

میکرواستخراج مایع مایع پخشی یون نقره در نمونه های غذایی و اندازه گیری با استفاده از طیف سنجی اتمی شعله ای

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Dispersive Liquid-Liquid Microextraction of Silver Ion in Food Samples and Determination by Using Flame Atomic Spectroscopy

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چکیده

در این کار یک دستورالعمل برای پیش تغلیظ نقره با استفاده از میکرواستخراج مایع-مایع پخشی به کمک معرف دایتیزون به عنوان عامل کمپلکس دهنده، توسعه داده شد. در $pH=2$ ، یون های نقره با دایتیزون کمپلکس داده و در قطرت حلال استخراج می شوند. محیط عمل شامل تتراکلرید کربن (به عنوان حلال استخراج کننده)، اتانل (به عنوان حلال پخش کننده) و محلول نمونه می باشد. بعد از استخراج فازها به وسیله سانتریفیوژ از هم جدا شده و نقره در فاز غنی شده به وسیله روش جذب اتمی شعله ای اندازه گیری شد. بعد از استخراج فاکتور غنی سازی 73.21 به دست آمد. حد تشخیص روش 30.4 نانوگرم بر میلی لیتر و انحراف استاندارد نسبی برای 10 اندازه گیری 0.1 میکروگرم بر میلی لیتر از نقره برابر 3.19% درصد بود. نتایج برای تعیین نقره در نمونه های آب های محیطی (آب چاه، آب آشامیدنی و آب معدنی) و چای نشاندهنده کارایی روش حاضر می باشد.

واژه های کلیدی

میکرواستخراج مایع-مایع پخشی؛ طیف سنجی جذب اتمی شعله؛ نقره (I)؛ آب؛ چای.

Abstract

In this work, a procedure for preconcentration of silver using dispersive liquid-liquid microextraction with the reagent dithizone as complexing reagent was developed. At pH 2, silver ions are complexed with dithizone and extracted into the fine droplets formed when mixing carbon tetrachloride (extraction solvent), ethanol (disperser solvent) and the sample solution. After extraction, the phases are separated by centrifugation and silver is determined in the enriched phase by FAAS. After extraction, the enrichment factor was 73.21. The detection limit of the method was 30.4 ng mL^{-1} and the relative standard deviation for ten determinations of $0.1 \text{ } \mu\text{g mL}^{-1}$ silver was 3.19 %. The results for the determination of silver in environmental water samples (tap water, well water, mineral water), tea and pepperbush have demonstrated the applicability of the proposed method.

Keywords

Dispersive Liquid-Liquid Microextraction; Flame Atomic Absorption Spectrometry; Silver; Water; Tea; Pepperbush.

1. INTRODUCTION

Due to the positive and negative effects and the toxicity of trace heavy metals on human health and the environment, many researchers are interested in the analysis of trace metal contents of the samples [1-2].

Separation and pre-concentration techniques are very important and significant in analytical chemistry. Modern trends are towards the simplification and miniaturization of sample preparation procedures as well as the miniaturization of solvent and reagent consumption [3-4]. There are different microextraction methods such

as single drop microextraction (SDME), cold induced aggregation microextraction (CIAME), solidified floating organic drop microextraction (SFODME), hollow fiber based liquid phase microextraction (HFLPME) and dispersive liquid liquid microextraction (DLLME). In this extraction method, any component in the solution is extracted and concentrated into a small volume of the remained phase. The principle advantage of DLLME is that the surface area between extraction solvent and aqueous sample initially is infinitely large, thus the equilibrium state is achieved quickly and the extraction time is very short [5-6].

This method has been successfully applied for the pre-concentration of organic and inorganic compounds in different matrices [7-10]. In recent years, a few articles based on DLLME method have been reported for silver determination such as, ligand-less DLLME coupled with FAAS [11], displacement DLLME (D-DLLME) coupled with graphite furnace atomic absorption spectrometry (GFAAS) [12] and DLLME-GFAAS [13]. In this work, a combination of DLLME and FAAS was employed as a sample preparation method and determination of silver. The parameters affecting the efficiency of extraction and determination were thoroughly investigated in detail. The applicability of the approach was demonstrated for the determination of trace amounts of silver in food samples, using dithizone as a proper chelating agent.

2. EXPERIMENTAL

2.1. Instrumentation

A Shimadzu atomic absorption spectrometer (Kyoto, Japan) Model AA-670 was used for the determination of silver using the manufacturer recommendations. A centrifuge Heraeus (Labofuge 400 model, Germany) was used to accelerate the sedimentation of the rich phase in the process of microextraction. The pH values were measured with a metrohm E-691 pH/mV meter equipped with a combined glass calomel electrode (Switzerland).

