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Significant sensitivity improvement of alternating current driven-liquid discharge by using formic acid medium for optical determination of elements

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ABSTRACT

A method has been developed to improve the performance of alternating-current electrolyte atmospheric liquid discharge (ac-EALD) optical emission spectrometry for the determination of elements. Significant enhancement of emission intensity was achieved by adding organic substance into the nitric acid electrolyte solutions. Under the optimized conditions, 3% (v/v) formic acid in nitric acid (pH 1.0) produced 13 times enhancement for Ag and 7% (v/v) formic acid resulted in 17 times enhancement for Cd. The emission of Pb was even enhanced 78 times in the presence of 3% formic acid. In addition, the signal stability was also improved compared with that in the absence of organic substances. Repeatability was 0.8% for 0.1 mg L^{-1} Ag, 0.7% for 0.2 mg L^{-1} Cd and 2.6% for 1 mg L^{-1} Pb standard solutions (n=5). The limits of detection of Ag, Cd and Pb were 1, 17 and 45 μg L^{-1}, respectively. The accuracy of the method was demonstrated by determination of elements in simulated natural water samples (GBW(E)080402 and GBW(E)080399).

1. Introduction

Liquid discharge microplasmas [1–3] have received increasing attention in the determination of metal ions in water and wastewaters. Compared to those high-performance instruments (eg., AAS, ICP-AES, ICP-MS), which require high temperature and high voltage, complicated equipment and manipulation, liquid discharge microplasmas offer the advantages of low power consumption, cost effectiveness, and reduced/no inert gas requirement. Several devices based on liquid discharge microplasmas are developed for the determination of metal ions.

The electrolyte as cathode glow discharge (ELCAD) [4–7], which involves a glow discharge being ignited between a metal anode and the surface of an electrolyte sample solution, becomes a possible emission source for measurements of metals in water samples. A shortcoming of the ELCAD apparatus is that high solution flow rates are typically required. Flow rates of 8–10 mL min^{-1} were usually employed in earlier designs [8–11]. An improved version of ELCAD, which is known as solution cathode glow discharge (SCGD) [6,12], exhibits better detection limits and operates at lower flow rate (2.5 mL min^{-1}). Shekhar et al. [7] reported a new apparatus ELCAD that leads to stable plasma even at low flow rates (0.96 mL min^{-1}) by attaching a V-groove onto the liquid glass-capillary. A variation of the ELCAD source, known as the liquid sampling atmospheric pressure glow discharge (LS-APGD) [3,13], was developed by Marcus and Davis for direct analysis of electrolytic solutions by optical emission spectrometry. The solution can be used as either the cathode or anode of the discharge circuit. The LS-APGD runs stably at rates of 0.5–1.5 mL min^{-1} and also permits direct, flow injection analyte solution introduction. In 2011, they even demonstrated the LS-APGD could be used as a low power ionization source for elemental MS analysis [14]. Tombrink et al. [15,16] proposed a new liquid analysis system based on a miniaturized capillary dielectric barrier discharge, where the flow rates could be just 1 μL min^{-1}. In our group, an ac-driven electrolyte atmospheric liquid discharge (ac-EALD) [17] was developed for elemental determination. It greatly reduced the consumption rate of sample solution, and therefore, can be operated at low flow rate (0.25 mL min^{-1}). Recently, we proposed a nonflowing liquid-film DBD (LFDBD) source [18] for elemental determination, which is a microanalysis system and requires sample volume $\leq$80 μL.

Although these liquid discharge microplasmas possess attractive features for elemental determination, the sensitivity/limits of detection are still unsatisfied, compared to inductively coupled plasma optical emission spectrometry (ICP-OES) [19]. Therefore, it is necessary to improve the analytical performance of these microplasmas sources for the determination of metal ions at very low levels in environmental samples. In arc emission spectrographic analysis, spectral buffers are usually needed to decrease

