

## THE USE OF SULPHOPHTALEIN DYES IMMOBILIZED ON ANIONITE AB-17X8 TO DETERMINE THE CONTENTS OF Pb(II), Cu(II), Hg(II) AND Zn(II) IN LIQUID MEDIUM

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**Abstract.** The conditions of the immobilization of xylenol orange, methylthymol blue, pyrocatechol violet, and chromazurol S at the surface of AB-17×8 anionite were studied. The interaction of Cu(II), Pb(II), Zn(II), Hg(II) ions with obtained solid-phase reagents was investigated. The efficiency of the purification of apple juice with such natural adsorbent of Cherkasy deposits (Ukraine) as palygorskite was studied. The optimum conditions of the reactions, quantitative characteristics of the composition and the surface compound stability, the efficiency of the anion exchanger with the immobilized sulphophthalein dyes were determined.

**Keywords:** solid-phase spectrophotometric determination of metal ions, immobilized sulphophthalein dyes, fruit juices.

### 1. Introduction

New requirements for analytical control of quality and safety of fruit juices have evolved due to the specifics that emerged in the modern domestic food market. A significant share of the market belongs to small producers; consumer is offered a great variety of names and brands of the same drink. More and more often consumers are doing their choice based on environmental considerations and nutritional value of food products. In line with global trends, the outlook for the food market should be associated with the production of organic foods. These are

products that consist of environmentally friendly components, obtained without the use of chemical fertilizers, pesticides, hormone supplements, etc., and contain much less contaminants than conventional products resulting from the technologies of large producers. Whereas previously the quality control of foods and fruit juices in particular implied determination of impurities at MAC level, the new conditions necessitate analytical methods for the determination of impurities at much lower level. This will compare the actual quality of different samples of the same type of products and the control of impurities in the ecologically clean agricultural products. Given the large number of producers and the realities of available national laboratories that monitor the quality of the foodstuffs, the necessary analytical methods should be as cheap as possible, simple and focused on the most common equipment.

The determination of metals, toxins and some other impurities uses commonly the methods of molecular and atomic absorption spectrophotometry. The ability to determine low concentrations is provided by preliminary concentration. The effective concentration is provided by solid-phase extraction, which is widely used to develop new methods for the determination of trace metals. However, the use of conventional sorbents requires either the extraction of the analyte from the solid-phase concentrate or the use of special spectral methods to register the signal of the analytical form at the sorbent surface. Direct photometry of the solid concentrate becomes possible with the use of transparent solid-phase extractants such as polymeric ion-exchange resin with chelating groups [1, 2]. Easy production of transparent solid extractants by the immobilization of some analytical reagents in conventional ion exchangers was reported; these were applied for the determination of toxic metals in the environmental objects [3-6].

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A promising approach, in our opinion, is obtaining a transparent solid-phase concentrate for the determination of microamounts of toxic metals in foodstuffs, in particular apple juice. This will enable concentrating analytes at the site of sampling, measuring of the light absorption of the analytical forms directly in the ion-exchanger phase, removing the analyte recovery stage from the extracts and related losses or pollutions, and reducing the duration and labor complexity of the analysis.

The development of techniques of the determination of toxic metals by producing transparent solid-phase extractants by the immobilization of analytical reagents on ion exchangers is of current interest for the analytical quality control and safety inspection of fruit juices. Due to the lack of the data in the literature, determination of metal ions in fruit juices purified with palygorskite using new solid-phase reagents was the purpose of this work.

## 2. Experimental

### 2.1. Reagents

The stock 0.1 M solutions of Cu(II), Zn(II), Pb(II), Hg(II) salts were prepared by dissolving weighed amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Zn in 0.1 M  $\text{H}_2\text{SO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Hg}(\text{NO}_3)_2 \cdot 0.5 \text{H}_2\text{O}$  in 0.1 M  $\text{HNO}_3$ .

The standardization of obtained salt solutions was performed by iodometric (Cu), complexometric (Zn), (Pb), and mercurimetric (Hg) methods [7].

We investigated metallochromic indicators xylenol orange (XO), pyrocatechol violet (PCV), chromazurol S (CAS), SPADNS (Chemapol), and methylthymol blue (MTB).