2.2. Reagents and materials

All chemicals used were of analytical-reagent grade. All aqueous solutions were prepared using doubly deionized water. Chloroform, diphenylthiocarbazone (dithizone), carbon tetrachloride, dichloromethane, methanol, ethanol, acetone, tetrahydrofuran and acetonitrile, dimethyl formamide, carbon disulfide, hydrochloric acid, nitric acid were obtained from Merck. The stock standard solutions of silver at a concentration of about 1000 mg L⁻¹ were prepared using AgNO₃ in deionized water (pH=2). Working solutions were then prepared by appropriate dilution of the standard solutions daily. The solution of dithizone was prepared by dissolving appropriate amount of dithizone in ethanol.

2.3. Dispersive liquid-liquid microextraction procedure

Five milliliters of the silver solution was placed in a 10 mL glass test tube with conical bottom, Then 1 mL phosphate buffer and 0.5 mL of a 0.1 g L⁻¹ dithizone solution were added. Next, a mixture containing 1.5 mL of ethanol and 100 µL of carbon tetrachloride were incorporated by using 5.00 mL syringe, and then the mixture was gently shaken by

hands for 1 min. A cloudy solution that consists of very fine droplets of CCl₄ dispersed into aqueous sample was formed, and the analytes were extracted into the fine droplets. After centrifugation at 1000 rpm for 5 min, the CCl₄ phase was sedimented at the bottom of the centrifuge tube. The sedimented phase was removed to another test tube and diluted with N,N-dimethylformamid (DMF) to 0.5 mL total volume. The final solution was directly nebulized into the flame without the need for special tools. The analyte concentration in final solution was determined by flame atomic absorption spectrometry.

2.4. Sample preparation

Water samples were collected in tap (pH 6.8, hardness 180 mg L⁻¹, conductivity 370 µmho cm⁻¹), well (pH 7.8, hardness 1800 mg L⁻¹, conductivity 890 µmho cm⁻¹), and mineral in sanandaj (Iran). These water samples were filtered; the pH was adjusted with buffer solution and analyzed immediately after collection.

The procedure used for the extraction of ions from tea sample was similar to that reported in the literature [14]. 10 mg of the dry tea sample (dried at 110 °C) was placed in a 50-mL beaker, followed by the addition of 7 mL of concentrated nitric acid and the beaker was covered with a glass watch. The beaker was allowed to stand overnight and the contents were heated on a hot plate (150 °C for 15 min). Then the sample was cooled, 8 mL of perchloric acid was added and the mixture was heated again at 200 °C until the solution became clear (about 1 h). The glass watch was removed and the acid evaporated to dryness at 150 °C. The residue was completely dissolved in 5 mL of 1 mol L⁻¹ nitric acid and the solution was transferred to a 100 mL calibrated flask. Then, the pH of solution was adjusted with buffer solution and diluted to the mark and the recommended procedure was followed.

One gram of pepperbush sample was placed in a 250 mL beaker, and 100 mL of concentrated HNO₃ (65% w/w) was added to the beaker. The mixture was evaporated near to dryness on a hot plate at about 130°C for 4 h. After cooling to room temperature, 3 mL of concentrated perchloric acid was added. The mixture was again evaporated near to dryness. The final solution was filtrated using deionized water. Finally, the recommended procedure described was applied to the sample solutions [15].

3. RESULTS AND DISCUSSIONS

In this study a recently presented microextraction method, dispersive liquid-liquid microextraction, was investigated for enrichment of silver ions from

aqueous samples followed by their determination by flame atomic absorption spectrometry.

During DLLME, a μL volume of an extracting solvent is dissolved into a dispersive solvent at the mL level. The extracting solvent must have a density higher than that of the aqueous sample and the dispersive solvent must be miscible with both the organic extracting solvent and water. To extract the analyte, the dispersive solvent containing the extracting solvent is added to the analyte solution by a syringe. There by the extracting solvent is dispersed into the aqueous phase as tiny droplets. If a pipette is used for adding extraction solvent, the upper part of sample will be cloudy while by using a syringe the extraction solvent is added to the sample under pressure and it dispersed in all parts of sample. This technique is very rapid and efficient but there are many factors that should be optimized before its application.

In this work, optimization was performed via one variable at a time method. Factors such as selection of the dispersive and extracting solvents and their volumes, pH, salting out effect, etc., were studied and the optimum conditions were selected. Enrichment factor was calculated using ratio of the analyte concentration in the sedimented phase to the analyte concentration in the aqueous sample. The analyte concentration in the sedimented phase was calculated from the direct calibration graph.

