

Spectroscopic characterization of ion and electron populations in a solution-cathode glow discharge

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The ion and electron populations of a glow discharge that uses an electrolytic solution as the cathode (an electrolyte-cathode discharge or ELCAD) were investigated. This paper presents the first determinations of electron number density, ionization temperature, and degrees of ionization in the ELCAD. Spectroscopic techniques were used to keep from perturbing the plasma, a range of conditions was explored, and two regions (the negative glow and the positive column) were observed. By using the Stark broadening of the hydrogen beta line, electron number densities near $8.5 \times 10^{14} \text{ cm}^{-3}$ for the negative glow and $2.5 \times 10^{14} \text{ cm}^{-3}$ for the positive column were found. From those results and measurements of the relative strengths of Mg neutral and ionic lines, ionization temperatures of 5000 K for the negative glow and 4600 K for the positive column were calculated. From these results, the degrees of ionization and norm temperatures were estimated for a variety of elements. Analytical implications of the study are discussed.

Introduction

The first use of a glow discharge incorporating a solution as the cathode for analytical atomic spectroscopy was in 1993 by Cserfalvi *et al.*,¹ who later named this source an electrolyte-cathode discharge (ELCAD).² Sporadic atomic emission from a similar source had been observed in 1959 by Couch and Brenner,³ and the basic technique, known as glow-discharge electrolysis, had been used in electrochemistry since its invention in 1887 by Gubkin.⁴ In an ELCAD, a solution with a pH lower than 2.5 is introduced upwards at a flow of 3.5–10 mL min⁻¹ through a tube whose outlet is 1.5–5 mm beneath a solid anode, and potentials on the order of 1 kV and currents greater than 30 mA are applied.^{1,2}

Initial detection limits were generally in the range of hundreds of parts per billion to single parts per million.² Since that time, a number of studies, which have been summarized in a review⁵ involving both practical considerations and fundamental characterizations, have expanded knowledge of the system and contributed to an improvement of analytical performance. Initial experiments showed that lower pH and higher current produced stronger emission.¹ Later experiments by Yagov and Gentsina⁶ revealed that emission decreases at higher electrolyte (acid or otherwise) concentrations than were initially employed. Mezei *et al.*⁷ showed that emission rises with pressure until around 2 bar, at which point it falls. Park *et al.*⁸ showed that emission intensity is somewhat, but not strongly, dependent on discharge-gas identity and that air yields more intense emission than He or Ar. Kim *et al.*^{9,10} showed that opening the discharge cell to the atmosphere improves analytical performance by enhancing stability. As a

result of the knowledge accumulated through these studies, typical detection limits have dropped by around two orders of magnitude so they are generally in the single to tens of parts per billion for steady-state measurements^{9–11} and comparable for those elements that have been studied in flow-injection analysis.¹²

In spite of the previously mentioned studies and others, there is much left to be learned about this type of discharge. The knowledge gained from fundamental studies has the potential to further improve analytical performance as earlier studies have. Among the parameters that are not yet known are the relative and absolute sizes of the electron and ion populations. The electron number density, in particular, has been proposed as an important variable in the mechanism by Cserfalvi *et al.*^{7,13,14}

The work presented here characterizes the electron number density, the ionization temperature, and element-specific ion-to-atom ratios. These characteristics are monitored as a function of location within the discharge and as functions of various changes made to the discharge. The consequences of the observed characteristics are discussed in relation to analytical performance.

Experimental

The ELCAD cell has been described previously¹¹ and is shown in Fig. 1. The solution enters the cell through a 0.3 mL portion of a 1 mL serological pipette that has been bent so the tip points upwards 3 mm below a 1.6 mm diameter Ti anode. A Kepco (Flushing, NY) BHK 2000-0.1MG high-voltage power supply operated in constant-current mode is connected to this anode through a 400 Ω ballast resistor. The solution overflows from the tip into an approximately 35 mL reservoir containing a grounded graphite electrode. This overflow creates an electrical connection between the solution at the pipette's tip and

