Talanta 84 (2011) 1215–1220

Contents lists available at ScienceDirect

Talanta

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Sequential injection dispersive liquid–liquid microextraction based on fatty alcohols and poly(etheretherketone)-turnings for metal determination by flame atomic absorption spectrometry

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ARTICLE INFO

Article history:
Available online 15 December 2010

Keywords:
Sequential injection
Dispersive liquid–liquid microextraction
Atomic spectrometry
1-Dodecanol
Silver

ABSTRACT

A novel, simple and efficient sequential injection (SI) on-line dispersive liquid–liquid microextraction (DLLME) procedure was described and was demonstrated for the assay of trace silver determination by flame atomic absorption spectrometry (FAAS). Fatty alcohols, such as 1-undecanol and 1-dodecanol, were examined as extraction solvents at microlitre volume, overcoming a major problem of the DLLME methods, the high toxicity of the extraction solvents used. Furthermore, the extractant fine droplets can be easily separated from the aqueous phase using a micro-column packed with a novel hydrophobic sorbent material, poly(etheretherketone)-turnings. In this method fine droplets of 1-dodecanol were on-line generated and dispersed into the stream of aqueous sample. By this continuous process, silver diethyldithiocarbamate (Ag-DDTC) complex was formed and extracted into the dispersed extraction solvent. No specific conditions such as ice bath for low temperature or special tools are required for extractant isolation. All significant parameters that influence the efficiency of the system such as sample acidity, concentration of complexing reagent and extraction solvent, flow-rate of disperser and sample solution as well as the preconcentration time were investigated and optimized by full factorial design. Under the optimized conditions a detection limit of 0.15 $\mu g\,L^{-1}$, a relative standard deviation (RSD) of 2.9% at 5.00 $\mu g\,L^{-1}$ Ag(I) concentration level and an enhancement factor of 186 were obtained. The developed method was evaluated by analyzing certified reference material and was applied successfully to the analysis of environmental water samples.

1. Introduction

In spite of its noteworthy analytical performances on metal determination, flame atomic absorption spectrometry (FAAS) often requires a suitable sample processing involving analyte preconcentration and/or matrix clean-up for the determination of trace level concentration of metals in various environmental samples, according to the tolerable levels imposed by European directives [1,2].

Liquid–liquid extraction (LLE) is a versatile sample preparation technique as well as the most commonly used one in routine analysis. However, there are some drawbacks such as the consumption of large amounts of high cost and potentially toxic organic solvents which are often hazardous and large volume of sample. In addition LLE is time-consuming, tedious, laborious and unfriendly to the environment. The trends in analytical processing are towards the simplification, miniaturization automation of all analytical steps and the compactness of the apparatus, which enhances the precision of the overall method [2].

Efforts have been focused on the miniaturizing of the LLE procedure by drastically reducing the organic solvent, introducing inexpensive liquid phase microextraction (LPME) methodologies [3–5]. LPME is achieved by extraction into a small drop of water-immiscible organic solvent (single drop microextraction, SDME) [6,7] or into small volume of acceptor solution, which is located inside the lumen of porous hollow fiber (HF-LPME) [8] and recently by dispersive liquid–liquid microextraction (DLLME), which is based on ternary component solvent system [9–11]. In DLLME methodology an appropriate mixture of extraction solvent and disperser solvent is injected into the sample (aqueous phase) containing the analytes. Consequently, a cloudy solution (high turbulence) is produced, which consisted of fine droplets of extraction solvent dispersed into the bulk aqueous solution [11]. The nature of the disperser solvent plays a key role that helps extraction solvent to form fine droplets in aqueous sample, affecting the mean droplet size and their distribution. The principal advantage of DLLME is the simplicity and the very short extraction time, due to the abundant surface contact between extraction solvent and aqueous phase,

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doi:10.1016/j.talanta.2010.12.017

which speeds up the mass-transfer processes of analytes from aquatic phase to organic phase. Nevertheless, the extraction solvent used in DLLME is generally highly toxic and not environmental friendly.

Although, it has been reported that DLLME has inherent difficulty on automation and the extraction solvent must have higher density than water (in order to be easily separated after centrifugation), which limit the choice of suitable solvents [4], a novel automatic sequential injection (SI) system based on DLLME has been presented by our group solving the above problems of the manual methods [10,12].