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the matrix effect and improve the performance [20–22]. Besides the conventional inorganic substances, some organic substances (e.g., sodium diethyldithiocarbamate, tetraethylammonium iodide) were also employed as spectral buffer in DC arc emission spectrometry [23,24]. As is well known, the presence of organic solvents in aqueous samples could also enhance the emission sensitivity for many elements in ICP-OES [25–28]. Korn et al. [26] evaluated the enhancement effect of aqueous-organic solvent solutions on the emission intensity of metals of the first transition series plus Cd and Pb. Ražić et al. [29] also demonstrated that low concentration of ethanol causes an enhancement of both atomic and ionic spectral lines (e.g., Ca, Cd, Mg). Several studies have also reported that presence of organic compounds could increase signal intensity in ICP-MS [30–32]. For example, Kovačevič et al. [33] reported that the signals for arsenic and selenium were enhanced by a factor of 4.2, when a 0.40 mol L^{-1} aqueous solution of acetone was introduced directly into the spray chamber. Guo et al. [34] observed that the signal intensity of As^+ or AsO^+ was improved 3–4 times by addition of 4% methanol in the analyzed solutions. It should be noted that Shekhar [35] recently demonstrated the usability of these organic solvents to improve the sensitivity of the ELCAD–AES for mercury determination. In 2006, we also reported that low molecular weight organic substances such as ethanol, formic acid, and acetic acid could enhance vapor generation efficiency of mercury in SCGD [36]. However, the effect of organic substances on emission signals of metals have not been reported in other liquid discharge systems.

In the present study, we demonstrated the significant improvement of sensitivity of ac-electrolyte atmospheric liquid discharge (ac-EALD) emission spectrometry in the presence of organic substances. It was found that the emission signals of Ag, Cd and Pb were significantly enhanced using formic acid. Different parameters including type of organic solvents, *pH* and sample introduction rate were investigated. The method had been developed for quantitative measurement of Cd, Ag and Pb by optical emission spectrometry. The proposed method was also successfully validated by analysis of Cd and Pb in simulated natural water samples (GBW(E)080402 and GBW(E)080399).

2. Experimental section

2.1. Instrumentations

Schematic diagram of the experimental setup is presented in Fig. 1. It consists of a discharge cell, a lens and a monochromator. The EALD was composed of a tungsten rod electrode (2 mm diameter × 60 mm length) and a reservoir containing a graphite electrode insert with a quartz capillary (0.3 mm i.d) from the bottom. Samples were introduced into EALD cell through the quartz capillary by a syringe pump (Harvard Apparatus PHD 2000, Holliston, MA). The distance between the top of the quartz capillary and the tip of the tungsten electrode was about 2 mm. The cell was mounted on a platform built with three independent micrometer screw gauges, which could be controlled precisely in the *x*, *y*, and *z* directions to adjust position of the plasma to obtain the maximum signal output. A peristaltic pump was used to reduce waste water for controlling the height of the electrolyte solution. Plasma power was provided from an ac power supply (Ozone generator power, Beijing Guoke Ozone Application Technology Co. Ltd., Beijing, China) with about 30 kHz frequency, 3.7 kV peak voltage, and 18 W maximum output power. The discharge was imaged 2.5:1 with a fused-silica lens (focal length = 100 mm, diameter = 25.4 mm) to the entrance slit of a monochromator (Princeton Instruments, Acton SP 2500, focal length = 0.5 m), which was equipped with a 1200 grooves/mm holographic grating. The monochromator has motorized slits whose width can be adjusted from 10 μm to 3 mm. The slit width was set at 70 μm for all experiments presented in this paper. A Hamamatsu R928 photomultiplier tube (PMT), set at −800 V was used as the detector. Integration time was set as 100 ms for each measurement.

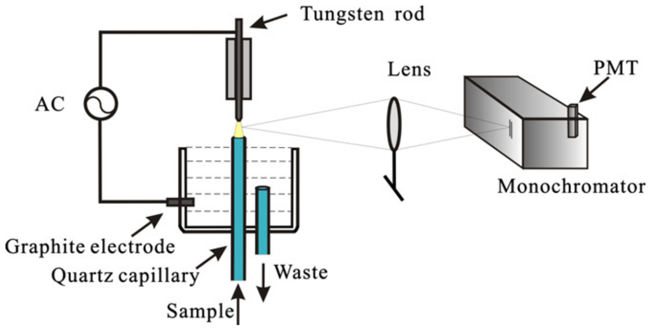

Fig. 1. Schematic diagram of the ac-EALD atomic emission spectrometry.