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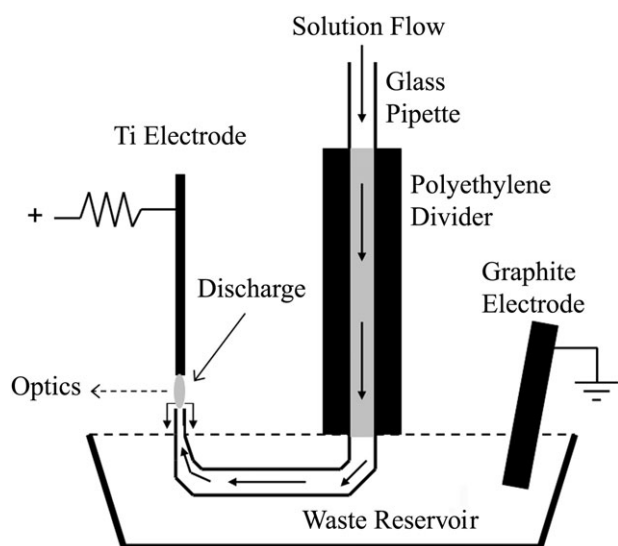


Fig. 1 Diagrammatic representation of solution-cathode glow discharge.

the graphite electrode. The discharge can be initiated by bringing the anode within approximately 1 mm of the solution or by using a metal syringe needle to make contact between the anode and the solution and then withdrawing the needle from the solution while maintaining contact with the anode to transfer the discharge to the Ti anode.

A black rectangular polyethylene divider supported by the pipette serves multiple purposes. It reduces the amount of hydrogen (produced at the graphite cathode) that reaches the discharge, it blocks some light from sources external to the discharge by impeding its path through the air, and it wicks moisture over the sides of the reservoir so a constant solution level is maintained within the reservoir. The hydrogen is blocked intentionally because its presence has been known to lower emission in other glow discharges; the light is blocked to reduce background noise; and the reservoir level is held constant to prevent fluctuations in the ohmic drop across the solution between the pipette tip and the graphite cathode.

Aside from what has been described to this point, two different sets of equipment are used in this work.

For the H_{β} measurements, solution is supplied by a syringe pump (Harvard Apparatus PHD 2000 (Holliston, MA)) at 3.5 mL min^{-1} . A Model HR1000 Jobin-Yvon (Longjumeau, France) monochromator was used in an arrangement which has been described previously.¹⁵ In brief, a collimating lens, dove prism, and focusing lens were used in series to rotate the image of the plasma 90° and project it onto the $20 \mu\text{m}$ wide entrance slit of the monochromator at a magnification of 0.4. A CCD camera (Roper Scientific, Trenton, NJ, Model CH350A) at the focal plane of the monochromator detected the lateral distribution of emission in one dimension and its spectral distribution in the other. A National Instruments (Austin, TX) LabVIEW program written by Starn *et al.*¹⁶ is used to calculate electron number densities based on Stark broadening of the H_{β} line.

In other measurements, solution is supplied by using a Global FIA MilliGAT (Fox Island, WA) flow-injection system. Before reaching the pump, the sample solution passes

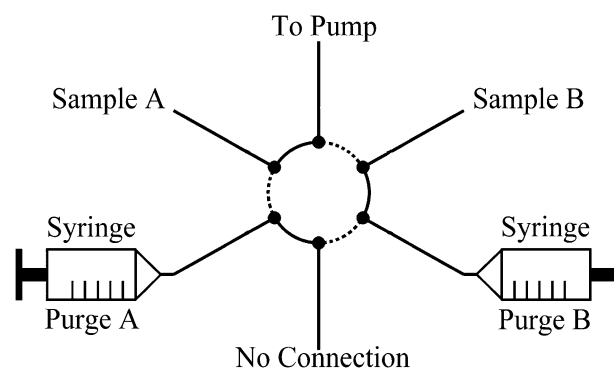


Fig. 2 2-way 6-port valve with sample A directed to the discharge.

through a 6-port 2-way switch, connected as shown in Fig. 2. This allows the sample to be changed without interrupting the solution flow so the discharge does not need to be extinguished between samples. The syringes are necessary to purge the intake lines of any air bubbles introduced as the tubing is moved between samples. The discharge is imaged 2.3 : 1 with a quartz lens onto the entrance slit of a Chromex (Albuquerque, NM) 500IS/SM 0.5 m Czerny–Turner spectrometer. Spatial resolution is accomplished by blocking portions of the imaged plasma with electrical tape affixed to the spectrometer entrance slit. Detection is accomplished with a Hamamatsu (Hamamatsu, Japan) R928 PMT biased at -850 V amplified by a Keithley (Cleveland, OH) 427 current amplifier. The output of this amplifier is recorded with a custom LabVIEW program that also controls the monochromator.