Recently, a novel liquid–liquid microextraction methodology based on solidification of a floating organic solvent droplet (SFO-LLME) was presented by Khalili Zanjani et al. [13]. In this method a small volume of an organic solvent with a melting point near room temperature (10–30 °C), like some fatty alcohols, is floated on the surface of the agitated aqueous sample in order to maximize the contact between the two solutions. The sample vial is then placed in an ice bath to solidify the droplet, which then can be easily removed by a special tool and it is subsequently melted for analyte determination. Leong and Huang [14] reported a variation of SFO-LLME based on DLLME methodology, achieving faster mass transfer and better extraction times. Both versions of SFO methods present speed, simplicity and high efficiency, consuming very small volumes of organic solvent in a "green operation" thanks to the fatty alcohols used. However, the limitation in the choice of proper extraction solvent, the need for centrifuging the cloudy solution and freezing the droplets can be mentioned as their major drawbacks.

The aim of present work was to develop a novel automatic sequential injection dispersive liquid–liquid microextraction (SI-DLLME) system combined with FAAS for trace metal determination. For this purpose, a fully automated interface was developed using a microcolumn packed with a novel hydrophobic sorbent poly(etheretherketone) (PEEK) in the form of turnings for extraction solvent separation instead of centrifugation. To meet recent concerns about environmental dangers of waste solvent disposal and the expenses, this method used fatty alcohols which are recognized as low-toxicity extraction solvent with a melting point near room temperature. To the best of our knowledge, the use of fatty alcohols and PEEK-turnings in an automated SI-DLLME format was demonstrated for the first time. The effectiveness and efficiency of the proposed SI-DLLME system have been demonstrated for silver determination in environmental water samples, because it is considered to be toxic and the recommendations of the World Health Organization (WHO) permit maximum concentrations of 100 μg L^{-1} of silver ions in drinking water, while the United States Environmental Protection Agency (USEPA) recommends 50 μg L^{-1} as maximum [15]. Sodium diethyl dithiocarbamate was implemented as a chelating ligand since it forms very stable hydrophobic complexes with silver ions in acidic medium, resulting thus to higher selectivity and sensitivity. The main parameters influencing the extraction efficiency were investigated and optimized by full factorial design. The accuracy of the proposed method was estimated by analyzing certified reference material and spiked environmental samples.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer, Norwalk, CT, USA (http://las.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer was exploited as detection system. A silver hollow cathode lamp (HCL) operated at 10 W was employed as radiation 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 adjusted to be slightly leaner than that recommended by the manufacturer, in order to compensate the effect of methyl isobutyl ketone (MIBK), which serves as an additional fuel during the measuring step. Thus the air and acetylene flow rate were set at 10.0 L min^{-1} and 0.9 L min^{-1}, respectively. By these flow conditions the nebulizer's free uptake rate was 5.6 mL min^{-1}. For better nebulization conditions, a flow spoiler inside the spray chamber was employed, according to the manufacturer recommendations.

A Perkin-Elmer Norwalk, CT, USA model FIAS-400 flow injection analysis system was combined with FAAS and SI system for automatic processing of the whole procedure. The FIAS-400 system was controlled by a personal computer and by the AA Lab. Benchtop version 7.2 software program. The FIAS-400 system consisted of two peristaltic pumps (only one was used in the proposed manifold) and a 5-port 2-position injection valve, IV. The connecting tubing between the IV and the FAAS nebulizer was as short as possible PTFE tube (20 cm length, 0.5 mm i.d.), in order to restrict analyte dispersion.

A FIAlab®-3000 sequential injection system (Alitea FIAlab, USA) equipped with an internally incorporated six-port multiposition valve (MV) and a syringe pump (SP, Cavro, Sunnyvale, CA) with a capacity of 1000 μL was adopted. The FIAlab®-3000 system was controlled by a personal computer and the FIAlab for windows v.5.9.245 application software, written by FIAlab instruments (http://www.flowinjection.com). The two programs (FIAlab and AA Lab.) were synchronized and activated in the same time.

