

THE EXTRACTION AND PHOTOMETRIC DETERMINATION
OF IRON AS THE COMPLEX
WITH ETHYLENEDIAMINE-N-N'-BIS-(*o*-HYDROXYPHENYLACETIC) ACID

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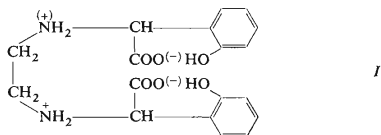
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Received February 24th, 1971

A new method for the extraction-photometric determination of iron has been developed based on the formation of the intensively red complex of iron with ethylenediamine-N-N'-bis(*o*-hydroxyphenyl acetic) acid and its extraction with a chloroform solution of trioctylmethylammonium chloride. Copper, cobalt, nickel, chromium, manganese, zinc, and a number of further elements do not disturb the determination even if present at high concentrations (up to the ratio 1 : 1000). By this method, less than 1 μg Fe can be determined in 1 ml of the extract, even after extraction from a large volume of aqueous solution.

Ethylenediamine-N-N'-bis(*o*-hydroxyphenylacetic) acid (EDHPA), or N-N'-ethylene-bis-2-(*o*-hydroxyphenyl)-glycine (EHPG) (I) is a very interesting substance of the "complexone type", since it forms an intensively red 1 : 1 complex with trivalent iron at pH 2–10 which can be considered as one of the most stable complexes of this type ($\log K_{\text{FeY}} 33.9$, see¹). Divalent iron is easily oxidized in the presence of the reagent to form the same complex, FeY.



The complex forming properties of this substance were studied in more detail by Martell and his coworkers². The stability constant of the iron complex was determined by Anderegg and L'Eplattenier¹. The colour reaction of EDHPA for iron was used by Underwood for the colorimetric determination of iron in aluminum alloys³ and for the spectrophotometric titration of very small amounts of iron⁴. In acid media, the Fe-EDHPA complex is less stable than the similar Fe-EDTA complex. For this reason, the described reagent can also be used as a complexometric indicator of the determination of iron at pH 1.2–2.0 (see¹). The absorption spectra of the Fe-EDHPA complex was measured by Hill-Cottingham⁵, who applied this measurement to the determination of free EDHPA and of its iron complex in soil extracts⁶.

The reaction of trivalent iron with EDHPA is disturbed by the presence of elements which form sufficiently stable and coloured complexes with the reagent. These are mainly copper, cobalt, and nickel, which, as is well known, also interfere in other methods for iron determination, such as the widely used reaction with *o*-phenanthroline. Johnson and Young⁷ attempted to decrease this interference by using a neutral citrate buffer and a relatively small excess of reagent compared to the expected amount of iron. Since the equilibrium between the citrate complex of iron and the reagent is established very slowly, the authors recommend measuring the absorption 18 hours after preparing the solution. However, even with these "optimum conditions", it is not possible to consider the results as satisfactory in the presence of copper, which strongly hinders the formation of the complex. Thus, for example, at a copper concentration of 40 p.p.m., the error in determining 6 p.p.m. of Fe was -92%, which can only be partially lowered by higher concentrations of the reagent. The situation is also similar in the presence of cobalt and nickel, which also compete with the formation of the Fe-EDHPA complex. All the experiments described to date were carried out in aqueous solutions.

During preliminary experiments, the present authors discovered that the Fe-EDHPA complex is easily extracted into a chloroform solution of trioctylamine and trioctylmethylammonium chloride, while the corresponding complexes of copper, nickel, and cobalt are either not extracted at all, or are only extracted slightly at higher concentrations of the element. This discovery became the basis for developing a new method for determining trace amounts of iron, in the presence of the mentioned elements, whose high selectivity and simplicity of operation exceed even that of the phenanthroline method.

EXPERIMENTAL AND RESULTS

Reagents and Apparatus

A 5% solution of trioctylmethylammonium chloride was prepared by dissolving 50 g (about 0.12 mol) of the substance (Aliquat 336-S, General Mills Inc., Kankakee, Illinois, U.S.A.) in 1000 g of pure chloroform. According to the manufacturer's specifications, the material contains a few percent of higher amines with nine or ten carbon atoms. The material was used without further purification.

