

**EXTRACTION MECHANISM THE COMPOSITION OF THE
EXTRACTED IRON (III) CHLORIDE COMPLEX WAS
DETERMINED BY THE EQUILIBRIUM SHIFT METHOD [7].
THE CONCENTRATION OF IRON (III) IN THE EXTRACT
WAS DETERMINED BY THE PHOTOMETRIC METHOD. THE
DATA OBTAINED (FIG. 1) SHOW THAT IN LOGARITHMIC
COORDINATES**

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Abstract. *The developed method for the extraction-photometric determination of iron with PAAF, which differs from existing ones in selectivity, sensitivity, simplicity and rapidity, is recommended for the analysis of industrial solutions, wastewater, ores, rocks, concentrates and other materials with a complex chemical composition without separating associated elements.*

Keywords: *express method, extraction, extraction-photometric, extract, selectivity, sensitivity, complexation, molar extinction coefficient, Beer's law, expressivity.*

Introduction. The development of science, industry and the introduction of new technological processes leads to increasing environmental pollution. To prevent an environmental disaster, it is necessary to create comprehensive environmental monitoring, which allows systematically obtaining information about the state of the natural environment.

Increasing requirements for environmental protection in the Republic put forward the task of analytical chemists to develop simple, rapid, sensitive and selective methods for determining micro concentrations of substances, in particular heavy and toxic elements.

As is known, many chemical compounds and toxic metals as a result of the operation of enterprises, plants and factories, with precipitation, dissolving in droplets of moisture, enter the soil and water as pollutants. Among pollutants, 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 humans themselves. Considering the ever-increasing scale of production and use of heavy toxic metals, high toxicity, carcinogenicity, ability to accumulate in the human body, and have harmful effects even in low concentrations, these chemical pollutants are considered a priority. Such ecotoxicants also include iron, copper, cadmium, nickel and others. Therefore, the relevance of the presented work is obvious and modern. The search for selective ecoanalytical methods for determining ecotoxicants in materials with complex chemical composition is an urgent task.

Research methodology. Modern environmental analytical methods of analysis, such as chromatometry, chromatography-mass spectrometry, atomic absorption, plasma, X-ray fluorescence and others, do not always allow solving this problem due to the complexity and inaccessibility of the equipment.

Existing photometric and extraction-photometric methods for determining iron using azoreagents are not selective enough [1, 2, 3], since the complexation of iron (III) with azoreagents

is carried out in an aqueous solution. In this case, many accompanying ions form compounds with the above reagents and are extracted together with iron.

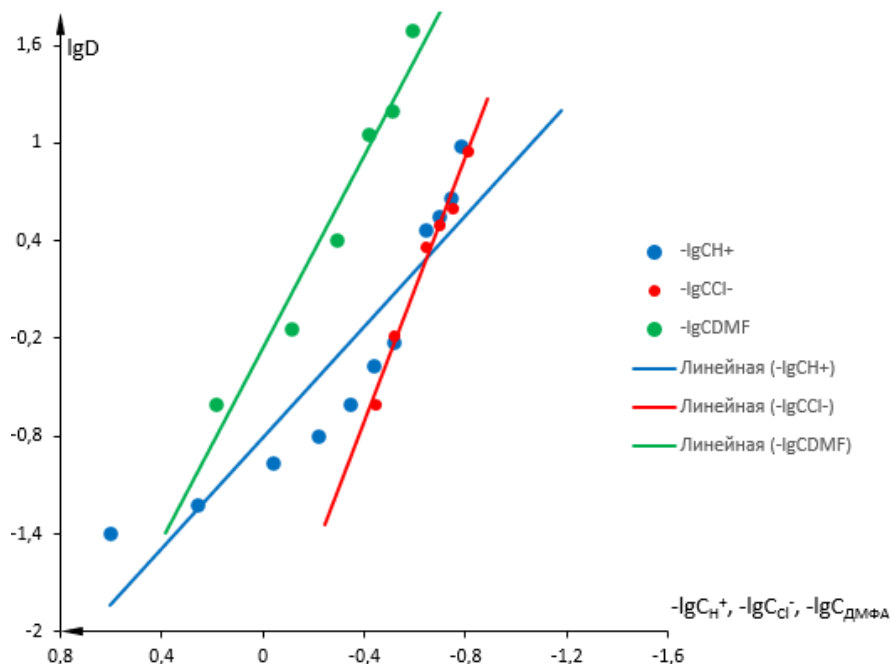
Recently, it is known that to increase the selectivity of methods for determining elements, a new technique is used - extraction of colorless complexes of elements with inert organic solvents, followed by the addition of organic dyes to the extract and their complexation directly in the organic phase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

This work investigates a new selective, simple method based on the selective extraction of iron (III) chloride complex with inert organic solvents and its complexation with organic dyes directly in the organic phase.

