Automatable On-line Generation of Calibration Curves and Standard Additions in Solution-Cathode Glow Discharge Optical Emission Spectrometry

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Abstract

Two methods are described that enable on-line generation of calibration standards and standard additions in solution-cathode glow discharge optical emission spectrometry (SCGD-OES). The first method employs a gradient high-performance liquid chromatography pump to perform on-line mixing and delivery of a stock standard, sample solution, and diluent to achieve a desired solution composition. The second method makes use of a simpler system of three peristaltic pumps to perform the same function of on-line solution mixing. Both methods can be computer-controlled and automated, and thereby enable both simple and standard-addition calibrations to be rapidly performed on-line. Performance of the on-line approaches is shown to be comparable to that of traditional methods of sample preparation, in terms of calibration curves, signal stability, accuracy, and limits of detection. Potential drawbacks to the on-line procedures include signal lag between changes in solution composition and pump-induced multiplicative noise. Though the new on-line methods were applied here to SCGD-OES to improve sample throughput, they are not limited in application to only SCGD-OES—any instrument that samples from flowing solution streams (flame atomic absorption spectrometry, ICP-OES, ICP-mass spectrometry, *etc.*) could benefit from them.

Keywords: Solution-Cathode Glow Discharge, Electrolyte Cathode Discharge, SCGD, ELCAD, Automation, Calibration, Atomic Emission Spectrometry, AES, Computer Control, Instrumentation

Introduction

In recent years, a large number of compact plasma sources that make use of solution electrodes [1] have been developed based on the design originally reported by Cserfalvi and co-workers [2]. One such device, the atmospheric-pressure solution-cathode glow discharge (SCGD), has garnered significant attention due to the advantages it offers over conventional plasmas for atomic optical emission spectrometry (OES) [3-11]. The SCGD is both inexpensive and simple, requires no compressed gases or sample-solution nebulizer, and operates at low direct-current power (~70 W). Despite its simplicity, the SCGD exhibits performance competitive with larger, more complex sources; detection limits are generally on par with, and in some instances, better than those achievable with radially viewed inductively coupled plasma (ICP)-optical emission spectrometry [6,7,9].

Regrettably, the SCGD suffers more from matrix interferences than does the ICP [5]. As a consequence, only relatively simple samples have been analyzed accurately with simple calibration methods [12-14]. More complex samples have necessitated use of standard additions in order to obtain accurate results [5,15-22]. Unfortunately, standard additions, though capable of overcoming the matrix interferences, are typically tedious, time-consuming, and reduce sample throughput. Methods that automate or increase the speed at which standard-addition analyses can be performed are therefore highly desirable for use with SCGD-OES.

Although automation is a common current theme in analytical instrumentation, most modern instruments automate only the sample-introduction and data-collection processes. As a result, the main bottleneck to analysis remains the off-line preparation of calibration standards and samples. To reduce human error and the time required for sample preparation and analysis, several studies have focused on instruments that prepare calibration standards and samples on-line, or obviate the need for several standards to be prepared. Among these studies are methods based on flow-injection [23,24], which enable on-line standard additions and calibration to be performed. Unfortunately, these methods suffer from poorer precision than traditional analyses and are difficult to fully automate. Other methods focused on the use of multiple peristaltic pumps to mix solutions on-line to generate linear concentration gradients from which calibration curves can be derived [25,26]. Though these techniques promote rapid calibration and standard additions, they suffer from inaccuracies caused by washout time of the pumping systems. Further, because

continuously changing concentration gradients were used, the concentration delivered to the detector did not remain constant long enough to yield good precision.

Starn and Hieftje [27] investigated the use of gradient high-performance liquid chromatography (HPLC) pumps for on-line solution preparation and delivery for atomic absorption spectrometry and ICP-OES [28]. These studies used stepped gradients to generate specific concentrations of a stock standard solution on-line, and were shown to exhibit performance comparable to traditional methods of calibration. Unfortunately, due to limitations of the available HPLC pumps, flow resolution was restricted and there were only two sample inlet lines; as a result, application of the method to standard additions was unsuccessful.

