

1092. *Submicro-methods for the Analysis of Organic Compounds. Part XXI.* The Determination of Nitrogen-containing Groups by Reduction with Titanium(III).*

By R. BELCHER, Y. A. GAWARGIOUS, and A. M. G. MACDONALD.

Nitro-groups have been determined in *ca.* 50- μ g. samples of organic compounds by reduction with excess of titanium(III) in the presence of citrate; an excess of iron(III) is then added, and back-titrated with titanium(III) in the presence of thiocyanate. An average relative error of $\pm 0.5\%$ was obtained. A modified Agla burette is described, in which solutions of titanium(III) sulphate can be stored for several months. The method is of wide applicability. Nitroso-groups have been determined similarly. A variety of compounds containing azoxy, azo, hydrazine, and oxime groups have been determined accurately, but the modes of reaction are uncertain in some cases and no general method could be developed.

A SURVEY¹ of the methods available for the determination of organic nitro-compounds by reduction to the corresponding amine indicated that, of the many possible reductants, titanium(III) was the most attractive reagent from the point of view of reaction rates, sensitivity to atmospheric oxidation, and selectivity. The method was suggested by Knecht and Hibbert,² and has been widely used on the macro- and semimicro-scales. In most procedures, nitro-groups are reduced with an excess of titanium(III) chloride solution in acidic medium, a variable boiling-period being needed, after which the excess of titanium(III) is titrated with iron(III) solution to a thiocyanate end-point. However, Kolthoff and Robinson³ have shown that boiling may cause variable errors, and Callan *et al.*⁴ have shown that reduction with titanium(III) chloride in dilute hydrochloric acid medium can be accompanied by chlorination side-reactions; moreover, the former workers demonstrated that reduction is complete in 3—5 min. at room temperature when conducted in a sodium citrate solution. Accordingly, the present work was based on reduction with titanium(III) sulphate in a citrate-containing medium.

Submicro-burette for Air-sensitive Solutions.—The first problem in this work was to find a suitable modification of the Agla micrometer burette, because titanium(III) solutions deteriorate rapidly in contact with air. Wilson and Sergeant⁵ have described a 5-ml. micrometer burette in which the syringe part can be connected either to the titanium(III) reservoir or to the burette tip through a two-way tap, and the titanium solution is stored under light petroleum (b. p. 100—120°). This idea was adapted for a 0.5-ml. syringe burette with unexpected ease. The reservoir was placed above, instead of below, the syringe level, in order to avoid air bubbles being drawn in from the end of the syringe during filling; a gravity effect also assisted filling with the present design [see the Figure (Experimental section)], and there was no evidence of seepage past the plunger of the syringe. A three-way tap was also tested, because it would be useful to flush the burette tip directly from the reservoir without having to fill the syringe, but there was a very slight seepage of titrant between the tap outlets in this case.

The titanium(III) solution was stored under heptane or pentane, the level of hydrocarbon in the top reservoir being maintained as the titrant was consumed. The stability of a 0.03—

* Part XX, R. Belcher, A. M. G. Macdonald, S. E. Phang, and T. S. West, *J.*, 1965, 2044.¹ Y. A. Gawargious, Ph.D. Thesis, University of Birmingham, 1963.² E. Knecht and E. Hibbert, "New Reaction Methods in Volumetric Analysis," 2nd edn., Longmans, London, 1925.³ I. M. Kolthoff and C. Robinson, *Rec. Trav. chim.*, 1926, **46**, 169.⁴ T. Callan, J. A. R. Henderson and N. Strafford, *J. Soc. Chem. Ind.*, 1920, **39**, 86T; T. Callan and J. A. R. Henderson, *ibid.*, 1922, **41**, 157T.⁵ A. D. Wilson and G. A. Sergeant, *Analyst*, 1962, **87**, 152.

0.04M-titanium(III) solution was excellent under these conditions, which may be ascribed partly to the extreme purity of the solution itself, and partly to the efficiency of the storage system. The loss in titre was 4% in the first 10 days; then the loss was very slow and gradual for about 80 days of constant use (1% over the period), but thereafter decomposition became increasingly rapid, amounting to 4% after 95 days, 12% after 128 days, and 40% after 150 days. This behaviour seemed quite reproducible, but more-dilute titanium(III) solutions deteriorated much more quickly. This apparatus appears to be much more effective for the storage of air-sensitive solutions than conventional systems with nitrogen atmospheres, even when zinc amalgam is placed in the reservoir and the solution is protected from light; for example, Ma and Early⁶ found that a 0.03M-titanium(III) chloride solution had a useful life of only 28 days under such conditions.

