AN INVESTIGATION ON THE EXTRACTION CONCENTRATION OF MICROELEMENTS FROM AQUEOUS SOLUTION FOR ATOM-ABSORBTION ANALYSIS

*Igor KOBASA[1], Vasyl BILOGOLOVKA[1], Mariya VOROBETS[1], Oxana PANIMARCHUK[2]

[1] *Yury Fedkovych National University of Chernivtsi, Ukraine, i.kobasa@chnu.edu.ua*
[2] *Bukovynian State Medical University, Ukraine, imk-11@hotmail.com*
*Corresponding author
Received November 27th 2014, accepted December 29th 2014

Abstract: *Some sodium diethyldithiocarbamate and 8-oxyquinoline based mixtures were tested as potential extractant to concentrate solutions containing ions of Cu^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+} while preparing the samples for atom-absorption analysis. The mixture of butylacetate/sodium diethyldithiocarbamate has shown the best performance. The method of the metal ions determination that combines the sample concentration using this extractant followed by the flame atom-absorption spectroscopy provides high sensitivity and selectivity outperforming characteristics as compared to the classical method of evaporation the concentration of samples.*

Keywords: *extraction, heavy metal ions, atom-absorption analysis, natural waters*

1. Introduction

The atom-absorption spectroscopy method (AAS) is a powerful analytical tool used widely in investigations of various environmental objects: soils, natural waters and wastewaters, air, biomaterials, foodstuff and raw materials.

A number of macro- and microelements can be successfully identified using this method along with proper chemical pre-processing of the samples.

Since regular contents of some microelements in the natural water samples and some other probes can be under the AAS sensitivity threshold, the preliminary concentrating of the probes is required prior to AAS measurements.

In case of heavy metals, such concentrating can be performed through extraction by dithiocarbamates, 8-oxyquinoline, dithi-

zone and some other [1, 2] while chloroform, carbon tetrachloride, a mixture of the polar oxygen-containing (spirits, ketones) or non-polar oxygen-free (benzene) compounds can be used as the organic solvents [3].

However, these organic compounds are hardly combustible and can produce side colorization of the flame hindering accurate AAS determination of the ingredients. Besides, some of them release toxic products of incomplete combustion [4].

This paper reports the results of investigation of performance of new extraction mixtures based on the butyl and amyl esters of acetic acid as extractants used for the AAS preconcentrating of the heavy metals compounds from the probes taken from natural waters.

2. Materials and methods

The following mixtures were used as extractants for the heavy metals ions: butylacetate/sodium diethyldithiocarbamate; amylacetate/sodium diethyldithiocarbamate; butylacetate/8-oxyquinoline; amylacetate/8-oxyquinoline. The 10 % solution of sodium diethyldithiocarbamate prepared on deionized water and 0.01 M solution of 8-oxyquinoline prepared on the heavy metals-free butylacetate or amilacetate [5] were used throughout all experiments as components for the working mixtures. According to [6], all extractants were used in excessive amounts (this does not effect the extraction degree), then the volatile organic compounds were distilled off and the heavy metals contents were analyzed in the distillation residue by AAS method. Aqueous solutions of some heavy metals (Cu^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+}) with concentrations close to the usual values occurring in natural water objects were used as model samples.

All solutions were prepared using deionized water with specific resistance 15 MOhm or above. pH levels were adjusted by adding some amounts of metals-free HCl or NH_4OH. All pH measurements were performed by pH-meter pH-150 equipped with the glass electrode ECL-47-07 and silver-chlorine reference electrode EVL-1M. All extraction processes were carried out according to the method [7] and the flame atom absorption spectrometer KAS-120-M1 was involved in the direct determination of metal ions concentrations.

3. Results and discussion

The atom absorption spectra of the pure extractants combustion products were investigated preliminary using the deionized water as the reference. The results of this investigation are shown in Fig. 1.
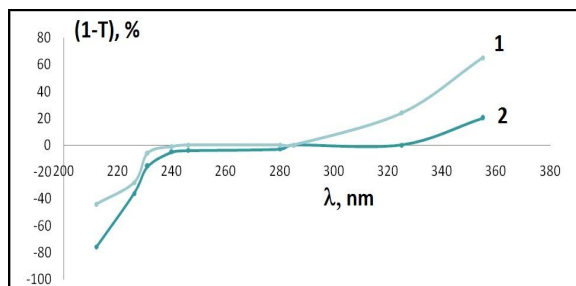

Fig. 1. Light absorbance for combustion products of amylacetate (1) and butylacetate (2).

