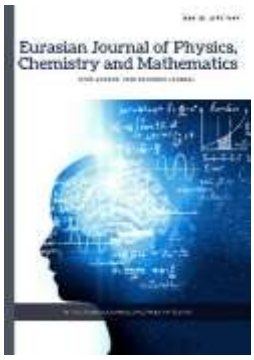

Determination of Heavy Metals in Food Products

Asqarov Ibrohim Rahmonovich — Doctor of Chemical Sciences, Professor, Andijan State University, 170100, Andijan, Uzbekistan
E-mail: xojiqulov76@inbox.ru

Xojiqulov Azizbek Sobirovich — PhD in Chemistry, Senior Lecturer, Andijan State University, 170100, Andijan, Uzbekistan
E-mail: xojiqulov76@inbox.ru

Kenjayeva Dilfuza Akbarali qizi — Master's Degree Student, Department of Chemistry, Andijan State University, 170100, Andijan, Uzbekistan

ABSTRACT

The article considers data on the solubilization of heavy metals in beef meat in the form of aqueous extracts, ensuring the complete separation of heavy metals in meat, potentiometric oximetric titration of the amount of mercury, cadmium, lead and iron in beef meat with a U-130 ion meter and spectrophotometric determinations were evaluated on a spectrophotometer KFK-3.

Keywords: aqueous meat extract, mercury, cadmium, lead and iron ions, potentiometric titration and spectrophotometry, redox pair, equivalent point, ionomer potential, optical densities, UV spectra, calibration diagram.

Introduction

In recent years, due to the seriousness of the ecological situation, attention has been paid to environmental objects, including food products. The seriousness of the ecological situation is connected with the uncontrolled dumping of various toxic substances into the environment. This is caused by the development of chemistry and related industries. In addition to chemistry and related industries, road transport, and geological exploration also have a significant impact on environmental pollution. In this regard, control of environmental objects has become an urgent problem today. The studied literature also shows that world scientists are paying great attention to this field. Scientists and researchers have developed various criteria for determining the contamination of the environment with heavy metal ions as a result of systematic examination of soil, air, water, one or another nutrient, plants, etc. For example, the degree of damage to the environment can be determined by the number of heavy metals in the leaves of trees.

Literature Revive

In the last few years, interest in this field has increased in our country. Several works have been carried out in this direction, and their results are published in various publications [1]. Most of these works are aimed at determining heavy metals in food products. The distribution of heavy metals in food products depends on the conditions of cultivation of these products, the places where cattle are fed and the proximity of these places to roads [2].

Heavy metals, including metals such as lead, cadmium, and mercury, which enter the human body through food products, cause many diseases. Heavy metals such as mercury, iron, cadmium and lead are distinguished by their high level of harmful effects on all forms of life. The rate of development and manifestation of clinical symptoms of the disease is determined by the intensity of the specific individual effect of heavy metals such as mercury, iron, cadmium and lead on the body. Cases of expressed chronic poisoning at concentrations of 0.035 mg/m3 and 0.2-1.3 mg/m3 are rare. The remaining signs of poisoning were observed in 2 out of 15 people working in an atmosphere polluted with mercury vapours at the level of 0.01-0.06 mg/m3. In general, chronic poisoning develops imperceptibly and continues for a long time without significant signs of morbidity [3].

It is 0.5 mg/l and 1.25 mg/l for heavy metals such as mercury, iron, and cadmium and leads in the waters of water bodies determined by the indicator of impact on the organism. It is 2.6 mg/l for the maximum concentration that does not disrupt biochemical processes and has a continuous effect for a long time, and 5 mg/l for halide salts of these metals [3].

When in contact with heavy metals such as mercury, iron, cadmium and lead and their compounds, the general harmful effect of the metal occurs, as a result of which it has an inflammatory effect on the upper respiratory tract. symptoms of pneumonia appear. Also, liver function disorders due to dust of heavy metals such as mercury, iron, cadmium and lead in workers; slow down the secretion of gastric juice; pathological changes such as monocytosis, and high levels of iron in erythrocytes have been observed [4].

