

# SELECTIVE EXTRACTION OF IRON CHLORIDE COMPLEX (III) AND ITS COMPLEXIZATION FROM 5-(PYRIDILAZO)-2-(MONOETHYLAMINE-PARACRESOL) (PAAC) DIRECTLY IN THE ORGANIC PHASE

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**Abstract.** The developed method of extraction-photometric determination of iron with PAAC differs from the existing selectivity, sensitivity, simplicity and rapidity and is recommended for the analysis of production solutions, waste water, ores, concentrates and other chemically complex materials without separation of accompanying elements directly in the organic phase.

**Keywords:** express method, extraction, extraction-photometric, spectrophotometric, complex ion, extract, selective extraction, selectivity, sensitivity, complexation.

**Introduction.** Scientific and industrial development and the introduction of new technological processes are leading to increasing environmental pollution. In order to prevent an environmental catastrophe, it is necessary to establish a comprehensive environmental monitoring system, which allows for systematic information on the state of the natural environment. The increasing requirements for environmental protection in the Republic pose a challenge for chemists to develop simple, rapid, sensitive and selective methods for determining micro concentrations of substances, particularly heavy and toxic elements.

Many chemical compounds and toxic metals are known to dissolve in droplets of moisture as pollutants into soil and water as a result of the operation of enterprises, plants and factories with atmospheric precipitation. Contamination environments heavy toxic metals and their compounds form a significant group of ecotoxicants, which largely determine the anthropogenic impact on the ecological structure of our environment and on mankind itself. Given the ever-increasing scale of production and use of heavy toxic metals, their high toxicity and ability to accumulate in the human body, they have harmful effects even in low concentrations. These chemical pollutants have been identified as a priority. These ecotoxicants also include iron, copper, cadmium, nickel and others. The relevance of the work presented is therefore obvious and up-to-date. The search for selective ecoanalytical methods for identifying ecotoxicants in materials with complex chemical composition is an urgent task.

## Research Methodology

The existing photometric and extraction-photometric methods for determining iron using azo reagents are not selective enough [1, 2, 3], as iron (III) complexation with azo reagents is carried out in an aqueous solution. However, many accompanying ions form compounds with the above reagents and are extracted together with iron.

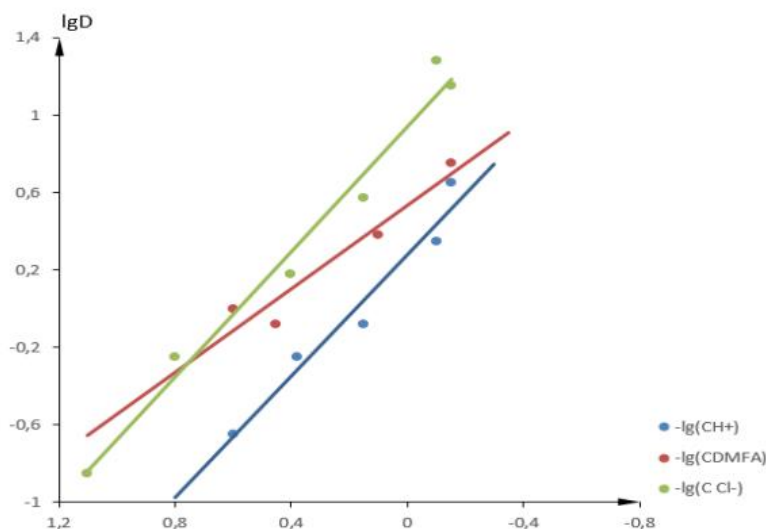
Recently it has been known that in order to increase the selectivity of the methods for determining elements, a new method is used to extract colorless complexes of elements with inert organic solvents, followed by the addition of organic dyes to the extract and their complexation directly in the organic phase [4,5].

#### Research results

Source solution of iron (III) was prepared from salt of iron nitrate (III), mark "Chemically pure" (CP). The titer of the solution was set potentiometric using potassium dichromate [6].

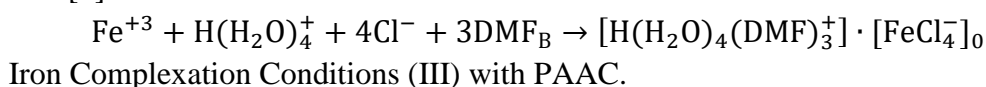
Experience has shown that iron (III) from a highly acidic environment in the presence of chloride ions and dimethylformamide (DMF) is well extracted by chloroform. In the absence of DMF, iron (III) is not extracted. A study of extraction of iron (III) by chloroform as a function of  $H^+$  ion,  $Cl^-$  ion and DMF concentrations has shown that the optimum conditions for extraction of iron (III) are: 5.55 m and above in hydrogen ions, 6.55 m and above in chloride ions, 30-45 vol % DMF and shaking phases for 10-15 seconds. If the volumes of the aqueous and organic phases are equal, the extraction of iron (III) at single extraction is 99.9% and does not change to a 3:1 ratio.