As seen from Fig. 1, light absorbance of the butylacetate and amylacetate combustion products within the range 200-240 nm is lower than that of water. Then both light absorbance values remain close within 240-320 nm. The former light absorbance becomes positive only after 320 nm. This unfavorable situation impedes accurate determination of AAS using water as the reference. However, pure extractants still can be used as reference solutions in case of the heavy metals ions contents analysis.

There were two experimental series performed in the framework of this investigation. Free metals ions were analyzed within one series while their chelate complexes were analyzed within the other. It was found that AAS of both series were quite close and lie within the experimental errors. Besides, an influence of pH on the extraction degree of the ions Cu^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+}, Cr^{3+} has also been investigated (Figs 2-8). As seen from Fig. 2, the highest (almost 100 %) extraction degree can be reached for the ions Pb^{2+} within quite a wide range of pH (2-9) for the system sodium diethyldithiocarbamate/butylacetate (curve 1) while only about 50 % of Pb^{2+} ions can be extracted out by the mixture sodium diethyldithiocarbamate/amylacetate within the pH range 2-5 (curve 2). The extraction activity of the mixtures amylacetate/8-oxyquinoline and butylacetate/8-oxyquinoline (curves 4 and 3) within the range of pH 6-8 is lower.
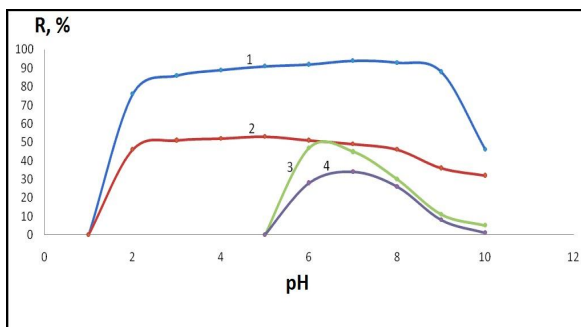
Fig.2. An influence of pH on the Pb^{2+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline (4).
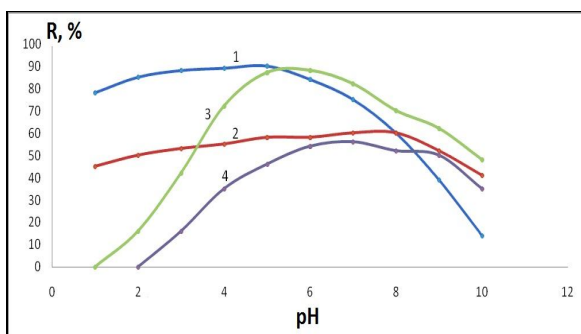

Fig.3. An influence of pH on the Cu^{2+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline.

Details of extraction of Cu^{2+} ions are shown in Fig. 3. It is seen that the pattern of both curves for the sodium diethyldithiocarbamate containing system is similar to the previous case while the degree of extraction for the 8-oxyquinoline containing systems is significantly higher and reaches 80 % for the system butyl acetate/8-oxyquinoline (see curve 3). The pH range of effective extraction is quite wide (2-6) for all the Cu^{2+} containing systems.

Details of extraction of Ni^{2+} ions are shown in Fig. 4. The range of effective extraction (about 90 %) by the mixture sodium diethyldithiocarbamate/butylacetate is also quite wide (see curve 1). The sodium diethyldithiocarbamate/amylacetate mix-

ture provides only 55 % efficiency of extraction within the same range of pH. Low solubility of the Ni^{2+}/8-oxyquinoline chelates causes very low efficiency of the corresponding systems (see curves 3 and 4).
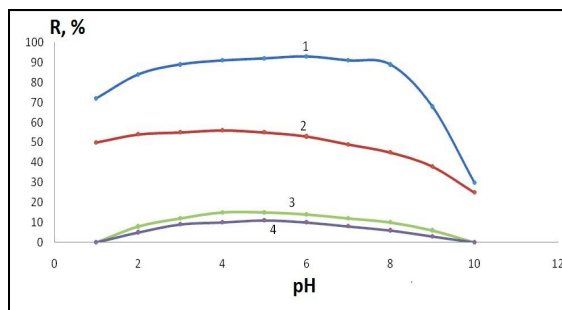

Fig.4. An influence of pH on the Ni^{2+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline.

