

PAPER

Solution–cathode glow discharge – optical emission spectrometry of a new design and using a compact spectrograph†

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A solution–cathode glow discharge is coupled to a compact spectrograph. Such a coupling results in a small, potentially portable instrument that can simultaneously detect a range of metals by optical emission spectrometry. Detection limits were calculated for Ag (1 ppb), Cd (2 ppb), Cu (8 ppb), Fe (40 ppb), Hg (20 ppb), Mg (3 ppb), Ni (12 ppb), Pb (10 ppb) and Se (3 ppm). These values are similar to those for an earlier, monochromator-based solution–cathode glow discharge system. All calibration curves showed good linearity ($R^2 \geq 0.9994$). Short-term precision ranged from 0.6–7%.

Introduction

Glow discharge plasmas are well established tools for the elemental analysis of solids. In 1993, Cserfalvi *et al.*¹ introduced the electrolyte–cathode discharge (ELCAD) – a glow discharge which could be used for the elemental analysis of aqueous solutions. A variety of electrical discharges which (like the ELCAD) use an aqueous solution as at least one of the electrodes have been introduced since then, as summarized in recent reviews.^{2,3} These plasmas can broadly be grouped as solution–electrode discharges. Such discharges often have advantages of cost, portability, and speed when compared to more established solution-phase elemental analysis techniques like inductively coupled plasma – optical emission spectrometry (ICP-OES). The solution–cathode glow discharge (SCGD), which is the subject of the present study, is an ELCAD-like design that produces detection limits ranging from 0.06 ppb for Li to 20 ppb for Hg.⁴

Aside from designs that are very similar to the ELCAD, the most thoroughly studied of the small atmospheric pressure discharges useful for elemental analysis is the liquid-sampling – atmospheric pressure glow discharge (LS-APGD).⁵ As an optical emission source, the LS-APGD has detection limits significantly higher than the SCGD, but it uses significantly lower flow rates. Because of the flow rate difference, the LS-APGD can detect similar absolute amounts (masses) of some elements (Hg, Pb) as the SCGD, although other elements (Mg, Na) required higher amounts for the LS-APGD than for the SCGD.^{4,5} The LS-APGD has also been recently shown to be useful as a mass spectrometry source, although such operation substantially

increases the construction cost compared to an optical emission instrument.⁶

In brief, the SCGD consists of a metal rod fixed approximately 3 mm above the exit of a glass capillary tube. A solution overflows from the glass tube and an electrical connection is made to this overflow. The solution surface at the exit of the capillary is held at a potential that is negative compared to the metal rod's potential. The potential maintains a glow discharge where the solution acts as the cathode and the metal rod acts as the anode. No discharge gas (aside from atmospheric pressure air) is required.

Aside from a few exceptions where the discharge was used as a sample introduction system,^{7–10} analyte detection using these systems has been through atomic emission excited by the discharge.^{1,4,11–20} An advantage of atomic emission over atomic absorption is that the former is more practically adaptable to simultaneous multi-elemental analysis. When the emission of several elements can be measured simultaneously, internal standardization and faster analyses are both possible. Although most solution–electrode discharge systems use atomic emission, almost no work has been done using a detection system capable of simultaneous multi-elemental analysis. Where spectrographs have been used, they have mostly been for characterizing the discharge emission rather than for analytical work.^{15,17} For the SCGD and similar designs, monochromators have always been used for the analytical portion of the work.

State-of-the-art miniature spectrometers with CCD solid state detectors are ideally coupled to a SCGD. These instruments are portable due to small size, low power requirements and mechanical ruggedness. These compact spectrographs are also significantly less expensive than some of the monochromators that have been previously used with the SCGD. Unfortunately, these spectrographs have significantly lower resolution (larger instrumental bandpass) than the monochromators used in previous SCGD studies. In other atomic

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emission instruments, resolution has a strong effect on detection limits. In particular, detection limits in ICP-OES have been found to be strongly dependent on the effective linewidth, where this linewidth is a combination of the instrumental bandpass and the physical linewidth of an analyte's emission line.^{21,22} The effect of resolution on detection limits in a SCGD system has not been previously studied, but the simple and low background of the SCGD suggest that such a combination may be worthwhile. The amount of light reaching the detector of a miniature spectrograph is also hindered by the small height of its entrance slit compared to the height of the entrance slit of the monochromator used in previous versions of the SCGD.

