Signal enhancement in solution-cathode glow discharge – optical emission spectrometry via low molecular weight organic compounds

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Abstract

HCOOH, CH₃COOH, and CH₃CH₂OH were used as chemical modifiers in a solution-cathode glow discharge. Emission was measured directly from the discharge, without a gas-liquid separator or a secondary excitation source. Emission from Ag, Se, Pb, and Hg was strongly enhanced, and the detection limits (DL) for these elements were improved by up to an order of magnitude using a combination of HCOOH and HNO₃ compared to using HNO₃ alone. The DL was measured for Mg (1 μ g/L), Fe (10 μ g/L), Ni (6 μ g/L), Cu (6 μ g/L), Pb (1 μ g/L), Ag (0.1 μ g/L), Se (300 μ g/L), and Hg (2 μ g/L). Coefficients of determination (R²) were between 0.9986 and 0.9999. A voltage of 1 kV was used, which produced a current of approximately 70 mA.

Keywords: glow discharge, vapor generation, optical emission spectrometry, solution cathode, atmospheric pressure

1. Introduction

Although glow discharges are typically used for elemental analysis of solids, several glow discharges designed for direct elemental analysis of aqueous solutions have been described in the past two decades [1-3]. These discharges tend to be small, low-cost devices. One such design, which we refer to as the solution-cathode glow discharge (SCGD), produces detection limits mostly in the single to tens of μ g/L in its latest version [4].

The core of the SCGD is a plasma in an approximately 3-mm gap between a metal rod and the surface of a solution exiting a glass tube. An electrical potential difference between the solution and the rod maintains a glow discharge, with the rod acting as the anode and the solution acting as the cathode. The solution is also the sample, and elements are generally detected by atomic emission. Unlike most atomic spectrometry atomization/excitation sources, no discharge gas (aside from ambient air) is used. The mechanism by which analyte atoms are transferred from the sample

solution to the plasma is not entirely clear, but some studies of the SCGD and similar plasmas have suggested that droplets play a role [5-8], possibly via an electrospray-like mechanism [5, 8]. Others have argued that sputtering plays a significant role [9].

In flame atomic absorption and inductively coupled plasma – optical emission spectrometry (ICP-OES), signal can be increased by changing the viscosity and other properties of the sample solution. This enhancement is credited to phenomena including increased total volume of droplets, smaller individual droplets, and more volatile droplets [10, 11]. If droplets are involved in analyte transport in the SCGD, it seems likely that a similar enhancement should occur. Altering the surface tension of the solution might also affect sputtering.

Another process through which analytes can be introduced into an atomization/excitation source is vapor generation. In this process, an analyte is converted into a more volatile form that is then introduced into the atomization/excitation source as a vapor. Typical vapors include metal hydrides, small organometallic compounds, and elemental mercury. These vapors can be generated in a number of ways, including chemically [12, 13], photochemically [14-16], and electrochemically [17]. Normally, the analytes' vapors are separated from water droplets and water vapor before being directed to the atomization/excitation source. In the atomization/excitation source, the vapors decompose into elements, and the analytes are detected using optical emission, atomic absorption, atomic fluorescence, or mass spectrometry.

An SCGD has been used as a vaporization source, where the vapor and aerosol produced by the discharge were passed through a gas-liquid separator and into a secondary excitation source in the form of an ICP-OES instrument [18-21]. The system has been used to detect Hg [18, 20], I [19], and Os [21]. Organic additives (HCOOH, CH₃COOH, and CH₃CH₂OH) enhanced the signal for Hg. A similar, earlier system was used to study analyte transport from the solution into the plasma but not for analyte quantitation [9]. For analytical work, adding an ICP-OES instrument sacrificed many of the advantages of the SCGD, including small size and low cost.

A drawback of vapor generation is that it reduces the ability of the atomization/excitation source to act as a multielemental detector. Not all elements are amenable to vapor generation, and those that are sometimes require different conditions from each other. The SCGD-ICP system is an extreme case of this; As, Se, Pb, Sn could not be detected even when 10 mg/L solutions were used [18]. One approach to circumvent this problem is to use normal sample introduction and vapor generation simultaneously [22]. For example, Sturgeon et al. inserted a UV lamp into a spray chamber in order to induce photochemical vapor generation in the aerosol [23]. Both the vapor and a fraction of the aerosol were directed to an ICP. All analyte elements were detected because of their presence in the aerosol, but the signals of some elements were enhanced by photochemical vapor generation.

