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DESIGN AND LOGISTICAL OPTIONS FOR THE CONDUCT OF THE ICES FIFTH ROUND  
INTERCALIBRATION FOR TRACE METALS IN SEAWATER

by

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ABSTRACT

This paper reviews the plans for the series of ICES intercalibrations for trace metals in seawater, particularly the Fifth Round Intercalibration already approved in full by Council. Recent related activities have demonstrated the utility and practicality of combining sampling intercalibrations with concurrent shore-based analytical activities. It is concluded that opportunities exist for the early completion of the entire sequence of ICES intercalibrations for trace metals in seawater including an assessment of sampling and sample pre-treatment methods, multi-ship intercomparisons and training functions. A set of options for the ICES Fifth Round Intercalibration is presented with a view to soliciting offers of research vessels and land-based laboratory facilities for the conduct of this exercise. Once the available facilities have been identified, the most appropriate design can be chosen and the final scientific and logistical planning completed.

RESUME

Cet article passe en revue les projets pour la série d'intercalibrations du C.I.E.M. pour les métaux à l'état de trace dans l'eau de mer et plus particulièrement la Cinquième Intercalibration dans cette série déjà entièrement approuvée par le Conseil. Des activités récentes reliées à ces projets ont mis en évidence la viabilité et l'utilité de combiner les intercalibrations d'échantillonnage avec des analyses parallèles réalisées en laboratoire basé au sol. On en conclut à la possibilité d'un achèvement prochain de la série complète des intercalibrations du C.I.E.M. pour les métaux à l'état de trace dans l'eau de mer, et ceci, en incluant une évaluation des méthodes d'échantillonnage et de traitement des échantillons, des

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comparaisons entre résultats obtenus de plusieurs navires et des activités éducationnelles.

Un ensemble de possibilités pour la Cinquième Série d'Intercalibrations du C.I.E.M. sont présentées dans le but de solliciter des offres de la part de navires scientifiques de recherche et de laboratoires basés au sol pour la conduite de ce programme. Dès que les installations disponibles sont identifiées, le plan de travail le plus approprié peut alors être rapidement élaboré et la planification logistique et scientifique finale complétée.

## INTRODUCTION

In an earlier ICES paper (Bewers et al., 1978) three of the present authors discussed the objectives and nature of the series of ICES intercalibrations for trace metals in seawater. At that time three of the six experiments in the series had been completed and the fourth was in progress. The fourth experiment has now been completed (Bewers et al, 1979) and approval for the conduct of the fifth experiment in the series has been given by Council (Council Resolution 1979/4:18). The main objectives of the fifth experiment were the intercomparison and assessment of different, commonly-used, sampling methods for the collection of sea water samples for trace metal analysis. The sixth and final experiment was intended to be a multi-ship exercise to examine any differences between samples collected from different oceanographic platforms. A small Coordinating Group comprising the authors, working within the forum of the Marine Chemistry Working Group, was made responsible for the planning of the Fifth Round Intercalibration.

In this paper we re-examine the objectives and scope of the previous plans for the Fifth Round Intercalibration in the context of recent related IOC activities and explore options for extending and improving its design to allow for earlier completion of the entire sequence of ICES intercalibrations for sea water. In stating these options we have tried to specify the resources needed for the execution of each in sufficient detail to permit member states of ICES to determine whether they are in a position to make the necessary contributions of ships and/or laboratory facilities for the successful conduct of the exercise.

## BACKGROUND

Before we present the various options which were discussed and developed by us at our last meeting in February, 1980, it is appropriate to outline some of the information and factors which were considered in the formulation of these options. The following sections therefore deal respectively with previous planning for the final stages of the ICES intercalibration series and the experience gained through the conduct of the IOC/UNEP/WMP Sampling Intercalibration (PANCAL-80).

### The Original Design of the Fifth Round Intercalibration

The preliminary design of the Fifth Round Intercalibration was first discussed during the meeting of the Sub-Group on Contaminant Levels in Seawater in Hamburg in 1977. It was agreed at that time that once; (1) a survey of the most commonly-used methods of sample collection had been made and (2) sufficient marine laboratories with good analytical precisions and detection limits for the trace metals of interest had been identified, it would be possible to examine the relative errors introduced through the use of particular combinations of seawater sampling devices and their methods of deployment. The first requirement was met by the results of a survey carried out by H.L. Windom (Windom 1979) that identified the most popular procedures for trace metal sample collection. These comprise the deployment of modified or unmodified GO-FLO, Hydro-Bios or Niskin bottles on kevlar, nylon or plastic-coated steel hydrowire. The survey also covers methods of sample pre-treatment, filtration and preservation that also need to be examined within the framework of the Fifth Round Intercalibration. The second requirement, namely the identification of a certain number of laboratories with adequate analytical precisions and detection limits to be able to detect small differences between samples collected by different techniques, was satisfied by the results of the ICES Fourth Round Intercalibration for Trace Metals in Seawater (Bewers *et al*, 1979). Some ten suitable laboratories were identified from among the participants of this experiment. The actual experimental design for the Fifth Round Intercalibration consists of the participants collecting, and subsequently analysing, water samples by a variety of common techniques from some suitably homogeneous water body using a single oceanographic platform. It would then be possible to determine the relative differences between sampling devices and their methods of deployment that result from contamination or other influences. As part of this experiment it was also intended to examine a variety of storage and pretreatment procedures and their effect on the results of sample analyses. The samples collected during the field operations were then to be returned to each participant's own laboratory for analysis. This approach was largely adopted for consistency with earlier rounds and to ensure that the conditions under which the participants' analytical performance were previously assessed would also apply to the analytical procedures employed within the Fifth Round.

