FORESTS DEPARTMENT

A COMPARISON OF SEVERAL TECHNIQUES FOR THE MICROESTIMATION OF SULPHATE IN WATER SAMPLES

by

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SUMMARY

Eight analytical techniques (1 atomic absorption, 3 colorimetric, 3 turbidimetric and 1 volumetric) were compared to test their suitability for the rapid analysis of sulphate present in water samples.

The most precise technique was the methylene blue reduction method of Johnson and Nishita (1952).

The turbidimetric method suggested by Loveday (1974) proved very satisfactory for the rapid, routine analysis of sulphate present in all water samples examined.

INTRODUCTION

The major water catchments in south-west Western Australia occur within the forest zone, and a large research programme is currently being carried out to investigate the effects of forestry and bauxite mining on water yield and quality. As part of this project, a regular stream sampling programme was commenced in 1973 to examine variations in electrical conductivity throughout the forest area. In addition, detailed chemical analyses were required for a number of samples, and these analyses included the sulphate ion concentrations. Preliminary studies had shown that sodium, magnesium, chloride and bicarbonate were the major ionic constituents of the water, and calcium, potassium, sulphate and phosphate were of minor importance (Hatch, in press).

The analysis of low concentrations of sulphates in water by the barium sulphate gravimetric method is tedious and subject to considerable errors, both positive and negative (APHA, 1969). To overcome the analytical problems associated with the microestimation of sulphate, a number of atomic absorption, colorimetric and turbidimetric techniques have been developed to permit the rapid and accurate analysis of sulphate in water samples. Of these techniques, the methylene blue reduction technique of Johnson and Nishita (1952) is regarded as the most sensitive and accurate, but this method requires special glass apparatus and does not readily lend itself to the rapid analysis of a large number of samples.

To check the suitability of some of these techniques, a comparison was made of eight methods (1 atomic absorption, 3 colorimetric, 3 turbidimetric and 1 volumetric) for the determination of microgram amounts of sulphate in water samples.

The experimental methods used were as follows.

1. Atomic absorption.

   Precipitation of sulphate with barium chloride, and the estimation of the excess barium by atomic absorption spectroscopy (Parker, 1972).

2. Colorimetric.

   a. Methylene blue reduction method (Johnson and Nishita, 1962).

   b. Precipitation of sulphate with 2-aminoperimidine and the spectro-photometric estimation of the residual amine cation (Jones and Stephen, 1973).

   c. Precipitation of sulphate with 2-aminoperimidine and the spectro-photometric estimation of the residual reagent after treatment with nitrous acid and alkali (Archer, 1975).

3. Turbidimetric. These techniques consist of the precipitation of finely divided barium sulphate under controlled conditions, and the measurement of the turbidity of the suspension in the presence of a conditioning reagent. Three different conditioning reagents are used to stabilize the precipitate, according to different authors.

   a. Gum acacia-acetic acid (Massoumi and Cornfield, 1963).

   b. Glycerol (Loveday, 1974).

   c. Gelatin (Tabatabai, 1974).

4. Volumetric

   Precipitation of sulphate with barium chloride and the estimation of the excess barium by ethylenediaminetetraacetic acid (EDTA) titration (Bond, 1955).

EXPERIMENTAL

Eight water samples were selected for the test analysis. These included both natural stream and runoff waters from experimental plots which had received heavy dressings of superphosphate (1 000 $kg \cdot ha^{-1}$). The sulphate concentrations (0.08 to 2.94 $me \cdot l^{-1}$ of SO_4) in these samples exceeded the range of sulphates normally present in forest streams, so the results are applicable to all waters sampled in the project. All waters were filtered through a 0.45 μm membrane filter to remove any suspended material prior to analysis.

The following analytical methods were used.

1. The precipitations were carried out according to the author's first method; but as no nitrous oxide-acetylene burner was available, an air-acetylene flame had to be used to estimate the excess barium.

