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Determination of trace heavy metals in environmental and biological samples by solution cathode glow discharge-atomic emission spectrometry and addition of ionic surfactants for improved sensitivity

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ABSTRACT

Solution cathode glow discharge-atomic emission spectrometry (SCGD-AES) was evaluated for its ability to determine toxic heavy metals, including cadmium (Cd), mercury (Hg), lead (Pb), and chromium (Cr), in environmental and biological samples. A significant enhancement in heavy metal signal was observed by addition of a small amount of cetyltrimethylammoniumchloride (CTAC, C₁₆H₃₃(CH₃)₃NCl) to the samples. The net intensity of atomic emission lines of Cd, Hg, Pb, and Cr increased by 2.1-, 4.8-, 6.6-, and 2.6-fold, respectively, after addition of 0.15% CTAC to the test solutions. The effects of ionic surfactants (CTAC) compared with non-ionic surfactants, e.g., Triton x-45 and Triton x-100, on the sensitivity of Cd, Hg, Pb, and Cr were also investigated in the present study. The enhancement effect is in the order Triton x-45 < Triton x-100 < CTAC for Hg, Pb and Cr and Triton x-45 < CTAC < Triton x-100 for Cd. Addition of CTAC to the electrolyte solutions decreased the background intensity and fluctuation of atomic emission lines of studied metals. It also changed the surface tension and the viscosity, and increased average discharge current of electrolyte solution. SCGD sensitivity to the heavy metals greatly improved by addition of the surfactant. The improved detection limits of Cd, Hg, Pb, and Cr were 1.0, 7.0, 2.0, and 42 ng mL⁻¹, respectively. The proposed method was validated by quantifying Cd, Hg, Pb, and Cr in certified reference materials, including human hair (GBW 09101b) and stream sediment (GBW 07310 and GBW07311). Measurement results obtained for the determination of Cd, Hg, Pb, and Cr in the reference materials agreed well with reference values. This study improves the application of SCGD-AES in quantifying very low levels of Cd, Hg, Pb, and Cr from biological and environmental materials.

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1. Introduction

Heavy metal pollution resulting from human activities and industrial development is an outstanding environmental issue that presents serious threats to human health. Determination of heavy metals in environmental and biological samples, especially lead (Pb), chromium (Cr), cadmium (Cd) and mercury (Hg), is a primary concern because these metals exhibit high toxicity and biological magnification [1–4]. Strict regulations for maximum allowable concentrations of poisonous and harmful heavy metals in the environment have been established around the world.

Several methods by which to determine and monitor low concentrations of heavy metals, such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry

(ICP-MS), have been developed. However, these methods present several shortcomings, often requiring complicated equipment and manipulation because of the size of the instruments, high gas and power consumption, and the need for vacuum equipment (for ICP-MS). These disadvantages limit the application of the methods to the laboratory and prevent their use in rapid analyses under field conditions. To meet the requirements of rapid detection and field utilization, more compact, low cost, and portable instruments are required for determining trace heavy metals.

In recent years, atmospheric pressure discharge technology has emerged as an important tool in atomic spectrum analysis [5–22]. Electrolyte cathode discharge (ELCAD), also called solution cathode glow discharge (SCGD), is considered a very promising alternative miniaturized excitation source that possesses potential advantages over commercially and analytically successful plasma sources [5–8]. In 1887, the first glow discharge (GD) apparatus to use a solution as an electrode was described by Gubkin [9]. Despite observations of atomic emissions from GD throughout the 1950s and 1960s, a GDE-like system, the ELCAD, was specifically

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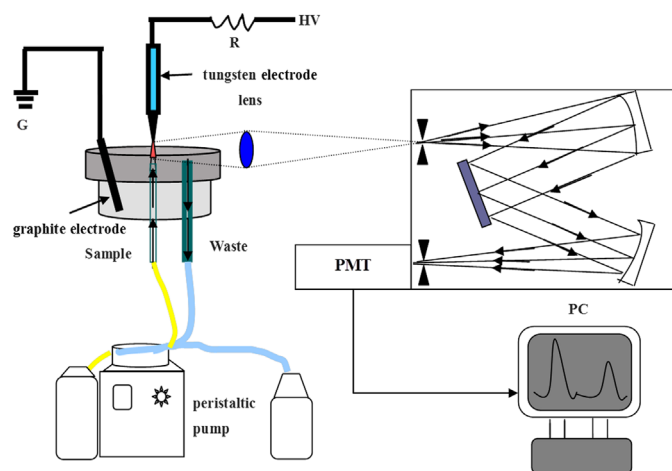


Fig. 1. Schematic diagram of the experiment setup.

designed for elemental analysis only in 1993 [10,11]. Since then, significant variations of the ELCAD design have been developed [12–22]. Aside from the solution-electrode sources described above, liquid sampling-atmospheric pressure glow discharge (APGD) [23], drop-spark discharge [24], electrolyte jet cathode glow discharge [25], and liquid electrode spectral emission chip [26] have also been studied. The use of aqueous solutions as electrodes has been summarized in recent reviews [27–30].

