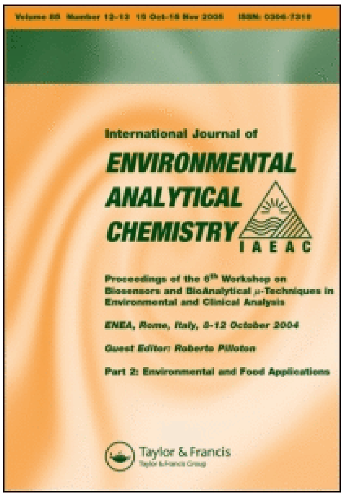

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Ripl, W. and Michel, J.(1988) 'Sulphur and Nutrient Analysis in Sediments and Sediment Interstitial Water', International Journal of Environmental Analytical Chemistry, 34: 2, 109 — 117

To link to this Article: DOI: 10.1080/03067318808027409

URL: http://dx.doi.org/10.1080/03067318808027409

Intern. J. Environ. Anal. Chem., Vol. 34, pp. 109–117
Reprints available directly from the publisher

Printed in Great Britain

Sulphur and Nutrient Analysis in Sediments and Sediment Interstitial Water

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(*Received 22 October 1987; in final form 28 February 1988*)

A suite of analytical methods for pretreatment and digestion of lake sediment samples, interstitial water sampling and Flow Injection Analysis (FIA) of nutrients in lake sediments and interstitial water is described. The methods are well suited to the requirements of laboratories with high workload where routine analysis of lake sediments and interstitial waters are necessary.

KEY WORDS: Sediment, interstitial water, pressure digestion, dialysis, Flow Injection Analysis.

INTRODUCTION

The bacterial reduction of sulphate and the disintegration of sulphurous, organic substances into elementary sulphur and hydrogen sulphide in the sediment is of special interest for the critical assessment of metabolic processes in waters. Like the comparable dentrification, the sulphate reduction is biggest in the upper sediment stratum and proceeds from there upwards into the free water zone. Hereby the solubility and the availability of iron and phosphorus—and thus the living conditions of all aquatic organisms—are fundamentally influenced. Total sulphur determination aims at transferring organic as well as inorganic sulphur components in the sediments into sulphate by help of a qualified digestion procedure. The sulphate is then to be determined analytically be means of Flow Injection Analysis. For this purpose a specific method has been developed, which permits quick and uncomplicated sulphur determination in connection with the analysis of phosphorus and nitrogen compounds.

In our laboratory the introduction of Flow Injection Analysis (FIA)[1] together with the development of special equipment for the sampling of interstitial solutions and for the rapid digestion of sediment samples improved the state of the art. FIA allows quick processing of large numbers of samples (40–150/h) at minimal sample volumes (50–500 μl) by extremely low consumption of chemicals (0.3–1.2 ml/min.).

The total analytical procedure consists of:

1) Pressure digestion in series for sediments.
2) Total sulphur determination in the sediment.
3) *In situ* sampling of interstitial water by means of dialysis technique.
4) Phosphate determination in interstitial water.
5) Nitrate determination in interstitial water.
6) Sulphate determination in interstitial water.

1. PRESSURE DIGESTION OF SEDIMENTS

For the determination of the proportion of metals (alkaline and heavy metals) as well as of the total of phosphorus and sulphur within a sediment sample an oxidative pressure digestion with nitric acid based on the Carius digestion is used. The method was recently proposed by Svensk Standard SS 028150[2] and modified in our laboratory. The determination of phosphorus and sulphur is made by FIA. Fe, Mn and Zn as well as Na, K, Ca and Mg are determined with flame–AAS whereas the analysis of heavy metals like Cu, Cr, Cd and Pb is conducted by means of graphite furnace (type Perkin Elmer 2380 and HGA 400).

1.1. Preparation of samples

In order to preserve the sample matrix the sediment samples are dried in a vacuum-freezedrier (Type Beta; Fa. Christ). Sediment samples are filled into small plastic bowls with perforated lids and frozen in a deep freezer for 2 hours. The frozen samples are then freezedried for 2 days. Subsequently the dry samples are brought to room temperature in the exsiccator. Then samples are pulverized for approx. 2 minutes in a ballgrinder (Type Pulverisette; Fa. Fritsch). The obtained stock is the original material for sediment digestion.

