

# Direct atomic-emission determination of metals on polyurethane foam sorbents

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**Abstract:** The principle feasibility of direct simultaneous determination of metals on polyurethane foam (PUF) sorbents by atomic-emission spectrometry was demonstrated. These metals were sorbed as thiocyanate acidocomplexes (Fe, Co) and complex compounds with dithizone (Hg, Pb) from water in batch mode. The proposed technique is based on partial destruction of PUF-sorbent with preconcentrated metals in plasma of AC-arc electric discharge and photoelectric registration of the analytical signal before the "torch" formation (exposure time  $\sim 1$  s). The range of the metal concentrations in water was  $10^{-2}$ - $10$   $\mu\text{g/ml}$ , the detection limits – units of  $\text{ng/ml}$ . The developed approach was applied for analysis of the water samples from Moscow River and water supply line, in particular. The validity of the analysis results was tested by diffuse reflection spectroscopy and X-ray fluorescence spectrometry.

## Introduction

Nowadays polyurethane foam (PUF) sorbents are widely used for preconcentration of metals from water. The advantages of this type of sorbents are high preconcentration factors (up to 10,000-fold), versatility, availability and low cost [1]. Metals can be sorbed either as acidocomplexes, chelates or ion associates. Preconcentration of metals by sorption on PUF is combined with subsequent determination by atomic-absorption spectrometry (AAS), atomic-emission spectrometry with inductively coupled plasma (ICP AES), photometry or diffuse reflection spectroscopy (DRS). There are two main ways of spectroscopic determination of metals with preconcentration on PUF-sorbents. The first 3-stage way includes solid-phase extraction in batch or dynamic mode, elution of metals from sorbent with ketones, low-molecular alcohols or strong acid solutions and determination of metals in eluate by ICP AES, flame or non-flame AAS [2, 3]. The possibility of simultaneous multielement analysis by ICP AES allows using PUF-sorbents for the group preconcentration of metals. It is very important for ecological monitoring of natural and waste water. This approach is characterized by excellent sensitivity and selectivity, but high cost of analytical equipment and analysis. Another 2-stage way includes solid-phase

extraction with subsequent direct determination of metals on PUF-sorbent by DRS [1, 4]. In this case the cost of equipment and analysis is low, and the sensitivity is sufficient. Moreover the accuracy of 2-stage technique is higher as a rule. However the photometric determination of metals has two evident restrictions – low selectivity and determination of colored compounds only.

Thus, for solution of the problems enumerated above it is necessary to employ a not very expensive method of multielement solid analysis with sensitivity comparable with sensitivity of DRS. The aim of our work was the study of principle feasibility of direct determination of metals on PUF-sorbents by AC-arc AES. Iron and cobalt were chosen as elements being determined. These metals were extracted from water as colored thiocyanate acidocomplexes. The choice of elements and ligands was stipulated first of all by the possibility of the result verification by DRS. Furthermore we have tried to get the preliminary information about the possibility of direct AE-determination of mercury and lead as complex compounds with dithizone on PUF-sorbents. To determine these elements by DRS is a difficult problem. That is why we used X-ray fluorescence spectrometry (XRF) for test of the determination results.

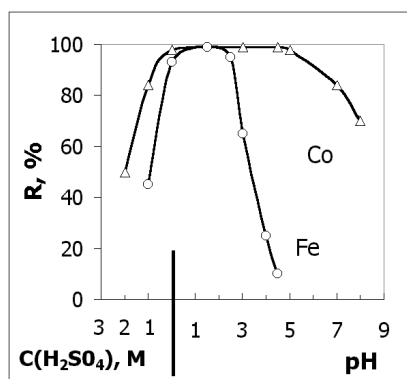


Fig. 1. The dependence of extraction degree of metal thiocyanate complexes by PUF from aqueous solution on pH value.

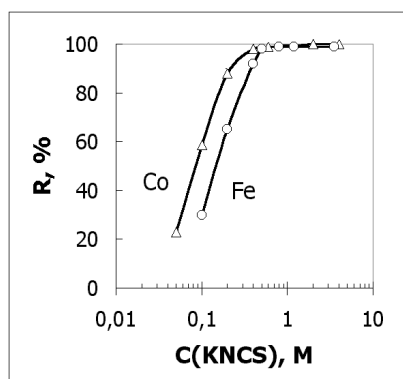


Fig. 2. The dependence of extraction degree of metal thiocyanate complexes by PUF on ligand concentration in solution.