Electrowelders and plumbers often have symptoms of inflammation in the upper respiratory tract. Chronic bronchitis, sometimes asthmatic bronchitis with emphysema is often observed in workers working in Fe ore mines and mining enterprises. In addition, dental diseases, inflammation of the gums, and whitening of the inner smooth wall of the oral cavity occur. When the worker who worked in the mines of mountain iron ore was dissected, it was found that destructive changes occurred in all areas of his lung bronchi [5].

Experimental part

For the detection of heavy metals in food products, cattle meat raised in the Buloq-boshi district of the Andijan region was taken from the meat stall in the farmer's market of the Buloq-boshi district of the Andijan region. A sample of 300 g of black beef was taken as an object of inspection. The obtained object samples are finely ground. This sample was then placed in a one-litre beaker and 300 mL of chemically pure concentrated acetic acid (CH_3COOH) was added. The solution from the acetic acid beef sample was filtered in a Buechner funnel with the mouth of the vessel sealed. The extracted meat sample was washed 5-6 times with distilled water. As a result, 1.5 litres of the solution was extracted from the beef sample. Separated solutions are concentrated using the distillation method at a temperature of 70-80 °C. The separated meat filtrate was concentrated by evaporation to a volume of 800 ml. Concentrates were used to determine heavy metals in meat [6].

After it was determined that the filtrates contained heavy metals, the remains of the meat samples were washed twice with distilled water. In the filtrates from the sixth washing, qualitative reactions were carried out to determine the ions of heavy metals. There were no changes as above. In this way, the complete transition of heavy metals in the sample to the solution was achieved. After collecting all the filtrates in one vessel, they were heated to 70-80 °C and concentrated using the distillation method. As a result, the volume of the meat sample filtrate was brought up to 800 ml. This solution was used to determine heavy metals in meat [6].

For potentiometric analysis of heavy metals in the meat sample solution prepared for analysis, 400 ml of the solution obtained from the meat sample was separated. This solution was divided into 3 parts for potentiometric determination of Cd^{2+}, Pb^{2+}, Hg^{2+} ions in the obtained solution. Then, the amount of Cd^{2+}, Pb^{2+}, Hg^{2+} ions was determined from this

solution. Before starting the potentiometric determination of Cd^{2+}, the U-130 ionomer was run. Then, 5 ml of the filtrate obtained from the meat sample isolated for Cd^{2+} was taken using a 10 ml graduated pipette and placed in a 50 ml titration beaker. 1 drop of 0.03 M K_3 $[Fe(CN)_6]$ solution was added to the solution to form a redox couple. Then 10 ml of distilled water was added to the solution in the beaker. A Pt indicator and a silver chloride reference electrode were washed with distilled water and immersed in the solution along with a steel piece of iron completely covered with polyethene. The solution in the beaker was placed in an MM-3M replica magnetic stirrer with electrodes and a magnetic stirrer rod. A magnetic stirrer was connected to a current and a constant rotation speed was set to continuously stir the solution during the titration. In this case, the main attention was focused on the solution not splashing and the formation of a funnel around the electrode, i.e. an air shell [7].

The ionomer was adjusted to measure the potential, and the titration was performed by adding portions of the titrant every 40-60 seconds from a standard solution of K_3 $[Fe(CN)_6]$ in a 25 mL micro burette. Since the amount of heavy metals in the tested filtrate is very low, it is advisable to perform the titration by adding portions of the titrant drop by drop.

After 40-60 seconds after adding each portion (drop) of titrant, the display of ions becomes constant, and the potential values during this period are recorded in the titration report. The volume of titrant to the drop corresponding to the largest potential jump was taken as the volume corresponding to the equivalence point. The amount of Cd^{2+} was calculated based on the results of 6-7 repeated experiments conducted in parallel. After each titration, the used vessels and electrodes were washed with distilled water. In addition to Cd^{2+}, the amount of Pb^{2+} and Hg^{2+} ions in meat solutions was determined in the same way as in the potentiometric titration of Cd^{2+} [7].

In this case, a 0.005 M $K_2Cr_2O_7$ solution was used as a titrant to determine Pb^{2+} and a drop of a 0.05 M $CrCl_3$ solution was used to form an oxidation-reduction pair, and the amount of Pb^{2+} was found.

In the potentiometric determination of Hg^{2+}, a 0.1 M solution of $NaJ*2H_2O$ was used as a titrant, and 1 drop of a 0.005 N solution of J_2 in alcohol was added to the solution to form a redox couple. Thus, the amounts of Cd^{2+}, Pb^{2+} and Hg^{2+} ions in the solution taken from the meat sample were determined by potentiometric titration and the obtained results were discussed.

