84. *The Volumetric Determination of Small Quantities of Barium and Sulphate with Barium Rhodizonate as an Indicator: the Determination of Sulphur in Iron Pyrites.*

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A stable and inexpensive suspension of the scarlet modification of barium rhodizonate in ethyl alcohol has been used, in dilute, slightly acid solutions, under certain standard conditions, as an indicator in the volumetric estimation of barium by means of sulphate, and of sulphate indirectly. The accuracy of the most satisfactory estimations is of the order of 1% for 4—20 mg. of sulphate. In the presence of 10 mg. of sulphate there may be at least equivalent amounts of many cations, including aluminium and ferrous ions; phosphate ions, in an equivalent amount and less, cause a positive error of 2%. When applied to the estimation of sulphur in 10 mg. portions of iron pyrites, the method yields results that agree to within about 1% with those obtained gravimetrically on decigram portions.

SODIUM rhodizonate and tetrahydroxybenzoquinone, which form reddish-brown and scarlet compounds with soluble barium salts (see, *e.g.*, Mutschin and Pollak, *Z. anal. Chem.*, 1937, **108**, 8), have been used for some time as indicators in the volumetric estimation of barium and sulphate. Aqueous solutions of the former indicator must be freshly prepared; the latter is made up in a solid stable form. Both indicators are expensive.

Strebinger and Zombory (*ibid.*, 1930, **79**, 1; 1936, **105**, 346) titrated somewhat concentrated neutral or slightly acid (0·3N-hydrochloric acid) solutions of barium chloride with ammonium sulphate in the presence of sodium rhodizonate. Direct titrations of the sulphate were impossible, owing to a lag in the transformation of the indicator in neutral solutions, and to its instability in acid solutions. An indirect method in neutral or slightly acid solutions involved the addition of an excess of barium chloride and a back-titration with sulphate. The sulphates of zinc, manganese, cadmium and copper were said to be titratable. The high concentrations and the large excesses of barium chloride used seem objectionable, and Mutschin and Pollak (*loc. cit.*) adversely criticised the work of the other authors.

Mutschin and Pollak (*ibid.*, 1936, **106**, 385), in direct titrations of sulphate in neutral or slightly acid (0·05N-acetic acid) solutions, improved on earlier methods of using papers impregnated with sodium rhodizonate for external testing, and later (*ibid.*, 1937, **108**, 8, 309), they determined sulphate in neutral solutions indirectly, using the indicator internally. To the sulphate solution containing 2% of ammonium chloride and 35% of acetone they added an excess of barium chloride, and then sodium rhodizonate to form the scarlet modification of barium rhodizonate (the brownish-red modification was unsuitable). A back-titration with sulphate followed, the colour change being from red to yellow. Iron, aluminium and phosphate ions had to be absent, and the results for 10—200 mg. of sulphate averaged 1·3% low. Finally, Abrahamczik and Blümel (*Mikrochim. Acta*, 1937, **1**, 354) buffered barium solutions to p_H 3, added an excess of methyl alcohol, and titrated with sulphate, in the presence of sodium rhodizonate, until the red colour disappeared. For 1·4—2·3 mg. of sulphate the maximum range in the error was ±0·8%. Interfering cations were adsorbed beforehand on permutit.

Schroeder (*Ind. Eng. Chem.*, *Anal.*, 1933, **5**, 403) found that tetrahydroxybenzoquinone could be used as an indicator in the direct titration, with 0·025N-barium chloride solutions, of 2—25 mg. of sulphate in 25 ml. portions of aqueous solutions at p_H 8, treated with the same volume of ethyl alcohol; 5 mg. of aluminium and at least 15 mg. of magnesium ions could be tolerated, but ferric ion in excess of 0·1 mg. had to be removed. The presence of 0·9 equiv. of phosphate ion caused the results for 2·7 mg. of sulphate to be about 30% high. Sheen and Kahler (*ibid.*, 1936, **8**, 127), by lowering the initial p_H to 4, reduced the phosphate error, for a similar amount of sulphate and 0·9—1·4 equiv. of phosphate, to + 2—17%. The indicator was somewhat readily destroyed at this lower p_H value; ferric, ferrous and aluminium ions interfered, and were removed with other heavy metals in applying the method (*ibid.*, 1937, **9**, 69).

