Spatially Resolved Measurements to Improve Analytical Performance of Solution-Cathode Glow Discharge Optical-Emission Spectrometry

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Abstract

Past studies of the solution-cathode glow discharge (SCGD) revealed that elemental and molecular emission are not spatially homogenous throughout the source, but rather conform to specific zones within the discharge. Exploiting this inhomogeneity can lead to improved analytical performance if emission is collected only from regions of the discharge where analyte species emit strongly and background emission (from continuum, elemental and/or molecular sources) is lower. Effects of this form of spatial discrimination on the analytical performance of SCGD optical emission spectrometry (OES) have been investigated with an imaging spectrograph for fourteen atomic lines, with emphasis on detection limits and precision. Vertical profiles of the emission intensity, signal-to-background ratio, and signal-to-noise ratio were collected and used to determine the optimal region to view the SCGD on a per-element basis. With optimized spatial filtering, detection limits ranged from 0.09–360 ppb, a 1.4–13.6 fold improvement over those obtained when emission is collected from the full vertical profile (1.1–840 ppb), with a 4.2-fold average improvement. Precision was found to be unaffected by spatial filtering, ranging from 0.5–2.6% relative standard deviation (RSD) for all elements investigated, closely comparable to the 0.4–2.4% RSD observed when no spatial filtering is used. Spatial profiles also appear useful for identifying optimal line pairs for internal standardization and for flagging the presence of matrix interferences in SCGD-OES.

Keywords: Solution-Cathode Glow Discharge, Optical-Emission Spectrometry, Instrumentation, Spatial Discrimination

Introduction

Studied as sources for atomic optical emission spectrometry (OES) for over twenty years [1, 2], solution-electrode glow discharges (SEGD), a class of atmospheric-pressure glow discharge where one or both electrodes is a flowing liquid, have garnered a great deal of interest within the spectrochemistry community [3-5]. Among the many SEG D designs reported in the literature [3-5], those based on the original system of Cserfalvi and co-workers [1, 2], often referred to as the electrolyte-cathode discharge or solution-cathode glow discharge (SCGD), have demonstrated important advantages over conventional plasma sources for solution analysis, such as inductively coupled plasma (ICP). Unlike the ICP, the SCGD is compact, utilizes no compressed or flowing gases, does not require a nebulizer and operates at low direct-current power.

Though initial evaluation of the SCGD and similar sources yielded poor figures of merit compared to the ICP [1, 2, 6-8], a myriad of advancements have bolstered analytical performance and expanded applicability. Reduction in cathode diameter [9], reversal of the discharge polarity [10], and solution modification [11-13] have improved limits of detection with SCGD-OES. Methods to overcome matrix effects and boost sample throughput have been realized through automated calibration schemes [14] and flow-injection analysis [15, 16]. Analysis of complex samples and expansion of SCGD-OES to the

determination of molecular species has been achieved through pre-concentration [17, 18] and replacement-ion chromatography [19]. The SCGD has also been coupled with smaller, more simplistic means of spectral sorting, including miniature spectrographs [20] and interference filters [21]. Combined, these advances have not only enhanced the potential portability, throughput, and applicability of SCGD-OES, but have also resulted in performance that is generally comparable to that obtained with radially viewed ICP-OES [9, 15, 16, 20].

Another means to improve performance in SCGD-OES is to exploit the spatial emission structure of the discharge. Earlier studies have shown that emission is not homogeneous throughout the source [7, 21–24], but rather conforms to specific zones. Exploiting this inhomogeneity can lead to better analytical performance if emission is collected only from regions of the discharge where analyte species emit strongly and background emission (from continuum, elemental and/or molecular sources) is lower. Indeed, in a recent study [21] that coupled the SCGD with interference filters, selection of an optimized emission region was shown to improve signal-to-background ratios (S/B) and detection limits by a factor of 2–4 and 10–100, respectively. Similarly, many earlier SCGD-OES studies [9, 12, 15, 16, 20] have utilized aperture stops to block emission from regions of the discharge closest to the anode, where background emission from molecular and continuum sources is stronger [7, 21]. Though utilized in earlier studies, no investigation of how spatial filtering affects SCGD-OES performance with traditional spectrometers has been reported in the literature.

