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**MICELLAR CLOUD POINT EXTRACTION IN THE SYSTEM:
LEAD (II) – DITHIZONE – OP-10*****Mozan Ali Amer Waheeb**

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Abstract. The presented data is about the application of the methodology based on the cloud point extraction for the selective determination of lead in liquids. For this aim it is proposed an extraction system dithizone – ethoxylated alkylphenol (OP-10) – NaOH. It allows to concentrate lead in the micellar phase of OP-10 without heating.

Key words: micellar cloud point extraction; heavy metals; lead; dithizone; nonionic surfactant.

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МИЦЕЛЛЯРНАЯ ЭКСТРАКЦИЯ НА ОСНОВЕ ТОЧКИ ПОМУТНЕНИЯ В СИСТЕМЕ: СВИНЕЦ (II) – ДИТИЗОН – ОП-10

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Аннотация. В работе представлены данные по методологии мицеллярной экстракции на основе точки помутнения для селективного определения свинца в растворах. Для данной цели выбрана экстракционная система: дитизон – оксиэтилированный алкилфенол (ОП-10) – NaOH, которая позволяет концентрировать свинец в мицеллярной фазе ОП-10 без нагревания.

Ключевые слова: мицеллярная экстракция на основе точки помутнения; тяжёлые металлы; дитизон; неионные ПАВ.

Determination of heavy metals in various objects is one of the actual problems of modern analytical chemistry. Lead is the priority pollutant among all of the heavy metals (limit of detectable concentration in the air – 0,003 mg/m³, in water – 0,03 mg/l, in the soil – 20,0 mg/kg) [1].

In this study the selective concentration of lead based on the cloud point extraction (CPE) is presented. It is well known, that cloud point extraction is one of the effective ways of selective extraction and concentration of lead. This method is based on the separation of a homogeneous surfactant solution into two isotropic phases: surfactant-rich phase of small volume composed mainly of surfactant with hydrophobic substance, which is distributed

throughout the volume until the phase separation, and aqueous phase containing surfactant with the concentration level less than critical concentration of micelle formation (CMC) with the residual amounts of not extracted substances (Fig. 1) [3, 4].

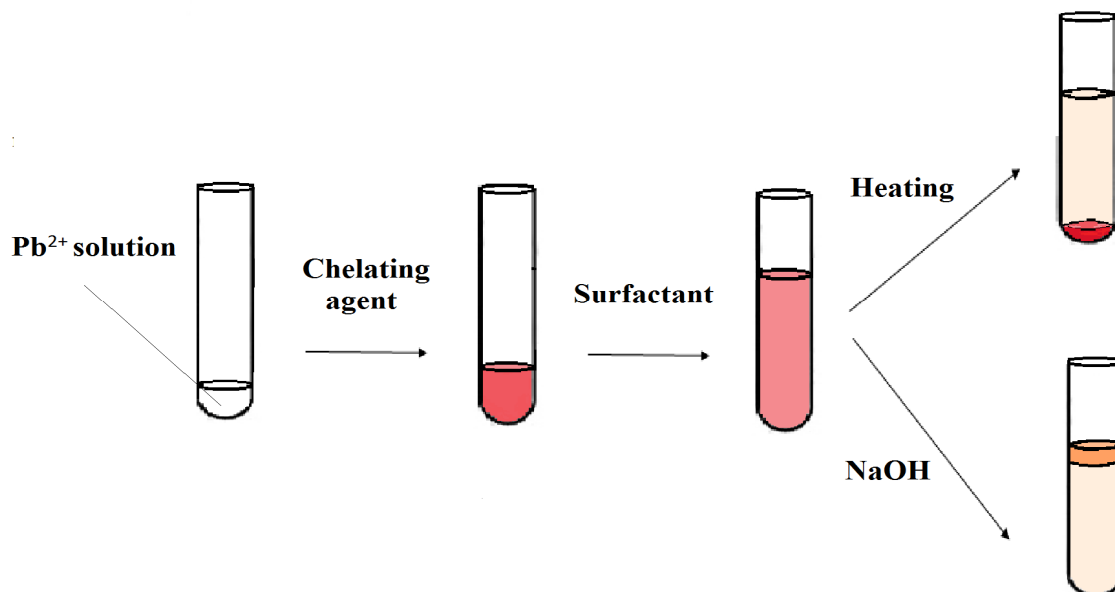


Fig. 1. Presentation of CPE process for lead preconcentration

It is known, there are different surfactants for CPE methodology. It was applied mostly nonionic surfactants, such as Triton X-114, Triton X-100, octanol, or PONPE (polynonylphenyl), also, in some cases, mixtures of nonionic and cationic/anionic surfactants: cetyltrimethylammonium bromide (CTAB), cetylpyridiniumchloride (CPC), benzyldimethyltetradecylammonium chloride (BDTAC) and sodium dodecyl sulfate (SDS), or only cationic surfactants (CTAB, and CPC) [5, 8].