Because the organic layer provided sufficient protection for the stock solution of titanium(III), a nitrogen atmosphere was required only for the reaction vessels; purified nitrogen, bubbled through the solution at a reasonably constant rate, gave sufficient protection with the vessels used.

Determination of Nitro-groups.—The reduction of a nitro-compound to the corresponding amine requires six equivalents of titanium(III); hence the method provides an excellent basis for submicro-work. Conventionally, the excess of titanium(III) is back-titrated with iron(III) solution in the presence of thiocyanate as indicator. The colour change to red could be detected in submicro-tests, but it proved easier to see the bleaching of the red complex; accordingly, after the main reduction, an excess of iron(III) was added, and then back-titrated with titanium(III) solution. Other indicators were tested, but were much less satisfactory than thiocyanate; either the ammonium or potassium salt was applicable.

The conditions for the titration of iron(III) were not critical: there was no significant variation in the results with titration volumes of 1.5–2.5 ml. at temperatures of 20–40°. The best end-points were obtained at acidities of 2.4–3.2N in sulphuric acid; if sufficient care were taken, reasonable results could be achieved over the range 1.6–4.8N.

Aromatic nitro-compounds were tested first; when the reduction was done in a citrate-containing medium, the conditions were not critical. Ethanol was the best general solvent for these compounds; with an end-volume of *ca.* 1.5 ml., up to 0.5 ml. of ethanol and up to 0.3 ml. of 20% potassium citrate solution had no effect on the end-point. A few compounds required dissolution in acetic acid: with glacial acetic acid, the end-points were very slow, but dilute solutions had no effect. It was shown that up to 0.3 ml. of acetone had no effect on the titration; however, this solvent did not prove necessary. Moderate amounts of formaldehyde and acetaldehyde caused poor end-points and turbidities, so that it was better to use aldehyde-free ethanol as solvent. Neutral salts, *e.g.*, sodium chloride, appeared to have no effect on the titration.

The blank introduced by potassium citrate in the specified amount was negligible; the sodium salt had a slightly larger blank. Sodium acetate was used in a few tests and was quite satisfactory, as has been shown on other scales of working,^{6,7} but appeared to have no advantage over citrate.

The pH of the solution during reduction in presence of citrate was 5–6, and a 70–100% excess of titanium(III) was generally quite sufficient, the reduction being complete in 3–5 min. As a general rule, 250 μ l. of titanium(III) were allowed to react for 5 min., but most mononitro-compounds could be reduced with 200 μ l. in 3 min., whereas with trinitro-compounds, addition of 300 μ l. and a standing time of 7 min. gave the best results. Neither the excess of reductant nor the time of reaction was critical in the presence of citrate; without citrate or acetate present, reduction was extremely slow, even on heating.

In a very few cases, the colour of the amine produced by the reduction was visible, *e.g.*, with 8-nitroquinoline or picramide, and the end-point was then taken as the change from red

⁶ T. S. Ma and J. V. Early, *Mikrochim. Acta*, 1959, 129.

⁷ P. G. Butts, W. J. Meikle, J. Shovers, D. L. Kouba, and W. W. Becker, *Analyt. Chem.*, 1948, 20, 947.

5700 *Belcher, Gawargious, and Macdonald: Submicro-methods*

to the amine colour; in no case was the end-point masked to an important extent, any doubt being resolved by addition of more indicator near the end-point, or by running a preliminary qualitative test to judge the final amine colour.

p-Nitroaniline was used as the initial test compound; it is customary on larger scales of working to use this as a standard. On the submicro-scale, at least, it was found that there was no significant difference between the factors based on standardisation against *p*-nitroaniline or against potassium dichromate after oxidation of iron(II). Repeated cross-standardisations showed that all the reactions proceeded stoichiometrically, despite the high dilutions involved. Standardisation against dichromate was normally applied.

A series of 20 determinations of *p*-nitroaniline showed an average percentage recovery of 100.15%, with an average error of $\pm 0.5\%$ (maximum 1.0%). No systematic bias was apparent and the precision and accuracy seem to be only slightly less than on larger scales of working. A series of research and commercial samples containing various substituents was then analysed. Representative results are given in Table 1; results for several di- and tri-nitro-

TABLE 1.
Typical results for nitro- and nitroso-compounds.