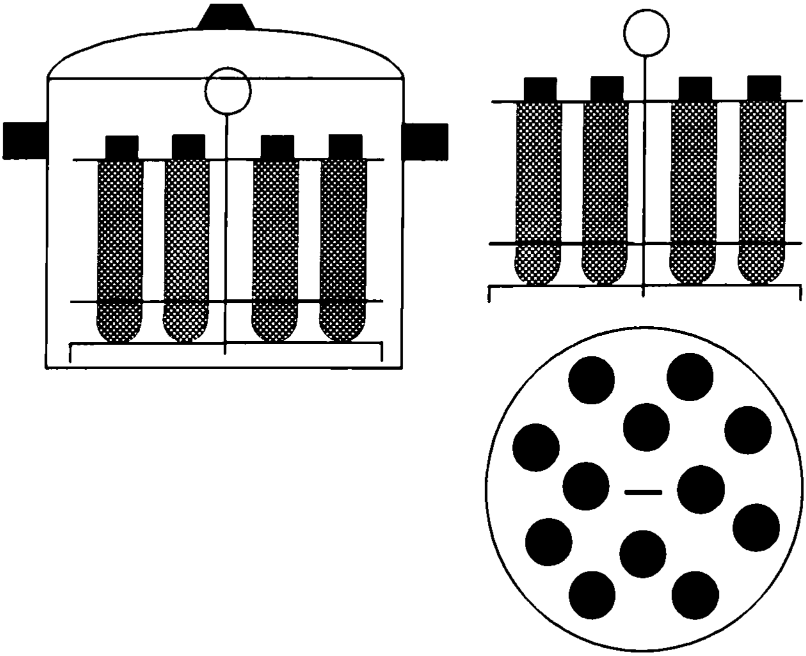

Figure 1 Cross section of a circular alumina container with borosilicate-glass vials with teflon screw caps.

1.2. Oxidative sediment digestion

Exactly 0.25 g of the pulverized sediment are weighed into borosilicate-glass vials (special making; length 12.5 cm, d = 1.5 cm) with screw caps made of teflon. Five millilitres 7 N HNO_3 are added to the samples and the lids are screwed on. After one hour waiting time samples are sorted into circular alumina containers (d = 23 cm) with a capacity of 43 samples (Figure 1). These containers are then inserted into a steam pressure cooker (Type Certoklav; Fa. Gruber & Kaja) filled with approx. 1.5 l aqua dest. Up to 86 samples can be digested in a single working process. In order to protect the cooker against aggressive vapours the sample inserts are first wrapped into transparent roasting foil (Kalle). Before using the cooker was treated with teflon spray. Digestion occurs at 2 bar overpressure, 140 °C in 45 minutes. After they have cooled off very slowly the glass vials are then shaken vigorously. After complete sedimentation the aggressive digestion solution is first prediluted at the rate of (in the ratio of) 1:10 with bidistilled water. For neutralizing 0.1 N $NaHCO_3$ is added to the samples at the rate of 1:2 and degassed in vacuum for the removal of minute gas bubbles.

2. TOTAL SULPHUR DETERMINATION IN THE SEDIMENT

2.1. Method

Until the working up of samples digestion proceeds analogous to the described metal resp. phosphorus procedure. In order to remove disturbing cations and to preserve the exchange column in the FIA-unit 0.2 ml ionic exchange resin is added per 20 ml of the resulting digestion solution and there must be a waiting time of approx. 5 minutes (Dowex ionic exchange resin Type 50 WX8, 20–50 mesh, Na charged). As a rule further dilution at the rate of 1:2 is necessary for the analysis in these cases. This dilution is advantageously made with a dilution automat (Type Microlab 1000, by Hamilton). For sample tubes 1.5 ml conic ampullae are used, which are suitable for the sampler of the Tecator 5020 analyzer.

Na_2SO_4 and cystine in the concentration range of 25 to 100 mg S/l were used as reference substances. The digestion described proceeds quantitatively. For each concentration fivefold determinations were carried through and the precision was up to ±4% relative standard deviation.

