Table I. Polarographic Results in Methanol

Salt, $M \times 10^3$	I_d/C, $\mu a./mM$			$-E^{1/2}$ volt vs. SCE	
	Wave I	Wave II	Total	Wave I	Wave II
Zr(SO₄)₂.4H₂O					
5.0	5.6	1.6	7.2	1.25	1.56
2.5	5.2	2.0	7.2	1.24	1.55
1.0	3.7	3.4	7.1	1.25	1.55
0.5	3.6	3.5	7.1	1.25	1.54
ZrOCl₂.8H₂O					
5.0	6.0	...	...	1.43	....
2.5	5.6	...	...	1.41	....
1.0	5.0	...	...	1.39	....
0.5	4.0	...	...	1.37	....

I_d/C values for wave I are seen to decrease with concentration of zirconyl chloride similar to the behavior observed with zirconium sulfate. Unfortunately, wave II for zirconyl chloride merges with the solvent-supporting electrolyte decomposition wave. Thus I_d/C values are not ascertainable for wave II in this case.

Diffusion current data for zirconium sulfate reduction waves at various drop times between 3.0 and 6.0 seconds were analyzed. I_d values obtained were in accordance with the Ilkovič equation, showing that kinetic currents are not involved in the present investigation.

The data presented in Table I indicate the possible application of the polarographic method to the analysis of hydrated quadrivalent zirconium salts such as zirconium sulfate tetrahydrate. The addition of a few tenths of 1% of water to the anhydrous methanol did not appreciably alter the polarographic data. Polarographic results obtained in a mercury pool cell were no better than those obtained in the H-cell, if the polarogram was recorded within about 5 minutes. In this way, diffusion of water through the agar plug in the H-cell was maintained below interfering quantities.

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Simultaneous Titration of Iron and Copper with Ethylenediaminetetraacetic Acid

Spectrophotometric End Points

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SEVERAL recent papers have pointed out the advantages of photometric end points in certain titrations (1, 2, 7, 8). Sweetser and Bricker (8) have shown that the principal disadvantage of ethylenediaminetetraacetic acid (Versene, Sequestrene) as a volumetric reagent for various cations—viz., lack of suitable indicators—may be overcome in certain cases by this technique. Studies in this laboratory have indicated that the photometric approach permits the simultaneous titration of two or more cations provided: (a) the stability constants of their complexes with ethylenediaminetetraacetic acid are sufficiently large, (b) the constants differ sufficiently, and (c) the spectra of the complexes permit selection of suitable wave lengths. Many of the stability constants have been measured, and a convenient compilation has been given (4). Although these constants may be expected to vary considerably with the medium, they may be used as rough guides in predicting the feasibility of titrating certain metals simultaneously. Proviso c may easily be checked experimentally.

Sweetser and Bricker have reported good photometric titrations of ferric and cupric ions, separately, with ethylenediaminetetraacetic acid (8). The stability constants reported for the complexes of these ions are large, and differ sufficiently to indicate the possibility of obtaining two consecutive end points when a mixture of the two is titrated with an ethylenediaminetetraacetic acid solution [ferric complex, log K = 25.1 (6); cupric complex, log K = 18.3 (5)]. Furthermore, the cupric complex absorbs strongly at a wave length (745 mμ) where the ferric complex exhibits no absorption. Since the ferric complex is the most stable, the formation of the cupric complex with the attendant increase in absorbancy serves as indicator for the titration of the iron. The copper end point is indicated, of course, by a plateau representing maximal formation of the cupric complex. This paper reports results obtained in this fashion, and includes application to an aluminum alloy containing low percentages of iron and copper.

REAGENTS AND APPARATUS

Ethylenediaminetetraacetic acid under the trade name Sequestrene AA was obtained from the Alrose Chemical Co., Providence, R. I. About 14.6 grams of this material was suspended in distilled water and treated with sodium hydroxide to dissolve the acid. The solution was diluted to 500 ml. with distilled water to give a 0.1M reagent, and standardize against the standard cupric solution, using the spectrophotometric end point.

As emphasized by Sweetser and Bricker (8), careful control of pH is essential for successful titrations with ethylenediaminetetraacetic acid. The buffer used in this work, 94.5 grams (1 mole) of monochloroacetic acid (Eastman Kodak Co. practical grade, distilled to remove dark-colored impurities), was dissolved in distilled water, adjusted to pH 2.0 with sodium hydroxide, and diluted to 1 liter.