SCGD in combination with AES (SCGD-AES) can be applied in process control or environmental monitoring studies for direct trace element analysis of various aqueous samples [7,12–22]. The performance of SCGD-AES is in many ways comparable with that of more expensive ICP optical emission instruments, and the technique features several advantages such as low power consumption (~ 75 W), no requirement for compressed gasses, small (~ 2 mm³) plasma, and low construction and operating costs [28]. Such distinctive features make it highly desirable for the direct and on-line optical emission spectrometric determination of trace metal impurities in different samples. Recent studies show that SCGD-AES can provide detection limits (DLs) for several metals, such as lithium, sodium, or potassium, at or below the tens of parts per billion ranges [31,32].

In many situations, available ELCAD or SCGD systems provide Cd, Hg, Pb, and Cr DLs higher than tens of parts per billion, which does not meet the requirements for quantifying heavy metals at very low levels in environmental and biological samples. The development of new approaches to improve the emission characteristics and analytical performance of current ELCAD systems may be achieved through modification of the composition and physicochemical properties of the electrolyte solutions serving as liquid cathodes. Addition of low-molecular weight organic compounds, such as alcohol, formic acid, and acetic acid [33], as well as non-ionic surfactants, including Triton X-45 and Triton X-405, results in higher emission signals compared with those obtained without the addition of such media [34,35]. In a previous study, in comparison with detection results obtained under conditions without addition of organic compounds to the electrolyte solutions, addition of 5% (v/v) acetic acid resulted in maximum enhancement of Hg detection [33]. The DL for Hg was also enhanced from 10 to 2 ng mL⁻¹, which is believed to be due to changes in the boiling point and surface tension of electrolyte solutions [33], as well as the presence of H and CO radicals involved in the reduction of Hg(II) ions to Hg(0) vapors [2]. On the other hand, the presence of non-ionic surfactants in electrolyte solutions serving as liquid cathodes in dc-APGD results in increases in viscosity and decreases in the dynamic surface

tension, leading to potential increases in the sputtering rate of dissolved components of the solution (metal ions) and potential decreases in the vaporization rate of water (particularly for Triton X-405) [34].

The use of low-molecular weight organic substances to improve sensitivity has been explored only for Hg. The effects of non-ionic surfactant addition on the spectral parameters as well as mechanism of APGD have been investigated. The performance of the proposed technique in elemental analysis has not been explored, and, to the best of our knowledge, no references on the usability of ionic surfactants with the SCGD-AES technique or applications of such a system are available. Considering that cetyltrimethylammoniumchloride (CTAC, C₁₆H₃₃ (CH₃)₃NCl) is a widely used cationic surfactant, its presence is likely to enhance sensitivity to metals.

In this work, the construction of an SCGD-AES system and the influence of different CTAC concentrations on its sensitivity were examined to predict changes in its performance as well as the atomic emission characteristics of heavy metals. The proposed method was then applied for the determination of Cd, Hg, Pb, and Cr in certified reference materials (CRMs), including human hair (GBW 09101b) and stream sediment (GBW 07310 and GBW07311).

2. Experimental

2.1. Instrumentation

A schematic diagram of the experimental setup is presented in Fig. 1. A Kepco (Flushing, NY) BHK 2000–0.1 MG high-voltage power supply was used in constant voltage mode. To limit the discharge current, a 1.2 k Ω ballast resistor was introduced in series with the anode. A peristaltic pump (Gilson, France) with two channels was used to pump sample solutions and carry waste solutions from the overflow reservoir. The discharge was imaged at a magnification of 2.3:1 by a quartz lens positioned on the vertical entrance slit of a monochromator (Princeton Instruments, Action SP 2500, USA) equipped with a photomultiplier biased at 700 V was used as the detector. Emission spectra were recorded with an integration time of 0.5 s at 0.05 nm intervals. Spectrasense (Princeton Instruments) version 4.4.6 software was used to operate the spectrometer, control its configuration, and collect and process the data. An Edmund Optics (Barrington, NJ, USA) GG 475 long-pass filter (greater than 88% transmission above 500 nm and less than 0.1% transmission below 460 nm) was used to block second-order emissions.

A closed microwave digestion system (Model: EXCEL 2010, PreeKem, China) was used for sample digestion. The digestion solutions were measured using a VISTA AX ICP-AES spectrometer with an axially viewed configuration (Varian, USA) and a Thermo X II Series ICP-MS spectrometer (Thermo Fisher, USA), and results were compared with values measured by SCGD-AES. Wavelengths used for SCGD determination are as follows Cd I, 228.8 nm; Hg I, 253.7 nm; Pb I, 368.3 nm; and Cr I, 357.9 nm. The spectrum line Cd I, 228.8 nm; Hg I, 253.7 nm; Pb II, 220.4 nm; and Cr, II 267.7 nm was used in axial-view ICP-AES. Isotopes of ¹¹²Cd and ²⁰²Hg were monitored by the ICP-MS spectrometer.

2.2. SCGD cell design and excitation source acquisition

The SCGD setup used in this work is similar to the one used in a previous study [31]. An SCGD cell was mounted on a platform equipped with three independent micrometer screw gauges so that it could be adjusted precisely in the x, y, and z directions to accurately position the plasma, obtain maximum signals, and focus the discharge image into the monochromator entrance slit. The sample-inlet pipette was oriented vertically in this SCGD cell. A second glass pipette was

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