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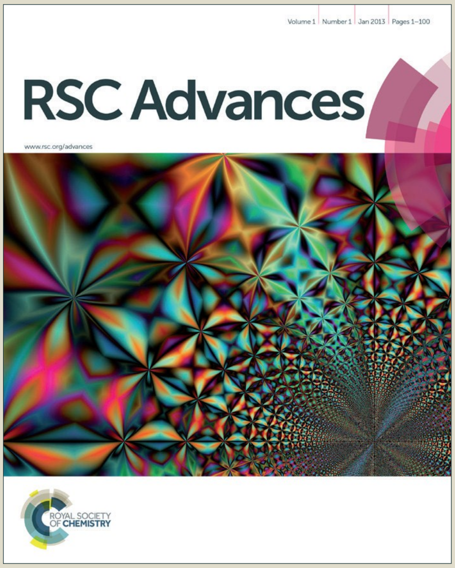

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Supramolecular solvent based liquid-liquid microextraction of aluminum from water and hair samples prior to its UV-Visible spectrophotometric detection

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Abstract

A new method for microextraction of aluminum from water and hair samples has been developed by using a supramolecular solvent (Undecanol-Tetrahydrofuran) prior to its UV-Visible spectrophotometric determination. 8-Hydroxyquinoline was used as chelating agent that forms chelate with Al(III) at pH 8.0. Al(III)- 8-Hydroxyquinoline chelate was quantitatively extracted to supramolecular solvent (Ss) phase. The molar absorptivity calculated for a complex was 1.8×10^3 $L.mol.cm^{-1}$ at 380 nm. Factors effecting extraction efficiency of the method like pH, amount of chelating agent, sample volume, type and volume of supramolecular solvent (Ss) and matrix effect were optimized. A pre-concentration factor of 30 was achieved with limit of quantification of 0.47 $\mu g\ L^{-1}$ with relative standard deviation of 0.3 %. The accuracy of the developed method was evaluated by the analysis of the certified reference materials (SPS WW2 Waste water, TMDA-53.3 fortified water and NCS ZC81002B human hair) and by the addition-recovery studies for water and hair samples.

Keywords: Supramolecular solvent based liquid-liquid microextraction, Spectrophotometric determination, Aluminum, 8-Hydroxyquinoline.

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1. Introduction

Aluminum is the third most abundant element on the earth crust and due to its low density. Aluminum has wide spread application in automobile, aerospace and automated industrial instruments. [1,2] The maximum permissible level of aluminum given by environmental protection agency (EPA) in drinking water is 0.2 mg L^{-1}. [3] Due to natural and human activity like industry and traffic, the amount of total dissolved aluminum in environmental samples including water and foods increasing. It may cause some serious complications in the nervous system, parathyroid gland, chromosomes and is also researched as a possible factor in the formation of Alzheimer disease, renal osteodýstrophy, and Parkinson's disease[4, 5]. Aluminum is also used for coagulation and flocculation for treatment colloidal and suspended particle from water effluents. [6-8] Due to both negative and positive aspects of aluminum, it is very important to develop analytical method for determination of aluminum at trace level both in environmental and biological samples. [9, 10]

Analytical methods, that largely used for determination of aluminum are chemiluminescence analysis [11], electrothermal atomic absorption spectrometry (ETAAS) [12], inductively coupled plasma optical emission spectrometry (ICP-OES) [13], electroanalytical techniques [14] and high performance liquid chromatography (HPLC) [15]. But due to lack of selectivity, sensitivity and interfering effect of the matrix, the direct determination of Al(III) by using these methods are not possible .[12] Other important factors related with these methods are highly expensive and expert analysts are required for their operation.