In potentiometric determinations, we converted the acetates in the sample to nitrates. For this purpose, a dilute solution of NaOH was added to the second part of the filtrates of the tested meat sample. As a result, heavy metal hydroxides precipitated. The resulting precipitate was separated and washed 3-4 times in distilled water. The washed precipitate was dissolved in HNO_3 (1:10) solution. The resulting solutions were used for spectrophotometric determinations. To determine the amount of Cd^{2+}, Hg^{2+} and Fe^{3+} ions in the filtrates, the solutions converted to nitrates were divided into three parts, and spectrophotometric determinations were made from the separated solution for each metal ion. 30 minutes before starting the spectrophotometric determinations, the KFK-3 photometer was started with the cover of the cuvette compartment open. We used the gradation plot method for spectrophotometric determinations. For this, standard solutions of $Cd(NO_3)_2*4H_2O$, $Hg(NO_3)_2*2H_2O$, $Fe_2(SO_4)_3*9H_2O$ were used, and the optimal conditions for detection were selected using these solutions. First, the extract of the complex formed by the effect of dithizone on a 0.1 M chloroform standard solution of the tested metal ion in a cuvette with a thickness of 10 mm, chloroform was added to the second, and the optical density of the solution was measured [8].

The determination of mercury is carried out in the same way as the determination of Cd^{2+} by the method of formation of dithizone complexes. A 0.001% solution of dithizone in chloroform was used to extract Hg^{2+} from the standard solution. The extracts obtained in several steps were combined, and a dilute

solution of ammonia was added to remove free dithizone from the extract and the mixture was shaken. The extract was then mixed with dilute acetic acid by shaking. As a result, a reddish-yellow solution was formed. The resulting reddish-yellow solution of mercuric dithizone was transferred from a separatory funnel to a 50 ml volumetric flask, and chloroform was added up to the volumetric level of the flask. In the above order, a ranking chart was created [9].

The Hg2+ ion from beef filtrates was extracted at pH=0 (as above). The extract is reddish-yellow in colour and has a maximum optical density at a wavelength of 540 nm. The resulting extract was tested at this length.

The optical density of the extract was measured at 630 nm (maximum absorption area of dithizone) to eliminate the effect of copper(II)-ion present in the extract. After that, KJ solution is added to the extract, and when shaken, the mercury dithionate in the extract breaks down, and Hg2+ turns into HgJ42- complex at pH=4. The amount of mercury was determined based on the difference in absorption by measuring the optical density of the equivalent amount of dithizone formed during the decomposition of mercury dithizone at 620 nm.

Spectrophotometric determination of Fe^{3+} was carried out in the presence of sulfosalicylic acid by the method of a calibration diagram. For this, a 0.1 M standard solution of $Fe_2(SO_4)_3{*}9H_2O$ was first prepared. Fe^{3+} ions were adjusted to the pH value of the 0.1 M $Fe_2(SO_4)_3{*}9H_2O$ standard solution prepared following the pH values of the filtrates of the samples separated for determination. Then, 10 ml was taken from the standard solution using a graduated pipette and placed in a 50 ml volumetric flask. It was mixed by adding 10 ml of 10% sulfosalicylic acid solution. After 1 minute, 10 ml of 10% NH_3 solution in water was also added. Then distilled water was poured up to the mark of the flask. After five minutes, the yellow solution formed in the first cuvette, the second cuvette was filled with a solution containing ammonia and sulfosalicylic acid (without iron) and the optical density of the solution was measured. 0.05, 0.025 using distilled water from the remainder of this solution; 0.0125; 0.00625; 0.003125; Solutions with a concentration of 0.0015625 M were prepared. The optical densities of these solutions were measured at a selected wavelength (680 nm). A gradation plot was constructed based on the measured values. Then, for the spectrophotometric determination of the amount of Fe^{3+} in the filtrates of the samples separated for the Fe^{3+} ion, 10 ml was measured in a pipette and placed in a 50 ml measuring flask. 10 ml of 10% sulfosalicylic acid solution was added to the solution and mixed. After 1 min, 10 ml of 10% NH_3 solution in water was also added and distilled water was added up to the volumetric level of the flask. The optical density of the resulting solution at a wavelength of 680 nm was determined and the obtained value was placed on the calibration chart. On this basis, the amount of Fe^{3+} in meat was determined [10].

