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# ATLANTIC REGION

# LABORATORY QUALITY CONTROL WORKSHOP

MARCH 5 - 6, 1980

PROCEEDINGS

Surveillance Report EPS-5-AR-81-5

Atlantic Region

# ENVIRONMENTAL PROTECTION SERVICE REPORT SERIES

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# ATLANTIC REGION
# LABORATORY QUALITY CONTROL WORKSHOP
## March 5-6, 1980
## PROCEEDINGS

Compiled under the auspices of the
Regional Laboratory Evaluation Committee

Members: Dr. H.S. Samant, Chairman
Environmental Protection Service

Dr. D.H. Loring
Marine Ecology Laboratory

Dr. S. Ray
St. Andrews Biological Station

Observer: A. R. McIver
Environmental Protection Service

Compiled
By: G.A. Packman
Environmental Protection Service

NOVEMBER, 1981

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# FOREWORD

Quality control is important in any enterprise which results in an end product. It is essential when the end product is laboratory data upon which scientific interpretations and regulatory decisions are to be made. Unless the quality of the data is precisely known, meaningful interpretations and decisions are difficult, if not impossible, to make.

The Environmental Protection Service is required to make decisions routinely on the basis of chemical analytical data submitted. This situation specifically applies to the administration of the Ocean Dumping Control Act where recommendations by the Regional Ocean Dumping Advisory Committee (RODAC) are dependent on the concentrations of specified contaminants in dredge spoils. In order to have some understanding of the laboratory capability in the Atlantic Region, RODAC established a Laboratory Evaluation Committee to develop a mechanism for close liaison and frequent exchange of scientific information between government, consultant, university and other laboratories in the Region. In consultation with all the interested organizations the Laboratory Evaluation Committee recommended an on-going quality control program, including periodic reciprocal laboratory visits and technical workshops. Although the quality control program was primarily developed for RODAC requirements it may also be applied to laboratory measurements relative to other programs.

After developing the mechanism the Laboratory Evaluation Committee conducted a quality control round robin covering trace metals in sediments with specific emphasis on cadmium. The results of this round robin have been reported in Samant et al (1979). As a follow-up this workshop was expected to discuss the findings of the round robin in detail

and to recommend a future course of action. In addition the participants also heard presentations on the U.S. Environmental Protection Agency laboratory certification program, overviews of quality control and sampling methods as well as standard reference materials.

The papers included in this publication have been presented as they were received.

## LITERATURE CITED

Samant, H.S., D.H. Loring and S. Ray. 1979. Laboratory evaluation program, First quality control round robin, EPS Surveillance Report Number EPS-4-AR-79-1.

## AVANT-PROPOS

Le contrôle de la qualité est important dans toute activité qui a un produit pour résultat. Ce contrôle devient essentiel lorsque ce sont des données de laboratoire sur lesquelles on se fonde pour faire des interprétations scientifiques et prendre des décisions régulatrices qui constituent le produit. A moins qu'on ne connaisse avec précision la qualité des données, il est difficile, sinon impossible, de faire des interprétations et de prendre des décisions.

Le Service de la protection de l'environnement est tenu de prendre couramment des décisions en se fondant sur les données résultant d'une analyse chimique, qui lui sont présentées. C'est expressément le cas en ce qui concerne l'administration de la Loi sur l'immersion des déchets en mer; c'est en effet en se fondant sur les concentrations de certains contaminants présents dans les déblais de dragage que le Comité consultatif régional sur l'immersion de déchets en mer (CCRIDM) établit ses recommandations. Afin de pouvoir connaître les possibilités des laboratoires de la région de l'Atlantique, le CCRIDM a mis sur pied un comité d'évaluation des laboratoires qui est chargé de mettre au point un mécanisme qui assure d'étroits rapports et de fréquents échanges de renseignements scientifiques entre les laboratoires du gouvernement, les laboratoires des experts-conseils, les laboratoires des universités et d'autres laboratoires de la région. Après avoir consulté tous les organismes concernés, le Comité d'évaluation des laboratoires a recommandé l'adoption d'un programme continu de contrôle de la qualité, comprenant des visites périodiques de laboratoires et des ateliers techniques. Bien que le programme de contrôle de la qualité ait d'abord été mis au point pour répondre aux besoins du CCRIDM, on peut également l'appliquer aux mesures de laboratoire relative à d'autres programmes.

Après avoir mis au point le mécanisme, le Comité d'évaluation des laboratoires a effectué une ronde préliminaire de contrôle de la qualité portant sur les métaux à l'état de trace dans les sédiments en mettant particulièrement l'accent sur le cadmium. Les résultats de cette ronde préliminaire ont été publiés dans le rapport de Samant, Loring et Ray (1979). On s'attendait à ce que, le présent atelier fasse fonction de suivi et qu'à cette fin, il discute en détail des résultats obtenus lors de la ronde préliminaire et recommande un plan d'action pour l'avenir. Les participants à l'atelier ont également entendu des présentations relatives au Programme de certification de laboratoires de la U.S. Environmental Protection Agency et se sont vu présenter des aperçus généraux portant sur les méthodes de contrôle de la qualité et d'échantillonnage ainsi que des documents de référence standard.

Les mémoires qui font partie de la présente publication sont présentés dans la forme où ils ont été reçus; ils n'ont pas été révisés.

## DOCUMENT CITE

Samant, H.S., D.H. Loring and S. Ray. 1979. Laboratory evaluation program, First quality control round robin, EPS Surveillance Report Number EPS-4-AR-79-1.

# ACKNOWLEDGEMENTS

The Laboratory Evaluation Committee would like to thank those contributing papers to the workshop, acknowledging that theirs was the major effort which resulted in this publication. The Committee would also like to thank all of the participants in the workshop for their input to the discussions, as well as those individuals and laboratories which participated in the Quality Control Round Robin exercise.

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# SUMMARY AND RECOMMENDATIONS

1. Several presentations were made in the workshop covering the various aspects of quality control and environmental measurements.
2. As anticipated in the design of the workshop the participation was somewhat unique, with representation from such varied agencies as the Department of Public Works (DPW), Department of Supply and Services (DSS) and Canadian Coast Guard (CCG) along with groups and agencies normally associated with environmental measurements. This approach was felt to be appropriate because in dealing with multi-faceted projects involving both scientific and non-scientific administrative agencies it is important that each party have a complete understanding of the others' responsibilities and associated complexities.
3. Discussion in the workshop began with a review of the First Quality Control Round Robin of the Laboratory Evaluation Program (Samant et al, 1979) by Dr. D. Loring. Dr. D. Loring pointed out that the noted discrepancies in values, as reported from the Round Robin, were functions of both methodology and laboratory while Mr. S. Abbey noted that the body of analytical data available in the literature for the distributed samples was meager. The conclusion, therefore, was that any ranking of laboratories based on the results of the Round Robin could be questionable.
4. After discussion there was almost unanimous agreement that the preferred methodology for conducting quality control Round Robins involves the use of blind and double blind spikes and standards in homogeneous samples. A compromise approach was recommended in which the Laboratory

Evaluation Committee would supply quality control samples in a Round Robin fashion to government and non-government laboratories to provide the participating laboratories with an additional mechanism for determining the quality of their analyses. This process would, in turn, allow the Laboratory Evaluation Committee to comment objectively to RODAC on results from participating laboratories and advise Public Works or Supply and Services on the suitability of a proposed contractor.

Several weaknesses in this approach were pointed out. Dr. Jamieson stated that successful analysis of a well characterized sediment did not necessarily mean that the collection and analysis of a sample from the field would demonstrate the same degree of accuracy, due to variability inherent in differing sampling techniques and the usual inhomogeneity of samples. Some representatives agreed that certification of a laboratory does not ensure that a given analysis will be accurate as analytical results are dependent upon the individual analysts.

5. The general concensus regarding continuous monitoring of the contractual work was that DPW/DSS should ensure that samples include a few duplicates/replicates and hidden standards. It was recommended that since DPW and DSS may not be familiar with monitoring the quality of analytical work a mechanism should be developed by EPS and other interested agencies to assist DPW and DSS in this regard. It was also recommended that DSS be requested to include clauses in contracts dealing specifically with quality control requirements and the withholding of funds if quality control performance, as determined by hidden standards and duplicates, is not satisfactory in a contractor's laboratory. It was suggested that the Laboratory Evaluation Committee might play an advisory role in assessing the quality of the work and co-ordinating activities related to quality control and split sampling.

6. It was agreed at a subsequent meeting of the Laboratory Evaluation Committee (March 6, 1980) that a second quality control round robin should be conducted as soon as additional standards are available. It is planned to use river sediment standards and MAG-1, and to determine concentrations of cadmium, copper, lead and zinc.
7. It was generally agreed that the workshop was a success and should be an on-going activity which should not be limited to the requirements of the Regional Ocean Dumping Advisory Committee.

# ASSURANCE OF ANALYTICAL EXCELLENCE UNDER THE SAFE DRINKING WATER ACT

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## ABSTRACT

The Safe Drinking Water Act, including most major pieces of U.S. legislation pertaining to the environment, requires regulations be developed to specify quality goals. These regulations, in turn, specify the nature of health related quality goals or standards and require that analytical data be obtained to demonstrate whether these goals are being met. With respect to the Safe Drinking Water Act, the supplier of water is responsible for monitoring the supply for chemical, microbiological and radiological contaminants. If the quality standards are exceeded the supplier is required to report the violation to the State and to the public.

To determine laboratory capability and assure data quality the U.S. Environmental Protection Agency has developed a laboratory approval program for those laboratories performing analysis of drinking water. EPA's program calls for on-site evaluation of Principal State Laboratories every 3 years and an annual performance evaluation of all laboratories analyzing public water supplies under the Act. The annual performance evaluation, which is the most critical part of the approval program, involves providing water supply laboratories with unknown samples for analysis. If the laboratory fails to perform acceptably on these samples it may be denied certification. To renew the initial certification at the end of 3 years a water supply laboratory must pass another on-site

evaluation, as well as a review of its quality control program and its annual laboratory performance records. States with primary enforcement responsibility (primacy) are required to have laboratory approval programs as stringent as the federal if all analyses are not performed in State laboratories.

## 1. INTRODUCTION

Congress, in passing the Safe Drinking Water Act in 1974 (42 U.S.C. 300 f. *et seq*.), Table 1, anticipated that there would be a sufficient number of laboratories available on a national basis to perform the monitoring that is presently required by the National Interim Primary Drinking Water Regulations (NIPDWR) and those anticipated in the future. Traditionally, States and a few commercial laboratories have performed most of the analyses for particular water supplies, however these regulations, in specifying mandatory monitoring frequencies and maximum contaminant levels (MCL's), have severely taxed the analytical capability of several States and many private laboratories. This occurrence continues to pose a dilemma for the Office of Drinking Water on how to provide a sufficient number of capable laboratories for the support of the drinking water program while assuring the Office that consistent data quality can be maintained.