2.2. Reagents and samples

Nitric acid was of superior-reagent grade. Other chemicals used in this work were analytical-reagent grade including lead nitrate, silver nitrate, cadmium nitrate, sodium nitrate, and potassium nitrate. Ultrapure water (> 18 MΩ cm, resistivity) was obtained from a water purification system (90005-02, Labconco water props, Canada). Stock solutions (1000 mg L^{-1}) of Cd^{2+}, Ag^+ and Pb^{2+} were prepared with nitric acid (pH = 1.0). Working standards were prepared from diluting stock solution. The pH of the solution was adjusted by concentrated HNO_3 and measured with a pH meter (HACH, HQ40d, America). The reference materials simulated natural water samples GBW(E)080339(Pb) and GBW(E)080402(Cd) (National Research Center for Standard Materials, Beijing, China) were used to validate the accuracy of our method. The samples were diluted by a factor of five for the analysis. Then except for the addition of formic acid and solution pH adjustment, no other pretreatment was performed. The spiked tap water was directly determined after the addition of formic acid and adjustment of solution pH.

3. Results and discussion

3.1. Enhancement effect of organic substances

In preliminary study, formic acid was selected to evaluate the enhancement effect of organic substance. The signal peak graphics were recorded in the presence and absence of formic acid in HNO_3 electrolyte solution. Taking the pH effect on the emission intensity into consideration, the pH of the electrolyte solution was maintained at 1.0 in this part. Fig. 2 shows the peak graphics of (a) Cd (228.8 nm), (b) Ag (328.1 nm) and (c) Pb (405.8 nm) in the presence of 1% formic acid (v/v) and without formic acid. The spectrums were subtracted by that of the corresponding blank solutions. It can be observed that the net emission intensities of each element increased significantly with the addition of formic acid. The signals of Cd, Ag and Pb emission in 1% formic acid were enhanced by a factor of 5, 10 and 43, respectively. This result indicated that the presence of formic acid could enhance the EALD emission signal especially in the case of Pb.

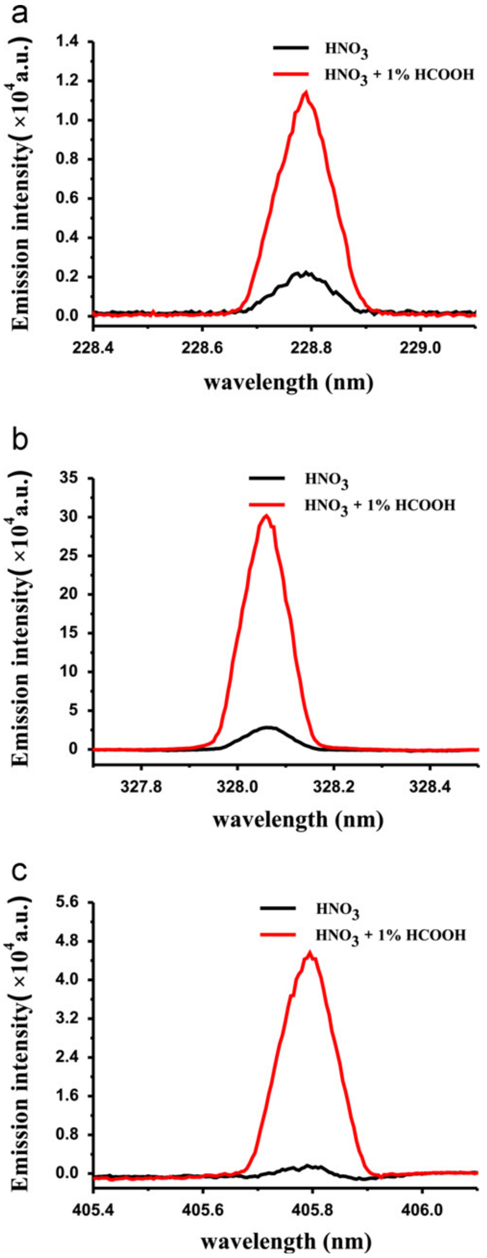

Fig. 2. Comparison of emission signals of (a) Cd (228.8 nm), (b) Ag (328.1 nm) and (c) Pb (405.8 nm) in the presence of 1% concentration of formic acid (v/v) and that without formic acid (electrolytes: HNO_3, pH: 1.0, flow rate: 0.4 mL min^{-1}).

