

*Dedicated to professor Gh. Marcu at his 80th anniversary*

## THE USE OF ORGANODITHIOPHOSPHORIC ACIDS FOR SEPARATION AND DETERMINATION OF SOME METAL IONS FROM RESIDUAL WATERS

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**ABSTRACT.** The U(VI), Cu(II) and Ni(II) separation was performed by thin layer chromatography on silica gel H, using o,m,p-xylene, methyl-ethyl-ketone (MEK) and N,N-dimethylformamide (DMF) (16: 2: 1, v/v) mixture as mobile phase. The di(n-pentyl)dithiophosphoric acid was used as complexing agent introduced in the mobile phase. This method was applied for quantitative determination of studied metal ions from waste waters.

**Key words:** thin layer chromatography, metal ions, di(n-pentyl)dithio- phosphoric, quantitative determination

### INTRODUCTION

In the last years many studies are devoted to the identification, separation and determination of trace metal ions in particular samples, because of their strong environment impact. Uranium, natural occurring actinide, is found at a trace level in the environment or associated with other metal ions in complex mixtures, nuclear fission products, and geological materials. Many methods have been proposed for the separation and determination of uranium and other metals. One of these techniques, more suitable due to the simplicity in handling radioactive elements is chromatography. In particular, extraction chromatography which combines the selectivity of organic extractants with multistage feature of chromatographic process has been extensively applied in the analysis of the radioactive materials [1-3].

In recent years thin layer chromatography (TLC), widely applied in pharmaceutical and food industries, biochemistry, and has been used in metal ions analysis because of their simplicity, low cost of qualitative analysis and short time of separation. TLC technique has been employed using different complexants fixed on silica gel or another supports or included in organic solvents used as eluents [4-9].

Organophosphorus compounds have been intensively investigated as complexants in separation of metal ions [8, 9]. Their analogues when one or more oxygen atoms have been replaced by sulphur atoms have been used in lesser extent.

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Dialkyldithiophosphoric acids are well known as good complexing agents for metal ions [10-12]. The metal chelates formed with organodithiophosphate anions are soluble in organic solvent which make these ligands useful in liquid-liquid extraction [13-18].

Dialkyldithiophosphoric complexants containing different alkyl chains were also investigated as extractants in the chromatographic technique. In our earlier work we have been investigated the extraction of U(VI), Th(IV) and lanthanides with various dialkyldithiophosphoric acids [19-23] and later we extended our investigations on the separation of metal ions by electrophoresis [24] and TLC [25-29].

The work discussed in this paper continues our investigations on the separation of the metal ions by TLC using dialkyldithiophosphoric acids. The work is undertaken to obtain information about TLC behavior of U(VI), Cu(II) and Ni(II) on silica gel H using di(n-pentyl)dithiophosphoric acid (HDPDTP) in mobile phase, in order to establish the optimum conditions for separation and quantitative determination of these elements in different water samples.

## **EXPERIMENTAL DATA**

### ***Apparatus***

Normal chromatographic chambers, Brand micropipettes (5  $\mu$ L), densitometer (DESAGA CD 60), Varian Tectron A 66 Spectrometer and Spekol Zeiss Yena were used.

### ***Materials***

TLC plates coated with silica gel H ("Raluca Ripan" Institute for Research in Chemistry), Arsenazo III and uranium nitrates (Sigma-Aldrich Chemie, Steinheim, Germany) were used. Copper and nickel nitrates and all other reagents were of analytical grade supplied by "Chimopar" Bucharest, Romania. HDPDTP were synthesized according to published procedure [30] and its purity was higher than 95%. Test solutions of metal nitrates were standardized gravimetrically and concentrations were obtained by successive dilutions.