Spectral interferences are potentially a problem when using low resolution. However, the SCGD has been shown to have a very simple emission spectrum.¹⁵ Ionic emission lines are rare, and only the strongest atomic emission lines are observed for most elements.

In this paper, we evaluate the combination of a small spectrograph with an SCGD. In addition, several changes to the design of the SCGD are described.

Experimental

The instrument used in this study bears some similarity to the one used in previous studies,^{4,16} but a number of changes have been made. Most notably, an overflow/waste reservoir was removed. This reservoir limited the portability of the discharge because it needed a constant level of solution with a flat surface. A diagram of the new system is shown as Fig. 1. A sample solution is delivered upwards through a glass tube. The tube is a 25 μ L micropipette (Corning) with a 0.6 mm inner diameter and a 1.3 mm outer diameter. A portion of this solution overflows and contacts a 6 mm diameter graphite rod positioned 3 mm below the top of the glass tube. Waste drips into a container below the discharge. The graphite rod has a hole drilled

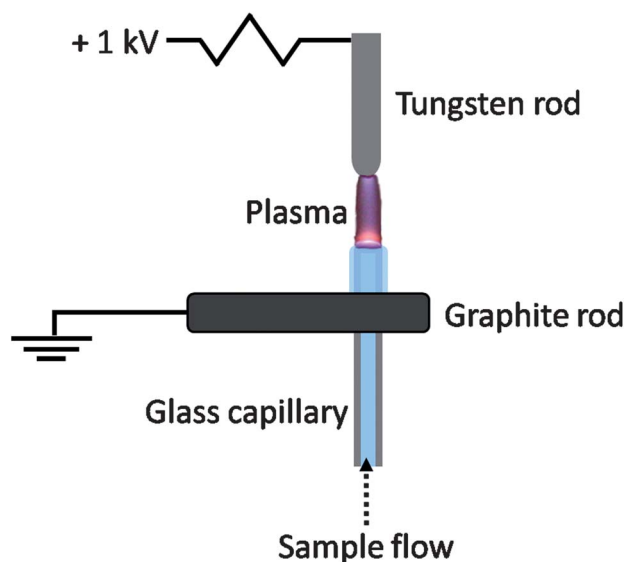


Fig. 1 Schematic of the solution-cathode glow discharge cell used in this study. The glass capillary is inserted through a hole in the graphite rod.

through it radially so that it can be placed around the glass tube. The solution is connected to electrical ground through the graphite. This arrangement is similar to the design of Shekhar *et al.*,^{13,14} but certain elements of that design were not used. For example, Shekhar *et al.* use a channel (or “v-groove”) cut into the glass tube, whereas the present system does not.

A 2 mm diameter tungsten rod with a rounded tip is located 3 mm above the glass tube and collinear to it. The rod is connected to the positive end of a dc power supply (Glassman High Voltage, model MR1.5P200L) through a 1 k Ω resistor. A plasma is maintained between the tungsten anode and the solution-cathode. Based on previous optimization of a similar system,⁴ the voltage was adjusted to provide a current of 65 mA. This required a voltage of 1.0 kV. The voltage was then held constant and the current was allowed to vary because this mode has previously been found to be less affected by the sample matrix than constant-current operation.⁴

