



Flow injection on-line displacement/solid phase extraction system coupled with flame atomic absorption spectrometry for selective trace silver determination in water samples

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ABSTRACT

A novel flow injection (FI) on-line displacement solid phase extraction preconcentration and/or separation method coupled with FAAS in order to minimize interference from other metals was developed for trace silver determination. The proposed method involved the on-line formation and subsequently pre-sorption of lead diethyldithiocarbamate (Pb-DDTC) into a column packed with PTFE-turnings. The preconcentration and/or separation of the Ag(I) took place through a displacement reaction between Ag(I) and Pb(II) of the pre-sorbed Pb-DDTC. Finally, the retained analyte was eluted with isobutyl methyl ketone (IBMK) and delivered directly to nebulizer for measuring. Interference from co-existing ions with lower DDTC complex stability in comparison with Pb-DDTC, was eliminated without need for any masking reagent. With 120 s of preconcentration time at a sample flow rate of 7.6 mL min⁻¹, an enhancement factor of 110 and a detection limit (3 s) of 0.2 µg L⁻¹ were obtained. The precision (RSD, *n* = 10) was 3.1% at the 10 µg L⁻¹ level. The developed method was successfully applied to trace silver determination in a variety of environmental water samples and certified reference material.

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1. Introduction

The widespread use of silver compounds and silver-containing procedures in industry, medicine, jewellery, cloud seeding and in the disinfection of drinking water has resulted in an increasing silver content of environmental samples. Silver impregnated filters are used in water disinfection, while silver concentrations up to 200 µg L⁻¹ are permitted for antimicrobial activities for human health [1]. Silver often presented as an impurity in Cu, Zn, As and Sb ores and thus it is possible to be entered into the environment from industrial wastes [2,3]. Bowen [4] suggested that silver may pose a potential risk as a water pollutant, because of the lack of recycling of mined silver. Also, recent information about the interaction of silver with essential nutrients, especially selenium, copper and vitamins E and B₁₂, has focused attention on its potential toxicity [1]. Consequently, determination of trace amounts of silver is important for many areas of chemical analysis.

Although, flame atomic absorption spectrometry (FAAS) is one of the most popular used techniques for metals determination with significant precision and accuracy, there are many limitations

to determine traces of analyte in environmental samples due to insufficient sensitivity or in some sample types matrix interference. Conventional off-line procedures for preconcentration and/or separation are usually effective, but they are time-consuming and tedious, requiring large quantities of sample and reagents, and thus potential prone to sample contamination and analyte losses. On-line flow injection (FI) preconcentration and/or separation coupled with atomic spectrometry has been shown to be very powerful in eliminating many of the above drawbacks for trace elements determination and offers advantages inherent in automatic methods of analysis [5,6].

Among on-line preconcentration techniques frequently used, FI micro-column based solid phase extraction presents many advantages, such as relatively high concentration factor and sampling frequency, simplicity of phase separation and suitability for automation [7,8]. Several methods have been reported to adapt FI on-line solid phase extraction coupled with FAAS, for the determination of silver in various types of samples. These methods usually make use of a packed column filled with a suitable stationary phase like: immobilized or modified silica gel [9–12], activated or immobilized alumina [13,14], sulfhydryl cotton fibers [3] and rhodamine fibers [15]. Alternatively, a knotted reactor (KR), which consists from a long polytetrafluoroethylene (PTFE) tube properly knotted, can be applied as a sorbent surface [16].

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However, preconcentration systems usually suffer undesirable interference from co-existing transition metals especially in complicated matrices, owing to metal competition for the complexing reagent and/or active sites of sorbent material in packed columns or in the inner walls of the KR [17]. Recently, Yan et al. [17] presented a FI on-line displacement solid phase extraction preconcentration method for interference-free determination of copper by FAAS. The methodology involved on-line formation, pre-sorption of the Pb-DDTC chelate onto the inner wall of the KR and subsequently retention of the analyte Cu(II) through a displacement reaction between the Cu(II) and the Pb(II) in the pre-sorbed Pb-DDTC complex because the stability of Cu-DDTC is greater than Pb-DDTC. Finally the retained analyte was eluted with ethanol and detected by FAAS. Interferences from co-existing ions with lower stability DDTc complexes relative to Pb-DDTC were eliminated without need for any masking agents, due to their competition with Cu(II) for DDTc and the active sorption sites on the inner walls of the KR. The same group also employed the above concept for mercury speciation and palladium determination, using cigarette filter as sorbent material [7,18–20]. To the best of our knowledge the above technique has not been applied for silver determination.

On the other hand PTFE-turnings have been proved as superior hydrophobic sorbent material for FI on-line column preconcentration systems for Cu, Pb, Cr, Co, As and Hg determination [8,21–25] but have not been used yet in on-line displacement solid phase extraction systems.

The aim of this work was to investigate the applicability of the micro-column packed with PTFE-turnings in FI on-line displacement solid phase extraction system in order to minimize interference from other metals, using sodium diethyl dithiocarbamate (NaDDTC) as complexing agent for selective and sensitive FAAS determination of trace silver in water environmental samples.