Here we present a comparative study of the effects of spatial selection on the analytical aspects of the SCGD, with emphasis on detection limits and precision. Maxima along the vertical profiles of emission, S/B and signal-to-noise ratios (S/N) are presented, and the optimal vertical region for analysis of chosen elements is determined. In addition to probing how spatial filtering affects detection limits and precision, we show that vertical emission profiles can be useful for identification of line pairs that function as effective internal standards, as well as indicating the presence of matrix interferences.

Experimental

SCGD Parameters, Optical Systems, and Data Analysis

The SCGD cell used in these experiments is identical to the one described earlier [21], so only differences in experimental parameters will be discussed here. Except where noted, the SCGD was operated at a power of 63–65 W (constant-current mode with 70 mA current and voltages that ranged from 911–934 V), interelectrode gap of 3 mm, and sample flow rate of 2.5 mL min⁻¹. For all experiments, samples were introduced into the discharge continuously throughout the data-acquisition period.

Figure 1 depicts the optical system used for collection of spatially resolved data. In this arrangement, radiation from the SCGD was imaged (1:1 magnification) by a plano-convex quartz lens (f/3) onto the 50- μ m wide entrance slit of an Andor (Belfast, Ireland) Shamrock 303i 0.3 m Czerny-Turner spectrograph outfitted with two diffraction gratings. The first grating (used for detection of radiation from 200–500 nm) had a groove density of 1200 grooves mm⁻¹ and 300 nm blaze, while the second (used for wavelengths longer than 500 nm) had 600 grooves mm⁻¹ and a 500 nm blaze. Radiation dispersed by the spectrograph was imaged onto an Andor Newton 971 two-dimensional (1600x400 array, where each pixel was 16x16 μ m in size) electron-multiplying charge coupled device (EMCDD) camera, thermoelectrically cooled to -25° C. In all experiments, the EMCCD was operated in conventional CCD mode (no gain).

Improvements in relative standard deviation (RSD) by use of internal standards were investigated with a second optical system, where radiation from the SCGD was imaged (2.3:1 magnification) by a plano-convex quartz lens (f/6) onto the 50- μ m wide entrance slit of an Andor Shamrock SR-750 0.75-m Czerny-Turner spectrograph with two diffraction gratings (1800 grooves mm⁻¹ blazed at 500 nm, and 1200 grooves mm⁻¹ blazed at 600 nm). Radiation that passed through the spectrograph was refocused onto a two-dimensional Andor iKon-M (model DU934P-BU2) charge coupled device (CCD) with an array of 1024x1024 pixels

(13x13 μm size), thermoelectrically cooled to -40°C . For detection of the Pb I 405.8 nm and Mn I 403.1 nm lines, the grating blazed at 500 nm was used, whereas the grating blazed at 600 nm was used for detection of the K I 769.9 nm and Rb I 780.0 nm lines.

Both optical configurations result in dispersion of various wavelengths along the horizontal axis of the detector, whereas the vertical axis corresponds to vertical position along the SCGD axis. A custom National Instruments LabVIEW® program was used to selectively bin pixels either horizontally or vertically on the collected EMCCD or CCD images, enabling vertical emission profiles to be generated or a desired emission region of the discharge to be selected for investigation. For both spectrographs, position in the images (relative to the surface of the SCGD electrodes) was calibrated by widening the entrance slit to 2.5 mm, whereon light from a collimated continuum source (white LED flashlight) was used to acquire an image of the SCGD cell shadow with the grating angled at zero order. With both spectrographs, spectral overlaps from higher-order diffraction were prevented by use of an Edmund Optics (Barrington, NJ) long-pass filter (>88% transmission above 500 nm, <0.1% transmission below 460 nm), positioned in front of the entrance slit when wavelengths longer than 500 nm were investigated.

Magnified white-light images of the SCGD were obtained with a stereomicroscope (Bausch and Lomb, Rochester, NY, Model 1955-RR-513). A Canon EOS Digital Rebel XTi camera (Lake Success, NY) was mounted on the objective lens of the microscope and images were collected with exposure times ranging from 0.17 to 0.33 s with an ISO speed of 400.

Vertical-emission, signal-to-background (S/B) ratio, and signal-to-noise (S/N) ratio profiles were determined from the average signal and standard deviation of 20 consecutive 10-s integrations of both an analyte (concentration ranging from 0.5–50 ppm, depending on sensitivity for a given element) and blank solution. Except where noted, all vertical profiles were subjected to a 5-point adjacent-averaging filter to reduce pixel-to-pixel noise.