UV-Visible spectrophotometric methods are preferable as compared to the above mention analytical methods. UV-Visible spectrophotometry method is more simple and cheap. But due to lack of selectivity and sensitivity, direct determination of Al(III) by UV-Visible spectrophotometry is problematic.[16] These problems for aluminum and other metal ions can be overcome by using specific separation-preconcentration methods like cloud point extraction [17, 18], solid phase extraction [19], and liquid-liquid extraction. [20]

Due to the excessive discharge of organic solvent in laboratories during liquid-liquid microextraction experiments, organic solvents cause some serious environmental hazards. To decrease discharge of the amount of toxic organic solvents, supramolecular solvent based liquid-liquid microextraction is an appropriate choice for researcher in the recent past. [24] Due to some unique properties of supramolecular solvents, like its hydrophobic nature and hydrogen bonding interaction with chelate, make the supramolecular solvent based liquid-liquid microextraction far superior in extraction efficiency then ordinary other kind of liquid-liquid microextraction. [25] The concept of supramolecular solvent-based extraction technique was first time given by Ballesteros-Gómez and co-workers [37]. Different supramolecular solvent system like 1-decanol, undecanol and decanoic acid have been used for liquid-liquid microextraction of heavy metals. [28]

Different researcher has been used different chromogenic reagents like chrome azurol S (CAS) [21], 8-hydroxyquinoline [16], eriochrome cyanine R (ECR) [22] and pyrocatechol violet [23] that form color complex with Al(III) for its UV-Visible spectrophotometric determinations. 8-hydroxyquinoline was selected as chromogenic reagents for the presented work.

The aim of the present work is, to develop supramolecular solvent based liquid-liquid microextraction method for aluminum from water and biological samples. A complexing reagent 8-hydroxyquinoline form a complex with Al(III) at pH 8.0 [29], which was then quantitatively extracted by supramolecular solvent based liquid-liquid microextraction. The concentration of Al(III) in supramolecular solvent phase was then determined by using UV-Visible spectrophotometer.

2. Experimental

2.1. Apparatus

Ultrapure water obtained from a MilliQ Direct-16 purification system (18.2 MΩ cm, Millipore) was used in all experiments. UV-Visible spectrophotometer (Hitachi 150-20) model with quartz micro–cell having path length of 10 mm and a volume of 0.7 mL was used for absorbance measurements. pH measurements was done by using pH meter Nel pH 900 model (Ankara-Turkey) with a glass electrode. A centrifuge (ALC PK 120 Model, Buckinghamshire, England) was used for phase separation. Vortex mixer (Wiggen Hauser, Malaysia) was used for thorough mixing of solutions.

2.2. Chemicals and solutions

Stock solutions of aluminum(III) as a $Al(NO_3)_3$ salt was produced by diluting a stock solution of 1000 mg L^{-1} of the given elements supplied by Sigma and Aldrich (, St. Louis, MO, USA). It was diluted for preparation of standard solutions of Al(III). 0.1 % (w/V) solution of complexing agent was prepared by dissolving 0.1 g of 8-hydroxyquinoline (Sigma-Aldrich, St. Louis, MO, USA) in 100 mL of ethanol. Extraction solutions Undecanol, 1-decanol and Decanoic acid were provided by E. Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA) respectively. Tetrahydrofuran (THF) was provided by Lab-Scan (Ireland). Buffer solutions were used given in literature. [16]

2.3. Supramolecular solvent based liquid-liquid microextraction (Ss-LLME) of Al(III)

The model studies for method development were performed by using 10 mL ultrapure distilled water. 100 µL of Al(III) was taken from a stock solution having 20 mg L^{-1} in 50 mL centrifuge tube. To this, 2 mL of ammonia/ammonium chloride buffer solution was added and the pH was adjusted to 8.0 with 0.2 M NaOH and 0.2 M HCl. The solution was diluted to 10 mL with ultrapure distilled water. After the addition of 0.3 mg of 8-hydroxyquinoline, the solution was become yellowish in color that shows that the complex formation takes place. The solution was allowed for 5 min to ensure that the complex formation is complete. For the extraction of complex, 0.2 mL of extraction solvent consisting of 0.1 mL of THF and 0.1 mL of undecanol was injected in to the sample solution. The supramolecular solvent spontaneously formed into this solution. The solution was subjected to vortex for 2 minutes having vortex speed of 40×100 rpm to ensure extraction of Al(III)-8-hydroxyquinoline complex. The test tube was centrifuged at 4000 rpm for 10 min to achieve phase separation. The water phase was separated from the bottom of the solution and discarded. The extraction phase was diluted to 1 mL with ethanol. The concentration of aluminum in last volume was measured at 380 nm by using UV–Vis double beam spectrophotometer.