Polyetherether ketone (PEEK) is a semi-crystalline thermoplastic with excellent mechanical and chemical resistance properties that are retained to high temperatures. It is a hydrophobic material and appears similarities with polytetrafluoroethylene (PTFE) concerning the retention of chelate complexes of metals and nonpolar organic solvents on its surface [16]. Due to the fact that PEEK is not accessible in the market in the form of beads, granules, fiber or turnings, we produced PEEK-turnings with 0.4 mm mean width, using a lathe. The image of the sorbent material is presented elsewhere [16]. The microcolumn (C) for retention of the extraction solvent was fabricated by firmly packing 750 mg of PEEK-turnings in a piece of narrow plastic tube (30 mm length, 3.2 mm id). First, the turnings were washed thoroughly by ethanol followed by 1.0 mol L^{-1} HNO_3 and finally with de-ionized water. No frits or glass wool were necessary at either end of the column to block the PEEK-turnings. The performance of the column was stable for more than 500 cycles and could be characterized as unlimited lifetime sorbent material.

A VICI AG (Valco International) four-section "cross" type confluence connector made of PEEK, with 0.5 mm i.d. bore size was used for intermixing aqueous (sample) and disperser solution. An Orion EA940 pH-meter was employed for the pH measurements being defined by NIST buffers.

2.2. Reagents and samples

All chemicals were of highest purity available from 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) were prepared daily 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 HNO_3. 1-Undecanol (1-UN-OH) (99%) and 1-dodecanol (1-DD-OH) (≥98.5%, GC) were obtained from Aldrich (Steinheim, Germany) and were used as the extracting solvents. Sodium diethyl dithiocarbamate (DDTC) was provided by Aldrich and the solution of sodium diethyl dithiocarbamate

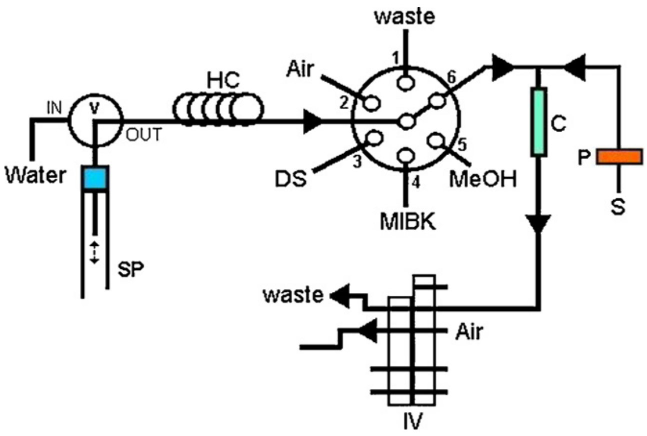

Fig. 1. Schematic manifold for SI-DLLME silver determination by FAAS (extraction). For details see text and Table 1. S, sample; DS, dispersive solution containing 2.0% (v/v) 1-dodecanol and 0.3% (m/v) DDTC; W, waste; P, peristaltic pump; SP, syringe pump; MV, multi-position valve; IV, injection valve in "load: position; V, valve in "out" position; HC, holding coil; C, microcolumn; MeOH, methanol; MIBK, methyl isobutyl ketone.

in methanol 0.3% (m/v) was prepared fresh daily by dissolving the appropriate amount of DDTC in methanol (MeOH). Methanol CHROMASOLV® gradient grade, for HPLC, ≥99.9% (Sigma–Aldrich) was used as disperser solvent for the study. The disperser solvent solution was prepared daily by dilution of appropriate amount of 1-dodecanol and DDTC in MeOH. Methyl isobutyl ketone (MIBK) was used after saturation with ultra-pure water, without any other purification.

Natural water samples (river and sea-water, from Northern Greece) and the industrial waste water treatment plant were filtered through 0.45 μm membrane filters, acidified to 0.1 mol L^{-1} HNO_3 and stored at 4 °C in acid-cleaned polyethylene bottles, in order to determine the "dissolved metal" fraction. The standard reference material NIST CRM 1643e (National Institute of Standard and Technology, Gaithersburg, MD, USA, http://www.nist.gov/) containing trace elements in water was also analyzed.

