Comparison of Inductively Coupled Plasma with Classical Analytical Techniques in the Analysis of Southern Oregon Lithia Water: Inclusion of a Local Resource in the Undergraduate Chemistry Curriculum

Steven C. Petrovic[a]; J. C. Clarkson[a]

[a] Department of Chemistry, Southern Oregon University, Ashland, Oregon, USA

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Comparison of Inductively Coupled Plasma with Classical Analytical Techniques in the Analysis of Southern Oregon Lithia Water: Inclusion of a Local Resource in the Undergraduate Chemistry Curriculum

S. C. Petrovic and J. C. Clarkson

Department of Chemistry, Southern Oregon University, Ashland, Oregon, USA

Abstract: Lithia water, a community resource of local historical significance, is described as a central theme in the undergraduate analytical chemistry sequence. A statistical comparison of the classical determination of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (HCO_3^-, Cl^-) reinforces statistical and charge-balance concepts covered in analytical chemistry. Subsequent determination of these major cations by inductively coupled plasma (ICP) enables students to statistically evaluate the presence of bias between instrumental and classical methods. The effect of easily ionized elements on ICP calibration sensitivity and linearity via the use of cesium as an ionization suppressor is reported.

INTRODUCTION

A variety of thematic approaches for teaching analytical chemistry in the undergraduate curriculum have been described in the chemical literature.[1−3]

The success of such themes is in part due to either community investment or the student's familiarity with the system under investigation. Southern Oregon University (SOU) is a public regional university whose students mainly come from the large and sparsely populated areas of Southern Oregon. This area has historically been known as a source for a variety of highly mineralized springs. Recognizing this as a local resource of historical significance, a module was developed for the SOU analytical chemistry laboratory, which focuses upon the determination of the major cations and anions from a local Lithia water spring in Ashland, Oregon.

Although the local economy is currently driven by both SOU and by visitors who come to enjoy the Oregon Shakespeare Festival, early attempts in community development began with some local hotels and a natatorium fed by local mineral springs in the 1880s. Subsequent chemical analysis of one mineral spring indicated a high lithium content, and the promise of healing mineral waters and a spa-based economy by early town leaders spurred capital investment, resort development, and the passage of a bond measure in 1914 to pipe Lithia water from its source 6 miles to the east of the downtown area.[4] Slogans such as "Ashland, Oregon, Lithia Springs 'The Carlsbad of America" and "Ashland Grows while Lithia Flows," which were promoted by the editor of the local newspaper, routinely appeared on the newspaper's masthead around the time of the 1914 bond passage. Although the dream of turning Ashland into a spa resort town faded in the 1920s, Lithia water still serves as a curiosity for tourists and a handful of local resorts and spas that depend upon the allure of mineral waters.

The influence of Lithia water in the early development of this region made its analysis an ideal theme for the analytical chemistry sequence at SOU. In the analytical chemistry laboratory, students perform a variety of titrations and potentiometric determinations on the major cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) and anions (HCO_3^-, Cl^-) in the local Lithia water. By the end of the term, the students turn in a report that provides a brief historical overview of Lithia water as a resource, a summary of the results for all six major cations and anions, and a complete statistical analysis on the charge balance in the Lithia water to ensure that all of the major ions have been determined.

Recently, the acquisition of a dual-view inductively coupled plasma optical emission spectrometer (ICP-OES) has allowed us to broaden the role of Lithia water in the SOU analytical chemistry sequence and explore some of the interesting chemistry that occurs in an emission source such as an ICP. In this paper, a statistical comparison of the Lithia water results obtained by both classical and instrumental methods is described. Lastly, because all major cations in Lithia water are either group I or group II elements, the effect of ionization suppression on the sensitivity and linearity of the ICP response for easily ionized elements (EIE) was also studied.

MATERIALS AND METHODS

Instrumentation

In the instrumental analysis laboratory, the significant metals in Lithia water were determined using a Perkin-Elmer Optima DV2100 ICP-OES (Perkin-Elmer Life and Analytical Sciences, Shelton, CT, USA) equipped with a glass Meinhard nebulizer. The major analyte emission lines are listed in Table 1, and the ICP-OES operating conditions are summarized in Table 2. All transitions were monitored in the axial position.

