

### 116. *An Improved Analysis of Fuming and Concentrated Sulphuric Acid by Water Titration.*

By J. C. D. BRAND.

The direct determination of sulphur trioxide in fuming sulphuric acid by titration with water (Parker, *J. Soc. Chem. Ind.*, 1917, **36**, 692) has been improved and shown to give results of considerable precision. The titration is applied further (a) to the analysis of concentrated sulphuric acid with a high order of accuracy, and (b) to the preparation of a standard normal solution of sulphuric acid without reference to analytical standards such as sodium carbonate or potassium iodate.

THE direct estimation by water of the sulphur trioxide contained in fuming sulphuric acid was proposed and carried out by Setlik (*Chem. Ztg.*, 1889, **13**, 1670) and by Parker (*loc. cit.*). However, in spite of the fact that Parker was able to show that the accuracy thus attainable is higher than that reached by any other means, the method does not seem to have gained much currency and receives only brief mention in works which describe the methods of analysis of oleum. This method for the determination of oleum strength amounts in principle to titration with distilled water of the "free" sulphur trioxide of the acid to an end-point at which the cooled liquid no longer fumes in contact with air. The familiar way of determining the strength of an oleum is by alkalimetry: the amount of alkali consumed by the sulphur trioxide, however, is only a small fraction of that required by the great bulk of sulphuric acid, and errors in estimation of the trioxide are commensurably magnified. It is clear that the water titration, which estimates sulphur trioxide directly, possesses an advantage over the alkali method; moreover, the distilled water of the titration is already an absolute standard.

The procedure of titration differs somewhat from that described by Parker (*loc. cit.*). Improved results were obtained by using a small drop in titration and by keeping the temperature of the liquid during the search for the end-point below 10°, rather than below 45° as recommended previously. Anhydrous sulphuric acid fumes perceptibly at about 13°, and an oleum will be over-titrated if the temperature at which the end-point

is reached is not lower than this. Analyses of oleum by water and by alkali are compared in Table I. An oleum which contains another substance dissolved in it cannot, however, be analysed straightforwardly by water titration, for most solutes combine chemically with a proportion of the sulphur trioxide of the oleum, and this quantity escapes estimation by water. *Direct* application of the water method is confined to pure

TABLE I.  
The strength of oleum by water-titration and by alkalimetry.

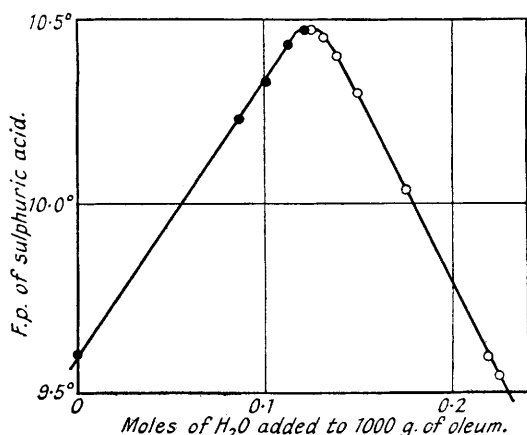
(Density of water = 0.998 g./ml. at 20°.)

No.	Water-titration.		H <sub>2</sub> SO <sub>4</sub> , %.	"Free" SO <sub>3</sub> , %.	% H <sub>2</sub> SO <sub>4</sub> by alkalimetry.	
	Ml. of H <sub>2</sub> O per 100 g. of oleum.	Mean, ml.*			Observed.	Mean.
1	3.98, 3.98, 4.00, 3.97, 3.95, 3.98, 3.95, 3.97	3.97 ± 0.01	103.96	17.6	103.9, 104.0	104.0 ± 0.1
2	3.84, 3.84, 3.84	3.84	103.83	17.0	103.9, 104.0	103.9 ± 0.1
3	3.07, 3.08, 3.05	3.07 ± 0.01	103.06	13.6	103.1, 103.0, 103.0, 102.9	103.0 ± 0.1
4	1.668, 1.667, 1.667, 1.664, 1.663	1.666 ± 0.002	101.66	7.39	—	—
5	0.495, 0.498, 0.498, 0.495, 0.487	0.495 ± 0.003	100.49	2.19	—	—
6	0.200, 0.195, 0.195	0.197 ± 0.002	100.20	0.87	100.1, 100.2, 100.1	100.1 ± 0.1

\* The error quoted is the mean deviation.

oleum by this fact, which will be examined in detail in a subsequent paper.