### Previous Intentions with regard to the Sixth Round Intercalibration

Following the successful completion of the Fifth Round Intercalibration there remained one variable to be tested within the present series of intercalibrations, namely the examination of the influence and effect of different oceanographic sampling platforms on water sampling. The Sixth Round was conceived to examine these influences and involved a multi-ship exercise in a marine area accessible to vessels from ICES member states. Such a multi-ship experiment should permit us to establish the overall comparability of trace metal data from various institutions involved in marine monitoring and research. This final experiment could also serve as a training programme for those scientists who had not participated in early ICES intercalibrations or who had limited experience in these matters.

### Related IOC Activities

Within its GIPME (Global Investigations of Pollution of the Marine Environment) Pilot Project, the IOC intends to conduct a number of intercalibration and training exercises for trace metals in seawater. The agency responsible for the design and execution of these experiments is the IOC's Group of Experts on Methods, Standards and Intercalibration (GEMSI) under the chairmanship of Dr. Neil R. Andersen. Although conceived during the course of the ICES series of intercalibrations for trace metals in seawater, the progression of planned IOC intercalibrations follows very closely the aims and objectives of the ICES experiments. Thus the IOC intercalibration series consists of a high-level standards round, very similar in scope to the first intercalibration in the ICES series; a low-level, or seawater, intercalibration similar in design to the ICES Fourth Round Intercalibration; and a sampling intercomparison designed to examine the influences of samplers and deployment procedures upon seawater samples collected with them. The IOC plans for the GIPME Pilot Project also include training aspects but it was understood that this could only be achieved on completion of the intercalibration activities.

Due to the advanced stage that the ICES intercalibration series had reached by 1979 and the considerable value of the results of these experiments to the design and conduct of the various IOC intercalibrations, it was possible for the IOC to proceed with their intercalibration of sampling procedures without the necessity of conducting its first and second intercalibrations, provided that enough previously calibrated and competent laboratories could be attracted to participate. Largely due to the progress made in the course of the ICES Fourth Round Intercalibration and the willingness of several of the participants of that experiment to be nominated to the IOC exercise by their national authorities, it was possible for the IOC to undertake a viable sampling intercalibration at Bermuda in January 1980. Participants in this experiment (identified by the acronym PANCAL-80) were drawn from 9 countries, of which 6 are ICES member states. The participants were brought together at the Bermuda Biological Station (BBS) in order to carry out a sequence of trace metal sample collection at Panulirus Station from the U.S. Research Vessel 'Kelez' which was temporarily based at St. George, Bermuda. Whilst the intercalibration design had been predicated on each of the participants taking samples back to his home laboratory for final metal analysis, intensive efforts by the staff of the BBS had resulted in the rapid construction of a clean laboratory suitable for the conduct of trace metal analyses and the acquisition of a number of atomic absorption spectrometers. Consequently it was possible for some participants to carry out preliminary analyses at the BBS during the course of the sample collection program. This feature, combined with the fact that some aspects of the PANCAL-80 experiment parallel portions of the original design of the ICES Fifth Round Intercalibration, convinced those of us who participated in PANCAL-80 that we can complete the ICES Fifth and Sixth rounds in one major exercise and furthermore include within it a training component or workshop.

## POTENTIAL REVISIONS OF THE ICES FIFTH ROUND INTERCALIBRATION

We had originally intended to treat the sampling intercalibration, the multi-ship intercalibration and the training workshop on marine analytical procedures for trace metals in seawater as separate experimental entities. From the experience gained during the PANCAL-80 exercise it now appears both feasible and potentially valuable to combine all these individual experiments into a single experimental format. The real possibility therefore exists to include in the design of the Fifth Round Intercalibration aspects of the projected Sixth Round plus a major training component. In the following sections we propose various options for the ICES Fifth, and potentially final, Intercalibration Exercise for Trace Metals in Seawater.