Stock 1.0 M solutions of nitric and hydrochloric acid and 0.2 M solution of sulphuric acid were prepared by the dilution of concentrated solutions.

The working solutions were prepared by the dilution of the stock solutions before the experiment.

### 2.2. Techniques

Anion exchanger AB-17×8 (A-Cl) of 0.25–0.50 mm fraction was prepared according to the technique in [7], namely 10 g of A was soaked in the saturated NaCl solution and left for a day. The prepared matrix was modified by the aqueous solution of the respective metallochromic indicator as follows: 0.1 g of the indicator was dissolved in 150 cm<sup>3</sup> of water, and 10 g of air-dry anion exchanger (A-Cl) was added to the obtained solution and stirred for 1 hr. The solid phase was filtered,

washed with water, and dried at room temperature. Obtained solid-phase reagents ( $\overline{\text{MTB}}$ ,  $\overline{\text{XO}}$ ,  $\overline{\text{PCV}}$ ,  $\overline{\text{CAS}}$ ) were transparent colored granules with good transmission of light.

The standardization of anion exchangers with immobilized sulphophthalein dyes was not performed as they were synthesized from the commercial anion exchangers and dyes, and their composition is determined by the manufacturer standards. This assumption later proved permissible as the investigation of chemical-analytical properties of anion exchangers with immobilized dyes showed for different batches of AB and dyes that the quantitative characteristics of sorption and complexation properties of the immobilized reagents remained unchanged.

The preparation of the solid sample for photometry consisted of forming the light-absorbing layer of the concentrate that is uniformly distributed in the cuvette. The measurements used quartz cuvettes. The concentrate was transferred by a pipette to a cuvette which was first filled with water while another cuvette was similarly filled with AB-17×8-Cl or AB-17×8-indicator of the same grain size. The light absorption of the analyzed samples was measured after achieving the densest possible packing of the granules in the cuvette. The solutions were agitated by a magnetic stirrer.

#### *Preparation of the experimental samples.*

The purification and clarification of apple juice were performed as follows: freshly-squeezed apple juice was treated with palygorskite fraction of 3.0–2.0 mm using static method with continuous stirring and palygorskite to juice ratio of 1:30 for 30–40 min at 343 K.

The destruction of juice was performed as follows: 25 cm<sup>3</sup> of apple juice was placed into 150 cm<sup>3</sup> heat-resistant flask, and 25 cm<sup>3</sup> concentrated  $\text{HNO}_3$  (66.97 %) was added. Standard additions of the solutions of the salts of the investigated metals were added to some of the batches. Then the mixtures underwent ultrasound bath treatment for 90 min. Obtained destructs were transferred to heat-resistant beakers by washing the flasks with small portions of water, and evaporated to wet salts. The latter were dissolved in 10 cm<sup>3</sup> 1 M HCl, transferred to 100 cm<sup>3</sup> volumetric flasks and filled with water to the mark.

*Determination of Cu(II), Zn(II), Pb(II), Hg(II) content using developed techniques [7-9].*

*Technique of the photometric determination of Cu(II).* The graduated 50 cm<sup>3</sup> beaker was filled with 10 cm<sup>3</sup> solution of juice destruct, 1 cm<sup>3</sup> 10<sup>-3</sup> M aqueous SPADNS, 1 cm<sup>3</sup> 10<sup>-3</sup> M sodium fluoride solution for the bonding of Fe(III) ions in a colorless complex, ~20 cm<sup>3</sup> distilled water, and creating pH ~6.8 with crystalline

methenamine. Then the mixture was transferred to 25 cm<sup>3</sup> volumetric flask, filled with distilled water to the mark, and stirred. Optical density was measured in a cuvette with  $l = 1$  cm at  $\lambda = 580$  nm against water.

