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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, $C_{16}H_{33}(CH_3)_3NCl$) 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.

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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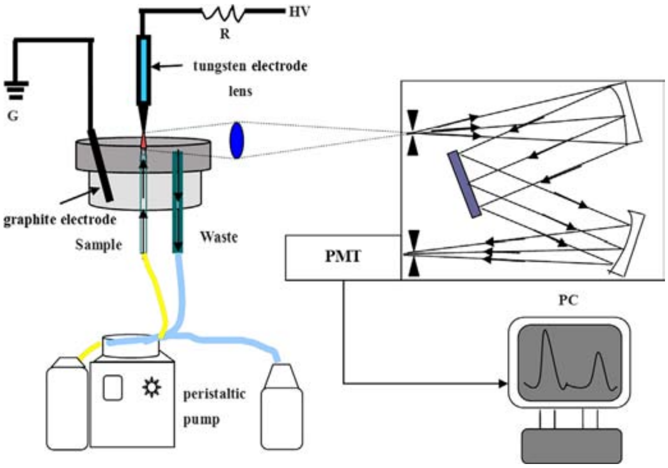

Fig. 1. Schematic diagram of the experiment setup.

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 mm^3) 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 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, $C_{16}H_{33}$ $(CH_3)_3NCl$) 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 kΩ 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 ^{112}Cd and ^{202}Hg 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 positioned vertically in the waste reservoir to draw waste solution away at the same rate by which new solution enters the cell, keeping the solution level in the waste reservoir constant. Electrolyte solutions adjusted to pH 1.0 with nitric acid (HNO_3) were delivered upward at a suitable flow rate through a glass tube. The quartz capillary used was s a 10 μL disposable micropipette (Fisher Scientific Co., Pittsburgh, PA, USA) with a 1.1 mm outer diameter and a 0.38 mm inner diameter. Stable plasma was maintained in an open-to-air atmosphere between a 2.4 mm outer diameter tungsten rod and the overflowing electrolyte solutions after application of a high voltage. A tungsten rod that tapered to a rounded point was positioned approximately 3 mm above the top of the glass tube as the anode, and the overflowing electrolyte solutions acted as the cathode. The solution was connected to an electrical ground through graphite. To reduce signal fluctuations induced by the pump, a simple and inexpensive custom-built pulse dampener consisting of a knotted peristaltic-pump tubing was inserted between the pump and the discharge.

2.3. *Reagents and samples*

Deionized water (≥ 18.25 MΩ cm^{-1} resistivity) was obtained by passing through a water purification system (AWL-1002-U, Aquapro, China) in our laboratory. Working standards of heavy metals (Cd, Hg, Pb, and Cr) of 1 mg L^{-1} were prepared by appropriate dilution from corresponding single-element 1000 mg L^{-1} stock solutions supplied by Shanghai Institute of Measurement and Testing. All of the sample solutions were acidified to pH 1.0 with HNO_3 (Sigma-Aldrich, ACS reagent, 65%). The pH of the solutions was measured by a pH meter (PHS-3E, INESA, China). CTAC (Sinopharm, analytical reagent-grade) was added to the working standards of metal solutions at mass percentages of 0%, 0.05%, 0.10%, 0.15%, and 0.20% for SCGD analysis. Non-ionic surfactants, e.g., Triton x-45[$C_{14}H_{22}(C_2H_4O)_{4.5}$] and Triton x-100 [$C_{14}H_{22}(C_2H_4O)_{9.5}$] were provided by Sigma-Aldrich. Values of CMCs were 0.10 and 0.24 mmol L^{-1}, respectively, for Triton x-45 and Triton x-100. Non-ionic surfactants were added to sample solutions and the final concentration of the surfactant corresponded to its 10 × CMC. CRMs, human hair (GBW 09101b) and stream sediment (GBW 07310 and GBW07311), were used to study the applicability of the proposed method.