2a. All analyses were carried out exactly as per the original method.

2b. 2-aminoperimidine was prepared from 1, 8 diaminonaphthalene and cyanogen bromide by McLure's (1973) method and used for the analyses. This reagent required an additional recrystallisation from ethanol after treatment with activated charcoal to remove coloured impurities. Appropriate aliquots (0.2 to 1.0 ml) of the water samples were pipetted into clean, dry 5 ml centrifuge tubes, diluted to 2 ml with distilled water, and the analyses were carried out by the author's procedure, using the variation outlined for the range 20-120 ppm sulphate.

2c. Similar aliquots of the water samples were pipetted into centrifuge tubes, diluted to 2 ml with water and the analysis carried out according to the

author's procedure, except that a final volume of 25 ml was adopted for all samples and standards.

3. For the three turbidimetric techniques, 5 ml aliquots of the water samples were tested according to the author's original methods.

4. Aliquots of 20 ml were used for the volumetric estimation of sulphates by EDTA titration.

All samples were analysed by two analysts on different days, and, in addition, aliquots of the water samples were spiked with 20 μg of sulphur (as K_2SO_4) and re-analysed, so that quantitative recovery tests could be carried out.

RESULTS

Techniques

The atomic absorption technique was not safisfactory because of the low sensitivity to barium exhibited by the air-acetylene flame. Consequently, small changes in barium concentration caused by the precipitation of barium sulphate could not be readily detected. The problem would have been reduced by the use of the nitrous oxide-acetylene flame; as this was not available, the technique had to be abandoned.

The methylene blue reduction technique proved very satisfactory and precise, and the only precaution necessary was that of using a reducing solution less than one week old. With older solutions, recovery of sulphate and agreement between duplicates were not satisfactory.

Both techniques involving the use of 2-aminoperimidine to precipitate sulphate proved very difficult to use as a rapid, routine laboratory method. With the former method (2b), precipitation occurred readily, but difficulties were experienced in withdrawing the 1 ml aliquots required for the subsequent estimation of the 2-aminoperimidine, despite the fact that the suspension was centrifuged for 15 minutes at 3000 r.p.m. In nearly every case, the supernatant liquid was probably contaminated

with the precipitate, because the absorbance at 305 nm was very variable with different runs on the same sample. In addition, the blank value was found to fluctuate widely, and absorbances of from 0.4 to 0.9 were recorded. Consequently, the standard graph varied widely for different sets of analyses.

With Archer's method (2c), very good standard graphs were obtained, but with the unknown water samples, widely differing duplicate values were obtained with different sets of analyses. In addition, recovery of added sulphate was very poor (of the order of 60%). Again, this could have been due to contamination of the supernatant liquid with some of the 2-aminoperimidine sulphate.

Because of the difficulty in obtaining satisfactory duplicates, it was considered that these two techniques were not suitable for the routine laboratory analysis of the small amounts of sulphate present in the water, so these methods were abandoned despite the evidence put forward by the original authors.

The three turbidimetric methods were both simple and rapid, and presented no problems in the analysis of the waters.

Bond's volumetric EDTA titration was also a relatively simple technique, but with very low sulphate water (<0.2 me$\cdot$l^{-1} of SO_4) difficulty was experienced in detecting the exact end-point of the titration with Eriochrome Black T indicator.

Analytical Results

The duplicate results for the five techniques that were finally used and the eight samples are shown in Table 1. Generally, the agreement between analyst's duplicates was quite good, and the colorimetric and turbidimetric methods gave similar results for all samples. However, the volumetric EDTA data showed considerable deviations from the other techniques, with samples 2, 4 and 6 showing higher values and sample 3 a lower sulphate concentration. This is despite the fact that 0.2 g of potassium cyanide were added to all samples prior to titration to eliminate any interference with the EDTA titration.

