Direct Spectrophotometric Determination of Sulphate Ion Based on the Formation of a Blue Molybdosulphate Complex

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In an aqueous medium containing 50% *V*/*V* acetone, sulphate ion reacts with a mixed reagent consisting of Mo^{V}-Mo^{VI}-HCl to give a blue molybdosulphate complex, the amount formed being proportional to the sulphate ion present. Using this colour forming reaction, sulphate ion could be determined spectrophotometrically, and the limit of detection (signal to noise ratio = 3) was 3.1×10^{-6}M. When combined with an extraction-concentration of the blue complex, the proposed method gave a lower limit of detection, *viz.*, 1.0×10^{-6}M. Phosphate, arsenate and germanate ions interfered owing to the formation of similar blue complexes at concentrations $\geqq1.0\times10^{-5}$M, but the presence of 1.0×10^{-4}M silicate ion and 1.0×10^{-2}M chloride ion caused no significant interference. Sulphate in natural waters, particularly saline waters, was determined and the results showed good agreement with those obtained by ion chromatography or inductively coupled plasma atomic emission spectrometry.

Keywords: *Sulphate determination;molybdosulphate blue; spectrophotometry; natural waters*

In spite of extensive studies on the determination of sulphate ion, few suitable colorimetric methods have been developed. Nearly all the spectrophotometric methods available for the determination of sulphate ion are based on indirect methods. In some instances, sulphate ion was first reacted with sparingly soluble reagents such as thorium borate-amarath,[1] barium chloranilate,[2] zirconium or thorium alizariun,[3] barium chromate,[4] barium iodate[5] and barium violurate,[6] and the liberated components from the respective reagents were then measured spectrophotometrically by taking into account the stoicheiometric replacement with sulphate ion. Alternatively, measurements were made using soluble reagents such as 2-aminoperimidine[7] and barium ion,[8] with remain in solution in excess after stoicheiometric precipitation with sulphate ion. These methods have subsequently been modified to improve their accuracy and sensitivity and have found a variety of applications.[9,10] However, these indirect methods require laborious procedures to ensure that the heterogeneous reactions are quautitative.

In the course of synthetic studies on heteropoly molybdate complexes in aqueous acetonitrile

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media, we found that sulphate ion reacted readily with an acidic molybdate solution to give a specific heteropoly complex.[11] This complex, which exhibited a yellow colour due to the fact that its absorption band occurred in the near ultraviolet region, could be electroreduced to a blue complex.[12]

We observed that a similar blue species could also be obtained directly by reacting sulphate ion with a Mo^{V}-Mo^{VI}-HCl mixture in the presence of acetonitrile or acetone. This reaction can be used as the basis of a simple, direct spectrophotometric method for the determination of sulphate ion.

Experimental

Reagents

A 500 mM Mo^{VI} solution was prepared by dissolving $Na_2MoO_4.2H_2O$ in water.

A 200 mM solution of Mo^{V} in 2.4 M HCl was prepared by controlled potential electrolysis. A 40-ml aliquot of the Mo^{VI} solution was mixed with 21 ml of 11.6 M (36% *m*/*m*) HCl and 39 ml of pure water and the mixture transferred into a 100-ml electrolysis cell. A three-electrode system was used: a bundle (*ca.* 1 g) of GC-20 glassy carbon fibres (Tokai Carbon) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. The acidic Mo^{VI} solution was stirred continuously and a potential of-0.1 V *versus* SCE was applied by means of a Hokuto Denko HA-301 potentiostat. Approximately 6 h were required for completion of the electrolysis; the electrolysis current decreased initially (for 15 min), then increased (for 30 min) and finally decreased again towards the residual current level. The transparent orange-red solution thus obtained was used as a standard solution of Mo^{V}, although it contained an equilibrium mixture[13] of $Mo_2O_4^{2+}$ and $Mo_2O_3^{4+}$. This solution was stable for at least 2 weeks when kept under ambient conditions and for more than 1 month when kept in the dark at 4°C.

A reagent mixture consisting of 50 mM Mo^{V}-117 mM Mo^{VI}-4M HCl was freshly prepared as required.

A 100 mM sulphate stock solution was prepared from K_2SO_4 and diluted appropriately to give the working sandard solutions.

Acetone and acetonitrile were of guaranteed-reagent grade and were used as received. Chloroform of guaranteed-reagent grade was washed before use by shaking it with water to remove the ethanol added as a stabiliser.

Apparatus

Unless stated otherwise, the temperature for the colour forming reaction was thermostated to 25 ± 1°C.