More recently, Shekhar [24] found that low molecular weight organic acids could be used to enhance Hg emission in an SCGD-like instrument. In

this study, emission was measured directly from the glow discharge rather than from a secondary source like an ICP. This method does not require significant changes to the SCGD instrument design, so it preserves the instrument's advantages. Other elements were not studied and the mechanism was not explored. Instead, the study concentrated on optimizing and validating the technique for Hg. The Hg emission signal was increased roughly five-fold in the presence of 5% CH₃COOH and the detection limit for that element was decreased by the same factor. The relative errors in accuracy for two certified reference materials were found to be 3.5% and 5.9% and the percent relative standard deviations for these reference materials were 4% and 5%. Greda et al. have recently shown that non-ionic surfactants can also enhance analyte emission for a range of metals [25, 26].

Xiao et al. [27] performed a study on the effects of HCOOH, CH₃COOH, and CH₃CH₂OH on a system related to the SCGD. Their system, which they refer to as an alternating-current electrolyte atmospheric liquid discharge (ac-EALD) differs from SCGD-like systems mainly in that it uses alternating current instead of direct current and that it uses very low flow rates (0.4 mL/min). They found a 13-fold increase in emission for Ag in 3% HCOOH and a 17fold enhancement of Cd emission under the same conditions. They also found a 78-fold enhancement of Pb emission in 7% HCOOH. In all cases pH 1.0 HNO₃ was used both in the solution with HCOOH and in the comparison solution. Xiao et al. also saw quantified enhancements for Na and K emission. They did not quantify these enhancements but described them as slight.

In this paper, we also treated samples with low molecular weight organic solvents in order to enhance the emission signals of various analytes in the SCGD itself, without a secondary excitation source. We build on the work of Shekhar by studying several elements.[24] Based on trends between those elements, the effects of different mineral acids, and the effects of different concentrations of low molecular weight organic compounds, we discuss possible mechanisms for observed signal enhancement, including vapor generation.

2. Materials and Methods

These experiments involved generation of known toxic and corrosive gasses as well as possible generation of unknown and potentially harmful gasses. The SCGD was operated in a fume hood in order to ensure adequate ventilation.

A discharge was maintained in a 3-mm tall gap between a tungsten anode and a solution cathode. The solution reached the discharge through a 0.6-mm inner diameter, 1.3-mm outer diameter glass tube and was electrically grounded through a graphite rod in contact with the solution that overflowed on the outside of the capillary. A potential of 1000 V and a current of 70 mA were used. Detection was accomplished using a Maya2000 Pro spectrograph. Further details on the SCGD cell and the optical detection arrangement have been described extensively in a previous paper [4]. Signal acquisition and background subtraction were performed as described in that paper and is illustrated here in Figure 1. Briefly, the emission signal and a signal at a nearby wavelength were both acquired during a 30second interval at a fixed delay after the injection time. Within this 30-second acquisition, a number of individual readouts of the charge coupled device (CCD) detector were made. For Ni, Se, and Hg, the CCD integration time was 5 seconds. For Fe, the CCD integration time was 4 seconds. For other elements, the CCD integration time was 3 seconds. The emission was roughly constant during the 30second period at the peak of the transient. The emission at the nearby wavelength was subtracted from the emission at the analyte wavelength. Emission at both wavelengths was also acquired after the analyte plug and was used to calculate a baseline, which was also subtracted. We refer to the result as the background-corrected emission.

The SCGD primarily produces emission from neutral atoms due in part to the low fractions of most elements that are ionized [4, 28]. Because of the weak ionic emission, atomic emission lines were chosen for all elements except Ca. The Ca atomic emission line (422.7 nm) that has been previously used [5, 6, 29-31] was outside of the range of the spectrometer. The strongest observable Ca line was

the Ca II 393.4 nm line, so this was used for the experiments described here.

