Evaluation of Matrix Effects and Mathematical Correction for the Accurate Determination of Potassium in Environmental Water Samples by Axially Viewed ICP-OES*

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ABSTRACT

The severe matrix enhancement effects for potassium determination in environmental water samples using axially viewed inductively coupled plasma optical emission spectrometry (ICP-OES) was investigated in this study. The severe enhancement caused by matrix interference components, such as Li, Na, Mg, and Ca, was demonstrated thoroughly, and the correlation between the enhanced K results and the interference concentrations was investigated. The results showed that both individual and combined interference elements contributed to this kind of enhancement effect. The enhancement ratios (enhanced K/expected K) range from 101%-212% due to the presence of Li, Na, Mg, and Ca, either presented individually or combined in the solution, in the concentration of 10–250 ppm of each interference element. In order to overcome matrix effects and to avoid the use of the time-consuming procedures (such as matrix matching, the method of standard addition, and gradual sample dilution), the approach of mathematical correction was implemented and adequate procedures were developed to handle this problem.

The analyses of Proficiency Testing and Quality Control Reference Standards and a series of test solutions evaluated the validity of this method. The accuracy of the reference standards was within 98.3–104.6%. The corrected spike recoveries from test solutions ranged between 90–110% (most of the recoveries were between 95–105%) and the precision (RSD%) was below 1%.

These preliminary experimental results suggested that this approach of mathematical correction provides a reliable and practical way to overcome the severe matrix enhancement effects for K determination by axially viewed ICP-OES. Precise and accurate K results were obtained by analyzing proficiency testing and quality control reference standards for environmental water samples and serial test solutions in the matrix concentration range of 10–250 ppm of each interference element.

INTRODUCTION

Potassium (K) is an important nutritional element for both plants and animals. Thus, K determination is essential in many different fields and applications, including agriculture, food and drug industries, clinical applications, and environmental monitoring. There are different instrumental techniques available for K determination. Traditionally, flame atomic absorption was used to determine K. But this single-element analysis capability limits productivity when multi-element analyses are required for the same sample. Alternatively, inductively coupled plasma optical emission spectrometry (ICP-OES) is the appropriate technique for the effective multi-element determination in the same sample, including K. Determination of Na, K, Mg, and Ca in urine and saline water and their relative matrix effects, using radial ICP-OES (1) and dual-viewed ICP-OES (2), respectively, are demonstrated and discussed.

Matrix interference effects in ICP-OES analysis have been of concern for application analysts and researchers. Numerous studies have demonstrated the trend of matrix effects under different operational conditions and different applications aspects. It is especially essential to investigate and understand the matrix effects for samples containing high concentrations of alkali and alkali earth elements when using axially viewed ICP-OES analysis since this method tends to present more matrix interferences in certain situations than radially viewed ICP-OES. An overall review of ICP-OES regarding both axially and radially viewed plasma, and the associated features and applications, has been presented and documented (3). The matrix effects of Na and Ca in multi-element analysis using axial and radial ICP-OES have been studied, and the degree of matrix interference and the impact on detection limit has been documented (4–6). Matrix effects in the

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presence of nitric acid, Ca, Na, K, and P have also been studied, and their impact on analyte transport rate, emission intensities, as well as correlation with excitation energy and plasma excitation conditions have been discussed (7). The study of matrix interferences in the trace element analysis of environmental samples addresses the concerns on changes that occur in the plasma or the nebulization device due to matrix differences between standards and samples (8). Meanwhile, the efficiency of using internal standardization in ICP-OES has been evaluated (9–11). In a more specific case, the matrix effect on dissolved phosphorus determination by axially viewed ICP-OES has been observed in the presence of Na and Ca (12). And the matrix effects under different ICP-OES operational conditions have also been described (13–15).

However, the severe enhancement effect in the determination of K using axially viewed ICP-OES has not been addressed specifically. Although the addition of an ionization buffer was considered and tested to overcome the matrix effect, a few problems emerged, for axially viewed ICP-OES, due to overloading the plasma. In order to compensate for this severe matrix effect sufficiently, introduction of a high concentration ionization buffer is required. This creates a dilemma itself over the potential benefit of compensating matrix effect, including instability of sample intensity, increased chance of system contamination, carryover while analyzing other trace level elements, increased instrument drift and gradual clogging of sample introduction components.

Therefore, there is a need to understand this matrix interference and, more importantly, to find an efficient and practical approach to deal with this problem. This study focuses on the demonstration of matrix enhancement effects for K determination using axially viewed ICP-OES in environmental water samples, with the objective of developing adequate and effective mathematical correction procedures to overcome matrix effects for routine analyses.