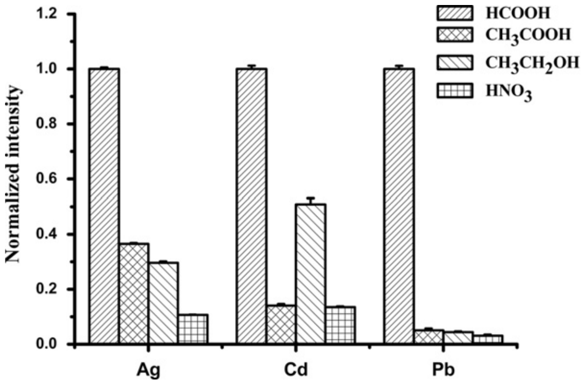

Fig. 3. Enhancement effect of different organic substances (formic acid, acetic acid and ethanol) on the emission intensity of Ag, Cd and Pb. (Concentration of organic substances 3% (v/v), pH: 1.0, flow rate: 0.3 mL min^{-1}.) Error bars in the figure represent standard deviations of five replicates.

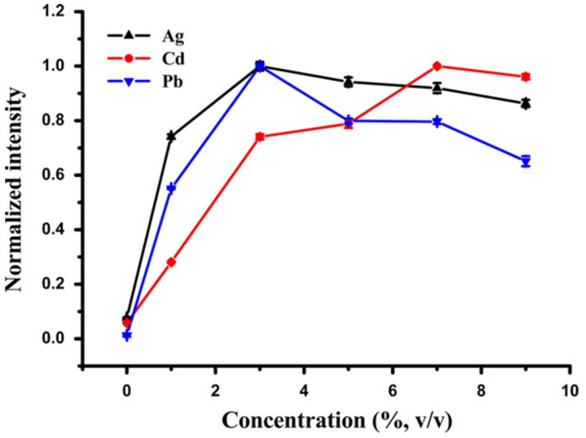

Fig. 4. Influence of formic acid concentration on the emission intensity enhancement of Ag, Cd and Pb (electrolytes: HNO_3, pH: 1.0, flow rate: 0.4 mL min^{-1}). Error bars in the figure represent standard deviations of five replicates.

It was reported by Shekhar [35] that the ELCAD emission intensity of Hg could be enhanced by several low molecular weight organic substances. Accordingly, the effects of ethanol, formic acid, and acetic acid on the sensitivity of lead, silver and cadmium were also investigated in the present study. Lead (20 mg L^{-1}), silver (5 mg L^{-1}) and cadmium (10 mg L^{-1}) solutions containing 3% (volume ratio) ethanol, formic acid, and acetic acid as well as their corresponding solutions without organic substances were prepared using nitric acid (pH 1.0). The results are shown in Fig. 3. It was observed that all these three organic substances could enhance the emission intensity of Ag, Cd and Pb. The enhancement effect is in the order $HCOOH > CH_3COOH > CH_3CH_2OH$ for Ag and Pb, and $HCOOH > CH_3CH_2OH > CH_3COOH$ for Cd. In addition, the enhancement effects of these organic substances at various volumetric ratios were also compared; formic acid was shown to present the maximum enhancement for all these three elements. This result is in agreement with the study of Hg vaporization by SCGD [36]. Therefore, formic acid was used in later research.

3.2. *Optimization of the concentration of formic acid*

The effect of the concentration of formic acid on the enhancement of the intensity was also investigated. Solutions of cadmium (10 mg L^{-1}), silver (5 mg L^{-1}) and lead (20 mg L^{-1}) with different volume percentages (0%, 1%, 3%, 5%, 7%, 9%) of formic acid were prepared in nitric acid (pH 1.0). Corresponding blank solutions (without elements) were also prepared. It was found that the emission intensities could be significantly enhanced even with the addition of a small amount (1%) of formic acid (Fig. 4). Maximum enhancement of Cd emission was enhanced by a factor of 17 with 7% formic acid, and Ag was enhanced by a factor of 13 in the presence of 3% formic acid. There was hardly any Pb emission in nitric acid without formic acid, but the emission intensity enhanced greatly by a factor of 78 and achieved maximum enhancement with 3% formic acid. On the basis of these results, solutions with 3% formic acid for Ag and Pb and 7% formic acid for Cd were selected in later research.