*Technique of solid-phase spectrophotometric (SPS) determination of Zn(II).* The graduated 50 cm<sup>3</sup> flask was filled with 10 cm<sup>3</sup> solution of juice destruct, pH = 2 was created in the 50 cm<sup>3</sup> volume using 0.01 M HCl, the mixture was transferred to a graduated beaker, 0.3 g solid XO was added for concentrating of impurities that interfere with the determination of zinc, the mixture was agitated for 10 min by a magnetic stirrer, ultrasound was applied for 2 s, and then magnetic stirring was continued for another 10 min. The solid phase was removed by filtering. In the liquid phase, pH = 3 was achieved using crystalline methenamine. Then 0.3 g of solid-phase MTB was added for concentrating and determination of zinc, and stirring for 20 min by a magnetic stirrer was applied. Optical density of the solid phase was measured in a cuvette with  $l = 0.1$  cm at  $\lambda = 500$  nm against A-Cl.

*Technique of SPS determination of Pb (II).* The graduated 50 cm<sup>3</sup> flask was filled with 10 cm<sup>3</sup> solution of juice destruct and 1 cm<sup>3</sup> 10<sup>-3</sup> M sodium fluoride solution for the bonding of Fe(III) ions, pH = 2 was created using 0.01 M HCl, the mixture was transferred to a graduated beaker, 0.3 g solid PCV was added, and the mixture was stirred for 20 min by a magnetic stirrer. Optical density of the solid phase was measured in a cuvette with  $l = 0.1$  cm at  $\lambda = 640$  nm against A-Cl.

*Technique of SPS determination of Hg (II).* The graduated 50 cm<sup>3</sup> flask was filled with 10 cm<sup>3</sup> solution of juice destruct and 1 cm<sup>3</sup> 10<sup>-3</sup> M sodium fluoride solution for the bonding of Fe(III) ions. Then pH = 2 was created in the 50 cm<sup>3</sup> volume with 0.01 M HCl, the mixture was transferred to a graduated beaker, 0.3 g solid CAS was added, the mixture was stirred for 10 min by a magnetic stirrer, ultrasound was applied for 2 s, and then magnetic stirring continued for another 10 min. Optical density of the solid phase was measured in a cuvette with  $l = 0.1$  cm at  $\lambda = 580$  nm against A-Cl.

### 2.3. Measurement and result processing techniques

The sorption of XO, MTB, PCV, CAS and Cu(II), Zn(II), Pb(II), Hg(II) ions by the ionites with immobilized dyes was studied under static conditions by controlling the composition of the solution at the ionite by spectrophotometry (the absorption of the dye or the complex of the metal and the photometric reagent) [8, 9] and by polarography using standard technique.

The absorption of light by the products formed in the ion-exchanger phase was measured using solid-phase

spectrophotometry techniques as described in [10]. A cuvette with the 0.1 cm thickness of the absorbing layer is filled with the suspension of the ion exchanger in distilled water to achieve the densest possible packing of the sorbent grains. The transmission scale is set at 100 % using another cuvette with the ion exchanger without the dye.

Based on the results of the study of the sorption kinetics for various volumes (25, 50, 100, 300, 500, 800, 1000 cm<sup>3</sup>) and the ion exchanger mass, we prepared series of solutions with set concentration of metal salts and pH. The dependence of the recovery degree ( $R$ , %) on pH, sorption duration and solution volume were studied.

The sorption constants of the sulphophthalein dyes  $k$  were calculated as  $k = \frac{1}{b} a_{\max}$ , where  $b$  is the segment

cut-off by the line in the coordinates  $\frac{[C]}{a_i} - [C]$ , where  $[C]$

is the equilibrium concentration of the respective form of the dye;  $a_i$  is the content of the absorbed dye, mol/g [8-10];  $a_{\max}$  is the maximum sorption capacity (MSC) of the ion exchanger for the immobilized dyes, mol/g.

The recovery degree ( $R$ , %) of the dye by the ion exchanger was calculated as  $R = \frac{C_R^0 - [R^-]}{C_R^0} \cdot 100$ , where

$C_R^0$  is the total dye concentration, mol/l;  $[R^-]$  is the equilibrium concentration of the dye in the solution, mol/l.

The sorption constants of metal ions were similarly calculated by the linearization of their sorption isotherms. The recovery degree  $R$  and the distribution coefficient  $D$  (cm<sup>3</sup>/g) were calculated as:

$$R = \frac{C_M^0 - [M^{+i}]}{C_M^0} \cdot 100$$

$$D = \frac{RV}{(100 - R)} \cdot m$$

where  $C_M^0$  is the total metal ion concentration, mol/l;  $[M^{+i}]$  is the equilibrium concentration of metal ions in the solution, mol/l;  $V$  is the solution volume, l;  $m$  is the sorbent mass, g.

