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SPECTROPHOTOMETRIC DETERMINATION OF SULPHATE
BY THE BARIUM PERCHLORATE - THORIN METHOD

Determination of sulphur dioxide in air and sulphate
in precipitation

1 PRINCIPLE

Sulphur dioxide in polluted air is absorbed by bubbling through an acidified solution of hydrogen peroxide, whereby the sulphur dioxide is oxidized to sulphate.

A known amount of barium perchlorate, $Ba(ClO_4)_2$, is then added to precipitate the sulphate as barium sulphate.

The excess concentration of barium(II) ions in the solution is determined spectrophotometrically through the reaction with Thorin (the sodium salt of 4-(ortho-arsenophenyl-azo)-3-hydroxy-2,7-naphthalenedisulphonic acid), at 520 nm.

The concentration of sulphate ions in rain water and melted snow can be determined in the same way as sulphate in the absorption solutions, but cations must be removed by ion exchange prior to the determination.

2 INSTRUMENTS AND EQUIPMENT

- Spectrophotometer for measuring absorbance at 520 nm
- 2 cm optical glass spectrophotometer cells
- 250 μ l micropipet
- Bulb pipettes: 1,2,3,4,5,6,7,8,9 and 10 ml
- 50 ml buret
- Ion exchange columns. 15 cm, diameter 1 cm.

- 30 ml test tubes
- volumetric flasks: 50, 100 and 1000 ml.

All glass should be borosilicate (Pyrex) and should be thoroughly rinsed in distilled water before use.

3. CHEMICALS

Sulphuric acid

30 % hydrogen peroxide, H_2O_2

Perchloric acid, $HClO_4$

Barium perchlorate, anhydrous. $Ba(ClO_4)_2$

Dioxane

Thorin (Disodium salt)

Cation exchange resin, strongly acidic (Dowex 50 W x 8, 50-100 mesh.)

All the reagents should be analytical reagent (a.r.) or pro analysis (p.a.) purity.

4. SOLUTIONS

1. 0,1 M perchloric acid, $HClO_4$

0,01 M "

2. Absorption solution for sulphur dioxide.

10 ml 30% hydrogen peroxide solution is diluted to 1000 ml with water. The pH of the solution is adjusted to 4.0-4.5 with 0,01 N perchloric acid. Store in a refrigerator and make up fresh every month.

3. Barium perchlorate stock solution.

210.0 mg anhydrous barium perchlorate, $Ba(ClO_4)_2$ is dissolved in 0,1 M $HClO_4$ to a volume of 100 ml in a volumetric flask.

4. Barium perchlorate reagent solution.

10,0 ml of solution (3) is diluted to 1000 ml with dioxane.

5. Thorin reagent solution.

125 mg of the disodium salt is dissolved in 5 ml 0,01 M $HClO_4$ and diluted to 50 ml in a volumetric flask.

6. Sulphate standard solutions.

- a. Stock solution. 31,25 ml 0,05 M (0,1 N) H_2SO_4 (made from Merck Titrisol solutions) is diluted to 1000 ml in a volumetric flask. The concentration is equal to 100 $\mu\text{g/ml } SO_4^{--}$.
- b. Standard solutions for the spectrophotometric determination containing 0,1,2... 10 $\mu\text{g/ml } SO_2$ (0-15 $\mu\text{g/ml } SO_4^{--}$) is made up by taking 0,1,2,3,... 10 ml of solution (a) and diluting to 100 ml with water or 3 % hydrogen peroxide solution.

Store in polyethylene bottles.

5 PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION

Pipet 4 ml of the solution to be analysed for sulphate. Add 10 ml barium perchlorate reagent solution and 250 μl Thorin solution. Use a test tube and a micropipette for the Thorin solution.

Blank:

4 ml absorption solution (or deionized water for precipitation samples).

10 ml barium perchlorate reagent solution.

250 μl Thorin solution.

Mix thoroughly (do not use rubber stoppers !).