In general, practical solutions for overcoming matrix effects such as sample dilution, matrix matching and/or the method of standard addition can be regarded as costly and time-consuming procedures for various and unknown sample matrices. Therefore, mathematical correction, based on the interference concentration, becomes an alternative and effective approach.

This study developed a series of mathematical equations to correct matrix enhancement effects for K determination using the enhancement correction ratio (R). The validity of this approach has been verified in the matrix concentration range of 10–250 ppm for Na, Ca, and Mg.

EXPERIMENTAL

Instrumentation

This study was performed using an Optima™ 3300 XL axially viewed ICP-OES (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The instrument was equipped with a GemCone™ nebulizer (Part No. N0690671), cyclonic spray chamber (Part No. N8122188), and 2-mm i.d. alumina injector (Part No. N0695442). The instrumental operating conditions are listed in Table I.

Reagents and Standards

Analytical grade nitric acid and deionized water (18.2 MΩ.cm, E-Pure, Barnstead, Dubuque, IA, USA) were used to prepare the standards and test solutions. Single-element stock standard solutions (K, Ca, Mg, Na, Li, Ba, Cs, Sr, and Y) were obtained from SpexCertiPrep (Metuchen, NJ, USA). Proficiency Testing and Quality Control Reference Standards, which are validated against NIST SRMs, were provided by NIST certified suppliers (AccuStandard, New Haven, CT, USA, and Resource Technology Corporation, Laramie, WY, USA). These reference standards were analyzed to validate the procedure and to verify the accuracy of this method.

Procedure

In order to investigate the matrix enhancement effects for K determination, serial test solutions were made to demonstrate the trend and level of enhancement from matrix interference elements. The test solutions were comprised of varying concentrations of individual and combined interference elements.

All test solutions were prepared to contain individual and/or combinations of elements at specific concentrations in 1% (v/v) HNO_3 by adequate dilution of the stock standards. For individual interference

TABLE I
Operating Conditions of the Optima 3300 XL for the Determination of K

RF Power	1350 W
Nebulizer Flow	0.55 L/min
Auxiliary Flow	0.5 L/min
Plasma Flow	15 L/min
Sample Pump Flow	1 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto-integration (min – max)	5–20 s
Read Delay	60 s
Rinse	60 s
Replicates	3
Background Correction	Manual, 2 points
Nebulizer	GemCone
Nebulizer Chamber	Cyclonic
Injector	Alumina, 2 mm

element effects, Ca, Mg, Na, and Li were investigated in the concentration range of 10–250 ppm. To evaluate the combined matrix effects, solutions that contained Na+Ca, Na+Mg, Ca+Mg, and Na+Ca+Mg were also prepared in the concentration range of 10–250 ppm. The test solutions were spiked with 20 ppm K to assess the trend and level of enhancement effects from the matrix interference on K determination.

The wavelength for K at 766.49 nm was used with two points background correction for instrument calibration. Blank solutions of 1% (v/v) HNO_3 and 20 ppm K in 1% (v/v) HNO_3 were used to generate calibration curves with a K linearity of 70 ppm.

Other Group I and II elements, such as Ba, Sr, and Cs, were studied briefly in the concentrations of 10, 30, and 50 ppm. Since there is no significant enhancement effect at these matrix concentration levels, no further evaluation was carried out.

To demonstrate other potential interferences from different blanks, two blank solutions [1% (v/v) HNO_3 + 5% (v/v) HCl, 100 ppm Ca +100 ppm Mg +100 ppm Na in 1% (v/v) HNO_3] were also analyzed for K.

The on-line addition of internal standard (IS), Y at 371.029 nm, was used to monitor instrument stability and to compensate for variations of different matrices.

RESULTS AND DISCUSSION

Matrix Effect

This study has demonstrated that Li, Na, Ca, and Mg contribute severe matrix enhancement effects at various element concentrations when K is determined by axially viewed ICP-OES. A comparison of 20 ppm K peak intensities in different matrices is given in Figure 1.

The enhancement effects of individual interference elements are shown in Figure 2 for 10–250 ppm of Ca, Mg, Na, and Li. As the curves demonstrates, the enhancement effects on K determination tend to increase in proportion to interference element concentrations. Twenty ppm K would be enhanced to have false reading of 25.8 ppm in the presence of 10 ppm Li. 250 ppm Li would enhance 20 ppm K to read as 42.4 ppm, which illustrated an enhancement ratio (enhanced K/expected K) of 212%. Similar enhancement trends occur on K determination caused by co-existence of single Na, Mg, and Ca with K. A series of test results indicated that the enhancement ratios of individual interference elements can range from 101–212% in the presence of 10–250 ppm of Li, Na, Mg, and Ca, and can reach as high as 134%, 147%, 174%, and 212% for Ca, Mg, Na, and Li matrices up to 250 ppm, respectively.