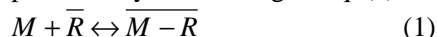
The composition, the stability of the metal-dye complexes, and the form of the ligand that is coordinated to the metal ions were determined by Bent-French method [11] using the technique of the shift of equilibrium. Series of solutions with  $C_M^0 = const$  and the increasing concentration of the immobilized ligand, and with the increasing concentration of metal ions and  $C_R^0 = const$  were prepared. Optical density of solid phases was measured using the technique in [12]. Dependences

$\lg \frac{A_i}{A_{\max} - A_i} - \lg[H_m R]$  (or  $\lg[M^{+i}]$ ) were plotted, and the

number of coordinated ligand molecules or metal ions was determined from  $tg\alpha$ .

The chemical species of metals in the solution at given pH value were determined from the stability constants of the metal hydroxocomplexes [13].

The sorption constant of metal equals the equilibrium constant of the reaction of metal ions with AB-immobilized sulphophthalein dyes according to Eq. (1):

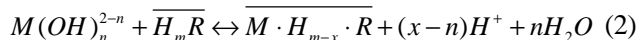


where  $M$  are metal ions in the solution ( $M^{z+}$  and its hydroxocomplexes),  $\overline{R}$  are immobilized dyes,  $\overline{M - R}$  are the metal complexes in the ion exchanger phase.

The number of protons of the ligand in the complexes was determined by preparing a series of solutions with the constant  $C_M^0$  and varying pH values, and using the ionite with the same concentration of the immobilized reagent  $C_R^0$ . The dependence of

$\lg \frac{A - A_R}{(A_{\max} - A)^2}$  on pH was plotted from the results of the

measurement of the optical density of the solid phase, and the slope of its dependence ( $tg\alpha$ ) was used to determine number of protons that the ligand loses during the formation of the complex in the reaction:



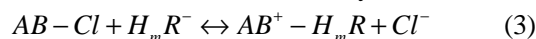
The coefficient  $n$  was found by the number of hydroxide groups in the metal species prevalent in the solution at the given pH value according to the stability constants of the metal hydroxocomplexes [13]. The coefficient  $m$ , *i.e.* the number of protons in the prevailing protolytic form of the immobilized dye at given pH value, was determined from the literature data on the protonation of the respective chelating groups in the chelate-forming ionites [14, 15] (incidentally, their protonation constants are close to the protonation constants of these groups in solution).

## 2.4. Equipment

Light absorption of the solutions was measured using CFC-3 photocolorimeter at the optimal wavelength ( $\lambda_{opt}$ ) relative to water or AB-17×8 anionite. The solution acidity was measured by I-160 ionometer using ESL-64 glass electrode as the indicator and EVL-1M3.1 Ag/AgCl as the reference electrode. Polarographic determination of metals was performed using the standard technique at PU-01 polarographer. Atomic-absorption determination of metal utilized the standard technique at C-115-M1 spectrometer. Atomic-absorption flameless determination of mercury was performed using Yulia-2 analyzer. Ultrasound sample preparation was performed using SELMI UP-1 [8].

## 3. Results and Discussion

The investigation of the conditions of the immobilization of XO, MTB, PCV, and CAS on AB-Cl established that the presence of sulphogroups in the sulphophthalein dye molecules leads to the sorption of their anion forms on the anionite surface by the reaction:



Functional-active groups of the dyes remain free for the formation of complexes. The use of AB in the chloride form was found to be optimal [8-10]. Ion exchangers obtained from  $OH^-$  form are less stable over time, and their chemical-analytical properties in some cases do not coincide with the properties of dyes in solution.

It was shown that the sorption of dyes depends on pH and the nature of the acid. The best results were obtained for the sulfuric acid solutions; the process is somewhat slower for the solutions of hydrochloric or nitric acids. It was determined that XO, MTB, PCV, and CAS are nearly fully (over 98 %) immobilized on AB in pH range of 2.5–5 [8]. The retention of dyes on AB weakens at  $pH < 2.5$ . Taking this into account, the immobilization of the analytical reagents on AB was performed in the range of  $3.0 < pH < 4.0$  to achieve high degree of the dye recovery and its one- or two-center bonding only by deprotonated sulphogroups by Eq. (3).

