Screening of cadmium and lead in potentially contaminated waters using a spectrophotometric sequential injection lab-on-valve methodology

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ABSTRACT

The present work describes the development of a μSI-LOV method for the simultaneous screening of cadmium and lead in potentially contaminated water samples. To attain the biparametric determination, dithizone was chosen as the spectrophotometric reagent as it forms a colored complex with both metal ions, at different pH conditions. The cadmium determination was attained in strong alkaline conditions (pH $\approx$ 12); the lead determination was calculated by the difference with the determination of both metals in mild alkaline conditions (pH $\approx$ 8). The colored complex was measured at 550 nm and the method presented a LOD of 34 $\mu g\,L^{-1}$ for cadmium and 56 $\mu g\,L^{-1}$ for lead, with a sample consumption of 20 μL per assay and a determination rate of 55 h^{-1}. The results obtained were in agreement with those obtained by FAAS. The developed method was efficiently applied to the screening of cadmium and lead in marine port waters.

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1. Introduction

Cadmium and lead continue to be discharged to the environment due to anthropogenic activities and in marine ports due to their release from ships paint pigments and fuel [1–4]. These hazards have an impact on water quality due to their high toxicity, so screening and quantifying both mentioned metal ions are vital to monitor possible pollution thus improving the safety in ports [3–6]. According to European legislation [7], the admissible level for cadmium discharge in the environment from the various industries is between 0.3 and 0.5 $mg\,L^{-1}$. For lead, the Environmental Protection Agency (EPA) [8] describes the Criteria Maximum Concentration (CMC) of 65 and 210 $\mu g\,L^{-1}$ for fresh and salt waters, respectively.

Sequential injection analysis (SIA) is an interesting approach for monitoring pollutants in the environment since it allows a real-time and faster determination of the analyte, automating the analysis with low sample and reagent consumption. Sequential injection lab-on-valve (SI-LOV) adds more advantages such as the miniaturization of the analysis with sample and reagents consumption to the microliter level [9,10].

In fact, the determination of cadmium and lead has been previously reported using SI-LOV coupled to different detection devices [11–19]. Also several sequential injection analysis methods have been described for the biparametric determination of both metal ions [20–26], listed in Table 1.

Some of those works [21,23] required a preconcentration step, resulting in a low determination rate. In the work by Siriangkhawut et al. [22] the use of the standard addition method also decreases the determination rate since there is a calibration curve for each sample. The work by Anthemidis and Ioannou [23] described the application of liquid–liquid extraction which employs the use of organic solvents (although at minimal volumes). Still, none of these works were aimed for application to potentially contaminated waters and, in some cases, like the work by Suteerapataranon et al. [26], it was not applied to any sample. Within the above mentioned works, the most common detection systems were voltammetry and atomic absorption spectrometry (AAS) [14–19,27,28], both very sensitive detection techniques. However, spectrophotometry represents an interesting, less expensive alternative with a simpler implementation and facilitated application in a flow analysis procedure.

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Table 1
Sequential injection methods for cadmium and lead determination in water samples.

System	Detection	Pre-concentration	Dynamic range ($\mu g\ L^{-1}$)	LOD ($\mu g\ L^{-1}$)	RSD (%)	Deter. rate (h^{-1})	Water sample	Reference
SI	CV & SWASV	–	0.1–50	0.07; 0.04	n. g	n. g.	Tap	[20]
SI	ASV	+	15–70; 0.5–15	0.01	2.56–5.67	n. g.	Drinking, pond, tap	[21]
SI	ASV	–	5–200; 10–200	0.1; 0.7	2.6; 3.1	n. g.	Ground water	[22]
SI DLLME	ETAAS	+	0.04–1.5; 0.006–0.15	0.002; 0.01	4.1; 3.8	10	Tap, river and coastal seawater	[23]
SI	ASV	–	5–120;4–100	1.4; 1.2	2.8; 2.6	20	Tap	[24]
SI	Spectrometry	–	1000–20,000	n. g.	< 2	27	Tap	[25]
SI	ASV	–	10–70;10–100	6;10	9.8; 2.6	n. g.	–	[26]
SI-LOV	Spectrometry	–	500–10,000	34; 56	7, 8, 5; 2, 4, 5	55	Marine and freshwaters	This work

*SI, sequential injection; DLLME, dispersive liquid–liquid microextraction; CV, cyclic voltammetry; SWASV, square-wave anodic stripping voltammetry; ASV, anodic stripping voltammetry; ETAAS; electrothermal atomic absorption spectrometry; n. g., not given.