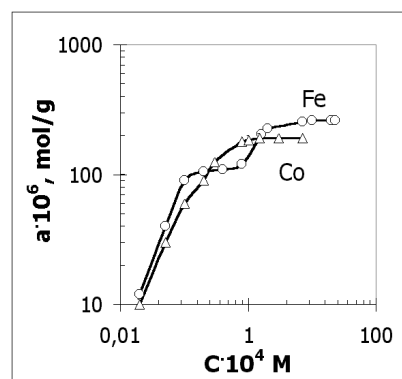


Fig. 3. The isotherms of sorption of metal thiocyanate complexes on PUF from aqueous solution.

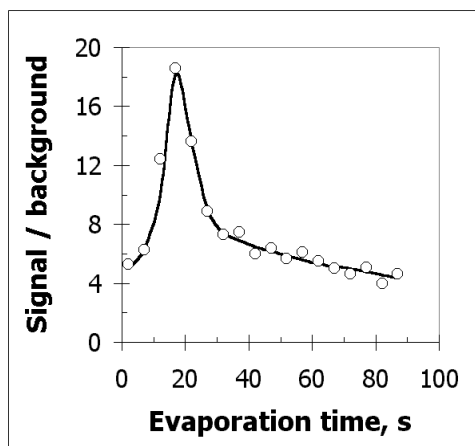


Fig. 4. The typical curve of the metal evaporation from a crater of bottom carbon electrode (Co on PUF, distance between working electrodes – 2 mm).

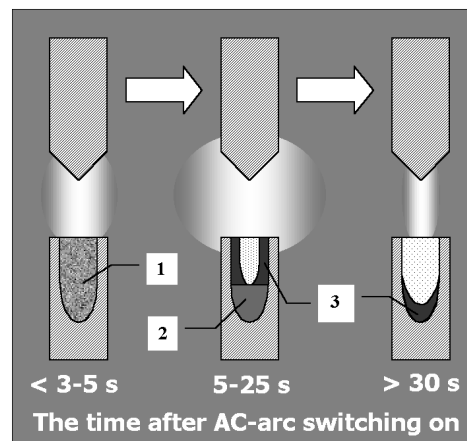


Fig. 5. Dynamics of the analyte transfer to AC-arc plasma (1 – porous PUF pressed in crater of carbon electrode, 2 – melted PUF with low porosity, 3 – carbonized PUF remains).

## Experimental

### PUF-sorbent preparation

As it is known the sorption of acidocomplexes on PUF from aqueous solutions proceeds on anion exchange or cation chelation mechanisms [5]. The last one prevails in case of  $\text{pH} > 2$ . The first stage of cation chelation mechanism is adsorption of alkaline metal ions on PUF surface. These ions interact with flexible spiral polyether chains of PUF macromolecules as with crown ethers. The flexibility of polyester chains is substantially less. As a result the polyether PUF sorbs metal acidocomplexes substantially better than polyester PUF [6]. For solid-phase extraction we used polyether PUF-sorbents. Ion-exchange mechanism of the sorption defines the features of technique of the sorbent purification for analysis:

1. treatment of PUF-pellets by 1M HCl during 1 hour;
2. washing the PUF-pellets by water until  $\text{pH} 4-5$ ;
3. washing the PUF-pellets by acetone;
4. air drying the PUF-pellets.

### Sorption of Fe and Co acidocomplexes

Earlier the sorption of thiocyanate complexes of iron and cobalt on polyether PUF-sorbent in batch mode was studied by

photometric method (Fig. 1-3) [1, 4]. The sorption efficiency depends on the nature of complex, the composition and pH value of working solution. The last factor has a decisive meaning. For joint sorption the optimal pH range is 1-2 (Fig. 1). Under higher pH values insoluble metal hydroxides are formed. Under lower pH values thiocyanate anions are associated with hydrogen ions. As a result the sorption efficiency decreases. The reasonable concentration of thiocyanate anions should exceed 0.5 mol/l (Fig. 2). For preliminary purification of KNCS from Fe-impurities we used the following technique:

1. addition of 0.1M  $\text{H}_2\text{SO}_4$  to warm 5M KNCS solution until  $\text{pH} 1.5$ ;
2. shaking up the solution with PUF in excess (4-5 pellets/100 ml) during 30 min;
3. removal of the PUF-pellets.