Here, a system similar to that of Starn and co-workers [27,28] was employed to enable automated, on-line generation of calibration curves and standard-additions plots with SCGD-OES. The new system uses a quaternary-gradient HPLC pump capable of providing and proportioning flows from up to four solution inlet lines. This system performed on-line mixing of a sample solution, stock standard and diluent, which enables standards and samples of specific concentrations to be prepared in a rapid and automated fashion. Results from the system were critically compared to traditional methods of calibration and standard addition and found to be comparable. Given that HPLC pumps are expensive to purchase and maintain, the method was extended to a system of three peristaltic pumps. This inexpensive arrangement could perform the same functions of the gradient HPLC pump and also provides analytical results comparable with traditional methods of calibration. Potential drawbacks to both methods (lag between changes in solution composition and pump-induced multiplicative noise) are described and evaluated.

Experimental

Pumps and Equipment for On-line Calibration Systems

Figures 1 (a) and (b) show schematic diagrams of the two setups used to perform on-line calibrations and standard additions with the SCGD. The first of these two systems, displayed in Fig. 1(a), employs a quaternary, gradient, HPLC pump (Hatachi, Japan, model L-7100) as a solution mixing and delivery device. This module is a dual-plunger type, series connection reciprocating pump that can provide solution flows from 0.001–10.000 mL min⁻¹ in 0.001 mL min⁻¹ increments with $\pm 2\%$ accuracy. It is equipped with four separate, solenoid-controlled solution inlets through which the fraction of total flow contributed from each line can be adjusted in increments of 1% with a range from 0–100%. The pump is also fitted with an onboard dynamic (stirring-mode) solution mixer with an approximate void volume of 2.0 mL. Solution delivery and flow ratios were automated with the system's onboard processor and gradient programming interface. A flow restrictor, made from a 45-cm length of polyether ether ketone (PEEK) tubing of 0.13-mm inner diameter, was placed at the outlet of the HPLC pump prior to the SCGD cell. This restrictor served to increase the backpressure of the pump to a level of approximately 3378 kPa (with a flow rate of 2.500 mL min⁻¹), which both dampened pulsations in the flow from the pump and prevented solutions from outgassing within the pump heads.

The second system, shown in Fig. 1 (b), makes use of three peristaltic pumps to perform on-line proportioning and mixing of solutions, similar to the gradient pump. In the setup used here, two Gilson (Middletown, WI) Minipuls 3 peristaltic pumps were used alongside one Perkin-Elmer Minipuls 2 (Norwalk, CT). All of these pumps were gravimetrically calibrated prior to their use in on-line calibration studies. Solution flows from the three pumps were fed into a PEEK cross connector, after which the combined flow was directed into a home-built pulse dampener. This dampener was comprised of an 11-cm length of polyethylene tubing with 3.5 and 7-mm inner and outer diameters, respectively. The polyethylene tubing was packed with glass beads, which both helped to dampen pulses from the pumps and provided a tortuous flow path to facilitate solution mixing. Void volume of the pulse dampener was measured to be approximately 0.5 mL. Solutions that exited the pulse dampener were directed into the SCGD.

SCGD Cell Design and Emission Optics

The present study employs a SCGD cell design similar to that used in earlier work, [8,11,20], so only a brief description will be provided here. Samples, diluents, and standards entered the SCGD cell *via* a vertically oriented glass-capillary pipet (internal diameter of 0.38 mm, external diameter of 1.1 mm, with a void volume of 10 μ L).