2.4. *Digestion of reference materials and preparation of samples with CTAC medium*

Human hair (0.2 g) was weighed into PTFE digestion vessels, mixed with concentrated HNO_3 (5 mL), and then left to pre-digest at room temperature for an hour. The process blank was prepared in an identical manner but without addition of the sample. All of the vessels were tightly capped, placed in the microwave oven, and subjected to program 1, as shown in Table 1. The vessels were then allowed to cool to ambient temperature.

Stream sediment samples (0.1 g) were accurately weighed into PTFE digestion vessels. After addition of a small amount of water to wet the samples, 6 mL of HNO_3, 2 mL of hydrogen peroxide, and 3 mL of hydrofluoric acid were mixed into the solution. Samples were left for pre-digestion at room temperature overnight. The process blank was prepared in an identical manner but without addition of the sample. All of the vessels were then tightly capped, placed in the microwave digestion instrument, and subjected to program 2, as shown in Table 1. The vessels were allowed to cool to room temperature. Two samples were evaporated to near dryness using a heating platform. These samples were then separately diluted to 20 and 10 mL and maintained at pH 1.0 with HNO_3.

Table 1
Digestion program of the microwave system.

Step no.	Ramp time (min)	Pressure limits (atm)	Temperature (°C)	Hold time (min)
Program 1				
1	2	10	100	2
2	2	15	150	2
3	3	20	180	10
Program 2				
1	5	20	120	5
2	5	25	180	5
3	5	30	210	25

Adequate amounts of CTAC were weighed into beakers separately. Samples were then added to beakers and left to rest until the CTAC had completely dissolved. The final mass percentage of CTAC in the beakers was 0.15%.

3. Results and discussion

In the SCGD system, each sample acting as an electrode was acidified to pH 1.0 with HNO_3. Under the applied voltage, the plasma self-ignited when the gap between the metal rod electrode and the solution electrode was reduced to approximately 1 mm. In the SCGD cell, low flows of 1.5 mL min^{-1} were adequate to produce stable plasma at atmospheric pressure. These findings, along with other analytical characteristics, are described in more detail in the paragraphs that follow.

3.1. *Initial characterization and optimization*

The analytical characteristics of the proposed technique were evaluated under preliminary conditions (electrode gap of 3 mm, slit width of 50 μm, and integration time of 0.5 s). Light was collected from the negative glow, a spot of approximately 0.6 mm diameter positioned 1 mm above the top of the center of the capillary. The background emission spectrum of the new SCGD was obtained using a solution of 0.1 M HNO_3, as shown in Fig. 2. Similar to most other solution-electrode discharges, the spectrum of the background was strong in several regions, particularly near the Mg I line at 285.2 nm. The most intense emission was obtained from OH radicals, atomic hydrogen, atomic and ionic oxygen, and molecular nitrogen. The plasma was notably in contact with the tungsten electrode but no tungsten lines were observed.

Based on the initial study, solutions of 1.0 mg L^{-1} Cd and Hg and the aqueous blank adjusted to pH 1.0 with HNO_3 were chosen as model analytes to further investigate the characteristics of the SCGD system. To optimize emission signals and DLs, the effects of voltage and sample introduction flow rate on the emission intensities of Cd and Hg were evaluated. Each of the 11 continuous measurements of

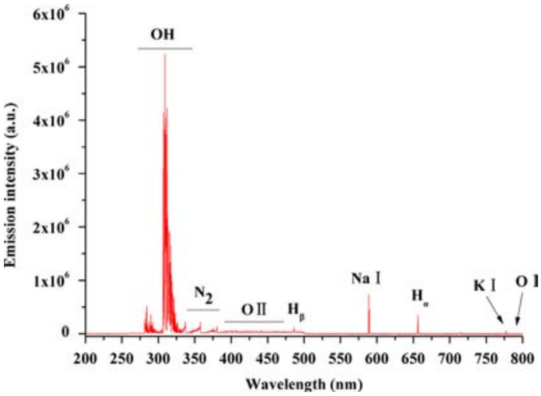

Fig. 2. Background (aqueous blank adjusted to pH 1.0 with HNO_3) spectrum of the SCGD.