Research results. The initial solution of iron (III) was prepared from iron (III) nitrate salt of the “chemically pure” grade. The solution titer was determined potentiometrically using potassium dichromate [6]. The spectrum of the iron complex with PAAF was recorded on an SF-26 spectrophotometer. The optical densities of the complexes were measured on a KFK-2 photoelectrocolorimeter.

Experiments have shown that iron (III) is easily extracted with chloroform from a strongly acidic medium in the presence of chloride ions and dimethylformamide (DMF). In the absence of DMF, iron (III) is not extracted. A study of the extraction of iron (III) with chloroform depending on the concentration of hydrogen ions, chloride ions and DMF showed that the optimal conditions for the extraction of iron (III) are: 5.55 g-ion/l and higher for hydrogen ions, 6.55 g-ion/l and higher for chloride ions, 30–45 vol. % (by volume) in DMF and shaking the phases for 10-15 s. With equal volumes of aqueous and organic phases, the extraction of iron (III) during a single extraction is 99.9% and does not change until the phase volume ratio is 3:1.

Extraction mechanism. The composition of the extracted iron (III) chloride complex was determined by the equilibrium shift method [7]. The concentration of iron (III) in the extract was determined by the photometric method. The data obtained (Fig. 1) show that in logarithmic coordinates: $\lg D_{\text{Fe}^{+3}} - \lg C_{\text{H}^+}$, $\lg D_{\text{Fe}^{+3}} - \lg C_{\text{Cl}^-}$, $\lg D_{\text{Fe}^{+3}} - \lg C_{\text{DMF}}$ (where D is the distribution coefficient, C is the equilibrium concentration), a linear dependence is observed with the tangents of the slope of the straight lines equal to 1, 4 and 3, respectively.



Puc. 1. Determination of molar ratios of Fe: H(1), Fe: Cl(2),

Fe: DMF (3) in the extract by equilibrium shift method.

$V_B = V_O = 10 \text{ ml}$; $l = 1 \text{ cm}$; $C_{Fe} = 1.07 \cdot 10^{-5} \text{ M}$.

Consequently, iron (III) is extracted by chloroform in the form of $H [FeCl_4]$. The solvate number in the extract is 3. The number of water molecules associated with $H [FeCl_4]$ in the extract, determined by the Fischer method [8], is 4.

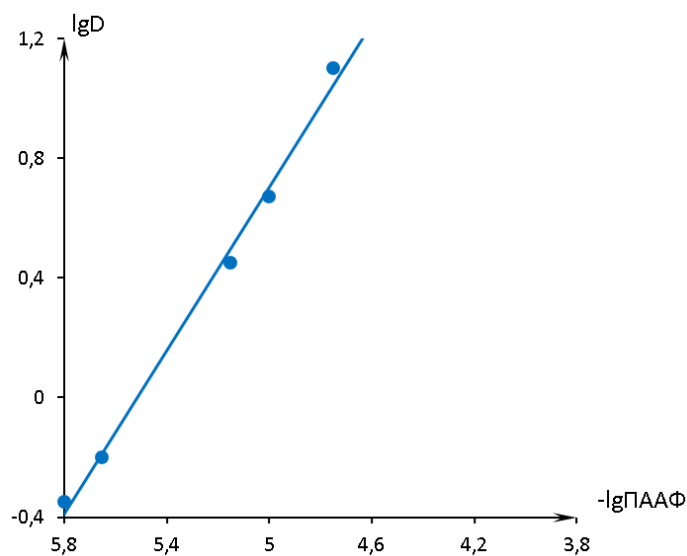
Thus, the iron (III) chloride complex from a strongly acidic medium in the presence of DMF is extracted with chloroform according to the hydrate-solvate mechanism [7]: $Fe^{+3} + H(H_2O)_4^+ + 4Cl^- + 3DMFA_{(B)} \rightarrow [H(H_2O)_4 (DMFA)_3]^+ \cdot [FeCl_4]_{(O)}^-$