Results and discussion

Electron number density

Several methods were considered for the determination of electron number densities; Stark broadening of the H_{β} line was chosen because it provides reasonable accuracy and precision with a relatively simple experimental setup and does not perturb the plasma or require an assumption of thermodynamic equilibrium.¹⁷ For Stark broadening to be a viable method, other sources of broadening need to be either insignificant or taken into account. The H_{β} peak width (full width at half maximum) from a typical ELCAD was measured to be 182 pm . Based on interpolation from tables¹⁸ that take plasma temperature into account, this half-width corresponds to an electron number density of approximately $8.7 \times 10^{14} \text{ cm}^{-3}$. Natural broadening is in the order of hundredths of picometers,^{19–21} and a 0.05 pm broadening would produce only a 0.04% error in this estimate, so this contribution can be neglected. Pressure broadening in an analytical flame, which is comparable to the ELCAD in terms of gas temperature and pressure, is from one to a few picometers.^{19–21} Even in an ICP, which has a higher temperature than either the ELCAD or a flame, pressure broadening is only a few picometers.²² From the cited tables, a 5 pm contribution from pressure broadening would produce a 4% error, which was judged to be acceptable and, ultimately, was several times smaller than the experimental uncertainty. Lower electron number densities in the

positive column make this error relatively larger than in the negative glow, but it is still smaller than the experimental error. Other broadening was accounted for as discussed below.

The H_β line profiles were measured at two locations: in the negative glow (approximately 0.2 mm above the cathode) and in the positive column (approximately 1.2 mm above the cathode). A LabVIEW program¹⁶ was used to calculate electron number densities after transformation of the data (which contained lateral information on one axis and spectral information on the other) by QuickBasic into a series of monochromatic images. Thomsen and Helbig²³ found that omitting the central portion of the H_β line profile yields better agreement between experimental and theoretical profiles because the assumption of static ions leads to predictions of a larger central dip than is experimentally observed. With this in mind, the central portion of the H_β line (the portion with intensity greater than approximately 70% of the maximum) was omitted from the fitting. To account for the contribution of Doppler broadening, the gas-kinetic temperature, which can be reasonably approximated by the OH rotational temperature, is required. Based on previous results,¹¹ a gas temperature of 3000 K was used. Another influence on the observed profile that must be accounted for is instrumental broadening. The measured profile of the 422.7 nm line of a Ca hollow cathode lamp was used for this purpose because it is narrow compared to the instrumental broadening and relatively close in wavelength to the H_β line.¹⁶

To calculate accurate electron number densities, lateral emission profiles are ordinarily transformed into radial profiles. If radial symmetry can be assumed, this procedure can be performed by means of an Abel inversion. Unfortunately, this process tends to amplify noise and therefore reduce precision, particularly near the center of the discharge. In some cases, particularly in measurements of the positive column, noise in the background emission was too great for Abel inversion to be feasible. To assess the impact of not using radially resolved profiles, Abel inversion was performed on one lateral profile by using the Nestor–Olsen algorithm.²⁴ As Fig. 3 shows, the results obtained using lateral and radial profiles for the negative glow region of a 60 mA discharge agree to well within the error of the measurement (calculation of the error is described below). Also shown in the figure is the lateral profile for the positive column under the same conditions. All three profiles show that the electron number density is very flat until the edges of the discharge, where it drops slightly before the emission becomes too weak for accurate measurement. It is no doubt this flatness that renders the Abel inversion unimportant.

To better analyse trends, average n_e were calculated for each region. For this purpose, the apparently constant n_e in the (horizontally) central region was assumed to be constant in fact. The mean and standard deviation of n_e were then calculated based on this assumption. The precision of the measurement was limited by both noise and the resolution of the results provided by the LabVIEW program. Twice the larger of the standard deviation or the program's resolution is given as the error for the remainder of this text. Based on these definitions, the laterally resolved n_e ($8.5 \pm 1.9 \times 10^{14} \text{ cm}^{-3}$), and radially resolved n_e ($8.3 \pm 1.9 \times 10^{14} \text{ cm}^{-3}$) are not