Extraction mechanism. The composition of the extractable iron chloride complex (III) was determined by the balance shift method [7]. The concentration of iron (III) in the extract was determined by the photometric method. The data obtained in Fig. 1 show that in the biogarithmic coordinates  $\lg D_{Fe} - \lg C_{CH}$ ,  $\lg D_{Fe} - \lg C_{Cl}$ ,  $\lg D_{Fe} - \lg C_{DMF}$  (where D - distribution coefficient, C - concentration) there is a straight-line relationship with the tangent angles of straight lines equal to 1, 4 and 3, respectively.



**Fig. 1. Determination of molar ratios in the extract by the equilibrium shift method**

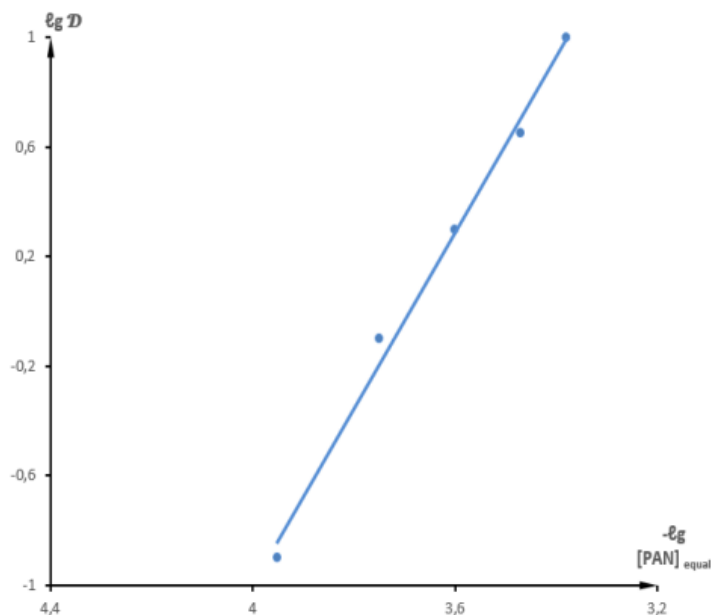
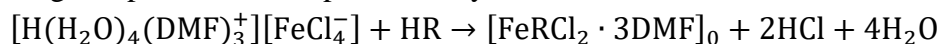
Consequently, iron (III) is extracted by chloroform as  $H[FeCl_4]$ . The solvate number in the extract is 3. The number of water molecules associated with  $H[FeCl_4]$  in the extract determined by spectrophotometry [8] is 4. Thus, the iron chloride complex (III) from a highly acidic medium in the presence of DMF is extracted by the chloroform by the hydro-solvate mechanism [8]:



Once iron (III) is extracted with chloroform under optimal conditions, the aqueous phase is separated, the PAAC chloroform solution, the acetate-ammonia buffer solution is added to the extract and the phases are shaken, iron (III) is complexed with PAAC in the organic phase.

Studies of iron complex (III) with PAAC depending on the optical density of the pH of the buffer solution have shown that the practical complete complexation of iron (III) with PAAC in the chloroform occurs in the pH range of the buffer solution 3-7.

The equilibrium shift method [7] found that iron (III) and PAAC interact in the organic phase in a molar ratio of 1:1 (Fig. 2). Therefore, the reaction of complexation of iron (III) with PAAC in the organic phase can be represented by a reduced scheme:



**Fig. 2. Determination of the molar ratio of Fe (III) to PAAC in an extract using the balance shift method**

$$V_B = V_0 = 10 \text{ ml}; l = 1 \text{ cm}; C_{\text{Fe}} = 1,07 \cdot 10^{-5} \text{ m}$$

Iron complex (III) with PAAC in the extract is stable for over three days. The maximum light absorption of iron complex (III) with PAAC is at 540 nm. The apparent molar yield at 540 nm is  $3.36 \cdot 10^4$ .

The Ber law is observed in the range of 0.5-150  $\mu\text{g}$  iron in 10 ml of the extract. Reproducibility of definitions is in the range of 1-5%. Three graduation diagrams have been constructed, covering the range of 0.5-10  $\mu\text{g}$ , 5-60  $\mu\text{g}$  and 60-150  $\mu\text{g}$  iron.

In iron (III) extraction, copper, molybdenum and gold (III) ions are partially extracted, but the presence of small amounts of these ions does not interfere with iron determination. The results of iron determination in the presence of foreign ions where the definition error does not exceed 1-5% are given in Table 1.