In all experiments where limits of detection or relative standard deviation (RSD) values were measured, analyte signals were determined as the background-subtracted peak area of the desired emission line. Background signals were measured with a blank solution over the same spectral band used to determine the analyte peak area (*i.e.* on resonance with the analytical line). In all cases, detection limits were estimated as three times the standard deviation of 20 consecutive 10-second integrations of a blank solution, divided by the sensitivity (cts ppb^{-1}) of the elemental line of interest. Sensitivities were determined from a single standard at a concentration approximately 2–20 times the detection limit. Relative standard deviation (RSD) values were computed from the average and standard deviation produced from 20 repeated 10-second integrations of the signal at a concentration at least fifty times the detection limit.

Reagents and Sample Preparation

Analytical grade (or better) carbonate, nitrate, or chloride salts were used for preparation of stock standards at 1000-ppm concentration. These standards were dissolved in 0.1 M nitric acid prepared with deionized water of 18.2 M Ω cm resistivity and concentrated (70% w/w) nitric acid stock solution. Concentrated nitric acid was purified in-house from reagent-grade nitric acid through sub-boiling distillation in a polytetrafluoroethylene distillation unit. All samples and standards of lower concentration were prepared by sequential dilution (in 0.1 M nitric acid) of the stock standards.

Results and Discussion

SCGD Structure and Vertical Maps of Signal, S/B, and S/N

Shown in Figure 2 are photographs of the SCGD before and after ignition on the surface of a 100-ppm In solution in 0.1 M HNO₃. In these images, the tungsten anode is located at the top middle of each frame,

and the sample-inlet capillary (along with the solution overflow) is located 4 mm below the pointed tip of the anode. It is clear that the physical structure of the SCGD conforms to that traditionally observed with reduced-pressure glow discharges [25], including the negative-glow (region of intense emission that ranges from the cathode surface to ~0.5-mm above the cathode), Faraday dark space (~0.5-mm tall region above the negative glow), positive column (~3-mm tall region above the Faraday dark space) and anode glow (region of strong emission at the anode surface). Past studies of the emission distribution in the SCGD have suggested that most analytes emit most strongly in the negative-glow region of the discharge, whereas background emission from molecular and continuum sources is strongest within the positive column and anode glow [7, 21, 24]. This and the structure of the discharge shown in Figure 2 suggest that analytical performance of the SCGD should be improved if emission were monitored from only the regions of the source where analyte emission is strongest and background emission is comparatively weaker.

To investigate how spatial discrimination affects analytical performance of the SCGD, fourteen atomic lines were selected for evaluation, including Ag I 338.3 nm, Al I 396.2 nm, Ca I 422.7 nm, Cd I 228.8 nm, Co I 345.4 nm, Cu 327.4 nm, Fe I 248.3 nm, In I 451.1 nm, K I 766.5 nm, Mn I 403.1 nm, Ni I 352.3 nm, Pb I 368.4 nm, Rb I 780.0 nm, and Zn I 213.9 nm. Since the SCGD produces weak ionic emission, no ion lines were chosen as they are not analytically useful. For these fourteen atomic lines, emission intensity was mapped over the region from 0.5 mm above the SCGD anode to 0.5 mm below the cathode surface, and is shown in Figure 3. These profiles revealed that analyte atomic emission generally conformed to one of four profile types, here deemed 'concentrated', 'semi-concentrated', 'semi-diffuse', and 'diffuse'. Those with concentrated profiles (In, K and Rb) exhibited intense emission within the negative glow, with weak emission elsewhere. Semi-concentrated profiles (Ag, Al, Ca, and Pb) all showed strong emission in the negative-glow region that extended into the upper regions of the discharge. Elements with semi-diffuse profiles (Co, Cu, Mn, and Ni) produced emission throughout the discharge volume that began to weaken beyond the position of each electrode. Finally, those elements with diffuse profiles (Cd, Fe, and Zn) displayed emission throughout the discharge volume that extended significantly beyond the position of the electrodes. Background profiles were also collected at the wavelength of each elemental line and are displayed in electronic supplementary Figure S1. Similar to earlier studies [7, 21], and for all wavelengths investigated here, background (from continuum, N₂, OH[•], and NO[•]) and analyte emission peak in different spatial locations within the plasma (*cf.* Figure S1A–N), which further suggests that spatial selection will enhance performance.