According to available literature data, micellar extraction of metal ions can be carried out in the presence of a chelating agent or without it. Among various organic ligands used in CPE it has employed 1-(2-pyridylazo)-2-naphthol (PAN), 1-(2-thiazolyazo)-2-naphthol (TAN), 4-(2-pyridylazo)resorcinol (PAR), 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP), ammonium pyrrolidinedithiocarbamate (APDC), diethyldithiocarbamate (DDTC), 2-amino-

cyclopentene-1-dithiocarboxylic acid (ACDA), O,O-diethyldithiophosphate (DDTP), 8-hydroxyquinoline (oxine, 8-HQ), dithizone and others [8].

In such a way, we have proposed non-ionic surfactant – ethoxylated alkylphenol (OP-10) – as an alternative and accessible surfactant for micellar cloud point extraction of lead. Moreover, the determination of lead must also be considered by the selectivity, which is achieved using either selective reagent or method. One of the most selective reagent for lead is diphenylthiocarbazonate (dithizone). The dithizone complex with lead can be formed with different tautomeric forms of the reagent (Fig. 2) [2].

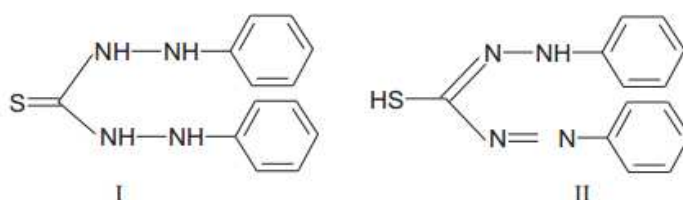


Fig. 2. Tautomeric forms of dithizone: ketone (I) and enol (II)

The complexation of lead with dithizone is depending on pH that varies from 7 to 10, according to [5]. Lead complexation is coming with dithizone form II, intensely colored in wine-red (Fig. 3).

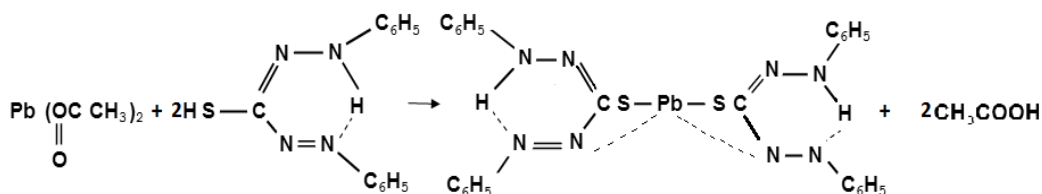


Fig. 3. Schematic reaction of complexation lead with dithizone (form II)

In this work we investigated the system: lead – dithizone – OP-10. It was compared two salts of lead as analyte solutions: lead acetate and lead nitrate. Furthermore it was varied the following parameters: concentration of lead salts

($1 \cdot 10^{-3} - 5 \cdot 10^{-5}$ mg/ml), concentration of dithizone ($1 \cdot 10^{-5} - 5 \cdot 10^{-5}$ mol/l), concentration of OP-10 (2-4 %), pH (3,5 – 10,8) and temperature (25 °C – 90 °C). The dithizone solution was prepared daily due to its instability. The color of dithizone complexes with lead independent of the chosen salt. The formation of lead dithizonate was proved by control of their electronic absorption spectra. The wavelengths of the pure reagent and its complex with lead ranged $\lambda = 490-493$ nm $\lambda = 501-505$ nm, respectively (Fig. 4). In the course of the experiment, results obtained were irreproducible, because of the reagent was oxidized [2].