2.4. Application to the actual environmental and human samples

The presented method was applied to water samples including tap water from Kayseri City-Turkey sea water from Marmara sea-Turkey underground water samples from Kayseri City-Turkey and hair sample were taken from male living in Kayseri, Turkey. The method was also applied to certified reference materials (SPS-WW2 waste water, TMDA-53.3 fortified water and NCS ZC81002B Human hair). All water samples were filtered through a cellulose membrane filter of 0.45 µm (Millipore) prior to use. In natural water analysis, 30 mL of water samples were used.

The NCS ZC81002B human hair certified reference material and hair samples were subjected to wet digestion method prior to its use, in which 0.04 g of NCS ZC81002B Human hair certified reference material and 0.1 g of hair sample were weighted in to the beakers and digested with 10 mL of concentrated HNO_3 at room temperature for 30 min, and then at 100 °C on hot plate till dry residue were obtained. After cooling, the residues were again digested with 15 mL mixtures of HNO_3 and H_2O_2 (2:1 v/v) follow the same procedure as discuss in above lines. The final residues in beakers were dissolved with 10-15 mL of distilled water and filtered to obtain clear solution. The resulting solution was used for supramolecular solvent based liquid-liquid microextraction (Ss-LLME) of Al(III) which is given in section 2.3.

3. Results and discussion

3.1. Effect of pH

In order to investigate the effect of pH on % recovery of Al(III), supramolecular solvent based liquid-liquid microextraction studies of Al(III) were carried at pH range of 2.0 to 10.0. The results were shown in Figure 1. The % recovery of Al(III) increases with increase in pH in the range 2.0 to 8.5 and reached to quantitative recoveries between at pH 7.5 and 8.5. It can be explained that the hydrophobic complex formation and the best formation of supramolecular solvent were achieved at these pH. [29] Hence, pH 8.0 was used for subsequent works.

3.2. Effect of amount of 8-hydroxyquinoline

The effect of amount of 8-hydroxyquinoline was examined in the range of 0.1-0.7 mg. The results are shown in Figure 2. The obtained results indicate that the quantitative recoveries for Al(III) were obtained after addition of 0.3 mg of complexing agent and further increase in amount of complexing agent has no significant change on % recovery of Al(III). Therefore 0.3 mg of 8-hydroxyquinoline was used in further works.

3.3. Effect of type and volume of supramolecular solvent (Ss)

In order to achieve the quantitative extraction of Al(III), the choice of best supramolecular solvent is important. Three supramolecular solvent including; 1-decanol–THF, undecanol-THF and decanoic acid-THF were tested. The results are given in Table 1. Undecanol-THF was a better choice having high extraction efficiency and used for formation of supramolecular solvent in rest of the proposed method.

The volume ratio of undecanol and THF was also optimized. For this purpose the SsLLME of Al(III) study was carried out at different volumes of undecanol in the range of (0.075-0.5 mL) keeping the volume of THF constant. The results are shown in Figure 2. The quantitative recoveries of Al(III) were obtained in the range of 0.1 and 0.5 mL of undecanol. In order to use minimum volume of undecanol, 0.1 mL of undecanol was selected for further experiments.

In the second step, the volume of undecanol was keep constant and the SsLLME method was carried out at different volumes of THF (0.075-0.5 mL). The results are given in Figure 3. It can be concluded from the graph that 0.1 mL of THF is enough for obtaining quantitative recovery of Al(III). Therefore 0.2 mL of Supramolecular solvent (undecanol-THF) was used in further microextraction experiment of Al(III).

3.4. Matrix effects

In order to check the selectivity of the method [30-34], the proposed supramolecular solvent based liquid-liquid microextraction method was carried out in the presence of coexisting ions given in Table 2. The effects of coexistent ions found in water and acid digested hair samples were studied on Al(III) determination. Quantitative recoveries of Al(III) even in the presence of high concentration of these interfering ions show that the method is highly selective and free of interferences.

3.5. Analytical parameters

Information about the extraction efficiency of the proposed method can be determined by calculating various analytical parameter like limit of detection (LOD), relative standard deviation (RSD), enhancement factor (EF), preconcentration factor (PF) and consumptive index (CIn) under the optimized experimental conditions. The value of LOD and LOQ are 0.16 μg L^{-1} and 0.47 μg L^{-1}, which were calculated as the ratio of three times standard deviation of ten blank absorbance's to the slope of the regression equation and ten times the standard deviation of the ten blank solutions to the slope of the regression equationrespectively. The values of (RSD), PF, EF and CIn are 0.3 %, 30, 29.6 and 2 which were calculated as given in the literature [35].

