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Flame atomic absorption determination of manganese(II) in natural water after cloud point extraction

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Abstract

The possibility to use 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) for manganese(II) concentrating by the micellar extraction at cloud point (CP) temperature and subsequent atomic absorption spectrometry (AAS) determination was investigated. Under the optimum conditions, preconcentration of 100 ml of water sample in the presence of 1% non-ionic surfactant (NS) OP-7, 1×10^{-4} M 1-(2-pyridylazo)-2-naphthol permitted the detection 5 $\mu g\,l^{-1}$ manganese. The proposed method has been applied to the AAS determination of manganese in water samples after cloud point extraction.

Keywords: Non-ionic surfactant; Cloud point extraction; Manganese determination

1. Introduction

The general trend of the modern analytical chemistry is the elaboration of simple, ecologically safe, sensitive, and selective methods for microcomponents determination combining previous concentration and further determination by physical or physico-chemical methods [1]. Micellar extraction with non-ionic surfactants (NS) at cloud point (CP) is a high effective, ecologically safe method for microcomponents preconcentration which has been developed intensively recent years [2,3]. High concentration coefficients, selectivity, simple combination with spectral, atomic absorption, chromatographic, and electrochemical analysis allow to use extraction with NS phases for elaborating high-sensitive and convenient analytical methods [4–7].

NS dissolves in water due to the hydrogen bonds formation between oxygen atoms of polyoxyethyl chain and water molecules [4]. Heating of aqueous NS solutions till definite temperature; namely, cloud point results in destruction of these bonds and further separation of the system into phases. Hence, the two phases are formed. The first one is the NS phase, which consists of large hydratated micelles, and the second one is the aqueous solution of NS with the concentration level near critical micelle concentration. The micellar phase is used for concentrating.

Manganese(II) is a biometal with low contents in natural waters. Thus, Mn^{2+} ions present in natural waters always participate biocycles. Lack of the manganese in the human organism leads to the bones and cartilages deformation and destroys platelet aggregation. As a rule, the overall manganese content in natural waters is determined by photometric method after oxidation of Mn^{2+} ions into MnO_4^- with peroxysulfate. However, this method is of low sensitivity (limit of determination, 50 $\mu g\,l^{-1}$) and labour-consuming [8]. The extraction–spectrophotometric procedures have been applied for manganese determination in water samples [9,10]. However, used organic solvents are hazardous causing damage to human health and the environment. On another hand, the application of cloud point extraction method is used for manganese preconcentration with 1-(2-thiazolylazo)-2-naphtol into the NS Triton X-114 phases [11]. The using of 0.05% Triton X-114 solution for the extraction of manganese allows to decrease the limit of metal determination to 0.28 ppb by the AAS.

Herein, the micellar extraction of manganese(II) with 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) into phase of non-ionic SAS OP-7 has been investigated. The reagents choice was caused by high stability of their complexes with manganese [12]. Also, it was possible to examine the influence of the ligand structure

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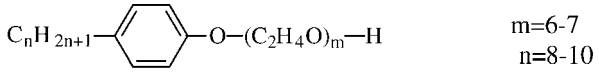
and hydrophobicity at the efficiency of the metal micellar extraction. Moreover, PAR and PAN were shown to be effective ligands for micellar extraction preconcentrating of the other metals; namely, Zn, Co, and Ni [13,14].

2. Experimental

2.1. Reagents and apparatus

Polyoxyethylated alkylphenol OP-7 with average oxyethylation degree 8–10 was used throughout the work. The choice of OP-7 is related to its ability to form phases under heating more quickly than other NS as well as high viscosity and the compactness of the micellar phase. The solutions of OP-7 were prepared by dissolving the exact mass of the substance in distilled water.



OP-7

The solutions of PAR and PAN (Merck) were prepared by dissolving of the exact masses of compounds in the aqueous micellar solutions of OP-7. For preparation of the manganese solutions, the standard samples "ДСЗРМ ПЩ-1" (Ukrainian State Standard Sample of Metal Solution) were used. Absorption spectra were measured with SF-46 and Specord M-40 spectrophotometers. Acidity of the solutions was controlled with pH-meter pH-340 using glass lithium electrode ESL-43-07.