Absorption measurements were made on a Shimadzu*

UV-200 spectrophotometer using silica cells with light path lengths of 1.0,0.2 and 0.1 cm. Absorbance values measured in 0.2- and 0.1-cm cells were calculated for a 1.0-cm cell.

Results and Discussion

Optimisation of Conditions for the Formation of the Blue Molybdosulphate Complex

The presence of acetonitrile aided the formation of the yellow molybdosulphate complex.[11] This was also true for the blue molybdosulphate complex. Without the organic solvent, no colour change was observed on addition of sulphate ion to the Mo^{V}-Mo^{VI}-HCI mixture;instead the orange-red colour of the reagent was unchanged. In the presence of acetonitrile or acetone at concentrations > 40% V/V, the solutions gave a characteristic blue colour on addition of sulphate ion. A blue complex with a Mo to S ratio of 9:1 was isolated from the reaction medium as the tetraalkylammonium salt. Details of the isolation procedure will be reported elsewhere. The present method is based on this complex formation reaction.

Fig 1 shows the absorption spectrum of the blue molybdosulphate complex, which has a broad $\lambda_{max.}$ at 720 nm. The absorbance increases with time over a period of several days (Fig. 1,B-D). A period of 24 h was used for all subsequent absorbance measurements.

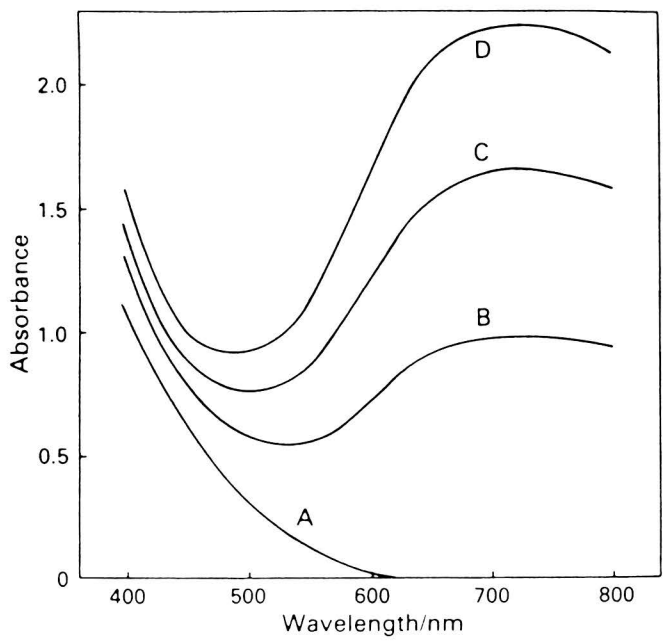

Fig. 1. Formation of the blue molybdosulphate complex in a reaction medium consisting of 15mM Mo^{V}-35mM M^{VI}-1.2M HCI-50% V/V acetone. A, Reaent blank; B, C and D, in the presence of 0.2mM sulphate ion after standing for 1, 2 and 5 d,respectively

Apart from the time needed for the reactoin to develop,the formation of the blue complex also depends on the concentrations of Mo^{V}, Mo^{VI} and HCI employed and on the temperature of the solution. The effect of the Mo^{V} and Mo^{VI} concentrations was examined first by keeping the other parameters constant,*viz.*, 1 mM sulphate, 1.2 M HCI, 50% V/V acetone and a temperature of 25°C. The concentration of molybdenum in each oxidation state (+5 and +6) was varied and the absorbance was measured at 720 nm after standing for 24 h. In Fig. 2, the absorbance is plotted as a function of the Mo^{V} and Mo^{VI} concentrations and each set of equal absorbance values is joined by a smoothed line. The shaded area in Fig.2 represents the region in which an interfering blue colour arises (*i.e.*, in the absence of sulphate ions) owing to the formation of a so-called isopoly molybdenum blue species. Excluding this region,the highest absorbance is attained on curve D. This curve was also used to determine the optimum composition for Mo^{V} and Mo^{VI} so that the total molybdenum concentration was kept to a minimum. This was found to be 15 mM Mo^{V} plus 35 mM Mo^{VI} (marked with an X on curve D).