Conditions for complexation of iron (III) with PAAF in the organic phase

After extraction of iron (III) with chloroform under optimal conditions, separation of the aqueous phase, addition of a chloroform solution, PAAF, acetate-ammonium buffer solution containing iodide ions to the extract, and shaking of the phases for 10-15 s, complexation of iron (III) occurs with PAAF in the organic phase. Studies have shown that almost complete complexation of iron (III) with PAAF in the extract occurs in the pH range of 4–8 of a buffer solution containing 0.10–0.30 g-ion/L iodide ions.

Using the equilibrium shift method [7], it was established that iron (III) interacts with PAAF in the organic phase in a molar ratio of 1:2 (Fig. 2).

Consequently, the reaction of complexation of iron (III) with PAAF in the organic phase can be briefly represented by the following scheme: $[H(H_2O)_4 (DMFA)_3]^+ [FeCl_4]_{(O)}^- + 2HR + NaI \rightarrow [FeR_2] I_{(O)} + 3DMFA + 3HCl + NaCl + 4H_2O$



Rice. 2. Determination of the molar ratios of Fe: PAAF in the extract by the equilibrium shift method: $V_B = V_O = 10 \text{ ml}$; $l = 1 \text{ cm}$; $C_{Fe} = 1.07 \cdot 10^{-5} \text{ M}$.

The iron (III) complex with PAAF in the extract is stable for more than three days. The maximum light absorption of the iron (III) complex with PAAF is located at 560 nm. The apparent molar extinction coefficient at 560 nm is $4.7 \cdot 10^4$. Beer's law is observed in the range of 0.5–120 μg of iron in 10 ml of extract. The reproducibility of determinations is within 1-5%. Three calibration graphs were constructed, covering the limits of 0.5 - 10 μg , 5 - 60 μg , and 60 - 120 μg of iron. The optical densities of the complexes were measured in cuvettes with absorbing layer thicknesses of 2, 1, and 0.3 cm, respectively.

Method for determining iron (III) in pure solutions.

Add 1 ml of the test solution containing 0.5 - 120 µg of iron (III) into a separating funnel, add 6.5 ml of HCl (pI = 1.19), 3 ml of DMF, 5 ml of chloroform and shake for 10-15 seconds. Then the extract is poured into another separating funnel, 5 ml of a 0.05% chloroform solution of PAAF, 5 ml of an acetate-ammonium buffer solution with pH 6 containing 0.1 M NaI are added to the extract, and shaken for 10-15 seconds. The colored extract is filtered into a cuvette through filter paper and the optical density is measured at 560 nm on a KFK-2 photoelectrocolorimeter relative to a blank solution prepared in a similar way.

Under the conditions of 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 the determination of iron. The results of the determination of iron in the presence of foreign ions, in which the determination errors do 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)	1 000	Au (III)	500 ¹	U (VI)	1 000
Zn (II)	10 000	Tl (III)	2 000	W (VI)	1 000
Pb (II)	10 000	Rh (III)	1 000	Cr (VI)	1 000
Cu (II)	50	Ru (III)	2 000	Te (VI)	10 000
Cu (II)	500 ¹	As (III)	5 000	Mn (VII)	1 000
Mn (II)	20 000	In (III)	5 000	Os (VIII)	500
Cd (II)	20 000	Ga (III)	50 000	F ⁻	не мешает
Hg (II)	10 000	Cr (III)	100	Cl ⁻	не мешает
Ca (II)	20 000	La (III)	20 000	Br ⁻	не мешает
Ba (II)	20 000	Sn (IV)	10 000	I ⁻	не мешает
Mg (II)	40 000	Ti (IV)	1 000	NO ₃ ⁻	не мешает
Pd (II)	2 000	Ge (IV)	5 000	PO ₄ ⁻	не мешает
Be (II)	5 000	Zr (IV)	50 000	CH ₃ COO ⁻	не мешает
Co (II)	400	Se (IV)	2 000	ЭДТА ⁻	50 000
Ni (II)	10 000	Th (IV)	5 000	C ₂ O ₄ ⁻²	50 000
Al (III)	10 000	Pt (IV)	2 000	Wine shop	doesn't interfere
Tl (III)	2 000	As (V)	1 000	Lemon juice	doesn't interfere
Bi (III)	2 000	Sb (V)	2 000	Thiourea	doesn't interfere

Au (III)	100	V (V)	500		
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M – ion or compound; M/Fe – permissible mass ratio of foreign ions to iron; 1 – in the presence of 50 mg of thiourea.