Sample	Sample wt. ($\mu\text{g.}$)	NO ₂ or NO (%)		Recovery (%)
		Found	Calc.	
Nitro-compounds				
<i>p</i> -Nitroaniline (20 detns.)	35—65	33.36	33.31	100.15
		(33.02—33.66)		
5-Amino-2-nitrobenzotrifluoride	79.06	23.09	22.32	103.4
	61.12	22.52		100.9
4-Nitro- <i>o</i> -anisidine	33.68	27.52	27.36	100.6
	47.28	27.33		99.9
1-Nitro-2-naphthol	72.45	23.90	24.32	98.3
	57.68	24.67		101.4
8-Nitroquinoline	45.00	25.97	26.42	98.3
	35.57	26.85		101.6
1-Chloro-2,4-dinitrobenzene	58.13	45.91	45.43	101.1
	51.70	45.10		99.3
2-(Pentafluorophenylamino)ethyl-3,5-dinitrobenzoate	36.85	21.35	21.84	97.8
	47.32	21.72		99.4
4,4'-Dinitrobiphenyl	53.50	37.68	37.68	100.0
	49.24	37.73		100.1
2,4-Dinitrophenylhydrazine*	49.30	46.55	46.44	100.2
	48.10	47.11		101.4
Picric acid	55.65	60.48	60.24	100.4
	39.95	60.44		100.3
Picramide	47.38	61.06	60.50	100.9
	36.64	60.36		99.8
Cyclohexanone 2,4-dinitrophenylhydrazone	51.99	33.41	33.07	101.0
	52.50	33.57		101.5
Nitroguanidine*	47.89	44.52	44.20	100.7
	56.00	44.04		99.6
Nitroso-compounds				
1-Nitroso-2-naphthol	59.28	17.61	17.33	101.6
	67.55	17.74		102.4
Sodium 2-nitroso-1-naphthol-4-sulphonate	61.54	10.62	10.90	97.4
	45.30	11.24		103.1
<i>N</i> -Nitrosodiphenylamine*	66.80	15.50	15.14	102.4
	57.33	14.95		98.7

* See text.

compounds are also included. The results on *p*-nitroaniline excluded, the average percentage recovery for nearly 50 analyses of 19 different mono-, di-, and tri-nitro-aryl compounds was 100.3%; the maximal error was slightly greater than with *p*-nitroaniline, probably owing to sample inhomogeneity.

Among the compounds analysed, there was no evidence of any effect of substituents on

the reduction of nitro-groups. Hinshelwood and his co-workers⁸ have shown that substituents have only a minor effect on the rate of reduction of substituted nitrobenzenes at acidities of about 0.5N. Increase in the acidity retards reduction so that the effects of some substituents become more apparent.⁶ The ease of reduction of all types of compound in the nearly neutral solution and at the comparatively high dilution used in the present work favours Hinshelwood's suggestion⁸ that the reducing species is actually a hydrolysed form of titanium(III), probably TiO(OH).

The results obtained for cyclohexanone 2,4-dinitrophenylhydrazone and 2,4-dinitrophenylhydrazine are of interest, because they confirm that the reactions on the microgram scale are generally the same as on larger scales of working. Thus, with the former compound, only the nitro-groups were reduced, whereas with 2,4-dinitrophenylhydrazine, the hydrazine group also reacted, 14 equivalents of titanium(III) being consumed. Arylhydrazines were not reduced unless the activating nitro-group was also present.

Very few aliphatic nitro-compounds were available for testing. There is little agreement in the literature about the optimum conditions for the reduction of these compounds.⁹ In this work, attention was concentrated on nitroguanidine; conditions similar to those recommended by Sternglanz *et al.*¹⁰ were found satisfactory, *i.e.*, dissolution in dilute acetic acid (0.3 ml. of 10% v/v solution), addition of twice the normal amounts of citrate and titanium(III) solutions, and a reaction time of 10 min. Recoveries obtained by the general procedure were about 30% low.