Light from the plasma is collected by a 50 mm focal length, 25 mm diameter (23 mm clear aperture) plano-convex fused silica lens located 50 mm from the plasma. An identical lens then focuses the light at 1 : 1 magnification onto the entrance of a fiber-optic cable with a 0.6 mm core diameter (Ocean Optics Xtreme Solarization-resistant Optical Fiber). The lenses were placed with their curved surfaces facing each other. This lens combination and arrangement was chosen to keep spherical aberrations small while matching the angle of acceptance of the fiber. The angle of the cone of focused light (26°) is close to the angle of the acceptance cone of the fiber optic (25°), which should lead to efficient light coupling. The other end of the fiber optic cable is attached to an Ocean Optics Maya 2000 Pro. The Maya 2000 Pro is a 15 $\times$ 11 $\times$ 5 cm spectrograph with a CCD detector. The 2048 $\times$ 64 pixel CCD (Sony ILX511) is backthinned and binned vertically to enhance sensitivity. The configuration used in this study had a spectral range of 189–413 nm, a 1200 line per mm grating, a 25 μ m entrance slit, and a resolution of 0.35 nm FWHM.

The solution is introduced to the SCGD using a peristaltic pump (Spetec Perimax 16) as shown in Fig. 2. Antipuls tubing (Spetec) is used in pairs with offset rollers to reduce pulsations. Two pairs of tubing were used in these experiments and are

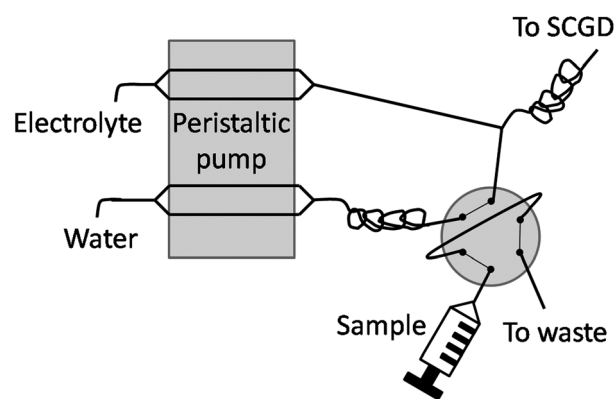


Fig. 2 Flow connections leading to the solution-cathode glow discharge. Solution flow is from left to right. Coiled tubing acts as pulse dampers and/or mixers.

referred to as the sample and electrolyte channels. The sample channel carries water at a flow rate of 2.7 mL min^{-1} . After the pump, the water passes through a length of knotted tubing that serves as a pulse damper. After the pulse damper, the water passes through a 6-port injection valve with a 3 mL sample loop. The electrolyte channel carries an aqueous solution of 0.25 M HNO_3 at a flow rate of 1.8 mL min^{-1} . The channels combine before entering a second length of knotted tubing which serves both as a pulse damper and a mixer. The mixed flows then enter the SCGD capillary. The combined channels have a flow rate of 4.5 mL min^{-1} and an HNO_3 concentration of 0.10 M. Lower flow rates may be possible, but it should be noted that this is a higher flow rate than has been used in previous systems. Although this arrangement simplifies sample and standard preparation by adjusting the acid concentration online, it also dilutes the sample and standards significantly (by a factor of 1.7). This dilution prevents small variations in the electrolyte concentration of samples from affecting the overall solution conductivity. All standards were prepared by dilution of high-purity 1000 ppm solutions (SPEX Certiprep for Cu, BDH Aristar Plus for all others). Nitric acid was Optima grade (Fisher Scientific).

Emission signals were acquired over a 30 second interval, during which corresponded to the flat portion of the peak. Integration times for individual measurement within this peak were 0.3–6 seconds. Background correction was performed by a two-step process. First, the background emission at a nearby wavelength was subtracted from the emission at the analyte wavelength. This process corrected for fluctuations in the background intensity. Second, the baseline was subtracted from the entire time trace. The baseline was measured at the analyte wavelength just after the sample plug passed through the discharge.