### ***Procedure***

Silica gel H was used as stationary phase for separation of U(VI), Cu(II), Ni(II). The mixture of o,m,p-xylene, methyl-ethyl-ketone (MEK) and N,N-dimethylformamide (DMF) (16 : 2 : 1, v/v), containing HDPDTP was chosen as mobile phase after preliminary experiments. Standard solutions of metal ions were spotted on the plates using Brand micropipettes (5  $\mu$ L). The plates were developed on 10 cm distance in unsaturated normal chromatographic chamber. After development the plate were dried for 15 min in a hood and visualized with 0.05% Arsenazo III aqueous solution for U(VI) and 0.1% rubeanic acid in ethanol for Cu(II) and Ni(II). All operations were performed at the room temperature.

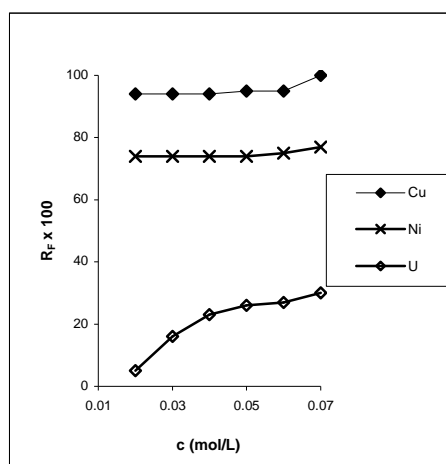
Calibration curves for U(VI), Cu(II) and Ni(II) determination were plotted using spots area determined by two methods, for chromatographic system containing HDPDTP in o,m,p-xylene – MEK – DMF mixture as mobile phase.

Unknown concentration samples were collected from Roşia Montana (Alba), Baia Mare (Maramureş) and Ştei (Bihor) mining exploitations.

## **RESULTS AND DISCUSSION**

The study of the chromatographic behavior of U(VI), Cu(II) and Ni(II) on silica gel H using HDPDTP as complexing agent in organic mobile phase show that  $R_F$  values depend on the HDPDTP concentration. From Figure 1 it can be observed the

increasing of the retention factor until almost constant value with the increase of complexing agent concentration especially for U(VI).

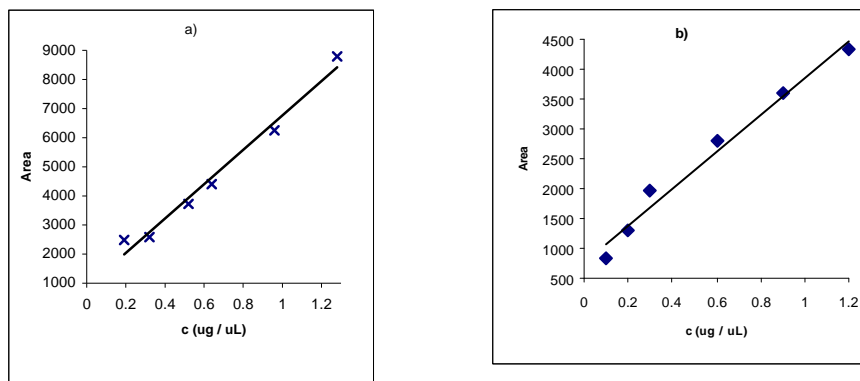


**Figure 1.** The influence of the HDPDTP concentration in mobile phase upon the  $R_F$  values of the metal ions studied

It can be seen also that the separation of U(VI) from Cu(II) – Ni(II) and the separation of Cu(II) – Ni(II) from each other can be achieved in all range of concentration investigated, 0.02 – 0.07M HDPDTP. The best separation with well defined zones is obtained with 0.05M HDPDTP in a mixture of o,m,p-xylene – MEK - DMF (16 : 2 : 1, v/v). In consequence this mobile phase system was used for TLC quantitative determination of U(VI), Cu(II) and Ni(II).

The calibration curve for Cu(II) and Ni(II) determination were obtained by two methods: a) densitometric determination using DESAGA CD 60 densitometer at 505 nm for Cu(II) and 600 nm for Ni(II), and b) scanning TLC plates with a classic scanner linked to a computer. UTHSCSA Image Tool PC based software was used for area determination. Detection limits were determined using the software Statistical Method in Analytical Chemistry [31]. In both cases the shape of the curve is similar.

Figures 2a and 2b show the calibration curves for Cu(II) and Ni(II), respectively.