2.2 Determination of sulphate with Flow Injection Analysis

In connection to digestion the resulting sulphate is determined with the 5020 Flow Injection Analyzer by Tecator. For this purpose a specific method for limnological purposes was tested and adjusted at our institute.[3] The procedure bases on the photometric detection of a complex from barium and methylthymole-blue (Ba-MTB).[4] This modified method was then published by Tecator as application note ASTN 15/84.[5]

Principle Methylthymole-blue (MTB, Na-salt) forms with barium ions in alkaline, ethanolic solutions a blue coloured complex with absorbance maximum at 620 nm. When sulphate ions are added, the barium ions will separate from the complex and form barium sulphate which results in an absorbance decrease. To eliminate on line the interference of many cations with the determination of sulphate, a cation exchange resin in the H^+-form is placed between the injector and the manifold (Figure 2). Suitable ion exchangers are Dowex or Merck 50×8 placed in a PVC tubing i.d. 2 mm, length 5 cm.

Reagents (1)116 mg MTB, 6 ml 1 N HCl in 80 ml H_2O and 14 ml $BaCl_2$-solution (1.526 g/l $BaCl_2$) filled up to 1 l with 95% ethanol; (2) 0.036 N NaOH in ethanol (44%).

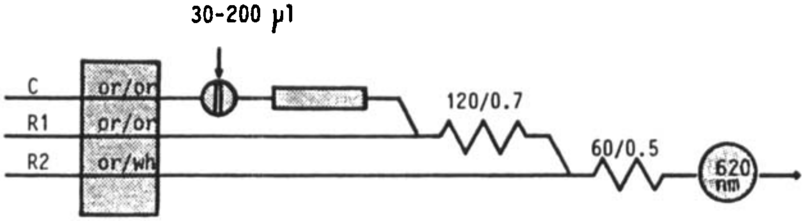

Figure 2 Manifold for the determination of sulphate by FIA. C: dest. H_2O, 1.40 ml/s; R_1: MTB/$BaCl_2$, 1.40 ml/s; R_2: NaOH, 0.75 ml/s.

Solvent resistant pump tubes and chemifold® should be used. Working range lies between 10–40 mg SO_4/l. Recovery attempts with repeated injection of calibration standards (10 fold) result in a precision of procedure of ± 1–2.5% relative standard deviation.

3. *IN SITU* SAMPLING OF INTERSTITIAL WATERS BY MEANS OF DIALYSIS TECHNIQUE

Conventional methods for the preparation of interstitial water samples are essentially based upon the filtration or centrifugation of relatively big sediment samples with nitrogen overpressure.[6,7,8] In contrast to these procedures we use a simple device made of borosilicate glass, the dialysis stick by Ripl.[9] (Figure 3.)

It is made up of a 525 mm long stick measuring 19 mm in diameter. The stick (special making by A. Lundberg and S. Klein, University of Lund) is divided into 13 chambers of variable size for the recording of different gradients of concentration. The special geometry of the stick is the basis for its high efficiency with regard to dialysis rates and stability. After the filling of the chambers the flattened front side of the stick is tightly closed by means of a dialysis membrane made of pure cellulosa. Experiments concerning incubation time showed that a period of 48 hours is sufficient to allow a yield range of >85% for the ions SO_4, PO_4 and NH_4-N at concentrations up to 100 mg/l and at temperatures above 4 °C. This relates to the applied geometry of the apparatus in use and for

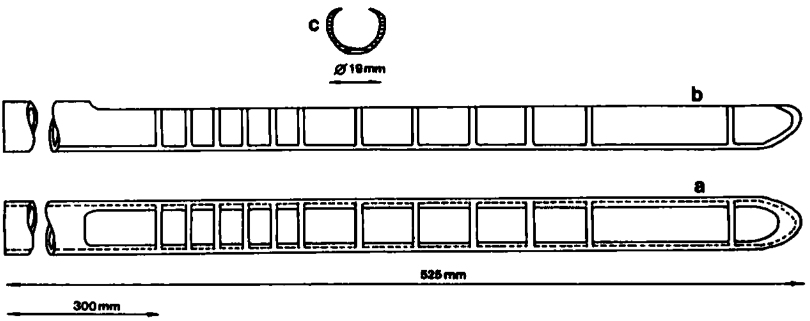

Figure 3 Segmented stick used for sampling interstitial water by dialysis (Ripl, 1978)[9]. (a) Front; (b) Side; (c) Cross section.

the organogenic sediments from lakes. Larger incubation times can lead to interactions between the dialysis membrane and the biologically active sediment surface.

