Photometric microtitration of iron by using 7-(o-carboxyphenylazo)-8-hydroxyquinoline-5-sulfonic acid

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The complex-forming equilibria of 7-(o-carboxyphenylazo)-8-hydroxy-quinoline-5-sulfonic acid (indicator OKFAZOX) with Fe(III) ions were investigated by spectrophotometric methods in the pH range 1.5—3. It has been found that OKFAZOX forms with Fe(III) complexes in the stoichiometric ratio $c_{Fe} : c_{ind} = 1$ 1 with conditional stability constant $\log \beta'_{Fe(ind)} = 5.60 \pm 0.02$ and in the stoichiometric ratio $c_{Fe} : c_{ind} = 1$ 2 with conditional stability constant $\log \beta'_{Fe(ind)_2} = 10.50 \pm 0.05$ (pH = 2.56, $I = 0.1$ mol dm^{-3}).

The indicator OKFAZOX is suited to chelatometric determination of iron with photometric indication. Provided the titration is carried out at pH = 3 and $c_{ind} = 8 \times 10^{-6}$ mol dm^{-3} and is photometrically observed at the wavelength of 510 nm, it gives correct and accurate results. The method is also applicable in the region of micromolar concentrations. The presence of Al, Cr, Mn, and Zn does not interfere. The interfering effect of Cu and Pb may be eliminated by reducing the pH value during determination to ≈ 1.7.

The developed method was applied to practical samples of drinking and utility water.

Спектрофотометрическими методами были изучены равновесия комплексообразования 7-(o-карбоксифенилазо)-8-гидроксихинолин-5-сульфокислоты (индикатор OKFAZOX) с ионами железа в интервале pH = 1,5—3. Было найдено, что OKFAZOX образует с Fe(III) комплексы в стехиометрическом отношении $c_{Fe} : c_{ind} = 1$ 1 с условной константой устойчивости $\log \beta'_{Fe(ind)} = 5,60 \pm 0,02$ и $c_{Fe} : c_{ind} = 1$ 2 с условной константой устойчивости $\log \beta'_{Fe(ind)_2} = 10,50 \pm 0,05$ (pH = 2,56; $I = 0,1$).

Индикатор OKFAZOX пригоден для хелатометрического определения железа с фотометрической индикацией. Если титрование проводится при pH = 3 с применением $c_{ind} = 8 \cdot 10^{-6}$ моль дм$^{-3}$ и фотометрически наблюдается при длине волны 510 нм, то получаются достоверные и точные результаты. Метод применим и в области микромолярных концентраций. Присутствие Al, Cr, Mn и Zn не мешает определению. Мешающее действие Cu и Pb можно отстранить снижением величины pH, при котором проводится определение, до ≈1,7.

Разработанный метод был применен на практических образцах питьевой и хозяйственной воды.

Several indicators were proposed for the chelatometric determination of iron. They are mainly simple substances such as KSCN [1], sulfosalicylic acid [2, 3], tiron [4], NaN_3 [5] and others. However, the sharpness of colour transitions of these indicators is very poor, especially at higher concentrations of iron where the yellow colour of the arising Fe—EDTA complex has a disturbing effect.

For this reason, it is not recommended in literature [6] to use the complexometric determination of iron and, on the contrary, other methods are preferred. The transfer of chelatometric titration into microscale and simultaneous spectrophotometric investigation of the course of titration, however, represent in the region of micromolar concentrations one of the most accurate and temporally as well as economically unpretending methods, i.e. the method of photometric microtitration.

The finding of a convenient metallochromic indicator for direct complexometric determination of trivalent iron which would exhibit a sharp colour transition in the point of equivalence and the corresponding photometric titration which could give correct results would be a contribution for analytical chemistry. The importance of such determination would manifest itself especially in practical and rapid analyses in which different mixtures of cations, e.g. Fe—Al, Fe—Cr, Fe—Mn, Fe—Cu, Fe—Mn—Al—Ca—Mg, etc. are to be determined without any separation.

This study is concerned with elaboration of a method of photometric microtitration which allows to determine low concentrations of iron and fulfils the above-mentioned conditions.