Reagents and Standards

All glassware was cleaned using a dilute Citranox detergent solution followed by copious rinsing with house-distilled water followed by three rinses with Type I (18 megaohm) deionized water (Aqua Solutions, Jasper, GA, USA). Concentrated nitric acid (Fisher Scientific, trace-metal grade) and Type I deionized water were used to prepare all blanks, standards, and dilutions. Standard stock solutions of 1000 μg/mL Ca, Mg (Alfa Aesar, Ward Hill, MA, USA) and Li (VWR International, West Chester, PA, USA) were used as purchased. Standard stock solutions of 10,000 μg/mL Na and K were prepared using an appropriate amount of oven-dried NaCl and KCl (Fisher Scientific, ACS primary standard grade) dissolved in Type I deionized water. A standard stock solution of 1000 μg/mL Y (Inorganic Ventures, Lakewood, NJ, USA) served as the internal standard at a level of 1.00 μg/mL. A 1% Cs stock solution (Inorganic Ventures) served as an ionization suppressor. The suppressor solution was added at a level of 500 μg/mL Cs to all appropriate blanks, standards, and samples. Samples of Lithia water were obtained from a free-flowing mineral spring piped into Lithia Park (Ashland, Oregon). In order to avoid clogging the ICP nebulizer and to avoid physical interferences as a result of the large dissolved solids content of Lithia water (>7000 mg/L), the sample was diluted 200-fold (500.0 μL Lithia water in 100.0 mL solution) prior to analysis.

Table 1. Lithia water analytes monitored by ICP-OES

Element	Wavelength (nm)
Li(I)	670.784
Na(I)	589.592
K(I)	766.490
Mg(I)	285.213
Ca(I)	422.673

Table 2. ICP-OES instrumental operating conditions

RF power	1300 W
Viewing distance	Plasma center (axial)
Coolant gas flow (Ar)	15 L min^{-1}
Nebulizer gas flow (Ar)	0.8 L min^{-1}
Auxiliary gas flow (Ar)	0.2 L min^{-1}
Peristaltic pump flow	1.50 mL min^{-1}

Analytical Equipment and Methods

In the analytical chemistry laboratory, four of the five cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and two anions (Cl^-, HCO_3^-) were determined by titrimetric or potentiometric procedures. Although the lithium ion is identified quite closely with Lithia water, it does not provide a significant contribution to the ionic strength of Lithia water. The methods are summarized in Table 3 and are adapted primarily from well-known analytical textbooks.[5,6] Approximately 200 mL of sample is needed to perform these analyses in triplicate.

RESULTS AND DISCUSSION

The students' first experience with Lithia water analysis is through classical techniques, specifically titrimetry and potentiometry. The major cations and anions were originally selected from a chemical analysis published in the local newspaper. Recent analysis of Lithia water performed by an environmental laboratory hired by the City of Ashland confirmed our choices. Once the determination of the major anions and cations in Lithia water is completed in the SOU analytical chemistry lab, including error propagation for uncertainty determinations, students are expected to apply their knowledge of univariate statistics and charge-balance relationships to decide whether all of the major ions have been taken into account. During the instrumental analysis lab, students use the ICP-OES to determine the major cations plus lithium in their Lithia water sample. They can once again use their knowledge of univariate statistics to determine whether the major cation concentrations agree between instrumental and classical approaches. The results of the Lithia water determination are shown in Table 4.

Confirmation of Major Ions in Lithia Water

Checking for electroneutrality begins with the proper charge-balance relationship, which should indicate the equality between the molar quantity of cationic

Table 3. Summary of analytical methods for the determination of major cations and anions in Lithia water

Analyte	Analytical procedure	Titrant	Indicator
$Ca^{2+}+ Mg^{2+}$	Complexometric titration, buffered at pH 10 (NH_4^+/NH_3)	5 mM EDTA standardized with a primary standard grade $CaCO_3$ solution	Eriochrome black T
Ca^{2+}	Complexometric titration after adjusting to pH $\sim$13 with 50% (v/v) NaOH	5 mM EDTA standardized with a primary standard grade $CaCO_3$ solution	Hydroxynaphthol blue ($\sim$0.1 g)
Mg^{2+}	By difference $[Ca^{2+}+ Mg^{2+}]$ $- [Ca^{2+}]$		
Cl^-	Fajans' method (precipitation titration)	0.02 N $AgNO_3$(99.9995% pure)	Dichlorofluorescein
HCO_3^-	Acid–base titration	0.10 N H_2SO_4 standardized with primary standard grade Na_2CO_3	1:1 Methyl red – bromcresol green mixed indicator
Na^+, K^+	Potentiometric determination by ion-selective electrodes Na^+: Glass electrode K^+: Polymeric electrode		

EDTA, ethylenediaminetetraacetic acid.

and anionic charges. The charge-balance relationship for the major ions in Lithia water is shown in Eq. (1):

$$[HCO_3^-] + [Cl^-] = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}]. \qquad (1)$$

Substitution of the classically determined molar quantities into Eq. (1), and the use of error propagation to calculate the overall uncertainty for the major anions and major cations, results in 0.11758 ± 0.00134 mol L^{-1} of anions and 0.11228 ± 0.00446 mol L^{-1} of cations. The students are expected to answer the question: Are these quantities statistically equivalent? To do this,

S. C. Petrovic and J. C. Clarkson

Table 4. Classical and ICP-OES determination of major ions in Lithia water[a]

