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Workshop Report No. 112



IOC-IAEA-UNEP
Group of Experts on Standards and References Material (GESREM) Workshop

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SUMMARY REPORT

1. BACKGROUND

GESREM was created as a forum for both users and producers of reference materials to jointly identify priorities for new reference materials and to define efforts for producing them.

GESREM Accomplishments:

(i) Catalog of reference materials - global perspective

(ii) Two reference materials composed of homogenized mussel tissue; one to be certified for trace metals, the other for organochlorine and other hydrocarbons.

(iii) workbook on proper use of reference materials.

Purposes of the workshop:

(i) review current status of availability of reference materials for inorganic nutrients in seawater, marine algal pigments, marine algal biotoxins;

(ii) develop appropriate collaborations that may accelerate availability of needed reference materials;

(iii) identify specific actions that the sponsors should take to further the availability of new reference materials.

2. TOPICAL REPORTS

2.1 INORGANIC NUTRIENTS IN SEA WATER

Don Kirkwood gave a brief history of the ICES nutrients intercomparison exercises from the mid-1960s to the present, with particular reference to the materials that were used as test samples.

The first two exercises involved a small number of research vessels, mainly from Baltic countries. These met by private arrangement and exchanged freshly-drawn seawater samples which were analyzed almost immediately afterwards in on-board laboratories.

Interest in these activities was growing and in 1970 a laboratory based exercise involving 45 laboratories worldwide was organized. Recognizing the problems of instability of natural seawater, standard solutions prepared by the Sagami Chemical Research Center (Japan) were used as the test materials.

There was a long gap after NUTS I/C 3, but for NUTS I/c 4, Kirkwood and Aminot (1991) decided they should aim for more realism by using materials that had at least began their life as natural seawater. One of the samples they used was a deep-water sample from near Greenland, simply bottled without any treatment, and although this material has since been shown to have only a limited stability, it proved to be reasonably satisfactory for the purpose and duration of that exercise.

Samples of naturally depleted shelf seawater were also included. These contained nutrients concentrations below the detection limits of most techniques, and were very useful in identifying biased results.

The most successful sample in terms of indicating the way forward to the eventual production of a reference material was a natural shelf-seas water that was filtered, bottled in glass, then heat-sterilized in an autoclave. This sample showed excellent stability for nitrate and only a small problem for phosphate, namely that prolonged storage gives rise to gradual dissolution of silicate from the glass bottle with simultaneous release of the small but significant phosphate impurity concentration naturally present in the glass.

In the interim between NUTS I/C 4 and 5, further work by Aminot confirmed that ammonia and nitrite concentrations could be stabilized by the

same procedure but the disadvantage remained that because the process involved glass bottles, silicate could not be included in the range of determinands studied.

The NUTS I/c 5 samples were distributed around the end of 1992 and 132 laboratories submitted results. A complete analysis of the data is contained in a draft report submitted to the ICES Marine Chemistry Working Group in February, 1994 at IFREMER, Brest, France. It is anticipated that ICES will publish the full report in its Cooperative Research Report Series, and all participants will be on the mailing list for the next exercise of this kind, probably commencing in late 1996.

To date participation in these exercises has been free of charge, but as their scope and size continue to increase financial support may be necessary to ensure their continuance. Particular thanks are due to IFREMER for their support for the development of techniques for the production of the necessary reference materials, full details of which will be included in the NUTS I/C 5 report. Kirkwood reiterated the intent of ICES to continue its series of nutrient intercomparisons, and that the current organizers (Aminot, Kirkwood) wanted to ensure participation on a global basis. He admitted there were limits to the number of labs that could be handled. The last intercomparison had 132 labs, the next (perhaps in 1996) will probably have 200. These efforts cannot be counted on as a source of reference materials for general use.

Shier Berman described a material that his organization (NRC-Canada) hopes to make available as a certified reference material in the near future. His water is from the Nova Scotian shelf from 200 m at a total depth of 250 m. The water has been "treated" (not chemically) but for commercial reasons the nature of the treatment cannot be disclosed at this stage.

Stability studies have been carried out over approximately 18 months. Despite some instrumental problems that initially suggested some instability, there is now reason to believe that the material has the required stability. Approximate concentrations are: phosphate 1.6, nitrate 20, silicate 15 and ammonia 1.5 micromole/1. Salinity is 34.8 psu.

The product will be packaged in high density polyethylene. He asked for the groups' advice on package size, and was informed that 50 ml would probably be the most generally suitable. Berman stated that a second large sample will be collected and processed, and submitted for certification. Unanswered questions are: can storage for at least 3 yrs be obtained; what is optimal sample treatment? Berman noted the need a second, independent, method for the certification process. The group suggested that a deep water (2000 m) sample should be obtained as well.