Determination of Nitroso-groups.—The reduction of nitroso-groups with titanium(III) has been studied by several workers (see, *e.g.*, refs. 2, 6, and 9). Sometimes a direct titration at 40–60° has been used, but usually an indirect method is preferred; nitroso-groups are much more rapidly reduced than are nitro-groups.⁸ In the present work, the method recommended for nitro-groups was found to be entirely satisfactory for the determination of nitroso-groups, with a 50–100% excess of titanium(III) and a reaction period of 3 minutes. Representative results are shown in Table 1. Because the nitroso-group consumes only 4 equivalents of titanium(III), the results were less precise than those obtained for nitro-groups, but there was no significant difference in the accuracy of mean values. *N*-Nitrosodiphenylamine had to be dissolved in 1:1 aqueous acetic acid, but this did not affect the results.

Determination of Other Nitrogen-containing Groups.—The methods described for the determination of nitro- and nitroso-groups are of reasonably general application, but no similarly general method could be developed for azo and other nitrogen-containing linkages because of the variability of the reactions involved. However, several useful applications are outlined below.

Azo-groups. Most azo-compounds appear to be reduced to the individual amines, and four equivalents of titanium(III) are consumed whether the titration is done directly² or indirectly.^{11,12} However, azobenzene is reduced only to hydrazobenzene, which is said to undergo benzidine rearrangement; with some derivatives of azobenzene, diphenylene or semidine rearrangements may intervene, depending on the nature and position of the substituents.

The first tests on the microgram scale were made with azobenzene; in sulphuric acid media, the amount of reduction increased as the acidity was increased to 5N, but quantitative reduction to hydrazobenzene could be achieved only on heating for 5 minutes. In a buffered medium, the reduction, with a consumption of 2 equivalents of titanium(III), was complete in 5 minutes at normal temperatures, but a slower reduction then continued for a considerable time. Veibel¹³ has indicated that the benzidine rearrangement does not necessarily require a strongly acidic medium, but if benzidine is formed, the slow reduction process is difficult to

⁸ S. A. Newton, F. J. Stubbs, and C. Hinshelwood, *J.*, 1953, 3384.

⁹ I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, 1957.

¹⁰ P. D. Sternglanz, R. C. Thompson, and W. L. Savell, *Analyt. Chem.*, 1955, 27, 392.

¹¹ T. S. Ma and J. V. Early, *Mikrochim. Acta*, 1960, 685.

¹² F. Fainer, K. F. Keirstead, and J. L. Myers, *Canad. J. Chem.*, 1952, 30, 498.

¹³ S. Veibel, *Canad. J. Chem.*, 1945, 32, 638.

explain, particularly in a solution containing sulphate. When attempts were made to reduce pure hydrazobenzene and other hydrazo-compounds in citrate media on the microgram scale, there was no significant reduction, but variation in the excess of titanium(III) and in reaction times led to some reduction, though this was never quantitative. Hinshelwood and his co-workers¹⁴ have indicated that, in slightly acidic media, hydrazobenzene mainly rearranges to benzidine, but is also partly reduced to aniline; this may explain the later slow reaction. Several azoates were analysed under similar conditions; again, only 2 equivalents of titanium(III) were consumed in the first relatively rapid reaction, so that a diphenylene rearrangement seems probable. Typical results obtained for such compounds, after a reaction time of 3–5 minutes, are shown in Table 2. The average recovery for 10 analyses of four pure

TABLE 2.
Analysis of azo, azoxy, and oxime compounds.

Sample	Sample wt. ($\mu\text{g.}$)	Group (%)		Recovery (%)
		Found	Calc.	
Azobenzene	61.57	15.74	15.37	102.4
	67.86	15.79		102.7
Ethyl azoate	45.61	11.12	11.02	100.9
	66.13	10.78		97.8
4,4'-Dimethoxyazoxybenzene	74.60	17.51	17.04	102.8
	75.47	17.60		103.3
Azoxybenzene	40.27	22.27	22.20	100.3
	62.75	22.24		100.2
Di-2-pyridyl ketoxime	54.18	21.69	21.60	100.42
	69.64	21.82		101.02
Pyridine 2-aldoxime	81.95	34.78	35.23	98.72
	67.53	34.99		99.32

samples was 100.5%, but the precision was worse ($\pm 3\%$) than that for nitro-groups, because of the poor conversion factor. Further tests were made with 3,3'-dimethylazobenzene and bistrifluoromethylazobenzene, but no reduction could be achieved under buffered or acidic conditions.