The spectrophotometer wavelength is set at 520 nm.

0 % transmission is adjusted as usual and gain and/or slit width is adjusted to give an absorbance reading of 0.80 absorbance units with the blank (0 $\mu\text{g/ml } SO_2$ or sulphate) in the sample compartment.

A calibration graph is constructed from the absorbance readings obtained from the standard solutions (6.b).

The SO_2 or sulphate content of unknown samples is determined from the absorbance readings using the calibration graph. Readings should be taken no more than 10 minutes after the addition of the Thorin solution. This is especially important for low concentrations of sulphate and for the blank because the barium-Thorin compound precipitates from the solution.

The calibration curve is not linear below 1 $\mu\text{g/ml}$, probably because of the solubility of the barium sulphate complex. This may be remedied by adding sulphate, corresponding to 1 $\mu\text{g SO}_2/\text{ml}$, to all samples and blanks. The detection limit (2σ) is then 0.1 to 0.2 $\mu\text{g SO}_2/\text{ml}$.

6 INTERFERENCES

Cations interfere by the spectrophotometric determination of barium with Thorin. When the method is used for sulphur dioxide in air, other sulphur compounds which may be oxidized to sulphate, e.g. hydrogen sulfide, interfere.

Detailed interference tests have been carried out. The results may be summarized briefly as follows:

1. Strong mineral acids (hydrogen chloride and nitrogen oxides) interfere if the pH of the solution is caused to fall below 3.
2. Phosphate interferes slightly. A 10^{-3}M solution gives a false corresponding to about $+0.3 \mu\text{g/ml SO}_4^{--}$.
3. Nearly all cations interfere. Common cations such as Ca^{++} , Mg^{++} and Pb^{2+} interfere strongly (equivalent to more than $-0.5 \mu\text{g/ml}$ of SO_4^{--}) when present in concentrations above $10^{-4} - 10^{-5} \text{M}$.
4. Mercury (II) does not interfere when present as the chlorides in concentrations less than 10^{-3}M .

7 STORAGE AND PRETREATMENT OF SAMPLES

The samples should be analysed as soon as possible after the sampling is finished. If the samples have to be stored, they should be kept in the dark and refrigerated.

No pretreatment is required for SO₂ absorption solution samples. Precipitation samples should be passed through an acidic cation exchange column before the spectrophotometric determination of sulphate.

NOTE: A small increase in the apparent SO₂ content of absorption solutions stored in polyethylene bottles has been noted. This effect could correspond to about 2,5 µg/ml SO₂ for samples stored up to 3 months. It was found that sunlight accelerated the process. Sulphuric acid solutions, with or without added hydrogen peroxide, were not affected.

8. AUTOMATION OF THE METHOD.

The spectrophotometric method may readily be automated, using the Technicon Autoanalyzer or another instrument based on similar principles. Persson¹ used mercury displacement bottles to overcome the difficulties with dioxane attacking the plastic tubings. This problem may be solved, however, by using ESCO silicone elastomer tubing. Isopropanol may also be used as the solvent medium. A description of instrument set-up and conditions for the use of isopropanol as solvent is given by Atkins². Below is given a description of the the setup, running conditions, and reagent solution strengths which have been used at the Norwegian Institute for Air Research³.

8.1 Equipment

Rotating sample carousel
8-channel peristaltic pump
Filter photometer with power supply
and recorder output.
Interference filter with peak trans
emission at 518-520 nm.

Recorder with zero suppression up to 100%.

Flow-through spectrophotometer cell 1.5 cm
pathlength.

Flexible tubing, glue, connections, pulse
suppressors and mixing coils.

8.2 Assembly

A schematic flow diagram is given in Figure A1. Table 1 lists the dimensions and types of flexible tubing which have been used to obtain suitable flow rates of sample and reagent solutions with a CENCO proportioning pump. When using dioxane as solvent it is advisable to place the equipment under a hood or in a fume cupboard to avoid the vapour which diffuses through tubing walls. Also it is preferable to use glass tubing with only short silicone rubber connections to carry the solutions containing dioxane.