The mixed element enhancement effects for the combined solutions of Na+Ca, Na+Mg, Ca+Mg, and Na+Ca+Mg, all in the concentration range of 10–250 ppm,

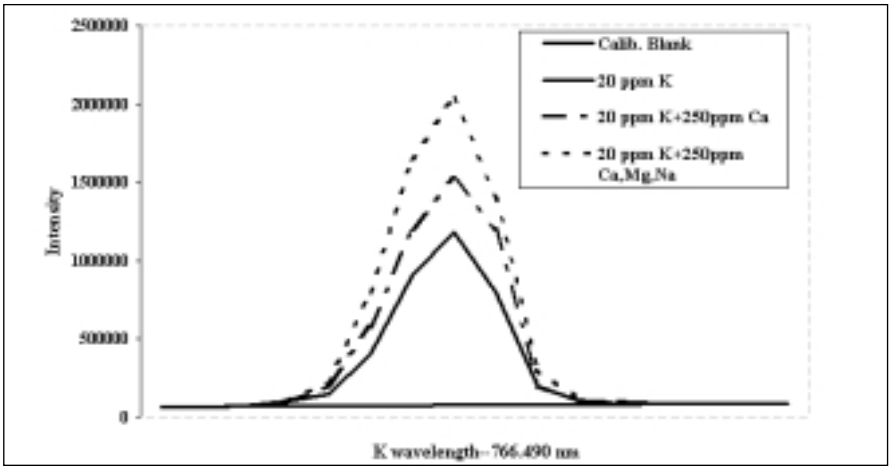

Fig. 1. Spectrum peak comparisons of enhanced K intensity in different matrices.

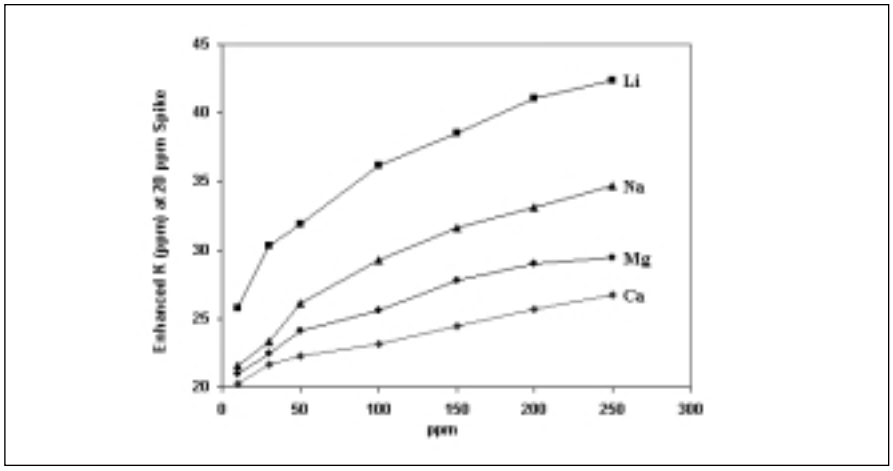

Fig. 2. Individual enhancement effect of Ca, Mg, Na, and Li on K determination.

are shown in Figure 3. For the mixed composition, the combined enhancement impacts are higher than the individual element matrix, but they are not simply additive. In general, the enhancement ratios of the combined matrices are as high as 153%, 182%, 184%, and 188% for Ca+Mg, Na+Ca, Na+Mg, and Na+Ca+Mg up to 250 ppm of each element, respectively. It is worth noting that Na contributed more impact on the combined enhancement (excluded Li). The results in Figure 3 show that there are no significant differences of enhancement ratios when Na was mixed with Ca or Mg only, compared with Na, Ca, and Mg mixed together.

The experimental results also show that Li has the strongest enhancement impact of the elements studied (Li, Na, Ca, Mg, Ba, Cs, and Sr). In general, the individual element enhancement presents the strength in the order of Li>Na>Mg>Ca in the same concentration ranges. Although Li demonstrated the strongest enhancement effect for K determination, it is less likely to find Li at concentrations of high ppm levels for general aqueous environmental samples, such as drinking water, surface water, and wastewater (excluding extreme cases). Meanwhile, Na, Ca, and Mg, which are commonly present in ppm levels in environmental samples, warrant further investigation to handle this matrix effect.

A brief study was conducted to verify the impact from Ba, Cs, and Sr on K determination. The results showed that matrices of 10, 30, and 50 ppm of each Ba, Cs, and Sr did not significantly enhance K determination with axially viewed ICP-OES.

Additionally, in order to demonstrate the impact from different acids and/or similar matrices without the presence of K, two blank solutions [1% (v/v) HNO_3 + 5% (v/v) HCl, 100 ppm Ca +100 ppm Mg +100 ppm Na in 1% (v/v) HNO_3] were analyzed for K, and no bias K intensity was observed. The blank tests suggested that the interference element alone does not elevate the K intensity without the presence of K in the solution. The K intensity will be enhanced only when K co-exists with the matrix-interfering elements.