These solutions overflowed from the tip of this capillary into a polytetrafluoroethylene (PTFE) waste reservoir of 60-mL volume. Submerged in the waste reservoir was an electrically grounded graphite electrode which, as a result of the overflow from the sample-inlet capillary, holds both the waste reservoir and incoming solutions at ground potential. Located 3 mm above the sample-inlet capillary was a tungsten rod that serves as the anode for the cell. The tip of this rod closest to the solution-inlet capillary was tapered at a contact angle of 45° to provide a pointed structure that results in a more stable discharge. Power to ignite and sustain the SCGD was sourced from a high-voltage, direct-current power supply (Kepco, Flushing, NY, BHK 2000-0.1 MG) through a current-limiting 1.25 kΩ ballast resistor. The discharge was operated in constant-current mode with power levels that ranged from 72–75 W (75 mA, 957–1000 V). A sample-solution flow rate of 2.5 mL min⁻¹ was used for all experiments.

An f/no.-matched (f/8), 20-mm diameter quartz lens was used to image the SCGD onto the 50-μm entrance slit of a 0.5-m Czerny-Turner monochromator (Chromex 500IS/SM) outfitted with two gratings (1200 grooves mm⁻¹ with a range of 250–800 nm, and 1200 grooves mm⁻¹ with a range of 600–1300 nm). Radiation that passed through the 50-μm exit slit of the monochromator was detected with an R928 photomultiplier tube (PMT) (Hamamatsu, Japan) biased at -950 V. Photocurrent from the PMT was subsequently amplified and filtered (low-pass, τ = 3.3 s) with a Stanford Research Systems (Sunnyvale, CA) low-noise current amplifier (model SR570) and read out with a custom National Instruments (Austin, TX) LabVIEW[®] program. The ultraviolet-visible grating (250–800 nm) was used for detection of emission from Ca I (422.67 nm), Na I (589.00 nm), Li I (670.78 nm), and K I (766.49 nm). For detection of Rb I (780.03 nm) and Cs I (852.11 nm), the near-infrared grating (600–1300 nm) was used. To prevent spectral interferences from second-order diffraction, an Edmund Optics (Barrington, NJ) long-pass filter (>88% transmission above 500 nm, <0.1% transmission below 460 nm) was placed in front of the monochromator entrance slit to block emission from the SCGD at wavelengths below 460 nm for analysis of the alkali metal species.

Reagents, Procedures and Plots

Samples and standards were prepared by dilution of stock solutions of 1000 ppm concentration prepared from analytical reagent grade (or better) carbonate, nitrate or chloride salts. Salts and standards were dissolved or diluted in 0.1 M HNO₃ prepared with deionized water of 18.2 MΩ specific resistance and distilled HNO₃ from an in-house sub-boiling PTFE distillation unit. In all cases, 0.1 M HNO₃ was used as the diluent solution for on-line calibrations and standard additions.

Unless otherwise stated, all data points plotted on calibration curves represent the average signal produced from 20 successive 10-s second integrations of the PMT photocurrent with a sampling rate of 1 kHz. Error bars on these plots represent the standard deviation computed from the 20 successive measurements. Except where noted, background subtraction was performed by measurement of a blank solution (0.1 M HNO₃) at the wavelength of interest. Limits of detection (LODs) were estimated as 3 times the standard deviation of 20 consecutive 10-second integrations of a blank solution, divided by the slope of the working curve of interest. Except where noted, relative standard deviation (RSD) values were computed from the average and standard deviation produced from 20 repeated 10-second integrations of the signal produced from samples at 500 ppb concentration.

Results and Discussion

Gradient Calibration with HPLC Pump

Figure 1 (a) exhibits the experimental setup used to evaluate the gradient pump system for on-line calibration. Only three of the four available sample-solution inlets (fed with stock sample, standard, and diluent, respectively) were required to perform on-line calibration and standard additions. Solution mixtures of the desired composition were generated on-line by adjusting the proportion of the total flow contributed by each inlet. In this manner, a concentration gradient of sample, standard, or mixture of both can be linearly generated or specific concentrations can be prepared and maintained for desired time intervals. The present work focused mainly on the latter of these two methods: stepped gradients to generate specific concentrations.