The quantitative recoveries of Al(III) were obtained at sample volume 30 mL. Therefore, high preconcentration factor 30 of Al(III) was achieved by using 30 mL of sample volume. The molar absorptivity calculated for a complex was 1.8×10^{3} L.mol.cm^{-1} at 380 nm. The straight line equation, based on relationship between absorbance (A) of Al(III) in the UV-Visible spectrophotometry measurement and the concentration of Al(III) (C) was A= 0.09+0.07C with a correlation coefficient (r^2=0.991).

3.6. Applications

The accuracy of the proposed Ss-LLME method was checked by applying this method to three certified reference materials (SPS-WW2 waste water, TMDA-53.3 fortified water and NCS ZC81002B Human hair). The obtained recovery results for Al(III) given in the Table 3 indicate that the method is highly accurate and valid for determination of aluminum at trace level.

The method was also applied to tap water sample from Kayseri City-Turkey, sea water sample from Marmara Sea-Turkey and underground water sample from Kayseri City- Turkey and hair sample were taken from male living in Kayseri, Turkey to prove accuracy of the developed Ss-LLME method. The known amount of Al(III) was added to these samples and recovery studies performed. The results given in the Table 4 shows that the method is valid for the determination of aluminum in hair and water samples. The addition-recovery tests to hair and water samples given in Table 4 show that the organic and inorganic matrices of real samples were not affected to our microextraction system.

The describe Ss-LLME method was compared with other preconcentration method for Al(III) in the literature based on analytical parameters including LOD and PF (Table 5). Low LOD value and high PF value confirm that the proposed Ss-LLME is comparable or more efficient as compared to other preconcentration methods in the literature.

4. Conclusion

The objective of the work was to develop a new supramolecular solvent (Ss) based liquid-liquid microextraction method for separation and preconcentration of Al(III) for water and biological samples prior to its determination by UV-Visible spectrophotometry. The presented method is highly sensitive with LOD low value of 0.16 µg L^{-1}. High extraction efficiencies were obtained with PF and EF value of 30 and 29.6 respectively. Cost effective because, there is no need of special laboratory equipment’s. The proposed method is comparable or more than the other preconcentration method regarding LOD. The method was successfully applied to water and hair samples.

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Figure captions

Fig. 1. Influence of pH on extraction efficiency of Al(III) (Volume of sample: 10 mL, volume of undecanol: 0.1 mL, volume of THF: 0.1 mL, amount of 8-hydroxyquinoline: 0.3 mg, N=3).

Fig. 2. Influences of undecanol volume and amount of complexing agent on extraction efficiency of Al(III) (pH: 8.0,Volume of sample: 10 mL, volume of THF: 0.1 mL, N=3).

Fig. 3. Influence of the THF volume on extraction efficiency of Al(III) (pH: 8.0,Volume of sample: 10 mL, volume of undecanol: 0.1 mL, amount of 8-hydroxyquinoline: 0.3 mg, N=3).

Table 1. Effect of type of extraction solution (pH: 8.0, Volume of sample: 10 mL, Volume of extraction solutions: 0.1 mL, volume of THF: 0.1 mL, Amount of 8-hydroxyquinoline: 0.3 mg, N=3).

Type of Extraction solution	**Recovery,%**
Decanoic acid-THF	<10
Undecanol-THF	102±2[a]
1-Decanol-THF	98±3

[a] Mean ± standard deviation.

Table 2. Interferences of the proposed method (pH: 8.0, Volume of sample: 10 mL, volume of undecanol: 0.1 mL, volume of THF: 0.1 mL, amount of 8-hydroxyquinoline: 0.3 mg, N=3).