The ion exchange column is a ca 100 mm length of polythene tubing, 2-3 mm in diameter. The tube is filled with ion exchange beads which are kept in position by loose plugs of quartz wool. Use of the ion exchange column slows down the responsetime and increase the memory effect in the system. It is therefore advisable to increase the size of the liquid sample from 2 to 4 ml's.

8.3 Reagents and solutions

The strength of the solutions below are adjusted for the sample and reagent flow conditions given in the diagram (Figure 1). A modification has been made in that the dioxane concentration in the final solution is now 68.5%, as compared with 70% for the manual method. This has been done to avoid precipitation of the slightly soluble barium-Thorin complex in the system.

Indicator solution

100 mg of the disodium thorin salt in 500 ml distilled water.

Reagent solution

670 mg anhydrous barium perchlorate dissolved in 1000 ml distilled water. Add 100 ml 1N HClO₄ in 1000 ml distilled water and dilute with distilled water to a final volume of 10 litre. (This solution will be 0.01 N with respect to HClO₄.)

Take 250 ml of this solution and dilute to 2500 ml with dioxane.

Standard solutions

Prepare standards containing 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 8.0 µg SO₂/ml as for the manual method.

8.4 Operation

Run the equipment on blanks and standards for approximately half an hour to stabilize the system. Adjust the scale expansion and zero suppression to give a low (10%) reading for the blank and near full (90%) reading for the highest standard (8 µg SO₂/ml).

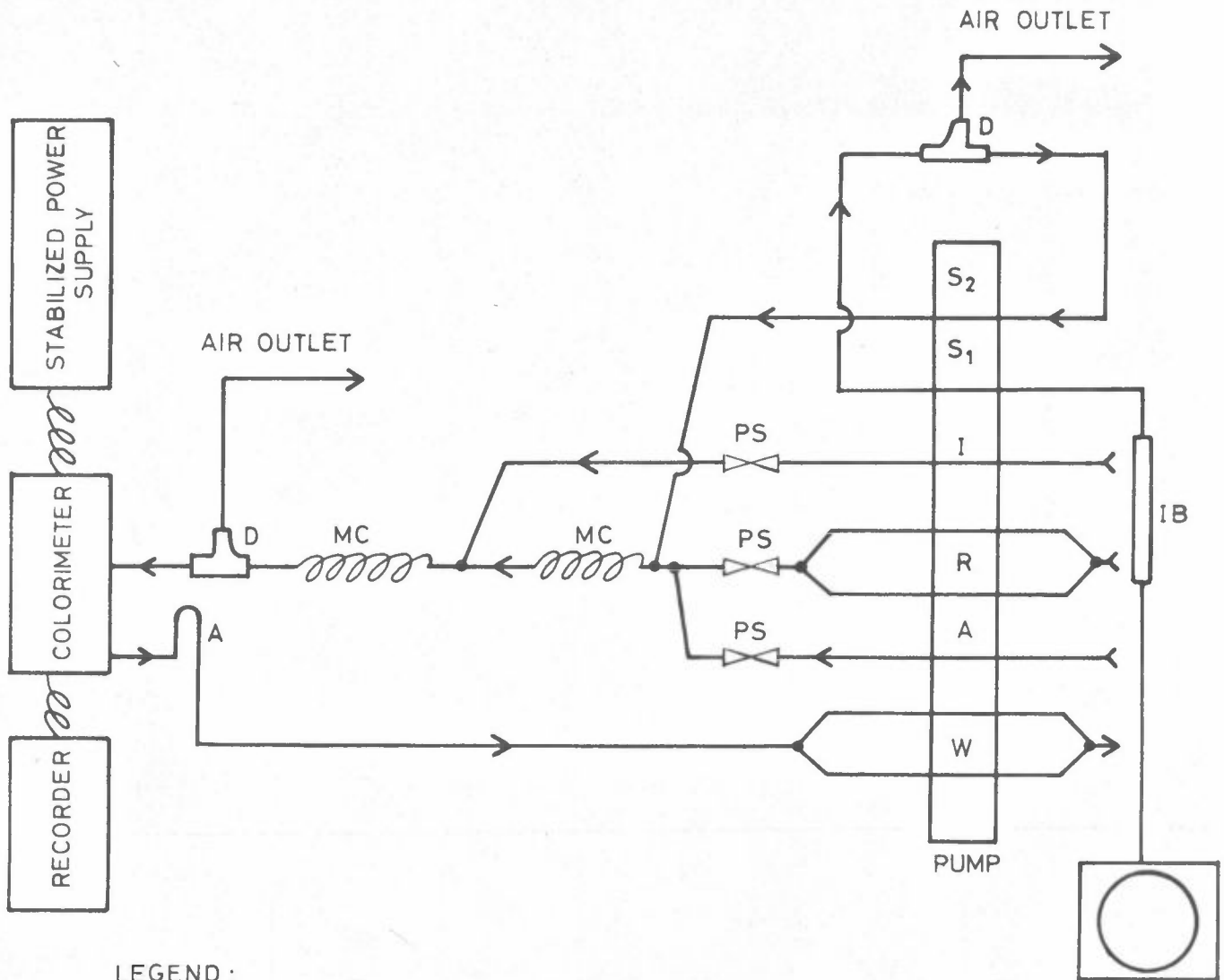
Run a full set of standards (0, 0.2, 0.5, 1.0, 2.0, 5.0, 8.0), and repeat once to see if the readings are reproducible.