The standard cupric solution was about 0.01M, prepared by dissolving accurately weighed electrolytic copper foil in nitric acid, boiling the solution to remove oxides of nitrogen, and diluting with distilled water. The standard ferric solution of about the same molarity was prepared from Baker's analyzed ferric ammonium sulfate. It was analyzed by passage through a Jones reductor, followed by titration with standard dichromate solution, and was kept sufficiently acidic to prevent hydrolysis of the iron.

The Beckman Model DU spectrophotometer was adapted as follows: The titration cell, which was a rectangular cuvette with a capacity of about 90 ml. designed for a Lumetron colorimeter, was mounted inside a Beckman test tube attachment with the test tube bracket removed. The cell, whose base projected beyond its sides, could be positioned and held securely by means of the setscrews designed to hold the test tube bracket. The cover for the test tube attachment was replaced by a flat wooden cover; molding around its edges gave a light-tight fit. Two holes in the cover, equipped with felt gaskets, admitted the glass stirrer and the 2-ml. microburet. The cover was painted with a flat black enamel. The exterior of the cell was likewise painted, leaving only small windows for the light beam. The stirrer and the buret were painted for a distance several centimeters above the cover down nearly to the tips, which were immersed in the solution. This arrangement was essentially light-tight; moving a strong light source about the exterior of the cell

compartment had no noticeable effect on the galvanometer. The light path (about 3 cm. in length) was near one end of the cell; the stirrer, operating near the opposite end, did not affect absorbancy readings.

PROCEDURE

The results described below were obtained with the standard ferric and cupric solutions.

Aliquots of the standard solutions furnishing the desired quantities of iron and copper were pipetted into the titration cell, followed by 25 ml. of the chloroacetate buffer solution. The pH was checked, and in cases where the acidity from the iron solution could not be handled by the buffer, sodium hydroxide solution was added to bring the solution to a pH of about 2. The total volume was adjusted to about 50 ml. with distilled water, and the solution was allowed to stand for at least 1 hour. The cell was then positioned in the instrument, and at a wave length of 745 mμ, the absorbancy was set at zero, using the slit width and sensitivity controls in the usual manner. The absorbancy was then measured after the addition of appropriate increments of titrate, and the titration curve plotted.
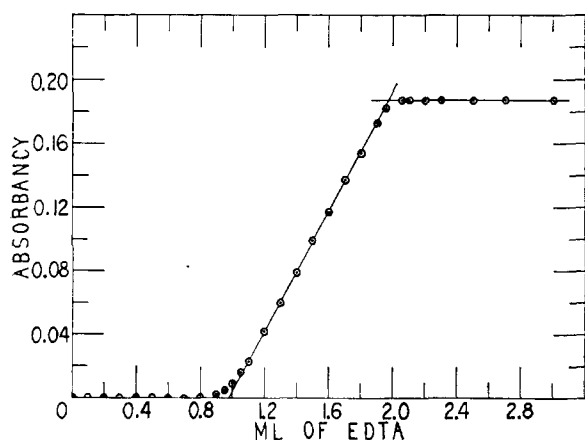

Figure 1. Titration of an Iron(III)–Copper(II) Mixture with 0.1M Ethylenediaminetetraacetic Acid

5.40 mg. Fe, 6.36 mg. Cu; 745mμ

To show a practical application of this method, an aluminum alloy obtained from the National Bureau of Standards (standard sample 603, wrought alloy), certified to contain 0.29% copper and 0.21% iron, was analyzed as follows:

A sample of about 2 grams was dissolved in dilute hydrochloric acid, and the bulk of the aluminum was precipitated as aluminum chloride, following the procedure of Hillebrand and Lundell (3). Great care was taken to wash the precipitate thoroughly. The resulting solution was evaporated to 15 to 25 ml., adjusted to a pH of about 2 with sodium hydroxide, buffered with 25 ml. of the chloroacetate buffer, diluted to about 50 ml., and titrated as described above.

DISCUSSION

Figure 1 shows a typical curve for the titration of a ferric-cupric mixture with ethylenediaminetetraacetic acid. The curve is linear with no change in absorbancy during the titration of the iron, because neither ferric ion in the chloroacetate medium nor its complex with the titrant absorbs appreciably at 745 mμ. It has been observed, however, that strongly acid ferric solutions approach zero absorbancy slowly after the pH has been raised to 2. Presumably a slow hydrolysis reaction is responsible for this phenomenon. In any case, it is desirable to wait at least an hour after raising the pH before starting the titration.

