

# Potentiometric Micro Determination of the Sulphate Ion

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In the measurement of fast neutrons, the amount of sulphur dispersed in the special films used is important. To determine their sulphur content a potentiometric titration has been studied in which sulphate ions, obtained by oxidation, are titrated with standard lead nitrate solution. The standard deviation in the titration value for 10- $\mu$ g amounts of sulphur is lower than 1 per cent. As constant potential is rapidly attained after each addition of titrating solution, an automatic titration is carried out.

THIS method was developed for the determination of micro amounts of sulphur contained in special films used at the Centro Studi Nucleari della Casaccia del Comitato Nazionale per l'Energia Nucleare, Roma, for measuring fast neutrons. These films consist of poly(vinyl alcohol), in which sulphur is homogeneously dispersed<sup>1</sup>; the amounts of sulphur to be determined may be as low as a few tens of micrograms, and the error in their determination must be less than  $\pm 1$  per cent.

We have, therefore, modified a method reported in the literature,<sup>2</sup> which consists in titrating the sulphate ion solution with a lead nitrate solution, after addition of potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III), with a platinum wire as measuring electrode and a silver reference electrode.

At the equivalence point, lead hexacyanoferrate(II) precipitates, with a resulting sharp change in the potential of the platinum electrode; the titration is carried out in a water-ethanol (1 + 1) solution.

The modifications introduced into this method, which are discussed below, have resulted in the rapid stabilisation of the electromotive force of the cell after each addition of titrating solution; this has made it possible to perform the titration automatically and to determine very small amounts of sulphur.

## EXPERIMENTAL

### APPARATUS AND REAGENTS—

A Metrohm E336 Potentiograph (supplied by Metrohm A.G., Herisau, Switzerland) connected with a 1-ml automatic Metrohm E336 microburette was used.

The measuring electrode consists of a 12  $\times$  12-mm platinum plate, which is washed in concentrated nitric acid and heated to whiteness with a blow lamp before use; the reference electrode consists of a silver rod, 1.7 mm in diameter, which is cleaned by abrasion, washed with distilled water and immersed for 4 hours in a freshly prepared solution containing 126 mg of potassium hexacyanoferrate(II) [ $K_4Fe(CN)_6 \cdot 3H_2O$ ] and 82.2 mg of potassium hexacyanoferrate(III) [ $K_3Fe(CN)_6$ ] in 100 ml; this electrode is washed and kept dry. An electrode prepared in this manner was used for fifteen titrations carried out within 3 days of its preparation.

All of the reagents used were of recognised analytical grade, except the Specpure sulphur (Johnson Matthey Ltd.) used for the determination of the titre of the lead nitrate solution.

### PROCEDURE—

The titre of the standard lead nitrate solution is determined by carefully weighing about 10 mg of sulphur into a 1-ml Pyrex-glass ampoule; 0.05 ml of 99 per cent. nitric acid is added and the ampoule sealed after drawing out into a capillary. The ampoule is heated for 10 minutes at 200° C, the sulphur being thus oxidised to sulphuric acid. After cooling, the ampoule is inserted, capillary downwards, into a 25-ml cylinder containing 7 to 8 ml of distilled water; the capillary at the bottom of the ampoule is broken, so that the gas bubbles through the water; the ampoule itself is then broken. The solution and washings from the

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cylinder are transferred into a dish, a slight excess of ammonia solution is added and the solution evaporated to dryness; the residue is dissolved in distilled water, which is made up to a suitable volume in a calibrated flask.

An aliquot containing the equivalent of between 40 and 100  $\mu\text{g}$  of sulphur is introduced into the titration cell and the volume made up to 18 ml with distilled water, 40 ml of isopropyl alcohol are added, the solution is stirred and the electrodes are introduced. The potential difference is immediately stabilised, and the automatic titration is carried out with a solution containing about 1 g per litre of lead nitrate. The titration rate is about 0.1 ml per minute; the potential drop, at the equivalence point, ranges between 30 and 60 mV. After each titration, the silver electrode is carefully washed with distilled water, dried and stored.

The amount of sulphur contained in a film is determined in the same way. A disc of film whose area is 1  $\text{cm}^2$ , which contains an amount of sulphur ranging between a few tens of micrograms and 500  $\mu\text{g}$ , with an organic-matter content of about 1000  $\mu\text{g}$ , is used; if the amount of sulphur present is small enough, 18 ml of distilled water and 40 ml of isopropyl alcohol are added, and the titration is carried out as indicated above.

## RESULTS

The results obtained for the standardisation are shown in Table I.

TABLE I

Amount of sulphur taken, $\mu\text{g}$	Volume of lead nitrate consumed, ml	Amount of sulphur corresponding to 1 ml of titrating solution, $\mu\text{g}$ per ml
30.24	0.343	88.16
50.40	0.555	90.81
58.20	0.638	91.22
70.56	0.770	91.64
82.15	0.897	91.58
82.50	0.899	91.77

As can be seen, when using amounts of sulphur between 38 and 83  $\mu\text{g}$ , the relative standard deviation of the titre of the standard lead nitrate solution is  $\pm 0.6$  per cent. We have not determined the relative standard deviation for the film analyses, because the lack of homogeneity of the film gives rise to a greater deviation than that of the analysis; on the other hand, the nitric acid oxidises the poly(vinyl alcohol) to carbon dioxide and water, which do not interfere. Therefore, assuming that the relative standard deviations of the standardisation of the titrating solution and of the titration value for the film solution are equal, then the relative standard deviation is  $\pm \sqrt{2} \times 0.6^2$  or  $\pm 0.8$  per cent. for the determination of sulphur in the film. This value relates to the amount of sulphur contained in the portion of the film destroyed during the analysis; it is therefore strictly applicable only if the disc of film used for measuring the fast neutrons is analysed.

If the piece of film used as a detector has to be preserved, two adjacent discs are cut from the film; one is used as the detector and the other is destroyed in the course of the analysis. The amounts of sulphur found in two adjacent 1- $\text{cm}^2$  discs differ by less than 1 per cent. when films prepared according to the method described<sup>1</sup> are used. The results of the potentiometric determination thus obtained were fully consistent with results obtained from experimental measurements with fast neutrons carried out at the Laboratorio Fisica e Calcolo Reattori of CNEN, C.S.N., Casaccia, Rome.

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