The selection of a metallochromic indicator for the determination of a given metal is determined by the value of dissociation constants of indicator, number and stoichiometry of arising complexes and their stability.

The preliminary determinations of the dissociation constants of 7-(o-carboxyphenylazo)-8-hydroxyquinoline-5-sulfonic acid [7] and the study of its complex-forming equilibria with the Cu(II) ions [8] have revealed the existence of very stable complexes from which it results that the investigated acid of the structural formula

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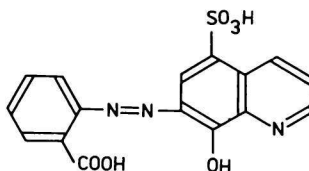
called OKFAZOX [8], is able to fulfil the conditions of a convenient metallo-chromic indicator for the determination of iron by photometric microtitration.

Experimental

Chemicals and solutions

The preparation and purification of 7-(o-carboxyphenylazo)-8-hydroxyquinoline-5-sulfonic acid were described in the preceding paper [7]. The data concerning current reagents and preparation of necessary solutions are given in papers [8, 9]. The volumetric solution of Fe(III) ions $(c = 10^{-3}\ mol\ dm^{-3})$ was prepared by weighing and dissolving $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$. The concentration of solution was ascertained by direct photometric titration of the Fe(III) salt with Chelaton 3 at the wavelength $\lambda = 390$ nm.

Instruments and equipment

The used instruments and evaluation of experimental data are described in preceding papers [7—9].

Results and discussion

Complex-forming equilibria of 7-(o-carboxyphenylazo)- -8-hydroxyquinoline-5-sulfonic acid with Fe(III) ions

First of all, the formation of complexes of the mentioned reaction system was investigated as a function of pH. For the concentration ratio $c_{Fe} : c_{ind} = 1\ \ 1$, the absorption spectra were measured from pH ≈ 1.5, where the ligand exists as H_3(ind) [7], up to pH ≈ 3 (Fig. 1). The obtained absorption curves intersect themselves in one point at $\lambda = 450$ nm. The A—pH curves also exhibit in the above pH range only one colour transition (Fig. 2). Though OKFAZOX represents a tribasic acid, it may be deduced from the plots in Figs. 1 and 2 that only a simple equilibrium is operative from the view-point of deprotonation of ligand in the investigated region. Higher values of pH were not subjected to measurement because the hydrolysis of Fe(III) ions takes place in this case.
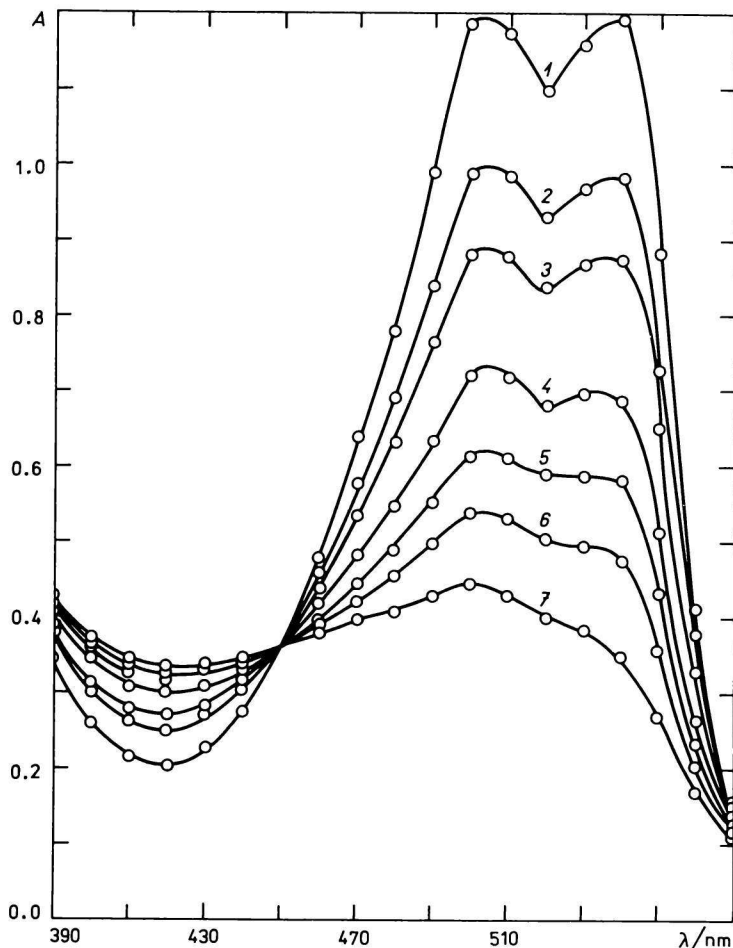
Fig. 1. Absorption spectra of the indicator OKFAZOX in the presence of Fe(III)
at varying value of pH.
$c_{ind} = 4.93 \times 10^{-5}$ mol dm^{-3}, $c_{Fe} = 4.92 \times 10^{-5}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}
(ClCH$_2$COOH + ClCH$_2$COONa), $d = 9.98$ mm, $\theta = 25$ °C.
pH Values of solutions: *1.* (1.72); *2.* (2.06); *3.* (2.19); *4.* (2.41); *5.* (2.58); *6.* (2.76); *7.* (3.12).