During the titration of the iron, each increment of titrant causes an increase in absorbancy, followed by a slow return to zero. Apparently cupric ion is complexed as a result of temporary high local concentrations of ethylenediaminetetraacetic acid, in spite of the stirring. However, this drift in the absorbancy persists for

only 5 to 10 minutes (somewhat longer in the vicinity of the end point). As only a few points are required to define the curve, this does not represent a serious defect in the method. Inconveniences of this type must be evaluated in the light of the fact that determinations of two metals accrue from each titration. The presence of cupric ion is necessary to indicate the iron end point. In cases where the sample to be analyzed contains no copper, cupric ion might be added by the analyst, or alternatively, the technique of Sweetser and Bricker based on the color of the ferric complex with salicylate might be used (8).

Table I. Results of Experiments

Standard Solutions

	Iron, Mg.			Copper, Mg.		
	Taken	Found	Error, %	Taken	Found	Error, %
1	2.70	2.61	3.3	3.18	3.23	1.6
2	5.40	5.42	0.37	4.45	4.48	0.67
3	8.10	8.03	0.86	5.09	5.08	0.20
4	10.81	10.83	0.19	6.36	6.41	0.79
5	10.81	10.78	0.28	3.18	3.20	0.63
6	8.10	8.14	0.49	4.45	4.43	0.45
7	5.40	5.41	0.19	5.09	5.10	0.20
8	2.70	2.65	1.9	6.36	6.38	0.31

Aluminum Alloy, NBS Certificate: 0.21% Iron, 0.29% Copper[a]

	Iron found, %	Error, %	Copper found, %	Error, %
1	0.20	4.8	0.27	6.9
2	0.20	4.8	0.28	3.4
3	0.21	0.0	0.30	3.4
4	0.21	0.0	0.29	0.0
5	0.20	4.8	0.28	3.4

[a] Other elements certified: Mg, 1.01%; Si, 0.52%; Cr, 0.24%; Ti, 0.037%.

That portion of the curve representing the titration of the cupric ion is similar to the copper curves reported by Sweetser and Bricker (8). As there is no drift during the titration of either pure ferric or pure cupric solutions, mixtures containing only these two ions exhibit no drift during the titration of the copper. Thus this portion of the titration can be performed as rapidly as one can manipulate the apparatus, if complex-forming ions other than ferric and cupric are absent. When titrations were attempted on solutions of the aluminum alloy which had been subjected to no prior separations, however, the drifting was very troublesome during the titration of the copper, and an inordinate length of time was required to complete the titrations. With sufficient patience it was possible to determine iron and copper even under these conditions. Presumably aluminum ions compete effectively with cupric ions until stirring has dissipated the high local concentration of ethylenediaminetetraacetic acid about the tip of the buret; a slow return to equilibrium conditions, favoring formation of the cupric complex, follows. (This effect is not so pronounced during the titration of the iron. As ferric ion forms a stronger complex than cupric ion, aluminum perhaps does not compete so effectively with the former. There is some drift in this part of the curve, due to the presence of cupric ions.)

The maximum quantity of aluminum which can be present without slowing down the titration in this way has not been determined. Sweetser and Bricker (8) have shown that small amounts of aluminum have little effect. It was found in the present study that removal of the bulk of the aluminum from the aluminum alloy solution by the precipitation of aluminum chloride [by passing hydrogen chloride gas into the solution to which ether has been added (3)] eliminated the aluminum interference completely, although this precipitation is known not to be quantitative. As about 2 grams of aluminum was being precipitated in the presence of only a few milligrams of iron and copper, the precipitate was washed more scrupulously than might ordinarily be necessary. When care was exercised in this regard, there were no appreciable losses of iron or copper. The troublesome drifting during the titration of the copper was completely eliminated by this separation.

The results shown in Table I indicate that the method is sufficiently accurate for many purposes. As pointed out by Sweetser and Bricker (8), interferences from other cations would be expected to be small because of the large stability constants of the ferric and cupric complexes with ethylenediaminetetraacetic acid. Furthermore, such interferences are minimized by working at a fairly low pH. This method is especially attractive for the determination of small quantities of iron and copper in aluminum alloys, because the bulk of the aluminum is so easily removed, and the small remainder does not affect the results appreciably.

Inspection of the stability constants of the metal ion complexes with ethylenediaminetetraacetic acid suggests other possibilities for the simultaneous determination of metals in various mixtures.

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Paper Chromatography of Some Alkoxy Acids

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IN CONNECTION with a pharmacological investigation being conducted in this laboratory, it became desirable to determine the presence and concentration of some alkoxy acids. Paper chromatography with its high sensitivity and simple procedure offers a straightforward approach to the qualitative and quantitative determination of small quantities of acids (100 to 500γ). This paper covers a number of compounds not elsewhere reported and is offered in the interest of increasing the knowledge of this useful analytical tool.

