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## Abstract

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# POTENTIOMETRIC METHOD FOR TITRATING ACIDS WITH QUATERNARY AMMONIUM BASES

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The analysis of weak and very weak acids and their mixtures presents great difficulties. These difficulties can easily be overcome by titrating acids in nonaqueous solutions ([1],[2]). The advantages of titration in nonaqueous media have been sufficiently well covered in the literature ([3]). At the present time, methods for titrating various substances in nonaqueous media have found wide application in the practice of scientific-research and factory laboratories ([4-6]).

We have developed a potentiometric method for titrating strong, weak, and very weak acids in nonaqueous media, making it possible to determine not only individual acids but also their binary and multicomponent mixtures. A striking example of the results that can be achieved by applying the method of differential determination of acids in nonaqueous solutions is the titration of five-component mixtures of acids, for example: hydrochloric, salicylic, trichloroacetic, acetic acids, and $\beta$-naphthol.

**Table 1**

Results of the quantitative determination of certain individual acids

| Substance determined | Taken, g | Found, g | Relative error, % |
|---|---|---|---|
| $\alpha$-Naphthol | 0.0303 | 0.0308 | +1.7 |
| $\beta$-Naphthol | 0.0205 | 0.0209 | +1.9 |
| Palmitic acid | 0.1101 | 0.1114 | +1.1 |
| Stearic acid | 0.0493 | 0.0496 | +0.5 |
| Oleic acid | 0.1697 | 0.1715 | +1.0 |
| *o*-Nitrophenol | 0.0432 | 0.0439 | +1.6 |
| *p*-Nitrophenol | 0.0528 | 0.0532 | +0.7 |
| 2,4-Dinitrophenol | 0.0371 | 0.0370 | −0.3 |
| 2,5-Dinitrophenol | 0.0169 | 0.0169 | 0.0 |
| 2,6-Dinitrophenol | 0.0531 | 0.0527 | −0.8 |
| 2,4,6-Trinitrophenol | 0.0635 | 0.0633 | −0.3 |

Fig. 1. Curves of potentiometric titration of individual acids with tetraethylammonium hydroxide in a methyl ethyl ketone medium: 1 – $\alpha$-naphthol; 2 –$\beta$-naphthol; 3 –palmitic; 4 –stearic; 5 –oleic; 6 – o-nitrophenol; 7 –m-nitrophenol; 8 –p-nitrophenol; 9 –2,4-dinitrophenol; 10 – 2,6-dinitrophenol; 11 –2,5-dinitrophenol; 12 –2,4,6-trinitrophenol

Figure 1: Fig. 1. Curves of potentiometric titration of individual acids with tetraethylammonium hydroxide in a methyl ethyl ketone medium: 1 –$\alpha$-naphthol; 2 –$\beta$-naphthol; 3 –palmitic; 4 –stearic; 5 –oleic; 6 –o-nitrophenol; 7 –m-nitrophenol; 8 –p-nitrophenol; 9 –2,4-dinitrophenol; 10 –2,6-dinitrophenol; 11 –2,5-dinitrophenol; 12 –2,4,6-trinitrophenol

## Experimental section

The objects of our study were various acids and their mixtures: 1) very weak acids, whose dissociation constants are so small that they cannot be titrated in an aqueous medium; 2) acids insoluble in water, which can be titrated only in a medium of nonaqueous solvents; 3) mixtures of weak and very weak acids, the differential titration of which is impossible in aqueous solution because of the leveling effect of water.

It was found that the best differentiating solvents for the determination of weak and very weak acids and their mixtures are ketones, especially methyl ethyl ketone. As the titrant we used a benzene–methanol solution of tetraethylammonium hydroxide (5 : 1), the titer of which was established with chemically pure benzoic acid. The titration was carried out in a stream of nitrogen; the change in potential was measured on an LP-5 potentiometer with glass and calomel electrodes.

**Titration of very weak acids.** As weak and very weak organic acids we titrated: phenol, *m*-, *o*- and *p*-cresols, thymol, hydroquinone, resorcinol, pyrogallol, $\alpha$- and $\beta$-naphthols, etc. The indicated compounds are very weak acids (pK  10); therefore in an aqueous medium it is impossible to determine accurately the equivalence point in the course of their titration. In a methyl ethyl ketone medium these compounds become stronger acids and can be titrated with tetraethylammonium hydroxide (Fig. 1). Analysis of the titration curves shows that the method of potentiometric titration in a nonaqueous medium can be successfully used for the quantitative determination of very weak acids, including phenols. The determination error is $±$2% (Table 1).