The solution was provided using a peristaltic pump (Spetec Perimax 16) with Antipuls tubing (Spetec). As described previously [4], the solution was provided via two different flows that were merged together and mixed online before reaching the SCGD cell. One flow, called the electrolyte flow, had a flow rate of 1.8 mL/min. The other flow, called the sample carrier flow, passed through a 6-port injection valve with a 3-mL sample loop. The sample carrier flow rate was 2.7 mL/min. It should be noted that this flow rate is several times higher than some recent related systems [30, 32]. Tubing-based pulse dampeners were used as described previously. In normal operation, the sample flow carries water and the electrolyte flow carries a 0.10 mol/L HNO₃ solution. In this study, the solution compositions were varied and will be described below.

Table 1 shows the elements used in this study, the concentrations used for all experiments except those involving calibration curves, and the wavelengths used to monitor emission in all aspects of this study. All solutions were prepared by dilution of 1000 mg/L standards from SPEX Certiprep (Cu) or BDH Aristar Plus (all other elements). HNO₃ (Optima grade, Fisher Scientific), HCl (trace metal grade, Fisher Scientific), HCOOH (analysis grade, Acros Organics), CH₃COOH (Optima grade, Fisher Scientific), and CH₃CH₂OH (USP grade, AAPER) solutions were all prepared by diluting concentrated solutions using water filtered by a Milli-Q system. To correct for any metal impurities, a matrix-matched blank was always used.

3. Results and discussion

3.1 Effects of organic modifiers and inorganic acids

The effects of HCOOH, CH_3COOH , and CH_3CH_2OH as organic modifiers were tested on all the elements used in this study. In these experiments, the sample and the sample carrier flow contained 0.17 mol/L HNO₃, and the channel usually used for electrolyte flow did not contain HNO₃. The final concentration

of HNO₃ in the merged flows was 0.10 mol/L. When present, the organic modifier was delivered using the channel usually used for electrolyte flow to give a final concentration of 3% by volume in the merged flows. The resulting background-corrected atomic emission was divided by the corresponding emission from an experiment where the channel usually used for electrolyte flow did not contain an organic modifier. The experiment was repeated 3 times for each organic modifier and 3 times without an organic modifier. The ratios calculated in these experiments are given in Table 1 as enhancement factors. The errors given are standard deviations calculated using the formula:

$$s_{R} = R \sqrt{\left(\frac{s_{U}}{U}\right)^{2} + \left(\frac{s_{E}}{E}\right)^{2}}$$

In that formula, R is the ratio or enhancement factor, U is the background-correct signal without organic modifier, and E is the background-corrected signal with organic modifier. The standard deviations are symbolized as s with subscripts to show which value they relate to.

For discussion purposes, it is useful to separate the elements into three groups. The justification for these groupings will become apparent as the results of various experiments are described. The first group (Pb, Ag, Se, and Hg) is composed of elements that readily form volatile species. The second group (Fe, Ni, and Cu) is made up of transition metals that do not as readily form volatile species. The final group (Ca and Mg) is made up of alkaline earth metals.

The emission signals from elements that readily form volatile species were enhanced by any of the organic modifiers. Except for Hg, the enhancement factors are substantially greater with HCOOH than with the other organic modifiers, and enhancements with CH₃COOH are greater than with CH₃CH₂OH. Mercury follows the reverse trend, but the differences in enhancement factors are small.

The emission signals of the remaining transition metals (Fe, Ni, and Cu) showed greater enhancement with CH₃COOH than they showed with HCOOH. CH₃CH₂OH reduced the emission signals from this

group of elements. Iron emission was reduced so much that an enhancement ratio could not be reliably measured. The emission signals of the alkaline earth metals showed little or no enhancement with either HCOOH or CH₃COOH and their emission decreased with CH₃CH₂OH.

While the alkaline earth metals are not known to be amenable to vapor generation, all of the metals that show enhancement in CH_3COOH can be analyzed by photochemical vapor generation under the right conditions [15]. Although there is insufficient evidence to credit vapor generation for the observed enhancements, these patterns suggest that the possibility should be investigated.