The objective of this work was the development of a μSI-LOV method for the biparametric determination of cadmium and lead with spectrophotometric detection. As far as we know, there is no previous work combining the use of spectrophotometry, coupled to SI-LOV, for the determination of cadmium and lead [28,29] with the same manifold. The challenge was to monitor both metals in potentially contaminated waters, namely marine/port waters with different matrix compositions according to the sampling location (near the sea or near the river). To achieve the determination of both cadmium and lead, dithizone (DTZ) was chosen as chromogenic reagent as it forms colored complexes with metals such as Pb, Cd, Zn, Cu, and others [30]. The detection was based on the spectrophotometric measurement, at 550 nm, of the dithizonate complex formed between DTZ and the metal ions at different pH values. The formation of the cadmium complex is more extensive at strong alkaline conditions, pH $\approx$ 13, while for lead complex formation the conditions should be neutral to slightly alkaline, pH $\approx$ 7–8 [30]. In the end, because cadmium also complexes at slightly alkaline pH, the determination of lead was attained by the difference of the cadmium assessment and the cadmium and lead assessment. With this approach, a single reagent was used for both determinations with the reaction conditions handled in-line.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with analytical grade chemicals and Milli-Q water (resistivity $> 18\ M\Omega$ cm, Millipore, Bedford, MA, USA) was used throughout the work.

The 0.01% dithizone (Riedel-de Haën, Germany) solution was daily prepared by dissolving 1 mg of the solid in 10 mL of 7.5% Triton X-100 ($d = 1.07$; Sigma-Aldrich, Germany).

The 2 M sodium hydroxide (Merck, Darmstadt, Germany) stock solution was prepared by dissolving 8 g of the solid in 100 mL of water and working solutions of 1 and 0.01 M NaOH were prepared from the stock solution.

Stock solutions of 100 mg L^{-1} of cadmium and lead were prepared by dissolution of the respective solids $Cd(CH_3COO)_2$ and $Pb(NO_3)_2$ (Merck, Darmstadt, Germany) in water. Mixed standards were prepared by dilution of the stock solutions in the range of 0.5–10 mg L^{-1}.

Artificial seawater was obtained by dissolving 41.5 g NaCl (Merck, Darmstadt, Germany) and 15 g $MgSO_4 \cdot 7H_2O$ (Merck, Darmstadt, Germany) in water to a final volume of 1.5 L, according to Liang et al. [31].

The solutions of the foreign ions used for interference studies were prepared from the respective solids and stock standard solutions: $Mg(NO_3)_2 \cdot 6H_2O$ (Fluka), $ZnCl_2$ (TCI Europe), $MnCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 2H_2O$, NaCl (Merck, Darmstadt, Germany), $Cu(CH_3COO)_2 \cdot H_2O$,

(Merck, Darmstadt, Germany), $CoSO_4 \cdot 7H_2O$, $Al(SO_4)_3$, Ni^{2+} and Fe^{3+} (AAS, Spectrosol). Several standards, with 3 mg $Cd^{2+}\ L^{-1}$ for cadmium determination and 3 mg $Pb^{2+}\ L^{-1}$ for lead determination and the tested concentration of interfering ions, were prepared and analyzed with the developed μSI-LOV method.

2.2. Sample collection and preparation

Inland and coastal water samples were collected in polyethylene plastic bottles of 0.5 L capacity at about 30 cm depth. The samples were filtered previously to the introduction in the system using a filter of 0.2 μm i.d. (Merck Farma e Quimica S 4531344 DS0215 – 4020).

Water samples from a marine port were collected in polyethylene plastic bottles of 0.5 L capacity at about 30 cm depth from different locations (near the sea and near the river).

2.3. Apparatus

The SI-LOV system, FIAlab-3500 (FIAlab Instruments, Medina, WA, USA) presented in Fig. 1, consisted on a bi-directional syringe pump (2500 μL of volume), a 1 m holding coil, a bi-directional variable speed peristaltic pump, and a lab-on-valve manifold mounted on the top of a six port multi-position valve. As detection system, a USB 2000 Ocean Optics charge coupled device (CCD) spectrophotometer equipped with two optical fiber cables (FIA-P400-SR; id: 400 μm) and a DH-2000-BAL UV/vis/NIR light source (Mikropack) was used. FIAlab for windows 5.0 software on a personal computer was used for flow programming and data acquisition.

2.4. Flow procedure

The μSI-LOV flow procedure for cadmium and lead determination is summarized in Table 2.

The initial steps of A–C consisted in the preparation of the port by filling the tube with sample. Afterwards, the steps D–F consisted in the sequential aspiration of NaOH, DTZ and standard/sample to the holding coil, followed by propelling the mixture to the detector with absorbance scanning (step G). The two final steps (H–I) consisted in washing the flow cell and the holding coil, preparing the system for the next cycle.

For cadmium determination, the NaOH solution of 1 M was used and for the simultaneous determination of cadmium and lead the solution used was 0.01 M NaOH.

The calculation of cadmium concentration was obtained directly from the calibration curve with the 1 M NaOH solution, as even though mixed standards were used the strong alkaline conditions ensure the reaction of only cadmium ion. With the 0.01 M NaOH solution both cadmium and lead are determined with equivalent sensitivity, so in the end the lead concentration was