

Determination of microquantities of sulphate by ion exchange spectrophotometry

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A simple method for the determination of microquantities of sulphate using ion exchange spectrophotometry is reported. Thiocyanate form of the Amberlite-IRA 400 resin is used as the ion exchanger. The optimum conditions such as column length and flow rate have been established. The method has been modified for the determination of sulphate in the presence of interfering halides and sulphide ions. It has been applied to the determination of total concentration of anions in water and soil samples.

The determination of sulphate anion in natural as well as waste water is important for monitoring ecological balance. Numerous analytical methods for sulphate determination have been proposed¹⁻⁵. However, most of these methods are either indirect, tedious or involve many steps like precipitation, dissolution and colour development, etc. In 1980's ion chromatography⁶⁻⁸ was introduced for sulphate determination. This technique is highly sensitive, selective, reliable, reproducible and fast. However, ion chromatogram is usually not available to small laboratories.

The method reported here for sulphate determination is simple, reproducible and sensitive. It is based on the displacement of equivalent amount of thiocyanate ion from the thiocyanate form of Amberlite-IRA 400 resin column by sulphate. The released thiocyanate, when treated with ferric ion, forms a complex absorbing at 480 nm. The interference due to other anions like chloride, bromide, iodide and chromate present alongwith the sulphate is removed by use of Ag^+ -form resin.

Experimental

AR grade chemicals and deionised water were used throughout the course of the work. Absorbance was measured on a Spectronic 20, Baush & Lomb photometer.

Preparation of SCN^- -form resin column

Amberlite-IRA 400 resin (10 g) was soaked in

water for 12 hr. and then treated with 100 ml of 0.5 M HCl to convert it into the chloride form. Excess HCl was removed by washing the resin with doubly distilled water and then it was treated with 100 ml of 0.5 M KCNS solution to convert it into the thiocyanate form. The excess of thiocyanate was washed with water till the washings did not develop any colour with ferric ion solution.

A glass column (18 cm in length, 1.5 cm o.d.) was used as the ion exchange column. The slurry of the resin in thiocyanate form was poured into the column to achieve a uniform packing. Excess water was drained and air gaps were avoided to overcome the eddy diffusion. The length of the resin bed was maintained at 10 cm.

Preparation of precolumn of Ag^+ -form resin

Two grams of cation exchange resin Dowex-50W-XB (mesh 20-50) was treated with 100 ml of 0.5 M HCl to convert it into hydrogen ion form. Excess HCl was removed by washing it with distilled water and then the resin was treated with 50 ml of 0.1 M AgNO_3 to convert it into silver ion form. Excess silver nitrate was removed by washing with doubly distilled water. A resin column was prepared as described earlier. The length of the resin bed was kept 5 cm.

Stock solutions of anions (10^{-2} M) were prepared by dissolving appropriate amounts of AR grade sodium salts in deionised water. Working solutions were prepared by diluting the stock solutions. Solutions of potassium thiocyanate and ferric chloride (10^{-2} M) were prepared by dissolving the corresponding salts in deionised water.

Determination of sulphate

Sodium sulphate solution (10 ml, 10^{-3} M) was passed through the SCN^- -form column at the flow rate of 1 ml min^{-1} . The column was washed with 10 ml of deionised water. The column effluents were collected alongwith the washings and diluted to 25 ml with deionised water. The absorbance of the iron-thiocyanate complex was measured after developing the colour by addition of 8.0 ml, 10^{-2} M ferric ion solution. The procedure was repeated for the sulphate solutions of 10^{-5} M to 10^{-3} M concentrations to construct a calibration curve.

Results and discussion

The method is based on the displacement of

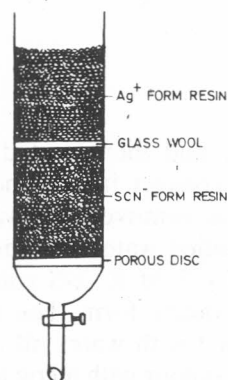


Fig. 1 – Column assembly

equimolar concentration of SCN^- from the anion exchanger by sulphate. A calibration graph was constructed for 1×10^{-4} – 6×10^{-4} M KCNS solutions using 1 ml of 10^{-2} M ferric ion solution at pH 1.5 to 1.8 and measuring the absorbance at 480 nm against reagent blank. Sulphate was determined at optimum conditions established earlier. It was observed that 90–95% displacement of SCN^- took place by sulphate ions. The results were reproducible with a standard deviation of 0.007 for 10 readings.