Elucidation of the cause of the elemental grouping and profile shapes of Figures 3 and S1 lies beyond the scope of the present work, though comments on the factors contributing to their origin are appropriate. The shape of the emission maps is dictated by a complex combination of several factors, including but not limited to desolvation and atomization processes (which includes factors such as dissociation energy) in the SCGD, propensity of the free-atomic form of an element to generate molecular adducts with reactive species in the SCGD (such as hydroxides, nitrides, oxides, *etc.*), excitation energy of the emission line, gas flow and electric-field dynamics in the plasma, and variation in the excitation temperature along the vertical axis of the SCGD. Attempts to correlate the location of the emission maximum of the curves in Figure 3 with the excitation energies or dissociation energies of each element showed no significant trends, further hinting that the behavior is complex.

In all profiles of Figure 3 and S1, emission does not terminate at the surface of each electrode, but extends beyond them. This behavior results from a combination of several factors. Most prominent is that the SCGD does not terminate at the surface of each electrode, but rather sheaths around them. Also contributing is scattering and reflection of emission from the surface of the electrodes and chromatic aberrations that degrade image formation. Indeed, the diffuse profiles of some elemental lines (Cd, Fe, and Zn) appear to result from chromatic aberration. All emission lines (including elemental and molecular background) at wavelengths shorter than 300 nm exhibited diffuse profiles similar to those of Cd, Fe, and Zn. In this study, a quartz lens was utilized for simplicity in optical alignment, though these results suggest that an achromatic means of radiation focusing (such as a parabolic or spherical mirror) would yield better results.

To identify the best spatial region for determination of each element, vertical maps of S/B ratio and S/N ratio were computed from the analyte and background signals (*cf.* supplementary Figures S2A–2N and S3A–2N). From Figures 3, S2, and S3, the point of maximum emission, S/B and S/N ratio were determined for each element and are compiled in Table 1. For elements that exhibited concentrated emission profiles (In, K, and Rb), the point of maximum emission and S/B all occur at nearly the same location in the plasma. Conversely, for elements that exhibited semi-concentrated, semi-diffuse and diffuse emission profiles, the point of highest S/B often occurred at a different location than the emission maximum, resulting both from background spectral interference and less defined analyte emission. For example, the Cu I 327.4 nm line has a semi-diffuse profile that overlaps strongly with background from OH* (*cf.* Figure S1F). Since the OH* emission weakens near the cathode surface, where the Cu emission is comparatively strong, the S/B maximum is shifted to a position lower in the plasma. Shifts in the location of S/B maxima of other elements (Ag, Al, Cd, Co, Fe, Mn, Ni, and Zn) can be rationalized similarly (*cf.* Figure S1).

Table 1 shows that the S/N maximum of several elements (Ca, Pb, Co, Cu, Mn, Ni, Cd, Fe, and Zn) occurs at a position lower in the discharge than the point of highest S/B. This finding suggests that the S/N in the SCGD depends upon factors apart from the relative analyte and background signal strength. One probable cause is differences in positional stability of the discharge zones. This hypothesis is supported by visual observations; a slight ‘wander’ in where the SCGD anchors to the anode is visually observable, which contributes to higher flicker noise in the upper regions of the plasma. Variation in discharge-to-anode anchoring can be reduced with a tapered electrode that limits the area in which the plasma can anchor, as utilized in this and earlier studies [9, 14–16, 19–21, 26]. Though electrode taper does reduce the flicker, the shift in S/N maxima to lower regions of the discharge suggests it is not eliminated entirely. Use of sharper tips might further improve stability but would do so at the cost of more frequent instrument maintenance since pointed anodes are more rapidly eroded.