TABLE 1

Comparison of analytical techniques

| Technique | Analyst | | Sulphate me·l⁻¹ | | | | | | | |
			1	2	3	4	5	6	7	8
Colorimetric	Johnson & Nishita	A	0.31	0.17	0.65	0.50	2.21	0.09	2.04	2.91
		B	0.32	0.17	0.64	0.53	2.23	0.06	2.05	2.96
Turbidimetric	Massoumi & Cornfield	A	0.23	0.23	0.61	0.51	1.94	0.05	1.90	2.62
		B	0.37	0.24	0.65	0.72	2.01	0.09	1.85	2.80
Turbidimetric	Loveday	A	0.26	0.23	0.62	0.59	2.31	0.15	2.21	2.68
		B	0.25	0.22	0.67	0.63	2.30	0.14	1.96	2.63
Turbidimetric	Tabatabai	A	0.30	0.27	0.64	0.49	2.17	0.10	2.14	2.70
		B	0.24	0.21	0.62	0.60	2.25	0.18	2.21	2.92
Volumetric	Bond	A	0.38	0.45	0.05	1.09	2.17	0.28	2.27	2.75
		B	0.30	0.40	0.10	0.88	2.07	0.33	2.10	2.37

TABLE 2

Analysis of variance

S		df	SS	MS	VR	
Techniques	(T)	4	0.0635	0.01588	3.16	*
Analysts	(A)	1	0	0	0	NS
Samples	(S)	7	75.4413	10.7773	2143.04	***
T x A		4	0.0905	0.02262	4.50	*
T x S		28	1.3066	0.04666	9.28	***
A x S		7	0.0229	0.003271	0.65	NS
T x A x S		28	0.1408	0.005029		
Total		79	77.0656			

TABLE 3

Percentage recovery of 20 μg sulphur (as K_2SO_4)

Technique		Mean μg	Recovery %	Variance	SD	SE	Confidence 95%	Limits 99%
Colorimetric	Johnson and Nishita	20.2	101.0	7.05	2.66	0.94	98.9-103.2	97.7-104.3
Turbidimetric	Massoumi and Cornfield	22.9	114.6	207.87	14.42	5.10	102.5-126.7	96.8-132.4
Turbidimetric	Loveday	19.4	97.2	128.14	11.32	4.00	87.7-106.7	83.2-111.2
Turbidimetric	Tabatabai	21.7	108.5	226.61	15.05	5.32	95.9-121.1	89.9-127.1

The statistical analysis of these data is shown in Table 2; it indicates a highly significant interaction (P = 0.001) between the techniques and the samples. There was also a significant interaction (P = 0.05) between the analysts and the techniques. The main effects showed significant differences between techniques (P = 0.05) and samples (P = 0.001).

Recovery Tests

It was not possible to carry out a recovery test on 20 μg of sulphate sulphur with the EDTA titration as this was only equivalent to 0.12 ml of 0.01N EDTA, and variations in duplicate titrations can differ by 0.1 ml. Previous tests had shown that it was almost impossible to titrate accurately less than 250 μg of sulphate (Hatch, unpublished data).

The recovery tests for the remaining four techniques are shown in Table 3, and it is clearly evident that only two methods (Johnson and Nishita, Loveday) were satisfactory, with recoveries in the range 100 ± 5 per cent. The other two turbidimetric techniques (Massoumi and Cornfield, Tabatabai) gave unacceptably high recoveries of 114.6 and 108.5 per cent respectively.

DISCUSSION AND CONCLUSIONS

The analytical work presented in this report indicates that the methylene blue colorimetric technique is the most accurate method for the microestimation of sulphate in water samples, and this method is recommended for all precise work.

However, the turbidimetric method suggested by Loveday is quite satisfactory for the rapid routine laboratory analysis of the sulphate normally present in uncontaminated water samples. Of course, difficulties would arise with this technique when dealing with waters coloured by organic matter, and in these cases a preliminary treatment with nitric and perchloric acids would be necessary prior to the analysis.

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