In testing qualitatively for barium with sodium rhodizonate, the author noticed that hydrochloric acid tended to dissolve brown barium rhodizonate, and also to convert it into the scarlet modification, which is less soluble in acid. The latter transformation was predominant when compact masses of the precipitate were stirred in the cold with small volumes of 2N or concentrated hydrochloric acid, or, at 80°, with alcohol containing 2% of concentrated hydrochloric acid. The centrifuged scarlet precipitates, washed with a little alcohol, and drained, but not dried, gave with ethyl alcohol, scarlet-coloured suspensions, which did not readily settle. The scarlet compound formed in the acid alcoholic medium provided the finest suspension. Since the scarlet compound is more stable towards hydrochloric acid than the brown, it was thought that its suspension in alcohol might serve as an indicator in titrations of barium with sulphate in solutions more acid than usual; in these solutions the tolerance towards phosphate ion and foreign cations, such as iron and aluminium, might be increased.

EXPERIMENTAL.

The Use of a Suspension of Scarlet Barium Rhodizonate as an Indicator.—The scarlet modification of barium rhodizonate, prepared from 40 mg. of sodium rhodizonate (see p. 406), was suspended in 250 ml. of absolute ethyl alcohol. When 1 ml. was added to 10 ml. of 0·1N-hydrochloric acid at 25°, the strong pink colour at first produced disappeared in 7 secs. The presence of a little sulphate did not noticeably affect the result, showing that there is a lag in the reaction between the barium compound and the sulphate. If, however, 0·1 ml. of 0·1M-barium chloride solution was present, the colour did not disappear, but became very pale, in 60 secs.; with 1 ml., the colour was still a very definite pink after 5 mins. The effect of adding an alcohol or acetone was to retard the disappearance of the pink colour; *e.g.*, 5 ml. of ethyl alcohol caused the pink colour, in the absence of barium chloride, to become very pale in 40 secs., but in the presence of 0·1 ml. of 0·1M-barium chloride solution it was still strong after 15 mins., and, in the presence of 1 ml., stable. Alcohol therefore helps to stabilise the barium rhodizonate, and to a more marked extent when the solution contains a little barium chloride.

In order to use the barium rhodizonate suspension satisfactorily as an indicator in the titration of barium with sulphate, one must be able, during the titration, to retain the pink colour until the concentration of barium ions is very small, and to ensure rapid fading at the equivalence point. Since, in gravimetric work, barium sulphate is best precipitated in dilute acid solutions, such solutions were used in a study of the rate of fading of the indicator under various conditions in the presence and absence of small amounts of barium chloride. The results are summarised in the following table.

	Composition of soln.				Approx. time (secs.) taken, at 25°, for the colour to equal a standard pale pink colour.	
Expt.	Indicator, ml.	H_2O, ml.	2N-HCl, ml.	EtOH, ml.	No $BaCl_2$.	0·06 Ml. of 0·02M-$BaCl_2$.
1	0·5	10	0·5	2	2	5
2	0·5	10	0·2	5	10	45
3	0·5	10	0·5	5	8	35
4	0·5	10	1	5	5	20
5	0·5	20	0·2	5	3	7
6	0·5	10	0·5	10	25	>120
7	1	10	0·5	10	>60	—
8	0·5	10	1	6	30 (15°)	>120 (15°)
9	0·5	10	1	6	10	40
10	0·5	15	1	11	12	50
11	0·5	26	1	22	12	50
						0·06 Ml. of 0·05M-$BaCl_2$.
12	0·5	10	2	7	5	> 60
13	0·5	26	2	23	8	> 60

Increasing acidity (expts. 2, 3 and 4), dilution with water (expts. 2 and 5), and increasing temperature (expts. 8 and 9) increase the rate of fading. Increasing amounts of alcohol (expts. 3 and 6) and indicator (expts. 6 and 7) have the reverse effect.