The specific analytical needs of the Office of Drinking Water are varied and include microbiological, chemical (including both inorganic and organic compounds) and radiochemical analyses. Sophistication in analytical procedures range from simple bacterial culturing techniques to gas chromatographic-mass spectroscopic analysis (Table 2).

## 2. IMPLEMENTATION

As indicated previously EPA's laboratory need for drinking water covers both laboratory "availability" and "capability". At issue, therefore, is how best to achieve the Agency's quality assurance goals of improving data quality and providing quantitative estimates of that quality to support the compliance aspects of the Act. To achieve these goals for drinking water EPA has developed a laboratory approval program that is based in regulation. According to 40 CFR 142.10 (b)(3) and (b)(4) a State has primacy (in part) if it:

> (b) Has adopted and is implementing adequate procedures for the enforcement of such State regulations, such procedures to include:
>
> (3) The establishment and maintenance of a State program for the certification of laboratories conducting analytical measurements of drinking water contaminants pursuant to the requirements of the State primary drinking water regulations, including the designation by the State of a laboratory officer, or officers, certified by the Administrator, as the official(s) responsible for the State's certification program. The requirements of this paragraph may be waived by the administrator for any State where all analytical measurements required by the State's primary drinking water regulations are conducted at laboratories operated by the State and certified by the Agency. Until such time as the Agency establishes a National quality assurance program for laboratory certification the State shall maintain an interim program for the purpose of approving those laboratories from which the required analytical measurements will be acceptable.
>
> (4) Assurance of the availability to the State of laboratory facilities certified by the Administrator and capable of performing analytical measurements of all contaminants specified in the State primary drinking water regulations.

Until such time as the Agency establishes a National quality assurance program for laboratory certification the Administrator will approve such State laboratories on an interim basis.

To implement EPA's laboratory approval program (Table 3), a three phased program was developed. This program is outlined in the Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies (EPA 600/878-008). Examples of the evaluation criteria are in Figures 1-4. In the first phase of the program all laboratories were granted Interim Approval. This was based either on prior knowledge of laboratory capability from some other EPA program or done administratively. The present phase, Interim Certification, is designed to improve laboratory quality where it is needed and not impair operations at laboratories which are functioning well. During the Interim Certification phase laboratories are evaluated on-site using the technical criteria contained in the Manual as guidance and only the analytical methods cited in Regulations or otherwise approved by EPA are considered mandatory. At some point in the future EPA is considering a regulatory certification program, a Certification phase, where the criteria used for the on-site visit would be mandatory requirements for the laboratories.

## 3. INTERIM CERTIFICATION

The Environmental Monitoring Support Laboratory in Cincinnati, Ohio (EPA) has initiated the national Interim Certification program for water supply laboratories by determining that EPA's Regional Offices and their laboratories have the capability to carry out the chemistry and microbiology portions of the program. Once this decision was made the Regions were ready to perform the on-site evaluations required for certification of Principal State Laboratories. In nonprimacy States the Regions have been conducting the evaluations and granting interim certification to Local Laboratories. Since certification of a Principal State

Laboratory may affect primary enforcement responsibility the State must be notified of any adverse action and given the opportunity for a hearing as provided in 40 CFR 142, National Interim Primary Drinking Water Regulations Implementation. Few, if any, EPA Regions have the expertise to certify radiochemistry laboratories, and the Environmental Monitoring and Support Laboratory in Las Vegas, Nev. (EMSL-LV) has assumed the same quality assurance responsibilities that the Regions have for chemistry and microbiology.

EPA is organized into 10 different Regional Offices and these Offices have primary responsibility for implementing the water supply certification program. This responsibility includes review, approval, and overview of State laboratories and certification programs to assure compliance with conditions for assumption of primary enforcement responsibility. Also, the Regions are responsible for on-site evaluation and certification of Principal State Laboratories; however Regional evaluation teams must be approved prior to conducting evaluations. Specific duties of the Regions include:

- Approve State programs to certify local laboratories.
- Conduct on-site evaluations of Principal State Laboratories
- Coordinate performance evaluations for all laboratories in the Region.
- Participate in the annual review of State certification programs and performance evaluation reports.
- Provide technical assistance to water supply laboratories that need to be upgraded.
- Operate certification program in nonprimacy States.

For radiochemistry, EMSL-LV will recommend to the Regional Offices renewed certification of Principal State Laboratories at 3-year intervals. Renewal criteria include annual performance records and an on-site evaluation conducted during the year of renewal.

Interim Certification starts when the laboratory makes a formal request to the Region stating the type of analysis to be evaluated. The Principal State Laboratory and its Local Laboratories must have the capability of performing all analyses; however an individual laboratory which is a part of a principal State laboratory may be certified for only one, several or all of the analyses included in the Interim Primary Drinking Water Regulations. A request for certification of a laboratory for which the Region has jurisdiction should come from the laboratory director. The Region should respond within 30 days and a mutually agreeable date and time should be set for laboratory evaluation.

Before conducting the on-site evaluation the Region shall:

- Hold a pre-evaluation conference with appropriate laboratory and field activity representatives to establish a schedule that would have a minimum impact on the laboratory activities.
- Request that a variety of tests be scheduled during the on-site evaluation.
- Arrange for the laboratory staff to be available during the on-site visit.

During the on-site visit the team, composed of a professional chemist, microbiologist and engineer, shall:

- Evaluate the procedures and equipment used for those specific analyses for which the laboratory has requested certification.
- Review the records and written standard procedures for compliance with the required sampling frequency; check sampling program, sample transit time and resample notices, if appropriate.
- Evaluate the Principal Laboratory's quality control program to determine:
  - Does the laboratory have a quality control program in effect?
  - Do quality control data show that this program is being implemented?

  - Does the data show that the laboratory is producing valid results?
- Examine and document general procedures including the following items:
  - Sampling location guidance
  - Sampling procedures
  - Sample identification
  - Prompt transport of samples to laboratory
  - Sample frequency
  - Follow-up of positive samples
  - Dissemination of data

  Note: This information should be obtained by the Regional Water Supply Division's engineer on the team and be included in the narrative report that is forwarded to the State; however only those items in the above list for which the laboratory is directly responsible shall affect certification.
- Complete the on-site evaluation form during the visit.
- Review the results of the evaluation with the director of the laboratory, the director of field activities and appropriate staff members. The review should:
  - Discuss deviations in the observed procedures and records.
  - Recommend procedural changes in equipment and supply needs, staffing requirements and facility improvements, as necessary.
- Conclude with a discussion of how the Region can aid the laboratory.

After the on-site visit the Region can take one of three actions for each analysis involved:

- Certified (interim) - a laboratory that meets the minimum requirements as determined by the evaluation team using the manual. The certification shall be for 3 years.

- Provisionally certified (interim) - a laboratory that has been given a grace period of up to 1 year to correct deficiencies. In no case should provisional certification be given if the evaluation team believes that the laboratory lacks the capability of performing the analysis. Laboratories placed in this category must be re-evaluated unless they can document, in some other way, that the deficiency has been corrected.
- Not certified - a laboratory that does not meet the minimum requirements as determined by the evaluation team using the manual. A laboratory in this category may appeal to the Regional Administrator by requesting re-evaluation by another Regional team or by a team from another EPA laboratory. Should the re-evaluation confirm the "not certified" classification the laboratory must correct the major deficiencies noted and then request re-evaluation, or the State can request that another laboratory be evaluated to perform the analysis.

## 4. QUALITY ASSURANCE SUPPORT

Documenting the ability of a laboratory to consistently produce valid data is the primary goal of the certification effort. Quality assurance is the backbone of the entire program. EPA will provide two types of samples to Regional and Principal Laboratories.

- Calibrated reference materials and quality control samples.

  Known-value quality control samples for microbiology and chemistry are developed and furnished by EMSL-CI directly to Regions and through the Regions to state and local laboratories. Calibrated radioactive samples will be provided by EMSL-LV. The known-value samples are to be used by the laboratories as independent checks on reagents, instruments or techniques; for training analysts; or for comparative analysis within the laboratory. However these samples are not intended to replace routine check samples or standards run as part of an internal quality control program. Although no certification or other formal evaluation function directly results from the use of these samples their routine use will provide evidence that an acceptable laboratory quality control program is in operation. Requests for samples are made through the appropriate EPA Regional Office.

- Performance Evaluation Samples

  Appropriate performance evaluation samples will be furnished to all Principal Laboratories as part of the Interim Certification program. Unacceptable performance could serve as a basis for denying the laboratory certification. In such cases, however, appropriate technical assistance, as well as additional performance samples, will be provided to the laboratory. Re-examination may be required if key analysts leave a particular laboratory during the 3 year certification period.

## 5. SUMMARY

The U.S. Environmental Protection Agency's laboratory certification effort for the drinking water program is in its infancy and we anticipate the need to resolve key issues such as reciprocity, decertification, chain of custody and perhaps separate Regional rules and procedures. However significant these issues may be, laboratories, and in fact analysts, have the major responsibility to insure only quality data is reported. The Safe Drinking Water Act requires that the public be notified when an MCL has been exceeded, and if the violation was based on faulty data then the public has been misused -- worse yet, if the error in some way affects the public health.

REFERENCES:

Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies, Office of Monitoring and Technical Support (RD-680), U.S. EPA, Washington, D.C., 20460, EPA 600/8-78-008, May 1978.

## TABLE 1. THE SAFE DRINKING WATER ACT (Public Law 93-523), 42 USC 300f *et seq.*, 1974

The Act provides for:

- Drinking water regulations applicable to all supplies serving more than 25 persons
- National Academy of Sciences review of regulations
- Extensive research programs
- Special surveys
- Improved analytical methods
- New treatment procedures
- New methods of delivery of safe water

TABLE 2. INTERIM PRIMARY DRINKING WATER REGULATIONS.

| Constituent | MCL | Analytical Method | Frequency of Measurement |
|---|---|---|---|
| Biological | | | |
| Coliform bacteria | Mean 1/month | MPN or MF | 1-500/month[1] |
| Turbidity | 1-5 NTU | Nephelometric | daily |
| Inorganic Chemicals | | | |
| Arsenic | 0.05 mg/1 | AA | 1-3 yrs |
| Barium | 1.0 | | |
| Cadmium | 0.010 | | |
| Chromium | 0.05 | | |
| Lead | 0.05 | | |
| Mercury | 0.002 | | |
| Selenium | 0.01 | | |
| Silver | 0.05 | | |
| Fluoride | 1.4-2.4[2] | Electrode or Colormetric | |
| Nitrate | 10. | Colormetric | |
| Organic Chemicals | | | |
| Endrin | 0.0002 mg/1 | GC | 3 yrs |
| Lindone | 0.004 | | |
| Methoxychlor | 0.1 | | |
| Tovaphene | 0.005 | | |
| 2,4D | 0.1 | | |
| 2,4,STP (silvex) | 0.01 | | |
| Trihalomethanes | 0.10 mg/1 | MS-GC | 4 samples/qtr |
| Radiochemistry | | | |
| Gross alpha | 15pCi/1 | EPA | 2-4 yrs |
| Ra-226 ¼ 228 | 5 | | |
| Beta | 4 millirem | | |

---

[1] Based on population served

[2] Based on average air temperature

## TABLE 3. TENTATIVE SCHEDULE FOR THE CERTIFICATION OF LABORATORIES

1. Interim Approval — Starting June 24, 1977

EMSL-Cincinnati grants Interim Approval to Regional certification programs.