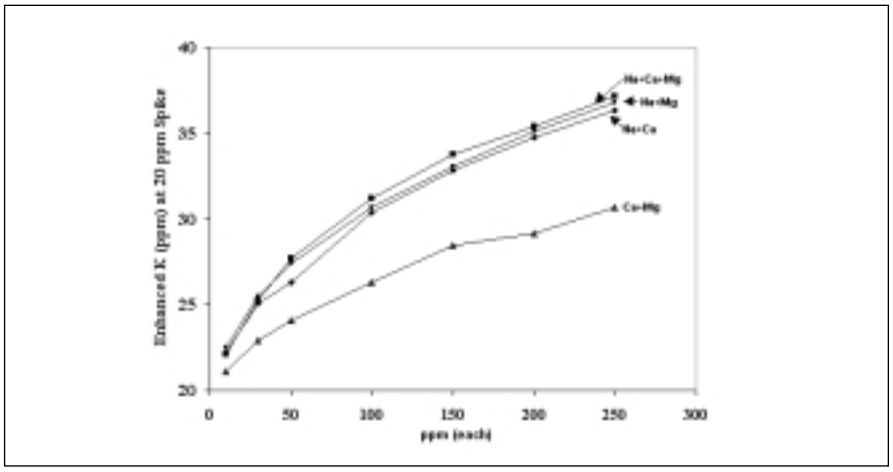

Fig. 3. Combined enhancement effect of Na+Ca, Na+Mg, Ca+Mg, and Na+Ca+Mg on K determination.

Further evaluation of the experimental results suggested that even though different elements and different combinations of elements in the matrices demonstrated various levels of enhancement effects, the enhancement ratio is related to the concentration of the interference elements. This trend describes the relationship between the matrix concentrations and the enhancement ratio. This approach was used for this study in order to develop a practical method for overcoming matrix effects for K determination by axially viewed ICP-OES.

Mathematical Correction – Overcoming Matrix Effects

Since the enhancement effects for K determination correlate to the concentration of a certain matrix composition, it is possible to generate mathematical equations to convert the enhanced K signals to the corrected K results by applying the enhancement correction ratio (R) based on matrix concentrations. Because this work focused on environmental application for general aqueous environmental samples, such as drinking water, surface water, and wastewater (excluding extreme cases), Na, Ca, and Mg enhancement impacts for K determination were studied thoroughly.

In order to develop the enhancement correction ratio (R), eight series of test solutions were prepared. Each series contained individual or combined matrix elements of Ca, Mg, Na, and Li with seven gradually increasing concentration levels -- ranging from 10 ppm to 250 ppm. Each test solution was spiked with 20 ppm K. All test solutions and K calibration standards were acidified to 1% (v/v) HNO_3.

The following mathematical equations were obtained through experimental data. The equations were applied for correction later by method validation, and the corrected results of Proficiency Testing and Quality Control Reference Standards were evaluated.

Kc = Ke / R

Kc---corrected K result (ppm)

Ke---enhanced K reading (ppm)

R---enhancement correction ratio

Since different matrix compositions contribute to different levels of enhancement, each situation was evaluated separately. The equations were obtained by finding the most suitable mathematical equations in order to illustrate the actual enhancement based on the experimental data. The developed equations are shown below:

1. Ca

$R = \{[(2\sqrt{Ca} - 4) / 100] + 1\} \times 100\%$

2. Mg

$R = \{[(2\sqrt{Mg} + 5) / 100] + 1\} \times 100\%$

3. Na

$R = \{[(4\sqrt{Na} + 2) / 100] + 1\} \times 100\%$

4. Na+Ca

$R = \{[(3\sqrt{Na} + 2\sqrt{Ca}) / 100] + 1\} \times 100\%$

5. Na+Mg

$R = \{[(3\sqrt{Na} + 2\sqrt{Mg}) / 100] + 1\} \times 100\%$

6. Ca+Mg

$R = \{[(\sqrt{Ca} + 2\sqrt{Mg}) / 100] + 1\} \times 100\%$

7. Na+Ca+Mg

$R = \{[(3\sqrt{Na} + \sqrt{Ca} + \sqrt{Mg}) / 100] + 1\} \times 100\%$

8. Li

$R = \{[(8\sqrt{Li}) / 100] + 1\} \times 100\%$

Note: √Ca, √Mg, √Na, and √Li represents the square root of concentrations in ppm for Ca, Mg, Na, and Li, respectively.