The stoichiometric ratio of the complexes arising in the reaction of OKFAZOX
with the Fe(III) ions at pH = 3 was investigated by the method of mole ratios and
Job curves. Fig. 3 represents the absorption spectra at different mole ratios. This
figure shows that the Fe(III) ions are able to form with OKFAZOX more than one
complex. The plots of absorption spectra intersect themselves up to the value of
mole ratio $c_{Fe}/c_{ind} \approx 0.5$ in a sharp isobestic point at $\lambda = 446$ nm while a less distinct

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Fig. 2. A—pH curves of OKFAZOX with Fe(III) and A—pH curves of pure indicator at different wavelengths.
$c_{ind} = 4.93 \times 10^{-5}$ mol dm^{-3}, $c_{Fe} = 4.92 \times 10^{-5}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} (ClCH$_2$COOH + ClCH$_2$COONa), $d = 9.98$ mm, $\theta = 25$ °C.
Wavelengths (λ/nm): pure indicator ○ 480; ● 470; OKFAZOX + Fe(III) □ 480; ■ 470.
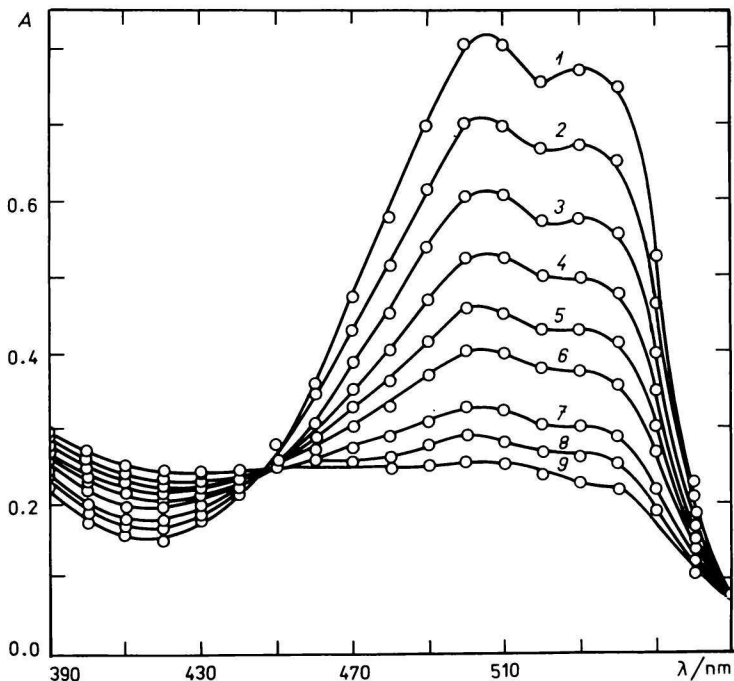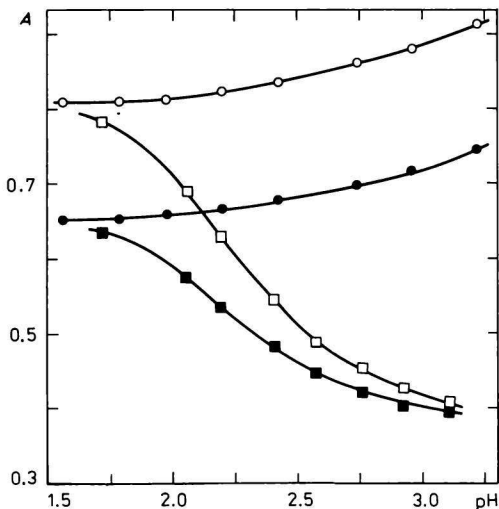