Spatial Window Optimization and Analytical Performance

To identify the optimal size of the spatial window for determination of each element, a region (0.1-mm tall) was selected on the EMCCD images centered at the S/N maximum of a given element. The pixel columns over this region were then vertically binned to obtain spectra representative of the emission from only the spatially selected location in the discharge. A series of subsequent spectra were collected where the spatial window was increased in height (in 0.1-mm increments) symmetrically about the S/N maximum up to a size of 2.0 mm. For each spatial window, the detection limits and precision of the analyte and background signals (as percent RSD) were measured for all fourteen elements. Precision of the analyte and background emission signals was found to be affected minimally by spatial-window size, varying by $\leq 5\%$ for all elements investigated. Conversely, detection limits were strongly influenced by the size of the window used for spatial discrimination. An example, shown in Figure 4, is the Pb I 368.3 nm line, where detection limits improve as window size is increased from 0.1 to 0.4 mm, but worsen with windows larger than 0.4 mm. The trend in Figure 4 can be rationalized from spatial-emission profiles (*cf.* Figure S1L). With an emission maximum 0.4-mm above the cathode and background emission (from N₂ and OH*) that is strongest near the anode, a larger proportion of total signal from Pb is collected in comparison to the background as window size is increased from 0.1 to 0.4 mm, and detection limits improve. As window size is increased beyond 0.4 mm, a larger portion of background emission (relative to the Pb emission) is collected and detection limits begin to degrade. Trends in the detection limits of other elements with window size (plotted in Figures S4A–N) can be understood similarly. Since background and analyte RSD were affected minimally by the spatial-window size, the optimal window for each element was defined as the one that produced the lowest (best) detection limit; these values are compiled in Table 2.

To assess how analytical performance of the SCGD is affected by spatial discrimination, detection limits and precision were measured when emission was monitored from only the optimized region for each element. These values were then compared to those obtained when emission was monitored from the full vertical profile (0.5-mm above the anode to 0.5-mm below the cathode) of the discharge, representative of

a situation where no spatial selection is used. These results are also shown in Table 2. With optimized spatial filtering, detection limits ranged from 0.09–360 ppb, superior to those obtained when emission is collected from the full vertical profile of the SCGD (1.1–840 ppb). Not surprisingly, the greatest improvement (a factor of 6.8–13.6) was for the concentrated emission profiles, where spatial discrimination can more readily isolate analyte emission from the background. For the semi-concentrated, semi-diffuse, and diffuse profiles, improvement in detection limits was more modest, ranging from factors of 1.4–4.9x. Although spatial filtering collects emission from a narrower region of the discharge, precision was generally unaffected. Relative standard deviation values ranged from 0.5–2.6% with spatial discrimination, closely comparable to the 0.4–2.4% obtained when the full vertical profile of the discharge is collected.

Compromise Window Spatial Selection

From the preceding, it is clear that spatial discrimination is effective in improving the analytical performance of SCGD-OES; however, because the method utilizes spatial windows individually optimized for each element, it is limited in application to spectrometers equipped with two-dimensional detector arrays (ex. EMCCD, CCD, *etc.*) or instruments capable of scanning an image across the entrance slit of a spectrometer [27]. Of course, if a single compromise spatial window were utilized, the method could be more readily expanded to instruments with single-channel detectors (such as a photomultiplier tube) or linear detector arrays. In such an arrangement, a specific region of the discharge could be selected through use of an aperture stop (horizontal slit, iris, *etc.*) placed at the entrance slit of a spectrometer or at an image plane formed by a focusing lens. Adjustment of the discharge position relative to the aperture stop would enable selection of emission from only the desired region.

To assess how detection limits would be affected by use of a single spatial selection window, a 1.0-mm tall region of the discharge, centered 0.75-mm above the cathode surface was selected on the EMCCD images. This “compromise” window was selected as it overlaps with strong regions of emission from all 14 elements investigated in this study. Pixel columns over this region were vertically binned to create spectra representative of emission from only the spatially selected region. Detection limits were computed for all fourteen elements and compared to those obtained with the optimized method of spatial selection; the outcomes are shown in Table 3. These data reveal that the “compromise” method of spatial selection provides detection limits that are generally similar (different by less than a factor of three) to those from the spatially optimized method. The single exception was Ag, which exhibited a detection limit significantly worse (factor of 7.2) with the compromise method. Surprisingly, some elements (Ca, Ni, and Fe) exhibited detection limits that were slightly better with the compromise method than with optimized spatial selection, likely resulting from the earlier method used to optimize size of the spatial window. The element-optimized method relies on symmetrically increasing the size of a spatial window surrounding the location of highest S/N. Unless the S/N declines nearly symmetrically around that location, the optimization process might not provide the best spatial window for analysis. This finding suggests that other methods of optimization with windows placed asymmetrically about the point of highest S/N might yield even better performance. Regardless, these results show that a single spatial window can be utilized effectively to enhance detection limits in SCGD-OES, and that spatial selection can thereby be applied to single-channel detection systems or linear detector arrays.