As the experimental data show, each individual element contributes to different levels of enhancement (see Figure 2). At the same time, the increased enhancements of the combination of these individual elements were not simply additive (see Figure 3). It becomes necessary to evaluate each individual element and each combination of matrices in order to obtain a more accurate mathematical equation to represent the actual enhancement for each situation, as shown in equations 1 through 8. Thus, it seems difficult to try to use one general equation to simplify the complex situations when multiple variables could impact the outcome of enhancement.

The results also showed that Na strongly impacts the enhancement when Na is mixed with Ca or Mg only, or mixed with Ca and Mg together. As Figure 3 shows, there are similar degrees of enhancement found when Na is present in the mixed solutions of Ca and/or Mg. Meanwhile, Ca and Mg show a similar degree of enhancement in mixed solutions in the presence of a significant quantity of Na (i.e., Na 10 ppm or more). Therefore, equation 7 for Na+Ca+Mg was almost converted to equation 5 for Na+Mg and to equation 4 for Na+Ca (i.e., $3\sqrt{Na} + \sqrt{Ca} + \sqrt{Mg} \approx 3\sqrt{Na} + 2\sqrt{Mg} \approx 3\sqrt{Na} + 2\sqrt{Ca}$). Thus, when samples contain Na, Mg, and Ca (excluding extreme or specific cases), it is recommended that equation 7 be used as the general solution to correct matrix effects in the concentration ranges specified for this study. In the cases of only individual interference element in the solution, the corresponding equation for the element should be applied for enhancement correction.

Impact of Internal Standard

All tests were analyzed with an added internal standard (Y 371.029 nm) to monitor instrument stability and to compensate for variations of different matrices. The results show that the absolute intensities of internal standard do not change significantly while matrix components and/or matrix concentrations vary. The relative percent differences (RPD %) of Y intensities compared to initial intensity of Y were less than 5% over four hours of continuous analyses (see Figure 4). On the other hand, the enhanced absolute K intensities responded directly to the changes of matrix components and/or matrix concentrations. As the interference concentrations increased, K intensities increased proportionally while no significant intensity changes were observed for the internal standard. Since the internal standard has less measurable impact over the severe enhancement of K caused by matrix effects, there are no significant differences between the absolute K intensities and the converted K intensities by the internal standard (see Figure 5). Therefore, neither the internal standard Y can

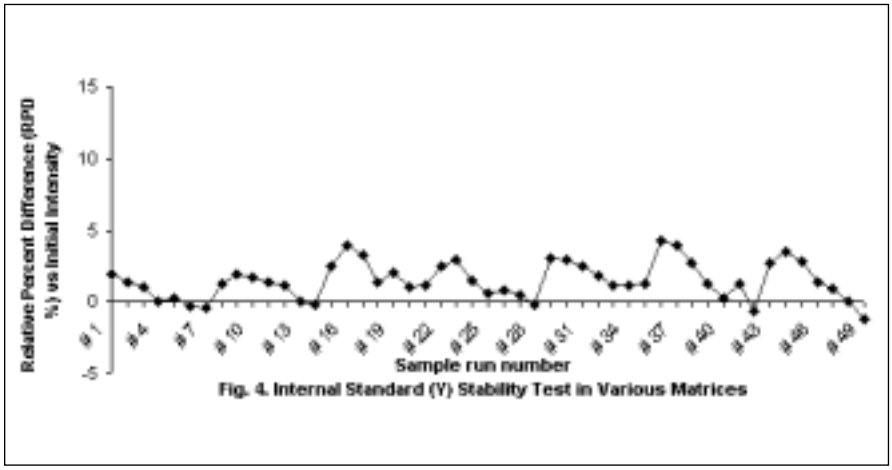

Fig. 4. Internal standard (Y) stability test in various matrices.

be used effectively to compensate for this matrix effect on K, nor does the internal standard Y itself show significant enhancement or suppression caused by these matrices.

Method Validation

When the developed equations were applied to the eight series of test solutions with various matrix concentrations, the corrected K results were agreeable with the expected K value (20 ppm). All recoveries ranged between 90-110% (most of the recoveries between 95-105%) in the interference concentration range of 10–250 ppm (see Tables II and III).

To further validate the applicable accuracy of this approach, several Proficiency Testing and Quality Control Reference Standards provided by NIST certified suppliers, which are validated against NIST SRMs, were analyzed in this study. These reference standards contain various concentration levels of interference elements (Ca, Mg, Na) along with K (see Table IV). The analyses of these standards are suitable to verify the mathematical correction of this method. All corrected results were found to be within the acceptance limits of the certified values, with recoveries between 98.3–104.6% (see Table IV and Figure 6), thus confirming the validity of this method.

Discussion

As a single interference element, Li generates the strongest enhancement on K determination, and we briefly studied the effect of Li on K. The results showed that 1 ppm Li tends to enhance K at approximately 5% or less. Most environmental water samples have Li levels significantly less than 1 ppm Li.

