

Table III. Recovery of Additions of Lithia

% Li ₂ O in Rock	% Li ₂ O Added	Total % Li ₂ O	% Li ₂ O Found
0.0015	0.0003	0.0018	0.0019
	0.0003	0.0018	0.0020
	0.0015	0.0030	0.0030
	0.0030	0.0045	0.0048
	0.0058	0.0073	0.0074
	0.0060	0.0075	0.0065
	0.0075	0.0090	0.0085
0.0113	0.0003	0.0116	0.0118
	0.0021	0.0134	0.0135
	0.0039	0.0152	0.0149
0.0111	0.0091	0.0202	0.0200
	0.0136	0.0247	0.0243

Table IV. Comparison of Flame Spectrophotometer and Spectrographic Methods

	% Li ₂ O	
	Flame spectrophotometer	Spectrograph
Standard granite G-1	0.0052	0.004
	0.0049	0.005
Standard diabase W-1	0.0030	0.002
	0.0033	0.002
	0.0027	

PRECISION AND ACCURACY

The sensitivity of the instrument at the settings used (full sensitivity, 0.4-mm. slit, 671 m μ) was 0.05 p.p.m. of lithia in solution, corresponding to 0.0005% of lithia in the sample. A difference of this amount of lithia could usually be detected (see Table III).

Because no standard materials are available for analysis, the only check on the accuracy is by adding known amounts of lithia to the rock powders before decomposition and checking recovery. This was done on rocks on which replicate determinations had been made, the average value being used as the true value. Results of these determinations are shown in Table III.

As an additional check a standard diabase and granite (5) were run several months apart. These results are compared in Table IV with spectrographic results (5) and indicate that the flame spectrophotometer compares favorably with the spectrograph.

Replicate determinations on a variety of samples showed a maximum deviation of 0.0005% of lithia in the sample or 0.05 p.p.m. of lithia in solution in the range 0.05 to 3 p.p.m. of lithia. Average deviation for multiple determinations is about 0.0003% of lithia. The method is considered to be accurate to 0.001% of lithia in the sample.

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LITERATURE CITED

- (1) Barnes, R. B., Richardson, D., Berry, J. W., and Hood, R. L., *IND. ENG. CHEM., ANAL. ED.*, **17**, 605 (1945).
- (2) Beer, H. L., *The Precambrian*, **24**, 8 (1951).
- (3) Broderick, E. J., and Zack, P. G., *ANAL. CHEM.*, **23**, 1455 (1951).
- (4) Brumbaugh, R. J., and Fanus, W. E., *Ibid.*, **26**, 463 (1954).
- (5) Fairbairn, H. W., and others, *U. S. Geol. Survey, Bull.* **980** (1951).
- (6) Lundegårdh, P. H., *Arkiv Kemi, Mineral. Geol.*, **A23**, No. 9 (1946).
- (7) McCoy, W. J., and Christiansen, G. G., *Am. Soc. Testing Materials, Special Tech. Pub.* **116**, 44 (1951).
- (8) Strock, L. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe, IV*, 171-204 (1936).
- (9) White, C. E., Fletcher, M. H., and Parks, J., *ANAL. CHEM.*, **23**, 478 (1951).
- (10) Williams, J. P., and Adams, P. B., *J. Am. Ceram. Soc.*, **37**, 306 (1954).

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Amperometric Titration of Iron with 1-Nitroso-2-naphthol

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An amperometric titration of iron(III), in acetic acid-sodium acetate buffer, with 1-nitroso-2-naphthol gave satisfactory results. It was the purpose of this investigation to determine optimum conditions for obtaining reproducible and accurate results in the direct titration of iron with this reagent. The titration is more rapid than the gravimetric methods, and necessitates fewer operations than other amperometric methods for the determination of iron. Of the cations studied, only lead interferes. Iron in iron ores was determined rather accurately, after it had been separated by ether extraction. This method should be especially suitable for determination of iron in selected steels.

SANDBERG (4) has performed amperometric titrations of iron(III) with bromoxine (5,7-dibromo-8-hydroxyquinoline) at 50° C. In his work the titration error is reported to be 2% for a 0.1*M* concentration of iron, and not more than 0.7% for concentrations of iron greater than 0.4*M*. Kolthoff and Liberti (2) have carried out satisfactory amperometric titrations of iron(III)

solutions with cupferron, the ammonium salt of phenyl-nitrosohydroxylamine, in tartrate and citrate buffers. They recommended that, in the presence of tartrate or citrate, the iron solutions be titrated in a cell covered with a coat of black paint, since iron(III) under these conditions is readily reduced by light to iron(II). These authors report an error of 1% for solutions not less than 1*mM* in iron, and an error of 2 to 3% for solutions which are 0.5*mM* in iron.