Fig. 3. Absorption spectra of solutions of OKFAZOX at varying concentration of Fe(III) and pH = 2.56.
$c_{ind} = 3.52 \times 10^{-5}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} (ClCH$_2$COOH + ClCH$_2$COONa), $d = 9.98$ mm, $\theta = 25$ °C.
Concentration ratios c_{Fe}/c_{ind}: 1. (0.051); 2. (0.152); 3. (0.254); 4. (0.355); 5. (0.457); 6. (0.559); 7. (0.761); 8. (0.965); 9. (1.27).

intersection appears at $\lambda = 452$ nm for higher mole ratios in the range $c_{Fe}/c_{ind} = 0.86$—1.27. Thus we may assume that two complex particles of the stoichiometry $c_{Fe}/c_{ind} = 1$ 1 and 1 2 are formed in the reaction system. The absorption spectra at different mole ratios were evaluated by the program SQUAD [10]. On the basis of regression matrix analysis of spectra, the supposed chemical model for the existence of two complex particles in the solution was, in principle, evidenced. The relationships between molar absorption coefficients and wavelengths were calculated for individual coloured particles in the solution (Fig. 4). Moreover, the distribution diagram for individual particles at varying mole ratio c_{Fe}/c_{ind} (Fig. 5) and the conditional stability constants of the arising complexes $\log \beta'_{Fe(ind)} = 5.6 \pm 0.02$ and $\log \beta'_{Fe(ind)_2} = 10.5 \pm 0.05$ (pH = 2.56, $I = 0.1$ mol dm^{-3}) were derived.

It is obvious from the obtained results that the arising complexes are relatively solid and their relative stabilities are close. This fact brings about that both complexes start to arise simultaneously at the beginning of the experiments with varying mole ratios, but the complex Fe(ind)$_2$ initially prevails. Besides, provided the mole ratio $c_{Fe}/c_{ind} \approx 1$, the complex Fe(ind) is not solely formed, but a considerable concentration of the complex Fe(ind)$_2$ also exists in the solution. Nevertheless, the complex Fe(ind) prevails.
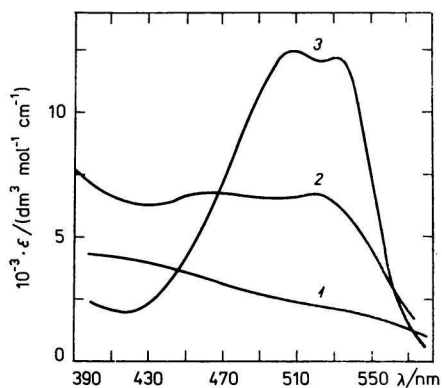

Fig. 4. Molar absorption coefficients ($\varepsilon /$ /(dm^3 mol^{-1} cm^{-1})) of complex particles in the system OKFAZOX + Fe(III) at pH = 2.56 calculated by matrix analysis from absorption spectra.
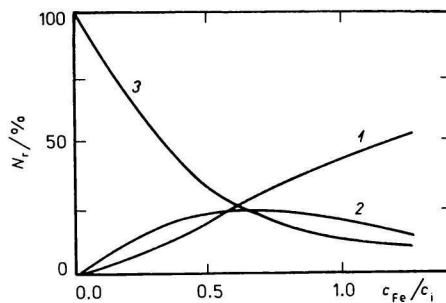Individual curves are for particles:
1. (Fe(ind)); 2. (Fe(ind)$_2$); 3. (ind).