Discussion

For potentiometric determination of heavy metal ions (Pb^{2+}, Cd^{2+}, Hg^{2+}), their ox radiometric capabilities were used.

Since the Pb^{2+} ion is electroactive in the aqueous solution under the given conditions, in order to determine the endpoint, the oxidation-reduction pair is formed at the expense of the titrant, that is, 1 drop of 0.02884 M CrCl3 solution is added to the solution to form the $Cr_2O_7^{2-}/Cr^{3+}$ pair. During the titration, $PbCrO_4$ precipitates. The resulting precipitate has low solubility,($K^0_s = 1{,}8{*}10^{-14}$).is enough.

$2Pb^{2+} + Cr_2O_7^{2-} + H_2O \rightarrow \downarrow 2PbCrO_4 + 2H^+$

The last drop of K2Cr2O7 added when the titratable Pb2+ in the solution was depleted caused an increase in the electrode potential. The rise of the potential after the equivalence point

$$E = 1{,}33 + \frac{0{,}059}{6} lg \frac{[Cr_2O_7^{2-}] * [H^+]^{14}}{[Cr^{3+}]^2}$$

can be explained using the formula

According to the results of the titration, the amount of Pb2+ ion in meat (lamb) was on average 9.02 mg/kg. The number of parallel detections was equal to 7 in the first case and 9 in the second case.

The following reaction was used to determine the Cd^{2+} ion:

$2Cd^{2+} + K_4[Fe(CN)_6] \rightarrow \downarrow Cd_2[Fe(CN)_6] + 4K^+$

Titration was performed by dropwise addition of titrant (0.004903 M $K_2Cr_2O_7$) as beef meat contained little Pb^{2+}. At the endpoint of the titration, the potential jump was around 15 mv. The solubility of the resulting precipitate is low and is Cos=3.2*10-17.

A drop of a 0.0291 M solution of K3 [Fe(CN)6] was added to the test solution to generate the redox potential.

Reduction of potential after the equivalence point:

$$E = 0{,}356 + 0{,}059\ lg\frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$$

is represented by the formula.

A titrant ($K_4[Fe(CN)_6]$ 0.004229 M) was also added dropwise in the determination of Cd^{2+} in meat. The potential jump at the equivalence point of the titrant was around 50 mv. The number of conducted parallel experiments according to (4 and 7). The amount of Cd^{2+} in meat (lamb) was 7.49 mg/kg.

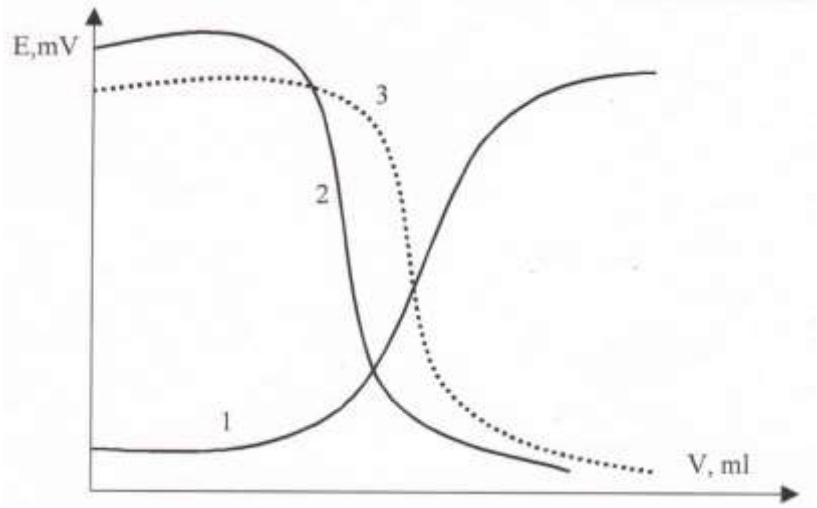

Figure 1. Potentiometric titration curves of heavy metal ions. 1 — Pb^{2+}, 2 — Hg^{2+}, 3 — Cd^{2+}

The determination of the Hg^{2+} ion was based on its binding to the complex by the J- effect:

$$Hg^{2+} + 2NaJ \xrightarrow[-2Na]{} HgJ_2 \xrightarrow{+2NaJ} [HgJ_4]^{2-}$$

A drop of 0.005 N solution of iodine was added to the test solution to form a redox couple. In this, the change in potential during the titration

$$E = 0{,}536 + \frac{0{,}059}{2} lg\frac{[J_2]}{[J^-]^2}$$

is explained using the formula.