To seek a similar matrix enhancement among other elements, a brief investigation was also performed to evaluate matrix effects

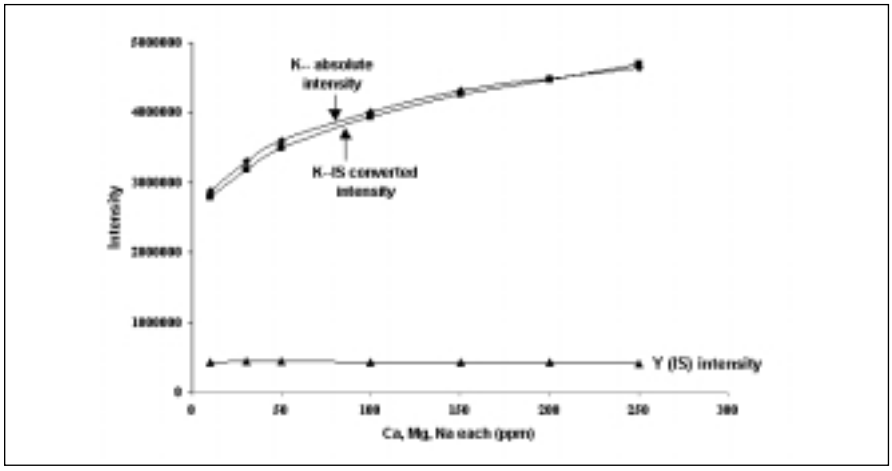

Fig. 5. Enhanced absolute K intensity vs. converted intensity by internal standard (Y). Matrices: Ca+Mg+Na.

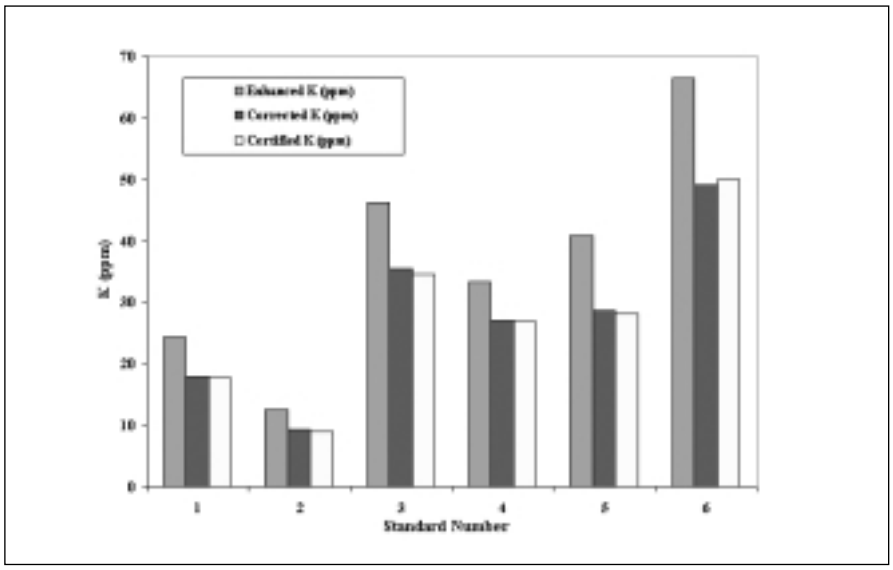

Fig. 6. Proficiency testing and quality control reference standards verification.

of Li, K, Mg, and Be on the determination of Na by axially viewed ICP-OES. The results showed that 20 ppm Li will enhance approximately 10% on the determination of 20 ppm Na, 60 ppm Li will enhance approximate 20% on the determination of 20 ppm Na. No enhancement effects were observed from single 20 ppm of K, Mg, and Be, respectively, on the determination of 20 ppm Na.

The advantages of using mathematical correction for the determination of K by axially viewed ICP-OES include (a) eliminating the time-consuming sample dilution process to overcome matrix effects, (b) better approach to understand the matrix effects of unknown and various sample matrices, (c) providing an alternate and effective method instead of using the costly method of standard addition, (d) avoiding the procedure of overloading the plasma with the addition of an ionization buffer, thus reducing the chance of sample contamination and the need of instrument maintenance.