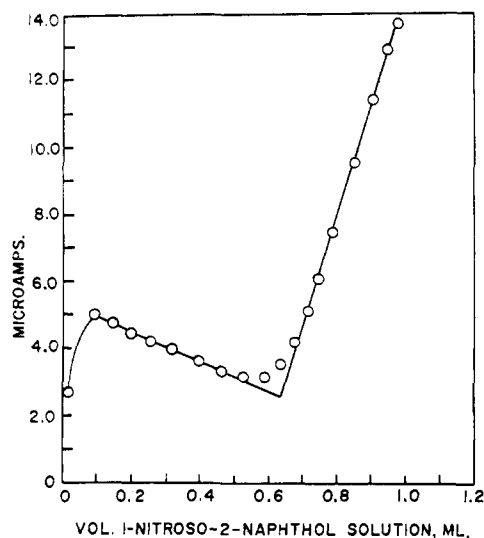
This investigation was undertaken to ascertain the possibility of obtaining reproducible and sufficiently accurate stoichiometric results in the direct titrations of iron(III) with 1-nitroso-2-naphthol in acetic acid-sodium acetate buffer. The precipitate formed in the reaction between iron and 1-nitroso-2-naphthol in acetic acid-water medium, has the composition (C₁₀H₅NO₂)₂Fe (?).

EXPERIMENTAL

Reagents and Solutions. The stock solution of iron was prepared by dissolving 27 grams of Baker's analyzed iron(III) chloride hexahydrate in distilled water. This solution was treated with 10 ml. of concentrated hydrochloric acid to prevent hydrolysis

Table I. Amperometric Titration of Iron(III) in Acetic Acid-Sodium Acetate Buffer at -0.5 Volt vs. S.C.E.

Iron Taken, Millimoles $\times 10^2$	1-Nitroso-2- naphthol, Millimoles $\times 10^2$	Mole Ratio, Fe/Titrant
0.197	0.59	1:3.00
0.394	1.18	1:3.00
0.984	2.97	1:3.02
1.968	5.89	1:2.99
2.952	8.85	1:3.00
3.936	11.9	1:3.02
4.919	14.8	1:3.01

**Figure 1. Titration of 20 ml. of $0.0984 \times 10^{-2} M$ iron(III) with $0.0920 M$ 1-nitroso-2-naphthol**

and was then diluted to 1 liter. The stock solution of iron was standardized using potassium permanganate which had been standardized by the sodium oxalate method (5).

1-Nitroso-2-naphthol, Eastman Kodak chemical No. P428, was recrystallized twice from alcohol and dried at room temperature. A weighed amount was dissolved in glacial acetic acid and was then diluted to volume with appropriate volumes of glacial acetic acid and/or distilled water to make the final solution 60% in acetic acid. This solution was filtered to determine whether all the reagent had dissolved, and any small residue remaining was washed and dried at room temperature and the weight of the residue was subtracted from the original weight of the reagent. The concentration of this solution was checked against a standard solution of palladium(II) chloride by the method of Kolthoff and Langer (1); the calculated concentration of 1-nitroso-2-naphthol agreed closely with the concentration determined by the method of Kolthoff and Langer. Fresh solutions of this reagent were prepared every 2 weeks. A buffer solution was prepared which was 2M in acetic acid and in sodium acetate. Water-pumped nitrogen (purity of 99.5% or greater), obtained from the Houston Oxygen, Inc., was used throughout this study. All other materials used were c.p. reagent grade products.

Apparatus. A Sargent Model XII polarograph was employed in this work. The titration cell contained a saturated calomel reference electrode in one compartment, as described by Kolthoff and Lingane (3). All current measurements were taken at $25^\circ \pm 0.1^\circ C$. Potentials are expressed versus the saturated calomel electrode (S.C.E.).

On the horizontal portion of the current voltage curve at -0.5 volt, the capillary characteristics for a mercury height of 66.4 cm. were: $m = 1.685 \text{ mg. sec.}^{-1}$, $t = 3.83 \text{ seconds}$, and $m^{2/3}t^{1/6} = 1.771 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$.

