

POTENTIOMETRIC TITRATION OF SULPHATE, SULPHITE AND DITHIONATE MIXTURES, WITH USE OF A LEAD ION-SELECTIVE ELECTRODE

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Summary—Simple methods are described for the analysis of sulphate, sulphite and dithionate mixtures by potentiometric titration with lead perchlorate (and use of a lead ion-selective electrode). The error and precision are both about 2–5% for the sulphate concentration range 3×10^{-3} – $6 \times 10^{-4}M$. The sulphur content in fuels derived from refuse was determined by potentiometric titration after bomb-combustion and the results compared favourably with those from the standard $BaSO_4$ gravimetric method.

The environmental significance of sulphur is being increasingly recognized¹ and the analytical chemistry of sulphur compounds has therefore received much attention.^{2,3} Sulphur dioxide is one of the most ubiquitous pollutants in ambient air. Its oxidation in clean, dry air is slow, but certain transition metals such as iron, copper and manganese, which are quite common constituents of urban atmospheres, may enhance it.⁴ The oxidation of sulphur dioxide may lead to dithionate ($S_2O_6^{2-}$) or sulphate.^{5,6} Dasgupta *et al.* first proposed the existence of dithionate in atmospheric aerosols.⁶

There are few satisfactory analytical techniques for determination of dithionates or mixtures of dithionates with other sulphur-containing anions.^{2,3} Dasgupta *et al.* have proposed a method for the analysis of sulphate, sulphite and dithionate mixtures.⁶ In this, sulphite is titrated with tri-iodide in one aliquot of sample. In another aliquot, sulphite is oxidized to sulphate with hydrogen peroxide and the total sulphate is titrated with barium perchlorate with Sulphonazo III or Thorin as indicator. In a third aliquot, sulphite is oxidized to sulphate, and the total sulphate is precipitated as barium sulphate and filtered off. The filtrate, containing dithionate, is oxidized with concentrated nitric acid and the resulting sulphate is determined gravimetrically. The error of this procedure for dithionate was about $\pm 3\%$, and the method is time-consuming and complicated.

The present paper describes the analysis of mixtures of sulphate, sulphite and dithionate, by poten-

tiometric titration with lead perchlorate. An aliquot of sample is titrated with lead perchlorate to obtain the sum of sulphate and sulphite. Another aliquot is acidified with perchloric acid, and the sulphur dioxide produced is removed from the solution by passage of nitrogen. The sulphate is then titrated with lead perchlorate. A third aliquot is oxidized with hydrogen peroxide to convert sulphite into sulphate and then with concentrated nitric acid to oxidize dithionate to sulphate, and the total sulphate is titrated. All the titrations are done at pH 4 in 50% aqueous methanol. The error and precision of each titration are both 2–5% for the sulphate concentration range 3×10^{-3} – $6 \times 10^{-4}M$.

The method is simple, fairly accurate and precise. It needs only one standard solution and may find application in the analysis of atmospheric and industrial particulates and aerosols for sulphite, sulphate and dithionate. It has been applied to the determination of sulphur in some fuels derived from refuse.

EXPERIMENTAL

Apparatus

An Orion model 94-82 lead electrode and model 90-02 double-junction reference electrode were used with a Corning model 12 pH/mV-meter. The salt-bridge compartment of the reference electrode was filled with 1M sodium nitrate to prevent precipitation of potassium perchlorate.

Reagents

All solutions were prepared with demineralized distilled water and reagent-grade materials.

Lead perchlorate solution, 0.1M. Dissolve 46.0 g of $Pb(ClO_4)_2 \cdot 3H_2O$ in water, dilute to 1 litre, and standardize by EDTA titration. Dilute further as needed.