Identification of Line Pairs for Internal Standardization

Apart from improvements in detection limits, spatial-emission profiles might also provide a means to identify line pairs that function effectively for internal standardization. Since the emission profiles of elemental lines are a function of processes such as desolvation, atomization, and excitation, line pairs that exhibit similar emission maps are also more likely to exhibit similar noise characteristics. Accordingly, when a target

analyte is paired with an internal standard that exhibits a similar emission profile, greater reduction in noise is probable.

To evaluate if emission maps can be used to identify line pairs that function as effective internal standards, two pairs of emission lines were evaluated. The first pair (Pb I 405.8 nm and Mn I 403.1 nm) exhibited mismatched vertical-emission profiles, and were compared to lines that display nearly identical emission profiles (K I 769.9 nm and Rb I 780.0 nm). Though the raw time traces of all four emission lines, shown in Figures 5A and 5B, each provided similar precision (0.89–1.02% RSD), significant differences in noise reduction were observed in the ratio of these lines. The ratio of the Mn and Pb emission traces resulted in a 3.2-fold improvement to precision (to 0.32% RSD, Figure 5C), whereas the ratio of the Rb and K emission lines exhibited a 14-fold improvement (0.07% RSD, Figure 5D). The much greater noise reduction for the Rb/K ratio suggests that emission lines with similar vertical profiles do exhibit better noise correlation and that spatial profiling can be utilized to identify effective internal standards.

Flagging Matrix Interferences

Earlier work by our research group [28-32] demonstrated that spatial emission profiles are effective in identifying the presence of matrix interferences in ICP-OES. When matrix interference exists, shifts in signal patterns occur (either as enhancement or depression) along the vertical axis of the plasma. If the signal of an unknown sample (I_{sample}) is ratioed with that of a reference standard known to be free of interference ($I_{\text{reference}}$), the shape of the resulting relative-intensity map ($I_{\text{sample}}/I_{\text{reference}}$) can be used to gauge whether an interference exists. The $I_{\text{reference}}$ is ordinarily taken from the standards employed to calibrate the instrument. If no enhancement or depression in I_{sample} occurs along its vertical profile, the relative-intensity profile will be flat, indicating that the sample behaves similarly to the calibration standards. If enhancement or depression occurs in the profile of I_{sample} , curvature is induced in the relative-intensity profile, indicating that matrix interference is present. Statistical analysis [30] of the “flatness” of the relative intensity profile can be utilized to alert an analyst to the presence of interference in unknown samples, and action (dilution, standard addition, etc.) can then be taken to correct for the matrix effect.

To determine if this method could also be applied to spatial mapping in SCGD-OES, the atomization interference of PO_4^{3-} ion on Ca [33] was investigated. Vertical-emission profiles of the Ca I 422.7 nm line were measured for a sample with interferent (20-ppm Ca in 0.1 M HNO_3 with 500- μM H_3PO_4) and for a reference standard, free of interferent (20-ppm Ca in 0.1 M HNO_3). The results are shown in the red and black traces of Figure 6A, respectively. Immediately apparent from these profiles is that enhancement and suppression of the Ca signal occurs in the presence of PO_4^{3-} , which suggests that the interference can be flagged. To confirm, the traces of Figure 6A were ratioed to create the relative-intensity profile in Figure 6B (red curve). Clear curvature is observed, signaling the existence of the PO_4^{3-} interference. To ensure that the curvature was the result of interference caused by the matrix and not of instrumental drift, the vertical profile of the Ca reference was reassessed at the end of the experiment. A relative-intensity profile computed from the two Ca reference measurements (black trace of Figure 6B) resulted in a “flat” curve, confirming that the curvature observed in the presence of PO_4^{3-} ion was the result of matrix interference and not instrumental drift.