Literature data on basic-acidic properties of certain chelate-forming ion exchangers with included dye fragments and modified silica indicate some similarity of the conditions of the ionization of functional-active groups of the reagents in the solution and in solid phase [8].

This allows one to forecast chemical-analytical properties of the immobilized forms of the analytical reagents and to plan the conditions of their application for the concentration and the determination of metal ions.

It was determined that XO, MTB, PCV, and CAS are absorbed by AB-Cl during 1–2 h both from organic and aqueous solutions. A short ultrasound (US) treatment of the system of ion exchanger and sulphophthalein dye cuts the immobilization duration in half [8-10]. From the literature data on the effect of US on anionite we can confirm that faster immobilization of dyes onto AB-Cl after US treatment is achieved due to conformational changes in the AB structure and accelerated mass exchange in its pores.

The sorption of the investigated dyes onto ion exchangers is described by the isotherms of L and H types (Table 1) which indicates their high affinity to the ion exchanger.

Table 1

**Parameters of the sorption of sulphophthalein dyes onto AB-17'8-Cl  
(pH range 2.5–5;  $2.5 < \text{pH}_{\text{opt}} < 4.0$ ;  $P = 0.95$ ,  $n = 3$ )**

Reagent	Isotherm type	$a_{\text{max}} \cdot 10^{-5}$ , mol/g	$k \cdot 10^5$ , dm <sup>3</sup> /mol
PCV	H	1.70 ± 0.10	–
CAS	H	1.67 ± 0.11	–
XO	L	1.48 ± 0.12	3.01
MTB	L	1.32 ± 0.14	2.69

Table 2

**Optimal conditions for the interaction of metal ions with  $\overline{H_m R}$**

System	pH <sub>opt</sub> in the sorbent	pH <sub>opt</sub> in the solution	$\tau$ , h	$V_{\text{max}}$ , cm <sup>3</sup>
Pb(II)–XO	1-7	5-6	0.3	500
Fe (III)–XO	1-5	1-2	0.3	500
Hg (II)–XO	5-7	5-6	0.3	500
Cu (II)–XO	5-9	5-6	0.3 (US)	500
Cd (II)–XO	5-9	5-6	0.3 (US)	300
Zn (II)–XO	5-8	5-6	0.3 (US)	300
Pb(II)–PCV	1-7	5	0.3	500
Zn (II)–MTB	3-9	6	0.3 (US)	300
Hg (II)–CAS	1	5-6	0.3	500

Notes:  $m_s = 0.3$  g;  $V = 50.0$  cm<sup>3</sup>;  $I = 0.1$  M, 2 s ultrasound treatment accelerates the equilibrium; pH<sub>opt</sub> (1) is the optimal pH value for the liquid phase from which sorption concentration is performed, pH<sub>opt</sub> (2) is the optimal pH value for the complex formation in the solution

Table 3

**Main parameters of the sorption of metal ions onto  $\overline{XO}$ ,  $\overline{PCV}$ ,  $\overline{MTB}$ ,  $\overline{CAS}$**

Metal	Isotherm type	$a_{\text{max}} 10^{-5}$ , mol/g	$k \cdot 10^5$ , dm <sup>3</sup> /mol	$R$ , %	$D$ , 10 <sup>4</sup> , cm <sup>3</sup> /g	$R$ , %, after US	$D \cdot 10^4$ , cm <sup>3</sup> /g, US
Fe(III)	L	1.63	2.20	99.0	16.50	99.0	–
Pb(II)	H	1.45	0.71	94.0	2.61	94.0	–
Zn(II)	L	1.18	0.90	97.5	3.90	97.5	–
Hg(II)	H	1.55	–	85.0	0.94	90.0	1.50

Notes:  $n = 5$ ;  $P = 0.95$ ;  $m_s = 0.3$  g;  $a_{\text{max}} \text{ XO} \cong 1.48 \cdot 10^{-5}$  mol/g;  $a_{\text{max}} \text{ PCV} \cong 1.55 \cdot 10^{-5}$  mol/g;  $a_{\text{max}} \text{ MTB} \cong 1.32 \cdot 10^{-5}$  mol/g;  $a_{\text{max}} \text{ CAS} \cong 1.67 \cdot 10^{-5}$  mol/g

It was determined that the immobilization of XO, MTB, PCV, and CAS does not achieve the complete bonding of all ion-exchanging groups of AB into ion associates but the sorption of dyes onto anion exchanger reaches a steady value. All immobilization centers are bonded to the dye molecules according to Eq. (3).