2.3. General procedure

The schematic diagram of the manifold and the operation sequences for the optimized SI-DLLME method for silver determination are presented in Fig. 1 and Table 1, respectively. Extraction, separation of extraction solvent (1-DD-OH) and measuring of absorbance were performed in the following steps: during step 4, 360 μL of methanol containing 2.0% (v/v) 1-dodecanol as extraction solvent and 0.3% (m/v) DDTC as chelating reagent were mixed on-line with the stream of sample solution. By this continuously mixing process a cloudy solution resulted from the dispersion of fine 1-DD-OH droplets in the aqueous stream and metal complexes were extracted from aqueous phase to organic phase (1-DD-OH). The extraction procedure was performed for 180 s which is defined as preconcentration time. The cloudy solution was passed through the micro-column and the fine droplets of 1-DD-OH were retained on the PEEK-turnings. With this operation, major problems of manual methods such as centrifugation and solidification with ice bath, for separation of the extraction solvent were solved. During step 7, a well-defined amount of 600 μL MIBK was delivered through the micro-column for extraction solvent elution and transportation directly to FAAS nebulizer for atomization and measuring. During the next steps complete washing of the micro-column and tubing was done. Three replicate measurements were made in all instances.

3. Results and discussion

Taking into consideration the sensitivity on the determination of silver ions, as well as the selectivity and precision of the SI-DLLME, the effect of the most important parameters such as type of disperser and extraction solvent, sample acidity, concentration of extraction solvent and chelating reagent in the disperser solvent, sample and disperser flow rate, and preconcentration time on the analytical signal was examined and optimized. The effect of the four variables: concentration of extraction solvent and chelating reagent, flow rate of sample and disperser solution on the analytical signal as well as their interactions with each other were studied by applying a two-level full factorial design. The total number of required runs is given by equation 2^n, where n is number of variables. The significant variables are found by analysis of variance (ANOVA) and using p-value at 95% significant level. Acidity of sample solution and preconcentration time were studied by univariate analysis, in order to study each variable in a wide range of values, separately. All experiments were carried out using standard aqueous solution 10.00 μg L^{-1} Ag(I) in 0.1 mol L^{-1} HNO_3.The experimental data were processed by using Statistica 9.0 software [17].

Acetone, acetonitrile ethanol and methanol have been examined as disperser solvents elsewhere [10,12] and proved that the recovery variations using the above disperser solvents were not remarkable. Thus, considering accessibility, low cost and toxicity, methanol was selected as disperser solvent for our work.

For effective elution of the extraction solvent, direct transportation to FAAS and atomization of the analyte, a segment of 600 μL MIBK at 40 μL s^{-1} flow-rate were adopted with the proposed manifold (Fig. 1) for all experiments, as it was optimized from preliminary experiments.

Table 1
Operational sequences of the SI-DLLME method for silver determination by FAAS (for manifold details, see Fig. 1).

Step	V position	MV position	SP flow-rate (μL s^{-1})	SP operation	IV position	P operation	Remarks
1	In	2	50	Aspirate 100 μL	Load	Off	Water into SP
2	Out	2	10	Aspirate 30 μL	Load	Off	Segment of air into HC
3	Out	3	50	Aspirate 380 μL	Load	Off	Dispersive solution into HC
4	Out	6	2	Dispense 360 μL	Load	On[a]	Cloudy solution generation/extraction/retention of 1-DD-OH
5	Out	1	50	Empty	Load	Off	Discard of air segment
6	Out	4	60	Aspirate 600 μL	Load	Off	MIBK into HC
7	Out	6	40	Dispense 600 μL	Elution	Off	Elution of 1-DD-OH/measuring
8	IN	2	50	Aspirate 200 μL	Load	Off	Water into SP
9	Out	2	10	Aspirate 30 μL	Load	Off	Segment of air into HC
10	Out	5	50	Fill	Load	Off	MeOH into HC
11	Out	6	50	Empty	Load	Off	Washing of microcolumn

[a] Sample propulsion with flow rate, 90 μL s^{-1}; V, valve; MV, multiposition valve; SP, syringe pump; IV, injection valve; P, peristaltic pump.