Determination of Hg^{2+} content in meat products was also performed based on dropwise titration. According to the obtained results, the amount of Hg^{2+} was 7.22 mg/kg. 5 and 7 parallel experiments were performed to evaluate the reproducibility of mercury determination. These values are above the permissible concentration limit. The results of the potentiometric determination of the number of heavy metals in beef are presented in Table 1.

Table 1. Potentiometric determination of heavy metal ions in meat products detection results

Object	R, mg			S, mg			Error, %		
	Pb^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}	Cd^{2+}	Hg^{2+}
Meat	9.02	7.49	7.22	0.04	0.03	0.03	0.98	1.23	1.15

The accuracy of the obtained results was evaluated using the spectrophotometric method. For the spectrophotometric determination of heavy metal ions (Fe^{3+} Cd^{2+}

Hg^{2+}), we used their formation of coloured complexes with various organic compounds. Iron (III) ion forms a yellow complex compound with sulfosalicylic acid in an ammonia medium. The Hg^{2+} ion forms an orange complex in chloroform solution, and the Cd^{2+} ion forms a pink complex.

The optimal conditions for detection were selected using a 0.05 M solution of the resulting colour solution. For this purpose, a corresponding solution was placed in a cuvette with a thickness of 10 mm, and its optical density was measured in the wavelength range from 310 nm to 998 nm in relation to the non-ionic solvent under investigation. The resulting spectra are presented in Figure 2. The experiments showed that the Hg^{2+} ion had the maximum optical density at a wavelength of 540 nm (Fig. 2, curve 1).

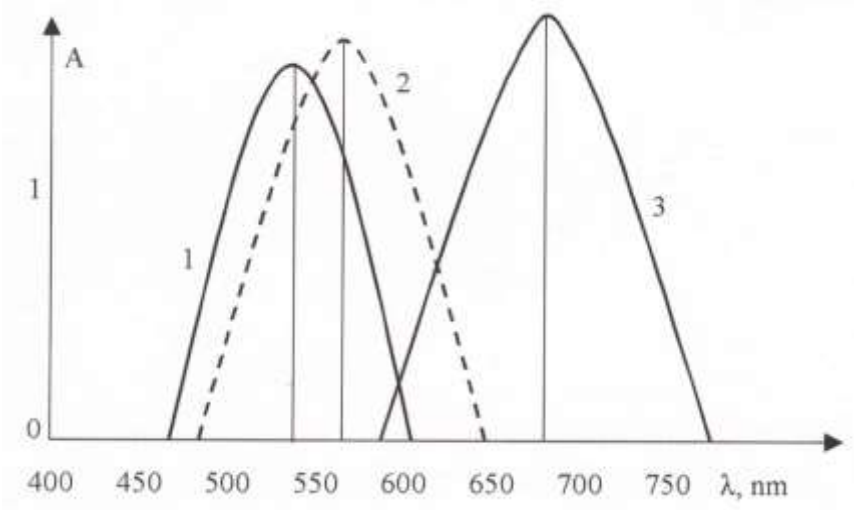

Figure 2. UV spectra of heavy metal solutions: 1 – Hg^{2+} ; 2 – Cd^{2+} ; 3 – Fe^{3+}