The Titration of Barium with Sulphate.—The following standard procedure, based mainly on the results of the above table, was applied. To 10 ml. of an aqueous barium chloride solution, equivalent to 2—20 mg. of sulphate, 0·2—1 ml. of 2N-hydrochloric acid was added, and ethyl alcohol equivalent to the total volume less 5 ml. This volume of alcohol ensured that the rate of fading at the equivalence point was not too slow, and yet considerably faster than that in the presence of a little barium chloride (expts. 1, 3 and 6). 0·5 Ml. of the indicator suspension was added and gave a sufficiently pink colour for end-volumes up to over 50 ml. The mechanically stirred solution was titrated dropwise, at room temperature, with a 0·02M-solution of ammonium sulphate, containing 50% by volume of ethyl alcohol. In this way the proportion of alcohol in the solution increased slightly during the course of the titration, and an approximately constant rate of fading at the equivalence point was maintained for final volumes ranging from 18 to 50 ml. (expts. 9—11). Experiments 2 and 5 show what would be the effect of titrating with an aqueous sulphate solution. Towards the end of the titration the temperature was adjusted to 25°, in order to avoid too slow fading of the barium rhodizonate (cf. expts. 8 and 9), and the titrant was added at the rate of one drop (0·015 ml.) in 10 seconds, until the pink colour disappeared. No delay was permissible in adding the last 0·06 ml. (expts. 9—11). Sometimes the precipitates were very pale pink beyond the equivalence point, owing to a slight adsorption of the indicator; this was most prominent in solutions containing small amounts of barium and the maximum amount of acid.

If the sulphate equivalent of the barium chloride in 10 ml. was 5—50 mg., and the titrant was 0·05M-ammonium sulphate, the amount of acid could range from 0·5 to 2 ml. The last drops of the titrant, when the maximum amount of acid was present, could be added at a slightly greater rate (cf. expts. 12 and 13).

Provided that the foregoing procedure was rigidly adhered to, errors averaging 1% and less were usually obtained, as shown below. With 0·02M-sulphate as the titrant, the most consistent results were obtained in solutions containing 0·5 ml. of 2N-hydrochloric acid in a final volume of 27—18 ml.

$(NH_4)_2SO_4$, M.	SO_4 equivalent in mg. of $BaCl_2$ in 10 ml.	Error, %, with various vols. of 2N-HCl initially present.		
		1 ml.	0·5 ml.	0·2 ml.
0·02	20	−0·5, −0·3	−0·1, +0·2	+0·5, +0·8
	10	−1·2, −1·6	+0·6, 0	+1·2, +0·8
	4	0, −0·5	0, 0	+0·5, +1·5
	2	+2, +3	0, −2	−1, +2
		2 ml.	1 ml.	0·5 ml.
0·05	50	−0·9, −0·4	−0·5	−0·6
	25	−0·8, −0·6	+0·4	+0·2
	10	−1·5, −0·5	−1	+1
	5	0, 0	−1	−1

Experiments with a 0·01M-sulphate solution were unsuccessful, except at low acidity, and slightly inferior results were recorded when the scale of the experiments was increased 2½-fold, due to a greater uncertainty in detecting the end-points.

