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Micro solid phase spectrophotometry in a sequential injection lab-on-valve platform for cadmium, zinc, and copper determination in freshwaters

Inês C. Santos [a], Raquel B.R. Mesquita [a, b], António O.S.S. Rangel [a, *]
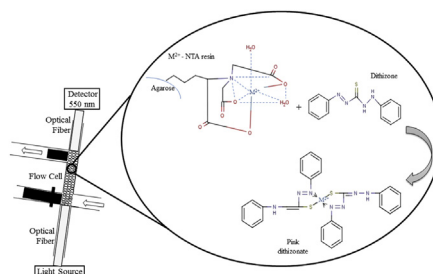
[a] CBQF—Centro de Biotecnologia e Química Fina — Laboratório Associado, Escola Superior de Biotecnologia, Universidade Católica Portuguesa/Porto, Rua Arquiteto Lobão Vital, Apartado 2511, 4202-401 Porto, Portugal
[b] Laboratório de Hidrobiologia, Instituto de Ciências Biomédicas Abel Salazar (ICBAS), Universidade do Porto, Rua de Jorge Viterbo Ferreira no. 228, 4050-313 Porto, Portugal

HIGHLIGHTS

- Multi-parametric determination of cadmium, zinc, and copper at the $\mu g\,L^{-1}$ level.
- In-line metal ions preconcentration using NTA resin.
- Minimization of matrix interferences by performing solid phase spectrometry in a SI-LOV platform.
- Successful application to metal ions determination in freshwaters.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

This work describes the development of a solid phase spectrophotometry method in a μSI-LOV system for cadmium, zinc, and copper determination in freshwaters. NTA (Nitrilotriacetic acid) beads with 60 −160 μm diameter were packed in the flow cell of the LOV for a μSPE column of 1 cm length. The spectrophotometric determination is based on the colourimetric reaction between dithizone and the target metals, previously retained on NTA resin. The absorbance of the coloured product formed is measured, at 550 nm, on the surface of the NTA resin beads in a solid phase spectrophotometry approach.

The developed method presented preconcentration factors in the range of 11−21 for the metal ions. A LOD of 0.23 $\mu g\,L^{-1}$ for cadmium, 2.39 $\mu g\,L^{-1}$ for zinc, and 0.11 $\mu g\,L^{-1}$ for copper and a sampling rate of 12, 13, and 15 h^{-1} for cadmium, zinc, and copper were obtained, respectively. The proposed method was successfully applied to freshwater samples.

1. Introduction

Sequential injection lab-on-valve (SI-LOV) appeared as the 3rd generation of flow injection analysis [1] bringing new advantages when compared to other flow techniques such as miniaturization and lower sample and reagents consumption. This technique is an interesting approach for monitoring pollutants in the environment as it allows a real-time determination of the analyte together with a miniaturization and automation of the analysis. The geometry of SI-LOV channels enables the manipulation of solid particles such as beads of resin, facilitating hyphenated techniques with bead

* Corresponding author.
E-mail address: arangel@porto.ucp.pt (A.O.S.S. Rangel).

injection (BI) [2] and solid phase spectrophotometry (SPS) [3]. Both approaches require aspiration and propelling of the beads suspension through the selection valve conduits, attaining analyte or reagent retention prior to the determination. This feature enables to perform in-line solid phase extraction (SPE), a highly advantageous approach for removal of possible matrix interferences together with analyte pre-concentration. In SPS, the beads are packed in the flow cell and the determination is made through the solid particles, which can be attained in a BI approach. In BI, the beads are removed at the end of the analytical cycle and replaced for another batch so, no interference from species accumulation is observed. However, BI turns out to be quite expensive due to high resin consumption. A reusable method of SPS is preferred since a single column of beads is packed, relying upon washing and reconditioning steps at each cycle to increase the lifetime of the solid material. According to SI-LOV equipment manufacturer [4], the beads that can be used for SPS must follow certain requirements in terms of size, format, material and optical transparency, characteristics fulfilled by the Nitrilotriacetic Acid (NTA) Superflow resin.

The SPS technique, not only allows the analyte retention and interferences elimination as it also reduces intrinsic sample and bead absorption by re-setting the absorbance baseline value after propelling the sample through the packed beads. The combination with the SI-LOV technique has proven to be advantageous with increased use and application [5].