3.3. *Spectral characteristics and enhancement mechanism*

The emission spectrums of the plasma were recorded in the presence of 3% formic acid and compared with that without

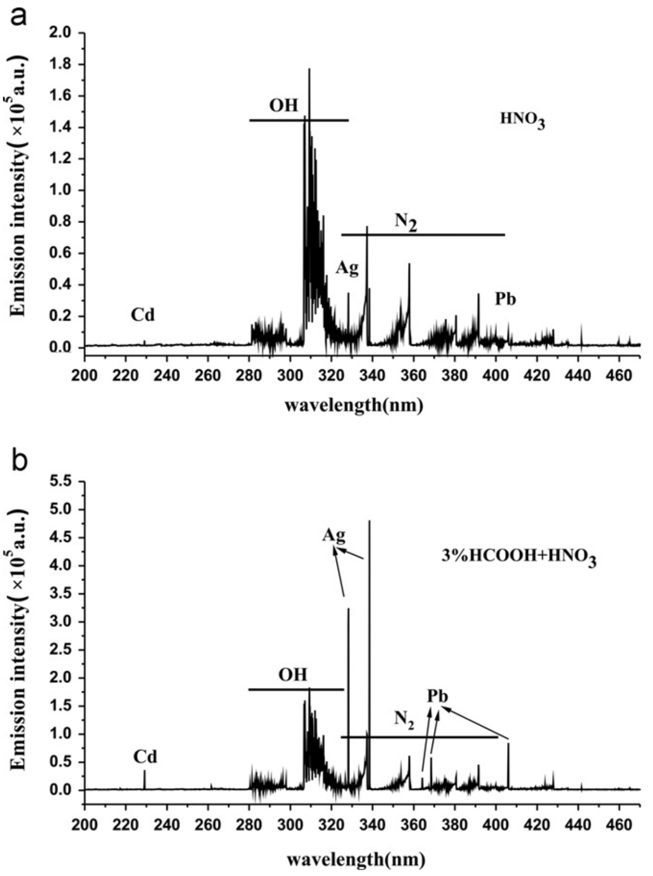

Fig. 5. Typical spectrum of atmospheric pressure EALD in the presence of 3% HCOOH (v/v) (b) and without HCOOH (a) (pH = 1.0) spiked with Cd (10 mg L^{-1}), Ag (5 mg L^{-1}) and Pb (20 mg L^{-1}). (Liquid flow rate: 0.3 mL min^{-1}.)

formic acid. Fig. 5 shows typical emission spectra ranging from 200 to 470 nm in the absence (a) and presence of 3% formic acid (v/v) (b). The background emission spectral characteristics in the presence of formic acid were similar to those without formic acid. From the spectra, background emissions are weak below 280 nm. Above this wavelength, there are several OH bands, with band heads at 281 nm and 309 nm, and N_2 second positive system, with band heads visible from 337 to 406 nm. The atomic spectral lines of Cd I (229 nm), Ag I (328 nm, 338 nm) and Pb I (406 nm) are very strong in the presence of formic acid, and those of Pb I (364 and 369 nm) are also obvious from (b) compared with that without formic acid from (a). It should be noted that slight increases in OH and N_2 emission intensities were also observed in the presence of formic acid, indicating that the discharge is more energetic with the addition of formic acid.

In addition to Ag, Pb and Cd, K (766 nm) and Na (589 nm) were also studied. However, only slight signal enhancements were observed for easily excited elements K and Na in the presence of formic acid. Based on all these observations, we proposed the possible enhancement mechanism of EALD by formic acid. Firstly, the signal enhancement may be caused by the change of the atmosphere of the plasma and then change of the characteristics (e.g., excitation temperature, ion density) of the plasma in the presence of organic substances. On the other hand, the presence of organic substances may also improve the sample introduction efficiency of EALD. Webb et al. [12,37] proposed that an electrospray-like mechanism might happen in SCGD. Similar mechanism may also exist in EALD as the presence of organic substances could change the surface tension of the solution, which could improve the electrospray sampling efficiency in EALD. Another possible explanation is the presence of organic substances especially in the case of formic acid may greatly improve the atomization of Ag, Pb, Cd (in this case, the sampling efficiency is also improved significantly). The process is similar to the vapor generation of Hg in SCGD [36]. Ongoing research will focus on the enhancement mechanisms in the presence of formic acid and the effect on other elements.