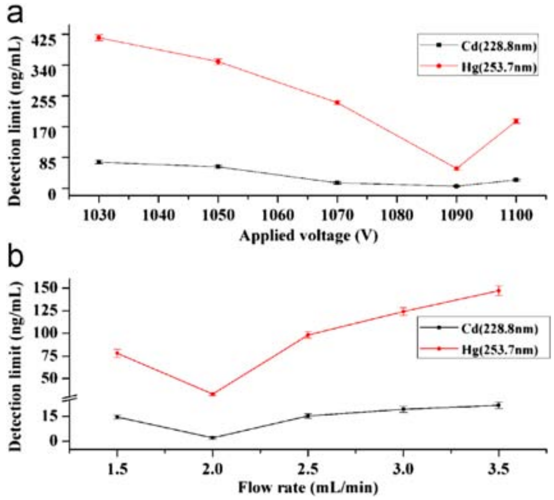

Fig. 3. Optimization of applied voltage (a) and solution flow rate (b). Electrode gap were held constant at 3 mm.

blank emission signals was obtained at the analytical wavelength from a blank solution for calculation. The DL was obtained using the definition $3km^{-1}$, where k is the standard deviation corresponding to 11 continuous measurements of the blank samples and m is the slope of the calibration graph. Multiple readings ($n=20$) for each analyte solution and the acid blank solution were recorded. For optimization studies, the minimum DLs were designated as the analytical parameter to be evaluated.

(a) Optimization of applied voltage. An aqueous standard solution containing 1 mg L^{-1} of both Cd and Hg was used as a test sample to further optimize the discharge performance of the SCGD system. The first parameter evaluated using this approach was the applied potential, the results for which are shown in Fig. 3a. For this test, the inter-electrode gap was maintained at 3.0 mm and the solution flow rate was maintained at 2.5 mL min^{-1}. From 1030 to 1090 V, an approximately linear increase in analyte emission with voltage was found. However, the emission began to level off at potentials ranging from 1090 to 1100 V. The DLs obtained at an applied potential of 1090 V (current, 70 mA; power, 76.3 W) were minimal. Thus, an applied potential of 1090 V was employed in subsequent experiments.

(b) Effect of solution flow rate. The effect of sample-solution flow rate on the system performance was determined with the electrode gap and applied voltage held constant at 3.0 mm and 1090 V, respectively. The atomic emission increased slightly at flow rates ranging from 1.5 to 2.0 mL min^{-1} and subsequently decreased slightly at flows ranging from 2.0 to 3.5 mL min^{-1}, as shown in Fig. 3b. Strong emissions at flow rates ranging from 1.5 to 2.0 mL min^{-1} may be attributed to increases in the amount of analyte entering the discharge. The slightly lower atomic emission observed at higher flows may be a consequence of additional water loading, which could reduce the energy in the discharge, and minimal effects of flow on the discharge gap. Because emission was highest at a flow rate of 2.0 mL min^{-1}, this rate was employed in further experiments.

3.2. Effect of surfactant addition on the atomic emission spectra of metals

Surfactants are known to decrease the surface tension of water samples. The effects of CTAC on the Cd, Hg, Pb, and Cr emission signals were investigated using SCGD-AES, and the usability of CTAC with the SCGD-AES technique for the determination of these heavy metals at 1 mg L^{-1} was examined.

An initial set of solutions of 1 mg L^{-1} Cd, Hg, Pb, and Cr and their corresponding blank solutions containing 0.05%, 0.10%, 0.15%, 0.20%, and 0.25% (mass fraction) CTAC were separately prepared using HNO_3. Emission signals of Cd, Hg, Pb, and Cr were recorded from all of the solutions using SCGD-AES. Higher currents were observed in sample solutions with CTAC than in solutions without CTAC. Moreover, the discharge plasma in the five sample solutions containing varying mass fractions of CTAC was unstable only with 0.25% surfactant. Corresponding blank solutions (without Cd, Hg, Pb, and Cr) were also prepared, and emission signals of Cd, Hg, Pb, and Cr were measured for all of the solutions using SCGD-AES.