Regions grant primary enforcement responsibility to qualified States. In States not qualified, the responsibility is assumed by the Regions.

States with primary enforcement responsibility grant Interim Approval to Local Laboratories.

Regions with primary enforcement responsibility grant Interim Approval to Local Laboratories.

2. Interim Certification — by December 1978

EMSL-Cincinnati completes on-site evaluations and grants Interim Certification to Regional Laboratories.

Regions complete on-site evaluations of Principal State and Federal Laboratories using the interim certification manual.

States with primary enforcement responsibility begin to conduct on-site evaluations of Local Laboratories using the interim certification manual or one prepared by a State.

Regions with primary enforcement responsibility begin to conduct on-site evaluations of Local Laboratories using the interim certification manual.

3. Certification — 1979-1980[1]

All water supply laboratories are certified using the certification manual or one prepared by a State.

[1] Estimated effective date of National Revised Primary Drinking Water Regulations.

Laboratory____________________ Evaluator__________

Location ____________________ Date__________

## QUALITY CONTROL

A written laboratory quality control program is available for review. . . . . . . . . . . . . . . . . ___

### *1. Analytical Quality Control*

A record containing results of analytical control tests available for review . . . . . . . . . ___

a. Verification of MF Colonies

At least five coliforms verified from each positive sample . . . . . . . . . . . . . . . . . . ___

Sheen colonies in mixed confluent growth reported and verified (optional)

b. Negative Coliform Controls

A start and finish MF control test (rinse water, medium, and supplies) run with each filtration series . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . ___

When controls indicate contamination occurred, all data on affected samples rejected and resampling requested . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . ___

c. Total Coliform Confirmed Test

Presumptive tubes with heavy growth but no gas production submitted to confirmed test to check for suppression of coliforms. Confirmation procedure carried out every 3 months on one sample from each problem water supply . . . ___

d. Duplicate analyses (optional)

Duplicate analyses run on positive polluted samples not to exceed 10 percent but a minimum of one per month (optional). . . . . . . . . . . . . . . . . . . . . . . . . . ___

e. Positive Control Samples (optional)

One positive control sample (polluted water) run each month (optional)

f. Colony Counting (If More Than One Analyst in Laboratory) (optional)

Two or more analysts count sheen colonies; all colonies are verified; analysts' counts compared to verified counts; procedure is carried out at least once per month (optional)

g. Check Analyses by State Laboratories (optional)

A minimum of samples, proportional to the local laboratory work load, processed by State laboratory (see criteria for recommendations) (optional)

FIGURE 1

## METHODOLOGY

## SAMPLE FORM ONLY

Laboratory____________________

Location____________________

Date__________

Evaluator____________________

| Parameter | Name or description of method | Method used (cite page and year) | | | | Number of analyses (frequency) | | | Satisfactory[1] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | SM | ASTM | EPA | Other | Daily | Weekly | Monthly | Yes | No |
| Arsenic | | | | | | | | | | |
| Barium | | | | | | | | | | |
| Cadmium | | | | | | | | | | |
| Chromium | | | | | | | | | | |
| Lead | | | | | | | | | | |
| Mercury | | | | | | | | | | |
| Nitrate | | | | | | | | | | |
| Selenium | | | | | | | | | | |
| Silver | | | | | | | | | | |
| Fluoride | | | | | | | | | | |
| Chlorinated hydrocarbons:<br>Endrin | | | | | | | | | | |
| Lindane | | | | | | | | | | |
| Methoxychlor | | | | | | | | | | |
| Toxaphene | | | | | | | | | | |
| Chlorophenoxys<br>2,4-D | | | | | | | | | | |
| 2,4,5-TP | | | | | | | | | | |

---

[1] For use only by certifying authority.

FIGURE 2

## QUALITY CONTROL

Laboratory ______________________

Location ______________________

## SAMPLE FORM ONLY

Date ______________

Evaluator ______________________

| Item | Done |  |  | Comments (system used) | Satis.[1] |  |
|---|---|---|---|---|---|---|
|  | Yes | No | Freq. |  | Yes | No |
| Minimum requirements:<br>Quality control data available for inspection |  |  |  |  |  |  |
| Use of unknown performance sample |  |  |  |  |  |  |
| Documented standard curve |  |  |  |  |  |  |
| Standard curve checked prior to each sample set |  |  |  |  |  |  |
| Verification of standards (every 20 samples) |  |  |  |  |  |  |
| Optional requirements:<br>Service contract on balances |  |  |  |  |  |  |
| Use of class S weights |  |  |  |  |  |  |
| Use of NBS-certified thermometer |  |  |  |  |  |  |
| Use of color standards |  |  |  |  |  |  |
| Dating of chemicals |  |  |  |  |  |  |
| For lab analyzing samples other than its own |  |  |  |  |  |  |
| Use of known reference samples |  |  |  |  |  |  |
| Use of duplicate samples |  |  |  |  |  |  |
| Standard deviation calculations |  |  |  |  |  |  |
| Quality control charts or tabulations |  |  |  |  |  |  |

[1] For use only by certifying authority.

FIGURE 3

## THIN WINDOW GAS-FLOW PROPORTIONAL COUNTER

Laboratory____________________

Location____________________

Date__________

Evaluator____________________

SAMPLE FORM ONLY

| Instrument number | Manufacturer | Model | Year | Sample changing | | |
|---|---|---|---|---|---|---|
| | | | | Manual | Automatic | Capacity |
| | | | | | | |

| Counting gas | Window density ($g/cm^2$) | Instrument background | | | |
|---|---|---|---|---|---|
| | | Alpha | | Beta | |
| | | Operating voltage | cpm | Operating voltage | cpm |
| | | | | | |

| Calibration frequency[1] | | | | Service maintenance frequency[2] | | | | Condition[3] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| D | W | M | Other | Q | S | A | Other | G | P | No |
| | | | | | | | | | | |

[1] Daily, weekly, monthly.

[2] Quarterly, semiannually, annually.

[3] Good, operating but needs repair, not operating.

| | |
|---|---|
| Are manufacturer's operating manuals readily available to the operator? | Yes __ No __ |
| Is there a calibration protocol available to the operator? | Yes __ No __ |
| Are calibrations kept in a permanent control chart record? | Yes __ No __ |
| Is a permanent service maintenance record kept on these instruments? | Yes __ No __ |
| Satisfactory | Yes __ No __ |

FIGURE 4

# ROUND ROBINS AND OTHER QUEER BIRDS

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## ABSTRACT

A general outline is presented concerning the problems that can arise in interpreting incoherent data gathered in round-robin collaborative analytical operations. The material presented is based on experience with programs in the evaluation of reference samples, but many of the pitfalls encountered can also occur in similar operations designed to evaluate the performance of participating laboratories.

When Dr. Samant first asked me to participate in this Workshop I protested that my work is far removed from your subject material. As one concerned mainly with the analysis of silicate rocks, and particularly in the evaluation of reference samples for that purpose, I wondered what I could possibly offer to those engaged in controlling the quality of data generated for use in environmental studies. On further reflection, however, I began to realize that our fields of interest have much in common -- i.e. our aims and the materials with which we work may differ but some of our techniques (and indeed our problems) have much in common.

For the benefit of those not familiar with rock analysis let me point out that, traditionally, it involves determination of $SiO_2$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$, FeO, MnO, MgO, CaO, $Na_2O$, $K_2O$, $H_2O$, $CO_2$, $P_2O_5$ and occasionally S and F as well. Those constituents are referred to these days as "major and minor" and to them have now been added the so-called "trace elements", which can mean nearly all of the rest of the Periodic Table. Thus a rock analysis is unique in involving so many constituents whose concentrations may vary from well over 50 percent (such as - $SiO_2$) to fractions of a part per million (such as - Sb or W). Don't ask me why so many constituents are expressed as oxides. That is the way the geologists want them, and we assume that the customer is always right -- except when he isn't.

Now, I understand that you often send samples of known composition (presumably as "blind" controls in a batch of regular samples) to laboratories involved in providing your analytical data. From the results obtained on those controls you can probably deduce something about the quality of data turned out by each laboratory. Our own work is in some respects the reverse of yours -- i.e. we attempt to establish the so-called "true" value of the concentration of each constituent of rock samples intended for use as reference materials. Please note that I do not speak of "standards" because I feel that that term implies a higher degree of reliability in the deduced compositional values than can realistically be expected with rocks.

There is no need to tell an audience like this one just why reference materials are required. To calibrate instrumental techniques, to test new methods, to act as controls in multi-laboratory or even within-laboratory operations, are but a few uses that come to mind.

Many years ago the historic giants in traditional rock analysis, W.F. Hillebrand and H.S. Washington, stated what they considered acceptable limits of deviation that might be expected in a careful rock analysis. Subsequent developments showed that they were much too optimistic. The limits they set might be valid for a careful classical analyst, doing repeat determinations in the same laboratory and, needless to say, using the same method because there were few alternatives available in those days. Thus the classical giants produced excellent precision, but there was really no way of knowing their accuracy. That point was well illustrated in the analysis of an ultrabasic rock intended for use as a reference material. The problem concerned the determination of very low calcium·content in the presence of nearly 50 percent MgO. One laboratory, actually the one with the best overall performance in the entire program, reported an average of 0.03 percent CaO based on the results produced by two different analysts using the identical classical procedure, the two results being very close to one another. Another laboratory, using so-called "rapid methods", reported 0.09 percent. When we tried the determination by atomic absorption measurements, after two different chemical pre-treatments, we found 0.18 percent and were sure that we were wrong. Subsequent atomic-absorption, flame-photometric and other measurements in many laboratories pointed to a value of 0.15. We are not certain how the best laboratory went wrong but we might guess that they followed the established practice of separating small amounts of calcium from large amounts of magnesium by precipitating it as the sulfate in alcoholic medium, apparently without realizing that the separation is not reliable where the magnesium-calcium ratio is as much as 300 to 1.