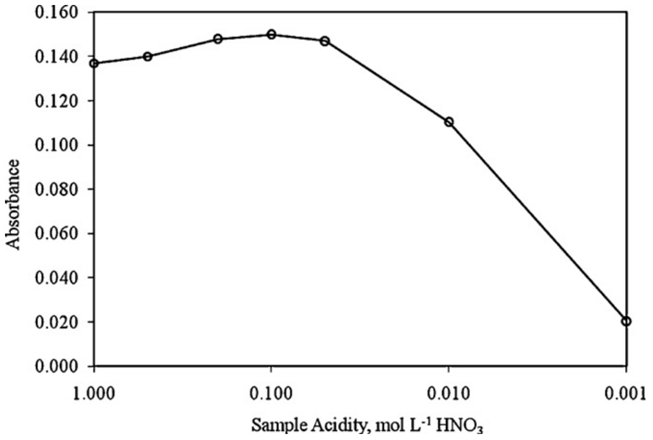

Fig. 2. Effect of sample acidity, expressed as nitric acid concentration, on the absorbance of 10.00 μg L^{-1} Ag(I). Preconcentration time 180 s, all other parameters as in Table 1.

3.1. Selection of extraction solvent

In solidification floating organic drop dispersive liquid–liquid microextraction (SFO-DLLME) batch methods an extraction solvent should fulfill several requirements: it must have a lower density than water, its melting point should be near room temperature (10–30 °C); it should have low volatility, low toxicity and low solubility in water and last but not the least should reveal good extraction capability of the compounds of interest [18]. In contrast to conventional (batch) methods, the extraction solvent was not necessary to have lower density than water, due to the fact that the formation of cloudy solution is generated in a moving stream and the separation of the fine droplets of the extraction solvent from the aqueous phase is accomplished on the hydrophobic sorbent PEEK-turnings. It means that the separation of the organic phase is based on the retention and not on the centrifuging of the cloudy solution. This is a silent advantage of the proposed on-line DLLME system.

Two extraction solvents such as 1-UD-OH (melting point: 16 °C) and 2-DD-OH (melting point: 23 °C) were compared for the extraction of Ag(I). The concentration of the studied organic solvents in methanol was fixed at 2.0% (v/v). Both fatty alcohols gave good extraction efficiency for silver anion. Finally, 1-dodecanol was selected for all experiments because it is cheaper than 1-undecanol.

3.2. Sample acidity

Acidity of the sample solution plays a significant role in the overall performance of the on-line solvent extraction by affecting Ag-DDTC complex formation and extraction efficiency. Sample acidity was studied by varying nitric acid concentration in standard aqueous solution of 10.00 μg L^{-1} Ag(I), from 0.001 mol L^{-1} up to 1.0 mol L^{-1}. As can be seen in Fig. 2 the recorded absorbance was higher and remained practically constant from 0.05 mol L^{-1} to 0.2 mol L^{-1} HNO_3. At the above-mentioned acidic range DDTC can be protonated, which results in forming stable Ag(I)–DDTC complex through its two donor sulphur atoms [19]. Thus, samples and standards solutions were prepared in 0.1 mol L^{-1} HNO_3, which is also used for common acid preservation of the environmental water samples.

3.3. Optimization study of the experimental parameters

The optimization of the on-line SI-DLLME system was performed with a multivariate approach using a 2^4-level full experimental design. High (+) and low (−) levels of the four studied factors were: concentration of extraction solvent (ES-C), 4.0% (m/v) and 2.0% (m/v); concentration of DDTC (R-C), 0.4% (m/v) and 0.2% (m/v); disperser solution flow rate (DS-FR), 8 μL s^{-1} and 3 μL s^{-1}; sample flow-rate (S-FR), 90 μL s^{-1} and 40 μL s^{-1}. The total number of experiments was 16 for the 4 factors and each experiment was carried out in duplicate. The preconcentration time was fixed at 180 s. The experimental matrix of the 2^4 full factorial design together with the recorded analyte responses is given in Table 2. An analysis of variance (ANOVA) was performed to examine whether the studied experimental factors as well as the 2nd order interaction effects, were significant in the performance of the proposed preconcentration system. The results are given in Table 3. An effect was considered significant when it was above the standard error at the 95% confidence level ($p > 0.05$), which is denoted by the vertical line on the Pareto chart (Fig. 3). According to this Pareto chart the factors, ES-C, DS-FR and S-FR, in the studied range were statistically significant at 95% confidence level, while R-C proved nonsignificant. The negative values indicate that decreasing these factors will result in an increase in the analytical signal. Among the second order interactions that of DS-FR and S-FR (3 by 4) was the most significant and the negative value (−3.78) indicates that a lower value of DS-FR combined with higher value of S-FR leads to a high response. Based on the negative value of interaction 2 by 3 (Fig. 3) and the fact that factor R-C is insignificant, 0.3% (m/v) DDTC was selected as optimum for the method.