Azoxy-groups. So far as is known, no analytical method based on reaction with a strong reductant has been described for azoxy-groups. Stephen and Hinshelwood¹⁵ indicated that, in acidic solution, azoxybenzene is partly reduced by titanium(III), through azobenzene, to benzidine, and partly reduced directly to aniline. In the present work, 4,4'-dimethoxyazoxybenzene could be determined with reasonable accuracy, by the general procedure based on consumption of 4 equivalents of titanium(III); prolonging the reaction period did not affect the results. However, azoxybenzene consumed only about 2 equivalents in 3 minutes, and 4 equivalents after 20 minutes; the latter results were accurate (Table 2) provided that a period of 5 minutes was allowed between the addition of acid and excess of iron(III) and the final titration, and subsequent reduction was slow. One could suggest that the reduction proceeds through hydrazobenzene to benzidine, but the same problems then arise as in the explanation of the reduction mechanism of azobenzene. No reduction of azoxybenzene could be obtained in acidic media.

Oxime groups. No quantitative application has previously been made of the reduction of oximes with titanium(III). On the microgram scale, several compounds were analysed. Excellent results were obtained for the compounds indicated in Table 2 by use of the general procedure, but quite similar samples (2-pyridyl methyl and 2-pyrrolyl methyl ketoximes) failed to show any reduction, presumably because of the electron-repelling effect of the methyl group.

A full account of this work has been given elsewhere.¹ For analyses, it appeared that most compounds containing azo, azoxy, or oxime groups could be determined with reasonable accuracy by the general procedure, where the reaction stoichiometry was known or could be

¹⁴ N. R. Large, F. J. Stubbs, and C. Hinshelwood, *J.*, 1954, 2736.

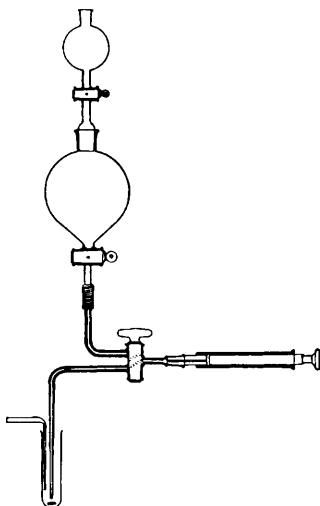
¹⁵ M. J. Stephen and C. Hinshelwood, *J.*, 1955, 1393.

deduced. A few compounds proved to be unexpectedly stable to reduction, and, therefore, no definitive conclusions should be made from zero results. Obviously, much more study is needed on larger scales of working in order to define the mechanism and products of reduction with these types of compound.

EXPERIMENTAL

Apparatus.—The microgram balance and accessories were as described previously.¹⁶ Analyses were carried out in Pyrex-glass test-tubes (ca. 65 mm. × 16 mm.) which were thoroughly cleaned and oven-dried before use. Agla micrometer glass-syringe burettes were used where accurate measurement of reagent solutions was required; other reagent solutions were added from calibrated capillary dropping bottles.

Modified Agla burette for air-sensitive solutions.—A capillary-type double-oblique tap (2 mm. bore) was inserted between the syringe and the capillary parts of the normal Agla burette. One of the tap outlets was fused to the male joint of the glass syringe and another to the capillary tip, as shown in the Figure; the third outlet was attached by PVC tubing to a reservoir (500-ml.



Assembly for storage and titration.

separatory funnel) above which was placed a 100-ml. separatory funnel. The tap was very lightly greased with silicone grease. Because it was convenient to leave the tip of the titanium(III) burette in the solution throughout a determination, the capillary bore was made fine (not greater than 0.2 mm. at the tip) in order to prevent diffusion effects. Before a series of titrations, the capillary tip was flushed several times with the titrant. When not in use, the tip was immersed in water with a slow nitrogen stream bubbling through it. The main reservoir was protected from light with black paper or aluminium foil.

Nitrogen supply. Nitrogen was purified by bubbling it through a titanium(III) sulphate solution containing potassium citrate over zinc amalgam in a Dreschel bottle, and was then scrubbed through two bubblers containing water. The last bubbler was connected, through a trap, to a suitable glass tube drawn to a capillary tip, which was placed into the sample solution slightly above the burette tip to prevent nitrogen entering the burette. The flow was controlled by a screw-clip on the rubber tubing between the cylinder and the purification train.

