

# Ionization Interference in Inductively Coupled Plasma-Optical Emission Spectroscopy

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Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is widely used in various high-sensitive and high-precision elemental analysis such as environmental analysis and material analysis. Although the influence of coexisting elements on ICP-OES is known to be relatively small, in the axially viewed ICP-OES, the measurement error due to ionization interference could be observed depending on the combinations of coexisting elements and analyte elements. The result of the study on elemental combinations clearly shows that the occurrence of ionization interference can be presumed from the magnitude of ionization potentials. After examining the methods for adding low ionization potential elements to both sample solution and standard solution, it was confirmed that ionization interference could be successfully suppressed by adding low ionization potential elements, especially excessive amounts of cesium.

## 1. Introduction

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is a quantitative method for determining trace elements in liquid samples. ICP-OES has characteristics such as high sensitivity, high reliability, wide dynamic range, and relatively less affected by coexisting elements. It is used in a wide range of fields, including purity analysis of environmental water and composition analysis and contaminant analysis of plating solutions and materials such as metals, ceramics, and plastics<sup>(1)</sup>. Recently ICP-OES is increasingly being applied for microanalysis of elements regulated by RoHS, REACH and other standards. When utilizing ICP-OES, the concentrations of coexisting elements in the sample solution and the calibration solution are usually adjusted to be the same in order to minimize the influence of coexisting elements on measurement. However, this approach cannot be used when a sample consists of high-purity materials or contains unknown elements. In some cases, whether or not the measurement was influenced by coexisting elements cannot be determined from measurement data. Therefore it is important to improve the reliability of analysis by preliminarily determining the conditions of interference by coexisting elements and how to avoid the occurrence of interference. In this study, the authors focused on ionization interference due to coexisting elements, and examined its influence in various combinations of coexisting elements and analyte elements. The authors report also on a measure for suppressing ionization interference and its success.

## 2. ICP-OES

**Figure 1** shows the schematic of typical ICP-OES equipment. The instrument is comprised of a sample introduction section, a plasma source, a spectrometer, a

detector, and a data processing system, and is customized for various purposes. ICP-OES works by spraying the sample solution into a high-temperature plasma generated by subjecting argon gas to a high frequency field. The elements in the solution are determined qualitatively and quantitatively from the wavelengths and intensities of the emissions from excited atoms and ions. Of the emissions spectra utilized for element determination, the emission spectra from atoms are classified as neutral lines, and the emission spectra from ions are classified as ionic lines. When ICP-OES is used for quantitative analysis, a calibration solution adjusted to a known concentration of the analyte element is generally prepared, and the concentration of analyte element is determined by comparing the intensity of emissions from the sample solution and the calibration solution.

As shown in **Fig. 1**, two different photometry methods are used in ICP-OES. Axial view is observation from the direction parallel to the plasma, and radial view is observation from the direction perpendicular to the

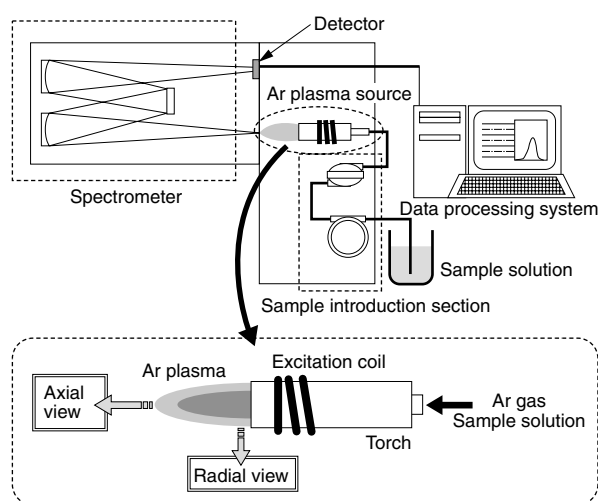


Fig. 1. Schematic of ICP-OES

plasma. Radial view is less affected by coexisting elements but has lower sensitivity, whereas axial view is greatly affected from coexisting elements but provides greater detection sensitivity, more than 10 times that of radial view for some elements. Recent ICP-OES instruments include models having both axial and radial view capabilities that allow the direction of observation to be selected to suit the sample and measurement range. Traditional ICP-OES instruments generally used photomultipliers as detectors and utilized diffraction gratings to scan the wavelengths. Recently, instruments using a semiconductor detector that can observe all wavelengths at the same time have become commercially available. As a result of these developments, ICP-OES instruments are becoming increasingly convenient to use.