Fig.5. An influence of pH on the Cd^{2+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline.

The highest extraction degrees for the Cd^{2+}-systems can be reached for the system sodium diethyldithiocarbamate/butylacetate (see Fig. 5, curve 1). This extractant remains active within very wide range of pH (1.8-9.0). Similarly to the above case, the amylacetate/sodium diethyldithiocarbamate mixture ensures extraction degree about 50 % within the same pH range (curve 2) while the 8-oxyquinoline based systems are inactive (curves 3 and 4).

Fig.6. An influence of pH on the Zn^{2+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline.
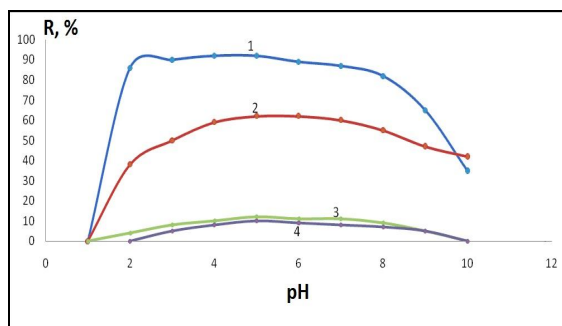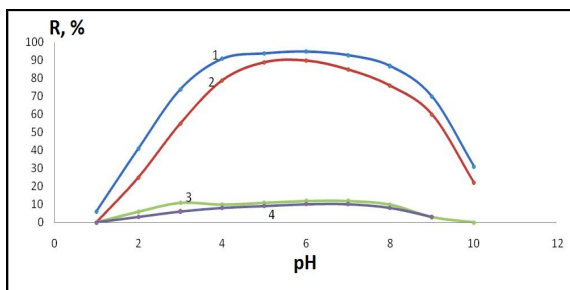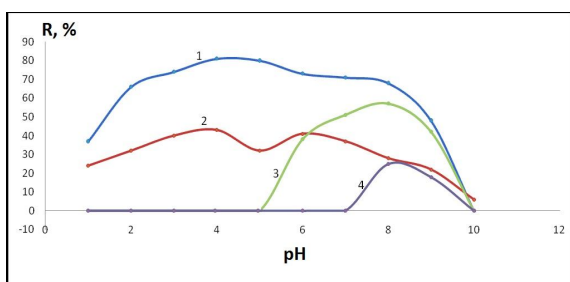

Fig. 7. An influence of pH on the Co^{2+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline.

Both sodium diethyldithiocarbamate mixtures ensure almost complete extraction of Zn^{2+} under pH 3.5-8.5 (with butylacetate) or 4.5-7.5 (with amylacetate) (see Fig. 7, curves 1 and 2). Both 8-oxyquinoline based systems in this case are also inactive (curves 3 and 4).

The extraction degree of ions Co^{2+} by the mixture sodium diethyldithiocarbamate/butylacetate within the pH range 1.5-8.0 is about 80 % (see Fig. 8, curve 1) and by the mixture sodium diethyldithiocarbamate/amyacetate – about 40 % (same pH range, see curve 2). The extraction degrees by the 8-oxyquinoline systems are also quite fair: 60 % for the system butylacetate/8-oxyquinoline (cobalt oxynate is formed within pH values 6.5-9.5, curve 3) and 30 % for the system amylacetate/8-

oxyquinoline, where the oxynate copound is formed within pH values 7.8-9.0 (curve 4).