A $5.10^{-3}M$ solution of EDHPA was prepared from 0.182 g of the material (CHEL-DP, Ciba-Geigy Corporation, Ardsley, New York) suspended in 50 ml of redistilled water. 1M-NaOH was added dropwise to the suspension to a pH of 8.5-9. After dissolving, the solution was diluted to 100 ml with redistilled water. The solution is sufficiently stable. If the substance is not sufficiently pure, and after dissolving in sodium hydroxide gives a yellow to yellow-brown coloured solution, purification may be carried out by extracting 100 ml of the reagent twice with 10 ml of 5% Aliquat and once with 10 ml of pure chloroform. After separation of the phases, if necessary after centrifuging the dispersed chloroform droplets, the solution can be used freely.

The copper solution (10 mg/ml) was prepared by dissolving 1 g of electrolytic copper free of iron (Outokumpu Oy, Popri, Finland) in an appropriate amount of nitric acid and evaporating almost to dryness with several drops of sulphuric acid. The damp residue was dissolved in 100 ml of redistilled water. Solutions containing 10 mg/ml nickel or cobalt were prepared by a similar method from 1 g of the p.a. metal. A 0.05M solution of trivalent iron was prepared from analytically pure ferric ammonium sulphate (or from the Mohr Salt), and the iron content was controlled

complexometrically. The corresponding diluted solution contained $27.92 \mu\text{g/ml}$ of Fe (5.10^{-4}M). The remaining chemicals used were of p.a. purity.

Photometric measurements were carried out on the spectrophotometer UVS-1 (Zeiss, Jena); pH was measured using the Precision pH Meter OP-205 (Radelkis, Hungary) and a glass electrode.

Absorption Spectrum of the Complex and the Calibration Curve

Measurement of the absorption spectrum of the Fe-EDHPA complex both in aqueous solution and in the extract (at the same Fe concentration) was carried out thus: to a 25 ml volumetric flask was pipetted 5 ml of the $5 \cdot 10^{-4} \text{M}$ iron solution, 1 ml of glacial acetic acid, and 5 ml of $5 \cdot 10^{-3} \text{M}$ reagent. After mixing, the mixture was diluted to the mark with redistilled water (Solution A). In the same way, a reference solution without iron was prepared. The spectrum of the solution was measured in a 1 cm cuvette in the wavelength range 400–630 nm (Fig. 1).

5 ml of solution A was pipetted into a 150 ml separating funnel, diluted with water to about 25 ml, 2 ml of saturated sodium sulphate were added, and the solution was extracted 1–2 minutes with 5 ml of a 5% chloroform solution of Aliquat. The spectrum of the extract was measured in the same way against a corresponding blank. In both cases the concentration of iron is the same ($5.3 \mu\text{g/ml}$) and, for this reason, the spectra are almost identical, with a maximum at 480 nm. This shape agrees with earlier results⁵. The lower curves in Fig. 1 show the absorption of the blank solutions against pure Aliquat. Under the described conditions their absorption is negligible and the solution can be measured directly against a chloroform solution of Aliquat.

0.2 to 2.0 ml of $5 \cdot 10^{-4} \text{M}$ iron solution were pipetted progressively into 150 ml separatory funnels, and were diluted to about 25 ml. 1 ml of glacial acetic acid and 5 ml of the reagent were added and extracted for 1–2 minutes with 5 ml of Aliquat solution and 2 ml of saturated sodium sulphate were then added. After extraction and filtering the extract through a dry filter, the absorbance was measured at 480 nm. The concentration dependence according to Beer's law holds for 5–56 μg Fe in 5 ml of the chloroform extract. The above described procedure was preserved during further measurements.

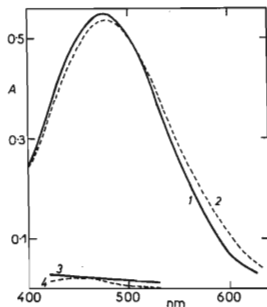


FIG. 1

The absorption Spectrum of the Fe-EDHPA Complex

Curve 1: $1 \cdot 10^{-4} \text{M}$ -Fe, $1 \cdot 10^{-3} \text{M}$ -EDHPA, 1 ml $\text{CH}_3\text{COOH}/25 \text{ ml}$; 1 cm cuvettes; an iron-free blank. Curve 2: the extract of the previous solution with the same amount of a 5% Aliquat solution in chloroform; curves 3, 4: the blanks against water.

Dependence on pH, Volume of the Solution, and Anions

In spite of the fact that the complex is stable in the pH range 2–10, a series of experiments demonstrated that the extraction is quantitative in the pH range 2–5.6 in solutions made acidic with acetic acid. Aqueous phase volumes from 50 to 150 ml were without effect on the yield of the extraction.