The analytical merit of gradient calibration was first assessed by generation of simple calibration curves. Only two of the sample lines are required to produce such curves; one line for a given calibration standard and a second that delivers the diluent (0.1 M HNO₃). An example of an on-line, stepped-gradient calibration is shown in Fig. 2, where the standard solution was 1000 ppb Li dissolved in 0.1 M HNO₃ and the dilution medium was 0.1 M HNO₃. A fit to the calibration curve obtained from 30-s integrations of the signal at each respective concentration exhibited exceptional linearity (slope = 0.556 ± 0.002 nA ppb⁻¹, intercept = $-3 \times 10^{-5} \pm 0.003$ nA, and $R^2 = 0.99991$), indication that the system seemed promising for further study.

One drawback of the gradient method is apparent in the temporal profile of Fig. 2. When the solution composition was stepped, a lag time of 62 ± 8 seconds occurred prior to signal stabilization. This lag was independent of the magnitude of concentration change, and therefore is likely determined by the internal void volume of the HPLC pump and its onboard solution mixer (which has a void volume of approximately 2.0 mL). To verify this hypothesis, the gradient calibration program was rerun with a flow rate of 1.75 mL min⁻¹ (reduced from 2.5 mL min⁻¹). Under the reduced-flow conditions, the lag time to signal stabilization lengthened to 83 ± 3 seconds, evidence that the effect is indeed caused by the time required to wash out the void volume of the pump and mixer. Regardless of the cause, this lag represents a challenge for high-throughput analysis with the system when stepped gradients are used. A mixer of smaller void volume could be used to reduce the lag if higher sample throughput is required. Though this change would reduce the length of the delay, use of a lower-volume mixer might also degrade precision, since less-fully homogenized solutions would exhibit greater signal variation.

To assess the accuracy of the gradient-calibration method, a series of calibration curves, shown in Figure 3, were obtained for the alkali metals for both samples prepared on-line by gradient calibration and by the traditional, “hand-made” approach. Visual inspection of the curves in Figure 3 reveals that the traditional and gradient methods exhibit good agreement. However, to evaluate these data more quantitatively, slopes, R^2 values, RSDs, and LODs are compared in Table 1 for both sets of calibration curves. Slopes were found to differ by 0.8–3.9%; these small differences are likely attributable to the intrinsic flow imprecision of the gradient pump ($\pm 2\%$) and precision of the equipment (balances, glassware, and pipets) used for preparation of the traditional samples. Curves generated on-line exhibited excellent linearity ($R^2 > 0.999$), also comparable to that obtained with the traditional method of sample preparation. Relative standard deviations for samples of 500 ppb concentration were found to be nearly the same (within 1%) for both gradient-prepared and traditionally prepared samples, which argue that the online method of solution mixing does not contribute to signal variation. Finally, LODs from both methods are also nearly identical, which indicates there is no loss in signal-to-noise ratio (S/N) by use of the gradient method for sample preparation; the values also reveal the exceptional LODs provided by the SCGD for alkali metals. Notably, the LOD for Na is limited in the present system by residual Na contamination of the deionized water supply available within our laboratory. An estimate of the LOD in the absence of this contamination was obtained by measurement of the background noise at a wavelength adjacent to the Na I 589.00 nm line (588.80 nm), and yielded LOD values of 0.020 ppb for both gradient and traditional calibration.

Most reported analyses of real-world samples with the SCGD required the use of standard additions in order to overcome matrix effects [5,15-22]. To evaluate the gradient method for on-line standard additions, a sample was prepared that was likely to exhibit a strong matrix effect. In particular, 10 ppm Ca and 25 mM NaCl (595 ppm Na) in 0.1 M HNO₃ was chosen, as moderate to high concentrations (>10 ppm) of Na⁺ have been shown in earlier work [5] to suppress emission from several analytes. Matrix suppression of Ca I emission at the 422.67 nm line was confirmed by analysis with a simple calibration curve, available as Online Resource (OR) 1, which yielded a Ca concentration of 4.4 ± 0.3 ppm, (56% error). This analysis also revealed that background emission from the matrix-containing solution was substantially suppressed compared to that from a blank solution (0.1 M HNO₃). As a result, background subtraction for the matrix-containing solutions was performed at a wavelength adjacent to the Ca I 422.68 nm line (422.50 nm), rather than on-resonance with use of a 0.1 M HNO₃ blank.