*The Correctness of the Water Titration.*—Agreement between the alkali and the water titration is not proof that the latter measures the sulphur trioxide content of an oleum exactly, but verification of this is possible.



The freezing point of anhydrous sulphuric acid is lowered by the addition of either water or sulphur trioxide. It is desired to find, therefore, whether, under the conditions of titration prescribed below, fuming ceases abruptly when a liquid of maximum freezing point is reached. That this is so is confirmed by experiment, the results of one series of which are displayed in the figure: water was added, in amount shown along the horizontal axis, to an oleum containing 1.00% of sulphur trioxide. The freezing points of the acids which were or were not seen to fume are marked by dots or circles respectively. As the freezing point of the liquid rose, fuming diminished, and no fume was seen upon the liquid after the freezing point maximum was reached. This observation was made at the freezing point of the acid (10.5°), but a fume could be seen over the terminal acid upon raising the temperature to only 13° or 14°, and Parker's statement (*loc. cit.*) that anhydrous sulphuric acid does not fume below 30° is therefore inexact.

Provided, however, that the temperature at which the end-point is sought is below 10°, water titration gives an exact measure of the "free" sulphur trioxide contained in an oleum.

*Determination of the Strength of Concentrated Sulphuric Acid.*—Attempts to analyse concentrated sulphuric acid by direct titration with oleum to the first appearance of a fume gave unpromising results, but the alternative

TABLE II A.  
Determination of the strength of concentrated sulphuric acid.

(Density of water at 20°: 0.998 g./ml.)

Acid.	Standard oleum.			Conc. H <sub>2</sub> SO <sub>4</sub> (g. used).	Water-titration of mixture, ml.	Water (ml.) present in conc. H <sub>2</sub> SO <sub>4</sub> .	H <sub>2</sub> O, %.	H <sub>2</sub> SO <sub>4</sub> , %.
	Ml. H <sub>2</sub> O per 100 g.	G. of oleum used.	Titre of sample used, ml.					
1	2.767	36.66 35.99 52.51	1.015 0.996 1.454	50.92 60.51 52.95	0.433 0.320 0.860	0.582 0.676 0.594	1.14 1.12 1.12	98.86 98.88 98.88
(By alkali: 98.8, 98.9%.)								
2	3.01	68.43 48.31 32.21 50.09	2.060 1.454 0.970 1.508	71.23 69.53 49.48 101.21	1.087 0.500 0.280 0.115	0.973 0.954 0.690 1.393	1.36 1.37 1.39 1.37	98.64 98.63 98.61 98.63
98.63 ± 0.01								

TABLE II B.

Acid.	Standard oleum.		Conc. H <sub>2</sub> SO <sub>4</sub> (g. used).	Wt. of mixture analysed, g.	Water- titration of mixture, ml.	Water (ml.) present in conc. H <sub>2</sub> SO <sub>4</sub> .	H <sub>2</sub> O, %.	H <sub>2</sub> SO <sub>4</sub> , %.
	G. of oleum used.	Ml. of H <sub>2</sub> O per 100 g.						
3	150.0	10.00	250.0	a. 21.72	0.554	0.260	1.91	98.09
				b. 25.84	0.659	0.309	1.92	98.08
				c. 23.19	0.595	0.275	1.89	98.11
	250.0	10.00	400.0	a. 59.31	1.593	0.688	1.89	98.11
				b. 72.03	1.923	0.847	1.91	98.09
				c. 48.86	1.300	0.579	1.92	98.08
	197.0	6.963	213.0	a. 22.78	0.535	0.227	1.91	98.09
				b. 75.80	1.787	0.749	1.90	98.10
				c. 31.35	0.737	0.312	1.91	98.09

98.09 ± 0.01

(The mean deviation is quoted for each series of results.)

method of back-titration was satisfactory. A weighed quantity of oleum of known strength was mixed with a weighed amount of concentrated sulphuric acid, and the remaining sulphur trioxide in the mixture estimated by water. The difference between the titration of the oleum and of the oleum-concentrated acid mixture is equal to the volume of water contained in the aqueous acid, from which its strength may be calculated (Table II). As the results quoted show, concentrated sulphuric acid may be analysed by this determination of the water content to within about 0.02% H<sub>2</sub>SO<sub>4</sub>, or with several times the accuracy of volumetric alkalimetry. The method can be used with advantage for the analysis of sulphuric acid stronger than about 90% H<sub>2</sub>SO<sub>4</sub>; application is still confined to pure acids which contain no dissolved substance.

