



## Sequential injection system with in-line solid phase extraction and soil mini-column for determination of zinc and copper in soil leachates

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### ABSTRACT

A sequential injection (SI) system equipped with in-line solid phase extraction column and in-line soil mini-column is proposed for determination of zinc and copper in soil leachates. The spectrophotometric determination (560 nm) is based on the reaction of both analytes with 1-(2-Pyridylazo)-2-naphthol (PAN). Zinc is determined after retaining copper on a cationic resin (Chelex100) whereas copper is determined from the difference of the absorbance measured for both analytes, introduced into the system with the use of a different channel, and zinc absorbance. The influence of several potential interferences was studied. Using the developed method, zinc and copper were determined within the concentration ranges of 0.005–0.300 and 0.011–0.200 mg L<sup>-1</sup>, and with a relative standard deviation lower than 6.0% and 5.1%, respectively. The detection limits are 1.4 and 3.0 µg/L for determination of zinc and copper, respectively. The developed SI method was verified by the determination of both analytes in synthetic and certified reference materials of water samples, and applied to the determination of the analytes in rain water and soil leachates from laboratory scale soil core column and in-line soil mini-column.

### 1. Introduction

Various kinds of human activities (e.g. industrial, urban, agricultural, gardening, or forestry) or inappropriate waste management can influence soil quality by inter alia its contamination with heavy metals. Soil contamination is a widespread problem in Europe. The most frequent contaminants are heavy metals and mineral oil [1]. Trace metals introduced to the soils on account of wide applications are subjected to constant accumulation, mainly in the surface soil which may lead to the pollution of groundwater and surface waters (indirectly). The effective monitoring of waters, affected by soil leachates from various activities, could help in identification of the potential sources of pollution.

Zinc and copper are micronutrients necessary for proper functioning of living organisms, but toxic when present in excess. The metabolically important influence is observed between zinc and copper, e.g. in animal and human organisms, many of symptoms associated with copper deficiency are explained by Cu-Zn antagonism [2]. Several ways of Cu-Zn interactions were also reported in relation to plants [3–7], among them

competitive inhibition of zinc on copper absorption [8]. Zinc is commonly regarded as one of the most mobile trace element in environmental samples [9] and easily absorbed by plants although soil conditions, pH value and Cu/Zn relation affect this absorption [10]. Both elements are better absorbed coming from anthropogenic sources than from natural occurrence in the soil [7] as higher levels of Cu and Zn were observed in the vegetables and wild plants in polluted soil [11].

Zinc and copper can be determined with reliable, but not portable, methods dedicated to elemental analysis like atomic absorption spectrometry (AAS) [12–15], inductively coupled plasma optical emission or mass spectrometry (ICP OES, ICP MS) [16,17] or neutron activation analysis (NAA). Flow-based systems are often combined with these methods to perform sample preparation. In the work of Nakatsuka et al. [16], a flow injection system with a column packed with chelating adsorbent of 8-hydroxyquinoline immobilized on fluorinated metal alkoxide glass (MAF-8HQ) was used for in-line separation of trace metals from seawater matrix. Another approach was used by Point et al. [17], two separate flow-based automated platforms consisting of an ultraviolet digestion unit and a chelation/pre-concentration/matrix

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elimination module were developed to process samples on-site before the ICP-MS detection for determination of total, labile and organically bound dissolved forms of seven trace metals in waters. Total dissolved and labile forms of copper, manganese and zinc were also determined in seawater samples by flow injection flame AAS spectrometry employing in-line fractionation of analytes with the use of chelating ion-exchange module packed with the Serdolit Chelite Che chelating resin (containing iminodiacetic acid groups) for separation and pre-concentration [12]. Total dissolved content of the analytes was determined after decomposition of organic complexes on-line by sonolysis.

Regarding electrochemical detection, anodic stripping chronopotentiometry [18] and anodic stripping voltammetry [19,20] methods were developed for determination of copper and zinc using FIA, SIA or both techniques, respectively.

Spectrophotometric methods are also still used to multicomponent determination, especially in combination with flow-based techniques, due to the possibility of developing relatively low-cost methods utilizing portable, automated and versatile systems for both in-line sample treatment and analysis. Regarding spectrophotometric detection, determinations can be based on the use of various chromogenic reagents. Bis(cyclohexanone)oxalyldihydrazone (cuprizone) and xylenol orange were applied to separate determination of zinc and copper, respectively [21,22]. Other complexing reagents like 1-(2-pyridylazo)-2-naphthol (PAN) [23,24], zincon [25–29], ditzone [30,31], sodium diethyldithiocarbamate (Na-DDTC) [32] or 4-(2-pyridylazo) resorcinol (PAR) [31,33] were also reported. Since these reagents form color compounds with both analytes, calibration, like H-point standard addition method [23], phase separation [24,29,30] or instrumental solutions were explored to enable simultaneous determinations and to enhance the selectivity of determinations. The use of resins and/or membranes results in a phase separation of the analyte or potential competitor ions. Using a flow-based system, multivariate calibration based on the substitution reaction of metal-nitrilotriacetic complexes (M-NTA) by PAR and employing spectral differences between the colored complexes in combination with differences in the reactions kinetics was described [33]. Different metal ions were also determined simultaneously using thin-film sequential injection extraction (SIE) with multivariate calibration, multi-wavelength detection and the dithizone-based method [31]. Differences in kinetics [25] and in the reaction pH [26–28] were also used for the determination of copper and zinc with spectrophotometric detection of metal-zincon complexes. To attain lower detection limit, two approaches have been reported: the use of a liquid waveguide capillary cell [26] and a pre-concentration unit with solid phase resin either in a solid phase extraction (SPE) approach [34] or in solid phase spectrophotometry (SPS) method with nitrilotriacetic acid (NTA) beads in a  $\mu$ SI-LOV system [30]. Copper and zinc were also simultaneously determined using a flow injection system with a chromatomembrane cell (CMC) to extract them separately and to pre-concentrate them before detection [24].

