

"Handbuch" the wave lengths for these lines were ascertained. These wave lengths plotted against the hydrogen-ion concentration of the solutions are shown in the accompanying graph.

The curves show two points of maxima at approximately a P_H of 5.5 and 6.6. These coincide surprisingly well with the two points of maxima found by Loeb and by Wilson and Kern, respectively. Two points of minima are also observed, one at P_H 4.69, a value coinciding with the so-called iso-electric point found in the literature, and a second at P_H 7.65. This figure differs but slightly from the value found by Wilson and Kern in their work on the swelling of gelatin (P_H 7.7).

Summary

The authors have made measurements of the absorption of light by gelatin sols as a function of the hydrogen-ion concentration (expressed in Sørensen values), using a spectrophotometric method, and have expressed these results in the form of curves in which Sørensen values are plotted against wave lengths for definite fractions of light absorbed, the fractions being 0.75, 0.6, 0.4 and 0 (transparent).

The curves for the different fractions absorbed are of the same general shape, as would be expected. The curious thing noted is the sharp shift of the absorption band toward the ultraviolet as the Sørensen values of 4.69 and 7.65 are approached. Just why this occurs we are unable to say. It might perhaps be argued that the second minimum point may represent the so-called "iso-electric point" of the "sol" form of gelatin which has caused so much confusion in the interpretation of results obtained with this substance. Just how a given colloidal system may have two iso-electric points is difficult to see, if the orthodox definition of iso-electric point is accepted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

THE DETERMINATION OF SULFUR BY MEANS OF A THERMOMETRIC TITRATION¹

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Dutoit and Grobet² have described a method of indicating the formation of compounds in solution by means of a thermometric titration. These investigators were of the opinion that the method could not be applied to volumetric analysis. In order to determine the applicability of thermometric titrations to precipitation reactions the following experiments were carried out.

¹ Extract from a thesis submitted by Otto O. Watts in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry at the University of Colorado.

² Dutoit and Grobet, *J. chim. phys.*, 19, 324 (1922).

The Determination of Sulfur in a Soluble Sulfate

An apparatus similar to that of Dutoit and Grobet was prepared. This consisted of a Dewar flask of about 150cc. capacity, fitted with a cork stopper through which extended a glass stirrer, the stem of a Beckmann thermometer and the tip of a goose-neck buret. The stirrer was driven at a uniform rate by a small induction motor. The neck of the buret was wrapped in asbestos and the portion above the stopcock was jacketed with a length of glass tubing to protect the standard solution from slight changes of temperature due to air currents.

Standardization.—An approximately 0.5 *N* solution of barium chloride was titrated against 0.5g. portions of a sample of soluble sulfate whose

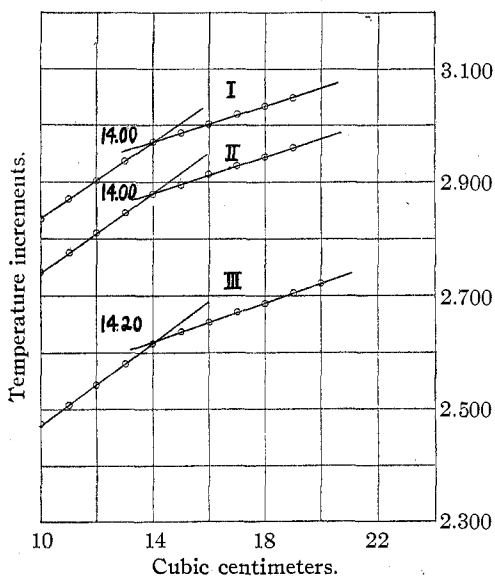


Fig. 1.—Standardization of barium chloride solution against a soluble sulfate.

sulfur content had been determined gravimetrically. The portions of the sulfate were dissolved in 100 cc. of water, the solutions acidified with hydrochloric acid, and cooled to a fraction of a degree below room temperature. In each case, the solution was then placed in the Dewar flask and the stirrer rotated. The standard solution, whose temperature should be that of the room, was run into the flask at a rate of 1 cc. per minute. The volume of solution used was plotted as abscissa and the temperature increments as ordinate. It is necessary to plot the curves only near the break, as the slope at other points

is not required. See Table I and Fig. 1.

When the values shown in Table I are plotted as shown in Fig. 1 it is seen that the breaks in the curves correspond to 14.00, 14.00 and 14.20 cc., respectively. A gravimetric analysis showed that the sample contained 22.38% of sulfur. Therefore 1 cc. of barium chloride solution was equivalent to 0.007927 g. of sulfur. This value was used in calculating the sulfur content of soluble sulfate Samples 1 and 2, of Table II. These results were in reasonable agreement with values obtained gravimetrically.

