

PHOTOCHEMICAL ANALYSIS.

PART III. VOLUMETRIC ESTIMATION OF FERRIC SALTS.

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In parts I and II of this series, Gopala Rao and Ramacharlu (1942, 1943) have described a method for the estimation of mercuric chloride employing a new technique based on the photochemical action of light. Using a similar technique we have now developed an easy method for the volumetric estimation of ferric salts.

The method, which we have now developed, is based on the reduction of ferric salts to the ferrous condition by oxalic acid, when exposed to sunlight for a short time and subsequent titration of the ferrous salt with a standard solution of sodium vanadate, by the method of Gopala Rao and Viswanadham (1944).

EXPERIMENTAL.

An approximately N/20 solution of ferric alum (Analar, B. D. H.) was prepared. 20 mls. of the ferric alum solution was taken in a conical pyrex glass flask, 20 mls. of approx. N/10 sodium oxalate (Merck, A. R.) was added followed by the addition of 10 mls. of approx. 4N sulphuric acid. The flask was then exposed to bright sunlight for the requisite interval of time. The ferrous salt formed by the photochemical reduction of ferric salt was estimated by titration with a standard solution of sodium vanadate, using diphenylamine or diphenyl benzidine as the internal indicator. Dichromate solution cannot be employed for the titration of the ferrous iron in the presence of oxalic, citric, tartaric or malic acids. The results recorded in the following table indicate that the ferric salt is quantitatively reduced to the ferrous condition in ten minutes :—

TABLE I.

20 mls. ferric alum solution (N/20) + 20 mls. sodium oxalate solution (N/10) + 10 mls. of sulphuric acid solution (4N).

Amount of ferric iron taken 0.05327 gm.

Time of exposure.	Amount of ferric iron reduced.
5 minutes	0.03663 gm.
10 minutes	0.05329 gm.
20 minutes	0.05323 gm.
30 minutes	0.05329 gm.
50 minutes	0.05329 gm.
60 minutes	0.05329 gm.
80 minutes	0.05329 gm.
100 minutes	0.05329 gm.

The results recorded in Table II show that the acid concentration can be varied within wide limits without appreciably altering the speed of reaction.

TABLE II.

20 mls. of ferric alum solution (N/20)+20 mls. of sodium oxalate solution (N/10)+10 mls. of XN sulphuric acid solution.

Amount of ferric iron taken 0.05327 gm.

Time of Exposure 30 minutes.

Value of X	Amount of ferric iron reduced.
4.0N	0.05337 gm.
2.0N	0.05337 gm.
1.0N	0.05351 gm.
0.5N	0.05310 gm.

We have found that sulphuric acid can be substituted by hydrochloric acid without any undue influence. We have also made experiments using sodium citrate or sodium potassium tartrate in place of sodium oxalate. We have found that the speed of reduction is much slower with these substances than with sodium oxalate. Moreover, the speed of reduction with citrate and tartrate is influenced by the acid concentration, decreasing with increasing acid concentration.

We have carried out a large number of determinations of ferric iron by the photochemical method now developed. Typical results are given below.

Amount of ferric iron taken.	Amount of ferric iron found by the authors' method.
0.01348 gm.	0.01344 gm.
0.02696 gm.	0.02687 gm.
0.05392 gm.	0.05387 gm.
0.03506 gm.	0.03510 gm.
0.07012 gm.	0.07030 gm.
0.08765 gm.	0.08742 gm.

It will be found that the method for the volumetric estimation of iron now proposed gives excellent results and is quite easy to carry out.

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