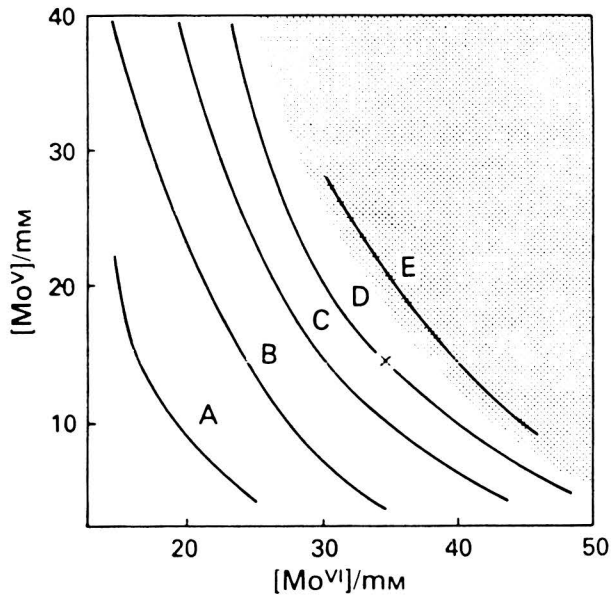

Fig. 2. Formation of the blue complex as a function of the Mo^{V} and Mo^{VI} concentrations. Sulphate ion (1 M m) is reacted in a medium consisting of 1.2 M HCI-50% V/V acetone and containing various concentrations of Mo^{V} and Mo^{VI}. Absorbances are measured at 720 nm after leaving the solutions to stand for 1 d. Absorbance values: A, 0. 1, B, 1; C, 3; D, 6; and E, 9. Path length, 1 cm. Shaded area, region of isopoly molybdenum blue formation. X, Optimum composition of Mo^{V}-Mo^{VI}.

Secondly, the effect of the HCI concentration was investigated. When the HCI concentration was greater than 1.5M, formation of the blue complex was extremely slow. In practice,moderate reaction rates were achieved only at HCI concentrations $\leqq$1.2 M. However,the interfering isopoly molybdenum blue species was also formed below 1.0 M HCI. From these observations, the optimum

HCI concentrations was found to be 1.2 M.

As regards the choice of auxiliary solvent,acetonitrile and acetone were compared and it was concluded that the latter was preferable because it gave a much greater rate of complex formation than the former. The rate could be increased by increasing the acetone concentration; however, large additions of this solvent caused an undesirably large dilution of the sample. A concentration of 50% V/V was chosen as a compromise.

Finally,the reaction temperature was varied from 5 to 45°C. Between 15 and 30°C there was virtually no change in the reaction rate;only at temperatures higher than 40°C or lower than 10°C was the rate decreased appreciably. On the basis of these data, subsequent experiments were carried out at room temperature.

Recommended Procedure

A 3-ml aliquot of the reagent mixture (*i.e.*, 50 mM Mo^{V}-117 mM Mo^{VI}-4M HCI) is placed in a 10-ml centrifuge tube having a tight stopper and then 2 ml of the sample to be analysed and 5 ml of acetone are added. The mixture is shaken well and left to stand for 24 h after which the absorbance is measured at 720 nm. The sulphate concentration can be determined by comparison with a calibration graph (Fig.3,A). The standard deviation of the blank absorbance (average of ten

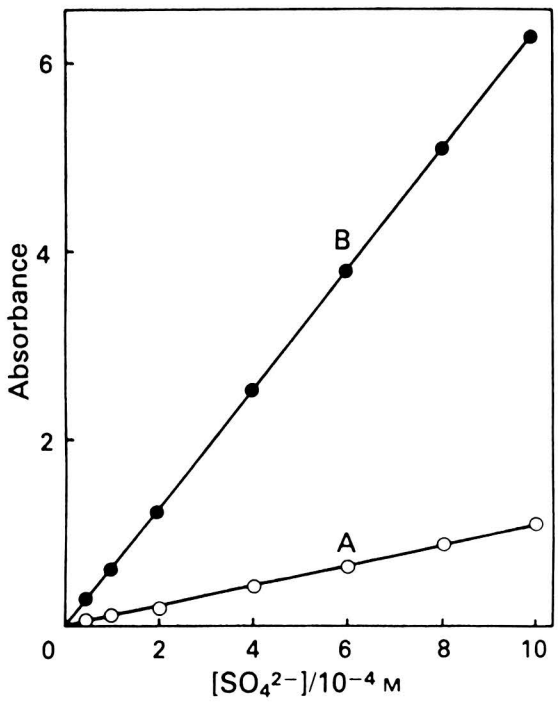

Fig. 3. Calibration graphs. Absorbance measured (A) before extraction and (B) after extraction of 10 ml of aqueous acetone solution with 0.5 ml of chloroform. Path length, 1 cm

