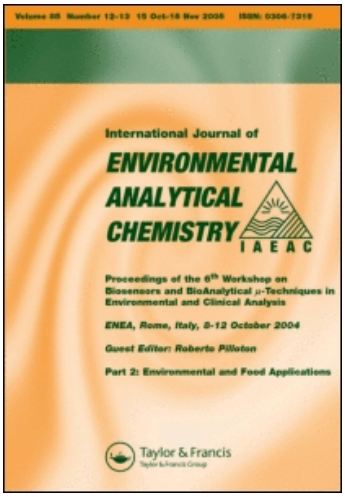

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SAMPLE STORAGE FOR INORGANIC COMPOUNDS IN SURFACE WATER – A REVIEW –

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Factors influencing water samples stability and methods of preservation for analysis of inorganic compounds are presented. Preservation techniques referred in the literature are relatively limited. They are intended generally to retard biological action, hydrolysis of chemical compounds and complexes and reduce volatility of constituents. Acidification and refrigeration at 4°C are the techniques usually recommended. Guidelines proposed by International Organizations and mostly used by environmental laboratories are compared.

KEY WORDS: Sample preservation, storage, inorganic compounds, surface water, sea water.

INTRODUCTION

A number of European Directives concerned with the quality of several types of water have been issued. They prescribe the determination of major elements and compounds as well as a wide range of trace elements.

Numerous laboratories produce per week sometimes thousands or more analytical data and results are the basis for decisions on the measures to be taken for the protection of the environment, the use of the water, treatment to be made, etc.

Whenever a sampling programme is devised all precautions should be taken in the definition of the position of sampling sites, frequency of sampling, duration of sampling, sampling procedures, subsequent treatment of samples and analytical requirements[1,2].

The samples collected should be as fully representative as possible of the environment to be characterised, in order that concentrations of the compounds are identical to those in the waterbody at the time of sampling. Moreover it is necessary to ensure that the concentrations of the compounds in the samples do not change between sampling and analysis and that the required information on any changes in water quality is obtained when repeating the sampling operation at times[3].

If these aims are not achieved the analytical results may be partially or completely invalid for their intended purposes. Sampling considerations are therefore of main importance being essential to devote sufficient time and effort to them to ensure that satisfactory techniques are applied.

In practice there is usually some delay between sampling and analysis and most parameters may show instability. Thus, it is essential to ensure both that instability is minimised and that analysis is made before any important changes in concentration occur.

Problems of preservation of the samples content since the time they are collected till the beginning of analysis is actually one of the most difficult tasks faced by researchers and laboratories responsible for the water quality control.

Considering that sample containers are stored in such a way that their contamination between sampling and analysis is avoided, the main factors affecting stability are nature of the samples, sample containers, time interval between sampling and analysis, addition of preserving reagents to the sample and storage conditions.

NATURE OF SAMPLE CHANGES

Once the sample has been collected changes in the concentration of the determinands may occur. Some may be fairly slow but few if any determinands exhibit permanent stability.

The most common changes that preservation techniques attempt to minimise are physical changes such as volatilisation, adsorption and precipitation and chemical changes including air oxidation, photochemical changes and microbiological degradation.

Volatilisation. In this process volatile species can be lost to the atmosphere, depending on the vapour pressure of the compound to be measured, the temperature of the sample and the surface area (e.g. hydrogen sulphide, hydrogen cyanide, oxygen, carbon dioxide).

The loss of volatile materials can be avoided by collecting the sample in a completely filled container, keeping the samples as cool as possible without freezing or changing the pH value of the samples so that the component is converted to a more stable form[4,5].

Precipitation. Components in a sample may form salts that precipitate in the container. This process results from the interaction of components present in the sample due to a change in the sample environment (e.g. pH) or from the reaction of components in the sample with components in the air environment[4].

The most common phenomenon is the precipitation of metal oxides and hydroxides as a result of metal ions' reactions with oxygen. For instance, iron and manganese are readily soluble in their lower oxidation states but relatively insoluble in their higher oxidation states; therefore, these cations may precipitate depending on the redox potential of the sample[5].

Changes in the pH-alkalinity-carbon dioxide balance may cause the precipitation of calcium carbonate and a decrease in the values for calcium and total hardness.

Adsorption and absorption. Components can adsorb sometimes irreversibly onto the walls of the sample containers. For instance, metals can be adsorbed onto glass surfaces. Therefore the usual sampling approach for metal determinations is to collect the samples in plastic containers and thus eliminate the glass contact[4].