Paul Ridout described a product which his organization (Ocean Scientific International) has already been marketing form some months. It is a North Atlantic surface water, naturally low in nutrients, which has been allowed to stand for several months in a polyethylene storage tank in sunlight to encourage further natural depletion of nutrients. This water is then filtered and is currently available in 1 liter polyethylene bottles.

It is described as Low Nutrient Seawater (LNS) and the following information on concentrations is given: phosphate less than 0.05, silicate less than 1.00, nitrate less than 0.08, nitrite less than 0.05 micromole/l. The product is described as being suitable for use as a matrix for the preparation of working calibration solutions for the determination of nutrients and it is particularly convenient for those laboratories which analyze seawater samples infrequently and do not wish to go to the trouble of producing their own LNS in bulk, as is customary in more oceanographically oriented laboratories. It is also useful for testing the analytical set-up by searching for biases due to presence of salt.

Bath Berman and Ridout indicated they would welcome the support of volunteer laboratories prepared to assist them in further stability studies and several attendees indicated their willingness. Both agreed to act as coordinators for the data produced by these volunteers on their respective materials, and report back to GESREM at a later date. (Note: Ocean Scientific International has begun testing a natural sea water reference

material. The origin and treatment of this material is not known, but it is available to expert laboratories for evaluation purposes.)

2.2 MARINE ALGAL TOXINS

Michael Quilliam stated that NRC-Canada has made good progress on toxin standards and reference materials, having now produced certified calibration solutions for domoic acid (DACS-1B), okadaic acid (OACS-1), and four PSP toxins Ø saxitoxin, neosaxitoxin, GTX2 and GTX3 (PSP-1), and certified mussel tissue reference materials for domoic acid (MUS-1) and DSP toxins (NUS-2). NRC will continue to work on addition of GTX1 and GTX4 to the PSP-1 calibration solution package; production of MUS-3, a mussel tissue reference material for PSP toxins; and possibly production of a DTX1 certified calibration solution.

He suggested that we should explore the interest and feasibility of plankton reference materials (e.g. Nitschia pungens or Gymnodinium brevis) that might serve a dual purpose as both a toxin and pigment reference material. Experiments to determine the stability of different types of preparations (e,g. thermally stabilized liquid slurry, or lyophilized material) would have to be conducted. NRC might be approached for this study.

There is a need to continue improvement of quantitative analytical methods for toxins in 'general. An AOAC collaborative study is being conducted an domoic acid analysis and it is possible that similar projects on DSP and PSP toxins might be conducted.

The proposed MUS-3 reference material for PSP toxins may be put through an intercomparison exercise first. This could help to evaluate and improve available analytical methods as well as assist in the certification of the material.

The state of the art for other toxins (ciguatoxins, maitotoxins, brevetoxins, etc) appears to be insufficient at this time to consider preparation of reference materials. Preparative isolation of sufficient quantities of toxins will be required. Possible collaboration between organizations should be explored (e.g. NMFS and NRC for calibration solution of ciguatoxin).

Dissemination of information on methodologies is important, and includes such available routes as AOAC, IUPAC, GESREM, NRC Technical Reports, etc. News groups on an electronic mall system, or bulletin boards would be useful. Better use of the Harmful Algal News should be explored.

2.3 MARINE ALGAL PIGMENTS

Rodger Dawson reported on recent discussions between himself and scientists at NIST regarding development of reference materials for algal pigments. The NIST is expanding its efforts on pigments in foods and might be able to take on some aspects of the marine pigment needs. Several exploratory studies were defined, to be undertaken as time permits. A sample of Sargassum from near Bermuda has been analyzed by Dawson and found to have a pigment suite of interest. Dawson stated that the final report from a SCOR working group on pigments would be out shortly. Once available, a community-based set of priorities would be established that could be used to guide the preparation of pigment reference materials.

3. CLOSING DISCUSSION

In those cases where a "certification" is based on a specific analytical method, rather than the preferred two independent methods, the workshop agreed that a complete description of the analytical method used for the certification should be widely available. The publication of reference methods was suggested as an additional responsibility for GESREM. This publication should not take the place of the peer-reviewed literature or publication of methods validated by collaborative studies (i.e. AOAC, ASTM), but should be a description of methods actually used in the certification process. It was agreed that this proposed new responsibility would be brought before the sponsoring organizations for consideration.

ANNEX I

AGENDA

1. BACKGROUND

2. TOPICAL REPORTS

2.1 INORGANIC NUTRIENTS IN SEA WATER
2.2 MARINE ALGAL TOXINS
2.3 MARINE ALGAL PIGMENTS

3. CLOSING DISCUSSION

ANNEX II

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