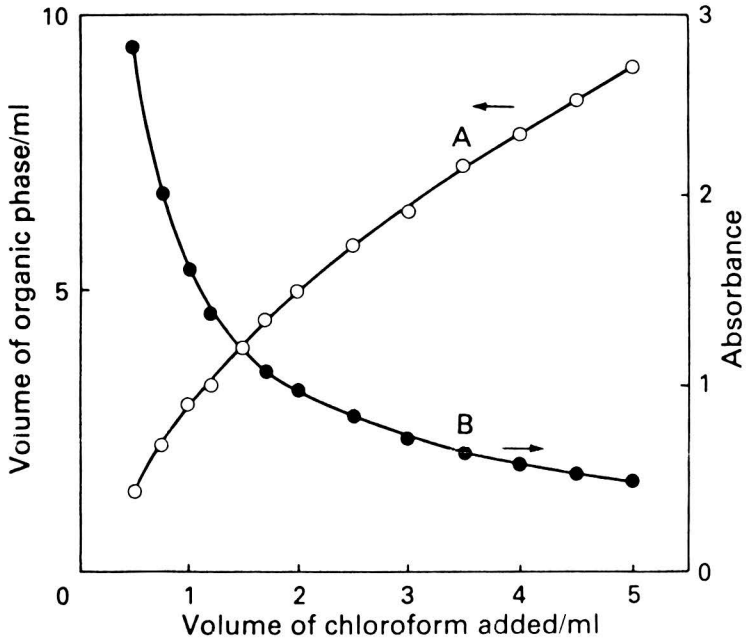

Fig. 4. Variation of(A) the volume of the organic phase and(B) the absorbance of the organic extracts as a function of the amount of chloroform added. Samples (10 ml) consisting of 1.0×10^{-4}M sulphate-15 mM Mo^{V}-35 mM Mo^{VI}-1.2 M HCl-50% V/V asetone were shaken with various amounts of chloroform

measurements) was 0.0012. The limit of detection was calculated as that concentration which gave an absorbance three times the standard deviation of the blank absorbance; the value thus obtained was 3.1×10^{-6}M. The reproducibilities (relative standard deviations of ten determinations) at the 1.0×10^{-4} and 1.0×10^{-3}M sulphate levels were 1.4 and 0.7%, respectively. The reproducibilities for lake and river water samples were 1.2% (3.49×10^{-4}M sulphate ion) and 0.6% (9.34×10^{-4}M sulphate ion), respectively, and those of the natural water samples, which were spiked with 1.0×10^{-4}M sulphate ion, had similar values.

As mentioned earlier (and as show in Fig.1,B, C and D), the reaction does not reach equilibrium even after standing for 24 h; in fact the absorbance continues to increase to increase with time. However, this presents no problem in the determination of sulphate ion because the increase in the absorbance is very slow; also,the change in the absorbance is less than 1% per hour after 24 h.

If the concentrations of sulphate ion in samples are found to be low for accurate measurements, then an extraction-concentration method can be applied to the blue complex by using chloroform. A 10-ml volume of the sample is shaken vigorously with 0.5 ml of chloroform for several minutes to extract the blue complex and the absorbance of the organic extract is then measured at 720 nm.

Owing to the presence of a large amount of acetone in the system,a larger volume of organic phase is recovered relative to the chloroform added. Fig.4 shows both the volume and the final absorbance of the organic phase as a function of the amount of chloroform added. The addition of

0.5 ml of chloroform produces 1.5 ml of organic phase, into which the dilute blue complex is concentrated. This leads to an approximately six-fold increase in the sensitivity of the method. The standard deviation of the blank absorbance was 0.0024 using this concentration method and the limit of detection was 1.0×10^{-6}M. The reproducibility at a 2.0×10^{-5}M sulphate concentration was 1.1%. The calibration graph obtained by this procedure is shown in Fig. 3, B.

Effect of Foreign Ions

Table 1 summarises the effect of a number of foreign ions that are often found in natural water samples. As can be seen from the table, phosphate, arsenate and germanate ions cause positive errors by forming a similar blue heteropoly complex at concentrations $\geqq 1.0\times10^{-5}$M. However,the concentrations of these ions in natural water samples are usually very low compared with that of