### 3. Ionization interference

ICP-OES and other methods of spectrochemical analysis are typically subject to errors due to the four different types of interference: 1) physical interference due to changes in viscosity, etc. of the solution, 2) chemical interference due to the generation of compounds that have low atomization efficiency, 3) spectral interference due to the superposition, etc. of emission/absorption lines, and 4) ionization interference due to changes in ionization equilibrium state.

Ionization interference is a phenomenon which shows a change in emission intensity, causing the ionization equilibrium to shift, when coexisting elements include easily ionizable elements such as Na, K, Rb, and Cs. Generally, this results in greater intensity of neutral lines and reduced intensity of ionic lines. It had been reported that ICP-OES is significantly affected by physical interference and spectral interference, but relatively less affected by the other two types of interference<sup>(1)</sup>. However, ionization interference is known to affect ICP-OES when the coexisting elements are easily ionizable elements, such as alkali metals. This is particularly a large problem in axial view, since the emissions spectra are observed over the entire range of plasma. It has been confirmed that while detection sensitivity is enhanced, the influence of ionization interference also increases. There are some reports discussing how the direction of observation affect measurement result<sup>(2)-(5)</sup>. Following the adoption by Sumitomo Electric Industries, Ltd. of an ICP-OES unit capable of both axial view and radial view, the authors investigated the influence of ionization interference and methods for suppressing such interference.

### 4. Instrument and conditions for measurement

The instrument used was an iCAP 6500 Duo ICP spectrometer manufactured by Thermo Fisher Scientific K.K. This instrument consists of a charge injection device (CID) detector and an echelle spectrometer,

enabling all wavelengths to be measured simultaneously. It also permits switching between axial view and radial view to be performed without reassembling the instrument. The ICP-OES measurement conditions are shown in **Table 1**.

**Table 1.** ICP-OES measurement conditions

Item	Condition
RF power	1150W
Flow rate of assist gas	1.5L/min.
Flow rate of nebulizer gas	0.65L/min.
Flow rate of coolant gas	12L/min.

### 5. Investigation of influence of ionization interference

#### 5-1 Experimental method

Coexisting elements and analyte elements for the experiment were selected arbitrarily from elements with first ionization potential up to about 10 eV. The selected elements are listed in **Table 2**. Neutral lines were selected as the measurement wavelengths, but ionic lines were measured for Ba and Y because these elements have no measurable neutral lines. For the sample solution, coexisting elements and analyte elements were added to attain the concentrations shown in **Table 2**, then after adding 5 ml of 60% HNO<sub>3</sub>, the solution was diluted to 100 ml with ultrapure water. The calibration solutions were prepared with the element added in three levels, 0, 1, and 3 µg/ml for an analyte element concentration of

**Table 2.** Lists of coexisting elements and analyte elements

Coexisting element			Analyte element			
Element	1st ionization potential (eV) <sup>(1)</sup>	Concentration (mol/l)	Element	1st ionization potential (eV) <sup>(1)</sup>	Concentration (µg/ml)	Wavelength (nm)
Cs	3.894	0.01	K	4.341	3	766.490
K	4.341		Na	5.139	3	588.995
Na	5.139		Ba	5.212	1	455.403
Ba	5.212		Li	5.392	1	670.784
Li	5.392		Al	5.986	1	309.278
In	5.786		Y	6.38	1	371.030
Al	5.986		Mo	7.099	1	317.035
Ga	5.999		Pb	7.416	3	216.999
Cr	6.766		Mn	7.435	1	279.482
Ni	7.635		Ni	7.635	1	232.003
Cu	7.726		Cu	7.726	1	324.754
B	8.298		Ge	7.899	1	265.118
Zn	9.394		B	8.298	1	249.773
P	10.486		Cd	8.993	1	228.802
			Zn	9.394	1	213.856

1  $\mu\text{g/ml}$  (0, 3, and 9  $\mu\text{g/ml}$  for an analyte element concentration of 3  $\mu\text{g/ml}$ ), adding  $\text{HNO}_3$  and diluting to 100 ml in the same way as for the sample solution. No coexisting elements were added to the calibration solution.

Measurements were performed by both axial view and radial view in order to evaluate how the determined concentrations changed with the difference in the direction of observation.