The Indirect Estimation of Sulphate.—Direct estimations of sulphate being out of the question, it was proposed to titrate sulphate solutions with an excess of a barium chloride solution, and then to prepare the solution appropriately for a back-titration with a standard sulphate solution, in the presence of the indicator suspension. In preliminary experiments low results were obtained for sulphate, owing, presumably, to the ready contamination of barium sulphate with sulphate when barium ions are added to an excess of sulphate ions. The errors were most marked when concentrated solutions were used, and when the barium chloride was added in the cold; the amount of hydrochloric acid was of less importance. The barium chloride had to be added to hot aqueous solutions, *i.e.*, at 80° or at the boiling point. Cooling immediately after, or after 10—30 mins.' further digestion at the precipitation temperature, led to very similar results. The excessively slow addition of the barium chloride, and the digestion at 80° of a precipitate formed in the cold, produced no beneficial effects. A considerable excess of barium chloride was required to prevent appreciable negative errors, particularly in solutions containing small amounts of sulphate and hydrochloric acid. The following standard procedure was devised : To 10 ml. of an aqueous solution containing 2—20 mg. of sulphate, 0·5—1 ml. of 2N-hydrochloric acid was added. The solution was titrated at 90°, at the rate of 1 ml. a minute, with 0·02M-barium chloride, until an excess of 1 ml. was present for amounts of sulphate under 10 mg., and at least 2 ml. for larger amounts. The precipitate was digested at 90° for 10 mins., and the beaker then immersed in cold water. Ethyl alcohol, equivalent to the total volume less 5 ml., and 0·5 ml. of the indicator suspension were added, and the solution was titrated with 0·02M-ammonium sulphate containing 50% by volume of ethyl alcohol. The end temperature was 25°, and 0·015 ml. drops were added at the rate of one in 10 secs. The results below show that better results were obtained with 1 ml. than with 0·5 ml. of 2N-hydrochloric acid in a final volume of 50—22 ml. Under similar conditions of acidity the most satisfactory results were obtained in direct titrations of barium chloride (p. 403). With 1 ml. of acid present the error in estimating 4—20 mg. of sulphate is under 1%. The more negative errors, observed when 0·5 ml. of acid was present, correspond to the positive errors associated with the titration of barium chloride solutions in the presence of 0·2 ml. of acid.

SO_4 in 10 ml. of solution, mg.	0·02M-$BaCl_2$ used in excess, ml.	Error, %, with various vols. of 2N-HCl initially present.	
		1 ml.	0·5 ml.
20	4	−0·5, −0·7	−1·5, −1·4
10	2	+0·2, +0·8	−0·8, −0·4
4	1	+0·5, 0	−1, −0·5
2	1	+3, +3	0, −2

Sulphate determinations, in solutions containing 1—2 ml. of acid, were also made with 0·05M-solutions, but the errors in general exceeded 1%, probably because adsorption errors were becoming more prominent. A few experiments made on a larger scale offered no advantage over those made on the smaller scale, which was preferred.

The Effect of Various Cations and Anions on the Estimation of Sulphate : the Adjustment of Acidity.—In estimating sulphate in solutions that may contain other salts, a means must be found for adjusting the acidity before the titration. A very satisfactory indicator was a solution of brilliant cresyl-blue, as supplied by The British Drug Houses, and diluted 10 times with ethyl alcohol. 0·1 Ml. added to 10 ml. of a neutral, aqueous sulphate solution gave a blue colour, which weakened as acid was added. About 1 ml. of 2N-hydrochloric acid was required just to discharge the blue colour; the extreme range was 0·8—1·1 ml., and this corresponds very well with the acidity most suitable for sulphate estimations with 0·02M-solutions. The adjustment of acidity may, in general, be effected by arranging that the blue colour of the indicator has just disappeared. For solutions initially too acid, the acidity was conveniently reduced by gradually adding magnesium acetate until a blue colour was just perceptible, and then discharging it with a little hydrochloric acid. Magnesium acetate does not affect the subsequent titrations (see p. 405). Even in slightly coloured solutions the method was applicable, especially if a reference solution was used. For solutions requiring adjustment of p_H to the lower value corresponding to the addition of 2 ml. of 2N-hydrochloric acid to 10 ml. of a dilute ammonium sulphate solution, it was necessary to double the amount of the indicator and to continue the addition of acid until a pinkish-brown colour developed. Here, one might add 2—3 ml. of 2N-hydrochloric acid, and the adjustment would be uncertain in slightly coloured solutions.

The subsequent addition of alcohol brought up the blue colour of the indicator, but this, instead of being a disadvantage, proved to be an advantage in the final titration. In association with the scarlet barium rhodizonate it gave a violet colour, which changed at the equivalence point to a pure, pale blue. This colour change was more readily observed than the fading to colourless of the pink rhodizonate solutions. In later work, brilliant cresyl-blue was added, whether or not it was required for the adjustment of acidity.

The effect on the estimation of sulphate of various salts was examined. The solid salt was added to 10 ml. of the solution containing 10 mg. of sulphate, the adjustment of acidity effected, and the standard procedure (p. 404) afterwards followed. The results of these experiments, practically all the average of two, appear below.