3.4. Effect of solution pH and flow rate

It is known that the element emission intensity strongly depends on the acidity of electrolyte solution in ELCAD [8,11] as well as in ac-EALD [17]. The effect of the solution pH was also optimized in the present study. It was found that the plasma was unstable when the pH was beyond 1.5. Therefore, solutions containing Ag, Pb with 3% HCOOH and Cd with 7% HCOOH, with various concentrations of nitric acid (pH = 0.5, 0.75, 1.0, 1.25, 1.5) were prepared and passed into the ac-EALD. The results are shown in Fig. 6. The emission intensities for all three elements increased from 0.5 to 1.0 and decreased from 1.0 to 1.5. Therefore, pH 1.0 was chosen for subsequent research.

The effect of flow rate in the range of 0.2–0.8 mL min^{-1} on the net-emission intensity of the analytes was also evaluated. The emission intensities of Ag and Pb increased with flow rate from 0.2 to 0.4 mL min^{-1} and then declined after a further raise in flow rate from 0.4 to 0.8 mL min^{-1}. However, the emission intensity of Cd increased from 0.2 to 0.5 mL min^{-1} and then reduced from 0.5 to 0.8 mL min^{-1}. The increase of the emission intensity with the increase of flow rate at lower range may be ascribed to the raised amounts of analytes which entered the discharge. The reduction of emission intensity at higher flow rate may be a consequence of additional water vaporization which may reduce the energy or number of electrons available for exciting the atoms. In the present study, the optimized solution pH and flow rate are different from our earlier study [17]. One possible reason is that the property of the discharge plasma altered (e.g., the discharge becomes more energetic) in the presence of formic acid, thus more solution is needed to support the discharge. As the emission intensity of Cd was only slightly enhanced from 0.4 to 0.5 mL min^{-1}, a flow rate of 0.4 mL min^{-1} was employed in subsequent experiments.

3.5. Analytical performance

The analytical performance of the proposed technique was evaluated under optimal operating conditions (flow rate: 0.4 mL min^{-1},

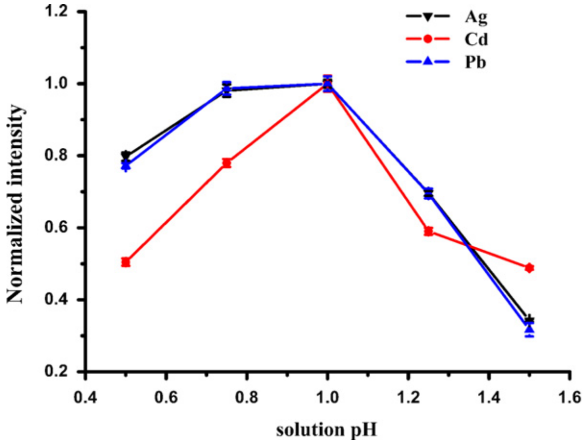

Fig. 6. The effect of pH on the emission intensities of Ag, Cd and Pb in the presence of formic acid (flow rate: 0.4 mL min^{-1}, concentration of formic acid: Ag and Pb 3%, Cd 7%). Error bars in the figure represent standard deviations of five replicates.

solution pH: 1.0, discharge power: 18 W, slit width: 70 μm), as shown in Table 1. A series of concentrations of Ag, Cd and Pb standard solutions with its optimal concentration of formic acid and the blank solutions were used to determine the detection limits and relative standard deviations. Five replicates were performed at each standard concentration and ten replicates were performed at each blank solution. With the signal height as a quantitative parameter, the calibration curves were linear for all studied elements. Repeatability, expressed as the relative standard deviation, was 0.8% for 0.1 mg L^{-1} Ag (328.1 nm), 0.7% for 0.2 mg L^{-1} Cd (228.8 nm) and 2.6% for 1 mg L^{-1} Pb (405.8 nm) standard solutions (n=5). The limits of detection (LOD), using the definition 3 s k^{-1} (s is the standard deviation corresponding to 10 blank measurements and k is the slope of the calibration graph), ranged from 1 to 45 μg L^{-1}. The LODs of EALD for those three elements were also compared with those in the absence of formic acid, as well as those in other liquid discharge systems. It can be observed that the LODs were significantly improved in the presence of formic acid and the LODs in EALD with formic acid were comparable with those in the latest reported ELCAD [7]. Although the LODs were still higher than that of SCGD [6], the absolute LODs should be also comparable with SCGD considering the flow rate of our proposed EALD (0.4 mL min^{-1}) lower than SCGD (2.5 mL min^{-1}).