### 5-2 Experimental results

**Figure 2** shows the results in radial view. Although the determined concentrations show some variations from the expected results, the variations are within a range of 5% measurement error, which is considered to be normal variation. These results show that the coexisting elements virtually have no influence. **Figure 3** shows the results in axial view. The results exhibit clear differences from those in radial view. There are significant increases in emission intensity in some combinations of elements, especially in the combinations where both coexisting element and analyte element have low ionization potentials. The combination of elements in this experiment that showed the largest emission intensity increase was where Na was used as the coexisting element and K was used as the analyte element, which exhibited three times larger emission intensity than the

case without Na.

**Figure 4** shows the experimental result data rearranged with the first ionization potentials of the coexisting elements being plotted on the X-axis. The Y-axis represents the ratio of the axial detection result to the radial detection result. No increase of detection sensitivity is observed in axial view when the first ionization potential is above 8 eV. This chart shows that the only possible case of sensitivity increase due to ionization interference is where the coexisting elements include elements whose first ionization potential is below 8 eV. **Figure 5** shows the experimental result data rearranged with the first ionization potentials of the analyte elements being plotted on the X-axis. This chart shows that sensitivity increase is observed when the first ionization potential of the analyte element is below 6 eV. The chart also shows that sensitivity increase due to ionization interference may occur in combinations where coexisting element has a first ionization potential of 8 eV or lower and analyte element has a first ionization potential of 6 eV or lower.

The measured results described above were for typical neutral lines, but similar sensitivity increase was observed for any neutral line of other wavelengths. It was also found that even when the elements were affected by ionization interference for neutral lines, there was

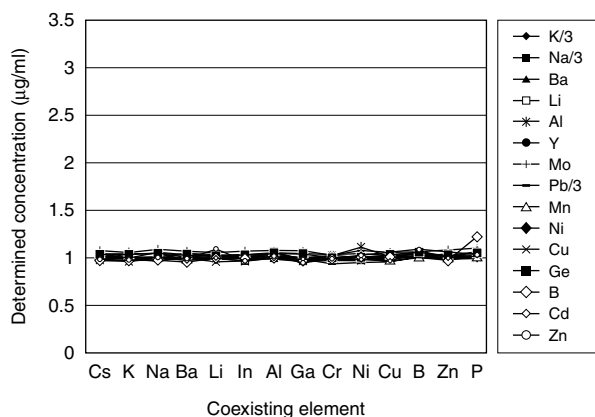


Fig. 2. Influence of coexisting elements in radial view

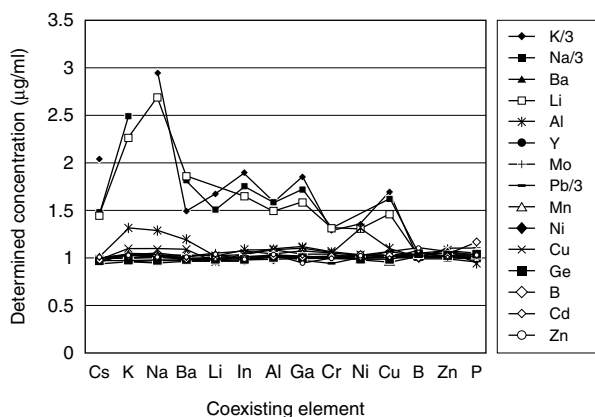


Fig. 3. Influence of coexisting elements in axial view

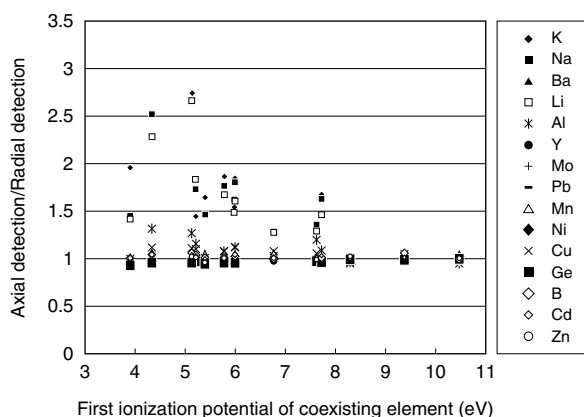


Fig. 4. Relationship between ionization potential of coexisting element and variation in determined concentration