The highest  $a_{\text{max}}$  values are observed for the dyes with the least branched structure (PCV, CAS) which allows their easy проникати through the hydrophobic AB matrix to the ion-exchanging groups. Immobilized dyes can be desorbed to the solution by 2–6 M solutions of strong acids and alkali. Ion exchangers with immobilized

XO, MTB, PCV, and CAS are well preserved under the layer of water during at least 6 months.

The recovery of Cu(II), Pb(II), Zn(II), and Hg(II) ions by ion exchangers with the immobilized dyes was then investigated as follows: study of the dependences of the recovery degree on pH, metal concentration, solution volume, duration of phase contact; determination of optimal sorption conditions; plotting sorption isotherms; determination of the composition of the complexes formed in the ionite phase and calculation of the stability constants; prediction of the selectivity of the sorption-spectrophotometric determination of ions.

Optimal conditions of the recovery of metal ions from aqueous solutions by AB-immobilized dyes under study are presented in Table 2.

The determination of the dependence of the recovery of metal ions on solution volume and sorbent mass showed that under the static conditions, the concentration is possible for  $V = 50.0\text{--}500.0\text{ cm}^3$  (Table 2) (for the sorbent charge of  $m_s \geq 0.3\text{ g}$ ).

The completeness of the metal ion recovery increases quickly with pH reaching maximum values for some metals (Pb, Hg, Fe(III)) already at  $\text{pH} = 1$  (Table 2). Further pH increase leads for all studied metal ions to the strengthening of the effect of the competing reaction of the formation of  $\text{M}(\text{OH})_n^{+z-n}$  and thus worsens the recovery. It should be noted that the pH range of the maximum yield of the complex in the ionite phase is substantially wider than the optimal pH range for the complex formation for the same reagents in the solution (Table 2, systems Pb(II)–XO, Zn(II)–MTB, Pb(II)–PCV, etc.).

The possibility of non-specific sorption of oxo- and hydroxo-anions by the anionite without dye was investigated for the easily hydrolyzing cations. Partial recovery of metal ions was observed under these conditions, Hg(II) – 13%; Cu(II) – 8%. It was established that metal sorption increases significantly in the transition from the original anionite to the immobilized-dye anionite, which agrees with the concept of the complex formation as the principal reason for the sorption of metal onto the anionite with immobilized dye.

The majority of the isotherms of the sorption of metal ions onto the anion exchanger with the immobilized dye belong to H- and L-types (Table 3).

Maximum capacity of metal ions for the ion exchangers with immobilized dyes is in all systems close to or practically coinciding with their capacity to the dyes (Table 3). This indicates the formation in the sorbent phase of the metal complexes of the equimolar composition.

The sorption equilibrium is established during 20 min of the phase contact for the majority of systems except easily hydrolyzing metal ions. There the equilibrium is reached slower and requires 3–12 h, which creates a challenge for the practical application of ion exchangers with immobilized dyes. The solution to this problem is the treatment with ultrasound. We have shown that the use of 2 s US treatment shortens the duration of the establishment of the sorption equilibrium in all systems to 20 min. The degree of the recovery of metal ions also increases by 5–26% [2, 8–10], which is explained by the conformation changes in the structure of the ion exchangers with immobilized dyes and by more active mass transfer in their pores. The increase of the recovery degree upon US treatment may be explained by the change of the local surrounding of the bonding centers whereby their larger numbers are available to metal ions,

*i.e.* the polymer chain acquires conformational mobility after US treatment. The data for the Hg(II)–CAS system are presented as an example.