Another notorious interference in SCGD-OES is the effect of moderate-to-high concentrations of alkali-metal cations on both background and analyte emission signals [33]. To determine if spatial profiles are effective for flagging this interference for a variety of analytes, emission profiles were measured for the Ca I 422.7 nm, Mn I 403.1 nm, and Pb I 405.8 nm lines with and without the addition of 25-mM NaNO_3 to the 0.1 M HNO_3 matrix. The relative-intensity profiles, and a drift test taken from a second measurement of the Ca reference, from this investigation are shown in Figure 7. Curvature is apparent in the ratio profile of all three emission lines, indicative of a matrix interference. Though the curvature in these profiles is visually apparent, a statistical protocol to determine the “flatness” of a relative-intensity profile might be required to

identify less-obvious interferences. Algorithms for this purpose have been described by Chan and Hieftje [30] and need not be discussed here.

Together, these early data show that spatial profiles can be used to effectively flag matrix interferences in SCGD-OES. The data also hint that the profiling could be effectively applied to reduce or eliminate interferences entirely; locations exist in both Figures 6 and 7 where matrix interference is reduced along the vertical profile of the discharge. If emission were selectively measured from these regions, matrix interference could be reduced or possibly eliminated. The potential use of spatial profiles to reduce matrix interference, either by selectively monitoring emission from discharge regions where the effect is reduced or by use of matrix crossover points [34], is presently under investigation and will be described in future publications.

Conclusions

Spatially resolved measurements provide a plethora of benefits to SCGD-OES analyses. All elements exhibited improved detection limits (ranging from a factor of 1.4–13.6) with optimized spatial filtering, but the greatest improvement was for species with emission profiles that facilitated isolating analyte emission from the background. Even though emission is collected from a smaller region of the discharge when spatial discrimination is utilized, no loss in precision was observed. Furthermore, spatial filtering can be effectively applied to instruments without a two-dimensional detector array, since use of a single, compromise spatial window provided similar results for most elements. Spatial emission profiles also appear useful for identification of line pairs that provide the best performance as internal standards. When the ratio of elemental lines that exhibited similar spatial profiles (K I 769.9 nm and Rb I 780.0 nm) was measured, a 14-fold reduction in noise was obtained, much greater than the 3.2-fold reduction for lines that had dissimilar spatial profiles (Mn I 403.1 nm and Pb I 405.8 nm). Finally, spatial profiling also appears to be effective in flagging the presence of matrix interferences in SCGD-OES, enabling an analyst to take action to correct them.

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Figure 1. Optical setup used for collection of spatially resolved SCGD data.

Intended for color both in print and online.

Figure 2. Photographs of the SCGD before and after ignition on a solution of 100-ppm indium in 0.1 M HNO_3 . Note the presence of the characteristic glow-discharge emission regions.

Intended for color both in print and online.

Figure 3. Vertical SCGD emission maps for several elements categorized as concentrated, semi-concentrated, semi-diffuse, or diffuse, depending on the profile structure. Surface of the anode and cathode are located at 0.0 and 3.0 mm on each x-axis, respectively.

Intended for color both in print and online.

Figure 4. Detection limits plotted as a function of spatial window height for the Pb I 368.3 nm line.

Intended for color online.

Figure 5. Time traces of the normalized emission signals from **(A)** Pb I 405.8 nm and Mn I 403.1 nm lines and **(B)** K I 769.9 nm and Rb I 780.0 nm lines. Signal ratios of both line pairs are shown in **(C)** and **(D)**, respectively. Signals of Mn and Rb in **(A)** and **(B)** have been offset by -0.05 AU for easier viewing. Each point on the plots is a 10-s integration of the respective signal.

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Figure 6. Effect of phosphate (PO_4^{3-}) on the emission profile of the Ca I 422.7 nm line **(A)**, and relative-intensity profile (signal with matrix divided by the signal of a matrix-free standard), demonstrating the curvature observed in the presence of the phosphate matrix **(B)**. Surface of the anode and cathode are located at 0.0 and 3.0 mm on the x-axis, respectively.

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Figure 7. Relative-intensity (signal with matrix divided by the signal of a matrix-free standard) profiles for several emission lines in the presence of a 25-mM NaNO_3 matrix. Surface of the anode and cathode are located at 0.0 and 3.0 mm on the x-axis, respectively.