**Titration of organic acids insoluble in water.** Some organic compounds constituting homologous series of saturated and unsaturated monobasic acids were titrated. As is seen from Fig. 1 (curves 3, 4, 5), saturated acids (of the stearic type) and unsaturated acids (of the oleic type) in a methyl ethyl ketone medium are fairly strong acids. Analysis of the curves shows that the method of potentiometric titration in nonaqueous media can be used for the quantitative determination of these compounds. The determination error is $±$1% (Table

Fig. 2. Curves of potentiometric titration of multicomponent mixtures of strong, weak, and very weak acids with tetraethylammonium hydroxide in a methyl ethyl ketone medium: 1 –2,4,6-trinitrophenol + 2,5-dinitrophenol; 2 – 2,4,6-trinitrophenol + p-nitrophenol; 3 –2,4,6-trinitrophenol + o-nitrophenol; 4 –2,6-dinitrophenol + o-nitrophenol; 5 –2,4-dinitrophenol + o-nitrophenol; 6 –2,4,6-trinitrophenol + 2,4-dinitrophenol + p-nitrophenol; 7 – 2,4,6-trinitrophenol + 2,6-dinitrophenol + o-nitrophenol

Figure 2: Fig. 2. Curves of potentiometric titration of multicomponent mixtures of strong, weak, and very weak acids with tetraethylammonium hydroxide in a methyl ethyl ketone medium: 1 –2,4,6-trinitrophenol + 2,5-dinitrophenol; 2 –2,4,6-trinitrophenol + p-nitrophenol; 3 –2,4,6-trinitrophenol + o-nitrophenol; 4 –2,6-dinitrophenol + o-nitrophenol; 5 –2,4-dinitrophenol + o-nitrophenol; 6 –2,4,6-trinitrophenol + 2,4-dinitrophenol + p-nitrophenol; 7 –2,4,6-trinitrophenol + 2,6-dinitrophenol + o-nitrophenol

1).

**Differentiated titration of acid mixtures.** To clarify the possibility of differentiated titration of acids, it is necessary first to obtain titration curves for the individual compounds. Comparison of the titration curves of separate acids with the titration curves of their mixtures makes it possible to establish that differentiated titration is possible if the beginnings of the titration jumps of the individual acids differ by more than 100 mV. Figure 2 presents titration curves of acid mixtures. Analysis of the titration curves

shows that dinitrophenols in methyl ethyl ketone medium are stronger acids than nitrophenols, while trinitrophenol is a stronger acid than dinitrophenols (Fig. 1). Since the beginnings of the titration jumps of the individual phenols differ by more than 100 mV, mono-, di-, and trinitrophenols can be differentially titrated in binary and three-component mixtures. The results of quantitative analysis of acid mixtures are given in Table 2.

**Table 2**

**Results of the quantitative determination of acid mixtures**

| Substance determined | Taken, g | Found, g | Relative error, % | Substance determined | Taken, g | Found, g | Relative error, % |
|---|---|---|---|---|---|---|---|
| 2,4,6-Trinitrophenol | 0.0519 | 0.0521 | +0.4 | 2,4-Dinitrophenol | 0.0326 | 0.0320 | −1.9 |
| 2,5-Dinitrophenol | 0.0176 | 0.0174 | −1.1 | *o*-Nitrophenol | 0.0545 | 0.0551 | +1.2 |
| 2,4,6-Trinitrophenol | 0.0403 | 0.0400 | −0.7 | 2,4,6-Trinitrophenol | 0.0468 | 0.0463 | −1.1 |

| Substance determined | Taken, g | Found, g | Relative error, % | Substance determined | Taken, g | Found, g | Relative error, % |
|---|---|---|---|---|---|---|---|
| *p*-Nitrophenol | 0.0594 | 0.0591 | −0.5 | 2,4-Dinitrophenol | 0.0406 | 0.0398 | −2.0 |
| 2,4,6-Trinitrophenol | 0.0529 | 0.0521 | −1.5 | *p*-Nitrophenol | 0.0645 | 0.0657 | +1.8 |
| *o*-Nitrophenol | 0.0591 | 0.0584 | −1.2 | 2,4,6-Trinitrophenol | 0.0605 | 0.0600 | −0.8 |
| 2,6-Dinitrophenol | 0.0353 | 0.0350 | −0.9 | 2,6-Dinitrophenol | 0.0336 | 0.0332 | −1.5 |
| *o*-Nitrophenol | 0.0385 | 0.0388 | −0.9 | *o*-Nitrophenol | 0.0765 | 0.0779 | +1.9 |

From the data obtained it is evident that the error in determining the individual components in binary and ternary mixtures lies within $±$2%.

Thus, on the basis of the data obtained by us, it should be concluded that with tetraethylammonium hydroxide in methyl ethyl ketone medium it is possible rapidly, and with accuracy sufficient for quantitative determination, to titrate strong, weak, and very weak acids and their mixtures.

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*Note: Figure translations are in progress. See original paper for figures.*

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