### First Option - Intercalibration of Sampling Procedure Only

The first option considered is to leave the experimental design as originally formulated. This experiment would include a comparison of different sampling devices and their methods of deployment using a single oceanographic vessel. Participation would largely be by invitation based upon laboratory performances in previous ICES intercalibrations. In this exercise land-based laboratory facilities would be used solely for the assembly and preparation of sampling equipment. The major requirement for this type of experiment is an oceanographic vessel capable of accommodating approximately 10 scientists and of deploying kevlar, plastic-coated steel and stainless steel hydrowire. Shipboard laboratory space (ca 40 m<sup>2</sup>) would be needed to rack, and process the water from, a variety of sampling bottles of volume up to 30 litres. Such space should be as clean as possible. If necessary, small laminar-flow bench units could be installed to provide clean working areas. We envisage such a vessel being of about 1000 tonnes displacement, or 60 metres in length, such as the FRG vessel 'Gauss', the Canadian vessel 'Dawson' or the UK vessel 'Scotia'. The choice of area of operations would be based upon the availability of a reasonably sized body of homogeneous water near to the home-port of the vessel donated. It should be noted that it would be possible to conduct such an intercalibration on a somewhat smaller vessel if a suitably convenient homogeneous water mass can be found, but this would require land-based facilities close to the site of oceanographic operations.

### Second Option - Intercalibration of Sampling Procedure combined with On-Site Analysis

A minor variant of the original design would allow for a portion of the intercalibration samples to be analysed at a single shore-based laboratory during the course of the experiment. This in turn would permit an increase in the number of laboratories participating in the exercise over those that would have participated by invitation. Furthermore, this approach provides a measure of security over the integrity of the experimental design and assumptions since it would allow a rapid assessment of

the homogeneity assumption and internal sample contamination during the course of the exercise. The requirements for oceanographic vessels would be identical to those in the first option but the requirements for land-based laboratory facilities would be more stringent. Such facilities should include a minimum of 60 m<sup>2</sup> of ultra-clean laboratory space equipped with class 100 laminar flow hoods. An adjoining area of 20 m<sup>2</sup> containing atomic absorption spectrometers and electrochemical analysers would also be required. Facilities of this type would permit up to 30 participants to carry out some analyses during the course of the experiment on a rotation basis and for them to undertake an on-site intercomparison of analytical procedures.

#### Third Option - Multi-Ship Intercalibration Exercise with On-Site Analyses.

In this option it would be possible to include the multi-ship intercomparison originally intended for inclusion in the ICES Sixth Round Intercalibration. The final experimental design would depend on the number and types of ships involved and the type of port facilities that are available. In this experiment it becomes mandatory that the site of oceanographic operations be close to a port or ports where scientists and equipment can be exchanged between vessels several times during the experiment. The requirements for laboratories on the vessels and those onshore remain similar to those required for the second option above.

#### Fourth Option - Multi-Ship Intercalibration Exercise with Training Components

The most ambitious format for the ICES Fifth Round Intercalibration would involve a substantial training component. The ship requirements for this exercise are identical to those contained in the previous option. There would be, however, rather larger demands for shore-based laboratory facilities. To a large extent these additional requirements are dependent upon the length of the period within which the experiment has to be conducted. In our view, the most appropriate manner in which to proceed with an exercise of this kind is in two stages. The first stage would involve a small number of participants undertaking the sampling intercalibration aspects of the experiment. In the second stage both the shore-based and shipboard facilities would be turned over to a general workshop within which both training and analytical intercalibrations could be conducted. Only a single oceanographic vessel would be required for the second stage. Thus it is possible to visualise a period of say 3 to 4 weeks being devoted to the sampling intercalibration which would include some on-site analyses of samples collected at sea. Once this stage had been completed the remaining participants could undertake shipboard sample collection and on-site analyses as part of a training and intercalibration workshop. We envisage that this latter operation could last from 3 weeks to 1 month depending upon the number of participants involved.

## CHOICE OF A FINAL FORMAT AND DESIGN FOR THE FIFTH ROUND INTERCALIBRATION

During the second meeting of the Marine Chemistry Working Group all the various options outlined above were considered by the Coordinating Group. It was concluded that it would not be possible to decide which of these options should be chosen until formal offers of ships and laboratory facilities for the conduct of the exercise had been made. Once the extent of such offers had been determined it would be a simple matter to choose the most appropriate experimental format for early completion of this series of intercalibrations. It was also agreed, based upon our experience during PANCAL-80, that the authorities responsible for the provision of vessel and laboratory facilities should take the lead in further logistical planning for the experiment. The Coordinating Group, however, is willing to assist in any way it can in developing more detailed plans once information on ships and facilities are known but trusts that the lead will be taken by those able to commit resources for the successful completion of this important experiment.

## CONCLUSIONS

A number of options exist for the ICES Fifth Round Intercalibration for Trace Metals in Seawater, some of which allow for early completion of the entire set of intercalibrations in this series. The final choice of the most suitable format for this experiment depends upon the availability and nature of oceanographic vessel and shore-based laboratory facilities. The early identification of those resources that can be committed by ICES member states and institutions will enable the most appropriate and beneficial format to be chosen rapidly. It is recommended that those authorities donating resources for the conduct of the intercalibration should be invited to take the lead in the overall design and planning of this experiment.

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