Analyte	Classical determination			ICP-OES determination[b]		
	mg/L	mmol/L	%RSD	mg/L	mmol/L	%RSD[c]
Li^+	—	—	—	6.6 ± 0.1	0.095 ± 0.001	1.5
Na^+	1960 ± 100	85.2 ± 4.4	5.2	1940 ± 20	84.5 ± 0.9	1.1
K^+	85 ± 1	2.18 ± 0.02	1.1	80 ± 2	2.04 ± 0.05	2.4
Ca^{2+}	273 ± 8	6.82 ± 0.20	3.0	261 ± 5	6.51 ± 0.13	2.0
Mg^{2+}	137 ± 7	5.64 ± 0.29	5.1	137 ± 4	5.64 ± 0.18	3.2
HCO_3^-	4030 ± 40	66.1 ± 0.6		—	—	—
Cl^-	1830 ± 40	51.5 ± 1.2		—	—	—

[a]All determinations are based on triplicate measurements except for the classical determination of Na^+ and K^+. For those two analytes, the determinations were based on duplicate potentiometric measurements.
[b]Analyte concentrations were obtained in the presence of 500 ppm Cs as an ionization buffer.
[c]Percent relative standard deviation.

students use the two-tailed *t*-test for two experimental means, shown in Eq. (2):

$$t_{\exp} = \frac{|\bar{x}_- - \bar{x}_+|}{s_{\text{pooled}}\sqrt{(N_- + N_+)/(N_- - N_+)}}. \tag{2}$$

The numerator represents the difference between the molar concentration of the anionic and cationic charges, N_- and N_+ are the number of anions and cations, respectively, and s_{pooled} is the pooled standard deviation of the anion and cation determinations, which is shown in Eq. (3):

$$s_{\text{pooled}} = \sqrt{\frac{(N_- - 1)s_-^2 + (N_+ - 1)s_+^2}{(N_- + N_+ - 2)}}. \tag{3}$$

Applying the results from Table 4 for the classical determination of the major anions and cations in Lithia water, a *t*-value of 1.56 was calculated. Students can either choose a predetermined confidence level (typically 95%, $\alpha = 0.05$) or they can use Microsoft Excel to calculate the confidence level at which the difference is significant. To accomplish this task, students can use the function TDIST($t_{\exp}$, degrees of freedom, no. of tails) to calculate the probability value at which the anion and cation concentrations are significantly different. In this case, TDIST(1.56, 4, 2) provides the probability value of 0.194, which indicates that the difference between the anion and cation concentrations in Lithia water becomes significant at a confidence level of 80.6%. This result is below the typical 95% confidence level, so a student with these results can safely say that the two concentrations come from the same population, and therefore all of the major cations and anions in Lithia water have been determined.

Major Cation Determination in Lithia Water: Classical versus ICP-OES Results

Students are asked to compare the results obtained by titrimetry and potentiometry to those obtained by ICP-OES for the major Lithia water cations. It is expected that the students again apply the two-tailed *t*-test for two experimental means, as shown in Eq. (4), for each of the four major cations to determine if there are any significant biases:

$$t_{\exp} = \frac{|\bar{x}_{\text{classical}} - \bar{x}_{\text{icp}}|}{s_{\text{pooled}}\sqrt{(N_{\text{classical}} + N_{\text{icp}})/(N_{\text{classical}} \, N_{\text{icp}})}}. \tag{4}$$

In this case, N represents the number of replicate measurements for a given analyte. Decisions about statistical difference were made at the 95% confidence level. These tests can be done manually or via the Data Analysis plug-in for Excel. Based on the results in Table 4, there were no statistically significant differences in the classical and instrumental determination

of the four cations, except for potassium. In this case, the difference between the potentiometric and the instrumental determination of potassium was statistically significant at the 96.4% confidence level. Out of the four classically determined cations, the precision of the potassium measurement was the best, and that would have a significant impact on the *t*-test results. Students should recognize however that a larger number of replicates would be desired when determining whether any bias between the two methods exists.

Although the same sample was analyzed in a straightforward manner for this report, the appearance of a bias may occur because of resampling the Lithia water or the length of time between the fall and winter term analyses. For example, in the absence of any bias in the methods, the possibility of sample evaporation between the fall and winter labs would result in larger concentrations reported by ICP. A one-sided *t*-test for two experimental means may be used to decide whether a statistically significant concentration increase has occurred. No study has been undertaken regarding Lithia water stability during storage between terms.

Effect of Easily Ionized Elements and Ionization Suppression on ICP Calibration

When interferences in emission spectroscopy are discussed in lecture, comparisons are made between flames and plasmas. Generally speaking, students learn that higher temperatures in ICP tend to minimize chemical interferences compared with flame emission. In contrast, the higher temperatures in ICP provide a greater amount of energy to excitation and ionization processes in plasmas than in flames. Therefore, spectral interferences tend to be of greater concern in plasmas compared with flame emission.

