

## 9. A MICROVOLUMETRIC DETERMINATION OF SULFATE IN PORE WATERS

B. S. Cescon and G. R. Macchi,<sup>1</sup> Osservatorio Geofisico Sperimentale, Trieste, Italy

### INTRODUCTION

The usual micromethod for determination of sulphate in pore waters uses a 0.5- to 1-gram sample and consists of the precipitation, collection, and weighing of the sulphate as BaSO<sub>4</sub>. The method is not especially suited to routine work since small samples are difficult to handle. The conditions for precipitation are unfavourable, and the operations are both tedious and time consuming. A more convenient procedure would be desirable. With this objective in mind, we have adapted the new method for the volumetric determination of sulphate in seawater, developed by Macchi et al. (1969), so that it can be used with suitable precision and accuracy for microanalysis of pore waters.

### REAGENTS

**Thorin solution:** 0.2 grams of thorin was dissolved in 100 ml of double distilled water.

**Barium chloride titrating solution:** Approximately 0.0052 moles of BaCl<sub>2</sub> · 2H<sub>2</sub>O was dissolved in one liter of 60 percent ethyl alcohol. The pH was adjusted to about 3.5 by adding one drop of concentrated HCl. This solution was standardized by titrating with standard sulphate solution under the same conditions as used during the analysis of samples.

**Standard sulphate solution 0.005 M:** One Normex ampoule of H<sub>2</sub>SO<sub>4</sub> (CARLO ERBA S. p. A.) is exactly diluted with 0.05 N HCl.

**Columns:** The elution columns were 40 cm long with an inside diameter of 0.5 cm. They were filled to 18 cm with cation exchange resin, BDH S. p. A. Amberlite IR-120 (H) "analytical grade" (50-100 mesh). The resin was regenerated by allowing 50 ml of 4 N HCl to flow downwards through the column then successively washing with double distilled water until the elute was neutral. The resin was kept wet until used and each column could be employed for several analyses.

**Diethylamine:** 99 percent (CARLO ERBA, analytical grade reagent).

**Hydrobromic acid:** 20 percent (CARLO ERBA, analytical grade reagent).

### INTERFERENCES

In order to avoid cationic interferences, cation exchange resins are employed. Atomic absorption analyses demonstrate that Ca, Mg, Na, and K are not detectable in the eluate. Among anions, chlorides represent the main source

of interference, but, as it has already been shown in a previous work (Macchi et al., 1969), this interference can be minimized by standardizing the titrating solution in the presence of a suitable concentration of chloride.

### PROCEDURE

A 2-ml pore-water sample was diluted to exactly 22 ml with double-distilled water. After mixing well, the dilute solution was passed through the cation exchange column at a rate of one drop every second. The first 8-ml portion was discarded and about 12 ml collected in a dry beaker. A 10-ml portion of this eluate was mixed with 40 ml of ethyl alcohol, 0.20 ml of thorin solution, and sufficient 99 percent diethylamine to bring the pH to neutrality (the indicator color changes from yellow to orange yellow). Afterwards, the pH was adjusted to the correct range (2.5-4) by the cautious addition of 20 percent hydrobromic acid, using the gradual change in the color of the indicator as a guide. Finally, the sample was titrated with 0.0052 M BaCl<sub>2</sub> at a rate of one drop every 2 seconds while continuously stirring. Near the equivalence point, the rate of addition is changed to about one drop every 15 seconds.

### RESULTS

In order to evaluate the precision of this method, six replicate analyses were performed on the same seawater sample. The coefficient of variation of these measurements is ±0.25 percent. Ten pore water samples collected on the Deep Sea Drilling Project Leg 15 have been analyzed using this method. Table 1 tabulates the results of an intercomparison between our microvolumetric analyses and the conventional microgravimetric determinations made at Woods Hole Oceanographic Institution. The mean deviation of the two sets of analyses is 2.13 percent. There does not appear to be a systematic difference. Sample 4 (DSDP Sample 15-147-1-5) was actually a tube filled with standard seawater having a salinity of 35‰. The 2.706 g/kg SO<sub>4</sub> determined with our microtitration method is in excellent agreement with the accepted value of 2.71 g/kg for standard seawater.

### ACKNOWLEDGMENT

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### REFERENCE

Macchi, G., Cescon, B., and Mameli d'Errico, D., 1969. A volumetric determination of sulphate in seawater. *Archo. Oceanog. Limnol.* 16, 163.

<sup>1</sup>Present Address: Programma Speciale per l'Oceanografia, C.N.R. - ROMA.

TABLE I  
Microanalyses Results

Sample	DSDP Designation	Squeezing Temperature (°C)	SO <sub>4</sub> (g/l)	Accepted Density	SO <sub>4</sub> <sup>a</sup> (g/kg)	SO <sub>4</sub> <sup>b</sup> (g/kg)
1	149-41-5	4	2.170	1.0203	2.127	2.014
2	148-2-3	4	2.229	1.0208	2.184	2.217
3	149-31-1	22	2.244	1.021	2.198	2.225
4	147-1-5	22	2.776	1.026	2.706	2.751
5	149-29-3	4	2.203	1.0206	2.159	2.091
6	149-42-2	4	2.186	1.0204	2.142	2.143
7	148-23-4	22	0.459	1.0043	0.458	— <sup>a</sup>
8	147B-1-3	22	0.494	1.0046	0.492	0.516
9	148-2-3	22	2.235	1.0209	2.190	2.222
10	147B-1-3	4	0.538	1.00504	0.536	0.539

<sup>a</sup>Cescon and Macchi.

<sup>b</sup>Woods Hole Oceanographic Institute.

<sup>c</sup>Not analyzed.