THE DETERMINATION OF MICROQUANTITIES OF SULFATES BY THE METHOD OF FILM POLAROGRAPHY WITH ACCUMULATION

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A method is proposed for the determination of microquantities of sulfates in specially pure materials, based on preliminary reduction of the sulfate ion with a solution of titanium (III) in phosphoric acid, absorption of the hydrogen sulfide formed, and subsequent determination of the sulfide by film polarography with accumulation. The minimum SO_4^{2-} concentration determinable was 0.005 μg/ml; the root mean square error was 15% relative. An analysis took 45 min.

Methods for determining sulfates, based on formation of the sparingly soluble barium sulfate, are unsuitable for the determination of ultrasmall quantities of sulfate ion in aqueous solutions, since their sensitivity is restricted by the solubility product of barium sulfate to about 4 to 10 μg/ml. Methods based on precipitation of sulfate as $PbSO_4$, $SnSO_4$, and Hg_2SO_4 are even less sensitive.

The most promising methods for determining microquantities of sulfates involve preliminary reduction of SO_4^{2-} to S^{2-}. Sulfides form considerably less soluble compounds with most metals than do sulfates, and the sensitivity for their determination can be much higher. Polson and Strickland [1] described a method for determining microgram quantities of sulfate after preliminary reduction in a stream of hydrogen and hydrogen chloride. Quartermain and Hill [2] used a method, based on reduction of the sulfate with a solution of titanium (III) in phosphoric acid, with subsequent absorption of the hydrogen sulfide formed in alkali, and determination of the sulfide ion mercurimetrically.

It was reasonable to suppose that, by using a more sensitive method for the final determination, it should be possible to extend the sensitivity of 2 μg/ml claimed by the above authors. We applied for this purpose the method of film polarography with accumulation [3], with which it was possible to determine down to $5 \cdot 10^{-8}$ g-ion of S^{2-} per liter [4, 5].

The reagent required for reducing the sulfates was prepared by dissolving 1.5 g of technical titanium in 50 ml of phosphoric acid with heating. A 10-ml portion of the resulting solution was placed in the apparatus shown in Fig. 1. A stream of carbon dioxide was passed through the apparatus, and, without stopping the gas flow, the solution was heated to boiling and boiled cautiously for 30 to 60 min. Any sulfate present in the reagent was reduced during this process, and the hydrogen sulfide formed was swept away. The resulting reagent could be used for 7 to 10 analyses.

The method for determining sulfates was as follows.

A 0.1 to 1 g sample of the material to be analyzed, or 0.2 to 0.5 ml of a standard sulfate solution, was placed in the apparatus containing the reagent, the absorber was charged with 5 N KOH, and carbon dioxide was passed through the whole at a rate of 2 to 4 bubbles per second while the solution was boiled cautiously for 30 min. The contents of the absorber were then transferred to the electrolyzer, the design of which has been described [4], and subjected to polarography.

The indicator electrode for the polarographic determination was a mercury drop, electrodeposited on a platinum microcontact from a saturated solution of mercurous nitrate, by a current of 30 mA flowing for 60 sec. After the electrodeposition of mercury, the electrode was cathodically polarized in N nitric acid by a current of 20 mA.

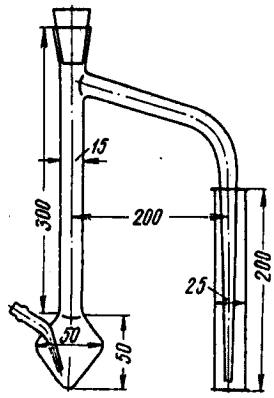

Fig. 1. Apparatus for the reduction of sulfate and absorption of hydrogen sulfide.

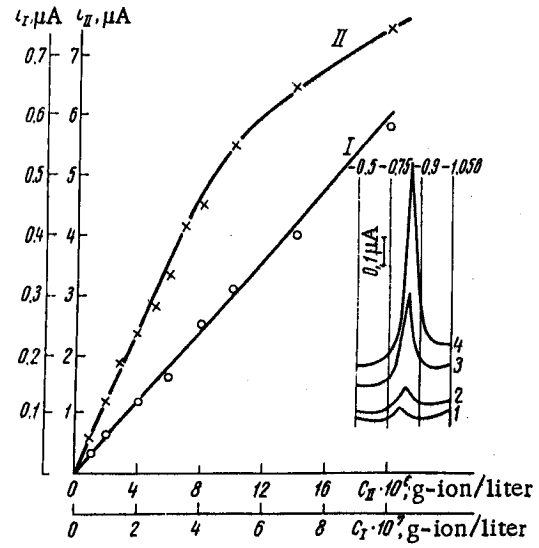

Fig. 2. Relation between the maximum electrodissolution current for mercury sulfide and the concentration of sulfate ion in the original solution. Also shown are the polarization curves corresponding to: 1) $5 \cdot 10^{-8}$; 2) 10^{-7}; 3) $5 \cdot 10^{-7}$; 4) 10^{-6} g-ion of SO_4^{2-} per liter.