Table 2
The experimental matrix of 2^4 full factorial design and the recorded analytical responses.

Experiment	ES-C	R-C	DS-FR	S-FR	Abs_1	Abs_2
1	–	–	–	–	0.114	0.109
2	+	–	–	–	0.065	0.061
3	–	+	–	–	0.102	0.107
4	+	+	–	–	0.066	0.062
5	–	–	+	–	0.058	0.072
6	+	–	+	–	0.041	0.039
7	–	+	+	–	0.058	0.064
8	+	+	+	–	0.056	0.051
9	–	–	–	+	0.140	0.145
10	+	–	–	+	0.112	0.114
11	–	+	–	+	0.152	0.153
12	+	+	–	+	0.136	0.132
13	–	–	+	+	0.114	0.116
14	+	–	+	+	0.060	0.056
15	–	+	+	+	0.078	0.075
16	+	+	+	+	0.056	0.058

Following results of the previous design (2^4-level full experimental design), a 2^3-level full factorial design was applied for the remaining three significant factors at different optimization range. In this case the two levels of the studied variables were: ES-C, 2.0% (m/v) and 1.5% (m/v); DS-FR, 3 μL s^{-1} and 2 μL s^{-1} and

Table 3
Analysis of variance (ANOVA) results for effect of the 4 factors and their 2nd order interactions.

Factor and interactions	df	MS	F_{exp}	p
(1)ES-C	1	0.007565	68.9809	0.000000
(2)R-C	1	0.000003	0.0285	0.867561
(3)DS-FR	1	0.016110	146.9088	0.000000
(4)S-FR	1	0.010225	93.2376	0.000000
1 by 2	1	0.000684	6.2420	0.020850
1 by 3	1	0.000098	0.8937	0.355237
1 by 4	1	0.000001	0.0103	0.920284
2 by 3	1	0.000378	3.4481	0.077406
2 by 4	1	0.000018	0.1641	0.689468
3 by 4	1	0.001568	14.2986	0.001095
Error	21	0.000110		
Total SS	31			

df, degrees of freedom; MS, mean squares.

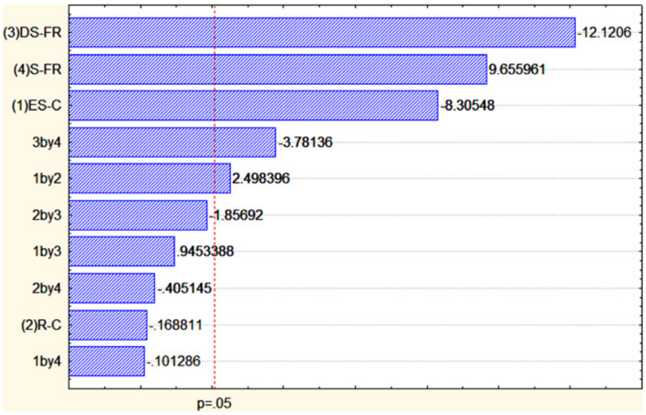

Fig. 3. Pareto chart obtained from the optimization study of the factors, with their significance, for the SI-DLLME determination of Ag(I). The experimental conditions are given in Table 2.

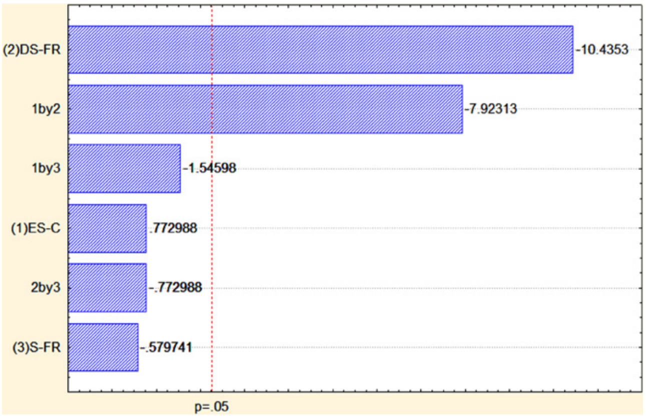

Fig. 4. Pareto chart obtained from the optimization study of the 3 variables, with their significance, for the SI-DLLME determination of Ag(I). The experimental conditions for the study of factorial optimization are shown in Table 4.