Fig.8. An influence of pH on the Fe^{3+} extraction degree for the mixture of butylacetate/sodium diethyldithiocarbamate (1); amylacetate/sodium diethyldithiocarbamate (2); butylacetate/8-oxyquinoline (3); amylacetate/8-oxyquinoline.
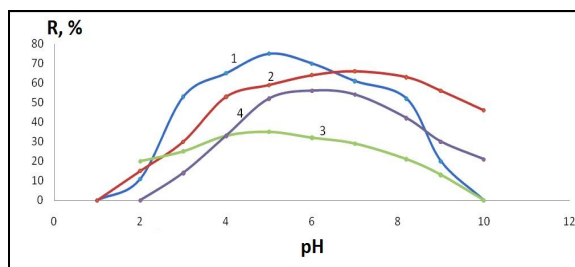
The data related to extraction of Fe^{3+} ions are shown in Fig. 8. It is seen that about 40 % of the ions can be extracted by sodium diethyldithiocarbamate/butylacetate mixture for the range of pH 1.5-5.0 while the mixture sodium diethyldithiocarbamate/amylacetate ensures extraction of about 40 % of Fe^{3+} only (pH = 3.0-7.0, see curves 1 and 2). The 8-oxyquinoline based systems exhibit higher extraction degrees: 70 % for the system butylacetate/8-oxyquinoline (pH = 5.0-8.5, see curve 3) and 55 % for the system amylacetate/8-oxyquinoline (weakly acid media, see curve 4). No tangible extraction activity has been determined for all the four mixtures under investigation and ions Cr^{3+} and Mn^{2+}. Therefore, the highest extraction degrees were found for the sodium diethyldithiocarbamate based systems. The heavy metals ions chelates are formed in such systems and then dissolve in butylacetate or amylacetate. It should also be noted that the chelates solubility in butylacetate is better than in amylacetate. Besides, butylacetate also facilitates further atomization and improves light absorbance (1.3-3.1 times depending on the metal nature).

Igor KOBASA, Vasyl BILOGOLOVKA, Mariya VOROBETS, Oxana PANIMARCHUK, *An investigation of the extraction concentrating of microelements from aqueous solution for atom-absorbtion analysis* ,Volume XIII, Issue 4 – 2014, pag. 342 – 348

345

The best extraction degrees can be achieved for the weakly acid (pH=4.0-6.0) solutions (see Figs 2-8). The above results were applied at the next stage when a series of experiments was carried out in order to build the calibrating lines for all the metal ions. The butylacetate/sodium diethyldithiocarbamate was used as the extracting while the same system without any heavy metals was used as the reference solutions. All experimental results were compared with the similar data obtained using the classical method of concentrating by evaporation of the samples. The concentrating coefficients were similar for the extraction and evaporation methods. The "extraction" calibrating lines are represented in Figs 9 and 10. They all are close to linear meaning that the experimental method was correct and adequate. The higher is the line slope, the better is the sensitivity of determination related to the corresponding metal. In this context we can state the this method exhibits the highest sensitivity towards ions Zn^{2+} and Cd^{2+} while the sensitivity of determination of Pb^{2+} is the worst. The sensitivities of determination of Co^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} are very close.
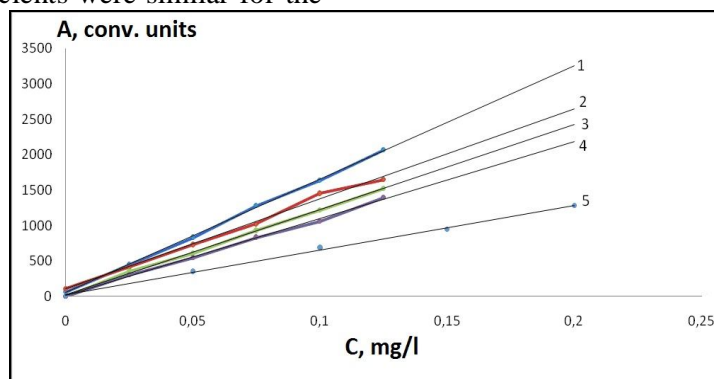

