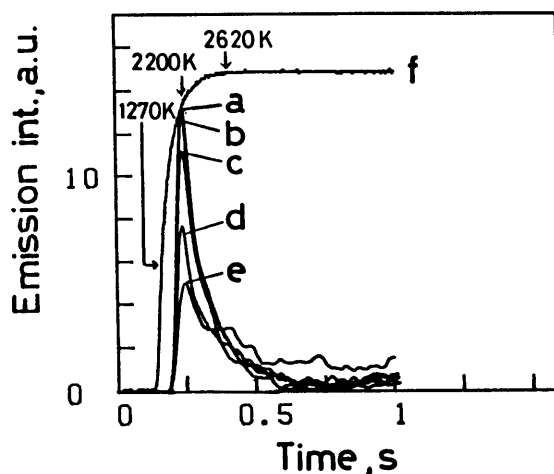


Fig.1 CRT display showing the effect of copper on atomic emission of lithium in 480 ml/min Ar and 20 ml/min H₂. (a) Li 10 pg only, (b) Li and Cu 100 pg, (c) Li and Cu 1 ng, (d) Li and Cu 10 ng, (e) Li and Cu 100 ng, (f) temperature increasing.

%. The typical interference of a matrix element (Cu) on the lithium signal is shown in Figure 1. The peak height of lithium signal was decreased as the amount of the interferent increased, as shown in Figures 1 and 2. In the presence of a large amount of sodium (Figure 2), a second peak in the lithium signal was observed. It was not understood what the peak resulted from. The appearance temperatures of lithium emission signal, which are defined as the temperature of the atomizer at the time when a RSD emission signal can first be perceived above the baseline noise, in the presence of the interferents were similar to the pure lithium signal. The peak temperature, which is the temperature at maximum emission, of the lithium emission signal in the presence of matrix elements was 2200K and the same as that of the pure lithium signal, except 100 ng of calcium and sodium matrix elements which shifted the peak temperature higher. The relationship between an intensity of lithium emission and logarithmic multiple of the interferent to the amount of lithium

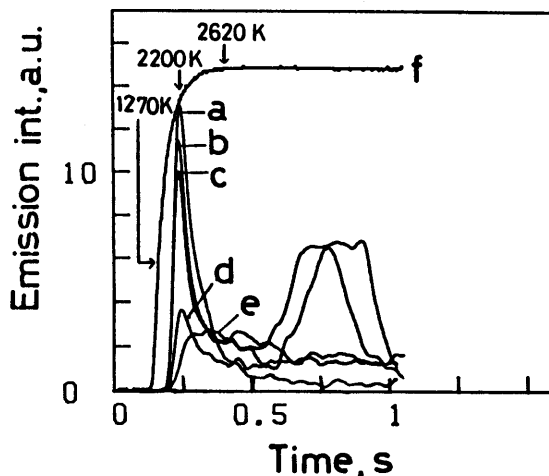


Fig.2 CRT display showing the effect of sodium on atomic emission of lithium in 480 ml/min Ar and 20 ml/min H₂.
(a) Li 10 pg only, (b) Li and Na 100 pg, (c) Li and Na 1 ng, (d) Li and Na 10 ng, (e) Li and Na 100 ng, (f) temperature increasing.

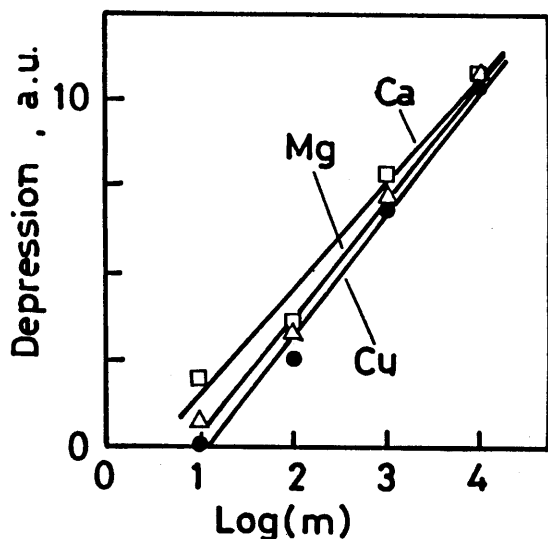


Fig.3 The relationship between the intensity of lithium emission ($I_{Li} - I_{int}$, Y) and \log (multiple of the interferent, m).
(□) Ca, (●) Cu, (Δ) Mg

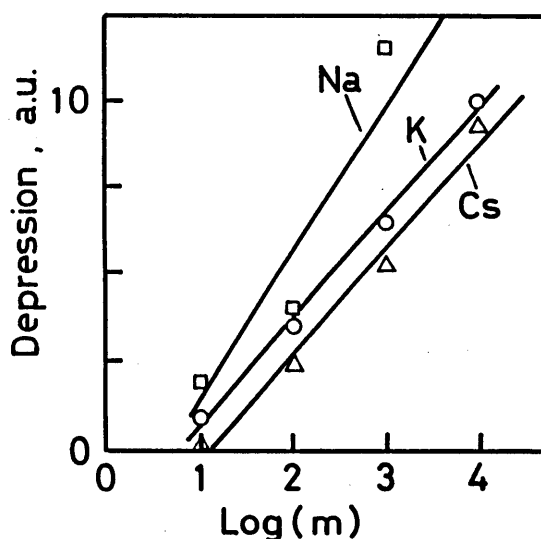


Fig.4 The relationship between the intensity of lithium emission ($I_{Li} - I_{int}$, Y) and \log (multiple of the interferent, m).
(Δ) Cs, (O) K, (□) Na

was linear. This is illustrated in Figures 3 and 4 with $Y = I_{Li} - I_I = a \cdot \log(m) + b$, Where I_{Li} and I_I are the emission intensities of pure lithium and lithium in the presence of interferent, respectively, m is the multiple of interferent to the analyte (10 - 10000 fold, corresponding to 0.1 - 100 ng), and a and b are constants. The experimental equation could not be theoretically explained at present. A coefficient and a constant in the equation are listed in Table 1. The intercept of the line at abscissa, m_0 (m value when $Y=0$), means the multiple of the interferent under which the lithium emission signal is not interfered. The intercepts were 3.5, 12.8, 11.8, 6.3, 8.1, and 4.6-folds of Ca, Cs, Cu, K, Mg, and Na, respectively, as shown in Table 1.

Table 1 The coefficient and constant in the equation ($Y = I_{Li} - I_I = a \cdot \log(m) + b$) for lithium atomic emission signal.

Interferent	$Y = a \cdot \log(m) + b$		Intercept at the abscissa m_0
	a	b	
Ca	12.2	-6.7	3.5
Cs	12.0	-13.3	12.8
Cu	13.9	-14.9	11.8
K	12.1	-9.7	6.3
Mg	13.5	-12.3	8.1
Na	16.7	-11.0	4.6

m : multiple of interferent (10 - 10000 fold, corresponding to 0.1 - 100 ng).

m_0 : m value when $Y=0$.

In conclusion, this experiment indicated that Ca, Cs, Cu, Mg and Na on atomic emission spectrometry with a tungsten tube atomizer offered additive interferences on the lithium emission signal. The results also suggest that it is feasible to determine these matrix elements by the use of the lithium emission line.

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