Oceanologia, 18 (1984)
PL ISSN 0078-3234

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PROCEDURE FOR CHEMICAL ANALYSIS OF SUSPENSIONS IN THE EZCURRA INLET*

(Received Sept. 1, 1981; in final form Apr. 20, 1982)

Abstract

The paper presents the results of chemical analyses of the suspensions. The procedure of their combustion on membrane filters has been developed. Total concentrations of Si, Al, P, Ti were determined by a spectrophotometric method. The contents of Na, K, Mg, Ca, Fe, Mn were determined using flame absorption and emission atomic spectroscopy. Trace metals: Cu, Zn, Pb were analyzed by an anodic stripping voltammetry. It was shown, that the main sources of impurities were chemical reagents used.

1. INTRODUCTION

Plankton and such minerals as carbonates, aluminosilicates and silicates are the main constituents of marine suspensions. Their mutual proportions affect significantly the accuracy of assaying particular elements, mainly suspended forms of trace elements in sea water.

In this paper results of chemical analyses of suspended matter have been discussed. A method of digestion on membrane filters has been developed. It has also been shown that chemical reagents provide the main source of contamination.

Total concentrations of Si, Al, P and Ti were determined spectrophotometrically. The levels of Na, K, Mg, Ca, Fe and Mn were assayed by the methods of atomic-absorption and atomic-emission spectrometry in the flame. Trace metals, Cu, Zn and Pb were determined by the anodic inversion chronovoltammetry.

ANALYTICAL METHODS

Massive progress has been made in the methods of assaying chemical elements in the marine environment after introduction of modern instrumental techniques such as neutron activation, isotopic dilution, polarography, atomic-absorption spectrometry and x-ray fluorescence.

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* The work was supported by grant M.R.I.15 topic 2.6 – see also Oceanologia 15, 1983.

The most widespread use has found atomic-absorption spectrometry [2, 7, 8, 12, 13, 14, 18, 19] which owing to the simplicity of operation, high sensitivity, good precision and non-complicated preliminary sample preparation enables analyses to be run routinely. In trace metal analyses, neutron-activation methods have been successfully used [10, 16, 17]. They ensure low detection limits and enable direct determination of a number of elements in one sample. A variety of heavy metals can be assayed in the marine environment by utilizing the polarographic technique which consists in electrolytic concentration of trace metals on the dropping mercury electrode and recording of the anodic current [4, 5, 15]. Ions of metals capable of formation of amalgams such as copper, lead, zinc and cadmium, can be assayed by this techniques in quantities of the order of a fraction of a microgramme. Classical spectrophotometric methods utilizing coloured complexes, have gained widespread popularity in the chemical analysis [1, 6, 11], in spite of the fact of being more labour-consuming than the mentioned instrumental methods. The choice of a suitable analytical method or instrumental technique depends on the mass of material to be analyzed, concentrations to be assayed and instrumental facilities available.

2. PROCEDURES

2.1. SAMPLING AND SAMPLE DIGESTION

Sea water was sampled with a 12 dm^3 poly(vinyl chloride) bathometer, and the samples were immediately filtered under reduced pressure of 0.5 atm. Membrane filters (Sartorius, G.F.R.), made of cellulose acetate, with a nominal pore diameter of 0.45 μm and an outer diameter of 47 mm were used for filtration. The effective filtration area was 12.5 cm^2 ($d=40$ mm), and the mean mass was of the order of 73.3 ± 0.2 mg. After filtration the surface of the filter was repeatedly rinsed with distilled water and sucked to wash off sea water that might have been retained in the pores of the filter. The filters were then dried in the air, under a cover, and placed in a desiccator over silica gel, where they were preserved until return. In the laboratory the filters were placed on a filter paper protected from dust and weighed on an analytical balance after three days. The mass of the suspended matter on a filter ranged from 2 to 13 mg and did not exceed 5 mg for the majority of samples.

There is a lot of methods for the digestion of silicate and biological materials [3, 6, 11]. The choice of the method depends on the nature of sample, its weight and the nature of chemical elements to be assayed.

Bearing in mind the nature of the material to be analyzed, our procedure for the digestion of suspended matter was developed under the following assumptions:

(i) Elimination of the fusing step, thus enabling the assay of alkaline metals and ruling out extraneous matter (foreign salts).