No one organic modifier provided the best enhancement for all elements. CH₃CH₂OH suppressed the signal from most of the elements, and it generally provided the lowest enhancement for the others. For the metals that had greater enhancement with than with CH₃COOH HCOOH. the enhancement was no more than 2-fold. HCOOH was chosen for further experiments because it produced large enhancement factors for several metals and did not suppress emission for any metals. The mechanism through which the organic modifier identity affects the enhancement is not known.

In their ac-EALD experiments, Xiao et al. [27] also found that HCOOH gave the greatest enhancement for Ag and Pb, although the differences were more dramatic in their work, with Ag in HCOOH providing approximately 5 times the signal of Ag in CH₃COOH or CH₃CH₂OH and Pb in HCOOH providing approximately 20 times the signal of Pb in CH₃COOH or CH₃CH₂OH.

The effect of HCOOH concentration on analyte atomic emission was tested. These experiments were performed as before except that the HCOOH concentration in the channel usually used for electrolyte flow was varied to give final concentrations in the merged flow of between 0 and 7% by volume. The experiment was repeated 3 times at each HCOOH concentration.

The same three groups will be used to discuss the results. As before, the background-corrected

emission was used. Figure 2 shows the effect of HCOOH concentration on the emission of elements that readily form volatile species (Pb, Ag, Se, and Hg). Figure 3 shows the same for several elements that do not readily form volatile species (Ca, Fe, Mg, Ni, and Cu). The error bars show the standard deviation of 3 replicate measurements for each HCOOH concentration and analyte. Both the signals and the standard deviations were normalized by dividing by the emission without any organic modifier.

The elements in Figure 2 all showed a similar trend with HCOOH concentration. Rising HCOOH concentration caused a sharp increase in emission at first, and then a more gradual increase at higher concentrations. The elements in Figure 3 showed less substantial effects. Their emission was either slightly enhanced or slightly depressed at low HCOOH concentrations. At higher concentrations, there was a gradual increase in emission with increasing HCOOH concentration. These results were in line with those found by Sturgeon et al. in a system where they performed photochemical vapor generation on an aerosol and directed both the vapor and a fraction of the aerosol to an ICP [23]. In that case, they saw evidence for vapor generation of Ag, Se, Hg, and Pb, but not for Cu and Ni. The remaining elements studied here (Fe, Ca, and Mg) were not included in that study.

Xiao et al. found similar trends for Pb, Ag, and Cd in their ac-EALD system [27]. For all three elements, a fairly steep increase in enhancement with rising HCOOH concentration was seen through 3% HCOOH, and the amount of enhancement was roughly constant as concentration rose past this point. Trends were not explored for other elements.

Gręda et al. also found enhancements in a similar system when non-ionic surfactants were added to the sample medium [25, 26]. Although there Pb also showed high enhancement in that study, most of the trends, either as a function of modifier concentration or as function of element, were different from the trends found in our study. For the surfactants that caused large enhancements (Triton x-405 and Triton x-705), the trends in enhancement with surfactant

concentration show sharp increases followed by more gradual increases (not unlike the trends in Figure 2) even for elements we show in Figure 3 (Ca, Cu, Fe, Ni) [26]. Although Hg always showed the greatest enhancement with HCOOH, CH₃COOH, or CH₃CH₂OH, it showed roughly average enhancement for most surfactant conditions, and always showed less enhancement than Pb and Cu [25]. Although there may be some similarities between the mechanisms behind the surfactant enhancement and the enhancement studied here, these differences suggest that the mechanisms are not entirely the same.

HCl was tested as an alternative electrolyte. The experiments were performed as above, but with HCl rather than HNO₃ in the sample and sample carrier flow and with HCOOH in the channel usually used for electrolyte flow. The merged flow was 0.10 mol/L HCl and 7% HCOOH by volume. The resulting enhancement ratios, along with those for the same concentration of HCOOH in 0.10 mol/L HNO₃, are shown in Table 1. No appreciable signal was produced by Ag or Se. The Ag signal suppression can be explained by the formation of insoluble AgCl, but the reason for the Se suppression is unclear. Generally, the difference between the enhancements in the two mineral acids was small, but enhancement factors of around 3 were found for both Ni and Cu in 7% HCOOH and 0.10 mol/L HCl. The mechanism through which the mineral acid identity affects the enhancement is not known.