The effect of concentration of sulphate on thiocyanate displacement

Aliquots (10 ml) of 10^{-3} to 10^{-5} M sodium sulphate solutions were passed through the SCN^- column at the optimum conditions. The displaced thiocyanate was measured as described earlier. A linear relationship was observed between the concentration of sulphate ions and the displaced SCN^- . 10^{-6} M sulphate also displaced SCN^- , but the absorbance measured was very small. By introducing the technique in flow injection system, the determination of sulphate at 10^{-7} M concentration was possible.

Effect of flow rate

Increase in the flow rate from 1 ml min^{-1} to 8 ml min^{-1} of the solution through the column did not decrease the percentage displacement of SCN^- from the column. Therefore, higher flow rates can be used during column operations. This increases the speed of the measurements.

The effect of column length

It was observed that a microcolumn of 2 cm length was sufficient for the quantitative displacement of SCN^- by sulphate ions. This makes the system economical.

Table 1 – Determination of sulphate in the presence of chloride

ml of 10^{-3} M chloride ion solution	ml of 10^{-3} M sulphate ion solution	SCN^- * column	$\text{Ag}^+ + \text{SCN}^-$ ** combined column
0	5	0.22	0.22
2	5	0.25	0.20
4	5	0.30	0.19
5	5	0.34	0.22
6	5	0.35	0.19
8	5	0.41	0.19
10	5	0.44	0.21
10	0	0.23	—

*Absorbance of Fe–SCN complex developed from SCN^- displaced due to single column assembly.

**Absorbance of Fe–SCN complex developed from SCN^- displaced due to combined column assembly.

Interference due to other anions

The displacement of SCN^- by other anions was studied by passing 10 ml of 10^{-3} M thiosulphate, chloride, nitrate and phosphate ion solutions through the resin columns. It was observed that equimolar solutions of these ions do not displace thiocyanate to the same extent. The displacement of SCN^- for equimolar solutions depends upon the charge present on the anion indicating the relationship between the concentration of anion in terms of normality and the absorbance. However, the interference due to chloride, bromide, iodide, sulphide, chromate, etc., can be overcome by introduction of precolumn in Ag^+ -form.

Determination of sulphate in the presence of chloride

Next to chloride, sulphate is the most abundant anion in sea water. Chloride interferes in the gravimetric or volumetric estimation of sulphate. In the proposed method, interference of chloride in sulphate determination is overcome by using a combined column of the Ag^+ resin and SCN^- resin (Fig. 1). When a mixture of 5 ml of 10^{-3} M chloride and sulphate was passed through the combined column chloride was removed and entrapped as AgCl in the Ag^+ -form resin column and only sulphate displaced the thiocyanate from the column. But the mixture when passed through a column containing only SCN^- resin gave the total concentration of chloride and sulphate in the mixture. Eight mixtures with varying ratios of sulphate and chloride were analysed by this method with a standard deviation of 0.00 to 0.01. The results are presented in Table 1. The absorbance

was also measured for 5 ml of 10^{-3} M sulphate solution and chloride solution separately by passing them through the combined column. It was observed that there was no variation in absorbance for sulphate whereas chloride solution did not show any absorbance due to the SCN^- displacement indicating quantitative removal of chloride by the precolumn. Sulphate solutions upto 10^{-3} M did not develop any turbidity during the use of combined column. Ag^+ -form column was efficient in the removal of interference due to bromide, iodide, sulphide, dichromate, phosphate, etc.

Determination of total anion concentration in water

The total anion concentration was determined by the proposed method by passing 5 ml of tap water through SCN^- -form column. The column was washed with deionised water. Column effluents along with deionised water were collected and displaced thiocyanate was determined as described earlier. It was observed that total concentration of the anions present in water was 4.5×10^{-3} N.

For the determination of sulphate in water, it is necessary to introduce an additional column of 2 cm length in the form of H^+ -resin to remove calcium and magnesium ions present in the water. However, the concentration of calcium and magnesium upto 10^{-3} M level did not show any displacement of Ag^+ from the column. Higher con-

centrations displaced Ag^+ , leading to erratic results. A study of displacement of SCN^- by SO_4^{2-} in the presence of 10^{-3} M Fe^{2+} , Ca^{2+} , Mg^{2+} , showed no change in absorbance, but higher concentration of these cations required their removal by a column containing H^+ -form resin.

Determination of water-soluble anions from soil

A sample of soil (0.3041 g) was treated with 100 ml of deionised water. It was stirred thoroughly and kept overnight, centrifuged and filtered through sintered glass funnel. Five ml of the filtrate was passed through the thiocyanate column. The displaced thiocyanate was determined using the calibration curve. It was observed that the total concentration of water soluble anions present in the soil was 2×10^{-2} Ng $^{-1}$ of soil.

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