Interfering ions	**Added as**	**Concentration, mg L^{-1}**	**Recovery, %**
Na^+	$NaNO_3$	5000	102±2[a]
K^+	KCl	2500	103±0
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	1000	99±1
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	1000	96±2
Cu^{2+}	$Cu(NO_3)_2.6H_2O$	10	100±3
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	10	99±4
Co^{2+}	$Co(NO_3)_2.6H_2O$	5	97±4
Ni^{2+}	$Ni(NO_3)_2.\ 6H_2O$	5	96±4
Mn^{2+}	$Mn(NO_3)_2.4H_2O$	5	97±1
SO_4^{2-}	Na_2SO_4	10	103±0
CO_3^{2-}	Na_2CO_3	10	102±1
F^-	NaF	5	99±2

[a] Mean ± standard deviation.

Table 3. Application of the proposed method to certified reference materials (pH: 8.0, volume of sample: 15 mL, volume of undecanol: 0.1 mL, volume of THF: 0.1 mL, amount of 8-hydroxyquinoline: 0.3 mg, N=3).

Certified Reference Material	Certified value, µg g^{-1}	Found value, µg g^{-1}	Recovery, %
NCS ZC81002B Hair	25	25.4±0.2	101
	Certified value, mg L^{-1}	**Found value, mg L^{-1}**	**Recovery, %**
SPS WW2 water	10	10.1 ± 0.1	100
TMDA 53.3 water	0.36	0.37 ± 0.04	102

[a] Mean ± standard deviation.

Table 4. Application of the proposed method to water and hair samples (pH: 8.0, volume of sample: 15 mL, volume of undecanol: 0.1 mL, volume of THF: 0.1 mL, amount of 8-hydroxyquinoline: 0.3 mg, N=3).

Sample	Added, µg	Found, µg	Recovery, %
Hair	0	1.8±0.01[a]	-
	3	4.7±0.06	95
	5	6.6±0.03	96
Tap water	0	BDL[b]	-
	3	3.0±0.01	100
	6	6.1±0.06	101
Sea Water	0	2.2±0.06	-
	4	6.2±0.05	99
	8	9.7±0.01	94
Underground water	0	3.8±0.03	-
	4	7.6±0.01	96
	6	9.4±0.00	94

[a] Mean ± standard deviation.

[b] BDL=Below of the detection limit.

Table 5. Comparison of the developed method with other preconcentration methods

Method	**Analysis**	**LOD, µg L^{-1}**	**REF**
Cloud point extraction	GFAAS	0.79	[36]
Cloud point extraction	ICP-OES	0.25	[37]
Solid phase extraction	ICP-AES	0.19	[38]
Solid phase extraction	AAS	2	[39]
Dispersive liquid-liquid microextraction	ICP-OES	0.8	[40]
Supramolecular solvent based liquid-liquid microextraction (SsLLME)	UV-Visible spectrophotometry	0.16	This work

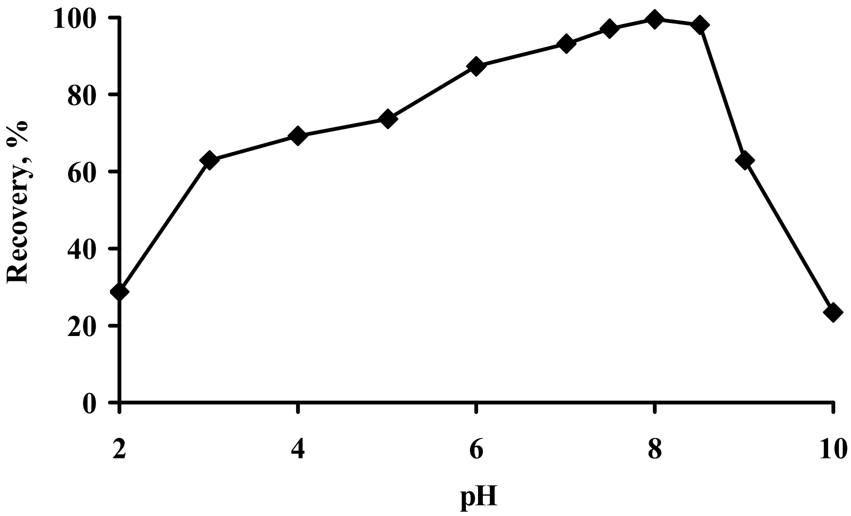

Fig. 1.