Addition of different concentrations of CTAC to the Cd, Hg, Pb, and Cr solutions yielded varying degrees of enhancement compared with results obtained without the surfactant. Amplification factors obtained with the addition of different CTAC concentrations are summarized in Table 2. All net intensities of the atomic emission lines were measured six times and averaged. Considering the net intensities of the atomic emission lines of the metals studied without the surfactant in the electrolyte solution, the magnitude of intensity amplification depended on the concentration of the surfactant (Table 2). The highest signal enhancement was obtained by addition of 0.15% CTAC to the samples. Maximum net intensities of atomic emission lines for Cd, Hg, Pb, and Cr solutions with 0.15% CTAC respectively increased by 2.1-, 4.8-, 6.6-, and 2.6-fold compared with sample solutions without CTAC. Among the studied metals, Pb showed the highest signal enhancement. Therefore, 0.15% of CTAC was selected for further studies.

In the present study, 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

Table 2
Amplification of the net intensities of atomic emission lines of Cd, Hg, Pb, and Cr solutions with addition of CTAC.

Element, nm	**CTAC**			
	0.05%	**0.10%**	**0.15%**	**0.20%**
Cd, 228.8	1.5	1.9	2.1	1.6
Hg, 253.7	2.3	3.1	4.8	3.0
Pb, 368.3	3.0	3.7	6.6	3.3
Cr, 357.9	1.7	2.4	2.6	2.0

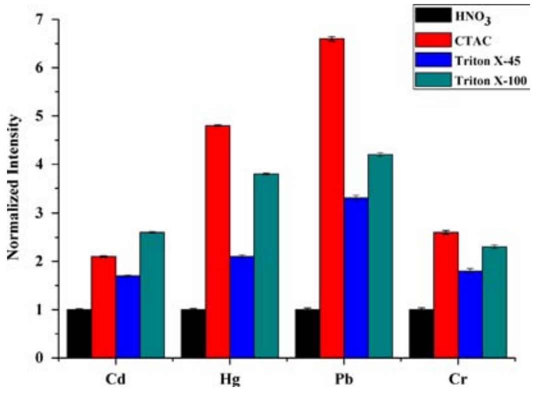

Fig. 4. Enhancement effect of different surfactants (0.15% CTAC, 10 × CMCs of Triton x-45 and Triton x-100) on the emission intensity of Cd, Hg, Pb and Cr, which used normalized intensity base on emission intensity of their corresponding solutions without surfactants. Error bars in the figure represent standard deviations of six replicates (electrolyte: HNO_3, pH=1.0; applied voltage: 1090 V; flow rate: 2.0 mL min^{-1}).

investigated. Solutions of Cd, Hg, Pb, and Cr at 1 μg mL^{-1} containing 0.15% CTAC, 10 × CMC of Triton x-45 and Triton x-100 as well as their corresponding solutions without such surfactants were prepared using nitric acid (pH 1.0). The results of the comparison were shown in Fig. 4. It was observed that all these surfactants could enhance the emission intensity of Cd, Hg, Pb and Cr. 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. The enhancement of CTAC is better than that of Triton x-45 and Triton x-100 in the present work, except for Cd. In addition, the enhancement result of Triton x-45 and Triton x-100 was in agreement with the study of Greda [35].

