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THE CANADIAN MARINE ANALYTICAL CHEMISTRY STANDARDS PROGRAM

by

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INTRODUCTION

Those who are actively pursuing research studies in marine chemistry are well aware of the high analytical standards required to obtain accurate data. This particular soup called sea water, politely defined as having a salinity of about 35‰, is undoubtedly one of the most complex phases existing in natural systems and presents extreme difficulties to professional analytical chemists. The challenges arise in a number of ways, e.g. in the analysis of extremely low concentrations of certain constituents in a matrix containing most/all inorganic elements and countless but unknown organic compounds in living and nonliving parts of the matrix. Anyone entering this field does so as a newborne babe blissfully unaware of the untold difficulties which lie ahead but hopefully with an enthusiasm that progress will result from the effort to be expended.

Just to give some examples of the experiences of those concerned with these difficulties I would like to present some data from two intercalibration experiments.

TABLE 1. Results from two trace metal intercalibration experiments.

1. Trace Element Intercalibration Study - P.G. Brewer and D.W. Spencer (1970)

	No. of Labs	Approximate Range (µg/kg)	Mean Concentration (µg/kg)	S.D.
Copper				
	12	0.9-14.8	3.5	4.2
Iron				
	13	5.7-31.6	12.2	9.9

2. Pilot Intercalibration I: Trace Metals in Fresh Water and Sea Water - I.D. Macaulay (1974)

Copper				
	7	0.3-40	7.1	13.5
Iron				
	3	5-15	9.3	(5.0)

Results such as these are common amongst laboratories active in the field and even with the passage of time and improved knowledge and capability it is doubtful whether significant advances have yet been made with the obvious problem. ICES, of course, has embarked on a step-by-step approach to the question of trace metal analysis in sea water and we hope that when the exercise has been completed that a much better understanding of the sources of these problems will emerge. IOC is also planning similar studies and has recently established an expert group, under the auspices of GIPME. Additional programs are being sponsored by IAEA and NATO in the field of intercalibration.

MARINE CONCERNS IN CANADA

In addition to the needs of the research workers in marine chemistry we have found, in recent years in Canada, that environmental legislation and other government policy decisions have led to increasing demands for high quality chemical analytical data from the marine environment. Almost all ICES countries are parties to the London Dumping Convention and/or similar regional agreements. In our national legislation enacted in 1975 certain quantitative values have been introduced in the accompanying Regulations to limit the amounts of particularly toxic substances which may be dumped in accordance with the Ocean Dumping Act. Substances such as lead, mercury, cadmium, organohalogen compounds and petroleum products are included in this category of Schedule 1 substances. The Environmental Contaminants Act also calls for strict controls on new and exotic materials which may find their way to the oceans and places a similar demand on the need for accurate analytical data on marine materials. Finally, we have the 'Make or Buy' policy which calls for increasing participation by the

private sector in all aspects of Government work including R & D in the marine environment. *In toto,* therefore, it has become apparent to marine chemists in Canada that these developments are creating a greater demand for accurate chemical analyses of marine materials which, from our knowledge of present capabilities, it is difficult to meet. This paper describes some of our attempts to remedy certain aspects of this situation.

RECENT DEVELOPMENTS IN THE MARINE ANALYTICAL STANDARDS PROGRAM

In spring 1976 the National Research Council of Canada (NRC), following the recommendations of the Canadian Committee on Oceanography, established a Marine Analytical Chemistry Standards Program and simultaneously a Committee on Marine Analytical Chemistry. This committee has, as its terms of reference:

- to review the status of marine chemistry in Canada
- to coordinate the development of standard reference materials, standard methods and interlaboratory calibrations
- to estimate long term developmental needs
- to study specific problems in reference to the analysis of marine materials

In addition to these tasks the Committee has a broader responsibility in terms of providing guidance and advice to the specific marine analytical problems being investigated in NRC laboratories and to the development of standards/reference materials in the Marine Analytical Chemistry Standards Program. The Committee held its first formal meeting in October 1976, established a program of activity, and attempted to assign priorities to the subject matter. Areas to be covered by the program are:

- Reviews and evaluations of sample collection, storage, preservation, handling, and contamination problems
- Evaluations of laboratory environments, reagents, materials, solvents, and analytical methodology
- Development of reference materials for trace metals and organic compounds and other exotic chemicals
- Initiation and coordination of literature surveys and assessments in marine analytical chemistry