3.1. Selection of dispersive and extracting solvents

The selection of the extracting solvent is critical and should meet the following criteria: (1) it should dissolve the analyte better than water, (2) it should be heavier than water and (3) it should form tiny droplets when it is added to the aqueous solution of analyte along with a dispersive solvent.

Almost all of the suitable extracting solvents are chlorinated. The miscibility of the disperser solvent in the extraction solvent and aqueous phase is the most important factor affecting the of disperser solvent in DLLME. These solvents can disperse extraction solvent as very fine droplets in aqueous phase. In this work methanol, ethanol, acetone, tetrahydrofuran and acetonitrile, were studied as a dispersive solvent and chloroform, carbon tetrachloride, CS_2 and dichloromethane were studied as a extraction solvent. The experiments were performed by using 1.5 mL of dispersive solvent containing 100 μL extraction solvent.

In Fig. 1 the recovery is shown for all combinations of dispersive and extracting solvents. Regarding the recovery, the combination of carbon tetrachloride as extracting solvent with ethanol or acetonitrile as dispersive solvent is the best one and an recovery higher than 95 is attainable. Finally,

the combination of CCl_4/EtOH was selected for subsequent experiments.

3.2. Dispersive solvent volume

Ethanol as a dispersive solvent in different volumes in the range 0-3mL along with 100 μL carbon tetrachloride as an extracting solvent was used for extraction of silver ions using the DLLME procedure. The obtained results show that in the case of 1.5 mL ethanol the highest recovery is attainable. At lower volumes of ethanol, the cloudy suspension of carbon tetrachloride droplets is not formed well, resulting in a decrease in the extraction efficiency. At higher volumes of ethanol, the solubility of complex in water increases and the extraction efficiency decreases (Fig. 2). With 3 mL or higher volume of ethanol no sedimented organic phase was achieved.

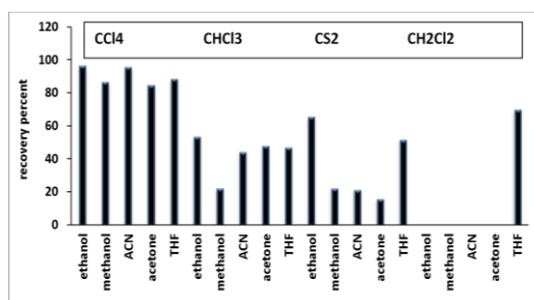


Fig. 1. Selection of extracting and dispersive solvents in DLLME. Conditions: sample, 5 mL silver ion 0.05 mg L^{-1} ; volume of dispersive solvent, 1.5 mL; volume of extracting solvent, 100 μL ; buffer, 1mL phosphate buffer ($C=0.1 \text{ mol L}^{-1}$, pH 2) and dithizone solution, 0.5 mL 0.1 g L^{-1} in ethanol.

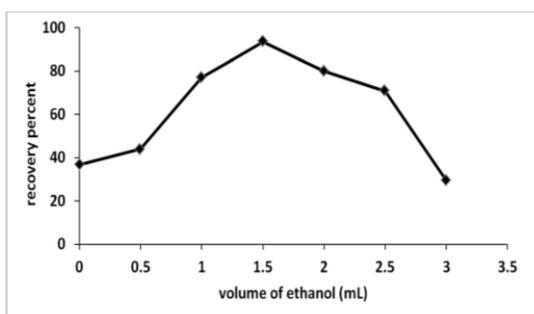


Fig. 2. Effect of dispersive solvent volume. Other conditions are the same as Fig. 1.

3.3. Extracting solvent volume

In order to study the effect of the volume of the extraction solvent on the extraction efficiency, different volumes of CCl_4 (50-400 μL) and a constant volume of the dispersive solvent ethanol (1.5 mL) were investigated. Fig. 3 illustrates the variations of the extraction recovery versus the volume of the extraction solvent. According to Fig.

3, the extraction recovery was increased with the increase of the volume of CCl_4 , by increasing the volume of extraction solvent from 100 μL , the volume of sedimented phase increases, but EF decreases because the volume of sedimented phase increases. On the basis of these results, 100 μL of CCl_4 was selected for subsequent experiments.