3.2 Possible enhancement mechanisms

The results discussed above raise the possibility that some form of vapor generation is involved in the enhancement of at least Ag, Se, Hg, and Pb, but further work is required to test this hypothesis.

In solution-electrode discharges, emission generally increases with H^+ concentration [29], although it decreases in at least some designs when very high H^+ concentrations are reached [33]. Adding 3% HCOOH to 0.1 mol/L HNO₃ increases the H^+ concentration by about 0.1%. Adding 3% CH₃COOH to 0.1 mol/L HNO₃ increases the H^+ concentration by about 0.01%. These increases are too small to convincingly explain the dramatic signal enhancements of Pb, Ag, Se, and Hg. They also do not explain the signal enhancements of those elements in CH_3CH_2OH . They may, however, contribute to or even fully explain the smaller enhancements for some other elements.

The physical properties of the solution may also contribute to the enhancement. In nebulizer-based systems, signals can be enhanced by modifying the sample medium. Properties such as viscosity and boiling point correlate with the degree of enhancement [10]. A strong correlation could not be established with these properties in the present study, but one might be found if a larger set of chemical modifiers were tried. It is not clear whether the viscosity can be easily established because there is a steep temperature gradient at the solution-plasma interface, and temperature affects viscosity. Although they were not formed through nebulization, droplets could be seen being ejected from the surface, and were particularly visible when illuminated with a green (532 nm) laser pointer. Schwartz et al. [8] have performed a detailed study on a similar system and have also seen droplets ejected from the cathode surface. A discussion of likely mechanisms can be found in their paper.

3.3 Analytical utility

Future research will be required to explore the various causes behind the observed enhancement, but the remainder of this study was dedicated to determining whether or not the signal enhancement also led to analytical improvements. Using the chemically modified SCGD system described in this paper, calibration curves were created for Mg, Fe, Ni, Cu, Pb, Ag, Se, and Hg. No calibration curve was created for Ca because no strong lines were within of the spectrometer's wavelength range. In these experiments, the electrolyte flow carried both the HNO3 and the HCOOH. After mixing with the sample carrier flow, the acid concentrations were 0.10 mol/L HNO₃ and 4% HCOOH. Information of the calibration curves can be found in Table 2. The upper end of the linear range was not tested for any element, but the highest concentrations included in these calibration curves were 100 μ g/L Ag, 250 μ g/L Hg and Mg, 500 µg/L Cu and Fe, 1000 µg/L Ni and Pb, and 25 mg/L Se.

The detection limits were calculated using the common $3\sigma/m$ definition, where m is the slope of the calibration curve and the σ is the standard deviation of 10 blank injections. The blank injections were treated identically to analyte injections. That is, the signal was acquired at the same delay after injection as was used for the injections containing analytes, the background was subtracted based on a nearby line, and the baseline from after the injection had passed through the system was subtracted. These detection limits are shown in Table 2. For comparison, previously reported detection limits for the same elements by the same SCGD-OES instrument [4] (without chemical enhancement), by a related system with enhancement due to the addition of surfactants [26], by ac-EALD with formic acid[27], and by ICP-OES [34] are also in the table. Detection limits for the elements that readily form volatile species are improved dramatically: Ag, Hg, Pb, and Se detection limits all improved by an order of magnitude. The detection limits of other elements also improved, but less dramatically. The relative standard deviation was measured for triplicate injections using just 0.1 mol/L HNO₃ and triplicate injections using a combination of 0.1 mol/L HNO3 and 4% HCOOH. The results are shown in Table 3. The two sets of relative standard deviations are not very different overall.