The analysis of Lithia water, however, presents a situation that runs somewhat contrary to the concerns just described. The major cations in Lithia water are either alkali metals or alkaline earths, which have low ionization potentials. Therefore, the major emission lines are located in the visible region of the electromagnetic spectrum, where there is little possibility for spectral overlap. Table 5 shows the first ionization potential for a series of alkali metals and alkaline earths.[7]

However, the emission intensity of atomic transitions for elements with low ionization potentials is sensitive to presence of other easily ionized elements in the sample or standards. The effect of EIEs has been widely reported in the chemical literature.[8–13] In the classroom, this phenomenon is explained via an ionization equilibrium.[7] For example, in the case of sodium:

$$Na \longrightarrow Na^+ + e^-$$

Table 5. Ionization potentials for metals in the Lithia water experiment

Element	First ionization potential (eV)
Cs	3.89
K	4.34
Na	5.14
Li	5.39
Ca	6.11
Mg	7.64

The equilibrium between the ionized and atomic forms of sodium is defined by the following relationship:

$$K_{eq} = \frac{[Na^+][e^-]}{[Na]}$$

The presence of other EIEs will increase the free electron concentration in the plasma and shift the equilibrium toward the reactant. However, if an EIE such as cesium is added to the solution in excess, a source of additional free electrons is contributed to the plasma through the following ionization equilibrium:

$$Cs \longrightarrow Cs^+ + e^-$$

The free electron concentration from these two equilibria can be expressed by the following mass-balance relationship:

$$[e^-] = [Cs^+] + [Na^+]$$

In the list of elements in Table 5, the ionization energy of cesium is smallest. Therefore, a shift in the analyte equilibrium toward the atomic state is predominately due to the excess cesium, and the enhancement of the analyte signal is independent of the concentration of the other analytes.

An example of this is shown in Fig. 1 for the Na(I) emission line at 589.592 nm. As the sodium concentration increases, the concentration of all the analytes increases in the multielement standards used to calibrate the instrument. This increases the concentration of EIEs and results in an upward curvature of the calibration plot.

The calibration curve with the ionization suppressor not only lacks an upward curvature but also exhibits greater calibration sensitivity. The effect of the ionization suppressor on the sensitivity of the atomic emission lines for all five cations is listed in Table 6. Notice that the magnitude of signal enhancement due to the ionization suppressor increases at longer wavelengths. Students should recognize the inverse relationship between the emission
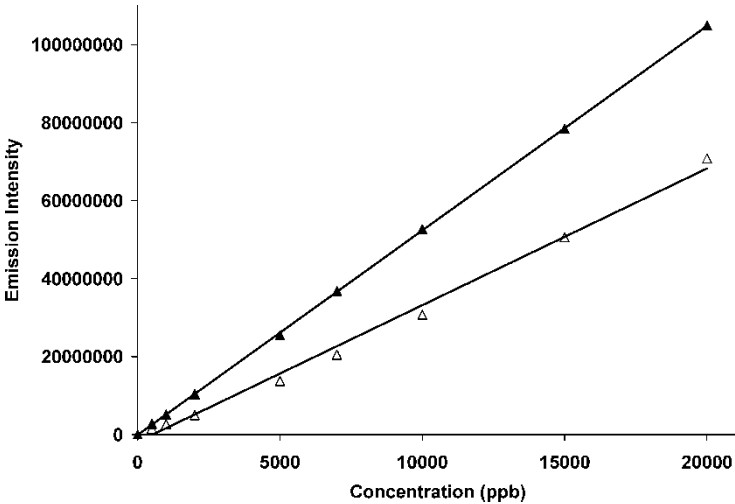
Figure 1. A comparison of Na(I) ICP calibration curves without an ionization sup-pressor (open triangles) and with 500 ppm Cs as an ionization suppressor (closed triangles).

wavelength and the energy of the transition and the fact that lower energy tran-sitions would be most affected by the increase in the EIE concentration.[13]

F-Test: Testing for Curvature

The effect of EIEs on the intensity of the ICP emission signal provides an opportunity for students to investigate the validity of the calibration model. Oftentimes, when presented with this question, students are told to character-ize the residuals. If the residuals are randomly distributed about the fitted line, then an appropriate calibration model has probably been chosen. However, if there is a distinct pattern of the residuals about the fit, then the calibration

Table 6. Calibration sensitivity enhancement in the presence of 500 ppm Cs

Atomic tran-sition (nm)	Calibration sensi-tivity (ppb^{-1}) (no added Cs)	Calibration sensi-tivity (ppb^{-1}) (with500 ppm Cs)	Enhancement ratio
K 766.490	1713	3029	1.77
Li 670.784	62,121	95,726	1.54
Na 589.592	3503	5244	1.50
Ca 422.673	4861	5927	1.22
Mg 285.213	2426	2429	1.00

model is not appropriate, and a new calibration model should be used. Such an example is shown in Fig. 2.