Amperometric Titration of Iron with 1-Nitroso-2-naphthol. The polarography of iron(III) and 1-nitroso-2-naphthol, in acetic acid-acetate buffer, was investigated briefly for the purpose of determining the shape of their current-voltage curves. These reduction curves, both for iron(III) and for 1-nitroso-2-naphthol,

started at or near zero applied potential and then became essentially parallel with the voltage axis between -0.2 and -1.0 volt.

Preliminary experiments showed that a high concentration of acetate ions was required, and that a large amount of ethyl alcohol was desirable to obtain reproducible results in the amperometric titration of iron(III) with 1-nitroso-2-naphthol; however, the precipitate formed was essentially insoluble in water. The following procedure was adopted for the titration of iron.

An appropriate aliquot of the standard stock solution of iron to give the final concentration desired was added to a 100-ml. volumetric flask, 5 ml. of 0.2% gelatin solution, 20 ml. of 2M acetic acid-acetate buffer, and 20 ml. of 95% ethyl alcohol were added, and the solution was diluted to volume with distilled water. A 20-ml. aliquot of this solution was transferred to an H-type cell, and oxygen-free nitrogen, which had been conditioned by passage through a blank solution that contained all the reagents in the usual concentration except iron or the titrant, was passed through for 15 minutes. After the passage of nitrogen had been completed, a microburet containing the 1-nitroso-2-naphthol solution was pushed through the remaining hole in the stopper of the titration cell. All current measurements were taken at -0.5 volt and were corrected for dilution effects. After the expiration of a few minutes, the current became steady and the mean of the galvanometer deflections was recorded. A small quantity of the titrant was run into the cell; the solution was stirred with nitrogen for 1 minute, and the current was read 3 minutes thereafter. After each addition of titrant, about 2 minutes were required for the current to become constant. This latter procedure was continued throughout the titration. The extrapolation method was employed in ascertaining the volume of titrant used in each titration.

Figure 1 is a typical titration curve for the amperometric titration of iron(III) with 1-nitroso-2-naphthol. The results are shown in Table I; each line in the table is the mean of three closely agreeing results on samples of the concentration indicated.

Effect of Diverse Ions. For application of the method to the analysis of iron ores and common compounds of iron, the possible interference from a number of metal ions should be considered. The metallic ions selected for this study were lead(II), calcium(II), nickel(II), zinc(II), aluminum(III), titanium(III), and chromium(III). The interference effects of these ions on the amperometric determination of iron(III) were studied by adding equal molar concentrations of the diverse ions, individually, to 1mM solutions of iron (in the final concentration); these solutions were made up in the usual way. The volume of 1-nitroso-2-naphthol required to titrate iron in the presence of equal molar concentrations of lead was approximately 4% greater than the volume of titrant required when lead was not present. Addition of titanium, in the same way, produced a precipitate which settled out almost immediately and did not interfere with the determination of iron. The presence of the remaining diverse ions produced no measurable effect on the end point for the determination of iron.

Table II. Determination of Iron in Iron Ores after Ether Extraction

Sample No.	Iron, %		Relative Error, %
	Amperometric method	Gravimetric method	
1	10.48	10.46	+0.19
2	15.23	15.26	-0.20
3	23.45	23.42	+0.13
4	32.70	32.61	+0.28

Determination of Iron in Iron Ores. Weighed samples of four iron ores (obtained from Standard Sample Co., Ames, Iowa) were dissolved using concentrated hydrochloric acid and sodium bisulfate. The iron was extracted from solution using the procedure of Scott (5).

The acid solutions of iron were evaporated to a sirupy consistency and then taken up in dilute hydrochloric acid and transferred to separatory funnels. Iron was extracted four times from

each of the cold acid solutions by shaking with ether; each time the ether which contained the iron was allowed to separate before the lower layer was drawn off for re-extraction. The iron was extracted from the ether layer by shaking the ether solution with water and drawing off the lower water layer. These extracted iron solutions were transferred to volumetric flasks and the solutions were diluted to volume with distilled water. Aliquots of these solutions were made up according to the standard procedure, duplicate amperometric titrations were performed on each solution, and the iron concentration was determined in the usual manner.

The averages of the results are shown in Table II along with the assays given by the manufacturer for the gravimetric determination of iron in the ores.