Method

For the preparation of dialysis sticks they are placed in a glass basin filled with distilled water at an approximate temperature of 40 °C. The flexible dialysis tubing (Type Visking 20/32, by Serva) is soaked and slipped over the stick carefully. Air bubbles in the chamber must be avoided. Sticks are only taken out of the water basin shortly before sampling in order to prevent drying or bursting out of the membrane. The sticks are exposed 48 hours *in situ* and rinsed with distilled water after removal from the sediment. For the working up of the samples a slight fissure is made into the membrane with the tip of a piston pipette and interstitial water is sampled from every chamber. Samples are then diluted in snaplock glasses with 0.1 N HCl at a rate of 1:5. This results in a sample matrix of approx. 0.08 N HCl.

The interstitial water samples obtained were then analyzed by means of Flow Injection Analysis in regard to parameters like molybdate reactive phosphorus (MRP), nitrate as well as sulphate. Further pretreatment of samples or conservation was not required. In order to utilize optimal working ranges of analytic determination methods, the samples are diluted with the dilution automat directly into the sample ampoules of the FIA-sampler.

4. PHOSPHATE DETERMINATION (MRP) IN INTERSTITIAL WATER

A modified molybdene-blue-method is used for the photometric determination of the phosphate. Basis of the procedure is a double step reaction; the formation of a heteropolyacid from orthophosphate and ammoniumheptamolybdate in sulphur acid solution and its reduction to molybdene blue. A sulphur acid $SnCl_2$-solution is used by means of reduction. The reaction product is measured at 690 nm. Determination occurs in compliance with Tecator application note AN 60/83 and ASN 60-01/83.[10,11] The working range covers 15–500 μg/l PO_4-P. To minimize matrix effects calibration standards are prepared in 0.08 N HCl and two carrier streams (aqua dist.) are used. For the control and correction of a possible drift in the system calibration standards are routinewise included in the analysis of every 10th sample. Recovery attempts with repeated injections of calibration standards (10 fold) result in precision of procedure of ±2% relative standard deviation.

5. NITRATE DETERMINATION IN INTERSTITIAL WATER

The method is exemplary for the flexibility of the chemical manifold (reaction distance between points of injection and detection) in a FIA-system. The determination of nitrate follows analytically from the determination of nitrite. The installation of a CD-reductor into the FIOA-system results in on-line reduction to nitrite. Nitrite is turned with sulfanilamide into a diazo-compound and subsequently reacts with N-(1-Naphthyl)-ethylendiamindihydrochlorid (NED) is a coupling component to a red diazodye. The reaction product is measured photometrically at 540 nm. Determination is made analogous to Tecator application note AN 62/83 and ASN 62-01/83.[12,13] The matrix of calibration standards and samples is 0.08 N HCl. In order to preserve the reductor column 0.1 M $NaCO_3$ is added to samples and standards at a rate of 4:1. Working range lies between 50–1000 μg/l NO_3-N. Recovery attempts with repeated injections of calibration standards result in a precision of procedure of ±0.5–1.5% relative standard deviation.

6. SULPHATE DETERMINATION IN INTERSTITIAL WATER

Determination of sulphate is made in compliance with application note ASTN 15/84, see also Section 2.2.[5] The matrix of calibration standards and samples is 0.08 N HCl.

GENERAL RESULTS

We have used these procedures for routine analysis of thousands of samples for the major nutrient constituents in sediments and interstitial waters. A rough estimate of the analysis throughout shows that for our comparatively small university laboratory (3 full time collaborators) approx. 150 samples per day could be dealt completely (including preparation, dilutions, evaluation and documentation). Furthermore sample size, consumption of reagents and costs have been essentially reduced in relation to the conventional analysis.

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