In the determination of trace elements precision and accuracy generally yield precedence to the need for high sensitivity, but one hopes at least for results that can be of use. How disappointed one can be is illustrated in Table 1, which lists results for silver in the collaborative analysis of three Canadian rocks intended for use as reference materials[1]. Here we really have no idea even of the order of magnitude of the true silver contents. One might conclude merely that MRG-1 contains more silver than do the other two. It happens that additional results, reported after the table was prepared, tended to support those from analyst A -- the lowest of all!

Things are not quite so bad in Table 2 where there is some slight consistency, but look at analyst C! Analyst A did not do so well this time either. Table 3 shows that even a major constituent like silica can show rather frightening dispersion in comparing results from different laboratories. What is particularly disturbing here is that the spectacular developments in analytical methodology between 1931 and 1974 seem to have done little to improve precision.

In the late 1940's workers at the U.S. Geological Survey, and several collaborating institutions undertook a "co-operative investigation of precision and accuracy" in the analysis of silicate rocks. Using the now well-known granite G-1 and diabase W-1 they eventually reported results from a number of laboratories that came as a shock to many people[2]. For silica in G-1, for example, a histogram of the reported

## TABLE 1

### REPORTED RESULTS FOR SILVER (PPM)

| SY-2 | SY-3 | MRG-1 | Analyst |
|---|---|---|---|
| <0.05 | 0.054 | | A |
| 2 | 3 | | B |
| <1 | <1 | < 1 | C |
| 0.4(5)* | 0.2(4) | 1.2(5) | D |
| <3 | < 3 | <3 | E |
| 2 | 2 | 3 | E |
| 1.9(4) | 2.0(5) | 3.5(5) | F |

*Mean of 5 determinations

## TABLE 2

### REPORTED RESULTS FOR BORON (PPM)

| SY-2 | SY-3 | MRG-1 | Analyst |
|---|---|---|---|
| 33(2)* | 45 | | A |
| | | < 5 | A |
| 77 | 98 | | G |
| 178 | 246 | 71 | C |
| 110 | 130 | | H |
| 95 | 110 | 5 | J |
| 83 | 108 | 13 | E |
| 84 | 108 | 9 | K |

*Mean of 2 determinations

## TABLE 3

## STANDARD DEVIATIONS OF SILICA DETERMINATIONS

| Year Reported | Sample Type | No. of Results | *Std. Devn. |
|---|---|---|---|
| 1931 | Glass | 5 | 0.28 (0.09)** |
| 1951 | Granite | 34 | 0.37 |
| 1963 | Tonalite | 14 | 0.26 |
| 1970 | Feldspar | 9 | 0.10 |
| 1972 | Granite | 30 | 0.18 |
| 1972 | Syenite | 36 | 1.06 |
| 1974 | Granodiorite | 35 | 0.46 |

*Per cent (absolute)

**After eliminating one result

results showed a major cluster between 72.2 and 72.5 per cent, with additional values up to 72.7 and a trail of lower values all the way down to 71.1. Other constituents showed a similar spread but the summations, for the most part, were concentrated between 99.7 and 100.2 per cent, suggesting the possibility of compensating errors. Such errors are to be expected in a scheme based on a series of separations, as is mainly the case in the classical analytical methods.

Much agonized soul-searching followed in an effort at finding the so-called "sources of error". The debate ultimately narrowed down to those concerned with sample inhomogeneity and those looking at inter-laboratory factors. The significance of sample inhomogeneity as a source of error has been shown to be minimal as a result of some studies involving experimental designs based on multiple sub-sampling from replicate bottles[3]. By subjecting the resulting data to analysis-of-variance it has been shown that most rock reference samples are sufficiently homogeneous for most purposes -- that is, as long as the analyst uses a sufficiently large sample. However we must remember that these tests were done on proposed reference samples that had undergone homogeneity testing before distribution for collaborative analysis. Errors due to sample inhomogeneity can and do occur in everyday analysis. Much study has been devoted to the science of sampling and there are many excellent references in the literature. In the special case of rocks (and probably of some environmental materials) sub-sample size must be governed not only by particle size and the extent to which the sample has been "homogenized" but also by consideration of the fact that the constituent of interest may occur in one or two particular phases of an essentially heterogeneous matrix[4]. The fact that different phases (in our own case, the constituent mineral species in the rock) may have different physical and mechanical properties does not help matters either.

Let us turn, then, to the question of "inter-laboratory factors", or what might less politely be referred to as "systematic errors". I would go a step further and cite a quotation whose original source I have forgotten: "Never underestimate the importance of stupidity as a force in human affairs". Now that is not a nice thing to say, is it? How can one accuse intelligent scientists of being stupid? Would you like an example?

Several years ago a well-established laboratory in a well-known institution reported results for a certain group of trace elements in a certain group of samples intended for use as reference materials. The procedure used involved pre-concentration via ion exchange, followed by measurement by means of a highly reliable and accurate technique. Unfortunately, in all cases where sufficient data were available for comparison purposes, the results for the particular group of elements produced by this particular laboratory averaged about 50 percent lower than those produced by other laboratories. Further, although those other laboratories had used a variety of different techniques, their results were comparatively well clustered together.

In his "thank-you note" to the laboratory with the low results, the organizer of the program provided, for each element, the median value of all results received from other laboratories, mentioning also that several different methods had been involved. Some months later a second report came from the laboratory in question. They expressed surprise that "everyone else was so high", so they had dismantled and thoroughly cleaned their equipment, re-calibrated it and repeated the analysis. Lo and behold! Their second set of data was very close to their first; therefore, they hinted, everyone else must be wrong! They even postulated some rather shaky reasons why and how others could have gone wrong, but offered no suggestion that anything might be wrong with their own results.

The organizer thereupon undertook some detective work. The original paper describing the method developed and used in the laboratory with the low results was found in the literature, read, and seen to be quite sound. A second paper of theirs was found, in which the same laboratory applied the same method to a number of established reference rocks, producing excellent results. Unfortunately no one seemed to note that those particular samples contained the particular group of trace elements of interest at much lower levels than did the samples where this particular laboratory reported the low results. It would appear that incomplete recovery in the case of samples with relatively higher concentrations of the elements in question was a distinct possibility. Evidently the workers in that well-established laboratory in that well-known institution had forgotten that there is a limit to the capacity of a given quantity of ion-exchange resin to hold certain ions. The possibility of that oversight was pointed out to them in a final letter. There was no reply.

Following the tragicomedy of G-1 and W-1 the U.S. Geological Survey, as well as institutions in many other countries, produced a number of additional rock samples for use as reference materials. All presumably had learned something from G-1 and W-1. Still, the results of all such programs showed at least as broad a dispersion as did those for the two original samples.

With such "wild and woolly" scattered results is it possible to arrive at reliable values for each constituent? To the uninitiated it would appear that, provided sufficient data were available, a mere arithmetic mean of all reported values for each constituent would give a most probably true value. However when that was done for the six samples in the second group produced by the U.S. Geological Survey, the summations of the means for the six samples were found to range from 100.12 to 100.88 percent -- and that without including those "trace elements" present at a sufficiently high level to affect the summations[5]. Although something was obviously wrong it must be admitted that, in most cases, the arithmetic mean was fairly close to the preferred values eventually derived by various special schemes. There were, however, some glaring exceptions, as shown in Table 4. It should be noted at this point that the constituents shown here are present at much lower levels than usual in most rocks. Therefore the methods used in determining them may well have been pushed rather close to their limit of usefulness. That possibility was emphasized by the marked skewness of the distribution of values reported for such constituents. Generally, it was found that skewness in the distribution eventually produced a significant difference between the original crude average and the eventual accepted value.

It should be noted that there appears to be no consistency in the terminology used in describing derived values for concentrations of constituents of reference samples. In the literature one finds terms ranging from the hesitant "preliminary", "provisional", "preferred", through the more assertive "proposed", "accepted", "recommended", all the way to the dogmatic "attested", "certified" and "guaranteed". Worse still, very few of the originators take the trouble to define the term they use. In our own work we have settled on the term "usable values", which I would describe as equivalent to an amber light on a railway signal -- i.e. proceed with caution, prepared to stop at the next signal.

Many different systems have been used for deriving the "best values" from a mass of reported data that is often highly incoherent. Generally these have involved using the mean of remaining values after rejecting those outliers that fail to pass one or another of several different statistical tests. In the case of ores, where comparatively few constituents are sought, where comparatively few collaborating

## TABLE 4

## ORIGINAL AVERAGES VS "PREFERRED VALUES"
(all in percent)

| Sample | Component | Average Flanagan (1969) | Preferred Flanagan (1976) |
|---|---|---|---|
| DTS-1 | $Al_2O_3$ | 0.55 | 0.24 a* |
| | $Na_2O$ | 0.46 | 0.007 R |
| | $K_2C$ | 0.02 | 0.0112 R |
| PCC-1 | $Al_2O_3$ | 0.85 | 0.74 a |
| | $Na_2O$ | 0.05 | 0.006 m |
| | $K_2O$ | 0.01 | 0.004 m |

*R: "recommended" a: "average" m: "magnitude"
(Courtesy: Geostandards Newsletter)

laboratories are involved, where all of them are probably expert in the particular type of material and where, possibly most important of all, all collaborating laboratories have a financial stake in the accuracy of the results, the work is often done according to a fixed experimental design -- i.e. a fixed number of sub-samples from each of two or three randomly selected bottles of sample material. From the observed variances it is possible to deduce whether or not the data are sufficiently coherent and, if so, acceptable recommended values and confidence limits[6].

With rock samples, unfortunately, the large number of constituents required and the highly variable expertise of the participating laboratories make it very difficult to take so rigorous an approach. The highly inconsistent and, one might say, heterogeneous data require rather more empirical treatment, hence my warning to "proceed with caution" in using published compositional values for rock reference samples.

A major shortcoming of many of the selection schemes is the real or apparent assumption of normal distribution of the results for a particular constituent. Such normality is to be expected in controlled experiments such as the collaborative analysis of ore samples, but is more the exception than the rule with the relatively "uncontrolled" work on rocks, particularly for trace elements. In recent years, however, several procedures have been published concerning the processing of skewed data. Generally they involve an approach to the modal value by means of data transformation, stepwise elimination of outlying values, graphical plotting etc.[7-11]

Our own studies have emphasized the importance of the variation in the quality of the work done by different participating laboratories. Although many changes have been made in our evaluation system over the last 10 years it involves essentially the "zeroing-in" on to the results reported by the comparatively few laboratories with the best overall performance. It includes a significant amount of what some might call empirical judgement, but which I prefer to call common sense[12].