These general subjects reflect, in the view of the Committee, the scientific and technical problems which are currently limiting progress of marine chemistry in the area of standards and reference materials. We have endeavoured to be much more specific in priorizing the actual efforts to be carried out and as far as inorganic analysis and standards are concerned we feel that, at the moment, two subjects should receive our attention. First we are concerned about the lack of a reference material for trace metal analyses at concentrations comparable to those which exist in sea water. At the levels which prevail in sediments there appear to be fewer problems and suitable reference materials are available from a number of centres throughout the world. Ideally, one would like to have a sea water matrix which is constantly available and which retains a constant composition. This is difficult to achieve because of the quantity which needs to be 'on tap,' the possibilities of physical, chemical, and biological alteration of the sea water and the problems, admittedly minor in contrast to the others, of shipment. For these reasons investigations are being pursued to develop a solid reference material from which a reference synthetic sea water can be conveniently and rapidly prepared in the laboratories of the NRC or those of the researcher. A second study in the inorganic field is being

carried out to investigate the applicability and limitations of solvent extraction techniques for the analysis of some of the more important metals present in trace quantities in the oceans, e.g. Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. Further definition of the limitations of the MIBK-APDC extraction procedure will be pursued together with evaluations and development of alternative extraction procedures.

A consideration of organic studies, on the other hand, has also led to two activities which are compatible with the overall priorities of the program and the capabilities presently available in the NRC laboratories. The first concerns the development of a marine oil reference material which can be 'spiked' with various analytes of interest to particular groups of research workers. Marine oils have, in the past, been used as reference materials in various national and international intercalibration exercises. It is unlikely that these particular samples will continue to be available for extended periods as the stocks are depleted. We feel, therefore, at least for Canadian purposes, that a large supply of marine oil should be prepared, and be available in sufficient quantities to last for several years. Fish oils are available in large quantities in the Maritimes region of Canada and a suitable type will be selected and attempts made to 'refine' it for the above purposes. The second subject for study at the present time concerns the everlasting question of the analysis of organic matter in sea water. A full understanding of the total quantities of organic matter in sea water in all its phases, its composition, and its role in biological reactions, productivity, and so on, has eluded marine scientists.

Particulate organic matter can be analyzed in a satisfactory manner at present and progress is being made, albeit slowly, toward the elucidation of natural and anthropogenic organic constituents of marine materials. As

far as dissolved organic matter is concerned several methods have been tried in various laboratories with varying degrees of success. A resolution of the specific problems in methodology remains outstanding together with a concerted effort by participating laboratories toward some form of standardization and intercalibration appears necessary at this time. In the marine analytical chemistry standards program, work has begun on this problem.

We look forward to opportunities to cooperate with marine scientists in Canada and other countries in such studies. The participation of interested scientists in methods comparison and intercalibration work would be most welcome.

ADDITIONAL FEATURES OF THE PROGRAM

Publications

It is our intention to publicize widely this particular Canadian activity. The output of the program will be varied and will include reviews of the state-of-the-art of critical areas of endeavour, results of research projects, descriptions and availability of reference materials as they are developed, results of intercalibration efforts and so on.

To achieve wide distribution of information it has been decided to establish a special series of publications in these particular fields. Distribution will be handled by NRC and publications will be available at a nominal cost. Where the information is clearly of a research nature as opposed to state-of-the-art reviews or information concerning standards/reference materials the normal method of publication in the scientific literature will be followed.

Composition of the Marine Analytical Chemistry Committee

While the Committee has been primarily established to serve Canadian needs the NRC recognizes the international aspects of these endeavours. It is hoped that members from other countries can be encouraged to participate in our deliberations for our mutual benefit. Naturally, we would welcome any expression of interest in this regard.

Resources Available

Activities in this program are supported by staff and resources of two NRC laboratories, the Division of Chemistry in Ottawa, Ontario, and the Atlantic Regional Laboratory in Halifax, Nova Scotia. The latter also has general responsibility for the program and coordination of the related NRC operations.

At the Division of Chemistry, expertise and facilities for trace inorganic analysis are available while at the Atlantic Regional Laboratory expertise and instrumentation for trace organic analysis are allocated to the program. The location of the Atlantic Regional Laboratory in the Halifax-Dartmouth area, a major centre of marine science activity, facilitates cooperative projects with marine scientists. Development of reference materials has so far been the major objective of operations in this program at the Atlantic Regional Laboratory. A horizontal-laminar-flow 'clean' room and related facilities have been established to aid in this.

Much of the work to date has been done in cooperation with analytical chemists and marine scientists in university and other laboratories in Canada, some of this supported by research contracts.

Staff and financial resources allocated to the program have been adequate to make a start with some of the urgent problems. It is hoped

sufficient resources can be made available to sustain a useful level of contributions to the problems of marine analytical chemistry.

CONCLUSIONS

The success of the effort which has been described will depend on the quality of the work being carried out. We are not under any illusions regarding the difficulty nor the extent of these activities but feel, nevertheless, that the problems have to be focussed at a sufficiently high level before substantial progress can be made. When reference materials become available which adequately represent natural systems, only then will we have confidence in the analytical data from our own and other laboratories.

It is our desire that these initiatives will stimulate others to give national consideration to the problems and that through mutual cooperation and endeavours progress will be made on what is undoubtedly an international problem.

REFERENCES

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