Samples can absorb air components such as oxygen or carbon dioxide which can have significant impact on the sample, e.g., sulphide may be converted to sulphate in presence of oxygen or the pH of the sample may suffer alteration due to the uptake of carbon dioxide[1,2,5].

Microbiological activity. The metabolic activity of micro-organisms in a sample can affect a large number of constituents, changing their oxidation state. It can be responsible for changes in nitrate, nitrite and ammonia content, phosphorus cycle and reduction of sulphate to sulphide[5]. Soluble constituents may also be converted to organically bound materials in cell structures.

There is no unanimously accepted method and the authors are divided regarding the technique to apply and its efficacy concerning the biological life destruction[2,4]. The methods most currently used are the following:

- Addition of a chemical compound to stop biological activity. Reagents mostly used are chloroform, sulphuric acid and mercuric chloride;
- Sample storage at low temperature (refrigerated or frozen).

Chemical Changes. Components in samples can undergo a variety of chemical changes[2,4,5]:

- Oxidation or more rarely reduction, e.g., sulphide, sulphite, ferrous iron, iodide, cyanide may be lost through oxidation and hexavalent chromium may be reduced to trivalent chromium;
- Cations may precipitate depending on the redox potential of the sample;
- Changes in the carbon dioxide content can result in changes in the carbonate system, composed of carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-) and carbonate ions ($CO_3^=$), and consequently in the pH of the samples. With changes in this balance, calcium carbonate may precipitate and cause a decrease in the values for calcium and for total hardness;
- Changes in pH my affect the degree of dissociation of weak acids or bases, e.g. rapid increases in pH value can cause increased ammonia concentrations and conversely lower pH values cause an increased concentration of hydrocyanic acid or hydrogen sulphide. Ferrous/ferric iron ratio may be affected by pH and Eh changes[5,6];
- Polymeric materials may depolymerise and vice versa. Condensed inorganic phosphates and polymeric silic acid can depolymerise and cause increases in the concentrations of orthophosphate and monomeric silic acid;
- Free chlorine can react with organic compounds to form chlorinated species.

Photochemical changes. Some components can undergo changes associated with light-catalysed reactions; however, they can be minimised by the collection of samples in opaque (e.g. brown) black glass containers.

Contamination. Contamination by container walls may occur, e.g. sodium, silica, boron may be leached from the glass container[5]. Contamination of the sample may also occur in the field during sampling (e.g. sample collection, handling, surrounding environment, storage, etc) which can be of great importance when trace elements are to be analysed.

SAMPLE CONTAINERS

The types of sample containers may have important effects on sample stability. Some authors advise the use of quartz or polytetrafluoroethylene (PTFE) bottles, however these containers are very expensive[5,7]. Polypropylene, linear polyethylene or glass bottles are most often used; in many cases both materials are considered equally satisfactory.

Glass bottles have the advantage that they are more efficiently cleaned and it is easier to see if they are properly cleaned. Polyethylene bottles are less liable to breakage or

damage by freezing. Dark brown or opaque glass bottles may be useful for reducing biological activity[1,2]. Glass bottles should not be used for silica analysis particularly for water with pH above 8 or for seawater for which a significant amount of silica in the glass can dissolve.

As well as the factors mentioned in the preceding paragraph, there are three chemical considerations in choosing sample containers[8]:

- Transfer from the container to the sample e.g. sodium, silica or boron from glass or organic material from plastics;
- Transfer from the water to the container e.g. sorption of trace metals by glass;
- Direct reaction with the container e.g. fluoride and glass.

In controlling contamination effects the following points must be considered[1,2]:

- Contaminants are not necessary major components of the container material, e.g. iron, manganese, zinc and lead may be leached from glass and lead and copper may be leached from polyethylene. Lithium chloride may occasionally be used in the manufacture of polyethylene;
- The nature and magnitude of contamination effects may depend on the manufacturing process of the container. Furthermore, bottles of identical type from the same manufacturer may differ among themselves. Therefore, in trace analysis it is advisable to check that each bottle is satisfactory from the standpoint of contamination;
- The caps of bottles sometimes contain inserts that may cause contamination. Some plastic caps or cap liners may introduce matal contamination; for example zinc has been found in black backlite-type crew cap, as well as in many rubber and plastic products[5]. Therefore it is necessary to ensure that caps contain only the material from which the bottles are made;
- Substances in a sample may be sorbed or deposited onto sample container and contaminate the next sample if used bottles are not adequately cleaned;
- Gaseous substances may diffuse, although rather slowly, through the walls of the bottles. Thus, contamination by gases in the air around the bottles or losses of gaseous substances from the sample may occur though these effects seem usually not important and not significant when high density polyethylene bottles are used;
- Sample containers may affect sample stability by sorption of substances from the sample. This effect is particularly important when small concentrations of metals are to be determined. The magnitude of this process depends on the nature and concentration of the substances in the sample, material and history of the container, temperature, nature and concentration of any preserving reagents added to the sample. Some metals (mercury and silver) are particularly liable to losses to the walls of the containers.

TIME INTERVAL BETWEEN COLLECTION AND ANALYSIS

On this subject all the authors agree that the shorter the time that elapses between the sample collection and its analysis, the more reliable will be the analytical results. It is difficult to state exactly how much time may be allowed between sample collection and analysis once it depends on the character of the sample, the analysis to be made and the conditions of storage[5].

Further research is needed in this field to establish clear guidelines for surface water analysis.

PRESERVATION METHODS

Various preservation methods are available but their effect is one of retardation of chemical, biological and physical reactions and they do not reduce the urgency and associated risks of sample transport. Complete and unequivocal preservation of samples is considered to be practically impossible. Regardless of the sample nature, the complete stability for every constituent can never be achieved. Methods of preservation referred in the literature are relatively limited and are intended generally to retard biological activity and hydrolysis of chemical compounds and complexes, prevent precipitation of components and reduce their volatility[8].

Methods most often referred in the literature may be classified as follows:

Refrigeration. The storage of the samples at about 4°C, preferably in the dark, retard biological activity substantially and reduce the rate of physical and chemical actions (e.g. volatilisation, biodegradation). This method has the advantage that it does not interfere with subsequent analytical determinations (no addition of reagents). However, analysis need to be performed not too long after collection.

Deep-freezing of seawater samples is used if storage for many weeks is necessary[9]. ICES also concludes that freezing is the method of choice of many workers for storage of sea water but recommends the following[10]:

– Bottles should be stored in a freezer in an upright position and they should not be completely filled, in order to prevent spillage from the bottle due to the expansion of the sample. The reason is that during the freezing process the last few millilitres of the sample will have a very different composition in comparison to the original sample and the integrity of the sample will be lost. The samples should also be thawed in an upright position;

– Dissolved silicate is reported to polymerise/crystallise during the freezing process and several authors warn that when samples are thawed prior to analysis, sufficient time must be allowed for depolymerisation/redissolution.

Chemical Preservation. Sample stability may often be achieved by the addition of a reagent to the sample directly after collection or to the empty sample container before collection. Different reagents can be used, often at different final concentrations in the sample.

The addition of a chemical preservative may affect the subsequent analysis by interfering with the analytical method, rendering the sample unsuitable for a number of determinations. They may also change the chemical and/or the physical forms of determinands[1].

(a) *Biocides.* An alternative approach is the addition of a biocide to inhibit biological action, particularly when storage at low temperature is not possible. Chemicals usually referred in the literature are chloroform and mercuric chloride. Several authors have reported the use of mercuric chloride at various concentrations but over the years it has lost favour, due to the concurrent increase in interest in the determination of mercury in water and its high toxicity. International Standard Organization (ISO) recommends to use it only when absolutely necessary[11].

Chloroform has the disadvantage that it may be lost by evaporation, especially from plastic containers. This compound actually acts as an anesthetic whereas mercury is a permanent poison.

The use of biocide (such as chloroform) is not recommended in phosphate analysis since it may accelerate the release of labile compounds from plankton cells.

(b) *Acidification* The addition of acid (usually nitric, sulphuric, hydrochloric) to produce a pH of about 2 is a common practice to prevent precipitation of components (e.g. metal oxides and hydroxides) and to inhibit biological activity.

Acidification is not recommended for samples to be analysed for phosphate since hydrolisis of polyphosphate and release of phosphate from plankton and bacteria may occur. Samples for silica analysis should not be acidified because silica precipitates in acidic solutions.

(c) *Special cases* Certain determinands may require special reagents for preservation. For example to preserve sulphide, zinc acetate and sodium hydroxide are added.