The detection limits found in this study are in a similar range to those found for an ICP-OES instrument in a recent paper [34]. Comparisons of detection limits should be treated cautiously, and other sample introduction or viewing modes can improve ICP-OES detection limits, but such comparisons can be tentatively made based on the information in Table 2. The most sizable differences are for Mg, Pb, Se, and Hg. Although the detection limit of Se was improved by an order of magnitude with HCOOH, it is still about an order of magnitude worse than the detection limit by ICP. The detection limits for Mg, Pb, and Hg are all about an order of magnitude or more better by chemically enhanced SCGD than by ICP. The detection limits for other elements are all somewhat worse for chemically enhanced SCGD than for ICP. The detection limits for chemically enhanced SCGD are about an order of magnitude better than for chemically enhanced ac-EALD. The ac-EALD uses significantly lower flow

rates, so the volume of sample needed for an analysis is likely to be smaller, but no sample volume was reported.

As was previously mentioned, an SCGD has been used in a hybrid SCGD-ICP system. The detection limit for mercury was 0.7 μ g/L in that instrument,[18] which is about a factor of 3 better than with the chemically enhanced SCGD system. Although the detection limit for Hg was somewhat better with the hybrid system than with the present system, it came with two important disadvantages. First, it took away the system's ability to detect most elements. In contrast, the present system enhances the detection limits of several elements. Second, the hybrid system is more complicated and expensive than the present system.

Shekhar used a similar instrument with 0.2 mol/L HCl as the electrolyte and 5% CH₃COOH to enhance emission [24]. The only analyte in that study was Hg, and the detection limit found for that element was 2 μ g/L, which is the same as the Hg detection limit found here for 0.1 mol/L HNO₃ and 4% HCOOH. Using Triton x-405 at 5 times its critical micelle concentration, Gręda et al. were able to improve their detection limits by similar or slightly greater factors than those found here [26], but the enhanced detection limits are substantially higher than the SCGD-OES detection limit (see Table 2).

Detection limits for Ni and Cu in 0.10 mol/L HCl and 4% HCOOH were also calculated. Aside from the substitution of HCl for HNO₃, the procedure was the same as was described above. The detection limit of Cu dropped from 6 to 4 μ g/L, and the detection limit of Ni dropped from 6 to 3 μ g/L. These changes are of minor practical and statistical significance, but they

suggest that different elements may have different optimal conditions. Similarly, CH₃COOH produced greater enhancement for Fe, Ni, and Cu. A chemical modifier of 4% HCOOH with 0.1 mol/L HNO₃ was chosen because it gave large enhancements for Pb, Se, Hg, and Ag without a large negative impact on other elements. Although that modifier was a reasonable compromise, different combinations and concentrations of inorganic and organic acids might significantly improve performance for some elements.

Future studies will be needed to evaluate the accuracy of chemically enhanced SCGD, particularly in the presence of metals that are known to interfere with conventional vapor generation. Similarly, future studies should determine what effect, if any, the initial chemical form of the analyte has on the emission signal.

4. Conclusions

Modifying the medium of the sample solution in an SCGD is a simple but potentially useful way to lower the detection limits of several metals. Based on the patterns of the enhancements, vapor generation may account for a large part of this enhancement, but other effects are also probably involved. Trends are similar to those found for a related technique, ac-EALD. Further studies into interferences with chemically enhanced SCGD will be required before it can be applied.

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Element	Wavelength (nm)	Concentration (mg/L)	Enhancement factor in			Enhancement factors in	
			0.1 mol/L HNO ₃ and 3% of:			7% HCOOH and 0.1 mol/L of:	
			HCOOH ^a	CH ₃ COOH ^a	CH ₃ CH ₂ OH ^a	HNO ₃ ^b	HCl ^c
Ca	393.4	1.0	1.10 ± 0.04	0.98 ± 0.03	0.6 ± 0.1	1.90 ± 0.06	2.1 ± 0.1
Mg	285.2	0.5	1.05 ± 0.03	1.11 ± 0.03	0.75 ± 0.02	1.50 ± 0.05	2.09 ± 0.08
Fe	252.3	0.5	1.16 ± 0.04	1.48 ± 0.08	-	1.7 ± 0.1	1.7 ± 0.1
Ni	341.5	0.4	1.04 ± 0.07	1.5 ± 0.1	0.61 ± 0.05	1.3 ± 0.1	3.1 ± 0.2
Cu	324.9	0.4	1.26 ± 0.02	1.99 ± 0.03	0.93 ± 0.07	1.65 ± 0.06	2.84 ±0.07
Pb	406.7	0.4	4.0 ± 0.5	2.5 ± 0.3	1.6 ± 0.2	4.8 ± 0.6	4.1 ± 0.6
Ag	328.1	0.4	6.0 ± 0.2	4.5 ± 0.1	1.93 ± 0.06	8.1 ± 0.3	-
Se	196.1	10	7.2 ± 0.4	2.3 ± 0.1	2.0 ± 0.2	9.1 ± 0.5	-
Hg	253.6	0.4	10.0 ± 0.7	10.6 ± 0.7	12.7 ± 0.5	10.4 ± 0.3	8.7 ± 0.6