To perform standard additions with the gradient system, the third solution-inlet line was utilized to provide flow from the sample itself (as shown in Fig. 1 (a)). In this arrangement, the sample solution was held at a constant dilution, and standards were spiked into the sample by replacement of portions of the diluent flow with that of the standard. This stepped-gradient method was employed to analyze the Ca sample by standard additions; the resulting curve (average of 20 repetitions) is available as OR2. The determined Ca concentration was found to be 10.02 ± 0.24 ppm (0.2% error), in excellent agreement with true concentration in the sample. This result was also compared to a

traditional standard-addition analysis (the curve, as the average of 20 repetitions, is available as OR3), which yielded a determined Ca concentration of 10.24 ± 0.18 ppm (2.4% error), in good agreement with the on-line method.

The standard-addition results here are superior to those in earlier experiments with gradient standard addition in ICP-OES [28], where errors as large as 11% were reported. Given that the Hitachi L-7100 pump used in the present study has similar specifications to the Beckman Gold Model 126 pump used in the earlier work [27,28], any difference in the gradient pumps seems unlikely to be the cause of the improved accuracy. One possible basis for the disparity is the concentration at which the samples were analyzed. In the earlier work [28], the analyte (Cu) concentration was approximately 150 ppb, much lower than the 10 ppm Ca sample used here. Analysis at lower concentrations inherently introduces more error than higher concentrations. However, a more likely cause for the dissimilarity could be differences in the standard-addition procedures. In contrast to the present work, the earlier study [28] employed only two inlets. The total flow, initially sourced from only the sample, was held at 3.0 mL min^{-1} and portions of this flow were replaced by a flow from the standard (specifically, 0.03, 0.08, 0.15, and 0.30 mL min^{-1}). This approach could introduce additional error into the measurement from two sources. First, precision of the flow proportioning in the earlier investigation was reported to be $\pm 0.003 \text{ mL min}^{-1}$. This would cause significant errors in spiking of the standard at low levels; a standard introduced at a flow of 0.03 mL min^{-1} would exhibit a $\pm 10\%$ error in effective analyte concentration. Second, since portions of the flow from the sample were replaced by flow from the standard, the sample (and thereby the matrix) was diluted to different levels throughout the analysis. If the changes in dilution were to alter the magnitude of matrix effects, significant error might be introduced. Further, the analyte signal from the sample would be reduced by addition of the standard during dilution, which might also add to the observed error. Regardless of any inaccuracies reported in the earlier study [28], the results reported here clearly indicate that the on-line gradient method provides accurate results when used for standard additions.

Peristaltic-Pump Based Gradient Calibration

From the foregoing, a gradient HPLC pump functions effectively as an automated, on-line platform for calibration. Gradient HPLC pumps, however, are comparatively expensive to purchase and maintain. Given that a system of three peristaltic pumps could perform the same operations as the gradient-pump system, a study was performed to assess the analytical merit of such a system. Figure 1 (b) shows the experimental setup of the peristaltic pump on-line calibration system. This setup enables on-line calibration through direct changes to the flow rate contributed from each of the pumps. If the pump flows are altered such that total flow remains constant, the resultant mixed solution composition will be determined by the fraction contributed by each pump (similar to the gradient pump). For this proof-of-principle investigation, the peristaltic pump flows were adjusted manually, although automation is possible as the pumps can be computer controlled.