**Table 1**

**Determination of iron in the presence of foreign ions  
 (10 mcg iron taken)**

M	M/ Fe	M	M/ Fe	M	M/ Fe
Ag (I)	1000	R u (III)	2,000	W(VI)	2,000
Zn (II)	40000	Jn (III)	50,000	Cr (VI)	1000

Pb (II)	50000	R a (III)	10,000	Te (VI)	10,000
Cu (II)	5000	Gr ( III)	5,000	Mn (VII)	10
Cd ( II )	1000 00	Rh (III)	2,000	Os (VIII)	20 00
Mn (II)	10 0000	La (III)	10,000	F <sup>-</sup>	10000
C o (II)	3 0000	Ti (IV)	50,000	Cl <sup>-</sup>	100000
Hg (II)	2 0000	Sn (IV)	10000	NO <sub>3</sub> <sup>-</sup>	50000
Ca (II)	10 0000	Zr (IV)	100,000	PO <sub>4</sub> <sup>-3</sup>	50000
Ba (II)	10 0000	Ge (IV)	50000	C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	Doesn't interfere
Mg (II)	10 0000	Se (IV)	10,000 <sup>1</sup>	CH <sub>3</sub> COO <sup>-</sup>	Doesn't interfere
Pd (II)	1 0 000	Th ( I V)	5,000	EDTA <sup>-</sup>	Doesn't interfere
Be (II)	10,000	As (V)	1000 0 <sup>1</sup>	Thiomochivin a	Doesn't interfere
Ni (II)	10000 0	Sl (V)	20 00	Wine acid	Doesn't interfere
Al (III)	10000	V (V)	2 000 <sup>1</sup>	Lemon acid	Doesn't interfere
Bi (III)	50,000	Nb (V)	20 00		
Au (III)	100	U(VI)	20,000		
Tl (III)	10000	Mo (VI)	200		

M - ion or compound; M/Fe- allowable mass ratio of foreign ions to iron;

1 - After a single washing of the extract with 10 ml of solution containing 8 ml of HCl ( $\rho=1,19$ ) and 20 vol % DMF, shaking phases 10-15 s.

Methodology for determining iron (III) in pure solutions. The dividing funnel is filled with 1 ml of the analyzed solution containing 0.5-150  $\mu\text{g}$  of iron (III), 6.5 ml of HCl ( $\rho=1.19$ ), 3.0 ml of DMF, 10 ml of chloroform and shaken for 10-15 seconds. Then pour the extract into another dividing funnel, add 10 ml of 0.02% PAAC chloroform solution, 5 ml of acetate-ammonia buffer solution with pH=5 containing 0.2 m NaCl and shake for 10-15 seconds. The colored extract is filtered into a cuvette through filtered paper and the optical density is measured at 540nm on the KFK-2 photoelectric colorimeter relative to the blank solution.

Optical complex densities were measured in ditches with an absorption layer thickness of 2.1 and 0.5 cm respectively.

In natural objects (minerals, ores, etc.), in various production solutions and in waste water, iron is present in the presence of elements such as Sb, Sn, Bi, Pb, In, Cd, Zn, Ga, Cu, Hg, Ag, Te, Mo, W, K, Mg, Al. Of such complex mixtures of cations and anions, the iron content is difficult to determine using known reagents. In this case, iron is usually separated from accompanying elements.

The extraction photometric method developed by the authors for determining iron makes it possible to determine microgram concentrations of iron in the presence of large amounts of all the above elements.

In order to find out the possibility of determining iron in various objects, the authors tested in model solutions based on the type of industrial samples of lead zinc production without separating the associated elements (Table 2), as well as in the analysis of silicate rocks and ores

(Table 3) in the analysis of industrial solutions took 1-2 ml of solution and determined the iron content of this method.

**Table 2**

**Results of determination of iron in model solutions (n=4, P=0.95)**

Composition of the mixture, mcg	Iron found, mg	Sr	$\Delta\bar{x} * 10^4$
Zn-123, 50; SiO <sub>2</sub> -7.50; Pb-50.00; Ag-1.73 Cl-1.00, Bi-0.25, Cu, Sn, Sb-0.50, In-0.25, Fe-0.025	0.0246	0.018	±7.13
Sublimation from fluming of copper slag Zn -177.50; Pb -5.00; SiO <sub>2</sub> -4.00; As -2.45; In-0.50; Sn,Sb-0.50 Bi-0.025;Fe-0.25	0.247	0.019	±7.54
Zinc-cadmium production solution Zn -75.00; Cd -12.50; In -0.175; As -1.75 Sn-0.50; Ti-0.3;Ge-0.2;Cu-0.05; Fe-0.025	0.0251	0.016	±6.60