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Table 1. Vertical profile emission maxima ($E_{\max}$), S/B maxima ($S/B_{\max}$), and S/N maxima ($S/N_{\max}$) of several elements with SCGD-OES, expressed as distance from the *cathode* surface.

Element, Wavelength	$E_{\max}$ (mm)	$S/B_{\max}$ (mm)	$S/N_{\max}$ (mm)
Concentrated Emission Profiles			
In I, 451.1 nm	0.2	0.2	0.3
K I, 766.5 nm	0.3	0.3	0.3
Rb I, 780.0 nm	0.3	0.3	0.3
Semi-Concentrated Emission Profiles			
Ag I, 338.3 nm	0.9	0.8	0.8
Al I, 396.2 nm	0.8	0.7	0.7
Ca I, 422.7 nm	1.6	1.6	1.5
Pb I, 368.4 nm	0.4	0.4	0.3
Semi-Diffuse Emission Profiles			
Co I, 345.4 nm	1.2	1.0	0.8
Cu I, 327.4 nm	1.4	1.0	-0.3
Mn I, 403.1 nm	1.5	1.4	1.1
Ni I, 352.5 nm	1.1	1.0	0.6
Diffuse Emission Profiles			
Cd I, 228.8 nm	1.1	1.0	0.8
Fe I, 248.3 nm	0.9	0.8	0.5
Zn I, 213.9 nm	1.3	1.2	0.5

Table 2. Optimized spatial window size, detection limits and RSD values for several elements with and without utilization of spatial selection with SCGD-OES.

Element, Wavelength	Optimized Window Size (mm)	Limit of Detection (ppb)		Improvement Factor	Relative Standard Deviation (%) (n=20)*	
		No Spatial Selection	Spatial Selection		No Spatial Selection	Spatial Selection
Concentrated Emission Profiles						
In I, 451.1 nm	0.7	13	1.9	6.8	0.6	0.9
K I, 766.5 nm	0.5	1.2	0.09	13.6	0.7	0.7
Rb I, 780.0 nm	0.7	1.1	0.15	7.3	0.5	0.5
Semi-Concentrated Emission Profiles						
Ag I, 338.3 nm	1.4	0.88	0.18	4.9	0.5	0.6
Al I, 396.2 nm	0.4	850	310	2.7	1.8	0.5
Ca I, 422.7 nm	0.9	81	30	2.7	0.7	0.7
Pb I, 368.4 nm	0.4	840	170	4.9	0.8	0.7
Semi-Diffuse Emission Profiles						
Co I, 345.4 nm	0.6	290	100	2.9	0.5	0.4
Cu I, 327.4 nm	1.7	12	8.5	1.4	2.4	1.9
Mn I, 403.1 nm	0.7	400	120	3.3	1.2	0.8
Ni I, 352.5 nm	0.6	840	360	2.3	0.7	0.5
Diffuse Emission Profiles						
Cd I, 228.8 nm	0.7	53	36	1.5	0.8	0.7
Fe I, 248.3 nm	1.4	660	200	3.3	0.6	0.4
Zn I, 213.9 nm	0.8	200	140	1.4	2.6	2.5

*Measured at a concentration at least 50 times the detection limit.

Table 3. SCGD-OES detection limits with per-element optimized spatial selection and with a single, compromise window of spatial selection.

Element, Wavelength	Limit of Detection (ppb)		Difference Factor (Compromise/Optimized)
	Optimized Spatial Selection	Compromise Window Spatial Selection	
Concentrated Emission Profiles			
In I, 451.1 nm	1.9	2.1	1.1
K I, 766.5 nm	0.09	0.10	1.1
Rb I, 780.0 nm	0.15	0.18	1.2
Semi-Concentrated Emission Profiles			
Ag I, 338.3 nm	0.18	1.3	7.2
Al I, 396.2 nm	310	390	1.3
Ca I, 422.7 nm	30	26	0.86
Pb I, 368.4 nm	170	250	1.5
Semi-Diffuse Emission Profiles			
Co I, 345.4 nm	100	110	1.1
Cu I, 327.4 nm	8.5	12	1.4
Mn I, 403.1 nm	120	140	1.2
Ni I, 352.5 nm	360	310	0.86
Diffuse Emission Profiles			
Cd I, 228.8 nm	36	36	1.0
Fe I, 248.3 nm	200	110	0.55
Zn I, 213.9 nm	140	330	2.3