Table 4
The experimental matrix of 2^3 full factorial design and the obtained mean analytical responses.

Experiment	ES-C	DS-FR	S-FR	Abs_1	Abs_2
1	–	–	–	0.143	0.145
2	+	–	–	0.156	0.155
3	–	+	–	0.140	0.140
4	+	+	–	0.139	0.130
5	–	–	+	0.144	0.145
6	+	–	+	0.155	0.156
7	–	+	+	0.143	0.141
8	+	+	+	0.128	0.130

S-FR, 110 $\mu L\,s^{-1}$ and 90 $\mu L\,s^{-1}$. In Table 4, the response of every experiment of the factorial design is presented. The response was taken as peak height absorbance and the preconcentration time was 180 s for 10.00 $\mu g\,L^{-1}$ Ag(I). ANOVA analysis results and the Pareto chart are presented in Table 5 and Fig. 4, respectively. In relation to the Pareto chart only DS-FR and the interaction 1 by 2 are significant at 95% confidence level. Considering the results, concentration of extraction solvent (1-DD-OH), 2.0% (m/v) combined with disperser flow rate of 2.0 $\mu L\,s^{-1}$ was adopted as optimum for the proposed method. Sample flow rate proved that for values higher than 90 $\mu L\,s^{-1}$ the effect was insignificant. Hence, for low sample consumption, the flow rate was fixed at 90 $\mu L\,s^{-1}$.

3.4. *Preconcentration time*

In liquid–liquid extraction the objective is to transfer the desired solutes from aqueous solution into an organic liquid. The process of mass transfer is time-dependent, and the extraction rate is reduced, as the system is approaching to a steady state condition. In the on-line systems, the equilibrium is not necessary, due to the fact that extraction conditions are very reproducible. In the proposed manifold the preconcentration time defines also the sample volume which takes place in the preconcentration procedure. Therefore, the effect of the preconcentration time on the absorbance was studied in the range 30–300 s. The results have shown that the absorbance was increased practical proportional by increasing the preconcentration time up to 240 s while for larger the absorbance was increased with lower rate. A preconcentration time of 180 s was adopted for the method, in order to compromise high sensitivity and low sample consumption.

Table 5
Analysis of variance (ANOVA) results for effect of the 3 factors and their 2nd order interactions.

Factor and interactions	df	MS	F_{exp}	*p*
(1)ES-C	1	0.000004	0.5975	0.459348
(2)DS-FR	1	0.000729	108.8963	0.000003
(3)S-FR	1	0.000002	0.3361	0.576312
1 by 2	1	0.000420	62.7759	0.000024
1 by 3	1	0.000016	2.3900	0.156512
2 by 3	1	0.000004	0.5975	0.459348
Error	9	0.000007		
Total SS	15			

df, degrees of freedom; MS, mean squares.

3.5. *Investigation of the potential interferences*

Although, FAAS has significant inherent selectivity, interferences from coexisting metals and ions should be investigated in order to define their influence on trace silver determination. The effect of some potential interfering species on 5.00 $\mu g\,L^{-1}$ Ag(I) determination was tested using the optimized manifold. Considering any deviation of the obtained recovery more than ±5% as criterion for interference, it was proved that, Cu(II) and Cd(II) were tolerated up to 1.00 $mg\,L^{-1}$, Co(II), Fe(III), Zn(II), Mn(II), and Ni(II) tolerated up to 5.00 $mg\,L^{-1}$ and Hg(II) was up to 0.5 $mg\,L^{-1}$. Some common matrix cations such as K(I), Ca(II), Mg(II) and Ba(II) at high concentrations were examined and it was found that they did not interfere at concentrations at least up to 10^3 $mg\,L^{-1}$. Also NaCl was tolerated up to 30 $g\,L^{-1}$.