**Table 3**

**Results of determination of iron in silicate rocks and ores  
(n=4; P=0.95)**

Name and number of the standard sample	Acestovania chem. Composition of standard samples, %	$\bar{x} \pm \Delta \bar{x}$ , %	Sr
<b>Breed</b>			
29-84 (PChKS)	SiO <sub>2</sub> -55.42; Al <sub>2</sub> O <sub>3</sub> -12.61; CaO-5.42; MgO-2.02 ; MnO-0.09 ; Pb-0.0013; Co-0.0021; Fe-3.92	3.91±0.05	0.008
28-84 (PSA)	SiO <sub>2</sub> -65.51; Al <sub>2</sub> O <sub>3</sub> -12.24; CaO-0.84; MgO-1.50; MnO-0.16; Pb-0.025; Co-0.0023; Fe-3.26	3.17 ± 0.02	0.001
<b>Ore</b>			
48-85 (SMR)	SiO <sub>2</sub> -83.77; TiO <sub>2</sub> -1.47; Al <sub>2</sub> O <sub>3</sub> -3.47; Fe-15.9; CaO-29.75; MgO-0.66; MnO-0.36; P <sub>2</sub> O <sub>5</sub> -0.11; K <sub>2</sub> O-0.13; Na <sub>2</sub> O-0.1; CO <sub>2</sub> -2.73; Cu-1.98; Mo-0.02;	15.45 ± 0.19	0.007
1347-78 (SNK-2)	SiO <sub>2</sub> -31.11; TiO <sub>2</sub> -0.32; Al <sub>2</sub> O <sub>3</sub> -7.10; Fe-4.22; CaO-18.7; MgO-4.24; MnO-0.25; P <sub>2</sub> O <sub>5</sub> -0.11; Na <sub>2</sub> O-0.1; CO <sub>2</sub> -2.73; Cu-0.39; Zn-0.039; Co-1.13; Ni-1.57; S-0.41	4.05 ± 0.11	0.017

Methodology for determining iron in silicate rocks and ores

When determining iron in silicate rocks and ores, the canopy (0.1-0.3 g) is placed in a platinum crucible (pre-treated with HCl), 1-2 ml of water is wetted, 1 ml of 70% chloric acid and 2-3 ml of hydrofluoric acid are added (for canopies greater than 0.3 g these quantities should be increased accordingly). The mixture is evaporated to dry. Add 1 ml of 70% chloric acid and 2-3 ml of hydrofluoric acid to the remainder and evaporate again to the dry residue. Dissolve the

remainder with 20-25 ml HCl (1:1). The solution is filtered into a measuring flask in a container of 100-150 ml and the volume of filtrate is brought to the mark by water. The iron content of the solution is determined from the aliquot of the solution using the method for determining the iron content of pure solutions, including a single washing of the extract.

#### Discussion of results

Research has focused on how to improve the selectivity and sensitivity of photometric definitions, as these analytical characteristics play an important role in analytical chemistry practice. We investigated the conditions of selective extraction of iron chloride complex in the presence of DMF inert organic solvents and the conditions of its complexation with azo reagents after their addition directly into the organic phase.

Research has shown that iron (III) from a highly acidic environment in the presence of chloride ions and DMF is selectively extracted by chloroform. At 10-15 second phase shaking, iron (III) is extracted by 99.9%. Under these optimal conditions, molybdenum (VI) and gold (III) ions are partially extracted together with iron, but the presence of small amounts of these ions does not interfere with iron determination. A research study of the composition of the extractable iron chloride complex (III) in the extract has shown that the iron chloride complex (III) is extractable by the hydro-salt mechanism. The chloroform extract of the iron complex with PAAC is stable over a long period of time and is subject to Bera Law in a wide range of concentrations. In aqueous solutions, the Ber law compliance interval is much lower than in the organic phase. The developed method of extraction-photometric determination of iron with PAAC has been tested on model solutions based on the type of industrial samples of zinc-cadmium and lead production without separation of accompanying elements. Iron determination methods were also tested on the analysis of silicate rocks and ores. The data obtained show the reliability and accuracy of the determination method.

The research therefore resulted in the development of a new method of selective iron extraction and complexation with the PAAC azoreagent in the organic phase. The mechanism of extraction and complex formation has been identified. The structure of the complexes was determined, and certain conclusions were drawn on increasing the selectivity and sensitivity of photometric reactions and the most analytically valuable reagents.

Therefore, the developed method of extraction and photometric determination of iron can be recommended for the analysis of production solutions, waste water, ores, rocks and other materials with complex chemical composition without separating the associated elements.

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