Purified PUF-pellets (40-50 mg) were used. The technique of sorption of Fe and Co thiocyanate acidocomplexes on PUF-sorbent in batch mode includes the following stages:

1. addition of  $\text{Fe}^{3+}$  ( $\text{Co}^{2+}$ ) aliquot (0.5-150  $\mu\text{g}$ ) to the acidified 5M KNCS solution (10 ml);
2. addition of water until 25 ml total volume;
3. addition of PUF-pellet and removal of air bubbles by stirring rod;

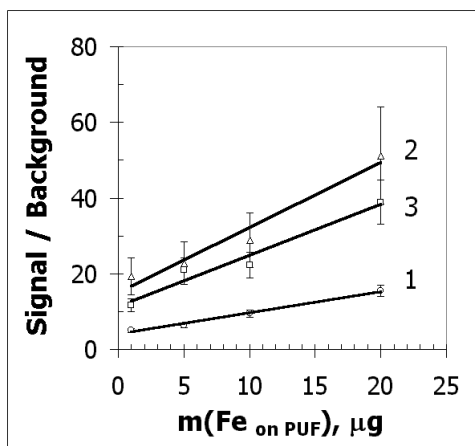


Fig. 6. The graduation graphs for direct AE-determination of Fe on PUF: distance between working electrodes – 1 (3) and 2 (1, 2) mm, evaporation time – 1 (1), 17 (2) and 40 (3) s.

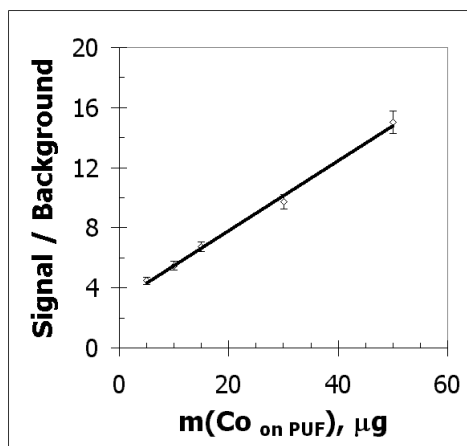


Fig. 7. The graduation graph for direct AE-determination of Co on PUF (distance between working electrodes – 2 mm, time of preliminary evaporation – 1 s).

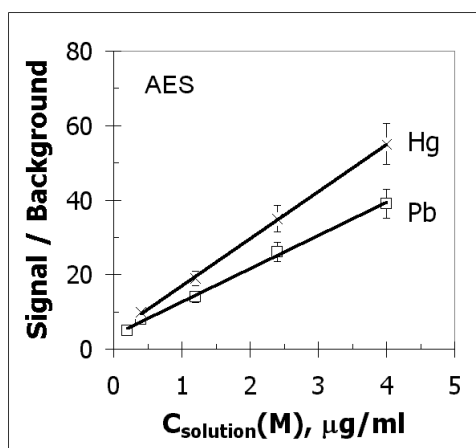


Fig. 8. The graduation graphs for direct AE-determination of Hg and Pb on PUF (distance between working electrodes – 2 mm, time of preliminary evaporation – 1 s).

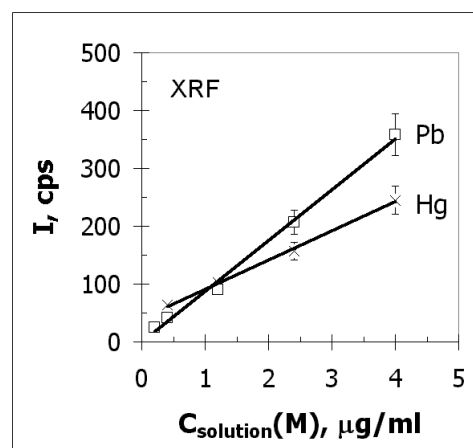


Fig. 9. The graduation graphs for direct XRF-determination of Hg and Pb on PUF (exposure time – 10 s).

4. shaking up the solution with use of vibrational mixer during 30 min;
5. drying the PUF-pellet.

#### Sorption of Hg and Pb complexes

The sorption of Hg and Pb complexes was realized under excess of dithizone in weakly alkaline solution. The reasonable pH range is 8.5-9. Under higher pH values insoluble metal hydroxides are formed. Under lower pH values dithizone molecules are protonized. As a result the sorption efficiency decreases. The technique of the sorption of Hg and Pb complexes on PUF-sorbent in batch mode includes the following stages:

1. addition of ammonium buffer to  $Hg^{2+}$  ( $Pb^{2+}$ ) aliquot (5-100 µg) until pH 8.5-9;
2. addition of 0.5 ml 0.04M solution of dithizone in acetone;
3. addition of water until 25 ml total volume;
4. addition of PUF-pellet and removal of air bubbles by stirring rod;
5. shaking up the solution with use of vibrational mixer during 1 hour;
6. drying the PUF-pellet.