TABLE II
Individual Element Enhancement Effect of Ca, Mg, Na, and Li on K Determination (20 ppm Spike)

Ca (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	20.26	0.069	0.34	101.3	102.3	19.80	99.0
30	21.62	0.022	0.10	108.1	107.0	20.21	101.1
50	22.27	0.044	0.20	111.4	110.1	20.22	101.1
100	23.18	0.006	0.03	115.9	116.0	19.98	99.9
150	24.42	0.048	0.19	122.1	120.5	20.27	101.3
200	25.68	0.031	0.12	128.4	124.3	20.66	103.3
250	26.74	0.013	0.05	133.7	127.6	20.95	104.8

Mg (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	21.00	0.030	0.15	105.0	111.3	18.86	94.3
30	22.45	0.100	0.44	112.3	116.0	19.36	96.8
50	24.10	0.170	0.72	120.5	119.1	20.23	101.1
100	25.57	0.080	0.33	127.9	125.0	20.46	102.3
150	27.79	0.080	0.29	139.0	129.5	21.46	107.3
200	29.03	0.060	0.22	145.2	133.3	21.78	108.9
250	29.46	0.100	0.33	147.3	136.6	21.56	107.8

Na (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	21.59	0.056	0.26	108.0	114.6	18.83	94.2
30	23.33	0.045	0.19	116.7	123.9	18.83	94.1
50	26.11	0.085	0.32	130.6	130.3	20.04	100.2
100	29.25	0.095	0.32	146.3	142.0	20.60	103.0
150	31.63	0.008	0.03	158.2	151.0	20.95	104.7
200	33.12	0.110	0.33	165.6	158.6	20.89	104.4
250	34.71	0.066	0.19	173.6	165.2	21.01	105.0

Li (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	25.76	0.078	0.30	128.8	125.3	20.56	102.8
30	30.28	0.088	0.29	151.4	143.8	21.05	105.3
50	31.92	0.061	0.19	159.6	156.6	20.39	101.9
100	36.15	0.046	0.13	180.8	180.0	20.08	100.4
150	38.49	0.122	0.32	192.5	198.0	19.44	97.2
200	41.05	0.070	0.17	205.3	213.1	19.26	96.3
250	42.41	0.039	0.09	212.1	226.5	18.72	93.6

[a] Enhanced K/20 ppm.
[b]Calculated using equations.

TABLE III
Combined Enhancement Effect of Na+Ca, Na+Mg, Ca+Mg, and Na+Ca+Mg on K Determination (20 ppm Spike)

Na (ppm)	Ca (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	10	22.22	0.07	0.31	111.1	115.8	19.19	95.9
30	30	25.08	0.02	0.01	125.4	127.4	19.69	98.4
50	50	26.32	0.07	0.27	131.6	135.4	19.45	97.2
100	100	30.39	0.04	0.14	152.0	150.0	20.26	101.3
150	150	32.83	0.08	0.23	164.2	161.2	20.36	101.8
200	200	34.75	0.07	0.19	173.8	170.7	20.36	101.8
250	250	36.35	0.07	0.18	181.8	179.1	20.30	101.5

Na (ppm)	Mg (ppm)	Enhanced K (ppm)	SD ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	10	22.49	0.09	0.40	112.5	115.8	19.42	97.1
30	30	25.48	0.05	0.21	127.4	127.4	20.00	100.0
50	50	27.39	0.06	0.20	137.0	135.4	20.24	101.2
100	100	30.68	0.07	0.23	153.4	150.0	20.45	102.3
150	150	33.04	0.05	0.16	165.2	161.2	20.49	102.5
200	200	35.09	0.01	0.02	175.5	170.7	20.56	102.8
250	250	36.80	0.02	0.05	184.0	179.1	0.55	102.8

Ca (ppm)	Mg (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	10	21.12	0.03	0.16	105.6	109.5	19.29	96.4
30	30	22.93	0.04	0.17	114.7	116.4	19.69	98.5
50	50	24.08	0.06	0.26	120.4	121.2	19.87	99.3
100	100	26.27	0.06	0.24	131.4	130.0	20.21	101.0
150	150	28.45	0.03	0.10	142.3	136.7	20.81	104.0
200	200	29.17	0.01	0.03	145.9	142.4	20.48	102.4
250	250	30.65	0.01	0.03	153.3	147.4	20.79	103.9

Na (ppm)	Ca (ppm)	Mg (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Ratio (%)[a]	Enhancement Correction Ratio (%)[b]	Corrected K (ppm)	Recovery (%)
10	10	10	22.12	0.02	0.10	110.6	115.8	19.10	95.5
30	30	30	25.23	0.16	0.65	126.2	127.4	19.81	99.0
50	50	50	27.69	0.05	0.19	138.5	135.4	20.46	102.3
100	100	100	31.22	0.03	0.09	156.1	150.0	20.81	104.1
150	150	150	33.74	0.08	0.02	168.7	161.2	20.93	104.6
200	200	200	35.37	0.03	0.08	176.9	170.7	20.72	103.6
250	250	250	37.16	0.02	0.04	185.8	179.1	20.75	103.8

[a] Enhanced K/20 ppm.
[b] Calculated using equations.