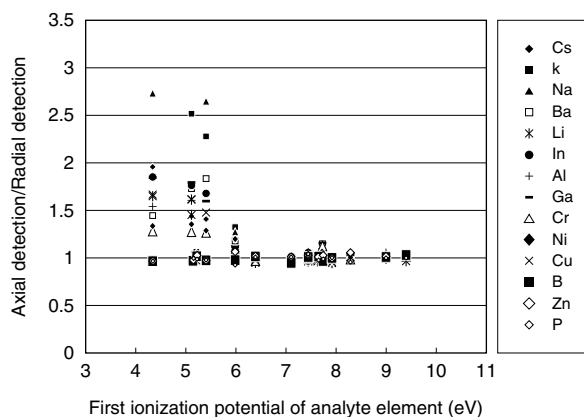


Fig. 5. Relationship between ionization potential of analyte element and variation in determined concentration

virtually no influence of ionization interference on the elements for ionic lines.

## 6. Study of ionization interference suppression methods

### 6-1 Experimental method

Through the examination of the influence that ionization interference has on analytical performance as described above, it was possible to identify the conditions under which ionization interference readily occurs. Since there are 50 to 60 elements having a first ionization potential 8 eV or below and 20 to 30 elements having a first ionization potential 6 eV or below, there are a large number of combinations in which interference may occur. Given this situation, the authors examined the effect of using interference suppressors as a simple and easy method of suppressing ionization interference.

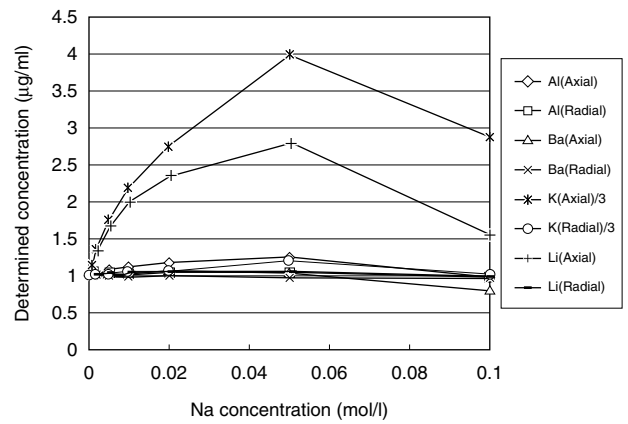
In atomic absorption spectrometry, in which ionization interference has a significant influence, ionization interference is sometimes suppressed by adding low ionization potential elements to both sample and calibration solutions. On the other hand, ICP-OES is considered as a measurement method that is very little affected by coexisting elements, and there are only few reports on the use of low ionization potential elements.

Based on the results of the investigation of the influence of ionization interference, an investigation was made on the method of saturating the sensitivity increase effect by adding an excess of element having a low first ionization potential as a suppressor.

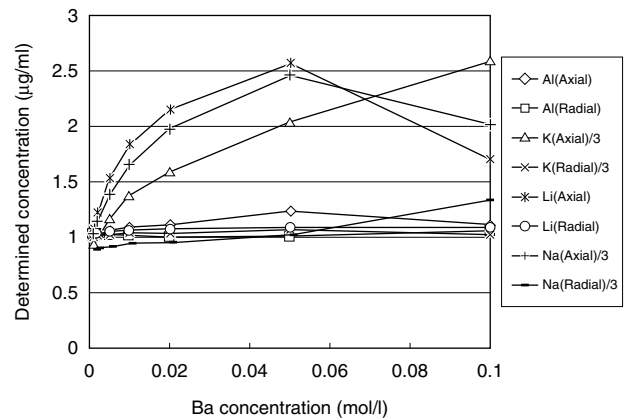
Using Cs, Na, and Ba as suppressors, an investigation was conducted on the combinations of analyte elements and coexisting elements shown in **Table 3**. The same amount of suppressor was added to both sample and calibration solutions, and the effect of each suppressor was confirmed by quantitatively determining the concentration of each analyte element (no coexisting element was added to calibration solutions). The suppressors used were water-soluble salts such as carbonates and chlorides. **Figures 6 to 8** show the dependence of each element on the suppressor concentrations. The authors then investigated the effect of the suppressors in concentrations of 0.005, 0.01, 0.03, and 0.05 mol/l.