In order to fit a greater proportion of the variance in the data, one can insert additional fitting terms in the calibration model. It is apparent from Fig. 2 that as the number of terms in the polynomial increases, not only does the goodness-of-fit of the calibration data increase, but also the residuals are more randomly distributed about the best-fit curve. At this point, students should start to pose the following question: At what point does an additional term in the calibration model fit an insignificant amount of variance in the data?

One useful and straightforward statistical method is the use of the F-test to test whether an additional term in the calibration model fits a statistically significant amount of variance in the data. The F-test is a statistical test taught in quantitative analysis and instrumental analysis courses to determine whether the variance of one data set is different from the variance of a second data set. An experimental F-ratio is calculated from Eq. (5):

$$F_{exp} = s_1^2/s_2^2 \qquad (5)$$

where s_1^2 and s_2^2 are the variances of data sets 1 and 2, such that $s_1^2 > s_2^2$. At a predetermined confidence level (usually 95% or $\alpha = 0.05$), the experimental F-ratio is compared with a critical F-ratio obtained from an F-table. If the critical F-ratio is larger than the experimental F-ratio, there is no statistical difference in the variance of the two data sets.
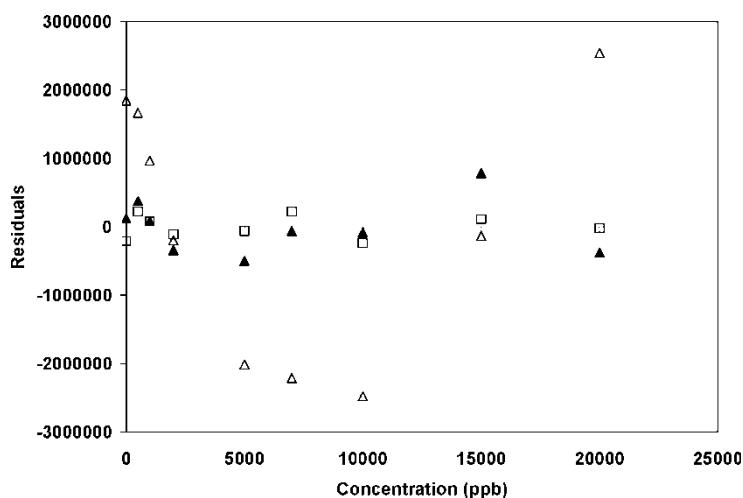

Figure 2. Residuals from linear, quadratic, and cubic calibration models applied to the Na(I) ICP emission data without ionization suppression. Open triangles represent residuals from the linear model, closed triangles represent residuals from the quadratic model, and open squares represent residuals from the cubic model.

The application of the F-test to evaluate calibration models has been pre-viously described by Miller.[14] The main advantage to this approach is that the coefficient of determination (R^2) is the only piece of information needed for the test. A spreadsheet (such as Microsoft Excel) or other statistical software package is a straightforward method for testing the significance of additional terms in a calibration model.

The success of a regression model is described by two parameters: the total variation of the measured y-values (y_i) with respect to the fitted y-values ($\hat{y}_i$) and the total variation of the fitted y-values about the mean y-value ($\bar{y}$). These are defined in Eqs. (6) and (7), respectively, as the residual sum of the squared deviations, SS_D, and the sum of the squares of the regression, SS_R:

$$SS_D = \sum (y_i - \hat{y}_i)^2. \tag{6}$$

$$SS_R = \sum (\hat{y}_i - \bar{y})^2. \tag{7}$$

The sum of these squared deviations represents the total variation of the y-values about the mean y-value. This is defined by the total sum of the squared deviations, SS_T, shown in Eq. (8):

$$SS_T = \sum (y_i - \bar{y})^2, \tag{8}$$

or in other words:

$$SS_T = SS_D + SS_R. \tag{9}$$

The relationship between SS_D, SS_R, and SS_T is shown in Fig. 3 for the largest calibration level. A widely used figure of merit for the goodness of fit of the model to the data is the coefficient of determination, defined in Eq. (10):

$$R^2 = \frac{SS_R}{SS_T}. \tag{10}$$

In other words, R^2 is the fraction of the total sum of the squared deviations represented by the calibration model. Rearrangement of Eqs. (9) and (10) provides the following useful relationships:

$$SS_R = R^2(SS_T). \tag{11}$$

$$SS_D = (1 - R^2)(SS_T). \tag{12}$$

The quantities SS_R and SS_D are related to the variances described by the cali-bration model and not described by the calibration model, respectively. The F-test, which is used to determine if the variance between two populations is statistically different, will be used here. To calculate the variance, each term
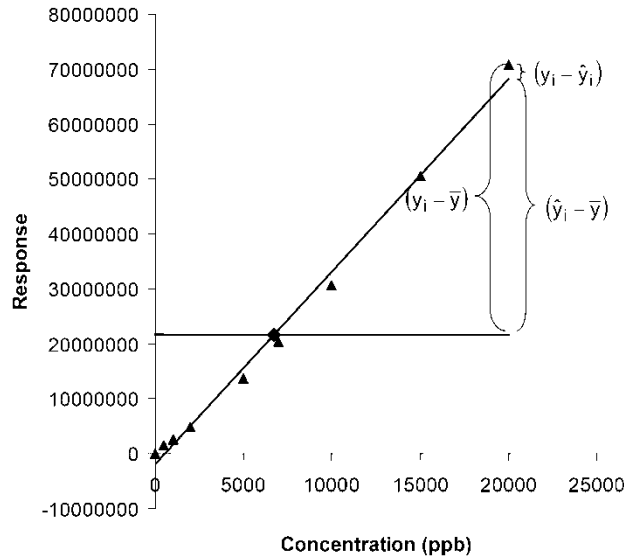
Figure 3. Na(I) ICP calibration curve with sum of squared deviations illustration for the largest calibration level. When summed over all calibration levels, the total sum of the squared deviations, SST, which is the largest bracket, is shown to be the sum of the squares of the regression (bottom right bracket), SSR, and the residual sum of the squared deviations (top right bracket), SSD.

is divided by the degrees of freedom associated with the sum of the square terms. These are called the mean square (MS) values, shown in Eq. (13):

$$F = \frac{MS_R}{MS_D} = \frac{SS_R/p}{SS_D/(N - p_t - 1)} = \frac{R^2(SS_T)/p}{(1 - R^2)(SS_T)/(N - p_t - 1)}$$
$$= \frac{R^2/p}{(1 - R^2)/(N - p_t - 1)}, \tag{13}$$

where N is the number of calibration levels, p is the degrees of freedom represented by the calibration term being tested (usually $p = 1$), and p_t is the order of the polynomial.

This method has been used in our lab to investigate the effect of an ionization suppressor on the linearity of the ICP calibration model for an EIE. The following example is based on the ICP calibration model for the Na(I) line, both with and without ionization suppression. The calibration data without ionization suppression is plotted in Fig. 4, and the calibration data with 500 ppm Cs is plotted in Fig. 5. The easiest method in Excel for comparing R^2 values is to plot the data and use the Add Trendline function to calculate and display the R^2 value for the linear, quadratic, cubic, and quartic calibration
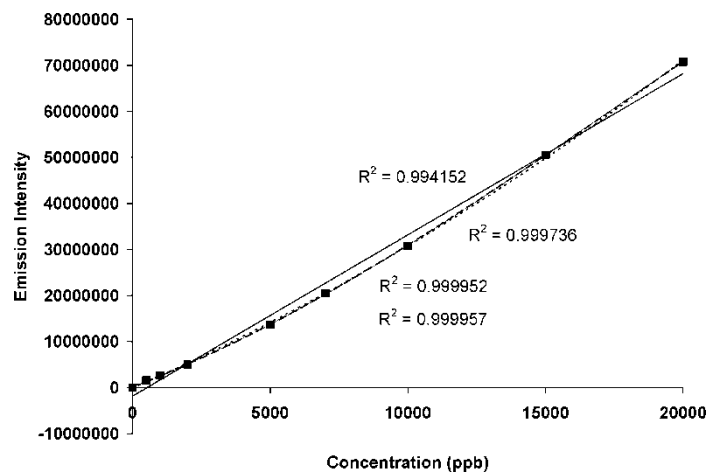
Figure 4. A comparison of linear, quadratic, cubic, and quartic calibration models for the Na(I) emission response without the use of an ionization suppressor. The coefficient of determination increases with an increase in the order of the polynomial (solid line, linear; short dotted line, quadratic; long dotted line, cubic). The quartic model essentially mimics the cubic model.

model. In this example, the R^2 values were utilized to the sixth decimal place to minimize rounding errors.