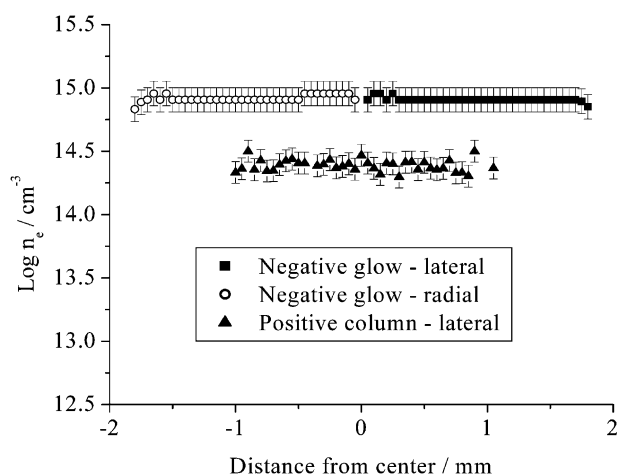


Fig. 3 Electron number densities in different regions of the ELCAD, estimated by means of lateral and radially resolved data. Negative glow and positive column are approximately 0.2 and 1.2 mm above the cathode, respectively. For clarity, only half the lateral and radial profiles are shown for the negative glow. Discharge current, 60 mA; solution pH, 1.0 (in HNO_3).

significantly different. The positive column n_e ($2.5 \pm 0.5 \times 10^{14} \text{ cm}^{-3}$) is significantly lower than that of the negative glow. These values approach those typically found for an inductively coupled plasma ($\sim 10^{15} \text{ cm}^{-3}$),¹⁷ and are quite a bit higher than those commonly found for a low pressure glow discharge ($\sim 10^{11} \text{ cm}^{-3}$).²⁵

Three variables were chosen for evaluation in this study. Solution pH was chosen because the dependence of emission on pH was proposed by Cserfalvi *et al.*^{7,13,14} to involve a higher electron number density at low pH. Discharge current was chosen because it affects the electron number density in low pressure metal-cathode glow discharges.²⁵ Electrolyte identity was chosen because it has been shown to affect emission.^{6,26} The effects of pH and current on n_e are shown in Figs. 4 and 5, respectively. No trend is apparent in either case. Electrolyte identity also did not have a statistically significant impact on n_e . At 60 mA and pH 1.0, HCl, HNO_3 , and H_2SO_4 produced electron number densities of $2.4 \pm 0.4 \times 10^{14} \text{ cm}^{-3}$, $2.5 \pm 0.5 \times 10^{14} \text{ cm}^{-3}$, and $2.5 \pm 0.3 \times 10^{14} \text{ cm}^{-3}$, respectively. In the negative glow under the same conditions, HCl, HNO_3 , and H_2SO_4 produced electron number densities of $8.1 \pm 1.8 \times 10^{14} \text{ cm}^{-3}$, $8.5 \pm 1.9 \times 10^{14} \text{ cm}^{-3}$, and $8.7 \pm 2.0 \times 10^{14} \text{ cm}^{-3}$, respectively.

Ionization temperature

By combining the Saha and Boltzmann equations,^{17,22,27} the ionization temperature can be calculated if the electron number density and the ratio of intensities of an atom and an ion line of the same element (as well as various constants associated with this element and these lines) are known.

$$\frac{n_e(I_{kl}^+ A_{pq} \lambda_{kl}^+)}{I_{pq} A_{kl}^+ \lambda_{pq}} = \left(\frac{2g_k}{g_p}\right) \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \exp\left(-\frac{E_i + E_k - E_p}{kT}\right)$$

Here the + superscript indicates the ion; subscripts indicate energy levels (subscripted k , l , p , and q are the ion upper level,

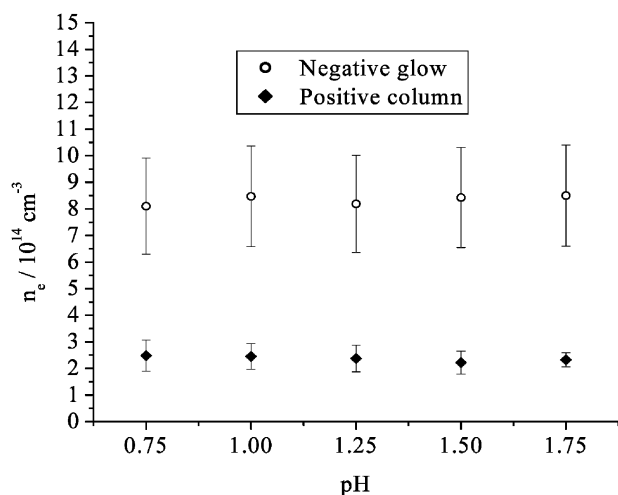


Fig. 4 Electron number densities as a function of pH. Discharge current was 60 mA and HNO_3 was used to provide the desired pH.