A number of attempts were made to standardize the barium chloride solution gravimetrically. Whenever the values so obtained were used to calculate the results of a thermometric titration an error of about 5% was found.

TABLE I
DETERMINATION OF TEMPERATURE INCREMENTS

BaCl ₂ Cc.	Temperature increments		
	I	II	III
10	2.836	2.74	2.472
11	2.870	2.775	2.505
12	2.902	2.810	2.540
13	2.935	2.842	2.575
14	2.965	2.872	2.610
15	2.981	2.890	2.632
16	2.998	2.910	2.650
17	3.015	2.925	2.668
18	3.030	2.940	2.684
19	3.045	2.955	2.701

The Determination of Sulfur in Pyrite Ore

Standardization.—Half g. samples of a chalcopyrite containing 34.52% of sulfur were fused with sodium peroxide, the fused masses extracted with water, and the solutions filtered, acidified, concentrated to a volume of 100 cc., cooled to room temperature and titrated with a solution of barium chloride. The three samples required, respectively, 20, 70, 20.75 and 20.80 cc. of the barium chloride. This gave a value of 0.008318 g. of sulfur per cc.

Determination.—Using the standard obtained from the chalcopyrite, three portions of a sample of pyrite ore were titrated thermometrically and found to contain 43.70% of sulfur. A gravimetric determination gave 43.92% of sulfur. See Table II.

TABLE II
DETERMINATIONS OF SULFUR

	Cc. of standard soln.			G. of S per cc. of standard solution	Sulfur found %	Sulfur in sample %
	I	II	III			
Sol. sulfate No. 1.....	12.75	12.85	12.85	0.007927	20.32	20.49
Sol. sulfate No. 2.....	8.95	8.95	8.85	.007927	14.14	14.11
Pyrite ore.....	26.25	26.25	26.30	.008318	43.70	43.92

Conclusions

1. Sulfur in various materials may be determined by means of a thermometric titration.
2. The results obtained by this titration agree closely enough with the gravimetric analysis to make the method available for most technical work.
3. The final precipitation, filtration, ignition, and weighing of the gravimetric analysis is replaced by the thermometric titration with a consequent saving of time.
4. As in certain other determinations it seems best to standardize the solution against a material similar to that to be titrated.

Summary

In this article a volumetric method for the determination of sulfur has been described. Sulfur has been determined thermometrically by titrating the sample at room temperature with a standard solution of barium chloride. To obtain the end-points, temperature increments are plotted against volumes. It has been noted that the barium chloride solution should be standardized thermometrically against a material similar to that to be analyzed. This latter point has not, however, been thoroughly investigated.

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THE OXIDATION OF HYDRAZINE. I. THE VOLUMETRIC ANALYSIS OF HYDRAZINE BY THE IODIC ACID, IODINE, BROMINE, AND HYPOCHLOROUS ACID METHODS

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Introduction

While numerous methods for the analysis of hydrazine, N_2H_4 , have been proposed, all of which depend upon its oxidation to nitrogen, Browne and Shetterly¹ have shown in many cases that some ammonia and hydronitric acid (or ammonia alone) are formed in addition to nitrogen, and that the amounts of these by-products can often be greatly increased by a suitable variation of the experimental conditions. The further study of the accuracy of methods of determining hydrazine, which was evidently necessary, was begun by Hale and Redfield¹ in 1911.

The methods suggested have usually been nitrometric, that is, the nitrogen evolved is collected and measured. In some cases the corresponding oxidimetric method has been used, in which a known amount of oxidizing agent in excess of 4 equivalents per mole of hydrazine is used and this excess determined by titration. However, we have found in the literature only two oxidimetric methods^{2,3} which are rapid, and which at the same time seem to be accurate within 0.2% on the basis of published experimental evidence. These will be referred to later.

We have investigated the accuracy of a number of rapid oxidimetric methods. In order to detect possible side reactions we have examined

¹ Browne and Shetterly, *THIS JOURNAL*, (a) (I) **29**, 1305 (1907); (b) (II) **30**, 53 (1908); (c) (III) **31**, 221 (1909); (d) (IV) **31**, 783 (1909). The various analytical methods are surveyed in these articles from the Cornell Laboratory, and in the fifth article of the series, (e) (V) Hale and Redfield, *ibid.*, **33**, 1353 (1911).

² Jamieson, *Am. J. Sci.*, [4] **33**, 352 (1912).

³ Kurtenacker and Wagner, *Z. anorg. allgem. Chem.*, **120**, 261 (1922).