It has already been shown that, even under standard conditions, one cannot expect to estimate barium and sulphate with an accuracy much better than 1%. If, in the presence of foreign salts, results of this accuracy are obtained, then the added salts have no important influence. From the table below, it may be deduced that the salts listed in the first column, in amounts equivalent to the sulphate (10 mg.), do not interfere. With some, the presence of much more than 1 equiv. is permissible. The salts mentioned in the fourth column interfere more—lead and calcium salts because of the partial precipitation of the sulphates, ammonium phosphate because of some precipitation of barium phosphate. A positive error of 2% seems to be unavoidable in the presence of phosphate. The error for 1·5 equivs. of phosphate (10 mg. of PO_4) and 10 mg. of sulphate is a marked improvement on Sheen and Kahler's result for one-fourth of these amounts (see p. 402). Ferric, nitrate, and potassium ions are well-known contaminants of barium sulphate. In the presence of the first, the colour change at the end-point was poor, and it was much better to reduce the iron to the ferrous state, with aluminium powder or hydroxylamine, neither of which appreciably influences the estimation of sulphate. The interference of cupric ions was eliminated by reducing them to the metal with aluminium; lead was incompletely deposited thus, and still interfered.

Added salt.	Equivs. of salt to one of SO_4.	Error, %, in detmn. of 10 mg. of SO_4.
NH_4OAc	7	−1·2
	33	−2·7
NH_4Cl	9	−1·2
	44	−3·2
Na_2HAsO_3	1	+0·2
	2	+1·6
Na_2HAsO_4	1	+0·1
	2	−0·3
NaCl	21	−1·8
$Mg(OAc)_2$	1	+0·5
	10	−0·2
$Zn(OAc)_2$	1	+0·3
	10	+4·9
$Cd(OAc)_2$	1	−0·8
$CoCl_2$	1·2	−1·1
$NiCl_2$	1	+0·2
$MnCl_2$	1	+0·8
$AlCl_3$	2·8 (5 mg. Al)	0
	14 (25 mg. Al)	−0·8
$FeCl_3$	1·5	−0·5 *
		−0·2 ‡
NH_2OH,HCl	30 mg.	−0·2
	250 mg.	−2·5
$FeCl_3$	1 } referred	+1·0
	2 } to FeS_2	†
KCl	1	−1·9
	1·3	−1·4
NH_4NO_3	1·5	+3·3
$(NH_4)_2HPO_4$	0·35	+2·6
	0·45	+1·8
	0·7	+1·6
	1·5	+2·4
	11·5	+4·4
$CuCl_2$	0·06	−1·1
	0·15	+2·0
	1	+3·2
	1·3 §	−1
$Pb(OAc)_2$	0·01	−1·0
	0·016	−3·6
$CaCl_2$	0·07	−1·0
	0·18	−2·6
	1·76	−8·2

* Ferric chloride had been reduced with 10—20 mg. of aluminium powder.

† See below.

‡ With 25 mg. of hydroxylamine hydrochloride, as in the analysis of iron pyrites (p. 406).

§ Metal precipitated by aluminium.

The Estimation of Sulphur in Iron Pyrites.—The foregoing results enable one to prescribe conditions for the volumetric estimation of sulphate, where an accuracy of 1% suffices, and its application to the determination of sulphur in iron pyrites was studied. Iron sulphide minerals, *e.g.*, pyrrhotite, pyrite, and marcasite, may contain small amounts of nickel, cobalt, copper, calcium, manganese, lead, arsenic, etc., but these elements are present in amounts which seemed, from the foregoing results, unlikely to affect the volumetric estimation of sulphate. Accordingly, a finely-ground sample of iron pyrites was analysed for sulphur as follows: 10 mg. portions were decomposed by the method of Allen and Bishop (see Kolthoff and Sandell, " Textbook of Quantitative Inorganic Analysis," 1936, 321), but with suitably reduced quantities of the reagents; ferric iron was reduced with aluminium or hydroxylamine, and the sulphate produced estimated under the standard conditions (p. 404). As a check, the sulphur was also determined gravimetrically in 0·1 g. portions of the pyrites, decomposed in the same way. The results (S, %) were as follows:

$$\text{Fe}^{\cdots} \text{ reduced by } \begin{cases} (1)\ \text{Al} & 47{\cdot}0 \pm 0{\cdot}2 \text{ (vol.)};\ 46{\cdot}6 \text{ (grav.)} \\ (2)\ \text{NH}_2\text{OH} & 46{\cdot}7 \pm 0{\cdot}3 \quad ,, \quad ;\ 46{\cdot}5 \quad ,, \end{cases}$$

These figures confirm the applicability of the method. Four volumetric estimations were made in 3 hrs. Many other applications are possible.