Taking the above mentioned into account, we can presume that of the two possible schemes of the sorption of metal ions on the  $\overline{H_mR}$  surface, specific and non-specific, the former prevails due to the formation of complexes with the immobilized dyes.

The comparison of the ion exchangers with the immobilized dyes on the efficiency of the recovery of metal ions and on the maximum capacity determines the boundaries of their use. It was established that the efficiency of the proposed ionites with the chromophore reagents is characterized by high values of distribution coefficients, especially after US treatment ( $D \geq 10^4$ , Table 3), at the optimal values of the acidity of the medium. The pH values of the solutions for 50% recovery of metal ions onto  $\overline{H_mR}$  ( $\text{pH}_{1/2}$ ) are listed in [8].

The investigated metal ions can be divided by this feature to two groups, those that may be concentrated and separated on the modified sorbents in the acidic medium ( $\text{pH} = 0.5\text{--}2.5$ ) and those that require weakly acidic or neutral medium ( $\text{pH} = 3.0\text{--}7.0$ ) [10]. For instance, it was established that  $\overline{XO}$  at  $\text{pH} = 0.5\text{--}2.5$  interacts with Fe(III), Pb(II), Hg(II), Cu(II), Sn(IV) ions, etc., whereas Zn(II) ions require the range of  $\text{pH} = 3.0\text{--}7.0$ . This led to the creation of the selective technique of the determination of Zn(II) ions with  $\overline{MTB}$  after the concentration of the interfering ions with  $\overline{XO}$ .

The data on the immobilization of MTB, XO, PCV, and CAS onto the anion exchanger and on the interaction of Cu(II), Pb(II), Zn(II), and Hg(II) ions with the immobilized dyes allowed to develop the technique of solid-phase spectrophotometric (SPS) determination of these metal ions and propose the method of fruit juices analysis (Fig. 1).

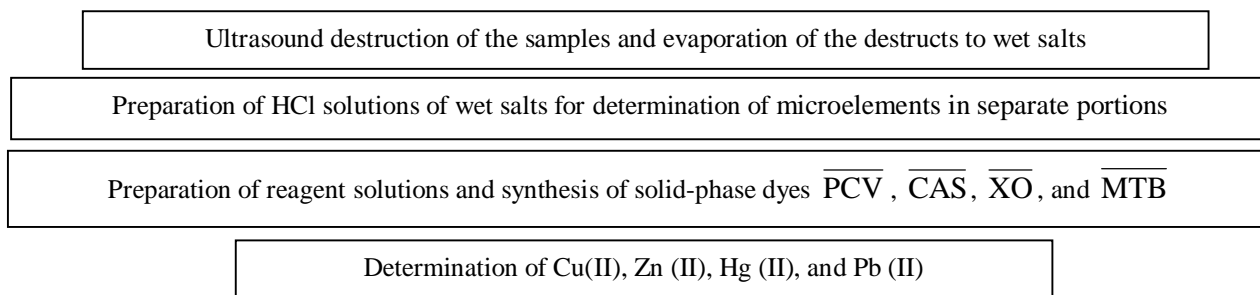
This method was used for the analysis of apple juice purified with palygorskite. The results of determination of Cu(II), Zn(II), Pb(II), and Hg(II) in apple juice samples by the developed techniques (A) and standard methods (B) are presented in Table 4.

The relative standard deviation of the results obtained by the developed techniques does not exceed 0.10, which indicates their satisfactory reproducibility.

High distribution coefficients ( $D \geq 10^4\text{ cm}^3/\text{g}$ ) of metal ions favor the decrease of the determination limits by using immobilized dyes vs the reactions in solution. By the  $C_{\min}$  values, the proposed techniques of sorption-spectrophotometric determination of metal ions yield only to atomic absorption (AAS) determination of Hg(II) ions. Still,  $C_{\min}$  of the proposed method is sufficient for the determination of Hg(II) ions in foodstuffs at the MPC

(maximum permitted content) level. In the case of Pb(II), Zn(II), Cu(II) ions the developed methods are advantageous over the standard techniques for the foodstuffs [16] as they permit the determination of these

ions at the level of  $\leq 0.1$ – $0.5$  MPC. The increase of the selectivity of the determination with anionite-immobilized dyes is explained by the change of the microsurrounding of MTB, XO, PCV, and CAS upon immobilization.