**Table 3.** Selected elements in the examination of suppressor

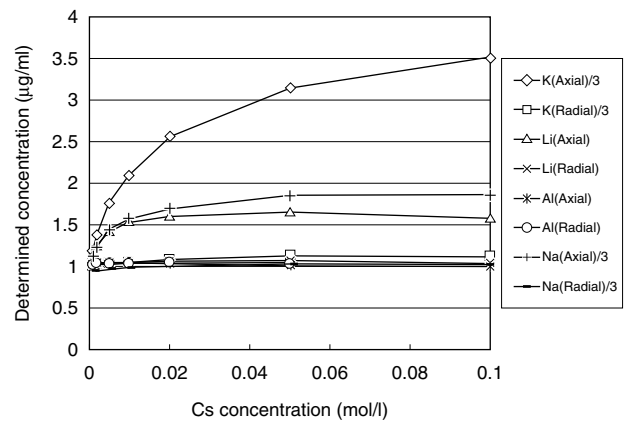
Coexisting element		Analyte element		
Element	Concentration (mol/l)	Element	Concentration (µg/ml)	Wavelength (nm)
K	0.01	K	3	766.490
Na		Na	3	588.995
Ba		Li	1	670.784
		Al	1	309.278



**Fig. 6** Relationship between Na concentration and variation in determined concentration



**Fig. 7** Relationship between Ba concentration and variation in determined concentration



**Fig. 8** Relationship between Cs concentration and variation in determined concentration

### 6-2 Experimental results

**Figures 9 to 11** show the effects the suppressors have on the results of axial view.

As can be seen, when the analyte element was Al, the influence of ionization interference was almost completely suppressed by adding a relatively small amount of suppressor 0.005 mol/l in all combinations of suppressors and coexisting elements.

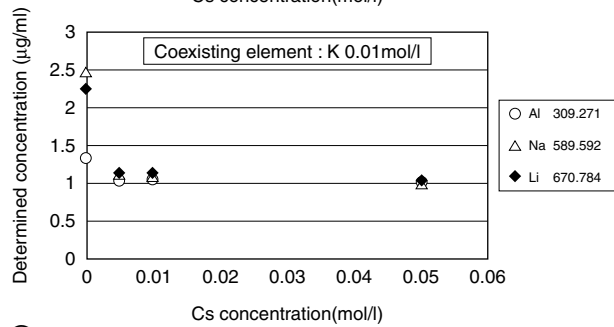
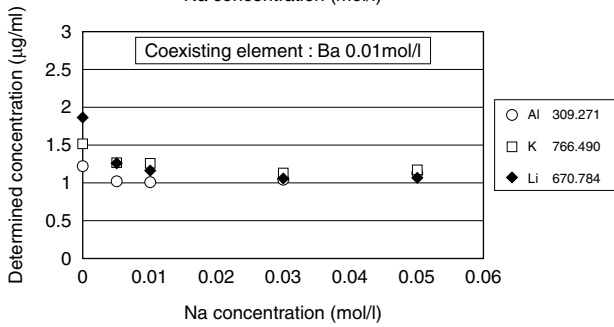
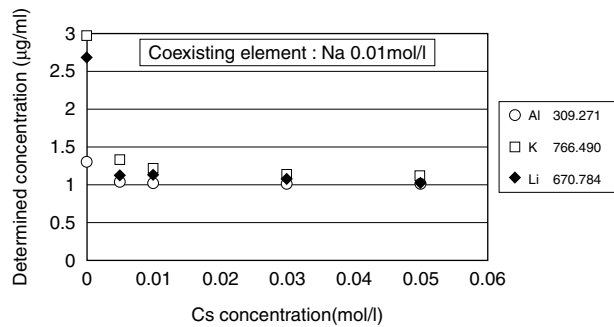
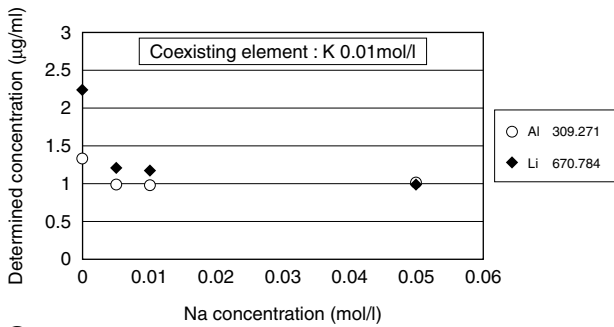