A series of experiments similar to those performed with the HPLC pump was used to evaluate the analytical merit of the peristaltic-pump system. First, simple calibration curves were generated for Li, Na, K, Rb, and Cs, and compared to those obtained with traditionally prepared calibration standards. Qualitative evaluation of the curves, which can be viewed in OR4, demonstrates that samples prepared on-line match closely the traditionally prepared samples. Table 2 assesses these curves quantitatively. Slopes generated from both methods are in good agreement, differing by 1.0–3.3%, comparable to the performance of the HPLC gradient system. Calibration plots generated on-line by the peristaltic pumps also exhibit excellent linearity ($R^2 > 0.997$), closely comparable to that with the traditional method of sample preparation and the gradient HPLC pump. Also like the HPLC gradient system, no apparent loss in S/N arises; LODs from both on-line and traditionally methods are nearly identical. Finally, relative standard deviation (RSD) values for samples prepared on-line were comparable to those obtained with traditionally prepared samples. The RSD values from the peristaltic pump system were also similar to those observed with the HPLC gradient system, indication that the home-built pulse dampener serves to adequately mix solutions, despite its comparatively small void volume (approximately 0.5 mL).

To evaluate the effect of the reduced void volume of the peristaltic-pump system, a time trace of K emission was monitored during a typical calibration sequence (cf. Fig. 4). It was found that the time from the change in solution composition to signal stabilization was 26 ± 6 s at a total flow rate of 2.5 mL min^{-1} , significantly shorter than the 62 ± 8 s required to stabilize the signal from the gradient HPLC pump system. Although this improvement is significant, an even greater improvement was expected, given that the void volume of the peristaltic pump mixer is lower by a factor of four (the void volumes were 0.5 and 2.0 mL, for the peristaltic pump and HPLC pump,

respectively). This limited improvement is likely attributable to the fact that the peristaltic pumps were operated manually, rather than automatically as with the gradient HPLC pump. In particular, each of the peristaltic pumps was manually adjusted sequentially to the desired flow rate when the solution composition was changed, which incurred an additional delay. If the peristaltic-pump system were under computer control, the lag time to signal stabilization would likely improve appreciably.

A prominent feature in Fig. 4 is the high noise level associated with the 2500 ppb K solution, enlarged in the inset trace. This noise appeared only when both peristaltic pumps were operated at identical rates of rotation simultaneously (for the 2500 ppb K sample, both the diluent and standard pumps provide 50% of the total flow) and occurred with all samples (not just K). The periodic oscillation in the time trace is likely multiplicative and results from pump-head rotation. To test this hypothesis, a Fast Fourier Transform analysis was performed on the portion of the trace that exhibited the periodic oscillations; their frequency was determined to be 0.175 Hz, significantly lower than the 2.23 Hz pulsation frequency of the pump heads. While the noise might be caused by a harmonic of the pump-head rotation, it is more likely caused by partial or fully in-phase oscillation of the pump heads. Even when operated at the same nominal rate of rotation, it is unlikely the pumps used here rotate with perfectly matched frequencies. Due to this, as the pumps drift in and out of phase with one another, a low-frequency pulsation in the solution flow is produced. This pulsation probably also happens under other conditions but, due to the faster rate of rotation of one of the pump heads, occurs at higher frequencies that are attenuated by the low-pass filter ($\tau = 3.3$ s) used here. Surprisingly, the added noise does not result in a significant increase in the RSDs for any of the species investigated. The RSD values (computed from the average and standard deviation of 20 repeated 10-s integrations) under the high-noise conditions were 1.8, 1.2, 1.1, 1.6, and 0.7% for Li, Na, K, Rb, and Cs, respectively, similar to those in Table 2. Nevertheless, the high noise is a drawback to the peristaltic-pump system compared to the gradient HPLC pump, but could be lessened through several methods. A longer time-constant low-pass filter or more sophisticated pulse dampener would attenuate the oscillations, or an internal standard could be used to correct for the noise by ratioing.