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

The extraction-photometric method for determining iron that we have developed allows us to determine microgram iron contents in the presence of large quantities of the above elements (Table 1).

To find out the possibility of determining iron in various objects, we tested it in model solutions prepared according to the type of industrial samples of zinc-lead production, without separating the accompanying elements (Table 2). To determine iron, 1–2 ml of a model solution was taken and analyzed according to the above method for determining iron from pure solutions, including washing the extract once with a washing solution containing 5 M HCl and 35 vol. % DMF. The method for determining iron was also tested on the analysis of production solutions, ores and concentrates of the Almalyk Mining and Metallurgical Combine (AMMC). When analyzing production solutions, 1–2 ml of solution was also taken and the iron content was determined using the above method (Table 3).

Table 3

Results of determination of iron in model solutions based on the type of industrial samples of AMMC (n = 4; p = 0.95)

Mixture composition, mg/l	Found iron \bar{x} , mg/l	S _r	Δ \bar{x} · 10 ⁴	± $\frac{\Delta\bar{x}}{\bar{x}}$ · 100
1	2	3	4	5
Zn – 123,5; SiO ₂ – 7,50; Pb – 50,00; Ag – 1,73; Cl – 1,00; Bi – 0,25; Cu, Sn, Sb – 0,5; In – 0,25; Fe – 0,025	0,0246	0,018	± 7,13	± 2,89
Sublimate from fluming of copper slag: Zn – 177; Pb – 5,00; SiO ₂ – 4,00; As – 2,45; In – 0,50; Sn, Sb – 0,50; Bi – 0,025; Fe – 0,25	0,247	0,019	± 7,54	± 0,305
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	± 2,62

To determine iron in ores and concentrates, a sample (1–2 g) was placed in a 250 ml conical flask, 20 ml of HCl was added, heated in a sand bath for 10 minutes, 10 ml of HNO₃ was added, the mixture was evaporated to wet salts, 50–60 ml of 0.01 M HNO₃ solution and boiled until the

turbidity disappeared; after cooling, the solution was filtered into 100 ml volumetric flasks and diluted with 0.01 M HNO₃ solution to the flask mark. Iron (III) was determined from an aliquot of the solution according to the method for determining iron (III) from pure solutions, also including a single washing of the extract with a washing solution (Table 4).

Table 3

Results of determination of iron in production solutions ($n = 4; p = 0.95$)

Content iron, mg/l	Found iron (\bar{x}), mg/l	S_r	$\pm \Delta \bar{x}$	$\pm \frac{\Delta \bar{x}}{\bar{x}} \cdot 100$
14,00	14,30	0,015	$\pm 0,35$	$\pm 2,44$
45,70	45,12	0,016	$\pm 1,14$	$\pm 2,52$
100,00	102,24	0,014	$\pm 2,32$	$\pm 2,26$
150,00	147,60	0,014	$\pm 3,40$	$\pm 2,30$

Table 4

Determination of iron in ores and concentrates ($n = 4; p = 0.95$)

Name and sample number	Fe content according to the passport, % 102	Found Fe (\bar{x}), % 102	$S_r \cdot 10^2$	$\pm \Delta \bar{x} \cdot 10^2$	$\pm \frac{\Delta \bar{x}}{\bar{x}} \cdot 100$
Руда:					
291 – 88	0,250	0,255	2,50	$\pm 1,00$	$\pm 3,92$
327 – 97	0,400	0,417	1,60	$\pm 1,10$	$\pm 2,63$
267 – 79	1,290	1,330	0,20	$\pm 0,50$	$\pm 0,37$
Concentrate:					
2192 – 18	0,270	0,280	1,90	$\pm 1,00$	$\pm 3,57$
2205 – 18	0,170	0,175	4,11	$\pm 11,00$	$\pm 6,28$
2191 – 18	0,460	0,590	0,95	$\pm 1,00$	$\pm 1,69$

The discussion of the results. Thus, the study allows us to conclude that heterocyclic azo compounds based on pyridine are very valuable analytical reagents for the determination of iron. This is facilitated by the high sensitivity of the reagents, the contrast of color changes in complex formations, and the stability of the resulting complexes.