#### Direct determination of metals

For direct AE-determination of metals we used electrodes made from spectro-pure carbon. After metal preconcentration and drying the PUF-pellet was pressed into the crater of bottom electrode. The crater depth was ~7 mm. The sample excitation was fulfilled by AC-arc electric discharge with use of universal generator *УТЭ-4* (Kazan, Russia). The discharge current was 2 A. The distance between working electrodes was 1 and 2 mm. AE-spectra were measured by improved grating spectrometer *СТЭ-1* (Peterburg, Russia) with the photoelectric detector *Slavna*

(Ekaterinburg, Russia). It is the cheap low-end detector completed by domestic Sony CCD-matrix without cooling system. The evaporation curves were measured for the study of dynamics of the analyte transfer from crater of bottom electrode containing PUF-sorbent to plasma of AC-arc electric discharge. The total time of evaporation was 3 min. The graduation graphs for the metal determination were plotted under following experimental conditions. The time of preliminary evaporation was 1, 17 and 40 s. The exposure time was 1 s. Analytical AE-lines – FeI (302.064 nm), CoI (340.512 nm), HgI (253.652 nm), PbI (283.307 nm). Before destruction of the PUF-pellets in electric discharge the contents of preconcentrated metals were determined by DRS and XRF. For this aim we used photoreflectometer *Spectroton* (Russia) ( $\lambda_{abs}=490$  ( $Fe^{3+}$ ) and 620 ( $Co^{2+}$ ) nm) and sequential wavelength-dispersive X-ray fluorescence spectrometer *Spectroscan* (Peterburg, Russia). Analytical X-ray lines –  $FeK_{\alpha}$  (0.194 nm),  $CoK_{\alpha}$  (0.179 nm),  $HgL_{\alpha}$  (0.124 nm),  $PbL_{\alpha}$  (0.118 nm). X-ray spectra were excited by low-power sharp-focused X-ray tube with Cu-anode. Working potential – 40 kV.

#### Results and discussion

For the study of dynamics of the analyte transfer from crater of bottom carbon electrode containing PUF-sorbent to plasma of AC-arc electric discharge the curves of sorbate evaporation were measured (Fig. 4, 5). These data and the results of visual observation indicate the following. The process of sample evaporation includes three stages at least (three time ranges respectively). The first one is negligible destruction of the sorbent as a result of indirect thermal action of plasma, in particular, through the sides

Table 1

The results of direct AE-determination of Fe and Co on PUF-sorbent (n= 5, p= 0.95).

System	Element	$C_{added}, \mu g/g$	$C_{found}, \mu g/g$	$S_r$
Single metal	Fe	0.20	$0.23 \pm 0.05$	0.08
	Co	2.0	$2.0 \pm 0.3$	0.05
Fe : Co = 2 : 1	Fe	0.40	$0.5 \pm 0.1$	0.09
	Co	0.20	$0.19 \pm 0.03$	0.07
Fe : Co = 1 : 2	Fe	0.5	$0.5 \pm 0.1$	0.08
	Co	1.0	$1.1 \pm 0.2$	0.06

Table 2

The comparison of the techniques of direct determination of Fe and Co on PUF-sorbent by DRS and AC-arc AES (preconcentration of metals from aqueous solution, V= 25 (**500**) ml, m(PUF)= 50 mg).

Method	DRS		AC-arc AES	
Element	Fe(III)	Co(II)	Fe(III)	Co(II)
Range of $C_M$ , $\mu\text{g/ml}$	0.004–0.6 ( <b><math>2 \cdot 10^{-4}</math></b> )	0.07–6.0 ( <b>0.0035</b> )	0.02–0.6 ( <b>0.001</b> )	0.3–6.0 ( <b>0.015</b> )
$C_{P,\min}$ , $\mu\text{g/ml}$	0.001 ( <b><math>5 \cdot 10^{-5}</math></b> )	0.008 ( <b><math>4 \cdot 10^{-4}</math></b> )	0.01 ( <b><math>5 \cdot 10^{-4}</math></b> )	0.12 ( <b>0.006</b> )
$S_{r,\min}$	0.03	0.02	0.08	0.05

