

Short Communication

Titrimetric determination of sulphate in natural waters using lead ion-selective electrode detector

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Abstract

A titrimetric method for the determination of sulphate in water samples using lead nitrate titrant and lead ion-selective electrode as end-point detector is described. A double junction reference electrode containing salt bridge of 1 M sodium nitrate is used. The determination is carried out in 75% methanol media. The range of the method is 5 to 500 ppm of sulphate, the end-point volumes being reproducible from ± 5 to $\pm 1\%$ and recoveries between 90-98% are obtained in river water, well water, and mine water samples.

Key words : Titrimetric method for sulphate determination, sulphate in natural waters, lead ion selective electrode detector, determination of sulphate.

1. Introduction

Sulphate ions are abundant in natural waters, the concentration varying from a few to several thousand ppm. In water required for industrial purposes, concentration of sulphate is of importance mainly where evaporative processes introduce potential-scaling problems. Determination of sulphate is necessary for regulation of allowable concentrations in boiler water and in cooling towers as often sulphate is a constituent of boiler deposits and heat exchanger scales. The sulphate concentration in potable water supplies is also of interest because high amounts of sulphate impart a faintly bitter taste to water and cause cathartic effects, especially in children.

The methods¹⁻³ based on precipitation and complexometric titrations for sulphate ion determination have not gained importance because below concentrations of 10^{-4} M, problems arise due to solubility of precipitate and diffuse colour changes of indicators at end-point. The turbidimetric method suffer from interferences due to colour of suspended matter and also requires controlled particle size precipitation. Thus, although a large number of sulphate determination methods have been reported, still no precise and accurate procedure is available to the analytical chemist. Using the method of Ross and Frant⁴, we report a potentiometric method for sulphate determination in water samples.

2. Experimental

2.1. Instruments

An Orion-Model 94-82A, lead ion-selective electrode along with an Orion-Model 90-02 double junction reference electrode (containing 1 M sodium nitrate in its outer chamber) fitted on an Orion-Model 901 digital mV-meter was used as end-point detector.

2.2. Reagents

All reagents were of analytical reagent grade including methanol which was used to obtain 75% v/v, methanol-water mixed solvent system. A stock solution (0.1 M) of sulphate was prepared by dissolving 7.1020 gm of anhydrous sodium sulphate (previously dried for 2 hours at 100° C) in 500 ml of water. 33.12 gm of lead nitrate was dissolved in one litre of water to obtain 0.1 molar stock solution of titrant and was stored in polyethylene bottle. 1 molar solution of ionic strength adjustor was prepared by dissolving 70 gm of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in 500 ml of water.

2.3. Ion-exchange columns

Zerolit 225 resin was used to prepare ion-exchange columns in acid and silver form. For acid form 100 gm of resin was treated with 500 ml of 2 M nitric acid, the mixture stirred for 5 minutes, separated on a sintered glass funnel and washed until neutral. For silver form 100 gm of resin was first brought into acid form and was further treated with 500 ml of 0.2 M silver nitrate, the mixture stirred for about 30 minutes separated on a sintered glass funnel and washed until free from Ag^+ ions.

3. Results and discussion

3.1. Titration media

The moderate solubility of lead sulphate in aqueous media makes it impractical to titrate water samples having low concentration of sulphate. Solvents of low dielectric constant such as 1, 4 dioxan or methanol can decrease the solubility of lead sulphate. Although dioxan can cause the greatest decrease, inconsistent results have been reported⁵ because formation of peroxide due to its decomposition has adverse effect on the

membrane of ion-selective electrode. Hence, methanol has been used in the proposed method.

The optimum methanol volume in the titration solution was found to be 50–75% because below 50% end-point breaks were found to be considerably smaller and above 75% sluggish establishment of equilibria was observed.

3.2. Titrant

Lead nitrate was used as titrant in the present method as lead perchlorate⁴ with sufficient purity was not readily available. While using 1, 4 dioxan as solvent serious interferences have been reported when only tenfold excess of NO_3^- is present over SO_4^{2-} , but in the present case when SO_4^{2-} was titrated in the absence and presence of even 200-fold excess of nitrate no difference was observed in the end-point of titration curve. Thus lead nitrate can be very safely used as titrant.

