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

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ABSTRACT

HCOOH, CH_3COOH, and CH_3CH_2OH 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 HNO_3 compared to using HNO_3 alone. The DL was measured for Mg (1 μg/L), Fe (10 μg/L), Ni (6 μg/L), Cu (6 μg/L), Pb (1 μg/L), Ag (0.1 μg/L), Se (300 μg/L), and Hg (2 μg/L). Coefficients of determination (R^2) were between 0.9986 and 0.9999. A voltage of 1 kV was used, which produced a current of approximately 70 mA.

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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 μg/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, CH_3COOH, and CH_3CH_2OH) 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

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system is an extreme case of this; As, Se, Pb, and 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% CH_3COOH 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, CH_3COOH, and CH_3CH_2OH 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 17-fold 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 HNO_3 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 Fig. 1. Briefly, the emission signal and a signal at a nearby wavelength were both acquired during a 30-second interval at a fixed delay after the injection time. Within this 30-second acquisition, a number
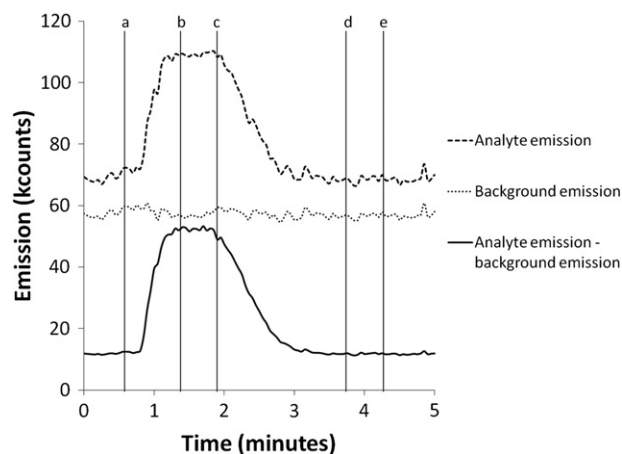

Fig. 1. Typical injection and signal processing, shown for 250 ppb Mg in 0.1 mol/L HNO_3 and 4% HCOOH. The following events are labeled: (a) injection, (b) beginning of peak integration, (c) end of peak integration, (d) beginning of baseline integration, and (e) end of baseline integration.

of individual readouts of the charge coupled device (CCD) detector were made. For Ni, Se, and Hg, the CCD integration time was 5 s. For Fe, the CCD integration time was 4 s. For other elements, the CCD integration time was 3 s. The emission was roughly constant during the 30-second 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 HNO_3 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). HNO_3 (Optima grade, Fisher Scientific), HCl (trace metal grade, Fisher Scientific), HCOOH (analysis grade, Acros Organics), CH_3COOH (Optima grade, Fisher Scientific), and CH_3CH_2OH (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.