2.2. Procedure for cloud point extraction

Aqueous solutions of NS containing all required components were placed into calibrated 10 ml cylinders placed into water bath. The temperature of the solutions was controlled by the thermometers dived both in the cylinders and in the bath. The heating was performed with $0.5\,^{\circ}\mathrm{C\,min^{-1}}$ rate. The cloud point was registered by the appearance of characteristic opalescence. The density of the micellar phase was some higher than that of the water and the NS phase was collected at the bottom of the cylinders.

Full phase separation was fixed when both precipitated phase volume and the NS concentration in the solution became constant. After the cloud point extraction, the aqueous phase was decanted. The micellar phase was diluted with distilled water to required volume before determination.

PAR and PAN distribution was controlled spectrophotometrically by measurement the optical density of aqueous micellar solutions before and after phases separation as well as of the micellar phase after its dilution at the λ_{max} of the corresponding analytical forms.

Manganese distribution between water and micellar phase was controlled by atomic absorption method at the wavelength 279.5 nm. The measurements were carried out with "Saturn" spectrometer with pneumatic nebuliser and tantalic impact beat. The aspiration rate composed $0.2\,\mathrm{ml\,s^{-1}}$. The flame gas mixture was propane–butane–air. The used mixture is cheaper instead of acetylene–air mixture. The gas flows were 0.35 and $8\,\mathrm{l\,min^{-1}}$ for propane–butane and air, respectively.

From the data obtained the extraction degree (R) and the distribution coefficient (D) of manganese in water–NS phase system were calculated. Distribution coefficients values calculations were performed with the consideration of the volumes of the aqueous and micellar phases. The volume of the micellar phase of OP-7 (V_{MP}) depended from the substance concentration in the starting solution. The V_{MP} value changed from 0.1 to 1.8 ml when NS concentration increased from 0.5 to 5%.

2.3. Preparation of water samples

The probes of natural water chosen for analysis were preserved by nitric acid addition at the place of the sample selection. Before manganese(II) determination, the water was treated with ultrasound energy to remove natural ligands such as fulvic and guminic acids. An ultrasonic bath, Ultrasons (Selecta), was used for sample sonication. The water solution was acidified to pH 1.0 using 65% HNO_3 (Merck) and exposed to ultrasound at 44 kHz, at an intensity of $\leq 10\,\mathrm{W\,cm^{-2}}$ for 3 min.

2.4. Procedure for manganese(II) determination in natural water

OP-7 (1.0 g) was dissolved in $100\,\mathrm{cm^3}$ of the water sample. PAN (0.012 g) and 1 ml of 1% aqueous sodium–potassium tartrate solution were added to the obtained solution and then it was stirred. The pH value was adjusted to 10.0 with KOH. The solution was heated in the water bath to the cloud point ($\sim 68\,^{\circ}\mathrm{C}$) and then was kept at this temperature for 20 min until complete phases separation. After cooling, the water phase was decanted, the micellar phase (V_{MP}=3 ml) was diluted to 5 ml with distilled water and the atomic absorption manganese determination was performed. The manganese content in the probe was found with calibration curve. To obtain it, the six probes were prepared as follows: 0.1, 0.2, ..., 0.6 ml of the standard manganese solution with concentration 1×10^{-4} M was diluted till 25 ml with 20% aqueous solution of OP-7 corresponding the NS concentration in the extract after dilution.

3. Results and discussion

3.1. PAR and PAN distribution between aqueous and micellar phases

First the distribution of PAR and PAN between water and micellar phase of OP-7 was investigated. It was found that

Table 1
Extraction degrees and distribution coefficients of different forms of PAR and PAN in the water–OP-7 phase system. $C_{HR} = 4 \times 10^{-5}$ M, $C_{OP\text{-}7} =$ 1%

Reagents form	PAR		Reagents form	PAN	
	R (%)	*D*		*R* (%)	*D*
H_3R^+	18	7.4	H_2R^+	54	38.3
H_2R	56	41.7	HR	82	148
HR^-	18	7.1	R^-	26	11.9
R^{2-}	1.7	0.6			

under conditions of its molecular form, i.e., PAN containing naphthol moiety, it was more effectively extracted into the micellar phase. Oppositely, PAR containing resorcinol moiety was less extracted into the OP-7 phase (Table 1). Therefore, the introduction of two hydrophilic hydroxy groups into the reagent molecule decreased the efficiency of the cloud point extraction of the substrate. Such character of the reagents distribution is in good agreement with the previously obtained data for the micellar extraction of aromatic carboxylic acids [15]. On the basis of the results obtained, the more effective manganese extraction should be expected with PAN due to its higher hydrophobic and amphiphilic properties comparatively to PAR.