ion lower level, atom upper level, and atom lower level, respectively); n_e is the electron number density, as determined previously; I is the observed emission intensity; A is the transition probability for spontaneous emission; λ is the wavelength of the emission line; g is the statistical weight of the level; m_e is the electron mass; k is the Boltzman constant; h is the Planck constant; E_k and E_p are the excitation energies of the repective levels; E_i is the ionization potential; and T is the temperature to be calculated as the ionization temperature.

Although the various temperatures are not in thermodynamic equilibrium, it is often necessary to assume they are for the purpose of calculations. The ionization temperature and excitation temperature are assumed to be equal in this case. Important considerations are that the lines be near in wavelength to reduce any wavelength bias of the detection apparatus and that the excited states involved be close in energy to minimize the impact of the excitation temperature. The lines used in this study, Mg II 279.6 nm and Mg I 285.2 nm, can be used for this purpose because they are separated by only

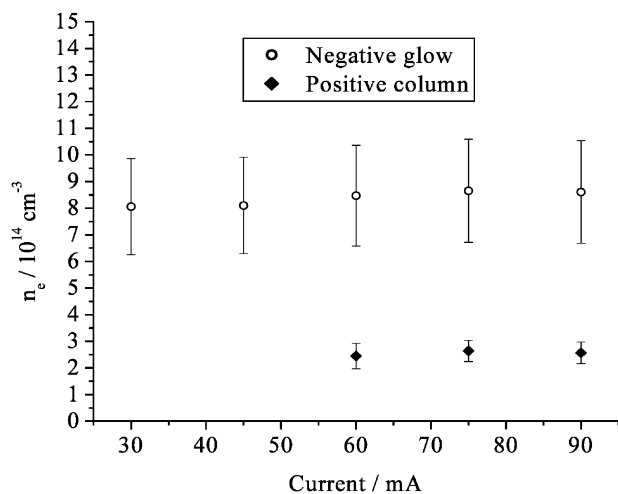


Fig. 5 Electron number densities as a function of current. Solution pH was adjusted to 1.0 using HNO_3 .

5.6 nm and the involved excited states are separated by only 0.09 eV. Mg II 280.2 nm, a more commonly used line, was not employed for this study because it is only approximately half as intense as the Mg II 279.6 nm line.

At 75 mA and pH 1.0 HNO_3 , the Mg I 285.2 nm : Mg II 279.6 nm intensity ratio was 38.0 ± 1.6 in the negative glow and 58.6 ± 9.8 in the positive column. Based on these values and the previously calculated electron number densities, T_{ion} was calculated to be 5038 ± 60 K in the negative glow and 4623 ± 34 K in the positive column under these conditions. No trend greater than the calculated uncertainty was seen with current or pH.

Analytical consequences

Based on the electron number density and the calculated ionization temperatures, the fractions of an element present as ions and atoms can be calculated from the Saha equation. For this computation, it is necessary to know the partition functions of the atoms and ions at the ionization temperature, which are obtainable from the polynomial approximations given by Irwin.²⁸ The element-specific degrees of ionization were calculated for the ELCAD negative glow ($T_{\text{ion}} = 5000$ K, $n_e = 8.5 \times 10^{14} \text{ cm}^{-3}$), ELCAD positive column ($T_{\text{ion}} = 4600$ K, $n_e = 2.5 \times 10^{14} \text{ cm}^{-3}$), and, for comparison, an argon ICP ($T_{\text{ion}} = 7500$ K, $n_e = 1 \times 10^{15} \text{ cm}^{-3}$). These last values are well within the range of values found in the literature,²⁹ and are the same as those used by Ohata and Furuta for a similar purpose.³⁰ The results are plotted *versus* ionization energy in Fig. 6.