A standard-addition analysis was also demonstrated with the peristaltic-pump system. In such calibrations, a third pump must be employed to provide the sample solution. Similar to the gradient pump, the sample can then be diluted to a constant value with the diluent flow line, and portions of the diluent flow replaced with the standard. As with the HPLC gradient-calibration system, the sample was 10 ppm Ca^{2+} and 25 mM NaCl in 0.1 M HNO_3 . Standard-addition calibration with the peristaltic pump arrangement resulted in a determined calcium concentration of 9.97 ± 0.46 ppm (0.3% error) for 20 repeated measurements (plot available as OR5). This result is in excellent agreement with the true Ca concentration of 10 ppm, and is comparable to the results obtained with both the gradient method and traditionally performed standard addition described earlier.

Alternative Methods of Calibration

Both the HPLC and peristaltic-pump gradient calibration systems offer a variety of alternative methods for generation of calibration curves or standard additions beyond the stepped concentration gradients described here. For instance, a linear concentration gradient could be used to generate calibration curves if the data sampling rate were faster than the rate of change in solution composition, as was noted in earlier work by Lopez-Garcia and co-workers [25]. Another alternative method that uses a linear concentration gradient was investigated with the gradient calibration system used here. In this method, a sample is diluted on-line and introduced into the SCGD and the resultant signal measured. After the signal from the diluted sample is obtained, the gradient pump is used to linearly replace portions of the diluent flow continuously with flow from a standard. This replacement maintains the constant dilution of the sample and simultaneously adds known amounts of analyte to the sample. If the signal is monitored as the standard replaces flow from the diluent, the concentration of the analyte can be determined when the signal reaches a magnitude twice that of the original diluted sample. At this point, the concentration of added standard and that of the analyte in the sample will be equal, as long as the analysis is performed within the linear working range. This approach, which is similar to the “null point” scheme [29], relaxes requirements on the dynamic range of all components in the instrument, including the source and photometric system.

A test of this concept was performed with the gradient system by use of a 2 ppm Li solution (sample), 5 ppm Li standard (standard), and a solution of 0.1 M HNO_3 (diluent). Originally, 50% of the flow was contributed from the sample of 2 ppm Li while the remaining 50% was contributed by the 0.1 M HNO_3 diluent, which resulted in a

solution composition of 1 ppm Li. After the signal was measured, the flow from the 0.1 M HNO₃ solution was linearly replaced with flow from the 5 ppm Li standard until it contributed 20% of the total flow. The resultant signal behavior is shown in Figure 5. When the percent of total flow contributed from the 5 ppm Li standard was equal to 20% (corresponding to an added concentration of 1 ppm Li), the signal was found to be 1.95 times that from the original sample. This result represents approximately a 2.6% error from the theoretical ratio of 2.00 (the signal should have been twice that of the original sample since the Li concentration had been doubled by addition of the standard). This new method of standard addition exhibits good accuracy and requires less time than a typical stepped-gradient standard addition.

Of course, this method would suffer from the signal lag noted earlier. As the standard solution replaces portions of the dilution medium, the resulting change in solution composition would not be observed at the detector until approximately 62 s later with the HPLC-pump system, or 26 s with the peristaltic-pump system. If the system were automated to stop the gradient when the signal was twice that of the original sample, this lag time would result in inaccuracies. A pump system designed for minimal void volume (and thereby low signal lag times) would remedy this issue.

Conclusions

Both the gradient HPLC pump and peristaltic-pump system function well as automatable, on-line methods of calibration and standard addition for SCGD-OES. These methods produced results that were comparable to those of traditional calibration methods; calibration-curve slopes differed by <4% and no loss in S/N arose for either on-line method. On-line solution mixing also does not appear to result in any loss of precision; RSD values for both on-line methods were similar to that from traditional standards. The on-line methods of standard addition also yielded excellent accuracy (errors of $\leq 0.3\%$) and precision (RSD <5%), better than had been obtained with past gradient calibration methods. Alternative methods of calibration that make use of linear gradients might further improve the speed and ease of analyses, but the void volume of both systems must be reduced for such methods to be attractive.