3.2. Manganese complexation with PAR and PAN in NS solutions

During the micellar extraction, the analytic reaction occurs in the pseudo-organic "organized" medium of the non-ionic surfactant solution. This affects the complexation parameters in comparison with water solutions [16]. Formation of the manganese complexes with PAR and PAN in the 1% OP-7 solution was observed in a wide pH range with the highest yields at pH 8–12.5. Using the method of equilibrium shift, complexes of ratio Mn:PAR(PAN) = 1:2 were found to be formed.

3.3. Manganese cloud point extraction with PAR and PAN

The study of the cloud point extraction of manganese with PAN exhibited complete metal extraction ($R > 99\%$) in the micellar phase of OP-7 in the pH range 9.7–11.8 (Fig. 1, curve 1). A decrease of the metal extraction efficiency at pH < 9.7 is explained by the complex destruction, whereas, at pH > 11.8, hydrolysis of the metal takes place upon heating of the solutions. At the same time, manganese was extracted by the PAR into micellar OP-7 phase for 58% only (Fig. 1, curve 2). Such distribution of the manganese complexes with PAN and PAR is in agreement with the results of the micellar extraction of the reagents themselves. Hydrophobic Mn–PAN complex with higher amphiphilic properties is more effectively extracted into the micellar phase than the hydrophilic Mn–PAR complex.

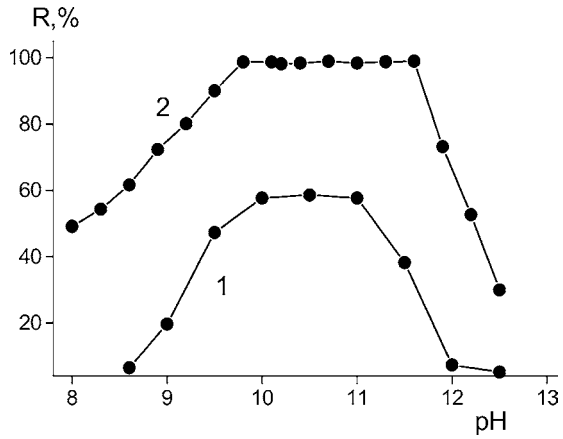


Fig. 1. Dependence of the manganese extraction degree into micellar phase of OP-7 with PAR (1) and PAN (2) via the pH value. $C_{Mn} = 1 \times 10^{-5}$ M, $C_{HR} = 5 \times 10^{-5}$ M, and $C_{OP\text{-}7} = 1\%$.

Complete extraction of the manganese into micellar phase of OP-7 with PAN was observed with three-fold excess of the ligand (Fig. 2). The analysis of the dependence $\log D = f(\log C_{PAN})$ permitted the determination of the ligands number in the extracted complex. The slope of curve on the Fig. 2 in $\log D = f(\log C_{PAN})$ coordinates is nearly ≈2; therefore, the unsaturated complex with Mn:PAN ratio 1:2 is extracted into the micellar phase.

3.4. Manganese determination in the natural water

On the basis of the data obtained the method for manganese(II), atomic absorption determination in the natural water with the use of preconcentrating by cloud point extraction with PAN has been elaborated (Section 2.4). The equation of calibration graph was $I = (5.9 \pm 4.2) + (0.064 \pm 0.002)C\ \mu g\,l^{-1}$, $r = 0.99$. The calibration equation is presented without taking into account the concentrating coefficient. The detection limit, calculated as three times the stan-