Fig. 9 Interference suppressing effect of Na (in axial view)

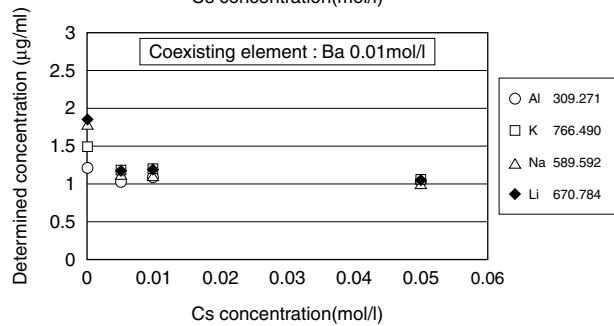
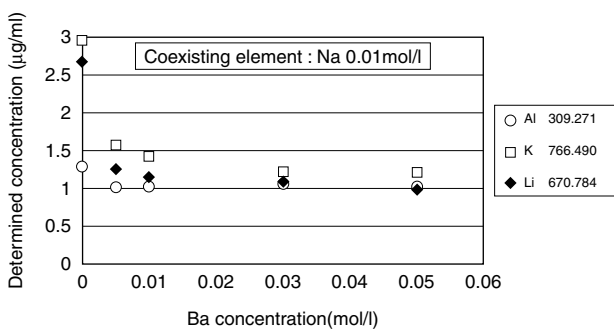


Fig. 11 Interference suppressing effect of Cs (in axial view)

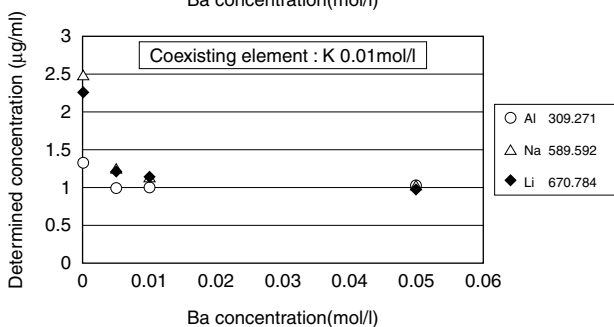


Fig. 10 Interference suppressing effect of Ba (in axial view)

a sensitivity increase of at least 20% was observed even when suppressor 0.05 mol/l was added. When Cs was utilized as a suppressor, the ionization interference suppression effect obtained at a low concentration was larger than that obtained by using other suppressors. Even when K was the analyte element, it was possible to suppress virtually all influence of interference by adding 0.05 mol/l of Cs.

From these results it was found that Cs has the largest ionization interference suppression effect among the three suppressors investigated in this report, and that the concentration of suppressor necessary for suppressing the influence of interference is 5 times that of the coexisting element.

## 7. Conclusion

Using an ICP-OES instrument capable of axial and radial view, the influence of ionization interference was investigated for the axial and radial observation directions. It was found from the investigation results that virtually no influence of coexisting elements was seen in the measurement with radial view, but the observation

with axial view was strongly affected by ionization interference when elements with low ionization potentials coexist in the sample. The detection sensitivity was enhanced to three times the expected level at a maximum. It was found that ionization interference was likely to occur when the first ionization potential of coexisting element is 8 eV or below and that of analyte element is 6 eV or below. Since it is not possible to determine the influence of ionization interference simply from measured result, it is very important to identify the conditions under which interference occurs. The investigations reported herein have made it possible to estimate the combinations of elements for which interference is likely to occur, and this result will contribute to the improvement of analysis reliability.

Methods for avoiding ionization interference include: 1) measuring with radial view, and 2) making the coexisting element concentration values in sample solution the same with those in calibration solution. However, in situations where both of these methods cannot be taken, other method of interference suppression is needed. This paper reports on the investigation on ionization interference suppression by adding an excess of element having a low ionization potential to both sample and calibration solutions. The ionization interference suppression effect was examined for the cases of adding Na, Ba, and Cs, and the effect was found to be particularly high with the addition of Cs. It was possible to almost completely suppress ionization interference by adding Cs at a concentration five times that of the coexisting element. This method can be implemented in a relatively simple and easy manner by adding water-soluble salt. By applying this method in conjunction with the determination of conditions under which ionization interference occurs as described above, it is considered possible to nearly completely eliminate measurement error due to ionization interference.

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