Fig. 9. Calibrating curves for the ions Fe^{2+} (1), Ni^{2+} (2), Co^{2+} (3), Cu^{2+} (4) and Pb^{2+} (5) after their extraction by the mixture butylactate/sodium diethyldithiocarbamate.
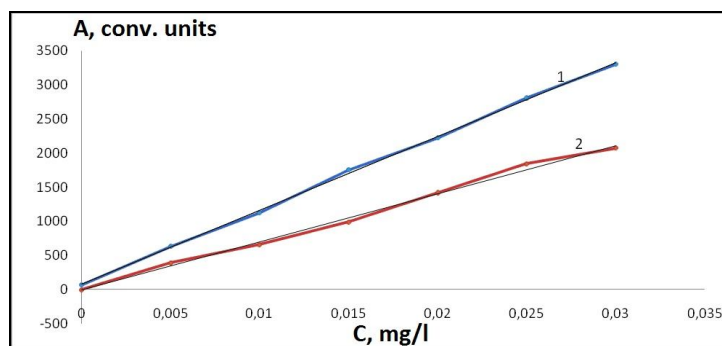
Fig. 10. Calibrating curves for the ions Zn^{2+} (1) and Cd^{2+} (2) after their extraction by the mixture butylactate/sodium diethyldithiocarbamate.

Then the calibrating lines were applied to determine the ions concentrations in the model solutions and then the results of the "extraction" analyses were compared to the results of evaporation" analyses. All related data and results of their statistical analysis are shown in Table 1.

Igor KOBASA, Vasyl BILOGOLOVKA, Mariya VOROBETS, Oxana PANIMARCHUK, *An investigation of the extraction concentrating of microelements from aqueous solution for atom-absorbtion analysis* ,Volume XIII, Issue 4 – 2014, pag. 342 – 348

<div align="right">**Table 1**</div>

Results of analysis of the model solutions

Metal	Tested concen-tration *mg/l*	Found concentration, *mg/l*		Statistical dispersion, S^2		Confidence interval limits $\mu = \bar{x} \pm \Delta\bar{x}$	
		Evapora-tion	Extraction	Evapora-tion	Extraction	Evapora-tion	Extraction
Co^{2+}	0.065	0.065 0.063 0.060 0.061	0.064 0.069 0.063 0.057	$4.917 \cdot 10^{-6}$	$2.425 \cdot 10^{-5}$	$0.0625 \pm 7.823 \cdot 10^{-6}$	$0.066 \pm 3.858 \cdot 10^{-7}$
	0.125	0.112 0.115 0.054 0.104	0.120 0.11 0.10 0.12	$5.00 \cdot 10^{-5}$	$1.076 \cdot 10^{-4}$	$0.096 \pm 7.955 \cdot 10^{-5}$	$0.112 \pm 1.712 \cdot 10^{-4}$
Fe^{3+}	0.065	0.048 0.053 0.066 0.077	0.056 0.062 0.065 0.059	$1.7 \cdot 10^{-4}$	$1.500 \cdot 10^{-5}$	$0.061 \pm 2.705 \cdot 10^{-4}$	$0.060 \pm 2.38 \cdot 10^{-5}$
	0.125	0.122 - 0.162 0.123	0.11 0.09 0.12 0.11	$3.933 \cdot 10^{-4}$	$1.87 \cdot 10^{-4}$	$0.130 \pm 6.257 \cdot 10^{-4}$	$0.107 \pm 2.975 \cdot 10^{-4}$
Pb^{2+}	0.125	0.124 0.120 0.134 0.121	0.118 0.119 1.122 0.125	$4.090 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	$0.124 \pm 6.507 \cdot 10^{-5}$	$0.121 \pm 1.591 \cdot 10^{-5}$
	0.250	0.245 - - 0.268	- 0.250 0.249 0.249	$1.806 \cdot 10^{-4}$	$1.250 \cdot 10^{-5}$	$0.0256 \pm 2.865 \cdot 10^{-4}$	$0.249 \pm 1.989 \cdot 10^{-5}$
Cu^{2+}	0.065	0.060 0.031 0.073 0.064	0.059 0.055 0.048 0.064	$3.3 \cdot 10^{-4}$	$4.56 \cdot 10^{-5}$	$0.57 \pm 5.25 \cdot 10^{-4}$	$0.56 \pm 1.453 \cdot 10^{-4}$
	0.125	0.146 0.142 - 0.118	0.110 0.121 0.115 0.125	$1.795 \cdot 10^{-4}$	$4.360 \cdot 10^{-5}$	$0.127 \pm 2.856 \cdot 10^{-4}$	$0.117 \pm 6.33 \cdot 10^{-5}$
Ni^{2+}	0.065	0.061 - 0.064 0.057	0.044 0.057 0.060 0.068	$8.667 \cdot 10^{-6}$	$9.963 \cdot 10^{-9}$	$0.060 \pm 1.379 \cdot 10^{-5}$	$0.057 \pm 1.585 \cdot 10^{-4}$
	0.125	0.116 0.119 0.120 0.121	0.125 0.123 0.118 0.120	$4.667 \cdot 10^{-6}$	$9.667 \cdot 10^{-6}$	$0.119 \pm 7.425 \cdot 10^{-6}$	$0.120 \pm 1.538 \cdot 10^{-5}$
Zn^{2+}	0.013	0.024 0.013 0.021 0.02	0.0125 0.011 0.013 0.0125	$4.823 \cdot 10^{-5}$	$7.507 \cdot 10^{-7}$	$0.016 \pm 7.673 \cdot 10^{-5}$	$0.012 \pm 1.194 \cdot 10^{-6}$
	0.025	0.039 - - 0.020	0.026 0.023 0.025 0.0265	$1.805 \cdot 10^{-4}$	$2.0 \cdot 10^{-6}$	$0.029 \pm 2.87 \cdot 10^{-4}$	$0.024 \pm 3.182 \cdot 10^{-6}$