Results and discussion

Based on previous studies,^{12,15} we chose to collect light from the negative glow. The light was collected from an approximately 0.6 mm diameter spot centered 1 mm above the top of the capillary. A background spectrum of this region of the SCGD is shown in Fig. 3. The dark signal of the detector has been

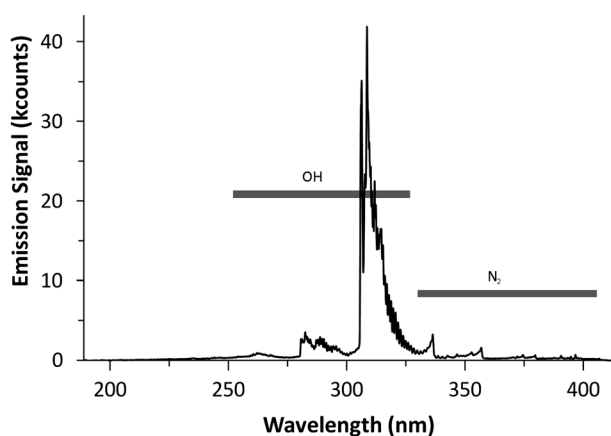


Fig. 3 Background spectrum of a solution-cathode glow discharge measured using a compact spectrograph.

subtracted. As with most other solution-electrode discharges, OH and N_2 are responsible for most of the background emission. As with the previous versions of the SCGD, the most intense background emission in the negative glow is from OH, and the N_2 emission increases closer to the anode (not shown).

The SCGD primarily produces emission from neutral atoms due in part to the low fractions of most elements that are ionized.¹⁷ Ionic emission can be observed from some elements with low ionization energies, but even this emission is very weak. For example, the ratio of the signal from the $\text{Mg II } 280.3 \text{ nm}$ line to that of the $\text{Mg I } 285.2$ was approximately 0.02. Details of this measurement can be found in the ESI.† For comparison, this ratio is approximately 10 in an ICP.²⁴ Because ionic emission in the SCGD is weak even for those elements where it is observable, atomic emission was used for analysis. Selection was simplified by the ability to observe all lines in the 189–414 nm range simultaneously. The wavelengths in Table 1 were chosen because they gave high signals and/or low backgrounds compared to other available lines.

Calibration curves were constructed for several elements based on calibration curves with four to five points. The wavelengths used for each element can be found in Table 1. Each standard was injected three times. The lowest point on each calibration curve was approximately the limit of quantitation (using the definition $10\sigma/m$, where m is the slope of the calibration curve and σ is the standard deviation of the signals for 10 blank injections). The curves show good linearity, with all R^2 values at least 0.9994, as shown in Table 1. The upper limit of linearity was not tested, but calibration curves remained linear with standards of 800 ppb Cu, 900 ppb Mg, 50 000 ppb Se, and 1000 ppb of all other elements. Relative standard deviations for these high concentration samples are given in Table 1.

Detection limits for each element were calculated based on the standard deviation of a blank signal and the slope of the calibration curve. The standard deviation of the blank signal was calculated based on 10 injections. The common $3\sigma/m$ definition of detection limit was used, where m is the slope of the calibration curve and the σ is the standard deviation of the blank.

These detection limits are shown in Table 2 alongside three other sets of detection limits for comparison. The first set of detection limits is from an earlier version of the SCGD,⁴ which used a monochromator with a narrower spectral bandpass. Assuming no diffraction or aberration-based broadening, the resolution of the earlier system for the lines used in both studies would be 0.01 nm, which is more than an order of magnitude narrower than the 0.350 nm spectral bandpass measured for the current system. The earlier detection limits are based on 10 second integrations. The other two sets of detection limits are for a commercially available ICP-OES instrument and are from a paper by Asfaw and Beauchemin.²³ One set was obtained using a pneumatic nebulizer and the other was obtained using an ultrasonic nebulizer. Both used radial viewing. Axial viewing would improve detection limits by factors of 2–10, but it would do so at the cost of increased susceptibility to interferences.²⁵ All three sets of comparison detection limits were obtained with clean standards and are based on the same $3\sigma/m$ definition of