(ii) Preliminary digestion of sample in a teflon autoclave with a mixture of hydrofluoric and hydrochloric acids. The digestion in a closed vessel enables silicon to be determined; this would be otherwise impossible due to the formation of the volatile SiF_4.

(iii) Expelling of hydrofluoric acid followed by destroying of organic matter by means of perchloric acid. This operation eliminates fluorides which would interfere with assaying aluminium and titanium, and sets free organic-matter-bound elements. The elimination of nitric acid in the wet digesion and the use of perhydrol offers the possibility of nitrogen determination.

Adhering to these assumptions, the suspended matter collected on membrane filters was wet digested by the following procedure.

The wet digestion was carried out with 0.5 cm^3 of 40% HF and 5 cm^3 of 6M HCl in a teflon autoclave (chamber dimensions: 35 mm in diam. × 80 mm), in which the filter with the suspended matter was placed. The autoclave was placed for 40 min in a drying oven at 110 - 120°C. After cooling the autoclave and centrifugation of its contents, 0.2 cm^3 of the supernatant was withdrawn for silicon assay. The remaining solution was evaporated to dryness on a hot plate, 1 cm^3 of 30% H_2O_2 and 0.5 cm^3 of 60% $HClO_4$ were added, and the mixture was heated until complete decomposition of H_2O_2. The closed teflon vessel was then kept at 180 - 190°C for 150 min. After cooling and centrifugation, $HClO_4$ was evaporated until white fumes ceased to evolve, and the digested residue was dissolved in 4 cm^3 of 0.1M HCl and, after closing the autoclave, it was kept at 80°C for 15 min. After cooling and centrifugation the solution was transferred to a previously etched with a 6M HNO_3/3M HCl mixture plastic bottle, and the autoclave was rinsed three times with 2 cm^3 of 0.1M HCl, and the washings were combined with main solution. In this way, 10 cm^3 of the wet digested suspension in 0.1M HCl was obtained. This solution served for the spectrophotometric assay of Al, Ti and P and for the atomic-absorption spectrometric assay of Na, K, Fe, Ca, Mg and Mn. Trace metals, Zn, Cu and Pb were determined polarographically.

2.2. SPECTROPHOTOMETRIC DETERMINATION

2.2.1. REAGENTS

All reagents were of analytical grade purity.

- Double distilled water. Distilled water was purified on a Dowex 50 × 8 cation exchanger (H form) and then distilled in a quartz still.
- 1.75% and 7% ascorbic acid solutions.
- 0.3% boric acid solution.
- 9.5% and 20% ammonium molybdate solutions.
- 3.25% antymonyl-potassium tartrate solution.
- 1.75% oxalic acid solution.
- Formate buffer solution, pH 3.5.
- Concentrated hydrochloric acid, concentrated sulphuric acid, 40% hydrofluoric acid.
- Quartz vool dried 2 h at 160°C.

– Reagent mixture for assaying silicon. To 100 cm^3 of the 20% ammonium molybdate solution, 100 cm^3 of 7.2N H_2SO_4 was added and the solution was kept in a plastic bottle.

– Stock solution of silicon. Quartz wool (300.5 mg) was dissolved in 10 cm^3 of 40% HF. The solution was transferred to a plastic vessel and its volume was made up to 500 cm^3 with double distilled water. One cm^3 of this solution contains 10 μmol of silicon.

– Reagent mixture for assaying phosphorus. Fourty-five cm^3 of the 9% ammonium molybdate solution was mixed with 120 cm^3 of 9N H_2SO_4 and 5 cm^3 of the antymonyl ammonium tartrate solution and 70 cm^3 of double distilled water were added.

– Stock solution of phosphorus. Dried KH_2PO_4 (131.6 mg) was dissolved in double distilled water containing 1 cm^3 of the 9N H_2SO_4 solution and the volume was adjusted to 100 cm^3 with the water. One cm^3 of this solution contains 10 μmol of phosphorus.

– 1% 8-hydroxyquinoline solution in purified chloroform.

– Complexing solution for assaying aluminium. The following solutions were diluted with double distilled water and transferred to a 1-dm^3 volumetric flask (in the given sequence; double distilled water throughout): 10 g of $NH_2OH \cdot HCl$ in 40 cm^3 of water; 3.4 g of CH_3COONa in 50 cm^3 of water and 0.2 g of $BeCO_3$ in 10 cm^3 of water acidified with 0.5 cm^3 of concentrated H_2SO_4. The volume was then adjusted to the mark with water.