Many of the procedures described in the literature have been concerned with column chromatography. Elsden (2) used silicic acid columns for the separation of acids, but the quantity of starting material was greater than was available in this laboratory. Most of the papers applied to paper chromatography have been developed for the separation and detection of amino acids. Lugg and Overell (7) have described a method of separation of nonvolatile organic acids, but volatile acids did not lend themselves to the procedure, as the material was lost during the process owing to heating. In addition, a swamping acid, acetic or formic, was included with the solvent and as this study concerned monocarboxylic acids, the procedure obviously was unsuitable.

The work of Fink and Fink (3) was investigated in which the acids were converted to nonvolatile hydroxamic acid derivatives. This method yielded excellent results qualitatively but, during the several steps, variable amounts of starting material were lost and quantitative analyses were impossible.

The technique of Kennedy and Barker (5) offered a reasonable approach and their general method was applied to the acids under consideration. In supplement, some aspects of the procedures of Brown and Hall (1) and Hiscox and Berridge (4) were incorporated in the work. Some of the solvent systems employed by Long, Quale, and Stedman (6) were used to extend the scope of the separation procedures.

EXPERIMENTAL

Whatman No. 1 filter paper was used for this study. Large sheets 18.25 × 22.5 inches were trimmed to 30 × 45 cm. before use. The sheets were washed with oxalic acid, following Kennedy and Barker, before use. It was found convenient to place the papers in a large tray and then add the wash. After sufficient rinsing, the papers were dried by placing an infrared light underneath the tray at a distance of 12 to 18 inches and heating overnight. This technique obviated any necessity for handling the wet paper, which tears easily.

The acids in the form of a solution of their ammonium salts containing 10 to 40 mg. per ml. of free acid were applied in 0.01-ml. quantities on a line 3 cm. from the bottom of the paper, spaced 3.5 cm. apart, and developed by the "ascending" technique in a cylindrical tank after the paper was stapled in the form of a cylinder. The developing solution was contained in a large Petri dish to which a handling rod of glass had been fused. The tank was sealed with a flat glass plate lubricated with stopcock grease.

After the development of the chromatogram had proceeded

6 to 8 hours, the paper was dried in an oven at 105° to 110° C. for 5 minutes, then placed against a large glass plate and sprayed with bromophenol blue (50 mg. of bromophenol blue plus 200 mg. of citric acid per 100 ml. water). The acid spots appeared blue against a yellow background with little or no "tailing." This spraying agent appeared to be the most satisfactory for general use. When several different concentrations of the same acid are spotted along the paper, the size of the spot and depth of color allow the ready estimation of the acid concentration of unknown quantities of the same acid, provided the original spot on the starting line was the same diameter as the known acid concentrations.

Table I. R_f Values × 100 of Some Semivolatile Acids

Acid	M.W.	Solvent						
		A	B	C	D	E	F	G
Methoxyacetic	90	10	8	18	..	8	28	6
Ethoxyacetic	104	19	17	17	..	17	36	9
n-Propoxyacetic	118	28	27	9	46	28	48	18
n-Butoxyacetic	132	42	39	18	52	39	54	26
3-Ethoxypropionic	118	22	26	4	46	28	44	17
4-Methoxy-n-butyric	118	19	24	4	46	29	48	14
n-Hexanoic	116	58	57	39	68	65	68	48
2-Ethyl-n-hexanoic	144	70	74	55	72	79	84	71

Solvent composition:
 A. 1-Butanol saturated with 1.5N aqueous ammonia.
 B. 1-Butanol, 75 ml.; 1-propanol, 25 ml.; 1.5N aq. ammonia, 10 ml.
 C. 1-Hexanol saturated with 1.5N aqueous ammonia.
 D. 95% Ethyl alcohol, 99 ml.; ammonium hydroxide, sp. g. 0.9, 1 ml.
 E. 1-Butanol, 50 ml., abs. ethyl alcohol, 50 ml.; ammonium hydroxide, sp. g. 0.9, 1 ml.
 F. Same as D but unwashed filter paper was used.
 G. Iso-octane, 40 ml.; acetone, 30 ml.; 95% ethyl alcohol, 30 ml.; ammonium hydroxide, sp. g. 0.9, 1 ml.

SUMMARY

The R_f values for a number of acids not yet listed in the literature have been reported. The values obtained were duplicable within 2 R_f units. Two aliphatic acids possessing the same molecular weight range and moderate volatility were included for purposes of comparison. It will be seen that in a homologous series, the R_f values have increased linearly with molecular weight in several of the solvent systems. This fact might find application in predicting the molecular weights and identities of unknown acids of a similar class.

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