Using the data in Fig. 4, there are nine data points, so $N = 9$. Starting with a linear regression model, $y = ax + b$, the order of the polynomial (p_t) is 1, and there is 1 degree of freedom (p) associated with that term. The degrees of freedom associated with the residuals is ($N - p_t - 1$), or 7 in this case.
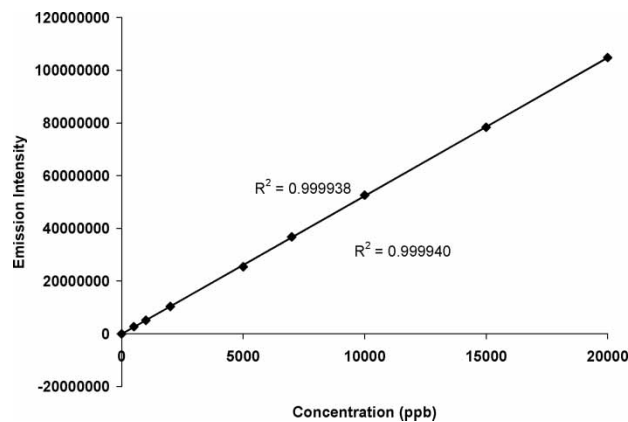

Figure 5. A comparison of linear and quadratic calibration models for the Na(I) emission response using 500 ppm Cs as an ionization suppressor.

The fraction of the variance described by the calibration model (R^2) is 0.994152, and therefore the fraction of the variance not described by the calibration model ($1 - R^2$) is 0.005848. Substituting these values into Eq. (13):

$$F = \frac{MS_R}{MS_D} = \frac{R^2/p}{(1-R^2)/(N-p_t-1)} = \frac{0.994152/1}{0.005848/(9-1-1)} = 1190.$$

The critical F-ratio (F_c) can be located either from an appropriate F-table or by using the FINV function in Excel. The function format is FINV(P, ν_1, ν_2) where P is the probability that the variances are actually the same, ν_1 is the degrees of freedom for the numerator, and ν_2 is the degrees of freedom for the denominator. In this case, FINV(0.05, 1, 7) provides a critical F-value of 5.59 at the 95% confidence level. Because $F \gg F_c$, the variance described by the calibration model is significant at the 95% confidence level. Testing the quadratic model, $y = ax^2 + bx + c$, the question to be answered is whether the variance fitted by the additional ax^2 term is significantly larger than the variance not fitted by the model. Adding the ax^2 term, $(R^2)_{quadratic} = 0.999736$, $(1 - R^2) = 0.000264$, and as $(R^2)_{linear} = 0.994152$, $= 0.005584$. There is still only 1 degree of freedom for the $(R^2)_{ax^2}$ term, and the residuals now have only 6 degrees of freedom:

$$F = \frac{MS_R}{MS_D} = \frac{(R^2)_{ax^2}/p}{(1-R^2)/(N-p_t-1)} = \frac{0.005584/1}{0.000264/(9-2-1)} = 127.$$

Because FINV(0.05, 1, 6) provides a critical F-value of 5.99, the quadratic term fits a significant amount of variance and should be included in the calibration model.

Testing the cubic model, $y = ax^3 + bx^2 + cx + d$, $(R^2)_{cubic} = 0.999952$. Therefore, $(1 - R^2) = 0.000048$, and $(R^2)_{ax^3} = (0.999952 - 0.999736) = 0.000216$. There is still only 1 degree of freedom for the $(R^2)_{ax^3}$ term, and the residuals now have only 5 degrees of freedom:

$$F = \frac{MS_R}{MS_D} = \frac{(R^2)_{ax^3}/p}{(1-R^2)/(N-p_t-1)} = \frac{0.000216/1}{0.000048/(9-3-1)} = 22.5.$$

Because FINV(0.05, 1, 5) provides a critical F-value of 6.61, the cubic term fits a significant amount of variance and should be included in the calibration model.

Finally testing the quartic model, $y = ax^4 + bx^3 + cx^2 + dx + e$, using the procedure shown above:

$$F = \frac{MS_R}{MS_D} = \frac{(R^2)_{ax^4}/p}{(1-R^2)/(N-p_t-1)} = \frac{0.000005/1}{0.000043/(9-4-1)} = 0.465.$$

The amount of variance fitted by the ax^4 term is less than the residual variance. Therefore, the ax^4 term is not a valid term to add to the calibration model.

This same procedure, when applied to the sodium calibration response in Fig. 5, indicates that higher order polynomials, beyond the linear calibration

Table 7. Significance of fitting terms at the 95% confidence level and the coefficient of determination for each ICP calibration model

Transition	Without ionization suppressor			500 ppm Cs ionization suppressor		
	ax	ax^2	ax^3	ax	ax^2	ax^3
K 766.490	Yes (0.991656)	Yes (0.999769)	No (0.999847)	Yes (0.999625)	Yes (0.999836)	No (0.999927)
Li 670.784	Yes (0.992647)	Yes (0.999921)	Yes (0.999984)	Yes (0.999513)	Yes (0.999954)	No (0.999955)
Na 589.592	Yes (0.994152)	Yes (0.999736)	Yes (0.999952)	Yes (0.999938)	No (0.999940)	No (0.999943)
Ca 422.673	Yes (0.997824)	Yes (0.999900)	Yes (0.999970)	Yes (0.999961)	No (0.999966)	No (0.999967)
Mg 285.213	Yes (0.999556)	Yes (0.999983)	No (0.999993)	Yes (0.999991)	No (0.999992)	No (0.999992)

model, fit an insignificant amount of variance. This indicates that the presence of the ionization suppressor minimizes any unexpected shifts in the ionization equilibrium that would increase the sensitivity of the emission response and provide curvature to the calibration model. A comparison of the significance of each term at the 95% confidence level is shown in Table 7. The presence of the ionization suppressor improves the linearity of the atomic emission signals for the all major cations in Lithia water.