Fig. 5. Distribution diagram of relative portion (N_r/%) of the products of complex-forming equilibrium of OKFAZOX with Fe(III) as a function of iron concentration.
$c_{ind} = 3.52 \times 10^{-5}$ mol dm^{-3}, pH = 2.56, $I = 0.1$ mol dm^{-3} (ClCH$_2$COOH + + ClCH$_2$COONa), $d = 9.98$ mm, $\theta = 25$ °C.
Individual curves are for particles: 1. (Fe(ind)); 2. (Fe(ind)$_2$); 3. (ind).

On the basis of this fact, we must regard the experimental intersections of the plots of spectra as some pseudoisobestic points (Figs. 1 and 3) which appear in spite of the fact that two equilibria take place in the solution.

In acid-base investigations involving the concentration ratio $c_{Fe}/c_{ind} \approx 1$ the complexes Fe(ind) and Fe(ind)$_2$ simultaneously arise, but the complex Fe(ind) prevails. As both complexes have similar relative stability and the calculated value of $\varepsilon_{Fe(ind)_2}$ at the wavelength $\lambda = 450$ nm is approximately the double of the value of $\varepsilon_{Fe(ind)}$ at the wavelength $\lambda = 450$ nm (Fig. 4), the measured A—pH relationships arise in equal ratio and an intersection like in simple equilibrium appears in the spectra.

If the method of mole ratios is used, the intersection in the plots of spectra appears almost up to the ratio $c_{Fe}/c_{ind} = 0.5$ because the concentrations of both complexes initially increase linearly and thus it is valid again that the calculated value of $\varepsilon_{Fe(ind)_2}$ for the wavelength 446 nm is approximately the double of the value of $\varepsilon_{Fe(ind)}$ of pseudoisobest, owing to which the resulting value of absorbance for a given value of λ is practically constant in the interval of linear increase in both concentrations.

The analysis of the plots of continual variations (measured at pH = 2.56 and $I = 0.1$ mol dm^{-3}) also confirms the existence of two complexes of the stoichiometric ratio $c_{Fe}/c_{ind} = 1$ 1 and 1 2. The maxima of the Job plots are not exactly over each other and vary in the interval between $x_{Fe} = 0.33$ and $x_{Fe} = 0.45$ (Fig. 6).
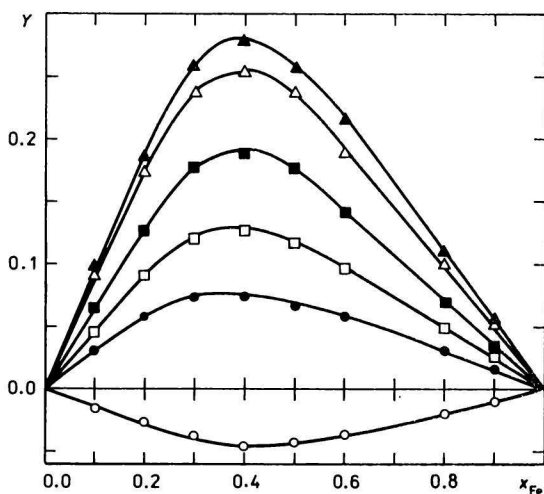

Fig. 6. The Job curves for the system OKFAZOX + Fe(III).
$c = 7.06 \times 10^{-5}$ mol dm^{-3}, pH = 2.56, $I = 0.1$ mol dm^{-3} (ClCH$_2$COOH + ClCH$_2$COONa),
$d = 9.98$ mm, $\theta = 25$ °C.
Wavelengths (λ/nm): $\bigcirc$ 410; $\bullet$ 460; $\square$ 470; $\blacksquare$ 480; $\triangle$ 490; $\blacktriangle$ 520.

*Photometric microtitration of Fe(III) by means of the
indicator OKFAZOX*

For delimitating the optimum conditions of the proper determination of Fe(III), the knowledge obtained from the study of protonation and complex-forming equilibria was used.