Blanks and two or three standards should be run regularly every 20 samples to compensate for baseline drift and changes in the response curve.

If the majority of the samples fall in the concentration range below 1.0 $\mu\text{g}/\text{ml}$, it may be advantageous to add a known amount of sulphate to each sample, corresponding to 1.0 $\mu\text{g}/\text{ml}$ of SO_2 . This will give better sensitivity for low concentrations (Cf. p. 4).

9. REFERENCES.

- ¹⁾ G A Persson(1966), Air and Water Pollut. Int. J., 10, 845.
- ²⁾ A E J Eggleton, D H Atkins, "Results of the Tees-side Investigation." AERE - R 6983. Atomic Energy Research Establishment, Harwell, Berks., 1972.
(Appendix: Analytical Methods, p 149).
- ³⁾ O Anda, "Automatisk kvantitativ bestemmelse av SO_2 i luft (Thorinmetoden)." NILU Teknisk notat nr 5/71, Norwegian Institute for Air Research, Kjeller, April 1971.



LEGEND :

- S₁ - SAMPLE INLET
- S₂ - SAMPLE AFTER DEBUBBLER
- I - INDICATOR SOLUTION (THORIN)
- R - REAGENT SOLUTION (Ba(ClO₄)₂)
- A - AIR INLET (SEGMENTING)
- W - WASTE (USED SOLUTIONS)
- IB - ION EXCHANGE COLUMN
 { 3 mm id }
 { 88 mm l }
- D - "DEBUBBLER"
- PS - "PULSE SUPPRESSOR"
- MC - "MIXING COIL"

Diagram code	Pump capacity, cm ³ /min		Dimension or type	Supplied by
	Nominal	Measured		
S ₁	0.79	-	white/white	Cenco
S ₂	0.465	0.56	black/black	Cenco
I	0.465	0.56	black/black	Cenco
R(2)	"2.05"	1.8	ESCO, 116-0189(0.081")	Technicon
A	1.41-1.9	-	Green/yellow or blue/black	Cenco
W	"2.05"	1.8	ESCO, 116-0189(0.081")	Technicon

Table 1: Types and dimensions of flexible tubing which give suitable proportions of sample and reagent flow rates with a CENCO (The Breda, Netherlands) proportioning pump.)