**Fig. 1.** Block layout for the determination of specific microelements in apple juice

Table 4

**Results of determination of metal ions in apple juice by methods A and B**

Metal	Reagent	MPC, $\mu\text{g}/\text{dm}^3$	Metal content, A, $\mu\text{g}/\text{dm}^3$	$S_r$	Metal content, B, $\mu\text{g}/\text{dm}^3$	$S_r$
Cu(II)	SPADNS	<5000	130.0 $\pm$ 7.0	0.02	135.0 $\pm$ 6.0	0.02
Zn(II)	$\overline{\text{MTB}}$	$\leq 10000$	0.65 $\pm$ 0.04*	0.02	0.64 $\pm$ 0.05*	0.03
Pb(II)	$\overline{\text{PCV}}$	$\leq 300$	28.0 $\pm$ 3.0	0.04	30.0 $\pm$ 5.0	0.07
Hg (II)	$\overline{\text{CAS}}$	<10	trace	–	4.0 $\pm$ 0.1	0.01

Note: \*( $\text{mg}/\text{dm}^3$ ),  $n = 3$

The rapidity of the proposed techniques is achieved by the ultrasound treatment of the analyzed sample during its preparation, and of the system of sample–ion exchanger with the immobilized dye during the establishment of the sorption equilibrium.

The ion exchangers with immobilized dyes and the presented methods of solid-phase spectrophotometric determination are environmentally friendly because they do not require the use of toxic organic reagents and are simple in execution and cost-effective due to the low cost of the used materials and reagents. The method of the photometric determination of Cu(II) using SPADNS is also environmentally safe.

The comparative analysis of the determination of the concentration of metals in apple juice samples showed that the content of Cu(II), Zn(II), Pb(II), and Hg(II) is significantly lower than MPC indicating the efficiency of the developed method of clarification (or purification) of apple juice with such natural adsorbent of Cherkasy deposits as palygorskite [17]. In addition to removing toxic metal ions, this clay mineral clears apple juice from pectin and colloidal substances, thereby increasing its

transparency degree by 25 % with virtually no reduction in vitamin C content and no changes to the content of carbohydrates, dry matter, active and titrated acidity. Moreover, it increases shelf life by 2–3 times due to the inhibition of pathogenic organisms [17], *etc.* Therefore, it can be recommended in the production of apple and other fruit juices.

## 4. Conclusions

The proposed method of the solid-phase spectrophotometric and photometric determination of several microelements in apple juice may be used for the determination of metal ions in other fruit juices.

The proposed techniques of metal ion determination are characterized by satisfactory correctness and reproducibility of results as well as high sensitivity and selectivity. They exceed known analogous and standard techniques by rapidity. The analysis is characterized by the simplicity of experiment and safety to the environment. It does not imply the use of complex or

expensive equipment requiring highly qualified staff and stationary laboratory.

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### ВИКОРИСТАННЯ СУЛЬФОФТАЛЕЇНОВИХ БАРВНИКІВ, ІММОБІЛІЗОВАНИХ НА АНІОНІТІ АВ-17Х8, ДЛЯ ВИЗНАЧЕННЯ ВМІСТУ Pb(II), Cu(II), Hg(II) ТА Zn(II) У РІДИННИХ СЕРЕДОВИЩАХ

**Анотація.** Встановлені умови іммобілізації ксиле-  
нолового оранжєвого, метилтимолового синього, пірокатехі-  
нового фіолетового та хромазуrola S на поверхні аніоніту  
АВ-17х8. Досліджена взаємодія йонів Pb(II), Cu(II), Hg(II) та  
Zn(II) з отриманими твердофазними реагентами. Показана  
ефективність очищення яблучного соку таким природним адсор-  
бентом Черкаського родовища (Україна) як палигорськіт.  
Визначені оптимальні умови реакції, кількісні характеристики  
складу та стійкості поверхневих комплексів та показники ефек-  
тивності аніонообмінників із іммобілізованими барвниками.

**Ключові слова:** твердофазно-спектрофотометричне  
визначення йон-металів, іммобілізовані сульфофталейнові  
барвники, фруктові соки.