Table 1 Calibration curves for several elements

Element	Analyte wavelength (nm)	Background wavelength (nm)	RSD ^a (%)	R ² of best fit	Sensitivity (counts per s per ppb)
Ag	328.1	326.9	0.6	1.0000	67
Cd	228.8	226.8	0.9	1.0000	11
Cu	324.8	323.9	1.6	0.9998	37
Fe	252.3	250.5	5	0.9998	0.4
Hg	253.6	252.9	7	0.9994	0.3
Mg	285.2	284.6	0.8	0.9997	97
Ni	341.5	339.7	1.1	0.9996	1.6
Pb	405.7	404.2	4	0.9999	0.8
Se	196.1		3	0.9994	0.007

^a RSD is for the highest concentration standard in the calibration curve as listed in the article text.

Table 2 Detection limits (in ppb) for several elements

Element	SCGD with spectrograph ^a	SCGD with monochromator ^b	ICP with pneumatic nebulizer ^c	ICP with ultrasonic nebulizer ^c	ICP wavelength ^c (nm)
Ag	1.1	0.3	—	—	—
Cd	2	2	0.8	0.2	214.438
Cu	8	4	3	0.2	324.754
Fe	40	—	3	0.2	259.941
Hg	20	20	50	—	184.950
Mg	3	0.2	20	30	285.213 (ultrasonic) 280.270 (pneumatic)
Ni	12	—	3	0.4	231.604
Pb	10	6	9	2	168.215
Se	3000	—	20	6	196.091

^a Present study. ^b Values from Webb *et al.* ^c Values from Asfaw and Beauchemin.²³

detection limit as is used in the present study. Most of the detection limits found in the present study are not very different from those found in the previous SCGD study or those of an ICP with pneumatic nebulization. The detection limits are also comparable to or better than those found with other solution-electrode discharges with similar designs to the SCGD.^{11,14}

Where there are differences in detection limits between the two SCGD systems, the present system has somewhat worse performance than the previous system. These differences are typically not much more than the 1.7-fold dilution factor used in the current system. The exception is Mg, which displayed a detection limit an order of magnitude worse with the present system than it did with the earlier one. This difference may be due in part to the order of magnitude difference in resolution of the two systems. Mg is likely to be affected the most strongly by the decreased resolution because of overlap with an OH emission band (Fig. 4). The CCD is less sensitive at this wavelength compared to the photomultiplier tube (Hamamatsu R928) that was used in previous versions,⁴ and that may play a role as well. However, it seems unlikely that detector sensitivity is the dominant factor because the difference in sensitivities is comparable at the Hg detection wavelength, and no degradation in detection limit was seen for that element.

Cu emission also overlaps with OH emission, but the detection limit of the present system is not very different from that of the previous system. This may be because the

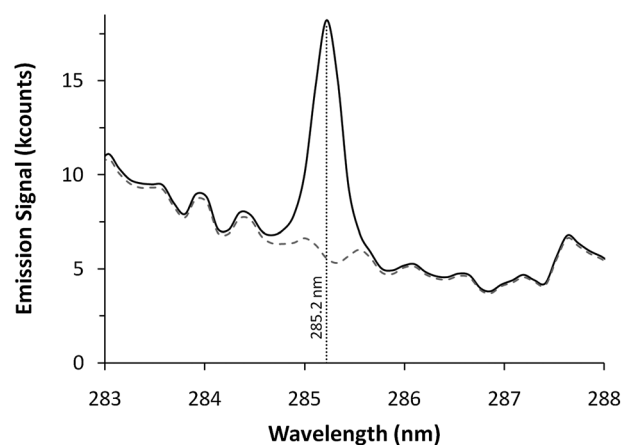


Fig. 4 Emission near the Mg 285.2 nm emission line. The dashed grey line shows a blank spectrum. The solid black line shows the spectrum of a solution containing 1 ppm Mg. Dark signal has been subtracted.

background is less intense (Fig. 5) and fluctuations are correspondingly less intense. The background, in counts at the Cu line was about 64% of that at the Mg line. This value was not corrected for spectrometer or detector efficiency, which would increase the difference. Although resolution may affect the detection limits of other elements, its effects were not isolated in the current study.