As seen from Table 1, the extraction method ensured lower deviation and better sensitivity for the majority of samples of Cu, Fe, Pb, Zn. Therefore, we can conclude that the extraction method of concentrating the traces of Co, Cu, Fe, Ni, Cd, Zn, Pb using butylacetate/sodium diethyldithiocarbamate extractant and AAS determination can ensure better concentrating degree, shorter processing time, higher selectivity and sensitivity (up to 1.3-3.1 depending on the metal nature).

4. Conclusion

The mixture of butylacetate and sodium diethyldithiocarbamate ensures the highest concentrating degree for the heavy metals ions extraction from aqueous solutions. Almost complete extraction of the metal ions can be reached within the pH range 4-6.

This result is based on rise in the AAS analytical signal intensity (1.3-3.1 times) caused by atomization of the chelate complexes formed by the heavy metals ions and butylacetate or amylacetate molecules.

The extraction method also ensures less laborious and more sensitive and selective analysis than the classical evaporation method. Besides, lesser number of the treatment stages in the method of extraction lowers chances of unwilled and uncontrollable probes pollution while processing.

5. References

[1]. KORENMAN I. Extraction in organic compounds analysis. Khimiya. Moscow. 392 p. (1977).
[2]. GONCHAROVA N. et al. Atom-absorption determination of metals-microelements in natural and industrial waters. *Chem. and Tech. of Water*. **6**. 152-157. (1984).
[3]. GRANZHAN A.. KUNUK G.. CHARYKOV A. Extraction atom-absorption determination of the heavy metals ions. *J. Analyt. Chem*. **4**. 711-717. (1991).
[4]. NOVIKOV Yu.. LASTOCHKINA K.. BOLDINA Z. Methods of the natural waters quality investigations. Medicine. Moscow. 181 p. (1990).
[5]. STARYI M. Extraction of chelates. Mir. Moscow. 392 p. (1966)
[6]. NOVIKOV M. Application of atom-absorption method of heavy metals analysis in natural objects. Khimiya. Moscow. 189 p. (1989).
[7]. KOBASA I. Atom-absorption method of determination of Selenium content in some raw materials and food. *J. Food and Environment Safety of the Suceava University*. 12. 233-239. (2013).

Igor KOBASA, Vasyl BILOGOLOVKA, Mariya VOROBETS, Oxana PANIMARCHUK, *An investigation of the extraction concentrating of microelements from aqueous solution for atom-absorbtion analysis* ,Volume XIII, Issue 4 – 2014, pag. 342 – 348

348