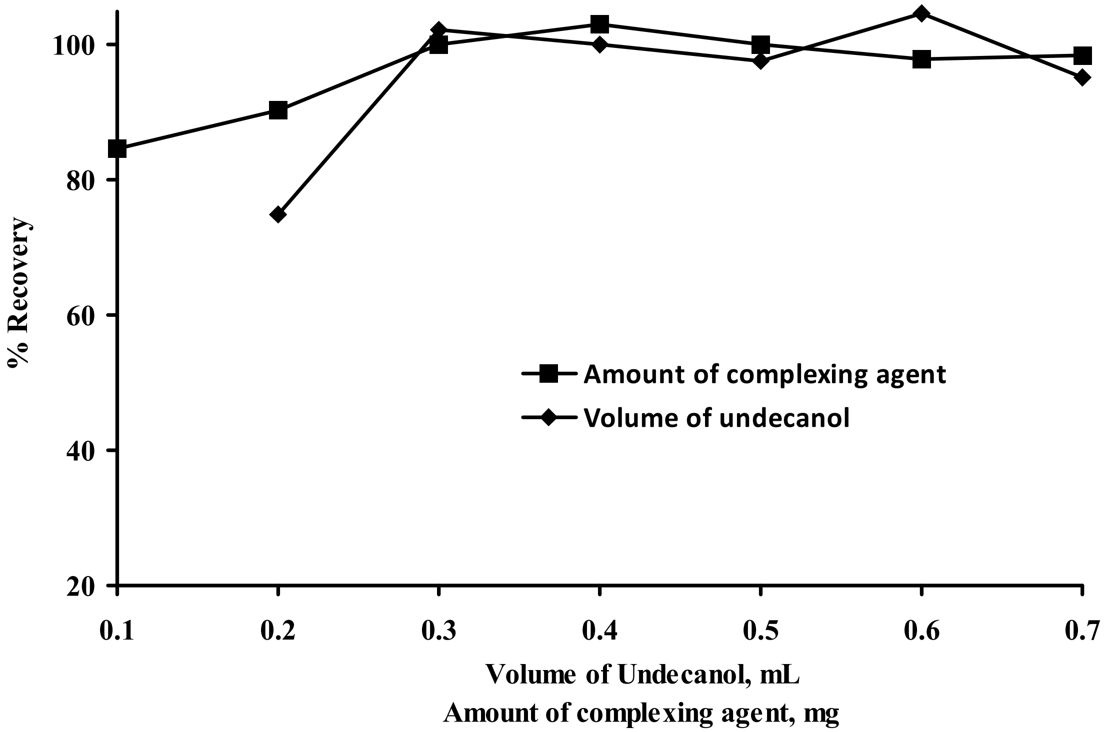
100
80
60
40
20
% Recovery
Amount of complexing agent
Volume of undecanol
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Volume of Undecanol, mL
Amount of complexing agent, mg

Fig. 2.

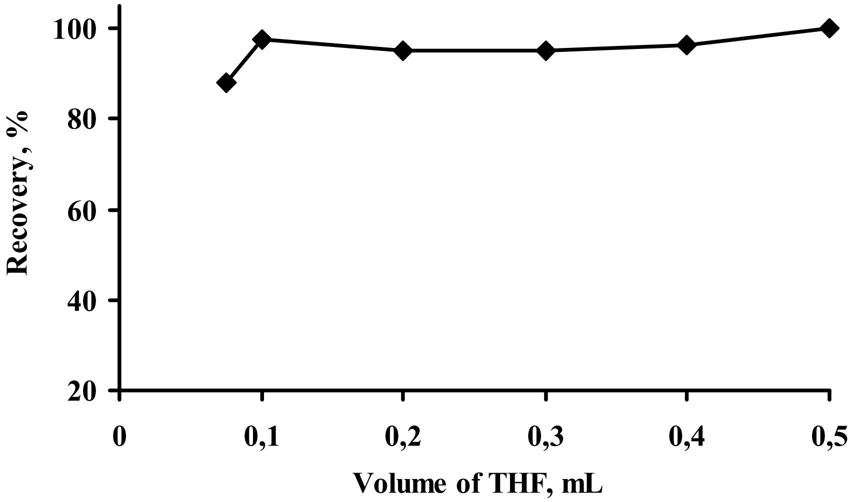

Fig. 3.