If there are so many different ways to deduce a "best value", is there any way of knowing which way produces the truly best result? No generally accepted test is known, but we have proposed two. One of these is the summation of the concentration values of all constituents in a so-called "complete analysis". In Table 5 the summations of values in certificates issued by one originating institution are compared with those of values derived from the same data by our "selective laboratories" method. For all six samples our summations are closer to 100 percent than are the others where, I believe, the values were established by determining the mean of remaining values for each constituent after eliminating all values which differed from the overall mean by more than three standard deviations[13].To be perfectly fair it must be pointed out that the originators of these samples subsequently published a set of recommended values, arrived at by what I consider a much more sensible approach than merely rejecting a few wild outliers[14].

At best the summation test is a rather uncertain one; it can be affected by compensating errors and by certain additional analytical phenomena that I do not propose to go into just now. Perhaps a more reliable test would involve comparing derived results for constituents that have a known relation to one another. For a number of reasons the only combination where this can be applied involves ferric, ferrous and total iron. In Table 6 a comparison is made between two values for total iron -- one derived from results reported as such, the other calculated from values derived for ferric and ferrous from results reported as such. In each case the pairs of values from the "selective laboratories" method are more closely matched than those from other methods. Again,

## TABLE 5

## COMPARISON OF SUMMATIONS OF DERIVED VALUES

| Sample | NIM Certificate | CSC "Usable" |
|---|---|---|
| NIM-D | 100.47 | 100.34 |
| NIM-G | 100.36 | 100.09 |
| NIM-L | 100.81 | 100.16 |
| NIM-N | 100.14 | 100.02 |
| NIM-P | 99.59 | 100.13 |
| NIM-S | 100.43 | 99.94 |

All figures in percent.

## TABLE 6

### Fe 0 (TOTAL) - PERCENT

| | NIM CERTIFICATE | | GSC "USABLE" | |
|---|---|---|---|---|
| Sample | A | B | A | B |
| NIM-D | 16.97 | 17.16 | 16.99 | 17.00 |
| NIM-G | 2.02 | 2.15 | 1.96 | 2.07 |
| NIM-L | 9.77 | 10.00 | 9.95 | 9.91 |
| NIM-N | 9.00 | 9.19 | 8.95 | 8.94 |
| NIM-P | 12.29 | 12.80 | 12.78 | 12.75 |
| NIM-S | 1.40 | 1.51 | 1.44 | 1.40 |
| | USGS 1973 AVERAGES | | | |
| DTS-1 | 8.64 | 9.24 | 8.59 | 8.51 |
| PCC-1 | 8.35 | 8.67 | 8.28 | 8.24 |

A - Derived values of Fe 0 (total)

B - Calculated from derived values of FeO and Fe 0 however, I must emphasize that later work by the originators of the NIM samples has provided better results -- probably because they use a more realistic method.

In Table 7 both tests are used to compare the relative merits of crude averages and selective usable values for three Canadian rocks. The comparatively less satisfactory agreement for MRG-1 has undergone improvement in later work involving more data and a somewhat refined selection procedure.

In Tables 8-11 the two tests are applied to comparing our most recently derived values for some samples from the U.S. Geological Survey with those in an earlier publication and those preferred by the originators[15].

Despite the claims made in the preceding tables regarding the supposed superiority of our method of selection we must admit the limitations of our approach and the limitations of the tests we have applied to compare the validity of derived values. Now let us look at Table 12, where common sense must be our only guide. Here we see a bewildering array of results for tin which seem to show no pattern of consistency; but please note the three sets of results marked by arrows. One of these sets was reported by an analyst who pre-concentrated tin by ion exchange and measured it by mass spectrometry; another by one who separated tin by solvent-extraction of a chelate and measured it by atomic absorption; the third from spectrographic analysis in a D.C. arc with fractional distillation. Incidentally, one analyst was in Australia, the second in Japan and the third in Canada. Yet there does appear to be an encouraging consistency in their results, and that was confirmed by some additional results received after this table was prepared.

We now come to a point that may well be of more direct concern to your work than what has gone before. That is the subject of "analytical method". In the case of tin you may have noticed that I did not say that one result was obtained

## TABLE 7

## "AVERAGES" VS "USABLE" VALUES
## CANADIAN SAMPLES

| | | | SY-2 | SY-3 | MRG-1 |
|---|---|---|---|---|---|
| Averages | Summation | | 100.34 | 100.88 | 100.66 |
| | $Fe_2O_3$ (total) | A* | 6.46 | 6.60 | 18.06 |
| | | B | 6.52 | 6.65 | 18.17 |
| Usable Values | Summation | | 100.21 | 100.29 | 100.16 |
| | $Fe_2O_3$ (total) | A | 6.34 | 6.45 | 17.84 |
| | | B | 6.32 | 6.47 | 17.93 |

All values in percent

*See preceding Table

## TABLE 8

### SAMPLE BCR-1

| | This work | GSC 77-34 | USGS 840 |
|---|---|---|---|
| Summation | 99.95? | 100.35? | 100.61 |
| $Fe_2O_3$ TR | 13.41 | 13.52 | 13.51 R |
| $Fe_2O_3$ TC | 13.44 | 13.54 | 13.58 |

## TABLE 9

### SAMPLE GSP-1

| | This work | GSC 77-34 | USGS 840 |
|---|---|---|---|
| Summation | 100.26? | 100.28? | 100.45 |
| $Fe_2O_3$ TR | 4.30 | 4.33 | 4.33 R |
| $Fe_2O_3$ TC | 4.28 | 4.34 | 4.34 |

## TABLE 10

### SAMPLE DTS-1

| | This work | $\overline{X1}$ | $\overline{X2}$ | GSC 77-34 | USGS 840 | |
|---|---|---|---|---|---|---|
| Summation | 100.31? | 100.31 | 100.31 | 100.41? | 100.75 | |
| Fe O TR | 8.70 | 8.69 | 8.66 | 8.60 | 8.64 | R |
| Fe O TC | 8.73? | 8.71 | 8.73 | 8.61 | 9.24 | |

## TABLE 11

### SAMPLE PCC-1

| | This work | GSC 77-34 | USGS 840 | |
|---|---|---|---|---|
| Summation | 100.38? | 100.45? | 100.34 | |
| Fe O TR | 8.28 | 8.28 | 8.39 | a |
| Fe O TC | 8.29? | 8.24 | 8.72 | |

## TABLE 12

## SOME RESULTS REPORTED FOR TIN (ppm)

| SY-2 | SY-3 | MRG-1 | Analyst |
|---|---|---|---|
| 2.5 | 4.8 | 3.2 | A |
| <10 | <10 | 18 | C |
| 2 | 2 | 2 | D |
| → 5.5 | 6.1 | 3.2 | L ← |
| → 4.1 | 6.4 | 3.5 | A ← |
| <4 | <4 | 4 | K |
| 3 | 4 | 28 | M |
| 10 | <10 | <10 | N |
| → 5.7 | 6.5 | 3.6 | P ← |

"by mass spectrometry", another "by AAS" and the third "by emission spectroscopy". I believe that such statements not only do not convey enough information but can be downright misleading. Far too much effort has gone into comparing the effect of so-called "different methods" on the results in a round-robin operation. Such comparisons overlook two very important factors. Firstly, most analytical procedures involve several stages, such as sample decomposition, separations if any and final measurement -- not to mention calibration technique, interference corrections, etc. The limitations of an analytical procedure would be recognizable only when one knows all the details -- if then. Secondly, I believe there is no such thing as a "bad method", only "appropriate" or "inappropriate" methods. There are, I regret to say, good and bad analysts. To me a good analyst recognizes the limitations of a particular method and takes corrective measures where required. In other words, WHO does an analysis is much more important than HOW it is done.

Tables 13 and 14 show how confusion about methods can affect results. For ferrous iron in DTS-1, we have here a comparison between different possible derived values. One of the earlier tables showed that the value marked "this work" did much better on the summation and iron-oxide tests than did the one from "USGS 840". However there is a complicating factor. Essentially all of the analytical methods used in providing the raw data involved an oxidimetric titration. Unfortunately a small but significant portion of the ferrous iron in the sample occurred in chromite, a mineral which is highly resistant to the gentle decomposition method designed to avoid oxidation of ferrous iron. Only three of the originally reported results were known to be based on methods where the ferrous iron in the chromite was included. So we are left in a quandry -- two derived values: one that appears superior on the basis of two tests, the other in closer agreement with analytical methods known to be more sound. To add to the confusion there is no way of knowing whether or not any of the other collaborating analysts corrected for the chromite effect. It is probable, but by no means certain, that none of them did.

Table 14 shows a good example of sloppy reporting. A little detective work in the literature revealed that the last two results were indeed a duplication. What is more, it also revealed that the decomposition technique used was probably inadequate to bring all zirconium into solution, possibly accounting for the low results. The "true value" in this case is anybody's guess.

Finally, we come to a case of which some of you may have read in a recent issue of Geostandards Newsletter[9]. In Table 15 we have a disheartening array of results for barium. Superficially these figures might suggest two conclusions:

(a) Atomic absorption is not a good method because its result is so far removed from the others.

(b) X-ray fluorescence is not a precise technique because its results are erratic.

Actually both of these conclusions are wrong. Let us look behind the figures.

(a) We know that the AAS result is incorrect because it originated in our own laboratory. However we did not report 90 ppm Ba, but 0.01 percent BaO, because we ran this sample along with others containing much more barium, using a procedure whose working range was about 0.01 to 1.00 percent BaO. Clearly we were wrong in not repeating the determination by a more sensitive procedure. The compiler of the data was also wrong in translating our 0.01 percent BaO to 90 ppm Ba, unless it was qualified as 90 plus or minus 90!