CONCLUSIONS

This manuscript describes the inclusion of a historically significant community resource into the analytical chemistry and instrumental analysis laboratory. The ability to apply classical and instrumental analytical methods to the major ions in Lithia water has the potential to illustrate and reinforce concepts addressed throughout the undergraduate analytical chemistry sequence.

In the analytical laboratory, students are able to successfully use error propagation, the *t*-test for two experimental means, and an appropriate charge-balance relationship to confirm that the major cations and anions in Lithia water have been determined. In the instrumental analysis laboratory, students can once again use the *t*-test for two experimental means to determine if any bias exists between classically and instrumentally determined concentrations of cations in Lithia water. Based on the results presented in this manuscript, both analytical approaches provide equally acceptable results.

Determination of major cations in Lithia water by ICP-OES after classical determination of these same analytes provides a wealth of information to the student. From a practical standpoint, students are aware that the classical determination of the four major cations in Lithia water requires approximately two 3-hour laboratory periods to complete and approximately 200 mL of sample. By contrast, students quickly recognize that the determination of these same cations plus lithium by ICP-OES takes less than half the time and less than 1 mL of sample. From an analytical standpoint, the fact that all four major cations in Lithia water are either alkali metals or alkaline earths provides an opportunity for students to study the effect of EIEs on the emission response for each analyte. The addition of 500 ppm Cs as an ionization suppressor increased the calibration sensitivity and/or linearity for all analytes, and the F-test allows students to evaluate calibration models in a quantitative manner.

ACKNOWLEDGMENTS

REFERENCES

1. Hughes, K. D. Marine microcosm: using an aquarium to teach undergraduate analytical chemistry. *Anal. Chem.* **1993**, *65*, 883A–889A.
2. Fitch, A.; Wang, Y.; Mellican, S.; Macha, S. Lead lab: teaching instrumentation with one analyte. *Anal. Chem.* **1996**, *68*, 727A–731A.
3. Wenzel, T. J. Community-based projects in analytical chemistry courses. *Anal. Chem.* **2002**, *74*, 279A–280A.
4. *Ashland Daily Tidings*; Mineral waters left legacy. June 14, 1984.
5. Harris, D. C. *Quantitative Chemical Analysis*, 5th ed.; Freeman, W. H. New York, 1999, p. 853.
6. Hargis, L. G. *Analytical Chemistry, Principles and Techniques*; Prentice-Hall: Englewood Cliffs, NJ, 1988, pp. 574–577, 590–591.
7. Skoog, D. A.; Holler, F. J.; Nieman, T. A. *Principles of Instrumental Analysis*, 5th edn.; Saunders: Philadelphia, 1998, p. 222.
8. Larson, G. F.; Fassel, V. A.; Scott, R. H.; Kniseley, R. N. Inductively coupled plasma – optical emission analytical spectrometry. A study of some interelement effects. *Anal. Chem.* **1975**, *47*, 238–243.
9. Larson, G. F.; Fassel, V. A. Comparison of interelement effects in a microwave single electrode plasma and in a radiofrequency inductively coupled plasma. *Anal. Chem.* **1976**, *48*, 1161–1166.
10. Dubuisson, C.; Poussel, E.; Mermet, J. Comparison of axially and radially viewed inductively coupled plasma atomic emission spectrometry in terms of signal-to-background ratio and matrix effects. *J. Anal. At. Spectrom.* **1997**, *12*, 281–286.
11. Brenner, I. B.; Zander, A.; Cole, M.; Wiseman, A. Comparison of axially and radially viewed inductively coupled plasmas for multi-element analysis: effect of sodium and calcium. *J. Anal. At. Spectrom.* **1997**, *12*, 897–906.
12. Brenner, I. B.; Vats, S.; Zander, A. T. A new CCD axially viewed ICP atomic emission spectrometer for simultaneous multi-element geoanalysis. Determination of major and minor elements in silicate rocks. *J. Anal. At. Spectrom.* **1999**, *14*, 1231–1237.
13. Todolí, J. L.; Gras, L.; Hernandis, V.; Mora, J. Elemental matrix effects in ICP-AES. *J. Anal. At. Spectrom.* **2002**, *17*, 142–169.
14. Miller, J. N. Basic statistical methods for analytical chemistry, part 2. Calibration and regression methods. A review. *Analyst* **1991**, *116*, 3–14.