TABLE IV
Proficiency Testing and Quality Control Reference Standards Verification

Standards	Na (ppm)	Ca (ppm)	Mg (ppm)	Enhanced K (ppm)	SD (ppm)	RSD (%)	Enhancement Correction Ratio (%)[a]	Corrected K (ppm)	Certified K (ppm)	Accuracy (%)	Acceptance Limits
1	53	71.6	33.8	24.39	0.032	0.13	136.1	17.92	17.7	101.2	15.1–20.3
2	72.5	26.2	11.8	12.58	0.011	0.09	134.1	9.38	8.97	104.6	7.53–10.5
3	62.9	28.1	1.05	46.14	0.16	0.35	130.1	35.46	34.5	102.8	29.9–39.3
4.	27.8	None	None	33.28	0.028	0.09	123.1	27.04	26.9	100.5	23.2–30.7
5	104	57.3	17.9	40.86	0.396	0.97	142.4	28.7	28.1	102.1	24.2–32.1
6	50	50	50	66.5	0.19	0.29	135.4	49.13	50	98.3	N/A

Standard 1: RTC PEI-027-12, Laramie, WY, USA
Standard 2: AccuStandard IPE-MET-005, lot #186493-68-01, New Haven, CT, USA
Standard 3: RTC QCI-027, lot #9, Laramie, WY, USA
Standard 4: AccuStandard IPE-MET-005, lot #186494-01-01, New Haven, CT, USA
Standard 5: AccuStandard IPE-MET-005, lot #156829-06-01, New Haven, CT, USA
Standard 6: SpexCertiPrep ICAL-1, Metuchen, NJ, USA

[a] Use equation 7 for standards 1, 2, 3, 5, and 6; use equation 3 for standard 4.

CONCLUSION

The severe magnitude of matrix effects was observed while using axially viewed ICP-OES for the determination of K. The group I elements (Li, Na) and group II elements (Mg, Ca) contribute to this matrix effect. The matrix effect varied depending on the concentration of the different interference elements and/or different combinations of interference elements. The level of enhancement ratio can range from 101–212% in the presence of 10–250 ppm of Li, Na, Ca, and Mg. The strength of enhancement is in the order of Li>Na>Mg>Ca.

To overcome the matrix effects in the determination of K in unknown and various aqueous environmental samples, a practical and effective approach is needed to handle this problem for the accurate determination of K. In this preliminary study, we developed a successful mathematical correction method using the enhancement correction ratio (R), which is based on the interference concentration in the sample matrix. Evaluation and accuracy of this method was validated by the analysis of several Proficiency Testing and Quality Control Reference Standards. The results of these reference standards are within acceptable limits and are quite satisfactory. This has proven that the suggested approach of mathematical correction provides a reliable and practical way to overcome the severe matrix effects for K determination by axially viewed ICP-OES in the matrix concentration range of 10–250 ppm for Na, Ca, and Mg.

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REFERENCES

1. A. Krejcova, T. Cernohorsky, and E. Curdova, J. Anal. At. Spectrom. 16, 1002 (2001).
2. K. Mitko and M. Bebek, At. Spectrosc. 21(3), 77 (2000).
3. I.B. Brenner and A.T. Zander, Spectrochim. Acta, Part B, 55, 1195 (2000).
4. I.B. Brenner, A.T. Zander, M. Cole, and A. Wiseman, J. Anal. At. Spectrom. 12, 897 (1997).
5. I.B. Brenner, M. Zischka, B. Maichin, and G. Knapp, J. Anal. At. Spectrom. 13, 1257 (1998).
6. I.B. Brenner, A. Le Marchand, C. Daraed, and L. Chauvet, Microchem. J. 63 344 (1999).
7. B. Budic, J. Anal. At. Spectrom. 13, 869 (1998).
8. M. Hoenig, H. Docekalova, and H. Bacten, J. Anal. At. Spectrom. 13, 195 (1998).
9, R.M. Belchamber and G. Horlick, Spectrochim. Acta, Part B, 37, 1037 (1982).
10. J.C. Ivaldi and J.F. Tyson, Spectrochim. Acta, Part B, 51, 1443 (1996).
11. X. Romero, E. Poussel, and J.M. Mermet, Spectrochim. Acta, Part B, 52, 487 (1997).
12.J. L. M. de Boer, U. Kohlmeyer, P.M. Breugem, and T. Van der Velde-Koerts, Fresenius' J. Anal. Chem. 360, 132 (1998).
13. J.M. Mermet, J. Anal. At. Spectrom. 13, 419 (1998).
14. M. Stepan, P. Musil, E. Poussel, and J.M. Mermet, Spectrochim. Acta, Part B, 56, 443 (2001).
15. C. Dubuisson, E. Poussel, J.L. Todoli, and J.M. Mermet, Spectrochim. Acta, Part B, 53, 593 (1998).