Magnetic stirrer. Because the modified burette was unwieldy and the nitrogen bubbling did not stir the bottom of the solution efficiently, a small magnetic stirrer, which could readily be moved from under the titration tubes, was constructed from a gramophone motor (47 mA, 9V).

Reagents.—Glass-distilled air-free water was used. AnalaR reagents were used unless otherwise specified.

Titanium(III) sulphate solution. Potassium titanium oxalate was twice recrystallised; 36 g. of the pure salt were converted to titanium(IV) sulphate by digestion with 80 ml. of concentrated sulphuric acid and 32 g. of ammonium sulphate, by the method of Roseman and Thornton.¹⁷

¹⁶ R. Belcher, P. Gouverneur, and A. M. G. Macdonald, *J.*, 1962, 1938.

¹⁷ R. Roseman and W. M. Thornton, *J. Amer. Chem. Soc.*, 1935, 57, 328.

This solution was diluted to give a 0.03—0.04M-titanium solution, and was then reduced with amalgamated (5%) zinc in the apparatus described by Stone and Beeson,¹⁸ being passed directly into the large storage reservoir of the modified burette, displacing a layer of heptane or pentane into the small reservoir. The final acidity of the solution was only 0.15—0.2N.

Ethanol. "Spectroscopically pure" ethanol was used.

Iron(III) ammonium sulphate solution. A 0.1M-iron(III) solution, ca. 0.25M in sulphuric acid (M.A.R.), was prepared. This was standardised against the titanium(III) solution.

Standardisation of the Titanium(III) Solution.—Two methods were used: (a) an empirical standardisation against *p*-nitroaniline (M.A.S.), following the procedure given below; and (b) a more accurate standardisation against potassium dichromate. The method described by Kolthoff and Belcher⁹ was readily scaled down. Iron(II) ammonium sulphate (3—3.5 mg.) was dissolved in 0.6 ml. of water, and 0.2 ml. of 12N-sulphuric acid and exactly 100 μ l. of standard 0.05N-potassium dichromate were added. The Agla tip was rinsed with 0.4 ml. of water, the titanium(III) burette was inserted, and nitrogen was bubbled through the solution for 3 min. A micro-drop of 10% ammonium thiocyanate indicator was then added, and the iron(III) formed was titrated with the titanium(III) solution, following the technique described below. Blank determinations were made in the same way, except for the addition of dichromate.

Procedure.—A sample of 30—80 μ g. was weighed into the cleaned tube, and dissolved in 0.2—0.3 ml. of ethanol. For complete dissolution of some compounds, heating for 1—2 min. to 50—60° was needed. A few compounds were dissolved in dilute acetic acid, as mentioned in the text. Then 0.4 ml. of water and 0.3 ml. of aqueous 20% potassium citrate solution were added. It should be noted that many solid nitro-compounds are sufficiently volatile for errors to arise if much time elapses between weighing and dissolution on this scale of working. The stirring magnet was introduced, and the tube was raised under the burette tip and the nitrogen outlet so that both were under the surface of the solution, with the stirrer in position. Nitrogen was bubbled through the solution for 3 min. at a rate of 1—2 bubbles per sec. This bubble-rate was maintained throughout the subsequent steps.

Exactly 250 μ l. of 0.03M-titanium(III) solution was added, and the solution was left for 5 min. (unless otherwise specified in the text). Then 0.2 ml. of 12N-sulphuric acid and exactly 100 μ l. of 0.1M-iron(III) solution were added, the tip of the iron(III) burette being rinsed with 0.2 ml. of water. Ammonium thiocyanate (0.04 ml. of 10% solution) was added, and, after 1 min., the excess of iron(III) was titrated with the titanium(III) solution under a close "daylight" bulb against a white background. Near the end-point, intervals of 10—15 sec. were allowed between the 0.1- μ l. increments of titrant.

A blank determination was taken through all the steps.

One of us (Y. A. G.) thanks the Ministry of Education (U.A.R.) for financial support. The work was sponsored, in part, by the Office of Research and Development, U.S. Department of the Army, through its European Research Office.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDGBASTON, BIRMINGHAM, 15.

[Present address (Y. A. G.): NATIONAL RESEARCH CENTRE, ANALYTICAL CHEMISTRY UNIT,

DOKKI, CAIRO, U.A.R.]

[Received, September 23rd, 1964.]

¹⁸ H. W. Stone and C. Beeson, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 188.