Results for the Comparative Determination of Sulfate and Sulfide Ions

SO_4^{2-} added, g-ion/liter	Max electrodissolution current, μA	S^{2-} added to electrolyzer, g-ion/liter	Max electrodissolution current, μA
$5 \cdot 10^{-8}$	0.03	$5 \cdot 10^{-8}$	0.03
$1 \cdot 10^{-7}$	0.065	$1 \cdot 10^{-7}$	0.07
$4 \cdot 10^{-7}$	0.25	$4 \cdot 10^{-7}$	0.3
$1 \cdot 10^{-6}$	0.58	$1 \cdot 10^{-6}$	0.7
$5 \cdot 10^{-6}$	2.8	$5 \cdot 10^{-6}$	3.0
$1 \cdot 10^{-5}$	5.5	$1 \cdot 10^{-5}$	6.0

The same mercury drop could be used repeatedly without any other preliminary treatment of the surface. A platinum electrode was used as auxiliary electrode during the deposition of the mercury drop, but a saturated calomel electrode was used as auxiliary electrode during the subsequent determinations.

The polarograph was a Hungarian instrument type ON-101. Mercury sulfide was deposited electrolytically for 1 min, at −0.5 V. The film produced was then dissolved cathodically with the potential changing linearly at a rate of 1 V/min, and the maximum dissolution current was determined.

Figure 2 shows polarization curves for the cathodic dissolution of the mercury sulfide film. These represent the relation between the maximum film electrodissolution current and the concentration of sulfate ion in the original solution.

In order to obtain reproducible results for the determinations, the apparatus for the reduction of sulfates and absorption of hydrogen sulfide should be well sealed and should have no rubber connections. Carbon dioxide should be used as carrier gas. If nitrogen was used as carrier gas the amount of hydrogen sulfide absorbed was found to be considerably less, because of inadequate intensity of displacement of hydrogen sulfide by nitrogen. The amount of hydrogen sulfide absorbed was also considerably less if the apparatus was fitted with a reflux condenser. Probably some of the hydrogen sulfide, liberated during the reduction of the sulfate, was absorbed by the condensing water vapor, so that only part of it passed on into the absorber.

It was necessary to use 4 to 5 N KOH to absorb the hydrogen sulfide. With a lower strength the requisite alkalinity was probably not achieved, owing to formation of K_2CO_3.

Absorption was continued for 30 min. Preliminary experiments showed that the amount of hydrogen sulfide absorbed only altered significantly in the first 15 to 20 min.

The table shows the results of comparative measurements of currents, associated with the reduction of mercury sulfide films, concentration from solutions obtained by reduction of sulfate and by addition of S^{2-} to the solution.

Statistical analysis of the results showed that the root mean square error for the determination of 0.005 to 0.01 μg of SO_4^{2-} per ml was 15%, and 0.1 μg/ml was 7% relative, and that the probable errors were 11 and 5% relative respectively.

The concentration range of sulfate which could be determined was $5 \cdot 10^{-8}$ to 10^{-5} g-ion/liter, i.e., 0.005 to 1 μg/ml. Within this range the sulfate concentration was proportional to the maximum current for the electroreduction of mercuric sulfide. At SO_4^{2-} concentrations greater than 10^{-5} g-ion/liter there was probably some combination of sulfide ions entering the absorber with heavy metal impurities. Results obtained by mercurimetric determination of sulfide showed that, in the course of time, there was some reduction in the concentration of S^{2-}.

The proposed method could be used for determining microquantities of sulfate in compounds of metals whose sulfides were insoluble in dilute acids, since the sulfides of such metals were soluble in hot concentrated acids [6]. The method could not be used for materials, the basis of which was easily reduced and also combined with mercury.

The method was applied to the analysis of high purity potassium and sodium carbonates. The sulfate content was obtained from calibration curves.

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