The short term stability of the plasma was also monitored by means of recording the emission intensities of elements at fixed wavelengths. Fig. 7 shows the emission intensities of solutions spiked with 1 mg L^{-1} Ag, 2 mg L^{-1} Cd and 10 mg L^{-1} Pb over 12 min after the plasma was stabilized. The RSD (n=24) of the signal was computed and found to be 0.6%, 1.2% and 1.3% for Ag, Cd and Pb, respectively, which is also improved with our earlier research measured without formic acid (2.2% for Cd, 5 mg L^{-1}, n=24) [17]. The results indicated that the stability of the emission signals in the presence of formic acid was also improved.

Table 1
Analytical characteristics of ac-EALD for elemental determination and other liquid discharge systems.

Element	Wavelength (nm)	RSD (%)	Present work without formic acid LOD (μg L^{-1})	Present work with formic acid LOD (μg L^{-1})	ELCAD LOD [7] (μg L^{-1})	SCGD LOD [6] (μg L^{-1})
Ag	328.1	0.8[a]	20	3	–	–
	338.3	1.3[a]	7	1	–	0.3
Cd	228.8	0.7[b]	163	17	5	2
Pb	405.8	2.6[c]	281	45	45	6

[a] Standard concentration, 0.1 mg L^{-1}, n=5.
[b] Standard concentration, 0.2 mg L^{-1}, n=5.
[c] Standard concentration, 1 mg L^{-1}, n=5.

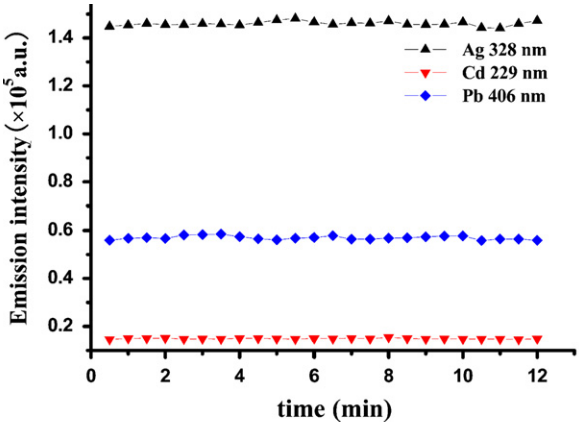

Fig. 7. Stability of emission signals of Cd (2 mg L^{-1}), Ag (1 mg L^{-1}) and Pb (10 mg L^{-1}) (HNO_3, pH: 1.0, concentration of formic acid: Ag and Pb 3%, Cd 7%, flow rate: 0.4 mL min^{-1}).

Table 2
The determination of Cd and Pb in simulated natural water samples (GBW(E)080402 and GBW(E)080399) and the recoveries of Cd and Pb in tap water samples.

Sample	Element	Reference value (mg L^{-1})	Measured value (mg L^{-1})
GBW(E)080402	Cd	1.00 ± 0.02	0.97 ± 0.04
GBW(E)080399	Pb	5.00 ± 0.10	4.93 ± 0.17
		Spiked concentration (mg L^{-1})	Recovery (%)
Tap water	Cd	0.5	99.7
Tap water	Pb	1.0	99.4

To validate the proposed method, two simulated natural water samples (GBW(E)080402 and GBW(E)080399) were applied to the determination of Cd and Pb by external standard method. The measured results agreed well with the reference values (Table 2). Recoveries, calculated from spiking 0.5 mg L^{-1} Cd and 1.0 mg L^{-1} Pb standard into tap water, were satisfactory: 99.7% and 99.4% for Cd and Pb, respectively. All these results indicated that the proposed method has the potential to be applied for the determination of metal in water samples.

4. Conclusions

It was demonstrated that the presence of low molecular weight organic solvents could significantly improve the performance of ac-EALD for elements determination. Formic acid exhibited better enhancement for all three studied elements (Ag, Cd, and Pb). The Cd emission intensity was enhanced by a factor of 17 with 7% formic acid, and Ag was enhanced by a factor of 13 with 3% formic acid. As for Pb, obvious emission intensity was observed with 78 times enhancement in the presence of formic acid, but hardly any emission was found without organic substances. The detection limits for Cd, Ag and Pb obtained from this method were also improved to a great extent. The proposed method was demonstrated for the quantitative determination of metals in water samples. With the improved performance, the ac-EALD device provides a promising technique for the *in-field* metal ion detection.

Acknowledgments

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