Generally in conventional liquid–liquid extraction addition of salt often improves extraction of analytes, as a result of the salting-out effect. The effect of ionic strength on the sensitivity was evaluated by adding various amounts of sodium chloride (NaCl) up to 3.5% (m/v). No significant statistical differences were recorded throughout the studied range.

3.6. *Analytical performance and analysis of natural waters*

Performance characteristics of the proposed SI-LLME method were obtained by processing standard solutions of silver ions and they are summarized in Table 6. Under the optimized conditions, the calibration graph was linear within the range 0.40–20.0 $\mu g\,L^{-1}$ with good correlation coefficient ($r = 0.991$). For preconcentration time 180 s, the detection limit, based on 3 s criterion, was $c_L = 0.15\ \mu g\,L^{-1}$ and the quantification limit was $c_Q = 0.40\ \mu g\,L^{-1}$. The regression equation of the calibration curve was calculated as $A = 0.0158\,[\mathrm{Ag(I)}] + 0.003$ ($\mu g\,L^{-1}$, $n = 10$). By using direct aspiration of aqueous standard solutions into FAAS without preconcentration, the calibration curve was calculated as $A = 0.0851[\mathrm{Ag(I)}] + 0.002$

Table 6
Analytical performance characteristics of the SI-DLLME-FAAS method for silver ion determination under the optimum conditions.

Enhancement factor	186
Preconcentration time (s)	180
Sampling frequency (h^{-1})	12
Sample volume (mL)	16.2
Linear range ([M] in $\mu g\,L^{-1}$)	0.40–20.0
Regression equation ([M] in $\mu g\,L^{-1}$, $n = 10$)	$A = 0.0158$ [Ag(I)] + 0.003
Correlation coefficient (r)	0.9991
Detection limit (3s), $\mu g\,L^{-1}$	0.15
Precision (RSD, $n = 10$) (%)	2.9 (5.0 $\mu g\,L^{-1}$)

Table 7
Analytical results of dissolved fraction of silver in certified reference material (CRM) and spiked natural waters samples with the SI-DLLME-FAAS method ([Ag(I)] in $\mu g\,L^{-1}$).

Sample	Certified	Added	Found[a]	Recovery (%)
CRM 1643e	1.062 ± 0.075	–	1.02 ± 0.05	96.0
River water		–	$<c_L$	–
		4.00	3.95 ± 0.25	98.7
Coastal seawater		–	0.64 ± 0.05	–
		4.00	4.50 ± 0.42	96.5
Waste water		–	0.85 ± 0.07	–
		4.00	4.73 ± 0.41	97.0

[a] Mean value ± standard deviation based on three replicate measurements.

(mg L^{-1}, $n = 5$). The enhancement factor was calculated by comparing the slopes of the calibration curves with and without preconcentration and was found to be 186.

The accuracy of the proposed method was estimated, by analysis of the certified reference material, NIST CRM 1643e (National Institute of Standard and Technology, Trace elements in water) and the resulted recovery (R) was satisfactory (Table 7). The method was also applied for the analysis of river and coastal sea-water samples, which had been collected from Northern Greece as well as of industrial waste water. All the determinations were performed using aqueous standard solutions for calibration, without further matrix specific optimization for the samples. The analytical results are presented in Table 7. The recovery varied within the range 96.0–98.7% showing the good performance of the method in various waters samples.

4. Conclusions

A new on-line sequential injection dispersive liquid–liquid microextraction approach for metal determination with FAAS was developed. The proposed procedure was based on very low consumption of organic solvents, such as MIBK, MeOH and less toxic extraction solvent 1-dodecanol, compared with others extraction solvent extraction methods achieving the objectives of the “green analytical chemistry”. For the separation of the fine droplets of the extraction solvent a novel sorbent material, PEEK-turnings were successfully adopted. Concerning other microextraction techniques, SI-DLLME offers simple manifold, fast function in micro-scale analysis, low cost and particularly low consumption of organic solvent due to the fact that it is a fully programmable flow system under enclosed conditions thereby eliminating possible contamination from/of the environment. The performance of the proposed system indicates that it could be applicable to the determination of other metals, which are capable to produce neutral complexes. To the best of our knowledge, fatty alcohols and PEEK-turnings have not been used before in SI-DLLME systems. The uncomplicated manifold and the appropriate sensitivity make the proposed method attractive for routine analysis of environmental water samples.

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