of bottom carbon electrode. This stage continues several seconds. The heat of PUF over its ignition point leads to intensive chemical combustion in air atmosphere. The bright torch forms. Its diameter exceeds the diameter of AC-arc halo by several times. The power ejection of the analyte to plasma is confirmed by intensive peak of the evaporation curve. The analytical signal has roughly 3-fold value. This stage continues about twenty seconds. The final stage is gradual transfer of melted and carbonized remains of PUF and the sorbate to plasma caused by temperature gradient. The metal concentration in plasma achieves certain stationary level that does not practically change during several minutes at least. Naturally this signal level decreases with the growth of the distance between working electrodes.

There are two serious problems preventing to direct determination of metals on PUF. The chemical combustion of sorbent results in unstable analyte transfer to plasma and substantial fluctuations of the analytical signal respectively. The second problem is an intensive background signal in the spectrum that is due to the presence of organic matrix. Therefore combustion of the sorbent is intolerable during direct AE-analysis. AE-determination of highly volatile elements (Cd, Hg, Pb, etc.) after 20–30 s of preliminary evaporation (after torch discontinuance) is impossible. The only reasonable time range for the analytical signal measurement is 1–2 seconds until torch formation. This conclusion is confirmed by the experimental results (Fig. 6, 7). Indeed it was established that the signal measurement during torch formation (2<sup>nd</sup> stage) is reasonable for sensitive semiquantitative analysis only, because of the relative standard deviation of the analysis results exceeds 20–30%. After torch discontinuance (3<sup>rd</sup> stage) this parameter is equal to 12–18%. Until torch formation (1<sup>st</sup> stage)  $s_r$  value is less than 10% that is quite admissible for quantitative analysis. The photographic registration is impossible in this case because of the exposure time is very small. For this problem to be solved we used the cheap photoelectric detector.

The results of test of new technique are shown in Tables 1, 2. The less sensitivity of our technique in comparison with photometric method is partially compensated by the possibility of simultaneous determination of metals. The result reproducibility for iron is worse than for cobalt. As appears it deals with the affect of iron contaminations on the analysis results in spite of preliminary purification of sorbent, reagents, flasks and carbon

electrodes. The table with results of direct AE-determination of iron in real subjects are presented in Table 3. They were obtained by AC-arc AES, DRS and XRF. The comparison of these data indicates an adequacy of new technique. The graduation graphs for direct AE-determination of mercury and lead as complex compounds with dithizone on PUF are shown in Fig. 8. Preliminary data that were obtained without optimization are quite satisfactory. It is partially confirmed by XRF data (Fig. 9).

## Conclusions

Thus AC-arc AES can be used for direct simultaneous determination of metals on PUF-sorbents. The average sensitivity is tens or hundreds of ng/ml. The preliminary estimations show that the use of DC-arc electric discharge, non-diffraction spectrometer with high transmission and photoelectric detectors completed by low-noise professional CCD-matrix with cooling system can substantially increase the determination sensitivity. For efficient group preconcentration of metals on PUF an application of heteropolyacids or ethylenediaminetriacetic acid is rather perspective. These organic reagents are universal. And corresponding compounds with metals have low density of charge on the complex molecule. It is very important for efficient sorption on PUF.

## References

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Table 3

The results of direct determination of iron in a number of environmental subjects and KNCS preparation by DRS, XRF and AC-arc AES (n= 5, p= 0.95).

Samples of water, snow and KNCS	The results of Fe determination					
	DRS		XRF		AC-arc AES	
	$C_{\text{found}}$ , $\mu\text{g/ml(g)}$	$S_r$	$C_{\text{found}}$ , $\mu\text{g/ml(g)}$	$S_r$	$C_{\text{found}}$ , $\mu\text{g/ml(g)}$	$S_r$
Moscow river	$0.16 \pm 0.02$	0.05	$0.15 \pm 0.03$	0.08	$0.16 \pm 0.03$	0.08
Water supply line	$0.7 \pm 0.1$	0.06	$0.8 \pm 0.2$	0.10	$0.9 \pm 0.2$	0.09
Snow near road	$0.26 \pm 0.06$	0.09	$0.32 \pm 0.06$	0.08	$0.28 \pm 0.06$	0.09
KNCS <sub>(solid)</sub>	$30 \pm 3$	0.04	$30 \pm 6$	0.07	$31 \pm 6$	0.08