Filtration. Algal and bacterial activity can often be sufficiently reduced by simply filtering (e. g. at 0.45 μm mesh) the sample during or immediately after collection.

RECOMMENDATIONS FOR SAMPLE PRESERVATION

The review presented in this paper is not exhaustive. In fact the objective has been mainly to compare recommendations and standards described in publications edited by International Organizations and mostly used by laboratories responsible for the water quality control[5,11–13].

As said before, there is not available absolute guidelines for the maximum time interval between sampling and analysis, prevention of all possible changes due to storage, preservation methods, etc.

During sample transport it is necessary to ensure that some precautions are undertaken. For example, samples should not be exposed unnecessarily to any source of light, facilities for refrigeration of samples should be arranged during transport, sample containers should be packed so that contamination of their outsides is avoided, etc.

ICES[10] considers that although several institutes have established procedures under which they can preserve and store seawater samples for selected nutrients (ammonium, nitrite, nitrate, silicate and orthophosphate) for a limited time, there is at present no procedure which can be recommended for general use i.e. for all nutrients, in all sea areas at all times of the year. Therefore analysis on board is to be preferred and is strongly recommended for nutrients. If this is not feasible for logistic reasons, each institute must verify storage procedures before they are used routinely. ICES recommends the use of glass bottles for storage of seawater intended for nitrate determination, considering that nutrients may be lost by absorption to the walls of plastic bottles.

For metals determined by hydride genweration/atomic absorption spectrometric method (e.g. arsenic and selenium), acidification should be done with hydrochloric acid[14]; however this recommendation is not usually referred.

A list containing methods of sample preservation and holding times for inorganic compounds is presented in Table 1.

Table 1 Preservation techniques for inorganic compounds.

Compound	*Ref*[a]	*Sample container*	*Preservation*	*Maximum recommended storage time*
Alkalinity	APHA	P, G	Refrigerate	24 hours
	EPA	P, G	Refrigerate	14 days
	ISO	P, G	Refrigerate	24 hours
	UNESCO	P, G	Analyse immediately or refrigerate	24 hours
Carbon dioxide	APHA	P, G	Analyse immediately	
	ISO	P, G	Analyse immediately	
	UNESCO	P, G	Analyse immediately or refrigerate	same day
Chloride	APHA	P, G	Unnecessary	28 days
	EPA	P, G	Unnecessary	No time limit
	ISO	P, G	Unnecessary	Several months
	UNESCO	P, G	Unnecessary	No time limit
Conductivity	APHA	P, G	Refrigerate	28 days
	EPA	P, G	Refrigerate	28 days
	ISO	P, G	Refrigerate (2–5°C)	24 hours
	UNESCO	P, G	Not possible	Several days
Cyanide (total)	APHA	P, G	Add NaOH to pH > 12; refrigerate in dark	24 hours
	EPA	P, G	Add NaOH to pH > 12; refrigerate	14 days; 24 h if sulfide present
	ISO	P	Add NaOH to pH > 12	24 hours
	UNESCO	P, G	Add NaOH to pH > 11; refrigerate or freeze	Same day
Fluoride	APHA	P	Unnecessary	28 days
	EPA	P	Unnecessary	28 days
	ISO	P	Unnecessary	Several months if neutral
	UNESCO	P	Unnecessary	No time limit
Hardness	APHA	P, G	Add HNO_3 to pH < 2	6 months
	EPA	P, G		6 months
	ISO	P, G	None or add HNO_3 to pH < 2	24 hours Several months
	UNESCO	P, G	Unnecessary/Bottles tightly capped	Immediately
Metals, general	APHA	P, G	Add HNO_3 to pH < 2	6 months
	EPA	P, G	Add HNO_3 to pH < 2	6 months
	JMG	P	Acidify to pH < 1–2	Several months
	ISO	P, G(B)	Acidify to pH < 2 .	1 month
	UNESCO	P, G	Add 2 mL conc. HNO_3/L	No time limit
Chromium VI	APHA	P, G	Refrigerate	24 hours
	EPA	P, G	Refrigerate, 4°C	24 hours
	ISO	P, G	Refrigerate (2–5°C)	As soon as possible
Copper:				
Polarographic method	(6)	P, G	Add perchloric acid to pH < 2	
Spectrometric method	APHA, (6)	P, G	Add hydrochloric acid to pH < 2	
Iron (II)	ISO	P, G(B)	Add HCl to pH < 2; without oxygen	1 week

Table 1 (cont.) Preservation techniques for inorganic compounds.