From Fig. 6, the majority of elements exist mostly as neutrals. Among the minority of elements that exist mostly as ions are the alkali metals, which produce only weak ionic emission because of their closed shell structure as ions. Based on this observation, atomic lines should be more analytically useful for most elements than ionic lines and line selection should be better aided by references for weakly ionizing sources such as flames and low-pressure glow discharges than by references to strongly ionizing sources such as the ICP. Indeed, all of the best ELCAD detection limits so far have

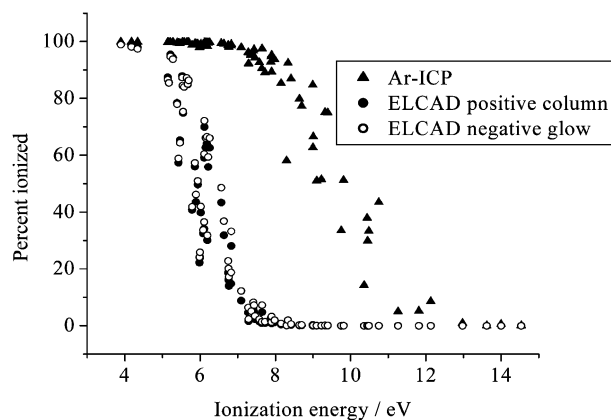


Fig. 6 Comparison of the degrees of ionization in the ELCAD and a typical argon ICP. ELCAD negative glow conditions were $T_{\text{ion}} = 5000$ K and $n_e = 8.5 \times 10^{14} \text{ cm}^{-3}$. ELCAD positive column conditions were $T_{\text{ion}} = 4600$ K and $n_e = 2.5 \times 10^{14} \text{ cm}^{-3}$. ICP conditions were $T_{\text{ion}} = 7500$ K, $n_e = 1 \times 10^{15} \text{ cm}^{-3}$.

been reported for atomic lines. Additionally, because ion lines are mostly absent, chances of spectral interference are reduced.

These predicted degrees of ionization are valid only as long as the electron density and temperature are unaffected by the presence of the analyte or concomitant elements. In flames, this assumption is not valid because the electron number density is highly dependent on the identities and concentrations of elements in the sample. For example, Luecke³¹ experimentally found that, in an air–acetylene flame at roughly 2200 K, magnesium was 46.2% ionized at a concentration of 25 ppb but only 1.5% ionized at a concentration of 400 ppb. As a result, the sensitivity (background-corrected signal divided by concentration) varies by almost a factor of two over this range, making quantization difficult. Further, because other elements from the sample will affect the electron number density in the flame, the degree of ionization (and therefore the emission and absorption) of a given element will depend on the concentrations of other elements. To combat this interference, an ionization buffer, commonly a caesium salt, is often used. This buffer raises the electron concentration to a level where changes caused by the presence of other elements become insignificant. In an ICP, in contrast, the background electron concentration is sufficiently high that the introduction of 1000 ppm of an easily ionized element should raise the electron concentration by only about 0.1 %, ¹⁷ so this type of interference is insignificant.

Because, as Fig. 6 shows, the ELCAD produces a lower degree of ionization than the ICP, fewer electrons will be added to the discharge for the same number of atoms introduced into it. At the same time, the background electron concentration in the ELCAD is nearly as high as in the ICP. The combination of these two factors implies that the sort of ionization interference seen in flames should not occur in the ELCAD. Correspondingly, we have seen no evidence of ionization interference in ELCAD calibration plots. To better evaluate whether or not there is an ionization interference, sensitivity is plotted as a function of concentration in Fig. 7.

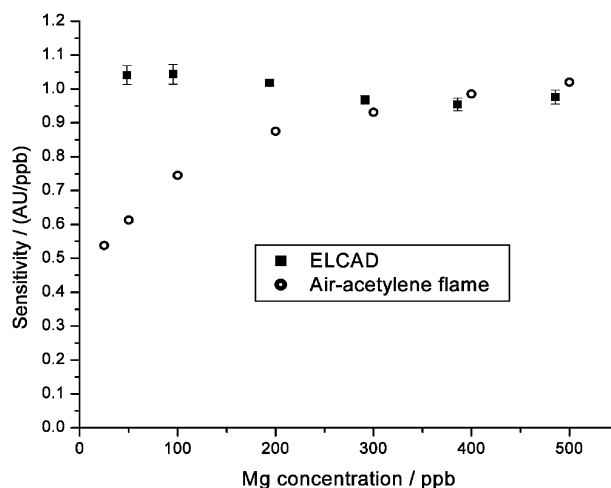


Fig. 7 Evaluation of the effect of concentration on sensitivity. ELCAD data are based on five ten-second integrations when the discharge was operated at 75 mA and solutions were adjusted to pH 1.0 with HNO₃. Flame data are from Luecke.³¹ Constant sensitivity for the ELCAD source suggests an absence of the classical ionization interference.