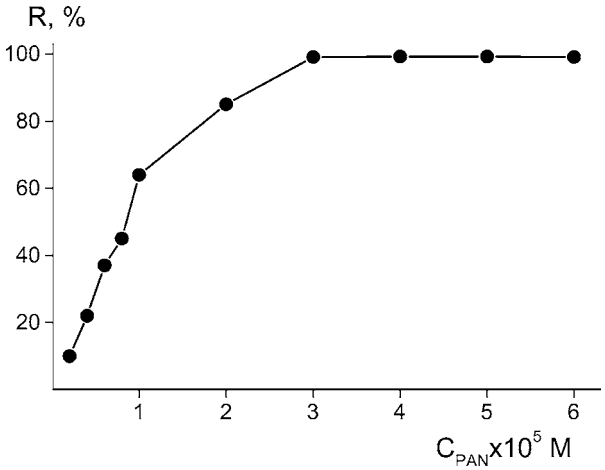


Fig. 2. The influence of the PAN concentration on the manganese extraction into the micellar phase of OP-7. $C_{Mn} = 1 \times 10^{-5}$ M, pH 10.0, and $C_{OP\text{-}7} = 1\%$.

Table 2
The model solutions content

Cations	Concentration ($mg\,l^{-1}$)	Anions	Concentration ($mg\,l^{-1}$)
Ca^{2+}	100	HCO_3^-	200
Mg^{2+}	40	Cl^-	50
Fe^{3+}	0.2	SO_4^{2-}	50
Zn^{2+}	0.02	HPO_4^{2-}	0.2
Cu^{2+}	0.02		

Table 3
Results of the manganese determination in the model solutions with the elaborated procedure using "added–measured" method ($n = 5$, $P = 0.95$)

Added ($\mu g\,l^{-1}$)	Measured ($\mu g\,l^{-1}$)	S_r (%)
15	14 ± 1	5.1
30	29 ± 1	2.0
50	48 ± 2	3.2

Table 4
Results of the manganese determination in some river waters of Ukraine with the elaborated procedure ($n = 5$, $P = 0.95$)

	Measured ($\mu g\,l^{-1}$)	S_r (%)	Measured [17] ($\mu g\,l^{-1}$)	t-test
River Lybid (Kyiv)	139 ± 2	1.4	137 ± 3	0.81
River Dnipro (Kyiv)	94 ± 2	2.1	93 ± 2	0.35
River Zbytynka (Rivne region)	143 ± 3	1.9	141 ± 3	1.64
River Sula (Poltava region)	83 ± 2	2.0	85 ± 3	−1.94
Lake (Kyiv)	33.3 ± 0.8	3.0	33 ± 2	−0.37

dard deviation (3σ) of the blank signal was $5\,\mu g\,l^{-1}$. The experimental preconcentrating factor was 20 (for 100 ml of sample solution).

Because the solubility of PAN in the micellar systems is limited, its complexation with Mg and Ca was prevented by addition of the sodium–potassium tartrate.

The procedure proposed was tested with "added–measured" method by manganese determination in synthetic sample spiked with several metal concentrations in the model solutions containing main macrocomponents of the natural water at their average contents [8]. The model solutions content is listed in the Table 2. Table 3 data exhibit satisfactory correctness and precision of the manganese determination results with the proposed procedure. The S_r value was calculated from parallel samples.

The procedure was used for manganese determination in natural waters. The correctness of the results obtained was controlled with atomic absorption method according to [17] with preconcentrating by the probe evaporation or extraction with dithizone. Table 4 data show the method to be suitable for manganese determination in the natural waters.

4. Conclusions

The micellar extraction of manganese(II) with PAR and PAN into the phase of non-ionic surfactant OP-7 has been investigated. Complete metal extraction was shown to be achieved with PAN due to the hydrophobic complex compound formation. The molar ratio of the extracted complex has been determined. The method for atomic absorption determination of manganese(II) in natural waters using preconcentrating by cloud point extraction with PAN has been elaborated. The sensitivity, metrological characteristics, ecological safety, simplicity, and convenience of the suggested procedure is competitive with respect to the methods based on the extraction with organic solvents. The limitation of elaborated procedure is rather long time of the analysis. The use of cheaper propane–butane–air burning mixture provides the decrease of gas flow and the low price of the suggested method in comparison with other procedure [11]. Moreover, the use of nonionic surfactant OP-7 for extraction permits to avoid the surplus step of solutions centrifugation after phase separation. Beside this, distilled water is used for surfactant rich phase dilution in the procedure suggested (instead of toxic methanol) that makes our procedure more ecologically safe.

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