Under the given acid conditions, sulphate acts as a salting out agent and hastens phase separation. Acetates have no effect. Chlorides do not interfere up to the concentration 0.4 g NaCl/100 ml. Higher concentrations of chloride (2 g NaCl/100 ml) decrease the absorption by about 10%. Nitrate interferes at the concentration 0.1 g KNO₃/100 ml. Fluorides already interfere in trace amounts, or prevent formation of the complex; however, their effect can be eliminated by adding boric acid. Chromate and vanadate can be directly extracted with an Aliquat solution before adding the reagent.

EFFECT OF OTHER METAL IONS

Determination of Iron in the Presence of Cobalt

In weakly acid media, cobalt also forms a red coloured complex with the reagent. At low cobalt concentration the Co-EDHPA complex is not extracted to a significant extent so that amounts of cobalt up to 10 mg are tolerable. The experiments were carried out in the same way as described for the concentration dependence. The blank solutions contained the same amount of reagent. A few results are given in Table I.

Considerable negative errors at higher cobalt concentrations are caused by the fact that the reaction of the reagent with iron is not quantitative because of formation of the Co-EDHPA complex. High positive errors are found at high concentrations of cobalt and of the reagent because of simultaneous extraction of the Co-EDHPA complex.

Much more favourable results were obtained when using a blank solution which contained the same amount of cobalt and reagent. The following procedure was employed: The same amount of cobalt solution was in each case measured into two 150 ml separatory funnels. To one was then added 0.5–1.0 ml of $5 \cdot 10^{-4}$ M iron

TABLE I
Effect of Cobalt on the Determination of 28 µg of Fe

mg Co added	—	10	20	50	50	50
ml $5 \cdot 10^{-3}$ M-EDHPA	5.0	0.5	1.0	0.5	1.0	6.0
$A_{480} \cdot 10^3$	511 ± 5	502	489	397	410	550

solution. After dilution to about 25 ml, to each solution was then added 5 ml of the reagent and 1 ml of glacial acetic acid. The extraction was extended to 10 min. The phases separated immediately after adding 2 ml of saturated sodium sulphate. Both chloroform extracts were filtered through small dry filters into 1 cm cuvettes and measured with respect to one another. The extract without iron was taken as the blank here. Under these conditions, the standard deviation for the determination of 14 to 28 μg Fe had the value, $s = 0.28\%$ without respect to the Co : Fe ratio, which varied in the range 178 to 3570. The absorbance of the blank is not negligible, as was shown by control measurement of these solutions against an Aliquat solution. At cobalt concentrations of 5, 10 and 20 mg, and 5 ml of the reagent, the following absorbance coefficients were found: 0.041, 0.093, 0.103.

This procedure ensures sufficiently precise results for iron even at Co : Fe ratios of 4000 : 1; however, it has the disadvantage that the cobalt concentration must be known with an accuracy of 0.5 mg of Co. In solutions containing only cobalt and traces of iron, the cobalt is determined by simple complexometric titration. During analysis of defined cobalt salts or metallic cobalt, the cobalt concentration is already known from the sample weight. It is assumed that we have a cobalt standard free of iron. The method can be used for determining iron in cobalts salts. Traces of copper, nickel, and other metals do not interfere in the determination.

Modification of the blank with sodium fluoride. It was found that iron is easily back extracted from the extracted Fe-EDHPA complex by a sodium fluoride solution acidified with acetic acid. However, the corresponding complexes of cobalt and nickel do not react with fluoride. The extract from which iron was removed in this way can be used as a blank. In this way the method becomes more accurate, since the parallel reaction for the blank is no longer necessary.

Procedure: To a solution of cobalt and iron in a 150 ml separatory funnel, after suitable dilution, are added 5 ml of the reagent, 1 ml glacial acetic acid, and 5 ml of Aliquat, and the extraction is performed for 10 minutes. After adding 2 ml of saturated sodium sulphate, the chloroform extract is filtered through a small dry filter into a 1 cm cuvette and measured at 480 nm against an Aliquat solution. Then the content of the cuvette is transferred to a 50 ml separatory funnel and several ml of water, 2 ml of saturated sodium fluoride, and 4 ml of glacial acetic acid are added. After extracting for 1 minute, 2 ml of saturated sodium sulphate are added to the solution. After separation of the phases, the chloroform solution is again filtered through a small dry filter into the original dried cuvette and measured against Aliquat at 480 nm. The difference in the two absorbance values gives the iron concentration.