An ionization interference, which is not present, would produce an increase in sensitivity at higher concentrations.

With optimization of emission as a goal, it is worthwhile to consider how a change in ELCAD temperature would affect emission. The fraction of an element present as neutrals can be calculated from the Saha equation and the fraction of those neutrals in a given excited state can be calculated by means of the Boltzmann equation. The product of those two fractions is proportional to the emission intensity at a given temperature and electron number density. This product was calculated for all elements for which detection limits by ELCAD have been reported in the literature. The emission lines used were those for which the lowest detection limit has been reported. Partition functions were calculated as described above.

Table 1 Norm temperatures and predicted temperature-dependent relative emission intensities of various analytes at wavelengths for which detection limits have been previously reported in the ELCAD

Element	Wavelength/ nm	Norm temperature/K	Intensity relative to maximum				
			3000 K	4000 K	5000 K	6000 K	7000 K
Cs	852.1	3260	88%	38%	10%	4%	2%
K	766.5	3610	55%	72%	16%	6%	3%
Na	589.0	4240	13%	93%	50%	16%	7%
Sr	460.7	4340	6%	84%	54%	16%	7%
Li	670.8	4390	15%	87%	46%	13%	6%
Ca	422.7	4620	2%	58%	79%	24%	9%
Al	396.2	5380	1%	18%	88%	76%	32%
Cr	357.9	5400	0%	16%	86%	69%	25%
Pb	368.4	5780	0%	5%	56%	95%	46%
Mg	285.2	5800	0%	3%	51%	96%	45%
Mn	279.5	5810	0%	3%	50%	95%	44%
Fe	248.4	6100	0%	1%	30%	99%	63%
Ag	338.3	6120	0%	3%	38%	99%	61%
Ni	341.5	6250	0%	3%	32%	96%	66%
Cu	324.7	6270	0%	3%	33%	95%	68%
Cd	228.8	6760	0%	0%	7%	61%	99%
Zn	213.9	7050	0%	0%	4%	41%	100%
Au	242.8	7330	0%	0%	4%	35%	93%
Hg	253.6	7530	0%	0%	2%	25%	85%

Degeneracies and excited-level energies were obtained from reference volumes.^{32–35} Although not strictly valid, equilibrium was assumed between the ionization and excitation temperatures, and the electron number density was assumed to be $8.5 \times 10^{14} \text{ cm}^{-3}$ regardless of temperature.

This calculation was performed for temperatures of 1000–9000 K in increments of 500 K. At first, emission rises with temperature as the fraction of atoms in the excited state grows. Simultaneously, the total number of neutral atoms declines due to ionization. At a high enough temperature, the effect of ionization is greater than the effect of excitation, so emission drops. The point of maximum emission is known as the norm temperature.¹⁷ This temperature was calculated by fitting the rising edge of the curve to a Gaussian function and the falling edge to a Lorentzian function. The peaks of the two curves agreed to within 1% in all cases and the average of these peaks is reported as the norm temperature in Table 1, alongside the relative emission at several temperatures.

Clearly, no single temperature is optimal for all elements. The temperature determined for the ELCAD negative glow (5000 K) gives a fair compromise between elements that are easy to ionize and those that are difficult to excite. If the temperature can be adjusted, a higher rather than lower temperature might be desirable because easily ionized elements, such as alkali and alkaline metals, are present in relatively high concentrations in many applications. However, no method for significantly increasing the excitation temperature of an ELCAD has yet been reported.

Conclusions

The electron number density, ionization temperature, and degrees of ionization in the ELCAD are presented for the first time. The variance of these values was surprisingly low. In particular, the insensitivity of electron number density to current differs from the behavior found in low pressure glow discharges, and its stability with pH contrasts with predictions that changes in electron number density will play a role in the ELCAD's pH-sensitive behavior.^{7,13,14} The relatively high electron number density suggests that calibration curves obtained using the source should not be subject to non-linearities from concentration-dependent degrees of ionization as those from flames are, which agrees with the authors' experience. Calculations based on the degree of ionization and the excitation in the source show that the ELCAD provides a good compromise between ideal conditions for detection of easily and less easily ionized elements, but that somewhat higher temperatures would give an even better compromise.

Acknowledgements

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