One of the main advantages in using the suspension of barium rhodizonate as an indicator is its cheapness. 40 Mg. of sodium rhodizonate, costing 5*s*. per g., suffice for 500 titrations. Abrahamczik and Blümel (*loc. cit.*) used 5 mg., in unstable aqueous solution, for 6—8 microtitrations. The use of tetrahydroxybenzoquinone would be much more expensive.

Experimental Details.—Reagents. As far as possible these were of analytical grade. Sodium rhodizonate was supplied by Messrs. Hopkin and Williams. Commercial, absolute ethyl alcohol was redistilled, and the carbon tetrachloride was " sulphur-free ". 0·1M-Solutions of barium chloride and ammonium sulphate were standardised gravimetrically by precipitation as barium sulphate in suitable portions, under Kolthoff and Sandell's conditions (*op. cit.*, p. 319). More dilute aqueous and alcoholic solutions were prepared from these.

Apparatus, etc. All the titrations, stability tests on solutions containing the indicator, and p_H adjustments were carried out in tall-form beakers, which were heated, when necessary, on a medium-temperature, electric hot-plate. For the final titrations in the presence of the indicator, they were placed in white surroundings. A simple glass stirrer was operated by a small electric motor. The volumetric ware was calibrated. Grade A burettes of ordinary size, delivering drops of 0·015 ml. with alcoholic solutions, were adequate. Owing to the sluggish end-points, the use of micro-burettes offered no advantage.

Preparation of the barium rhodizonate suspension. 40 Mg. of sodium rhodizonate were dissolved in 20 ml. of water, and treated with 0·1 g. of barium chloride dissolved in a little water. The flocculent, brownish-red precipitate was centrifuged, and washed with a little water and then with ethyl alcohol. 5 Ml. of ethyl alcohol containing 0·1 ml. of concentrated hydrochloric acid were poured over the precipitate, and the tube was placed for a few minutes in a beaker of hot water, in order to convert the complex into the scarlet form. The centrifuged precipitate was drained of alcohol, and at once suspended in 250 ml. of ethyl alcohol. The suspension was kept in a glass-stoppered bottle and invariably shaken before use. No deterioration was noted during 3 months' use.

Volumetric determination of sulphur in iron pyrites. 10 Mg. of the finely ground pyrites in a tall, 6 ml. micro-beaker were treated with 0·2 ml. of bromine in carbon tetrachloride (2 : 3), followed after ¼ hr. by 0·2 ml. of concentrated nitric acid. After a further ¼ hr. the bromine was carefully expelled, and the mixture evaporated to dryness, by placing the beaker in a suitable holder (see, *e.g.*, Emich, " Microchemical Laboratory Manual," 1932, 13) on an electrically heated water-bath. Nitrates were destroyed by two evaporations with 0·2 ml. of concentrated hydrochloric acid, and the residue was heated for 10 mins. in an oven at 100°, before being dissolved in 0·2 ml. of hydrochloric acid and 1 ml. of water. Ferric iron was reduced by adding either 10 mg. of aluminium metal powder or 25 mg. of hydroxylamine hydrochloride, and heating the solution on the hot-plate until it became colourless (2 mins.). After transference to a 50 ml. beaker, and dilution to 10 ml. with cold water, the solution was adjusted to the correct acidity as outlined on p. 404, and sulphate estimated under the conditions prescribed on p. 404. An excess of fully 2 ml. of a 0·02M-barium chloride solution was used in the first titration.

A solution of cupric ions could be reduced with aluminium in the same manner, but with deposition of the metal, which did not, however, interfere in the subsequent titrations.

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