(b) Note that the XRF results are in two clusters: a high group, ranging from 24 to 39 ppm, and a low group, running

## TABLE 13

### FeO in DTS-1

| No. of results | 48 | Range | 3.70-8.16 |
|---|---|---|---|
| Median | 6.92 | "This work" | 6.94? |
| $\bar{X}$ | 6.86 | GSC 77-34 | 6.98 |
| $\bar{X}_1$ | 6.91 | USGS 840 | 7.23 a |
| $\bar{X}_2$ | 6.91 | | |

Results by methods including chromite: 7.48
7.27
7.24

## TABLE 14

### Zr in PCC-1

| ppm | "Method" | |
|---|---|---|
| 37 | Optical Emission | |
| 30 | " " | |
| 28 | " " | |
| 8.1 | Neutron Activation | |
| 5.9 | Spectrophotometry ) | Duplication? |
| 5.9 | Ion Exchange ) | |

## TABLE 15

## Ba IN A DUNITE

| Ba, ppm | "Method" |
|---|---|
| 90 | AAS |
| 39 | XRF |
| 36 | XRF |
| 26 | XRF |
| 24 | XRF |
| 20 | OES |
| 15 | XRF |
| 12 | MS |
| 10 | XRF |
| 10 | XRF |
| 6.4 | XRF |
| 6.3 | OES |

from 6.3 to 15. When these values were referred to our own XRF specialist he asked whether those who reported high results had allowed for possible interference by the titanium L-alpha line. Unfortunately that information was not available. (Insufficient information is a chronic problem in round-robin data on proposed reference samples of rocks.)

So now that we have looked behind the figures we can see that there is little ground for the conclusions from the superficial examination. Unfortunately there is a fly in the ointment: the quantity of titanium in the sample is probably not enough to cause any interference!

After all that I have said in the course of this talk I am sure you will recognize why I was so hesitant to accept the invitation to participate in this workshop. My field of interest is indeed far removed from yours. I can only hope some of the points raised may prove of some use to you.

Thank you very much.

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# QUALITY CONTROL ROUND ROBINS - INTERCALIBRATION STUDIES CARRIED OUT UNDER THE AUSPICES OF THE INTERNATIONAL COUNCIL FOR THE EXPLORATION OF THE SEA

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The International Council for the Exploration of the Sea is an organization composed of 18 member nations and is charged with co-ordination and investigation of various aspects of oceanic useage and research. Its area of operation is essentially the North Atlantic Ocean and its attached bodies of water (e.g. North Sea, Baltic Sea). Member countries are those which surround these water bodies ranging from the United States in the southwest around to Portugal in the southeast and including the U.S.S.R., Poland and the German Democratic Republic. Twelve committees are responsible for the generalized activities of the Council, including the Marine Environmental Quality Committee whose role is to deal with the scientific study of man-made impacts, including pollution on the marine arena. Each member nation has two Committee members. Major Committee roles are carried out through Working Groups. Membership on Working Groups is open to experts from all member nations. The Working Group on Pollution Baseline and Monitoring Studies in the North Atlantic was set up in 1971 as a more limited group charged with implementing an international study of pollution problems in the North Sea, a base from which it has expanded to the generalized ICES area. From its foundation the Working Group has been active in carrying out intercalibration studies of both trace metals and organochlorine residues of interest. Although the Working Group is interested in intercalibration studies in water, sediments and biota this paper will briefly describe only the trace metal studies in biota and results obtained. Brief reference will be made to the findings of the organochlorine intercalibrations as well. Details of the first three trace metal intercalibrations and the first two organochlorine intercalibrations are available in Topping and Holden (1978). In this and all subsequent trace metal inter- calibrations no attempts were made to impose standard methods of analyses other than to judge the use of a standard method against the individual method.

Trace metal intercalibration utilized dried, ground fish preparations (fish meals). The first intercalibration exercise utilized a commercial fish meal which was finely ground. The results are shown in Table 1.

TABLE 1 - RESULTS OF THE FIRST TRACE METAL INTERCALIBRATION STUDY

| Element | Range (ug/g) | Range after exclusions | Number (N) |
|---|---|---|---|
| Copper | 11-20 | 17-20 (1)(a) | 6 |
| Zinc | 39-80 | 66-80 (2) | 7 |
| Mercury | 0.09-1.1 | 0.09-0.23 (1) | 7 |
| Cadmium | 1.1 -2.4 | - | 5 |
| Lead | 1.0 -9.0 | - | 6 |

(a) - number of exclusions

In the case of copper, exclusion of one set of results resulted in a very acceptable range of values. Zinc analyses also yielded an acceptable range of values if two low results were excluded. With the exception of one high mercury value a reasonable range of mercury values was also obtained. Cadmium results also fell within a reasonable range. In the case of lead the results were distributed over the total range suggesting difficulties in lead analysis were being encountered. The analysts, upon seeing these results, suggested that some of the variation in results was due to inhomogeneity in the fish meal preparation. This would not have been unexpected since commercial fish meal contains skin, bones and a large amount of visceral tissue. The second intercalibration sample was prepared from skin-on codfish fillets. In addition to analyzing this preparation with a standard method in addition to their own method, participants were requested to analyze solutions of known (but undisclosed) metal concentrations. The results of the fish meal analyses obtained by the individual and standard methods are shown in Table 2.

TABLE 2 - RESULTS OF THE SECOND TRACE METAL INTERCALIBRATION STUDY (Fish Meal)

| | Range | |
|---|---|---|
| Element | Standard Method (N) | Individual Method(N) |
| Copper | 8.7 - 10.1 (5) | 8.3 - 10.1 (7) |
| Zinc | 23 - 29.5 (5) | 23 - 32 (7) |
| Mercury | 0.47 - 0.83 (5) | 0.6 - 0.83(8) |
| Cadmium | 0.2 - 0.55 (5) | 0.02 - 1.1 (7) |
| Lead | 0.25 - 2.5 (5) | 1.3 - 2.5 (4) |

As in exercise one, it appears that analysts do not have appreciable problems in obtaining comparable values of copper concentrations. No significant differences were found between the common and individual methodologies. A multiple range test of six of the laboratories showed that they all produce comparable data for copper as do all four highest value laboratories (see Topping and Holden, 1978 for details of all multiple range tests). Both the standard and individual methodologies yielded essentially similar results for zinc. Multiple range testing of six laboratories supplying sufficient data indicated that the two laboratories submitting the highest and lowest zinc values were outliers while the next two lowest and the four remaining highest laboratories were overlapping groups, each group producing equivalent data.

Mercury values obtained by both methodologies did not differentiate between the methods but the relative range of the results was greater than the relative ranges of copper and zinc data. The intralaboratory precision was very high, however, suggesting consistent intralaboratory errors were prevalent. Multiple range testing of seven laboratories indicated that the three lowest laboratories produced equivalent values, as did the next three highest laboratories. The highest laboratory was also an outlier.

With respect to cadmium the standard and individual methods yielded different ranges of results. In both cases rather wide ranges of results were obtained, precluding any multiple range testing. This suggests that serious analytical problems were being encountered in determining cadmium at the level present in the second fish sample. This level was lower than the cadmium level in the first study.

The ranges in lead values obtained from the standard and individual methods were overlapping but significantly different. The wide range in results precluded multiple range testing and it appears that significant analytical difficulties are also being encountered in lead analysis.

The results of the analyses of the acidified metal solutions are shown in Table 3.

TABLE 3 - RESULTS OF THE ACIDIFIED METAL SOLUTION INTERCALIBRATION STUDY*

| Element | Range of Results | (N) | True Value | Accuracy Ratio |
|---|---|---|---|---|
| Copper | 0.39 - 0.50 | (5) | 0.40 | 2/5 |
| Zinc | 0.50 - 0.61 | (5) | 0.50 | 1/5 |
| Mercury | 0.10 - 0.18 | (6) | 0.10 | 1/5 |
| Cadmium | 0.07 - 0.20 | (5) | 0.10 | 0/5 |
| Lead | 0.07 - 0.49 | (4) | 0.30 | 0/5 |

* number of laboratories reporting accurate values/total number (N)

Two laboratories reported accurate values of copper concentrations in the acidified solution. The rest of the laboratories reported higher values, the maximum difference was 25% higher. This suggests that laboratories were employing working standards containing less copper than believed.

One laboratory reported an accurate value for zinc concentration in the acidified solution. All of the rest produced higher values, the maximum difference being 20% higher.

With one exception reported mercury values were higher than the true values, the maximum difference being 80%. The exceptional value was equal to the true value.

It should be noted that in the case of the above three elements no laboratory reported accurate results for more than one element. Every laboratory was employing working standards containing lesser amounts of the element than believed in more than one case.

Reported values for cadmium were higher or lower than the true value for cadmium concentration in the acidified solution. No laboratory was able to report the true value accurately.

Reported values were higher or lower than the true value for lead concentration in the acidified solution, demonstrating that analytical difficulties with lead and cadmium analyses are encountered even in analysis of standard stock solutions.

In general, assessment of the first two studies indicated that significant improvement had been made by analysts in terms of comparability of data. Cadmium and lead results still indicated that improvement would have to still be made to allow intercomparison of results among laboratories. The discovery of a generalized working standard problem led to the inclusion of stock standards being included in the third intercalibration study. The fish sample for the third study was prepared from skinned cod fillets. Twenty-one laboratories participated in the third exercise. The results of the third study are shown in Table 4.

TABLE 4 - RESULTS OF THE THIRD TRACE METAL INTERCALIBRATION STUDY

| Element | Range (9/9) | (N) | Grand Mean ± S.D. |
|---|---|---|---|
| Copper | 2.69 - 5.68 | (20) | 3.76 ± 0.67 |
| Zinc | 27.8 - 52.7 | (22) | 37.5 ± 6.0 |
| Mercury | 0.74 - 1.26 | (16) | 0.8 ± 0.12 |
| Cadmium | 0.03 - 0.552 | (17) | 0.14 ± 0.16 |
| Lead | 0.16 - 4.00 | (21) | 1.24 ± 1.07 |

Given the large increase in the number of participants who took part in the third exercise it is not surprising that a wider range is observed in the results from this exercise as compared with the previous exercises. Also, in this exercise, analysts were requested to include every determination made. It is likely, in practice, that individual laboratories would exclude outliers which would improve the data. Multiple range testing was again applied to the copper, zinc and mercury results. The wide variation found in cadmium and lead reported values again precluded the statistical analysis. Multiple range testing showed that of 19 laboratories an intermediate group of 13 laboratories produced equivalent values. In the case of zinc the maximum number of laboratories (out of 16) producing equivalent values was four (3 groups) while in the case of mercury out of 13 laboratories the highest 7 produced equivalent data.

Isolation of the laboratories which had participated in all three exercises and calculation of an overall coefficient of variation for copper, zinc and mercury over the three experiments indicated that the coefficient of variation for copper had decreased from 21% in the first exercise to 10% in the third. In the case of zinc the coefficient of variation had decreased from 23% in the first exercise to 8% in the third one. The coefficient of variation was 38% for mercury in the first exercise and decreased to 5% in the third exercise.