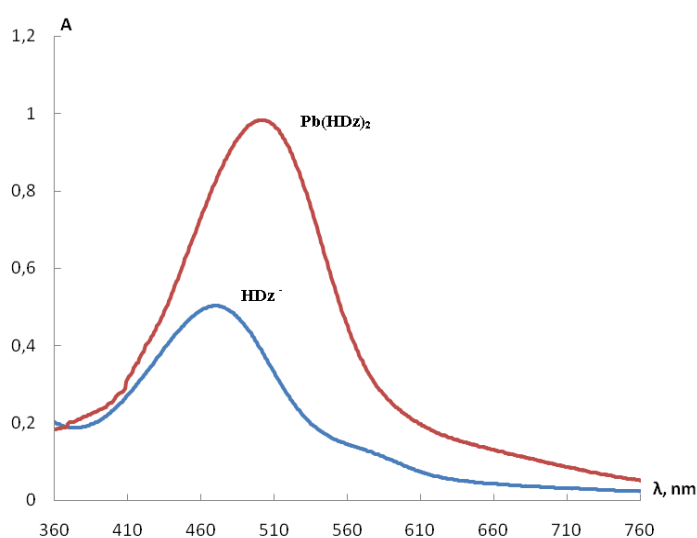


Fig. 4. Electronic absorption spectra of dithizone (HDz⁻) and lead dithizonat (Pb(HDz)₂), pH = 10,5 (borate buffer)

The purification procedure of dithizone was tested according to technique [10] for enhancing the reproducibility of the results. A new recrystallized reagent was used again in the experiments. Wherein, the reproducibility of the results has been not achieved. CPE was carried out in the first case by heating for 15 minutes at the temperature range 85-90 °C. The density of the micellar phase was above than the density of the solution. The separation of the layers at the bottom of the tube was observed. Micellar phase included dithizone complex with lead was colored in wine-red (pH = 10,8). In the second case, CPE conducted by adding the NaOH (concentration of alkali – 2,8

mol/l) (Fig. 1). In this case, the density of the micellar phase was lower than the solution density, and it was noted the separation on the top of the tube. In this mode, the dithizone complex with lead in micellar phase was destroyed. The color of the solution changed from wine-red to orange.

Hereby, the experimental results indicated the possibility of applying the system: dithizone – OP-10 for the selective concentration of lead by CPE. However, the usage of this system is impractical without additional dithizone stabilization.

СПИСОК ИСПОЛЬЗОВАННЫХ ИСТОЧНИКОВ

1. Brajter K., Slonawska K. Determination of lead in waters by AAS after preconcentration // *Water Research*. 1988. V. 22. Is. 11. P. 1413-1416.
2. Budesinsky B.W. Stability constants of some metal dithizonates // *Talanta*. 1973. V. 20. Is. 2. P. 228-232.
3. Citak D., Tuzen M. A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry // *Food and Chemical Toxicology*. 2010. № 48. P.1399-1404.
4. Gil R.A., Salonia J.A., Gásquez J.A., Olivieri A.C., Olsina R., Martinez L.D. Flow injection system for the on-line preconcentration of Pb by cloud point extraction coupled to USN– ICP OES // *Microchemical J.* 2010. № 95. P. 306-310.
5. Karel G. von Eschwege, Jannie C. Swarts. Chemical and electrochemical oxidation and reduction of dithizone, South Africa. *Polyhedron* 29 (2010). P. 1727-1733.
6. Mahmoud M.E., Osman M.M., Hafez O.F., Hegazi A.H., Elmelegy E. Removal and preconcentration of lead (II) and other heavy metals from water by alumina adsorbents developed by surface-adsorbed-dithizone // *Desalination*. 2010. № 251. P. 23-130.

7. Manzoori J.L., Karim-Nezhad G. Selective cloud point extraction and preconcentration of trace amounts of silver as a dithizone complex prior to flame atomic absorption spectrometric determination // *Analytica Chimica Acta*. 2003. № 484. P. 155-161.
8. Pytlakowska K., Kozik V., Dabioch M. Complex-forming organic ligands in cloud-point extraction of metal ions: A review // *Talanta*. 2013. № 110. P. 202-228.
9. Xioadong Wen, Qingwen Deng, Shoulian Ji, Shengchun Yang, Li Peng. Design of rapidly synergetic cloud point extraction of ultra-trace lead combined with flame atomic absorption spectrometry determination // *Microchemical J.* 2012. 100. P. 31-35.
10. GOST 18293-72. Potable water. Methods for determination of lead, zinc and silver. P. 100.