Optical densities showed a linear relationship (Fig. 3, curve 2) in the concentration range of 0.00625 – 0.05 M. And the Cd^{2+} ion has the maximum optical density at a wavelength of 560 nm (Fig. 2, curve 2), and the optical densities show a straight line in the concentration range of 0.0125 - 0.1 M got the appearance (Fig. 3, line 1). The maximum optical density of Fe^{3+} ion (Fig. 2, curve 3) corresponded to the wavelength of 680 nm. Iron (III) ion had a straight line (Fig. 3, line 3) in the concentration range of 0.0015625 – 0.05 M. Parallel experiments were performed to ensure the reproducibility of the analysis. Ranking plots were made based on the average of the results of 3-4 parallel experiments. 4 parallel experiments were conducted to determine the amount of iron in beef. The obtained results (Table 2) show that the average amount of iron in meat was 0.48 mg/kg. This is very close to the established norm. 5 and 9 parallel experiments were conducted to determine the amount of mercury (in beef extracts), respectively. Based on the obtained results (Table 2), shows that the amount of mercury in beef is 7.24 mg/kg, which is much higher than the prescribed values. The results of the determination of the number of metals in meat products using the spectrophotometric method are presented in Table 2. 5 and 9 parallel experiments were conducted to determine the amount of mercury (in beef extracts), respectively.

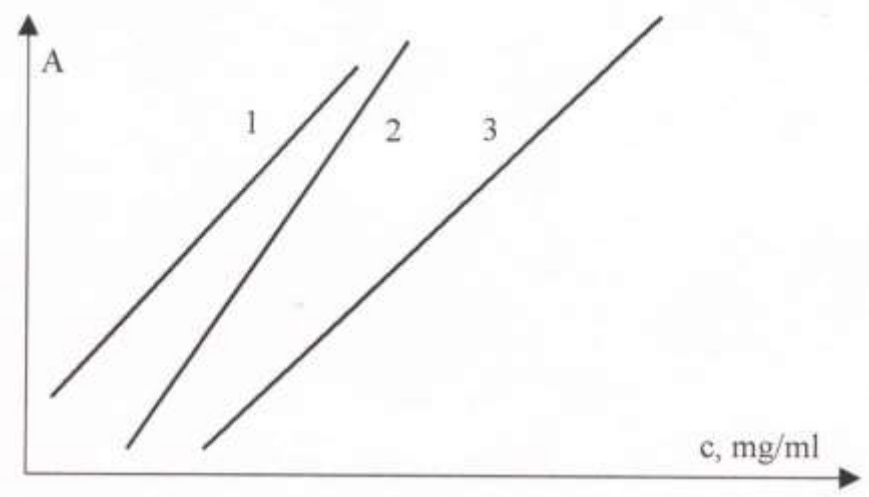

Figure 3. Grading charts of heavy metal ions:
1 — Cd^{2+}; 2 — Hg^{2+}; 3 — Fe^{3+}

5 and 7 parallel experiments were performed to evaluate the reproducibility of the results, with the cadmium content of the meat being 7.48 mg/kg, respectively. All obtained results were evaluated using mathematical statistical methods. The standard deviation did not exceed 0.05 mg. This indicates that they are sufficiently accurate.

Table 2. Spectrophotometric determination of heavy metal ions in meat detection results

Object	X, mg			S, mg			Error, %		
	Fe^{3+}	Cd^{2+}	Hg^{2+}	Fe^{3+}	Cd^{2+}	Hg^{2+}	Fe^{3+}	Cd^{2+}	Hg^{2+}
Meat	0.48	7.48	7.24	0.02	0.03	0.04	10.60	1.11	1.53

The results of spectrophotometric determinations were compared with the results of potentiometric titration and their accuracy was assessed. The closeness of the results obtained using both methods, and in many cases the compatibility, indicates the correctness of the results.

Conclusion

1. The method of transfer of heavy metal ions in beef meat to the solution was developed. Taking advantage of the fact that the nitrates of the examined heavy metal ions are well soluble in water, it was possible to transfer them to the solution in the form of nitrates.
2. Potentiometric oxradiometric titration and spectrophotometric methods were used to determine the number of heavy metal ions in beef.
3. Potentiometric oxradiometric titration of mercury ion in beef meat with NaJ (with J2), titration of a lead ion with $K_2Cr_2O_7$ (Cr^{3+} (with Cr^{3+}) and titration of Cd^{2+} ion with K_4 $[Fe(CN)_6]$ (K_3 $[Fe(CN)_6]$ with the participation) was conducted using.
4. For spectrophotometric determination of the amount of heavy metal ions in beef meat, coloured complexes of Fe^{3+} formed with sulfosalicylic acid, Hg^{2+} and cadmium in chloroform solution with ditozone were used.
5. The values obtained by potentiometric and spectrophotometric methods were used to assess the accuracy and correctness of the results. The mutual compatibility of the obtained results indicates their correctness.

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