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Table 1. Results for the analysis of sulphate-sulphite mixtures

Taken, mM	Found, mM		Error, %	
$[\text{SO}_4^{2-}] + [\text{SO}_3^{2-}]$	$[\text{SO}_4^{2-}]$	$[\text{SO}_3^{2-}]$	$[\text{SO}_4^{2-}]$	$[\text{SO}_3^{2-}]$
2.000 + 0.500	2.030	0.440	+1.5	-12.0
0.500 + 2.000	0.458	1.960	-8.4	-2.0
1.000 + 2.000	1.000	1.980	0	-1.0
2.000 + 1.000	1.970	0.980	-1.5	-2.0
1.000 + 1.000	1.010	0.960	+1.0	-4.0

Sodium sulphate solution, 0.1M. Dissolve 14.20 g of anhydrous Na_2SO_4 in water and dilute to 1 litre. Dilute further as required.

Sodium sulphite solution, 0.1M. Dissolve 1.260 g of anhydrous Na_2SO_3 in freshly boiled water and dilute to 100 ml. Prepare daily and standardize by iodometric titration. Dilute further with freshly boiled water, as needed.

Sodium dithionate solution, 0.1M. Dissolve 24.20 g of dried $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (97.0%) in water and dilute to 1 litre. Standardize by oxidation with concentrated nitric acid, followed by titration with lead perchlorate as in procedure (a) below. Dilute further as required.

Procedures

(a) **Determination of sulphate and sulphite.** Pipette a 20-ml sample into a 100-ml beaker. Adjust the pH to 4 with sodium hydroxide solution or perchloric acid. Add 25 ml of methanol, immerse the electrodes in the solution, start stirring at the maximum speed at which air bubbles are not formed, and titrate with 0.01M lead perchlorate.

(b) **Determination of sulphate.** Pipette a 20-ml sample into a 100-ml beaker. Add 1.0 ml of 3M perchloric acid and bubble nitrogen vigorously through the solution for 15–20 min. Adjust the pH to 4 with 5M sodium hydroxide, add 25 ml of methanol and continue as in (a).

(c) **Determination of sulphate, sulphite and dithionate.** Pipette a 20-ml sample into an Erlenmeyer flask. Add 2 or 3 drops of 0.025M sodium hydroxide and 0.5 ml of 30% hydrogen peroxide. Allow 5 min for oxidation of sulphite to sulphate. Add 30 ml of concentrated nitric acid and put the loosely stoppered flask in a heated water-bath for 4 hr. The dithionate is quantitatively oxidized to sulphate. Evaporate the solution almost to dryness to remove the nitric acid, add 20 ml of water and adjust the pH to 4. Add 25 ml of methanol and continue as in (a).

Calculations

Plot the e.m.f. against volume of titrant and take the point of inflection as the end-point. Calculate the sulphite content from the difference between titrations (a) and (b). Calculate the dithionate content from titrations (a) and (c), remembering that 1 mole of dithionate is converted into 2 moles of sulphate.

RESULTS AND DISCUSSION

Potentiometric titration of sulphate

Ross and Frant first described the potentiometric titration of sulphate with lead, with use of a lead

ion-selective electrode.⁷ They used 50% aqueous dioxan medium to suppress the solubility of lead sulphate. The detection limit is $5 \times 10^{-5}M$ sulphate. Major interference is caused by cations which give an electrode response (Cu^{2+} , Hg^{2+} , Ag^{+}), anions which form insoluble lead salts (PO_4^{3-}) and high concentrations of chloride and nitrate. Lokka used a water-acetone mixture to suppress the solubility of lead sulphate,^{8,9} but we use 50% aqueous methanol in accordance with the electrode manufacturer's instructions,¹⁰ but no formaldehyde. The pH used (4) is the middle of the optimal range (4 ± 1).⁷⁻¹⁰

When sodium sulphate solutions in the range $4-20 \times 10^{-3}M$ were titrated with 0.1M lead perchlorate as in procedure (a), the error and precision were about 1%. The potential break at the equivalence point was about 85 mV. For $4-20 \times 10^{-4}M$ sodium sulphate titrated with 0.01M lead perchlorate the error and precision were about 1–2%, and the potential break about 45 mV.