**Figure 2.** Calibration curve for the determination of: a) Cu(II), b) Ni(II); Stationary phase: silica gel H; mobile phase: o,m,p-xylene – MEK – DMF (16 : 2 : 1, v/v) with HDPDTP 0.05 M

Good linearity is obtained in the concentration range 0.20 – 1.28  $\mu\text{g}/\mu\text{L}$  for Cu(II) and 0.3 – 1.2  $\mu\text{g}/\mu\text{L}$  for Ni(II). The statistic parameters a (intercept), b (slope of the regression lines,  $y = ax + b$ ), and r (regression factor) are included. The regression factor, detection limit (LD) and quantitative limit (QL) are presented in Table 1.

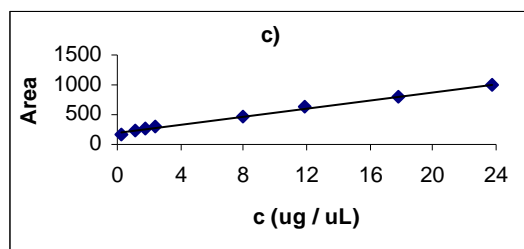
**Table 1**

Regression factor, DL and QL values for Cu(II) and Ni(II)

Cation	Method	r	LD ( $\mu\text{g}/\mu\text{L}$ )	LQ ( $\mu\text{g}/\mu\text{L}$ )
Cu(II)	Photodensitometry	0.9931	0.132	0.244
	UTHSCSA Image Tool software	0.9872	0.176	0.322
Ni(II)	Photodensitometry	0.9864	0.170	0.310
	UTHSCSA Image Tool software	0.9929	0.118	0.215

The calibration curve for U(VI) was obtained only by scanning TLC plates with classic scanner, because of the strong signal noise. Figure 3 show that good linearity is obtained in the concentration range 0.24 – 24  $\mu\text{g} / \mu\text{L}$  and r is 0.9973. DL and QL determined by SMAC software are 1.102 and 2.130 respectively.

Calibration curves (Fig. 1-3) were used for the determination of studied metal ions from mining exploitation waters and the results obtained are presented in Table 2. Cu(II), Ni(II) and U(VI) were also determined by other methods: Flame Atomic Absorbion Spectrometry (FAAS) (Cu(II), Ni(II)) and spectrophotometric method (U(VI)) [32-34].



**Figure 3.** Calibration curve for U(VI); Stationary phase: silica gel H; mobile phase: o,m,p-xylene – MEC – DMF (16 : 2 : 1, v/v) with HDPDTP 0.05 M

**Table 2**

Analysis of Cu(II), Ni(II) and U(VI) content from water samples

Observed cation	Sample origin	Method/Found concentration (mg / L)		
		FAAS	TLC	e <sub>r</sub> (%)
Cu(II)	Ore processing waste water (Baia Mare)	1.50	1.49	-0.67
Ni(II)		2.09	2.12	+1.44
U(VI)	Natural running mine water (Băița)	Spectrophot	TLC	e <sub>r</sub> (%)
		1.50	1.48	-1.33

It can be seen a good agreement between TLC data and those obtained by FAAS and spectrophotometric method. Determination by TLC analysis requires preconcentration of the sample, but TLC method has some advantages: short time of analysis, inexpensive and easy getting equipment, rapid qualitative results with no necessary treatment of the sample.

### CONCLUSIONS

It was found that U(VI), Cu(II) and Ni(II) can be separated by TLC using HDPDTP as complexing agent in the mobile phase, a mixture of organic solvents: o,m,p-xylene – MEK – DMF (16 : 2 : 1, v/v). The mobile phase containing 0.05 M HDPDTP was chosen for TLC quantitative determination of the studied metal ions. Calibration curves plotted for Cu(II), Ni(II) and U(VI) were used for the analysis of unknown samples collected from waste water (Cu(II), Ni(II)) and mine water (U(VI)). The results obtained by TLC method are in a good agreement with those obtained by FAAS and spectrophotometric method.

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