Chelex-100 is a strong complexing resin containing the iminodiacetic group resin and it was selected as a cationic resin for metal ion retention/separation/pre-concentration. It has been reported to be used: in metal species separation [35]; quantitative pre-concentration of metals from sea water [36]; discrimination between very labile, moderately labile, slowly labile and inert metal fractions [37]; separation of labile copper fractions in various environmental samples [38] or separation and pre-concentration, of Cu(II), Pb(II), Fe(III), Co(II), and Cr(III) ions in natural water and black tea samples [39]. Furthermore, the authors' previous experience using Chelex-100 in a sequential injection approach [40] has proved quite efficient for specific retention through pH adjustment.

Various factors, namely soil properties like pH, soil fraction, organic matter, sorption capacity or redox potential, influence the mobility and bioavailability of metal ions and affect the leaching of trace elements from contaminated soils. To study these processes may provide practical insights for soil remediation efforts and assessment of risk for the

environment, so the effect of rainwater on trace metal leaching were investigated [11]. Attempts were also made to miniaturize columns and applied them to study metal-partitioning and release-rate under environmentally simulated conditions using both flow injection [41] and sequential injection [42,43] systems with various modes of leaching, like continuous leaching, static extraction and recirculation mode [44].

The objective of this work was to develop a simple sequential injection method with in-line solid phase extraction (SI-SPE) for the bi-parametric determination of copper and zinc with spectrophotometric detection enabling both the application to leachate samples from laboratory soil columns and to study the in-line soil mini soil columns. The determination of copper and zinc ions was based on reaction with PAN as a chromogenic reagent on account of high molar absorptivity of the formed complexes. To this aim, the system comprising two channels for sample introduction was designed. One of the channels was equipped with a solid phase extraction (SPE) mini-column of Chelex100 resin (mRC) used as a sorbent to retain copper. This way, in the optimized conditions, zinc was determined directly, after retaining copper on the mRC. Using the second channel, sample was introduced directly, and copper was determined based on the difference between the signal for the sum of both analytes and the signal for zinc.

Then, the system was equipped with an original in line soil mini-column (ILSM). The idea was to downscale the laboratory scale soil core column to enable the in-line simulations of environmental conditions with the use of rain water to collect the soil leachates. The approach was verified by the determination of both analytes in synthetic and certified reference material of water samples, and applied to the determination of the analytes in rain water and soil leachates from laboratory scale soil core column and in-line soil mini-column after irrigation with rainwater.

## 2. Experimental

### 2.1. Reagents and solutions

All solutions were prepared with analytical grade chemicals and deionized water (specific conductance less than  $0.1 \mu\text{S cm}^{-1}$ ). To minimize potential air bubbles interference, deionized water was boiled before its use.

Stock solutions of  $10 \text{ mg L}^{-1}$  of copper and zinc were prepared by 100-fold dilution with  $0.01 \text{ mol L}^{-1}$  nitric acid of the standard solutions of  $1000 \text{ mg L}^{-1}$  (Spectrosol, England). Working standard solutions in the ranges  $0.005$ – $0.30 \text{ mg L}^{-1}$  for zinc and  $0.01$ – $0.20 \text{ mg L}^{-1}$  for copper  $0.02$ – $0.30$  were weekly prepared by dilution of the  $10 \text{ mg L}^{-1}$  stock solution and acidified to final concentration  $0.01 \text{ mol L}^{-1}$  nitric acid.

The 1-(2-Pyridylazo)-2-naphthol (PAN) stock solution ( $0.1\%$  w/v) was prepared by dissolving  $50 \text{ mg}$  of PAN (Sigma Aldrich, USA) in  $50 \text{ mL}$  of ethanol ( $99.5\%$  AGA, Portugal). PAN intermediate solution of concentration  $0.02\%$  (w/v) was prepared by dilution  $20 \text{ mL}$  of PAN stock solution in  $35 \text{ mL}$  of ethanol ( $99.5\%$  AGA, Portugal) and making it up to  $100.0 \text{ mL}$  with water. A stock solution of Triton X-100 was prepared by dissolving  $20 \text{ g}$  of the surfactant Triton X-100 (Sigma Aldrich, USA) in  $80 \text{ g}$  of water. The PAN working solution of  $0.03 \text{ g L}^{-1}$  was prepared by mixing  $15 \text{ mL}$  of PAN intermediate solution and  $7.5 \text{ mL}$  of Triton X-100 stock solution and dilution with water to a final volume of  $100 \text{ mL}$ .

The  $0.6 \text{ mol L}^{-1}$  hydrogen carbonate buffer solution was prepared by dissolving  $10.08 \text{ g}$  of  $\text{NaHCO}_3$  (Merck, Germany) in  $200 \text{ mL}$  of water and adjusting the pH to  $10.0$  with  $10 \text{ mol L}^{-1}$  NaOH.

The stock solution of nitric acid,  $0.5 \text{ mol L}^{-1}$ , was prepared by dilution of concentrated acid ( $d = 1.4$ ;  $65\%$ , Merck, Germany).

For interference assessment studies, the solutions of the tested ions were obtained by appropriate dilution with nitric acid ( $0.01 \text{ mol L}^{-1}$ ) the respective atomic absorption standards (Spectrosol, Spain).

The cationic resin – Chelex 100 sodium form ( $200$ – $400$  mesh, Bio-Rad, USA) was used for in-line solid-phase extraction. The resin was

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