Determination of sulphite

It was found that sulphite can also be titrated directly by the procedure for sulphate. Titration of $2-10 \times 10^{-3}M$ sulphite with 0.01M lead perchlorate at pH 4 [procedure (a)] gave an error and precision of about 1–2%, and a potential break of about 35 mV. The detection limit was $5 \times 10^{-4}M$. An alternative is to oxidize the sulphite to sulphate with hydrogen peroxide, heat to dryness to remove peroxide, which interferes with the titration,¹¹ dissolve the sodium sulphate in water and titrate by procedure (a).

Analysis of sulphate-sulphite mixtures

The sum of the sulphate and sulphite is determined [procedure (a)] and then the sulphate alone [procedure (b)] after decomposition of the sulphite. The accuracy for analysis of mixtures is shown in Table 1. There is a small systematic negative error in the determination of the sum of sulphate and sulphite,

Table 2. Results for the analysis of sulphate-sulphite-dithionate mixtures

Taken, mM	Found, mM			Error, %		
$[\text{SO}_4^{2-}] + [\text{SO}_3^{2-}] + [\text{S}_2\text{O}_6^{2-}]$	$[\text{SO}_4^{2-}]$	$[\text{SO}_3^{2-}]$	$[\text{S}_2\text{O}_6^{2-}]$	$[\text{SO}_4^{2-}]$	$[\text{SO}_3^{2-}]$	$[\text{S}_2\text{O}_6^{2-}]$
1.000 + 1.000 + 1.000	1.020	0.900	1.030	+2.0	-10.0	+3.0
1.000 + 3.000 + 1.000	1.007	2.960	1.034	-0.7	-1.3	+3.4
3.000 + 1.000 + 1.000	2.985	0.930	0.960	-0.5	-7.0	-4.0
1.000 + 1.000 + 3.000	0.996	0.958	2.925	-0.4	-4.2	-2.5
2.000 + 2.000 + 2.000	2.060	1.894	1.954	+3.0	-5.3	-2.3

Table 3. Results for the determination of sulphur in fuels derived from refuse

Sample	Sulphur, %*†	
	Gravimetry (X)	Titrimetry (Y)
1	0.250	0.220
2	0.462	0.446
3	0.238	0.234
4	0.238	0.231
5	0.095	0.100
6	0.188	0.199
7	0.463	0.478
8§	0.224	0.226

*Referred to dry weight.

†Correlation equation $Y = 0.990X$ ($r = 0.9934$, $N = 8$).§Standard deviations ($N = 5$): gravimetry 0.012, titrimetry 0.008.

which is possibly due to the greater solubility of the lead sulphate.

Analysis of sulphate-sulphite-dithionate mixtures

Dithionate is remarkably stable towards oxidizing agents, being attacked by only by a few strong oxidants, the most suitable of which is concentrated nitric acid, but prolonged heating is needed for complete oxidation.⁶ The sulphite present is oxidized first with peroxide, as otherwise there would be loss of sulphur dioxide during addition of the nitric acid. After the oxidation of dithionate the surplus nitric acid is expelled by heating almost to dryness, as nitrate interferes in the titration.¹⁰ Table 2 shows the accuracy of the method.

The proposed methods may find application in analysis of atmospheric and industrial particulates.¹²

Determination of sulphur in fuel derived from refuse

The bomb-combustion and classical gravimetric procedure for this analysis¹³ is time-consuming and

tedious. We have compared the gravimetric finish with procedure (a), after decomposition of the sample by bomb-combustion. Table 3 shows the results.

The precision of the two methods was checked by burning five samples of the same material and analysing the resulting solutions by both methods. The means and standard deviations were 0.224 ± 0.012 and $0.226 \pm 0.008\%$, for the gravimetric and titrimetric methods, respectively. The agreement is good but the titrimetric method is more precise and takes only 30 min, whereas the gravimetric method needs 3 hr.

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