Determination of Iron in the Presence of Nickel

Nickel forms a less stable complex than cobalt with EDHPA and practically does not interfere, since its complex is almost not extracted. For solutions containing only nickel and iron can be used the very simple method of measuring against a blank containing the same amount of reagent. Working conditions are the same as those

described for cobalt. However, the amount of the reagent used up is governed by the nickel content, as shown in Table II. At very unfavourable nickel-reagent ratios, the results are lower, which, however, can be considerably improved by increasing the extraction time, by which the iron-nickel-reagent equilibrium is shifted toward formation of the iron-EDHPA complex. However, the method using blank solutions treated with sodium fluoride is completely reliable.

TABLE II
Effect of Nickel on the Determination of 28 μg of Fe

mg Ni added	—	30	50	50	50	50
ml $5 \cdot 10^{-3}$ M-EDHPA	1	1	1	5	7	10
$A_{480} \cdot 10^3$	510	506	230	348	498	503

Determination of Iron in the Presence of Copper

Copper forms an intensively blue complex with the reagent which is partially extractable at high concentrations of copper and the reagent. However, the presence of copper predominantly slows down the formation of the Fe-EDHPA complex. Thus, experiments carried out in the two above ways, *i.e.* by measuring against the reagent, or measuring against the reagent with the same amount of copper did not give reproducible results at higher copper concentrations. However, it was found that, on extending the extraction to 20 minutes, and measurement against a blank treated with sodium fluoride, the results are quite satisfactory. The sodium sulphate addition must be carried out after the extraction.

Determination of Iron in the Presence of Cu, Co, and Ni

Since the method should be usable in the presence of copper, cobalt, and nickel, and of other divalent elements, a general method for determining iron in the most variable combinations with the mentioned elements was developed. In the determination of 14–28 μg of Fe in the presence of 20–50 mg of Co, Ni, or copper at the ratio (Cu + Ni + Co): Fe within the range 700–7800, the standard deviation has the value, $s = 0.32$.

Procedure: To a weakly acid solution of iron, nickel, cobalt, and copper in a 150 ml separatory funnel, 5 ml of the reagent are added and the solution is neutralized with sodium hydroxide to the appearance of hydroxide cloudiness. The precipitate is dissolved by dropwise addition of glacial acetic acid and an additional 1 ml of acid is added. After 10 minutes, 5 ml of Aliquot are added and the extraction is performed, usually by shaking 20 minutes. A milky emulsion

is formed. After adding 2 ml of saturated sodium sulphate, the two phases quickly separate. The extract is filtered through a small dry filter into a 1 cm cuvette and measured against Aliquat at 480 nm. The contents of the cuvette is then transferred into a 150 ml separatory funnel, and a few ml of distilled water, 2 ml of saturated sodium fluoride, and 4 ml of glacial acetic are added, and, if necessary, saturated sodium sulphate. A 1 minute extraction is performed. After separation of the phases, the chloroform extract is filtered through a small dry filter into the original, dry, 1 cm cuvette and measured against Aliquat at 480 nm. The difference between the two absorbances read on a calibration curve gives the concentration of iron.

DISCUSSION

In the work is described only the study of the interference of copper, cobalt, and nickel since a number of the so-far developed methods for iron usually fail at high concentrations of these elements. However, the effect of other elements was also studied, which, although they form colourless complexes, could still interfere by forming competing EDHPA complexes. For example, the effect of aluminum, manganese, zinc, cadmium, calcium, magnesium, *etc.* was studied. The method is so sensitive that, for example, various aluminum sulphate preparates, which were available, themselves gave a "strongly positive" reaction for iron (up to 10–15 μg in 1 g, which corresponds to 10–15 p.p.m. iron). In these cases, it was necessary to determine, by the above described method, the iron content in the added compounds. The method was applied to a number of alloys containing copper, chromium, nickel, cobalt, and other elements, and also to granite (American standard G1), and various kinds of silicates, dolomites, limestones, *etc.* The appropriate procedure will be published elsewhere.

R.P. considers it his pleasant duty to thank Dr H.W. Zussman, Ciba-Geigy, New York, for providing a sample of the pure reagent. J.A. also thanks Dr M. Gross, Highland Park, Illinois, U.S.A., for providing a sufficient amount of Aliquat.

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Translated by M. Štulíková.