DISCUSSION

The amperometric titration of small amounts of iron, in acetic acid-sodium acetate buffer, with 1-nitroso-2-naphthol has been performed in which satisfactory results were obtained. Of the several diverse ions studied, only lead interfered with the titration of iron; however, iron may be quantitatively extracted from lead using ether (8). Iron in iron ores was determined with a good degree of accuracy, after this element had been separated by ether extraction. The percentage of iron in the ores ranged from 10 to 33%. In no case was the relative percentage error of

a result of this method, as compared with the assay reported by the manufacturer, greater than $\pm 0.28\%$. Results were duplicated on each of the samples with an average precision of less than $\pm 0.1\%$. This method as compared with other methods for the amperometric titration of iron(III) (2, 4) saves time and necessitates fewer operations for carrying out the determination.

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LITERATURE CITED

- (1) Kolthoff, I. M., and Langer, A., *J. Am. Chem. Soc.*, **62**, 3172 (1940).
- (2) Kolthoff, I. M., and Liberti, A., *Analyst*, **74**, 635 (1949).
- (3) Kolthoff, I. M., and Lingane, J. J., "Polarography," 2nd ed., Vol. 2, p. 903, Interscience, New York, 1952.
- (4) Sandberg, B., *Svensk Kem. Tidskr.*, **58**, 197 (1946).
- (5) Scott's "Standard Methods of Chemical Analysis," N. H. Furman, editor, 5th ed., Vol. 1, pp. 465, 475, Van Nostrand, New York, 1939.
- (6) Swift, E. H., *J. Am. Chem. Soc.*, **46**, 2375 (1924).
- (7) Welcher, F. J., "Organic Analytical Reagents," Vol. 3, p. 314, Van Nostrand, New York, 1948.

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Spectrophotometric Determination of Esters in Mixtures Benzyl Benzoate and Dibutyl Phthalate

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In a study of cloth impregnations with a mixture of benzyl benzoate and dibutyl phthalate it was necessary to determine the components of this mixture in cloth patches. A method was devised in which the quantity of an alkali used in a saponification and the absorbance reading at 230 $m\mu$ were used to determine the quantity of each of these esters. Analyses of five known mixtures showed average recoveries of 100.08% for benzyl benzoate and 99.97% for dibutyl phthalate. Analysis of six impregnated cloth patches showed average recoveries of 101.43% for benzyl benzoate and 99.66% for dibutyl phthalate. The procedure in which titration and spectrophotometric readings are used to analyze for mixtures of the same type of compound is new and has many applications.

AN IMPORTANT phase of research in this laboratory is the investigation of repellents and repellent formulations for use by the military services for the protection of troops against insects, mites, and ticks. One part of this research is the development of procedures for impregnating clothing with repellents. In these procedures it is necessary to have methods of chemical analysis that can be utilized to identify the repellents individually and in mixtures, and to measure the amounts deposited on cloth. Final recommendations as to concentrations of repellents and procedures for impregnation are based largely on the results of analytical determinations of the amounts of repellent deposited on the cloth in experimental trials.

One of the clothing impregnants in use by the army is a mixture which, according to military specification (1), contains 45% each of benzyl benzoate and dibutyl phthalate and 10% of a

nonionic emulsifier. Both esters have a maximum absorption in the lower ultraviolet region, but their peaks are so close, 230 $m\mu$ for benzyl benzoate and 225 $m\mu$ for dibutyl phthalate, that a method based on readings at these wave lengths would be difficult. Since both esters are easily saponified, a method using the saponification and a spectrophotometric reading has been devised.

The emulsifier used in these experiments does not have an ultraviolet peak that interferes with the spectrophotometric reading. It reacts slightly with alkali but not sufficiently to interfere with the analysis. In the analysis of cloth extracts an electrometric Titrimeter is used, since the extracted dye interferes with the reading of a colorimetric end point. In the analysis of emulsifiable concentrates, either an internal indicator or an electrometric Titrimeter may be used.

The calculations are similar to those used in the spectrophotometric determination of multicomponent systems (2).

APPARATUS AND REAGENTS

The absorbance measurements are made in matched 1-cm. silica cells with a Beckman Model DU spectrophotometer.

All titrations are performed with a Fisher potentiometric Titrimeter.

The alkalimetry titrations are made with approximately 0.1N standard sulfuric acid.

Approximately 0.1N standard ethanolic sodium hydroxide is used for the saponification of the esters. It is prepared by dissolving 4.0 grams of sodium hydroxide in 10 ml. of water, diluting to 1 liter with 95% ethyl alcohol, and titrating with the standard acid.

Ethyl alcohol, 95%, is used as the solvent in the spectrophotometric determinations. When ethyl alcohol from the same lot is used for dilutions and as a reference in the blank cell of the spectrophotometer, further purification is not necessary.