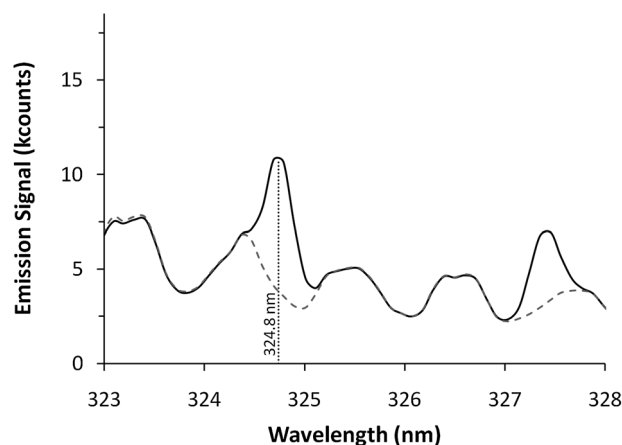


Fig. 5 Emission near the Cu 324.8 nm emission line. The dashed grey line shows a blank spectrum. The solid black line shows the spectrum of a solution containing 2 ppm Cu. Dark signal has been subtracted.

The detection limits for Cu, Ni, and Pb with the present system are close to, but somewhat higher than, those with the pneumatic nebulization ICP system. The detection limit for Hg with the present system is similar to, but somewhat ($2.5\times$) better than, the detection limit with the ICP. The detection limit for Mg is an order of magnitude better by SCGD than by ICP, and the detection limit for Fe is an order of magnitude worse by SCGD than by ICP. Given that different emission lines are used for the two systems and that the SCGD uses atomic emission for all elements while the ICP uses ionic emission for most elements, differences on this scale are not surprising. The most substantial difference in detection limits between the SCGD and the ICP is for Se, which has a 2-order of magnitude higher detection limit by SCGD than by ICP. This difference may result from the lower excitation temperature of SCGD-like plasmas compared to ICPs.^{12,17,26} The emission line used for Se was the deepest into the UV of the lines used in this study, so it will be subject to significant absorptive losses, and it has a fairly high excitation energy of 6.32 eV.²⁷ Oxygen is usually removed from ICP spectrometers when measurements at such short wavelengths are used, but this was not attempted for the SCGD here. The detector has lower sensitivity for this wavelength than it does for longer ones and the SCGD may not have a high enough excitation temperature to efficiently excite this level.

As noted in the introduction, the detection limit of an ICP is strongly affected by effective linewidth, which is largely determined by instrument bandpass.^{21,22,28} The spectrometer used in the ICP study has an instrument bandpass 40 times smaller than that of the spectrometer used in the present SCGD study. Based on this resolution difference, an ICP would be expected to produce detection limits significantly worse than those in given in the table if that ICP were used with our 0.35 nm bandpass spectrometer. It is not clear whether, or by how much, the SCGD detection limits would improve if a spectrograph with higher resolution was used. Future studies may include a controlled evaluation of the effect of resolution on instrument figures of merit.

Conclusions

The performance of a solution-cathode glow discharge that uses a compact spectrograph for wavelength separation has been evaluated. The detection limits are mostly comparable to those found with earlier SCGD systems that used higher resolution monochromators. The ability of the SCGD-spectrograph system to detect many wavelengths at once should speed analyses and open up the possibility of using internal standards. The modifications to the instrument design add to the instrument's portability.