– Stock solution of aluminium containing 36.52 mg $Al \cdot cm^{-3}$.

– Chromotropic acid for assaying titanium. 1 g of the disodium salt of chromotropic acid was dissolved in double distilled water, 20 cm^3 of the 2% ascorbic acid solution was added and the volume was made up to 100 cm^3 with water.

2.2.2. EQUIPMENT

– Quartz-glass distillation still.

– A VSU-2P spectrophotometer (VEB Carl Zeiss, Jena).

– A set of quartz cuvettes.

2.2.3. DETERMINATION OF SILICON

In acid medium silicon compounds form molybdosilicic acid with molybdate, which occurs in two isomeric forms. The α-isomer is formed over the pH range 2.5 - 4.5, and it is stable in this pH region. At lower pH values, a considerably less stable β-isomer is formed which absorbs the 390-nm spectral line twice as strong as the α-isomer [6, 9, 11]. The reduction of the molybdosilicic acid with ascorbic acid in an acid medium (pH 0.8 - 2.5) affords a blue-coloured complex. The addition of oxalic acid prevents the formation of a similar complex with phosphorus, while the addition of boric acid binds an excess of hydrofluoric acid used to dissolve the silicate material and destroys H_2SiF_6 to form a stable BF_4^- complex.

2.2.3.1. Procedure

A sample (0.2 cm^3) of a solution to be analyzed and 1 cm^3 of the reagent mixture are pipetted with a plastic pipette into a 50-cm^3 Erlenmeyer flask containing 35 cm^3 of the boric acid solution. The flask is left for 20 min, and 1 cm^3 of the 1.75% solution of ascorbic and oxalic acids is added under agitation. After 1 h, the absorbance of the solution is measured at 810 nm in a 1-cm cuvette. A calibration graph was constructed for the concentration range 0 - 2.5 μmol Si/sample.

2.2.4. DETERMINATION OF PHOSPHORUS

Phosphorus was determined by means of ammonium molybdate with the addition of a Sb(III) salt, in an acid medium ($pH < 1$). Under these conditions, a blue complex underlying phosphorus determination is formed [6, 11].

2.2.4.1. Procedure

One cm^3 of a solution to be analyzed and 1 cm^3 of the reagent mixture were placed in a 50-cm^3 Erlenmeyer flask containing 34 cm^3 of double distilled water. The solution was left for 15 min and then 1 cm^3 of the 7% ascorbic acid solution was added under agitation. After 30 min the absorbance was measured at 880 nm in a 5-cm cuvette. A calibration graph was constructed for the concentration range 0 - 0.3 μmol $PO_4^{3-}-P$/sample.

2.2.5. DETERMINATION OF ALUMINIUM

8-hydroxyquinoline (oxine) forms a complex with Al^{3+} ion extractable with chloroform over the pH range 6.8 - 8.0 [9]. This complex underlies aluminium determination. The interference is due to iron which can be masked with 1,10-phenanthroline.

2.2.5.1. Procedure

To a 50-cm^3 separating funnel, 0.5 cm^3 of a solution to be analyzed was pipetted and it was diluted with double distilled water to 10 cm^3. Then 10 cm^3 of the complexing reagent was added, the solution was agitated and left for 5 min. After this time, 20 cm^3 of the 1% chloroformic solution of 8-hydroxyquinoline was added and the mixture was set aside for phase separation. The extract was transferred to a 1-cm cuvette and the absorbance was measured at 410 nm. A calibration graph was constructed for a range of aluminium solutions containing 0 - 70 μg Al/sample.

2.2.6. DETERMINATION OF TITANIUM

Depending on the acidity of the medium, chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) forms with titanium brown-red complexes [9]. At pH 3.5 the molar absorptivity of the titanium complex is 1.7×10^4 at 460 nm. Fe(III), which interferes, can be reduced with ascorbic acid.

2.2.6.1. Procedure

To an acidic solution, containing less than 100 μg of titanium, 1 cm^3 of the 2% ascorbic acid solution was added and the mixture was heated to 80°C. After cooling, 1 cm^3 of the disodium salt of chromotropic acid was added followed by an ammonia solution (to adjust pH to 2) and 5 cm^3 of the formate buffer solution. The volume was made up to 10 cm^3 with double distilled water and the solution was agitated. After 10 min the absorbance was measured at 460 nm in a 1-cm cuvette.