The influence of medium on the course of photometric titration and coherent form of titration curves with possibility of their evaluation was verified by means of a series of titration curves obtained at certain values of pH, ionic strength, and concentration of indicators. pH ≈ 3 may be recommended as the most convenient value. At higher values of pH the hydrolysis of the Fe(III) ions takes place while the colour transition of the metallochromic indicator becomes less distinct at lower
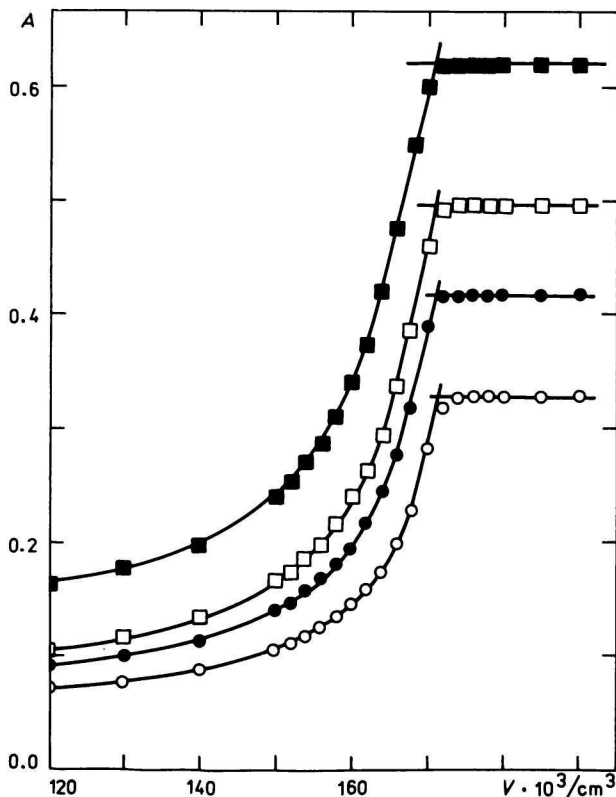

Fig. 7. Photometric titration curves of Fe(III) for different concentrations of OKFAZOX.
$\lambda = 510$ nm, pH $= 3.06$, $I = 0.1$ mol dm^{-3} (ClCH$_2$COOH + ClCH$_2$COONa), titrated with a solution of EDTA ($c = 9.86 \times 10^{-3}$ mol dm^{-3}).
Concentrations of indicator (c/(mol dm^{-3})): ○ 4.9×10^{-6}; ● 6.5×10^{-6}; □ 8.1×10^{-6}; ■ 9.8×10^{-6}

values of pH. The greatest differences in colour of the investigated reaction system occur in the range of wavelengths 510—530 nm and for this reason, the photometric titration curves give a good possibility of graphical extrapolation for evaluating the end-point of titration. The photometric titration curves of Fe(III) for different concentrations of indicator are represented in Fig. 7. It is obvious from the form of these curves that an increased concentration of indicators has no influence on the position of the end-point of titration and is more convenient for graphical extrapolation.

The photometric titration of Fe(III) performed under described conditions gives titration curves with sheer ascending linear section which is abruptly broken in the point of equivalence. The results of determinations by this method are given in Table 1. All values were corrected with respect to blank test. For completeness, the

Table 1

Reproducibility of the determination of Fe(III) by means of OKFAZOX under optimum conditions $\lambda = 510$ nm, pH = 3.02, $I = 0.1$ mol dm^{-3} (CH$_3$COONa + HClO$_4$), $c_{ind} = 7.62 \times 10^{-6}$ mol dm^{-3}; titrated with a solution of EDTA ($c = 9.77 \times 10^{-3}$ mol dm^{-3})

Experiment	Consumption EDTA $V \ 10^3/\text{cm}^3$	Found Fe(III) $m/\mu\text{g}$	Relative error %
	Theoretical consumption $V_e = 96.20 \ 10^{-3}$ cm^3 EDTA given 52.49 μg Fe(III)		
1	96.36	52.58	0.17
2	96.36	52.58	0.17
3	96.06	52.42	− 0.13
4	95.87	52.31	− 0.34
5	96.36	52.58	0.17

Arithmetic mean: $\bar{x} = 52.49$ μg.
Estimation of standard deviation: $s_r = 0.12$.
Interval of reliability for the significance level $1 - \alpha = 0.95$: (52.49 ± 0.14) μg.

dependence of consumption of the titrating agent on concentration of the determined metal was investigated. The obtained results are given in Table 2. It is evident from this table that the results obtained by graphical extrapolation of the photometric titration curves correspond to the determined amount of the Fe(III) ions.

