

Notes

THE DETERMINATION OF SMALL AMOUNTS OF SULPHATE BY REDUCTION TO HYDROGEN SULPHIDE AND TITRATION WITH MERCURIC OR CADMIUM SALTS WITH DITHIZONE AS INDICATOR

(Presented at the meeting of the Society on Wednesday, October 5th, 1955)

REDUCTION of sulphate to hydrogen sulphide and determination of the latter by the methylene blue method is probably the most sensitive method so far described for the determination of traces of sulphate. Polson and Strickland¹ have described a procedure in which barium sulphate is co-precipitated with barium chromate and then reduced to hydrogen sulphide in a stream of hydrogen. Sulphates can also be reduced to hydrogen sulphide with hydriodic - hypophosphorous acid mixtures as in Luke's procedure²; but within our experience this simpler method of reduction cannot be used satisfactorily in conjunction with the methylene blue method. Karabash³ has described a procedure for the titration of sulphides with dithizone as an extraction indicator. It has been found, however, that sulphides can be more readily titrated with dithizone as indicator when a single-phase system is employed. In the method described, hydrogen sulphide is evolved from sulphates by using a reduction mixture similar to Luke's reduction mixture. The hydrogen sulphide is carried over by a stream of nitrogen and absorbed in a dilute alkali - acetone mixture to which a little dithizone has been added. On titration with mercuric or cadmium salts, insoluble sulphides are precipitated, but at the end-point a bright red dithizonate is formed.

EXPERIMENTAL

In the experiments described, mercuric acetate was used as titrant; cadmium sulphate can also be used, but results are not so accurate when very small amounts of sulphur are present. This is possibly due to slight solubility of cadmium sulphide.

The work carried out so far has only been on pure sulphate solutions; further work is at the moment in progress on various applications of the method, notably on the determination of traces of sulphur in organic liquids after burning in a lamp.

To prepare the reduction mixture, take 100 ml of hydriodic acid, sp.gr. 1.7, 25 ml of 50 per cent. w/w hypophosphorous acid, 100 ml of concentrated hydrochloric acid and 50 ml of hydriodic acid, sp.gr. 1.9, and boil under reflux for 1½ hours with a stream of nitrogen blowing through the mixture. This treatment is necessary in order to reduce the reagent blank and to achieve complete reduction with the mixture under the conditions employed. With a shorter period of reflux, the reagent may not reduce sulphates at 100 °C. Several batches of reagent have been prepared as described, and all were found to reduce sulphates readily at 100° C. The reagent can be used immediately after preparation. When kept in a dark-coloured bottle, it appears to retain its reducing properties indefinitely.

The apparatus used is a 25-ml round flask with a small water reflux condenser attached. The flask has a side-arm with a B14 standard joint into which fits a tube reaching to the bottom of the flask. This tube is connected to a nitrogen cylinder fitted with a reducing valve. The top of the condenser has a B10 standard joint into which fits a tube with two right-angled bends, and pulled out to a jet at the end. This acts as a delivery tube, and the end dips into a 1-inch × 3¼-inch specimen tube, which acts as receiver. For titration a 5-ml burette with two right-angled bends below the tap, so that the jet can go inside the specimen tube, is used. A small beaker containing water with a micro-burner underneath is used to heat the flask to 100° C.

To determine the sulphate in a solution, by pipette put an aliquot portion of it in the flask via the side-arm (0.2 ml was the largest volume taken in the experiments described). Add 5 ml of the reduction mixture to the flask and 3 ml of *N* sodium hydroxide and 3 ml of acetone to the specimen tube used as receiver. Set up the apparatus, filling the burette with 0.001 *M* mercuric acetate solution. Blow a slow stream of nitrogen (about 15 ml per minute) through the apparatus. Heat the water bath to boiling and keep just at the boil. When the water boils, add to the receiver a few micrograms of dithizone. Then add one drop of the mercuric acetate solution from the burette, changing the colour of the solution from yellow to bright red. The first evolution of hydrogen sulphide is indicated by the colour changing back from red to yellow. Continue to heat for 20 minutes after this. Then, with the stream of nitrogen still passing, titrate with the mercuric acetate until a permanent red colour is reached. When more than about 20 µg of sulphur are present, a black precipitate of mercuric sulphide is apparent, but this does not mask the dithizone colour change.

Carry out a blank on each batch of reducing mixture, and deduct it from the net titration. On two batches of reducing mixture used this was 0.22 and 0.06 ml of 0.001 *M* mercuric acetate.

RESULTS

The following results were obtained on aliquot portions of a standard potassium sulphate solution—

Sulphur present, μg	6.4	32	64	128
Sulphur found, μg	5.8, 5.8	32.3, 30.4	60.2, 64.7	125.5, 128.0

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REFERENCES

1. Polson, D. S. C., and Strickland, J. D. H., *Anal. Chim. Acta*, 1952, **6**, 452.
2. Luke, C. L., *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 602.
3. Karabash, A. G., *J. Anal. Chem., U.S.S.R.*, 1953, **8**, 140.

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