2.3. DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, CALCIUM, IRON AND MANGANESE BY THE ATOMIC-ABSORPTION AND EMISSION SPECTROMETRY IN THE FLAME

The determinations were run on an IL-151 atomic-absorption spectrophotometer (Instrumentation Laboratory, U.S.A.). Sodium and potassium were determined by the emission technique, whereas the remaining elements by atomic absorption in the air-acetylene flame. The conditions of determination of particular elements are shown in Table 1. With the exception of manganese, which was assayed directly in

Table 1. Conditions of the determination of the elements in suspended matter by atomic spectrometry in flame

Specification		Mn	Fe	Na	K	Mg	Ca
Technique used[a]		AAS	AAS	AES	AES	AAS	AAS
Analytical wavelength	[nm]	279.5	248.3	589.0	766.5	285.2	422.7
Voltage on the photomultiplier	[V]	530	530	620	530	380	530
Hollow-cathode lamp current	[mA]	4	10	–	–	15.5	5
Slitwidth	[μm]	160	80	10	40	80	80
Burner height	[mm]	9	9	17	9	10	13
		Stoichiometric					
Acetylene flow rate	[SCFH]	2.5	2.5	2.5-3	2.5-3	2.5	3
Air flow rate	[SCFH]	15	15	15-17	15-17	15	17
Integration period	[s]	1	4	4	4	4	4
Sensitivity range	[x]	2	1	1	1	1	5
Suction rate	[$cm^3 \cdot min^{-1}$]	4-5	4-5	4-5	4-5	4-5	4-5

a – AAS = atomic-absorption spectrometry; AES = atomic-emission spectrometry.

samples, all other elements were determined in 25-fold diluted solutions in 0.1M HCl. Calibration graphs were constructed by using mixed standards containing 0.05 - 6 mg of the particular element in 1 dm^3.

2.4. DETERMINATION OF ZINC, COPPER AND LEAD BY ANODIC INVERSION CHRONOVOLTAMMETRY

The analyses were run on a Hungarian Radelkis OH 102 polarograph in sample solutions diluted (1 : 40) with double distilled water. Ten cm^3 of the solution was dea-aerated by bubbling nitrogen through it during 5 min, and then the solution was electrolyzed on the dropping mercury electrode. The surface area of a drop was 3 mm^2 during a turn by 180°. With copper and lead the duration of electrolysis was 5 min, the electrode potential was -0.65 ± 0.05 V and pH 3; with zinc the duration was 3 min, the potential -1.1 V, and pH 4.5 - 5. The decomposition potentials for Zn, Pb and Cu were $-0.75--0.8$ V, -0.2 V and $+0.15$ V respectively. All the potentials were determined vs. saturated calomel electrode (S.C.E.).

3. RESULTS AND DISCUSSION

The developed analytical methods were verified on a large number of samples collected during the second Antarctic expedition of the Polish Academy of Sciences organized from 20th November 1977 to 24th April 1978 to the Henryk Arctowski Station.

The methods are characterized by high sensitivity, but the minimum detectable concentrations of particular elements are limited by the magnitudes of the blanks which were treated identically as virtual samples. The magnitudes of the blank samples are shown in Table 2.

Table 2. Mean contents of the analyzed elements in the blanks (µg/sample)

No.	Element	Membrane filter with reagents	No. of samples	Standard deviation (S.D.)	Reagents	No. of samples	S.D.
1	Silicon	200	17	139	206	13	176
2	Aluminium	4.69	23	5.56	4.42	15	4.59
3	Sodium	17.10	8	2.13	11.97	9	2.71
4	Potassium	14.19	13	3.04	9.12	10	2.17
5	Iron	9.37	12	2.77	12.29	9	4.94
6	Magnesium	2.40	12	0.81	1.30	10	0.56
7	Calcium	15.9	9	3.9	15.4	8	4.7
8	Phosphorus	0.477	21	0.483	0.344	14	0.373
9	Manganese	0.175	11	0.044	0.171	10	0.044
10	Titanium	0.419	14	0.082	0.285	15	0.134
11	Zinc	7.7	13	2.3	5.8	16	1.9
12	Copper	0.32	12	0.16	0.23	9	0.09
13	Lead	0.21	12	0.19	0.17	11	0.04