Table 2

Determination of Fe(III) ions by photometric microtitration with OKFAZOX under optimum conditions at different iron concentrations

Experiment	Theoretical consumption $V \ 10^3/cm^3$	Real consumption $V \ 10^3/cm^3$	Given Fe(III) $m/\mu g$	Found $m/\mu g$	Relative error %
		Titrated with EDTA ($c = 9.77 \times 10^{-3}$ mol dm^{-3})			
1	192.38	192.38	104.97	104.97	0
2	153.91	153.97	83.98	84.01	0.04
3	96.19	96.36	52.48	52.58	0.19
4	57.72	57.85	31.49	31.56	0.22
		Titrated with EDTA ($c = 3.96 \times 10^{-3}$ mol dm^{-3})			
5	71.54	71.44	15.81	15.79	− 0.13
6	50.07	49.44	11.07	10.93	− 1.26
7	35.77	36.32	7.91	8.02	1.39
8	21.46	21.49	4.74	4.75	0.21

Determination of Fe(III) by means of OKFAZOX in the presence of some bivalent and trivalent metals

The fact that the Fe(III) ions rarely occur alone in practical samples inspired the investigation of the influence of the presence of some bivalent and trivalent metals on the proper determination of iron. It has been found that the presence of Al(III), Cr(III), Mn(II), and Zn(II) does not interfere under the described conditions. However, an increased consumption of the titrating agent appeared in the presence of Cu(II) and Pb(II). The influence of Cu(II) ions was eliminated by reducing the pH value of the titration solution. If Fe(III) is determined in the presence of Cu(II) at pH = 1.72 a differentiation appears on the photometric titration curve in the form of two jumps and not only the quantity of iron can be determined but also the quantity of copper (Fig. 8). In contrast to expectation, the Fe(III) ions are titrated after the Cu(II) ions under the above-mentioned experimental conditions. This observation was verified for a great number of the concentration ratios c_{Fe}/c_{Cu} and an exact explanation would require a detailed study of the structure and stability of all participating complexes.

The interfering effect of Pb(II) can be also eliminated by reducing the pH value. If the photometric titration of a mixture Fe(III) + Pb(II) is carried out in acid medium at pH = 1.72, the consumption of Chelaton 3 corresponds only to the content of Fe(III). The bivalent lead is not titrated under these conditions.
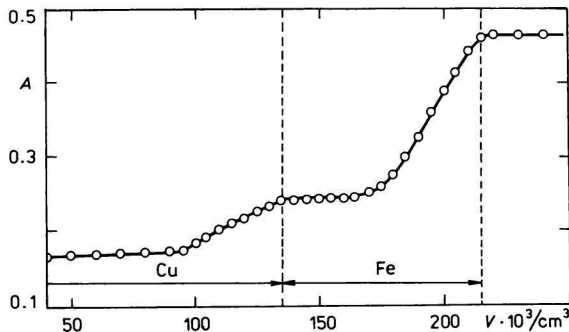
Fig. 8. Photometric titration curves of Fe(III) obtained by means of OKFAZOX in the presence of Cu(II).

$\lambda = 510$ nm, pH $= 1.72$, $I = 0.1$ mol dm^{-3} (ClCH$_2$COOH + ClCH$_2$COONa), titrated with a solution of EDTA ($c = 1.28 \times 10^{-2}$ mol dm^{-3}).

The elaborated method of the determination of Fe(III) by means of OKFAZOX makes possible to determine iron reliably even in the region of micromolar concentrations. The virtue of the method is a relatively good selectivity which enables to determine iron in the presence of different admixtures, *i.e.* Al, Mn, Cr, Cu, Pb, and Zn without preceding separation. This method was applied to analysis of the samples of drinking and utility water.

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