Drawbacks of the on-line systems include the signal lag observed between changes in solution composition and (for the peristaltic pump system) pump-induced multiplicative noise. The signal lag could be lessened by reducing the void volume of either system. Pump-induced multiplicative noise could be remedied by a variety of means, particularly that of a longer time-constant low-pass filter or by ratioing the signal from an internal standard.

Together the results here suggest that the new methods would substantially improve sample throughput for SCGD-OES analyses, and minimize the time required for off-line sample preparation. Of course, the new on-line methods are not limited in application to SCGD-OES; any instrument that samples from flowing solution streams (flame atomic absorption spectrometry, ICP-OES, ICP-mass spectrometry, *etc.*) could benefit from them.

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(A)

(B)

Figure 1. Schematic diagrams of the two systems used for on-line calibration interfaced to the SCGD. Figure 1 (A) exhibits the gradient HPLC pump system, while (B) shows the peristaltic pump system.

Intended for color on the web and in print.

Figure 2. Temporal profile of an on-line, stepped calibration of Li performed with the gradient pump system. Photocurrent was monitored at the 670.78 nm Li atomic emission line.

Figure 3. Comparison of calibration curves generated on-line with the gradient pump system (solid lines and symbols) with calibration curves obtained by traditional sample preparation (dotted lines and open, X-indicated symbols).

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Figure 4. Temporal profile of an on-line, stepped calibration for K with the peristaltic-pump system. The inset trace is an enlarged view of the signal at 2500 ppb concentration. Photocurrent was monitored at the 766.49 nm K atomic line.

Figure 5. Temporal profile for Li I emission at the 670.78 nm line which demonstrates an alternative method of on-line calibration. The red trace represents a moving average (smoothed representation) of the signal. Signal averages and standard deviations were computed from 10 repeated, 10-s integrations of the photocurrent. See text for discussion.

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Table 1. Quantitative comparison of on-line calibration with the gradient HPLC pump and traditional calibration.

Analyte	On-line Gradient Calibration				Traditional Calibration			
	Slope of Calibration Curve (nA ppm ⁻¹)	R ²	RSD at 500 ppb (%)	LOD (ppb)	Slope of Calibration Curve (nA ppm ⁻¹)	R ²	RSD at 500 ppb (%)	LOD (ppb)
Li	304 ± 2	0.99992	2.0	0.050	295 ± 3	0.99941	1.1	0.051
Na	576 ± 3	0.99923	1.1	0.53	570 ± 4	0.99953	1.0	0.53
K	131 ± 1	0.99986	0.7	0.18	130 ± 1	0.99983	0.7	0.18
Rb	60.6 ± 0.2	0.99992	1.0	0.12	62.3 ± 0.3	0.99874	0.7	0.12
Cs	3.03 ± 0.01	0.99966	0.7	1.2	2.92 ± 0.02	0.99992	0.7	1.2

Table 2. Comparison of the analytical aspects of calibration curves generated on-line with the peristaltic pump system and that of traditional calibration.

Analyte	On-line Peristaltic Pump Calibration				Traditional Calibration			
	Slope of Calibration Curve (nA ppm ⁻¹)	R ²	RSD at 500 ppb (%)	LOD (ppb)	Slope of Calibration Curve (nA ppm ⁻¹)	R ²	RSD at 500 ppb (%)	LOD (ppb)
Li	466 ± 1	0.99996	1.4	0.045	451 ± 3	0.99981	1.2	0.046
Na	753 ± 5	0.99976	1.2	0.20	760 ± 6	0.99971	1.1	0.21
K	119.2 ± 0.6	0.99988	1.5	0.17	117.1 ± 0.8	0.99978	1.3	0.17
Rb	42.0 ± 0.3	0.99980	2.1	0.23	42.9 ± 0.2	0.99989	0.8	0.22
Cs	2.23 ± 0.05	0.99767	0.9	1.9	2.26 ± 0.01	0.99993	0.8	2.0