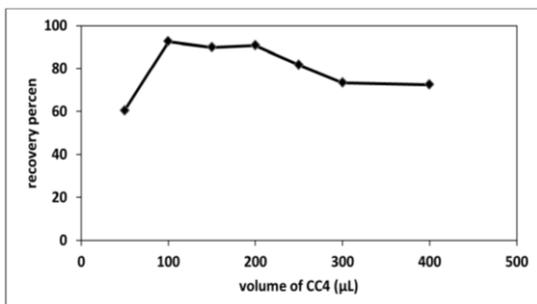


Fig. 3. Selection of extracting solvent volume. Other conditions are the same as Fig. 1.

3.4. Influence of pH

The separation of metal ions by dispersive liquid-liquid microextraction involves prior formation of a complex with sufficient hydrophobicity prior followed by extraction into a small volume of the sedimented phase, obtaining the desired preconcentration. The pH plays a unique role on metal-chelate formation and its subsequent extraction. The effect of pH on the complex formation and the extraction of silver from water samples was studied by using HCl, NaOH, Na_2HPO_4 . As Fig. 4, shows at very low pH values, the low adsorption amount was due to the competition of silver ions with hydrogen ions and at higher pH values, the hydrolysis of cations may occur, so the highest recovery for silver ion was observed in pH 2. Hence the pH value of 2 was taken as optimal value for silver ion.

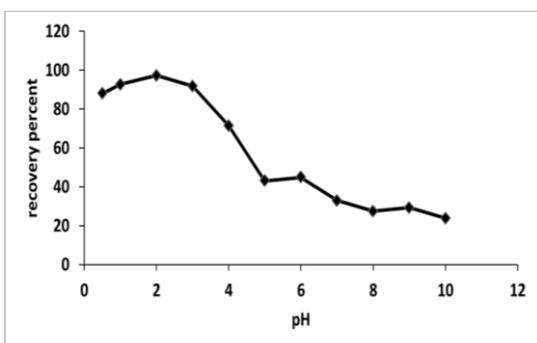


Fig. 4. Effect of pH on the absorbance of silver ion. Other conditions are the same as Fig. 1.

3.5. Influence of dithizone

The influence of the quantity of dithizone reagent in preconcentration of silver was evaluated, varying the concentration of the solution of this

reagent. Dithizone solutions at different concentrations in ethanol were prepared. Each of these solutions injected in aqueous solutions of silver. The result obtained for each solution is shown in Fig. 5. Basically, when the concentration of ligand is low the possibility to form of complex decreases, therefore low recovery was obtained. Best result was obtained when concentration 0.1 g L^{-1} was used. Hence, this amount of reagent was taken as optimal amount for the silver.

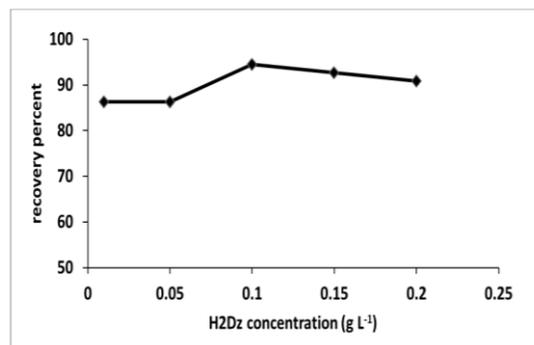


Fig. 5. Influence of complexing reagent concentration. Other conditions are the same as Fig. 1.

3.6. Effect of ionic strength

To evaluate the possibility of salting out effect, the extraction efficiency was studied with the sodium chloride concentration over the range from 0 to 10% (w/v). The results showed the addition of salt has no significant effect on the extraction recovery. Therefore, all the extraction experiments carried out without the addition of salt.

3.7. Effect of extraction time

In DLLME, extraction time is defined as interval time between injecting the mixture of dispersive solvent (ethanol) and extraction solvent (CCl_4) and before starting to centrifuge. The effect of extraction time was examined in the range of 1–10 min with constant experimental conditions. The obtained results showed that the variations of recovery percent versus extraction time were not remarkable. It is revealed that the DLLME method is time-independent, because of the infinitely large surface area between extraction solvent and aqueous phase after the formation of cloudy solution lead to the transition of analytes from aqueous phase to extraction solvent is very fast and equilibrium state is achieved quickly. This is the most important advantage of DLLME technique. In this method, the most time-consuming step is the centrifuging of sample solution in the extraction procedure, which is about 5 min.

3.8. Study of interferences

Interferences were studied in the presence of a constant concentration of analyte and different

amounts of interfering ions. Tolerable concentration of interfering ions was considered that concentration in which less than 5% deviation in absorbance reading was observed in comparison with the case in which interfering ion was absent. The obtained results are given in Table 1.