Time prohibits detailed investigations of further ICES intercalibrations. In 1979 Topping reported on the latest study. Essentially cadmium and lead analyses were still plagued with wide ranges and high variances. Arsenic was added to this intercalibration and the reported range of results was 0.50-20.7 ug/g. These results readily split into 2 groups, one of 5 lower values (0.50-8.9 ug/g) the other of 7 higher values (12.2-20.6 ug/g). This study also included activation and x-ray, fluorescence analysis, both values falling within the higher group. The majority of the lower values were obtained by wet digestion followed by reduction to arsine, generally with sodium borohydride, although two laboratories employing this procedure fell into the higher group. This suggests that this method can easily give low arsenic results but is capable of giving equivalent values to other procedures when used under appropriate conditions.

As stated earlier, intercalibration studies have also been carried out on the common organochlorine materials, polychlorinated biphenyls, and common organochlorine pesticides. In summary, each intercalibration study was composed of spiked and unspiked oil. The first intercalibration fish oil naturally contained relatively high levels of organochlorines 80-2000 ug/kg (excluding o,p'-DDT) and was spiked to 800-10,000 ug/kg. Recoveries (spiked and unspiked, excluding outliers) ranged from 94-105% with coefficients of variation of from 7-20%. The second intercalibration oil was a corn oil containing from about 1-50 ug/kg (spiked to 50-1100 ug/kg). Recoveries ranged from 80-104% with a coefficient of variation of from 7-40% when outliers were excluded. Recently (Holden, 1979) reported little improvement in organochlorine intercalibration performance had occurred in spite of continued intercalibrations. Readers should consult Topping and Holden (1978) and Holden (1979) for details regarding the organochlorine intercalibration details.

In conclusion we wish to summarize what has been learned through the continuing program of intercalibrations:

(1) Intercalibrations should be carried out with substrates as close as possible to the materials of analytical interest and containing levels of contaminant in the range expected to occur in the material of analytical interest.

(2) Extreme care must be taken in preparing standards, particularly standards which appear from these studies to often contain lesser amounts of the element of interest than intended.

(3) A common procedure for preparing stock and working standards is recommended.

(4) Methods of analysis should have detection limits of at least one order of magnitude lower than the lowest levels expected to occur in samples.

(5) Cadmium and lead levels in marine fish do not appear to be accurately determined in most laboratories as yet. Further work will be required to enable intercomparison of data from various laboratories.

(6) Intercalibration studies on trace elements should attempt to include laboratories employing x-ray fluorescence and non-destructive activation analysis in addition to the more general chemical techniques such as atomic absorption.

(7) Every laboratory appears to have trouble determining a certain element at a certain time. Analysts must ensure rigorous intralaboratory quality control is maintained.

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# SOME INTERNATIONAL MARINE QUALITY-CONTROL PROGRAMS

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## ABSTRACT

Intercalibration programs of the International Council for the Exploration of the Sea and the Intergovernmental Oceanographic Commission related to trace metals in seawater will be briefly described. Reference will also be made to planned activities of these organizations for further trace metal and petroleum hydrocarbon intercalibrations in seawater and marine sediments.

## 1. INTRODUCTION

There has long been an interest in improving the comparability of marine analytical data. Recently, as a result of their interest in determining the extent of pollution of the marine environment, several international organizations have taken up the cudgel and applied considerable effort to the conduct of intercalibration exercises for a variety of contaminants in marine biota and seawater. This discussion will primarily concern itself with intercalibrations involving trace metals in seawater fostered or sponsored by international organizations.

One of the earliest international intercalibrations for trace metals in seawater was that undertaken by Brewer and Spencer (1970 among potential participants in the Geochemical Ocean Sections (GEOSECS) program of IDOE (The International Decade of Ocean Exploration). The results of this experiment (summarized in Table 1) served to emphasize the discrepancies between data from different laboratories derived from assumed identical water samples. Intercalibrations for lead in seawater (Participants 1974, 1976) were subsequently organized by Dr. C.C. Patterson of

## TABLE 1

## SUMMARY OF RESULTS FROM THE GEOSECS TRACE METAL INTERCALIBRATION

(Brewer and Spencer, 1970)

| | Mn | Fe | Ni | Cu | Zn | Cd | Pb |
|---|---|---|---|---|---|---|---|
| $\overline{x}$ (μg/l ) | 1.37 | 12.2 | 3.5 | 3.5 | 4.92 | 0.50 | 5.0 |
| V (%) | 92 | 81 | 63 | 120 | 93 | 40 | 114 |
| Range (μg/l ) | 0.07-3.6 | 3.7-47.5 | 0.88-8.9 | 0.8-15 | <0.02-99.2 | 0.03-2.1 | 0.42-14.1 |

the California Institute of Technology and funded by the U.S. National Science Foundation under the IDOE program. These intercalibrations were conducted largely as training exercises for the participants and it is much to Dr. Patterson's credit that this approach was adopted. It does, however, require a leader, or organizing laboratory, with internationally-recognized abilities in the determination of the metals concerned at real environmental levels. Such a condition, while applying to lead, has not, until very recently, prevailed in case of other metals in seawater. Nevertheless the value of such intercalibrations in increasing the participants' experience and assisting them in improving accuracy and precision is often neglected whereas it should always be fully exploited.

The intercalibrations mentioned above have been reported in the open literature and I use them by way of introduction only and will not refer to them further. I wish now to discuss the activities of three international organizations - the International Council for the Exploration of the Sea (ICES), the Intergovernmental Oceanographic Commission (IOC) and the Joint Monitoring Group of the Oslo and Paris Commissions (JMG) - in relation to intercalibrations for trace metals in seawater. It should be remembered, in the following discussion, that determinations of oceanic constituents involves three distinct phases; sampling, pretreatment and/or preconcentration and instrumental analysis. Sample storage is also a potentially important aspect of this sequence but for convenience I shall consider it as part of sample pretreatment. In most cases the approach to examining data intercomparability has been to pay initial attention to the purely analytical stages (pretreatment and instrumental analyses) and then, if adequately precise and accurate methods can be shown to exist, to pay attention to sampling procedures.

## 2. ICES ACTIVITIES

Four intercalibrations for trace metals in seawater have been organized and conducted under ICES auspices since 1975. ICES has made plans for two additional intercalibration rounds; the fifth having been outlined in more detail than the sixth since invariably the results of one experiment in the series influence, to some extent, the design of its successor. The primary metals of interest are Iron (Fe), Manganese (Mn), Chromium (Cr), Cobalt (Co), Nickel (Ni), Copper (Cu), Cadmium (Cd), Zinc (Zn), Lead (Pb) and Mercury (Hg).

The overall objective of these intercalibrations is to permit the chemical characteristics of different marine areas or basins to be compared. Since various laboratories are producing data pertaining to the distribution of trace metals in the ocean the achievement of this objective depends largely upon finding a mechanism for intercomparison of these data. This is the underlying raison d'etre for the series of ICES intercalibrations on trace metals in seawater. Obviously there exists a related desire to acquire a better appreciation of the procedures which improve accuracy and precision.

These ICES intercalibrations have been organized by representative laboratories on a voluntary basis at the behest of the ICES Working Group on Marine Chemistry which has been responsible in large part for the experimental design. The organizing laboratories, or their governments, have borne the entire costs of these experiments. The following sections describe ICES intercalibrations already conducted.

### 2.1 Round 1 (High Level Aqueous Standards Intercalibration)

The first intercalibration in the series involved the preparation, distribution and analysis of trace metal standard solutions. The purpose of this experiment was to assess the accuracy and comparability of metal determinations at levels higher than those in seawater. In essence the experiment was one of standards intercomparability which is a fundamental precursor to conducting intercalibrations using seawater samples.

Two artificial aqueous solutions containing between 100 and 300 mg/1 of the metals Mn, Co, Cr, Cu, Ni, Zn, Cd, Pb and Hg were distributed to 45 potential participants in early 1976. The experiment was conducted by P.G.W. Jones of the Fisheries Radiobiological Laboratory, Ministry of Agriculture, Fisheries and Food, Lowestoft, Suffolk, United Kingdom and the results reported in a paper (Jones, 1976) presented at the 1976 ICES Statutory Meeting, Copenhagen. Thirty participants in 13 countries reported a total of 232 analyses of which 80% were within ±10% of the expected values. Mercury and chromium results tended to be low while reported iron values tended to be high (Figure 1). Nevertheless it was concluded that standards intercomparability was sufficiently good to permit the two subsequent intercalibrations on seawater samples to proceed as planned.

## 2.2 Round 2 (Intercalibration for Mercury in Seawater)

This was the first intercalibration in the series to be conducted on natural seawater samples. It was organized by J. Olafsson of the Marine Research Institute, Reykjavik, Iceland and involved the distribution of two seawater samples and a mercury-spiked seawater sample to 14 laboratories in 10 countries on April 5th, 1976. The results were first presented in a paper (Olafsson 1976) to the 1976 ICES Statutory Meeting in Copenhagen and later described in the scientific literature (Olafsson 1978). They show that there did not then exist a basis for interlaboratory comparison of determinations of mercury in seawater (see Tables 2 and 3). Olafsson concludes, "This exercise indicates that some five of the participating laboratories have methods sensitive and accurate enough to determine mercury in unpolluted seawater with a reasonable agreement. It further suggests that at the spike level of 130 ng/1, as might be encountered in polluted seawater, 11 or possibly 12 of the 14