Compound	*Ref*	*Sample container*	*Preservation*	*Maximum recommended storage time*
Mercury	APHA	P, G	Add HNO_3 to pH < 2, refrigerate (4°C)	28 days
	EPA	P, G	Add HNO_3 to pH < 2	28 days
	ISO	G(B)	Add HNO_3 to pH < 2 and $K_2Cr_2O_7$ (0.05% (m/m))	Several months
	UNESCO	P	Add 10 mL H_2SO_4/L	Several days
Nitrogen, Ammonia	APHA	P, G	None or add H_2SO_4 to pH < 2	As soon as possible 7 days
	EPA	P, G	Add H_2SO_4 to pH < 2, refrigerate	28 days
	ISO	P, G	Refrigerate (2–5°C) or add H_2SO_4 to pH < 2 and refrigerate (2–5°C)	6 hours 24 hours
	UNESCO	P, G	Refrigerate (3–4°C) or add H_2SO_4 to pH < 2	Same day
	(9, 15, 16)	P, G	Refrigerate; dark or Deep-freezing at –20°C	1–2 hours 1–2 days
Nitrogen, Nitrate	APHA	P, G	None or refrigerate	As soon as possible 48 hours
	EPA	P, G	Refrigerate (4°C)	48 hours
	ISO	P, G	Add H_2SO_4 to pH < 2; refrigerate (2–5°C)	24 hours
	UNESCO	P, G	Add 0.8 mL H_2SO_4/L or 2–4 mL $CHCl_3$/L; refrigerate (3–4°C)	Same day
	(9, 15, 16)	P, G	Refrigerate, dark or Deep-freezing	12 hours Several weeks
Nitrogen, Nitrite	APHA	P, G	Analyse as soon as possible or refrigerate	None
	EPA	P, G	Refrigerate, 4°C	48 hours
	ISO	P, G	Refrigerate, 4°C	As soon as possible
	UNESCO	P, G	Add 0.8 mL H_2SO_4/L or 2–4 mL $CHCl_3$/L; refrigerate (3–4°C)	Same day
	(9, 15, 16)	P,G	Refrigerate; dark or Deep-freezing at –20°C	5–10 hours 1–2 days
Oxygen, dissolved (electrode)	APHA ISO		In situ	Immediately
Oxygen, dissolved (Winkler method)	APHA	BOD bottle	Titration may be delayed after acidification	8 hours
	EPA	BOD bottle		8 hours
	ISO	P, G	Add reagents immediately; dark	4 days
	UNESCO	BOD bottle	Refrigerate; dark	Immediately
	(9)	BOD bottle	Add reagents	1 hour
pH	APHA	P, G	Analyse immediately	2 hours
	EPA	P, G	Analyse immediately	
	ISO	P, G	Analyse immediately or fill completely; refrigerate	6 hours
	UNESCO	P, G	Not Possible	Immediately
Phosphate	APHA	G	Refrigerate	48 hours
	EPA		Refrigerate	
	ISO	P, G	Refrigerate (2–5°C)	24 hours
	UNESCO	P, G	Refrigerate (3–4°C)	Same day
	(9, 15, 16)	P, G	Refrigerate; dark or Quickly freezing at –20°C	1/2–2 hour Several months

Table 1 (cont.) Preservation techniques for inorganic compounds.

Compound	*Ref*	*Sample container*	*Preservation*	*Maximum recommended storage time*
Silica	APHA	P	Refrigerate, no freeze	28 days
	EPA	P	Refrigerate	28 days
	ISO	P	Refrigerate(2–5°C); filtration; add H_2SO_4 to pH < 2	24 hours
	UNESCO	P	Analyse immediately or freeze	Several days if frozen
	(9)	P	Refrigerate; dark Deep-freezing at –20°C	1 day Several months
	(15, 16)	P	Add H_2SO_4 to pH < 2.5; refrigerate; dark	Several months
Sulphate	APHA	P, G	Refrigerate, 4°C	28 days
	EPA	P, G	Refrigerate	28 days
	ISO	P, G	Refrigerate (2–5°C)	1 week
	UNESCO	P, G	Refrigerate (3–4°C)	No time limit
Sulphide	APHA	P, G	Refrigerate; add 4 drops 2N zinc acetate/100 mL; add NaOH to pH > 9.	28 days
	EPA	P, G	Refrigerate, 4°C, add zinc acetate	7 days
	ISO	P, G	Add 2 mL zinc acetate till 1 mL/L; add 2 mL NaOH till 1 mol/L.	1 week
	UNESCO	P, G	Add 10 mL of a 10 % cadmium acetate or zinc acetate solution	Same day
	(9)	P, G	Refrigerate; dark	1 hour