Table 1.
Effect of foreign ions

Ion	Concentration/ M	Absorbance at 720nm	Error,%	Ion	Concentration/ M	Absorbance at 720nm	Error,%
None*		0.091					
Na^+	10^{-4}	0.091	0	BO_3^{3-}	10^{-3}	0.091	0
	10^{-3}	0.092	1		10^{-2}	0.090	-1
	10^{-2}	0.088	-3		10^{-1}	0.090	-1
K^+	10^{-4}	0.092	1	SiO_3^{2-}	10^{-5}	0.094	3
	10^{-3}	0.092	1		10^{-4}	0.096	5
	10^{-2}	0.091	0		10^{-3}	0.145	59
Ca^{2+}	10^{-3}	0.090	-1	PO_4^{3-}	10^{-6}	0.090	-1
	10^{-2}	0.086	-5		10^{-5}	0.120	32
	10^{-1}	0.091	0		10^{-4}	0.322	254
Mg^{2+}	10^{-3}	0.093	2	AsO_4^{3-}	10^{-6}	0.093	2
	10^{-2}	0.087	-4		10^{-5}	0.114	25
	10^{-1}	0.092	1		10^{-4}	0.354	289
Fe^{3+}	10^{-6}	0.090	-1	NO_3^-	10^{-3}	0.092	1
	10^{-5}	0.092	1		10^{-2}	0.089	-2
	10^{-4}	0.096	5		10^{-1}	0.015	-84
Al^{3+}	10^{-5}	0.089	-2	GeO_3^{2-}	10^{-6}	0.091	0
	10^{-4}	0.093	2		10^{-5}	0.100	10
	10^{-3}	0.090	-1		10^{-4}	0.223	145
Cl^-	10^{-3}	0.091	0				
	10^{-2}	0.091	0				
	10^{-1}	0.082	-10				

*Sulphate concentration, 1.0×10^{-4}M.

sulphate ion and, therefore, they have a negligible effect on the analysis of such samples.* The presence of 1.0×10^{-4} M silicate ion causes no significant interference. Nitrate ion at concentrations $\geqq 0.1$ M causes negative errors due to the oxidation of Mo^{V} in the reagent. Chloride ion also reduces the absorbance at concentrations $\geqq 0.1$ M by the formation of chloride complexes with molybdenum ions. None of the cations studied interferes.

Application to Natural Water Samples

To ascertain the utility of the proposed method, sulphate ions were determined in natural saline and other water samples such as sea water from the Pacific Ocean and lake and river waters from the

Table 2

Analytical results on sulphate concentrations in natural saline and other water samples

Concentration/mM

Sample	proposed method	ICP-AES *	IC †
Sea water ‡—			
KH87-4/25-0[a]	27.6	28.2	—
KH87-4/43-0[b]	27.2	27.9	—
KH87-4/43-1000[c]	26.9	27.9	—
KH87-4/43-3000[d]	27.7	28.0	—
KT86-2[e]	25.8	26.7	—
Lake water §			
85519-01	7.58	7.75	7.38
85521-03	8.14	8.38	8.45
85526-01	2.15	2.23	2.18
85526-02	3.57	3.63	3.36
85526-05	7.31	7.48	7.74
85608	0.934	0.939	0.916
River water §			
85521-04	3.67	3.81	3.68
85527-02	47.2	49.5	49.5
85527-03	484	515	492
85617-01	0.349	0.368	0.361

*Inductively coupled plasma atomic emission spectrometry.

† Ion chromatography.

‡ Sea water samples were collected from the Pacific Ocean (location: a, 42° 30.3' N, fii° 59. 3' E; b, c and d, 39° 38. 7' N, 144° 54. 5' E; and e, 34°46.0' N, 141° 47.2' E. Depth: a, b and e, O; c, 944; and d, 2805 m).

‡ Lake and river water samples were collectd from the Tibet Plateau,China.

Tibet Plateau, China. The analytical results are shown in Table 2 together with those obtained by two other methods, *viz*., inductively coupled plasma atomic emission spectrometry (ICP-AES) and ion chromatography (IC). It can be seen that the results show good agreement within experimental error. This indicates that the proposed method is a useful alternative for the determination of sulphate ions in natural waters, particularly saline waters.

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*When present in amounts comparable to sulphate ion, phosphate, arsenate and germanate ions should be removed before analysis. This can be achieved by using hydrated iron(III) oxide as a scavenger. The following procedure is recommended. Hydrated iron(III) oxide is prepared as described previously[14] and suspended in a pH 8 buffer solution to give a concentration of 5 mg ml^{-1} of Fe.A 2-ml portion of the buffer solution containing the iron oxide is taken and added to a 50-ml aliquot of the sample solution in a 50-ml centrifuge tube. The sample is shaken for 30 min and the iron oxide separated by centrifugation. The supernatant solution is then subjected to the sulphate determination procedure.

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