*Preparation of a Standard Aqueous Solution of Sulphuric Acid.*—It is a straightforward matter to analyse a pure oleum by water so that its strength is known to ± 0.01% H<sub>2</sub>SO<sub>4</sub>. By dilution of this acid with water (without loss of fume) one may obtain an aqueous acid of strength known to one part in 10,000 parts. A very weak oleum, containing 1% or less of sulphur trioxide, can be diluted with water without a significant loss of fume. By diluting a weighed amount of weak oleum, three approximately N-solutions of sulphuric acid were prepared, and the strengths of each found independently by use of a standard solution of potassium iodate. The results were as follows:

100.20% H <sub>2</sub> SO <sub>4</sub> was diluted with water to the following concn.	Concn. found by reference to KIO <sub>3</sub> .
0.8908N	0.8902N
1.043N	1.042N
1.189N	1.189N

It is therefore possible to prepare a standard solution of sulphuric acid by this means without resort to standard analytical substances other than distilled water.

## EXPERIMENTAL.

Oleum was prepared by distilling sulphur trioxide in an all-glass Pyrex apparatus from a strong (commercial) oleum into concentrated sulphuric acid; purification was repeated until the product was colourless. No residue remained upon ignition of the acids, which contained less than 0.003% of sulphur dioxide. The type of flask used for storage had a ground glass cone at the neck, and was closed by a ground glass cap.

*Method of Titration.*—Distilled water was added from a micro-burette, graduated to read to 0.02 ml., the tip of which was drawn out into a capillary so that the drop size was about 0.01 ml. Choice of the amount of oleum used in an estimation depends upon the strength of the oleum under analysis and the precision required; with the burette used it was clearly desirable that a titration should not be of less than 0.5 ml. About 25 g. of oleum were used to obtain the comparatively crude results 1—3 of Table I, whereas more than 150 g. was sometimes taken for the remaining analyses. The oleum was titrated in a glass-stoppered conical flask, to which water was added in such amounts that there was no escape of fume. Fume within the flask was absorbed by vigorous shaking after each addition, and the acid cooled in ice; the temperature at the end-point of a titration must be below 10°. Fuming diminished near the end of a titration. When necessary the liquid was tested to see whether it still fumed by blowing a puff of air (from a bellows) into the flask, through a tube held with its opening only a few mm. above the surface of the liquid. Any fume was thereby swept out of the flask leaving the air within momentarily clear, but, if the liquid was still an oleum, fume formed again rapidly and was seen as a mist upon the surface. Water was added dropwise, and this observation repeated at each step until no fume could be detected over the liquid. Near the end-point the fume which formed was slight and was seen only in a good light. Titrations are best carried out in bright daylight, the flask being held for inspection against a dark background. Immediately before the end-point a mere wisp of fume develops, which lies on the surface of the oleum in the centre of the flask, and is seen from an eye-level slightly above the plane of the surface of the liquid.

If, in testing for the end-point, the air within the flask is changed too often the effect of the moisture introduced become detectable. Air used to locate the end-point cannot be dried, since the fume forms by reaction of sulphur trioxide with water vapour. The number of times air may be blown over the liquid without effect upon the titration obviously depends upon the humidity, and the volume of air enclosed in the flask. (0.005 Ml. of water, *i.e.*, half a drop in titration, is contained in some 300 ml. of air of maximum humidity at 20°.) For comparison, the results of Table I are expressed in ml. of water consumed by 100 g. of oleum. Denoting this quantity by *v*, the strength of the oleum (if the density of water be taken as unity) is (100 + *v*)% H<sub>2</sub>SO<sub>4</sub>, or (*v*/0.225)% "free" SO<sub>3</sub>.

Analyses by alkali were made by dilution of the acid to give a roughly N-aqueous solution, which was analysed by titration with normal alkali, methyl-red being used as indicator. Estimations were not reproducible to better than one part in 1000 parts, the consequent error being 0.1% H<sub>2</sub>SO<sub>4</sub> in the calculated oleum strength. To obtain more accurate

results by alkalimetry, however, the method of gravimetric titration with sodium carbonate (Richards and Hoover, *J. Amer. Chem. Soc.*, 1915, **37**, 108) needs to be adopted.

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KING'S COLLEGE, LONDON.

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