APHA - American Public Health Association[5]
EPA - Environmental Protection Agency[13]
ISO - International Organization for Standardization[11]
UNESCO - United Nations Educational, Scientific and Cultural Organization[12]

P - Plastic (polyethylene or equivalent)
G - Glass
G (B) - Glass, borosilicate

CONCLUSIONS

Recommendations and guidelines found in the various publications often differ and sometimes are contradictory. Acidification and refrigeration at 4°C are the techniques generally recommended. There is no agreement for the time interval between collection and analysis for the different parameters. However, there is a general consensus in what concerns sample containers (glass and/or polyethylene). At present, there is no procedure recommended for all the nutrients. This is particularly important if analytical methods common to different parameters are used. There is general agreement that acidification of samples is necessary when trace metals are to be determined, though different acids and acidities are referred. Establishment of guidelines on preservation methods based on existing information and recent studies are necessary. They should identify the influence of sample matrix on physical and chemical changes for each parameter and the corresponding preservation method recommended.

References

1. A. L. Wilson, *The Chemical Analysis of Water—General Principle and Techniques* (Analytical Sciences Monograph n°2, The Society for Analytical Chemistry, London, 1974), 188 pp.
2. M. Suess, *Examination of Water for Pollution Control, Vol. 1-Sampling Data Analysis and Laboratory Equipment* (World Health Organization, Pergamon Press, Paris, 1982).
3. ISO 5667/1, *Water Quality-Sampling-Part 1: Guidance on the Design of Sampling Programmes* (ISO, Geneva, 1980).
4. J. Parr, M. Bollinger, O. Callaway and K. Carlberg, in: *Preservation Techniques for Organic and Inorganic Compounds in Water Samples, in Principles of Environmental Sampling,* (ACS Professional Reference Book, The American Chemical Society, Ed. Lawrence Keith, Washington, 1988), pp. 221–230.
5. American Public Heatlh Association, American Water Works Association and Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater,* (American Public Health Association, Washigton, 1992), 18th ed.
6. M. Suess, *Examination of Water for Pollution Control, Vol. 2-Physical, Chemical and Radiological Examination,* (World Health Organization, Pergamon Press, Paris, 1982) 1st ed., 555 pp.
7. Joint Monitoring Group, *Guidelines for the Sampling and Analysis of Trace Metals in Seawater under the Joint Monitoring Programme of Paris and Oslo Commission,* **JMG 15/6/4,** (1990).
8. L. Keith, *Principles of Environmental Sampling,* (ACS Professional Reference Book, The American Chemical Society, Ed. Lawrence Keith, Washington, 1988).
9. J. L. Strickland and T. Parsons, *A Practical Handbook for Seawater Analyses,* (Fisheries Research Board Canada, Bull. 167, Ottawa, 1972), 2nd ed.
10. International Council for the Exploration of Sea, *Basic Guidance for Sampling and the Determination of Nutrient in Seawater,* **MCWG/7.3.1- ANNEX 9,** (1991).
11. ISO 5667-3, *Water Quality-Sampling- Part 3: Guidance on the Preservation and Handling of Samples,* (Geneva, 1992).
12. United Nations Educational, Scientific and Cultural Organization and World Health Organization, *Water quality Surveys—A Guide for the Collection and Interpretation of Water Quality Data,* (United Kingdom, 1978) 350 pp.
13. Environmental Protection Agency, *Required Containers, Preservation Techniques and Holding Times,* (EPA, Washington, 1987).
14. E. Pruskowska, P. Barrett, R. Ediger and G. Wallece, *Atomic Spectroscopy,* **4, n°3,** (1983).
15. A. L. Aminot and M. Chaussepied, *Manuel des Analyses Chimiques en Milieu Marin,* (CNEXO, Brest, (1983).
16. K. Grasshoff, M. Ehrardt, K. Kremling, *Methods, of Seawater Analysis,* (Verlag Chemie GmbH, Weinheim, 1983) 2nd Ed.