3.3. Spectral characteristics and enhancement mechanism

The emission spectrums of the plasma were recorded in the presence of 0.15% CTAC and compared with that without CTAC. Solutions of cadmium (5 μg mL^{-1}), mercury 10 μg mL^{-1}), lead (10 μg mL^{-1}) and chromium (10 μg mL^{-1}) with 0.15% CTAC in nitric acid (pH = 1.0) were prepared and tested. It showed typical emission spectra ranging from 200 to 500 nm from Fig. 5. The background emission spectral characteristics in the presence of CTAC (Fig. 5b) were similar to those without CTAC (Fig. 5a). A considerable decline in the intensity of background and fluctuation from 200 to 500 nm, and substantial decreases in OH and N_2 emission intensities were also observed in the presence of CTAC. However, the atomic spectral lines of Cd I (228.8 nm), Hg I (253.7 nm), Pb I (368.3 nm) and Cr I (357.9 nm) were much more stronger in the presence of CTAC and those of Pb I (406.1 nm) were also obvious (Fig. 5b) compared with that without CTAC (Fig. 5a).

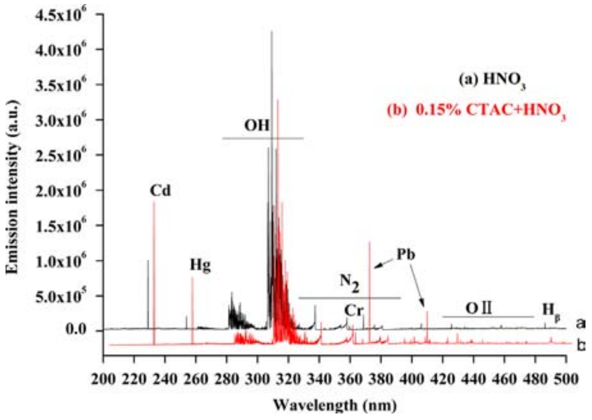

Fig. 5. Typical spectrum of SCGD in the presence of 0.15% CTAC (m/v) (b) and without CTAC (a) spiked with Cd (5 μg mL^{-1}), Hg (10 μg mL^{-1}), Pb (10 μg mL^{-1}) and Cr (10 μg mL^{-1}). In order to better distinguish and contrast results, curve b (red) is relative to curve a (black) on the horizontal displacement of 5 nm and on the vertical displacement of 2.5×10^5 a.u. in the same coordinate system (electrolyte: HNO_3, pH = 1.0; applied voltage: 1090 V; flow rate: 2.0 mL min^{-1}).

According to above observations, we proposed the possible enhancement mechanism of SCGD by CTAC. First, the signal enhancement may be due to decreases of the background intensity and fluctuation of atomic emission lines of studied metals achieved in conditions of the presence of CTAC in the electrolyte solutions. Signal enhancement as well as fluctuation decrease of the background signal directly resulted in the improvement of detection limits. Second, the presence of added CTAC may change the surface tension and increase the viscosity of electrolyte solution, which could allow metals to stay in their excitation states longer in SCGD. Longer excitation states improve vaporization rates and might directly increase the concentration of positive ions in the near-cathode zone of the discharge [34]. Finally, the increased average discharge current with addition of CTAC to the electrolyte solution caused a corresponding increase in excitation temperature and ion density of the plasma, which directly resulted in improvement in element excitation efficiency.

3.4. Analytical performance of SCGD-AES with CTAC

The analytical performance of SCGD-AES with addition of CTAC to the test solutions was evaluated in terms of heavy metal DLs and repeatability, which was expressed as relative standard deviation (RSD), as shown in Table 1. The bias voltage of the photomultiplier tube was set to 700 V and an integration time of 0.5 s was used. Cd, Hg, Pb, and Cr solutions of 1 mg L^{-1} mixed with 0.15% CTAC, as well as blank solutions, were used to determine the DLs and measurement precision of the technique. The DLs of the proposed SCGD system were compared with those of other liquid discharge systems (cf. Table 3). SCGD heavy metal