Acknowledgements

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Notes and references

- 1 T. Cserfalvi, P. Mezei and P. Apai, *J. Phys. D: Appl. Phys.*, 1993, **26**, 2184–2188.
- 2 M. R. Webb and G. M. Hieftje, *Anal. Chem.*, 2009, **81**, 862–867.
- 3 P. Mezei and T. Cserfalvi, *Appl. Spectrosc. Rev.*, 2007, **42**, 573–604.
- 4 M. R. Webb, F. J. Andrade and G. M. Hieftje, *Anal. Chem.*, 2007, **79**, 7899–7905.
- 5 W. C. Davis and R. K. Marcus, *J. Anal. At. Spectrom.*, 2001, **16**, 931–937.
- 6 R. K. Marcus, C. D. Quarles, C. J. Barinaga, A. J. Carado and D. W. Koppelaar, *Anal. Chem.*, 2011, **83**, 2425–2429.
- 7 Q. He, Z. L. Zhu, S. H. Hu and L. L. Jin, *J. Chromatogr., A*, 2011, **1218**, 4462–4467.
- 8 Z. L. Zhu, G. C. Y. Chan, S. J. Ray, X. R. Zhang and G. M. Hieftje, *Anal. Chem.*, 2008, **80**, 7043–7050.
- 9 Z. L. Zhu, Q. A. He, Q. Shuai, H. T. Zheng and S. H. Hu, *J. Anal. At. Spectrom.*, 2010, **25**, 1390–1394.
- 10 T. Cserfalvi and P. Mezei, *J. Anal. At. Spectrom.*, 2005, **20**, 939–944.
- 11 T. Cserfalvi and P. Mezei, *J. Anal. At. Spectrom.*, 2003, **18**, 596–602.
- 12 P. Mezei, T. Cserfalvi and L. Csillag, *J. Phys. D: Appl. Phys.*, 2005, **38**, 2804–2811.
- 13 R. Shekhar, D. Karunasagar, K. Dash and M. Ranjit, *J. Anal. At. Spectrom.*, 2010, **25**, 875–879.
- 14 R. Shekhar, D. Karunasagar, M. Ranjit and J. Arunachalam, *Anal. Chem.*, 2009, **81**, 8157–8166.
- 15 M. R. Webb, F. J. Andrade, G. Gamez, R. McCrindle and G. M. Hieftje, *J. Anal. At. Spectrom.*, 2005, **20**, 1218–1225.
- 16 M. R. Webb, F. J. Andrade and G. M. Hieftje, *Anal. Chem.*, 2007, **79**, 7807–7812.
- 17 M. R. Webb, G. C. Y. Chan, F. J. Andrade, G. Gamez and G. M. Hieftje, *J. Anal. At. Spectrom.*, 2006, **21**, 525–530.
- 18 R. Shekhar, *Talanta*, 2012, **93**, 32–36.
- 19 A. J. Schwartz, Z. Wang, S. J. Ray and G. M. Hieftje, *Anal. Chem.*, 2013, **85**, 129–137.
- 20 Z. Wang, A. J. Schwartz, S. J. Ray and G. M. Hieftje, *J. Anal. At. Spectrom.*, 2013, **28**, 234–240.

- 21 P. Boumans and J. Vrakking, *J. Anal. At. Spectrom.*, 1987, **2**, 513–525.
- 22 P. Boumans and J. Vrakking, *Spectrochim. Acta, Part B*, 1987, **42**, 553–579.
- 23 A. Asfaw and D. Beauchemin, *Spectrochim. Acta, Part B*, 2010, **65**, 376–384.
- 24 M. Carre, K. Lebas, M. Marichy, M. Mermet, E. Poussel and J. M. Mermet, *Spectrochim. Acta, Part B*, 1995, **50**, 271–283.
- 25 G. Tyler and L. Goldstone, *Today's Chemist at Work*, 2003, **12**, 51–53.
- 26 P. Jamróz and W. Żytnicki, *Plasma Chem. Plasma Process.*, 2011, **31**, 681–696.
- 27 A. Kramida, Y. Ralchenko and J. Reader, *NIST Atomic Spectra Database (ver. 5.0)*, <http://physics.nist.gov/asd>, accessed April 11 2013.
- 28 J. M. Mermet, *Spectrochim. Acta, Part B*, 2001, **56**, 1657–1672.