Table 3. Mean contents of the elements in suspended matter and in streams in per cent based on dry matter (Zn, Cu and Pb in µg·mg^{-1} dry matter) and their statistical evaluation

No.	Element	Mean contents in marine suspension	No. of samples	Standard deviation (S.D.)	Confidence level	Mean contents in streams	No. of samples	S.D	Confidence level
1	Silicon	13.1	18	4.4	2.2	12.2	15	6.4	3.6
2	Aluminium	6.6	19	1.6	0.8	6.9	18	2.8	1.4
3	Iron	3.6	15	0.8	0.4	4.8	17	1.0	0.5
4	Sodium	1.6	18	0.7	0.4	1.1	18	0.4	0.2
5	Potassium	1.5	23	0.4	0.2	1.0	15	0.3	0.2
6	Magnesium	1.1	23	0.5	0.2	1.8	19	0.7	0.4
7	Calcium	0.4	21	0.2	0.1	1.1	14	0.5	0.3
8	Manganese	0.063	25	0.018	0.008	0.093	18	0.023	0.011
9	Phosphorus	0.468	24	0.244	0.103	0.068	15	0.012	0.007
10	Titanium	0,236	25	0.052	0.021	0.324	20	0.095	0.044
11	Zinc	0.564	12	0.241	0.153	0.473	12	0.306	0.194
12	Copper	0.035	19	0.014	0.007	0.006	9	0.002	0.002
13	Lead	0.018	10	0.011	0.008	0.004	14	0.002	0.001

The results indicate that each blank contained the elements to be determined. Two main features of the blanks should be taken into account: contaminants introduced with the reagents and those due to air-borne particles, contamination of laboratory glassware and fortuitous contact with metallic utensils. Elements such as copper, zinc, manganese and iron are ubiquitous components of laboratory contaminants and their removal in trace analysis has been faced with serious difficulties. The main source of contamination provided, however, the acids. The membrane filters introduced 5.13 μg of Na, 5.07 μg of K, 1.1 μg of Mg and 1.9 μg of Zn to the blanks. In some brands of the filters, a high phosphorus content (of the order of 39.4 μg) was ascertained, the quantity exceeding that present in a sample of suspended matter. The highest absolute contents of the elements were found for silicon and sodium, this being indicative of their ubiquity in the environment and the inherent ease of sample contamination.

Suspended matter in the waters of Ezcurra Inlet originates mostly from a rocky material present in the immediate vicinity, from which water washes off and transports detritus of differentiated size. The results of analyses of the material carried away with waters flowing down the rocky slopes from glaciers (referred to as streams throughout) are representative of those constituents of the suspended matter that are of continental origin. A comparison of the mean contents of particular elements in the suspended matter and in the streams is shown in Table 3.

These results indicate that the suspension of the continental origin (in streams) contains about 2.8 times as much calcium, 64% more magnesium, 48% more manganese, above 37% more titanium and 33% more iron, proportionally equal amounts of silicon, aluminium and zinc, about 7 times less phosphorus, almost 6 times less copper, 4.5 times less lead, and more than 40% of sodium and potassium. These differences are due to the fact that the suspended matter in sea water contains also organic matter produced by photosynthesis, i.e. mostly phytoplankton.

When comparing the results of the blanks with those of samples it was noticed that almost all the net values for Zn, Cu and Pb were lower than those of the blanks. The reason for this is a small weight of the suspended matter, mostly falling in the range 2 to 5 mg. Beginning from 10 mg this problem became less significant. The results for silicon were frequently obtained with a large random error due to the variability of the results for the blanks. The net values for calcium are usually higher than those of the blanks. On the other hand, the contribution of the blanks to the results for iron, aluminium, sodium and phosphorus falls within the range 10 to 30%. The results for manganese, potassium, magnesium and titanium were most reliable, determined with the smallest errors, owing to the relatively small contribution of the samples. With polarographic assays, using the developed method of wet digestion of the suspended matter, total quantities of trace metals (Zn, Cu, Pb) bound with both the mineral and organic matter were determined. The average concentrations of the metals amount from several to a thousandth of microgramme per cm^3 of solution after wet digestion. With such small quantities, interferences due to chemical reagents can be expected. The sum of the main mineral constituents of the suspended matter, based on their oxide forms, does not amount to 100%, as the analyses of all constituents were incomplete. Among missing constituents which affect the balance are: hygroscopic water, water bound in the crystal structure of the mineral components, and organic matter.

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