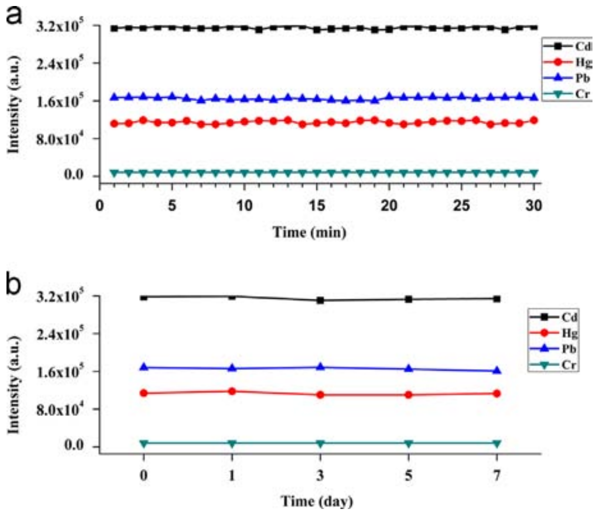

Fig. 6. Stability of emission signals of 1 μg mL^{-1} Cd, Hg, Pb and Cr after adding 0.15% CTAC over half an hour (a) and in a week (b) (electrolyte: HNO_3, pH = 1.0; applied voltage: 1090 V; flow rate: 2.0 mL min^{-1}).

Table 3
Analytical performance of SCGD-AES after addition of CTAC to Cd, Hg, Pb, and Cr solutions.

Element, nm	LD (ng mL^{-1})						
	Present Work	Present Work RSD (%)	Continuous[7] SCGD	Earlier[5] SCGD	ELCAD[36]	ICP-AES[b]	ELCAD[33]
Cd, 228.8	1	1.8	2	9	5	2	
Hg, 253.7	7	1.1	22	350	15	30	2
Pb, 368.3	2	1.7	6	82	45	20	
Cr, 357.9	42	0.8			200[a]	10	

[a] Values are from Kim et al. [16].

[b] Values are from axial-view ICP-AES. The more sensitive ion lines of Pb II 220.4 nm and Cr II 267.7 nm were used.

Table 4
Comparison of Cd, Hg, Pb, and Cr concentrations determined by SCGD-AES and ICP-AES/MS in CRMs with corresponding certified values.

Sample	Element	Certified value ($\mu g\ g^{-1}$)	SCGD-AES value ($\mu g\ g^{-1}$)	ICP-AES/MS value ($\mu g\ g^{-1}$)
Human hair (GBW09101b)	Cd	0.072 ± 0.010	–	0.067 ± 0.009[a]
	Hg	1.06 ± 0.28	1.01 ± 0.09	1.03 ± 0.07[a]
	Pb	3.83 ± 0.18	3.68 ± 0.19	3.74 ± 0.22
	Cr	8.74 ± 0.97	8.66 ± 0.59	8.68 ± 0.81
Stream sediment (GBW07310)	Cd	1.12 ± 0.08	1.04 ± 0.11	1.07 ± 0.15
	Hg	0.28 ± 0.03	–	0.26 ± 0.01[a]
	Pb	27 ± 2	25 ± 3	24 ± 3
	Cr	136 ± 10	132 ± 9	133 ± 9
Stream sediment (GBW07311)	Cd	2.3 ± 0.2	2.0 ± 0.1	2.1 ± 0.2
	Hg	0.07 ± 0.009	–	0.06 ± 0.006[a]
	Pb	636 ± 22	637 ± 15	633 ± 17
	Cr	40 ± 3	39 ± 2	38 ± 2

For ICP-AES determination of Pb and Cr, sensitive lines at 220.4 and 267.7 nm, respectively, were used.

[a] ^{112}Cd and ^{202}Hg isotopes were determined by a Thermo X II Series ICP–MS spectrometer.

sensitivity greatly improved with the addition of CTAC. The improved DLs are comparable with, and even better than, published values. For example, the DLs of SCGD-AES were better than those obtained by axial-view ICP-AES, except for Cr, which uses the more sensitive ionic line Cr II, 267.7 nm. In case of Cr, the less sensitive atomic line Cr I 357.9 nm used in the present study and its interference in the vicinity of the analytical line are likely related to higher DL than ICP-AES (Table 3). The DL of Hg determined by SCGD-AES was 7 ng mL^{-1}, which is better than published values except for reported by Shekhar (2 ng mL^{-1}) [33]. In addition, repeatability, which is expressed as the RSD of six replicates, ranged from 0.8% to 1.8% for analytes at 1 mg L^{-1}.