3.3. Effect of pH

In alkaline media lead may get precipitated as lead hydroxide and in acidic media ($\text{pH} < 3.5$) solubility of electrode membrane increases thereby decreasing the sharpness of end-point. However, the titration curves were independent of pH in the range 3.5 to 5.5.

3.4. Effect of cations

As lead electrode suffers interferences from Cu^{2+} , Hg^{2+} and Ag^+ these ions should be absent from the samples. Fortunately, they are in trace concentrations in water. In addition to these ions, calcium in water was found to cause negative error in sulphate determination. The end-point appeared prematurely in presence of increasing amounts of calcium. However, it was observed that interference due to calcium can be suppressed by addition of inert electrolyte, *i.e.*, by increasing ionic strength. Although the potential change at end-point was found to be smaller in presence of ionic strength adjustor, the addition of 0.05 M sodium perchlorate eliminated interference from a 5-fold excess of calcium and 0.1 M sodium perchlorate from a 20-fold excess of calcium. When calcium is present at high concentration, CaSO_4 may precipitate on addition of methanol but as ionic strength adjustor increases solubility of calcium sulphate, it should be added before the addition of methanol. When expected calcium concentration is still greater, it is advisable to pass the solution through cation exchange resin.

3.5. Effect of anions

Anions such as molybdate and tungstate which form less soluble precipitate with lead will react preferentially with the titrant, however, they are seldom present in water. To investigate the influence of other common anions occurring in water, titrations were carried out with synthetic samples. Fluoride and phosphate normally found in waters

had no interference. Carbonate and bicarbonate ions could have interfered but their interference was removed by acidifying titration solution. Nitrate ions even up to 200-fold excess of sulphate showed no interference, but chloride ions interfered above 10-fold excess. In order to eliminate interference due to chloride an ion exchange separation procedure⁷ was followed. Water sample (50 ml) containing around 100-fold excess of chloride over sulphate was passed at a flow rate 5 ml/min through two columns fitted one above the other. The upper column contained ion-exchanger in silver form and lower column contained the acid form. Cations present in water sample displaced silver ion from ion exchanger in upper column precipitating silver chloride and making sample chloride free. The sample while passing through the lower column gets rid of excess silver ions. This procedure also destroyed carbonate and bicarbonate ions because when the sample leaves second column, it gets acidified to pH 3.5 ± 0.5 which is well below the pH of carbonic acid (6.4). This procedure is suitable for a series of samples, but for occasional samples, an alternative procedure was followed, in which 50 ml of sample was placed in a beaker, about 2 gm of resin in silver form was added and the mixture was stirred for about 20 minutes. It was then filtered through a sintered glass funnel and to the filtrate about 2 gm of resin in acid form was added. After stirring for another 20 minutes, it was again filtered. The filtrate was found free from chloride, carbonate and bicarbonate.

Table 1

Recovery studies for sulphate determination in natural water samples by proposed method

Water sample	Sample no.	Sulphate found, ppm	Sulphate added, ppm	Sulphate recovered, ppm	% recovery ppm
Well water	1	26	10	34	94.4
	2	44	10	52	96.4
	3	85	10	91	95.8
	4	39	10	47	96.0
	5	52	10	59	95.1
Mine water	1	256	100	351	98.6
	2	313	100	403	97.5
	3	186	100	273	98.7
	4	472	100	561	98.0
	5	391	100	488	99.5
River water	1	9	5	13	92.8
	2	17	5	20	90.2
	3	22	5	24	89.7
	4	14	5	17	89.4
	5	11	5	15	93.7

3.6. Precision and accuracy

To check the precision of the method, tests on synthetic samples were carried out for sulphate determinations. The end-point volumes were found to be reproducible to $\pm 1\%$ at concentrations around 250 ppm. Precision was found to decrease at low concentrations to $\pm 2\%$ around 50 ppm and approached $\pm 5\%$ around 10 ppm.

The accuracy of the method was tested by titrating series of unspiked and spiked natural water samples at different concentration levels and the results are summarised in Table I. Recoveries of 98% were obtained with samples containing more than 250 ppm sulphate, 95% with samples containing 50–100 ppm sulphate, and around 90% with samples containing 10–25 ppm sulphate.

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