3.9. Figures of merit

The calibration graphs for silver was linear in the range of 0.05 – 0.8 $\mu\text{g mL}^{-1}$. The RSD values ($n=10$, 0.1 $\mu\text{g mL}^{-1}$ Ag) was 3.19%, the enrichment factor was 73.21 (Table 2).

A comparison of the DLLME-FAAS and some of previously reported methods for the extraction and determination of silver are summarized in Table 3.

Table 1. The effect of the interfering ions on dispersive liquid phase microextraction of silver ion using dithizone.

Ion	Added as	Tolerance limit ^a ($C_{\text{ion}}/C_{\text{Ag}}$)
Mg ²⁺	Mg(NO ₃) ₂ .6H ₂ O	1000
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	100
Ca ²⁺	Ca(NO ₃) ₂ .4H ₂ O	100
Ba ²⁺	Ba(NO ₃) ₂	100
Cd ²⁺	Cd(NO ₃) ₂ .4H ₂ O	100
Zn ²⁺	Zn(NO ₃) ₂ .6H ₂ O	100
Fe ³⁺	Fe(NO ₃) ₃ .9H ₂ O	100
Cu ²⁺	Cu(NO ₃) ₂ .3H ₂ O	10
Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	10
Pb ²⁺	Pb(NO ₃) ₂	10
Hg ²⁺	Hg(NO ₃) ₂ .H ₂ O	1 ^b
Cl ⁻	MgCl ₂	100
SO ₄ ²⁻	MgSO ₄	100

^aAt this ratio interfering effect was observed.

^bEDTA was used as a masking agent for Hg²⁺.

Table 2. Analytical characteristics of the method for silver ion.

Parameter	Analytical feature
Linear range ($\mu\text{g mL}^{-1}$)	0.05-0.8
R ²	0.998
Limit of detection (LOD) (ng mL ⁻¹)	30.4
Repeatability (RSD, %)($n=10$)	3.19 (0.1 $\mu\text{g mL}^{-1}$)
Enrichment factor	73.21
Sample volume (mL)	5

3.10. Application to real samples

The proposed method was applied to the determination of silver in real samples (tap water, well water and mineral water). The accuracy of the method was verified by the analysis of the samples spiked with known silver amount. The relative

silver recovery from tap, well and mineral water at the spiking level of 0.1 $\mu\text{g mL}^{-1}$ (Table 4) demonstrated that the matrices of the well, tap and mineral water samples had little effect on the DLLME method for determination of silver.

Table 3. The analytical characteristics of the different extraction methods.

Enrichment method	Detection method	Enrichment factor	Detection limit($\mu\text{g L}^{-1}$)	Reference
Coprecipitation	FAAS	26	0.6	14
LLE	FAAS	30	13	15
SPE	FAAS	25	1.05	16
CPE	FAAS	46	2.2	17
SPE	FAAS	110	0.2	18
DLLME	FAAS	73	30.4	This method

The method was also validated for determination of silver in tea and peppercorn. The results in Table 4 indicate that the method can be successfully applied to the determination of silver in food samples.

Table 4. The analytical results (mean \pm s, $n=3$) for determination of silver ion in real samples.

Sample	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$) SD($n=4$)	Recovery (%) \pm very
Tap water	0	<LOD	-
	0.1 $\mu\text{g L}^{-1}$	0.095 \pm 0.001	96
Mineral water	0	<LOD	-
	0.1 $\mu\text{g L}^{-1}$	0.095 \pm 0.001	95
Well water	0	<LOD	-
	0.1 $\mu\text{g L}^{-1}$	0.0965 \pm 0.003	96.5
Peppercorn	0	1.013 \pm 0.010 ($n=3$)	-
	2 $\mu\text{g g}^{-1}$	2.980 \pm 0.059 ($n=3$)	98.3
Tea	0	1.162 \pm 0.089 ($n=3$)	-
	10 $\mu\text{g g}^{-1}$	10.679 \pm 0.212	95.2

4. CONCLUSIONS

In the proposed procedure, the reagent dithizone was successfully used as complexing for preconcentration of silver using dispersive liquid-liquid a microextraction. The method is simple, easy to use and economic. The low cost is related mainly to small amounts of solvents required. The small amounts of carbon tetrachloride and ethanol also minimizes the toxicity of the method. Another interesting feature of the method is speed. After injection of the mixture ethanol/carbon tetrachloride, the solution was immediately

cloudy. The rich phase is injected into the FAAS after rapid centrifugation. The advantages cited and the analytical characteristics obtained make the method a good alternative to the determination of silver in routine analysis.

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