The stability of the plasma was also monitored by means of recording the emission intensities of elements at fixed wavelengths. Fig. 6 showed the emission intensities of solutions of 1 μg mL^{-1} Cd, Hg, Pb, and Cr mixed with 0.15% CTAC over half an hour (a) and in a week (b) after the plasma was stabilized for 30 min. The RSD (n=30) of the signal over half an hour was computed and found to be 1.7%, 2.8%, 2.0% and 2.3% for Cd, Hg, Pb, and Cr, respectively, which were better than those without CTAC (2.3%, 3.8%, 3.4% and 4.3%, respectively). In addition, The RSD (n=5) of the signal in a week was also computed and found to be 3.8%, 4.9%,4.3% and 6.2% for Cd, Hg, Pb, and Cr, respectively. The results indicated that the emission signal in the intra-day or inter-day in the presence of CTAC has a good stability and reproducibility.

3.5. *Determination of elemental impurities in certified references*

SCGD-AES was used for the direct determination and quantification of Cd, Hg, Pb, and Cr in CRMs. Two CRMs, human hair and stream sediment, were used, and the materials were accurately weighed prior to digestion by a microwave system.

The conditions used for SCGD-AES quantitative measurement were identical to those described above. Concentrations of Cd, Hg, Pb, and Cr in the CRMs were determined using the standard addition method. All of the measurement results and reference values are listed in Table 4. Measurement results obtained by SCGD agreed well with the reference values as well as corresponding values obtained by ICP-AES/MS. Such results indicate that SCGD can be employed for the quantitative determination of trace elements in biological and environmental samples. The concentration of Hg in human hair can be directly detected by SCGD-AES but not by ICP-AES, which indicates that the former technique has a slight advantage over the latter method. The concentration of Cd in human hair and that of Hg in the stream sediment were below the DL of the improved method. Thus, determination of these elements may require pre-concentration of the elements or matrix separation.

SCGD has a very simple emission spectrum. Ionic emission lines are rare and only atomic emission lines are observed for most elements. Although very low ionic emission is expected in the SCGD spectra, matrix interferences do exist to some extent in the improved method. Matrix effects caused by sample constituents other than the analyte are a problem in any analytical method. Therefore, the standard addition method was used to directly measure the samples in the presence of a matrix. The effectiveness of Mn, Ti, Al, Fe, Mg, Ca, Na, K, Zn, PO_4^{3-}, and SO_4^{2-} as matrices was investigated. The maximum total matrix concentrations of Mn, Ti, Al, Fe, Mg, Ca, Na, K, Zn, PO_4^{3-}, and SO_4^{2-} in the solution were 25, 20, 400, 50, 25, 70, 40, 30, 5, 50, and 10 μg mL^{-1}, respectively. Thus, these interfering elements do not significantly affect the determination of heavy metals.

4. Conclusions

Addition of the ionic surfactant CTAC to electrolyte solutions resulted in a decrease in dynamic surface tension, an increase in power density, and improvements in excitation efficiency, resulting in the enhanced sensitivity of SCGD-AES toward Cd, Hg, Pb, and Cr. CTAC at 0.15% (mass percentage) showed maximum enhancement of emission signals. The net intensity of atomic emission lines of Cd, Hg, Pb, and Cr solutions with CTAC improved by 2.1-, 4.8-, 6.6-, and 2.6-fold, respectively, compared with solutions without CTAC. The DLs of Cd, Hg, Pb, and Cr were 1.0, 7.0, 2.0, and 42 ng mL^{-1}, respectively. The proposed method was used to determine Cd, Hg, Pb, and Cr concentrations in human hair and stream sediment, and results confirmed the improved sensitivity of SCGD-AES for quantifying heavy metals at very low concentrations in biological and environmental samples.

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