Table 1. Standard concentrations, and analytical lines, and enhancement factors. Enhancement factors by organic modifiers expressed as the signal ratio relative to 0.1 mol/L HNO_3 or HCl without organic modifiers.

^a Ratio of signal in 3% organic modifier and 0.1 mol/L HNO₃ to signal in 0.1 mol/L HNO₃.

^b Ratio of signal in 7% HCOOH and 0.1 mol/L HNO₃ to signal in 0.1 mol/L HNO₃.

^c Ratio of signal in 7% HCOOH and 0.1 mol/L HCl to signal in 0.1 mol/L HCl.

All errors are standard deviations calculated by propagating the on the standard deviation of the unenhanced signal (n=3) and the standard deviation of the enhanced signal (n=3).

Element	Coefficient of determination (R ²)		Detection limit (µg/L)					
		Slope (counts s ⁻¹ $\mu g^{-1} L$)	Chemically			dc-APGD-OES	Chemically	
			enhanced	SCGD-OES ^b	ICP-OES ^c	with Triton x-	enhanced ac-	
			SCGD-OES ^a	1		405 ^d	EALD ^e	
Mg	0.9990	53	1	3	20	8	-	
Fe	0.9986	0.63	10	40	3	180	-	
Ni	0.9998	1.2	6	12	3	50	-	
Cu	0.9999	11	6	8	3	20	-	
Pb	0.9997	12	1	10	9	120	45	
Ag	0.9999	100	0.1	1	-	-	1	
Se	0.9988	0.064	300	3000	20	-	-	
Hg	0.9995	3.6	2	20	50	130	-	

Table 2. Calibration curve information and comparison of detection limits

^a Present study, using a sample medium of 0.1 mol/L HNO₃ and 4% HCOOH.

^b Earlier study with the same instrument, using a sample medium of 0.1 mol/L HNO₃ [4].

^c ICP-OES using pneumatic nebulization and radial observation [34].

^dDirect-current atmospheric pressure glow discharge with Triton x-405 at 5 times its critical micelle concentration [26].

^eAlternating-current electrolyte atmospheric liquid discharge with 3% HCOOH.[27]

Table 3. Comparison of short term precision (n=3) for chemically enhanced SCGD-OES (0.1 mol/L HNO₃ and 4% HCOOH) and SCGD-OES (0.1 mol/L HNO₃)

		Relative standard deviation (%)			
Element	Concentration (µg/L)	Chemically enhanced SCGD-OES	SCGD-OES		
Mg	250	1.0	2		
Fe	250	3	4		
Ni	100	3	4		
Cu	250	1.1	3		
Pb	250	3	3		
Ag	100	0.9	-		
	250	-	3		
Se	10000	4	8		
Hg	250	3	6		



Figure 1. Typical injection and signal processing, shown for 250 ppb Mg in 0.1 mol/L HNO₃ and 4% HCOOH. The following events are labeled: (a) injection, (b) beginning of peak integration, (c) end of peak integration, (d) beginning of baseline integration, and (e) end of baseline integration.



Figure 2. Enhancement (with standard deviation error bars, n=3) as a function of HCOOH concentration for elements that readily form volatile species.



Figure 3. Enhancement (with standard deviation error bars, n=3) as a function of HCOOH concentration for Ca, Fe, Cu, Mg, and Ni.