The low selectivity of metal ion determinations using azo compounds, as well as when using other organic reagents during complex formation in the aqueous phase, is the main disadvantage of existing methods.

In our research, much attention is paid to ways to increase the selectivity and sensitivity of photometric determinations, since these analytical characteristics play an important role in the practice of analytical chemistry. We have studied the conditions for selective extraction of the ferric chloride complex in the presence of DMF with inert organic solvents and the conditions for complexation with azoreagents after their addition directly to the organic phase.

Studies have shown that iron (III) is selectively extracted with chloroform from a strongly acidic medium in the presence of chloride ions and DMF. With 10-15 second shaking of the phases, 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 the determination of iron.

The study of the composition of the extractable iron (III) chloride complex in the extract showed that the iron (III) chloride complex is extracted by the hydrate-solvate mechanism. The chloroform extract of the iron complex with PAAF is stable for a long time and obeys Beer's law over a wide concentration range. In aqueous solutions, the range of compliance with Beer's law is much lower than in the organic phase.

The method is also valuable because after the extraction of iron in the organic phase, it becomes possible to form complexes with more sensitive azoreagents, which, due to low selectivity, are not widely used.

The developed method for the extraction-photometric determination of iron with PAAF was tested on the analysis of model solutions compiled according to the type of industrial samples of the Almalyk mining and metallurgical production without separating associated elements. The method for determining iron was also tested on the analysis of production solutions of the Almalyk mining and metallurgical plant. The data obtained indicate the reliability and accuracy of the determination method.

Conclusions. As a result of the research, a new method for the selective extraction of iron (III) and its complexation with the PAAF azoreagent in the organic phase was developed.

The mechanism of extraction and complex formation has been revealed. The composition of the structure of the complex was determined, certain conclusions were made about increasing the selectivity and sensitivity of photometric reactions and about the most analytically valuable reagents.

Thus, the developed method for the extraction-photometric determination of iron with PAAF is characterized by high selectivity, sensitivity, ease of implementation and rapidity and is recommended for the analysis of industrial solutions, wastewater, ores, rocks, concentrates and other materials with complex chemical composition without separating associated elements directly into organic phase.

REFERENCES

1. И. В. Пятницкий, Л. Л. Коломинец, В. И. Симяненко, В. С. Баршевская. Высокоизбирательный метод фотометрического определения железа (III) с глицинкрезоловым красным // Завод. лаборатория. – 1989. – Т. 55. – № 7 – С. 1-3.
2. Е. Б. Сендел. Колориметрическое определение следов металлов. – М.: Госхимиздат. – 1949. – С. 210-230.
3. И. Г. Периков, А. В. Дрозд, Г. В. Арцебашев. Селективное экстракционно-фотометрическое определение железа (III) с 1-(2-пиридилазо)-2-нафтолом // Ж. аналит. химии. – 1987. – Т. 42. – № 12. – С. 2193-2196.
4. К. Рахматуллаев, Б. Г. Закиров. Экстракция йодидного комплекса индия в присутствии диметилформаида и его комплексообразование с 1-(2-пиридилазо)-2-нафтолом в органической фазе // Известия вузов. Химия и хим. технология. – 1979. – № 6. – С. 663-666.
5. К. Рахматуллаев К., А. Ш. Гиясов. Экстракция таллия (III) в присутствии хлорид-ионов и диметилформаида и его комплексообразование с 1-(2-пиридилазо)-2-

- нафтолом в органической фазе // Известия вузов. Химия и хим. технология. – 1984. Т. 27. – Вып. 9. – С. 1028-1031.
6. А. П. Крешков. Основы аналитической химии. М.: Химия. – 1970. – С. 65-66.
 7. Ю. А. Золотов, Б. З. Иофа, Л. К. Чучалин. Экстракция галогенидных комплексов металлов. М.: Наука. – 1973. – С. 25, 59.
 8. Дж. Митчелл, Д. Смит. Акватметрия. М.: Химия. – 1980. – С. 345-354.