Metal ions determination is still of great importance due to their continue release by anthropogenic activities and to their high toxicity. In this context, determination of cadmium, zinc, and copper was aimed. Cadmium assessment is important due to its high toxicity [6] as for zinc and copper, although essential micronutrients, when in excess they are also toxic [7]. According to Yu et al. [8] SI-LOV is an appropriate platform for metal ions analysis coupled to different detection systems namely spectrophotometry, atomic spectrometry and electrochemical detection. In fact, several works were developed for determination of metal ions using SI-LOV [8] and a compilation of the developed methods for cadmium, zinc, and copper determination in water samples using a sequential injection approach [9–32] was made (Table S1 in the Electronic Supplementary Material). About half of the listed works were based on spectrophotometric detection, an evidence of the interest in developing alternatives to atomic absorption or emission detection. To achieve the expected low levels of metal ions in water samples using spectrophotometric detection, some works have included a pre-concentration step by coupling microcolumns with packed beads into the flow system [13,31]. This has resulted in an effective improvement of the detection limit.

The objective of this work was to develop an SI-LOV method to perform SPS for the determination of cadmium, zinc, and copper in freshwaters. The idea was to retain the metal ions prior to the determination in an NTA resin column packed in the flow cell, using a reusable SPS approach. The chosen NTA resin is known for its efficiency to retain metals [33,34] and has been effectively used in SPS-SI-LOV approach [35,36]. The idea was to pack the NTA in the flow cell and then send the sample through for the retention of the metal ions (Cd^{2+}, Zn^{2+}, Cu^{2+}) attaining both matrix elimination and metal ion pre-concentration. Afterwards, the dithizone (DTZ) reagent was propelled through the beads column for complexation with the metal ions and colour formation registered by absorbance measurement at 550 nm. As the dithizonates are formed, they are measured and displaced from the NTA to waste. The choice of dithizone was based on its reported reactivity towards different metal ions by manipulation of reaction pH [37]; this feature was previously exploited for the simultaneous determination of Cd and Pb [9]. So, combining the appropriate retention pH and reaction pH,

together with carrying out the absorbance measurement at specific wavelength enabled the quantification of each targeted metal ion using the same manifold configuration. Table 1 presents the optimal pH range for NTA adsorption and DTZ colouration. The cadmium and zinc were measured under strong alkaline conditions for retention and for the colourimetric reaction; zinc was assessed individually with retention in acidic medium and alkaline conditions for the colourimetric reaction; and copper was also assessed individually with acidic retention and colourimetric reaction at neutral pH. In the end, the cadmium concentration was calculated using a two equation system.

2. Experimental

2.1. Reagents and solutions

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

All glassware was decontaminated in 10% (v/v) nitric acid solution and rinsed with ultra-pure water.

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 4 mol L^{-1} sodium hydroxide (Merck, Darmstadt, Germany) stock solution was prepared by dissolving 8 g of the solid in 50 mL of water.

The carbonate buffer was prepared by dissolving 0.76 g of $NaHCO_3$ (Merck, Darmstadt, Germany) in 50 mL of water and by adjusting the pH value to 7 with the concentrated hydrochloride acid (d = 1.19, 37%, Merck, Darmstadt, Germany).

Cadmium, zinc, and copper stock solutions of 100 mg L^{-1} were prepared by dilution of the 1000 mg L^{-1} atomic absorption standard solution (VWR-Spectrosol) in 0.02 M HNO_3 solution.

A 0.5 mol L^{-1} HNO_3 stock solution was prepared by dilution of the concentrated nitric acid (d = 1.39, 65%, Merck, Darmstadt, Germany). The 0.02 mol L^{-1} HNO_3 solution was prepared by dilution of the stock solution.

The bead suspension used was a dilution in water 1:1 (w/w) of the commercial stock solution (NTA Superflow resin, highly crosslinked 6% agarose, 60–160 μm of bead diameter, 50% suspension in 30% ethanol, 30,510, Qiagen).

The solutions of the tested foreign ions for interference studies were prepared from the 1000 mg L^{-1} atomic absorption standard solution (VWR-Spectrosol) for metal ions and from the solids $NaNO_3$, $NaNO_2$, Na_2SO_4 and $NaH_2PO_4 \cdot H_2O$ (Merck, Darmstadt, Germany) for the anions.

2.2. Sample collection and preparation

Freshwater samples were collected from the northwest of Portugal, in polyethylene plastic bottles of 0.5 L capacity at about 30 cm depth and acidified at sampling as recommended [40]. In situ measurements (Table S2) were performed using an YSI 6920 multiparameter probe.

Table 1
Optimal pH conditions for cadmium, zinc, and copper retention on NTA and complexation with DTZ.

Analyte	NTA retention [33]	DTZ reaction
Cadmium	>5	12–14 [38]
Zinc	>4	4–11 [37]
Copper	>1.7	1, 1.4 [37,39]