2. Experimental

2.1. Instrumentation

A PerkinElmer, Norwalk, Connecticut, USA (<http://las.perkinelmer.com>) model 5100 PC flame atomic absorption spectrometer with deuterium arc background corrector was exploited as detection system. A silver hollow cathode lamp (HCL) operated at 10 W was used as light source. The wavelength was set at 328.1 nm resonance line and the slit at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. The flame conditions were slightly leaner than those recommended by the manufacturer, in order to compensate the effect of organic solvent isobutyl methyl ketone (IBMK), which serves as additional fuel during elution step. The air and acetylene flow rate was set at 10.0 L min⁻¹ and 0.9 L min⁻¹, respectively. In that case the nebulizer's free uptake rate was 5.9 mL min⁻¹. A flow spoiler was employed into the spray chamber for better nebulization conditions. The spectrometer was set to work in the FI-FAAS mode.

A PerkinElmer Norwalk, Connecticut, USA model FIAS-400 flow injection analysis system was coupled to the flame atomic absorption spectrometer for automatic processing of the method and operated in preconcentration mode. The whole system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 application program. The FIAS-400 system consisted of two peristaltic pumps P1, P2 and a 5-port 2-position injection valve, while it was connected to the spectrometer's nebulizer, using a short PTFE capillary 20.0 cm length/0.35 mm i.d., in order to minimize the eluent dispersion. A third peristaltic pump P3 (Watson Marlow model 205U/BA) was also elaborated for the FI on-line displacement solid phase extraction method. A flow compensation (FC) unit was used

just before the nebulizer inlet, in order to compensate the lack of nebulizer free uptake flow rate. Peristaltic pump tubing of "Tygon" type was adopted to deliver the aqueous solutions and a displacement bottle (Tecator, Hoganas, Sweden, <http://www.foss.dk>) was used to deliver the organic solvent, isobutyl methyl ketone. All other conduits used for various connections were of 0.5 mm i.d. PTFE tubing.

The micro-column for retention of Ag-DDTC derivative complex was fabricated by firmly packing 100 mg of PTFE-turnings in a piece of narrow PTFE tube (20 mm length, 2.1 mm i.d./3.2 mm o.d.). PTFE-turnings were mechanically produced in our laboratory by lathe as described elsewhere [8]. The image from PTFE-turnings using an optical microscope has been given previously [25]. The turnings were washed thoroughly by ethanol followed by 1 mol L⁻¹ HNO₃ and finally with de-ionized water. No frits or glass wool were necessary at either end to block the PTFE-turnings. The column was initially flushed with de-ionized water and subsequently with IBMK. The performance of the column was stable at least for 1000 preconcentration cycles.

An Orion EA940 pH-meter was employed for the pH measurements with absolute accuracy limits at the pH measurements being defined by NIST buffers.

2.2. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, <http://www.merck.de>). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA, <http://www.millipore.com>). Working standard solutions of Ag(I) and Pb(II) were prepared by appropriate stepwise dilution of a 1000 mg L⁻¹ stock standard solution (Titrisol, Merck) to the required µg L⁻¹ levels. The acidity of the standards was adjusted with dilute HNO₃. The chelating reagent 0.1% (m/v) DDTc was prepared fresh daily by dissolving the appropriate amount of sodium diethyl dithiocarbamate (Aldrich) in water. Isobutyl methyl ketone was used after saturation with water, without any other purification.

Natural water samples (tap, lake, and coastal sea-water, from Northern Greece) and the industrial waste water treatment plant, filtered through 0.45 µm membrane filters, acidified to 0.1 mol L⁻¹ HNO₃ and stored at 4 °C in acid-cleaned polyethylene bottles, in order to determine the "dissolved metal" fraction. The standard reference material NIST CRM 1643d (National Institute of Standard and Technology, Gaithersburg, MD, USA, <http://www.nist.gov/>) containing trace elements in water, was also analyzed.

2.3. Procedure

The operation sequence (three steps) and the schematic diagram of the manifold for the FI on-line displacement solid phase extraction (FI-D/SPE-FAAS) method for silver determination are presented in Table 1 and Fig. 1, respectively. In step 1 (Fig. 1, Pre-sorption), the injection valve (IV) was set in the load position. Pump P2 fed a mixed solution 1.0 mg L⁻¹ Pb(II) and 0.05% (m/v) DDTc as complexing agent, through the column C for 30 s. The formed Pb(II)-DDTC complex was adsorbed on the surface of the PTFE-turnings of the packed column. In the mean time, pump P1 remained inactive and the nebulizer of the FAAS aspirated air through the flow compensation adapter (FC). During step 2, pump P2 was off, while pump P3 was activated and propelled the sample solution through the column for 120 s. In this step, the silver ions were retained onto the surface of the PTFE-turnings, by replacing the Pb(II) ions of the pre-sorbed Pb(II)-DDTC complex. Such displacement reaction could not be established between other co-existing metal ions and

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