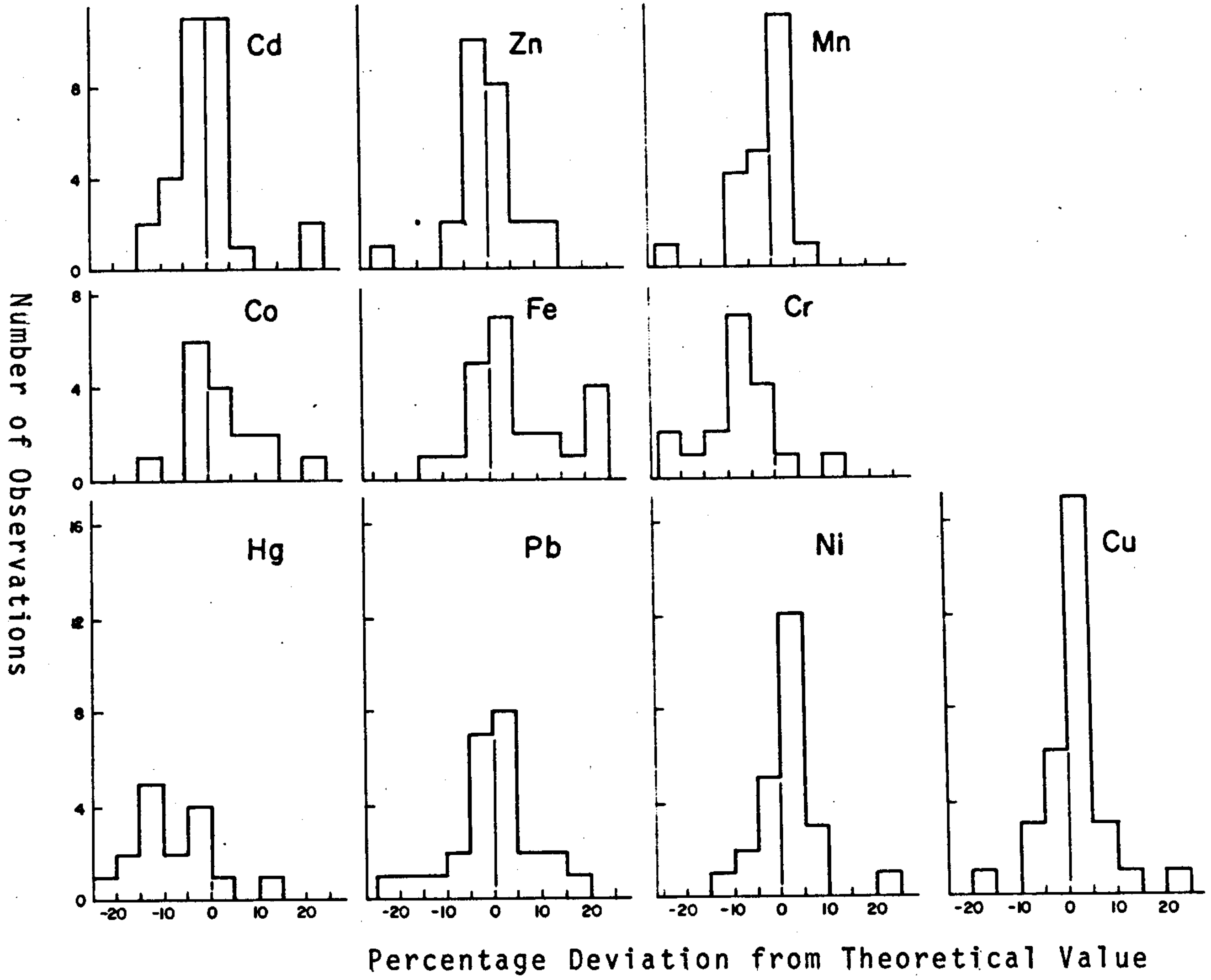

FIGURE 1: RESULTS OF TRACE METAL INTERCALIBRATION EXERCISE

participants could be expected to be able to determine the mercury concentration". Thus the experiment has indicated that the wide ranges of concentration for mercury in seawater reported in the literature are not likely to represent wholly real variability but partly reflect deficiencies in analytical procedures. The reports of the experiment include descriptions of each of the analytical procedures employed and it is, therefore, possible for readers to determine which of these gave the most comparable results.

### 2.3 Round 3 (Intercalibration for Trace Metals Using North Sea Water)

This round involved the distribution to 65 laboratories of two frozen samples of filtered seawater and was organized again by P.G.W. Jones of the United Kingdom. The samples were collected and distributed in early 1977. The results of analyses of these samples by 28 participants in 16 countries was reported at the 1977 ICES Statutory Meeting in Reykjavik (Jones, 1977). As in the case of the preceding intercalibration for mercury the range of values reported for most of the metals was large and coefficients of variation were between 18 and 201% (Tables 4 & 5). The results for cadmium, lead and nickel showed the greatest variation with manganese and zinc showing the best agreement among participants. A group of marine institutes, selected on the basis of their manganese results, showed improved agreement for most metals compared with the participants as a whole (Table 6).

### 2.4 Round 4 (Intercalibration for Trace Metals using Scotian Shelf Water with inherent replication and spiked samples)

At the conclusion of round 3 it was realized that a further seawater intercalibration was required in which replication could be used to determine analytical precisions and low-level spike recovery to attempt to assess accuracy. As a result the two intercalibration rounds had unequivocally demonstrated the extent of disparity in trace metal analyses of common seawater samples. Originally it had been intended to conclude with a multi-ship

## TABLE 2

### REPORTED MERCURY CONCENTRATIONS IN UNSPIKED SEA WATER SAMPLES

| Lab | Sample | Hg ng $l^{-1}$ | Days From Collection | Hg ng $l^{-1}$ Unoxidized | | |
|---|---|---|---|---|---|---|
| A | | 4.48 ± 0.4 | 2 | 1.40 ± 0.4 | | |
| B | a | * 31 ± 3 | 19 | | Contamination? | |
| | b | 6 ± 3 | 19 | | | |
| C | a | | 88 | 10.5 ± 1.0 | | |
| | a | | 90 | 11.2 ± 0.7 | | |
| | b | | 88 | 4.0 ± 0.6 | | |
| | b | | 90 | 3.9 ± 1.1 | | |
| | a | * 19.7 ± 2.4 | 90 | | Contamination? | |
| | b | 8.5 ± 0.9 | 90 | | | |
| D | a | 5.0 | ~60 | | 3.0 ng $l^{-1}$ | Obtained additionally by rinsing sample bottles with $KMnO_4/H_2SO_4$ solution. |
| | b | 5.9 | ~60 | | 1.0 ng $l^{-1}$ | |
| E | a | * 34 | 13 | | Estimated precision ± 10 ng $l^{-1}$ | |
| | b | * 42 | 13 | | Unusually high blanks. | |
| F | a | < 50 | 14 | | | |
| | b | < 50 | 14 | | | |
| G | a | 9.5 | 60 | 6 | Detection limit 2 ng $l^{-1}$ | |
| H | a | < 50 | 21 | | | |
| | b | < 50 | 21 | | | |
| I | a | < 20 | 14 | | | |
| | b- | < 20 | 14 | | | |
| J | a | * 14 | 27 | | Close to the limit of detection. | |
| | b | * 15 | 27 | | | |
| K | a | * 50 | 20 | | Close to the limit of detection. | |
| | b | * 50 | 20 | | | |
| L | a | * 55 | 29 | | Estimated precision ± 12% | |
| M | a | * 30 | 13 | | Estimated precision ± 20 ng $l^{-1}$ | |
| | b | * 30 | 13 | | | |
| N | a | * 60 | 70 | | | |
| | a | * 100 | 77 | | | |
| | b | * 80 | 70 | | | |
| | b | * 90 | 77 | | | |
| All | $\bar{x}$ | 35.2 | | | | |
| reported | S | 29 | | | | |
| results | c.v. | 82.3% | | | | |
| Results | $\bar{x}$ | 6.56 | | | | |
| marked* | s | 2.0 | | | | |

$\bar{X}$ : mean

s : standard deviation

c.v. : coefficient of variation

## TABLE 3

## REPORTED MERCURY CONCENTRATIONS IN SPIKED SEA WATER SAMPLES

| Lab | Hg ng l$^{-1}$ | Days from Preparation | Hg ng l$^{-1}$ Unoxidized | |
|---|---|---|---|---|
| A | 131 ± 1.7 | 0 | | |
| B | 131 ± 7<br>121 ± 7 | 16<br>16 | | |
| C | | 88 | 97.7 ± 3.6 | |
| | | 90 | 84.9 ± 4.9 | |
| | 114 ± 6 | 90 | | |
| D | 106<br>106 | ~ 60<br>~ 60 | | 8.0 ng l$^{-1}$<br>6.0 ng l$^{-1}$ Obtained additionally by rinsing sample bottles with $KMnO_4/H_2SO_4$ solution.<br>Received two aliquots of spiked samples. |
| E | 167 | 10 | | Estimated precision ± 10 ng l$^{-1}$<br>Unusually high blanks |
| F | *250 | 11 | | |
| G | *220 | 58 | 210 | |
| | 170 | 58 + 6 hrs. | 170 | |
| | | 61 | 160 | |
| | | 64 | 150 | |
| H | 110 | 18 | | Estimated precision ± 14 ng l$^{-1}$ |
| I | 100 | 11 | | |
| J | 140 | 24 | | |
| K | 140 | 17 | | |
| L | *300 | 26 | | Estimated precision ± 12% |
| M | 200 | 10 | | Estimated precision ± 20 ng l$^{-1}$ |
| N | *220<br>180 | 67<br>74 | | |

| | | |
|---|---|---|
| All reported results | $\bar{x}$ | 161 |
| | s | 57 |
| | c.v. | 35.2% |
| Results marked* excluded | $\bar{x}$ | 137 |
| | s | 31 |
| | c.v. | 22.8% |

$\bar{x}$ : mean

s : standard deviation

c.v. : coefficient of variation

TABLE 4

THE ANALYSIS OF SAMPLE A ($\mu g\ l^{-1}$)

| Institute and Method | Co | Fe | Ni | Pb | Cd | Cr | Cu | Mn | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. AA (2) A |  | 4.1 |  | 0.20 |  |  | 0.45 | 1.5 | 8.6 |  |
| EC |  |  |  |  |  |  |  |  | 6.2 |  |
| 2. AA (1) A (Mn*) |  | <1.0 | <2.5 | <0.5 | 0.03 | < 0.5 | < 0.5 | < 10 | 5.6 |  |
| 3. AA (1) A | 0.2 | 2.3 | 0.6 | 0.8 | 0.3 | 0.4 | 0.6 | 0.4 | 4.8 |  |
| 4. EC (Hg AA (3)) |  |  |  | 0.18 | 0.09 |  | 1.22 |  | 4.72 | 38.6 |
| 5. AA (2) A | <0.5 | <1.0 | <1.0 | <0.5 | <0.1 | <10 | 0.4 | <20 | 6.5 |  |
| 6. EC |  |  |  | 5.6 | 0.6 |  | <1.0 |  | 22.2 |  |
| 7. AA (2) A (Zn (1) A) |  |  |  | 0.37 | 0.07 |  | 0.5 |  | 5.5 | 0.15 |
| 8. EC |  |  |  | 0.315 | 0.047 |  | 0.49 |  | 3.59 |  |
| 9. AA (2) B |  |  |  |  |  |  | 0.36 |  |  |  |
| 10. AA (1) A (Cd, Pb, Mn (2) A) |  | 3.0 |  | 0.51 | 0.09 |  | 0.6 | <0.06 | 9.9 |  |
| EC pH 8.1 |  |  |  | 0.18 | 0.11 |  | 0.4 |  | 4.7 |  |
| EC pH 1.85 |  |  |  | 2.0 | 0.10 |  | 0.8 |  |  |  |
| 11. AA (2) A |  | 4.9 | 0.5 |  | 0.19 |  | 0.9 | 2.2 |  |  |
| EC |  |  |  | 2.1 | 0.14 |  |  |  | 17 |  |
| 12. EC |  |  |  | 0.90 | 0.18 |  | 0.88 |  |  |  |
| 13. AA (1) A |  |  | < 0.1 | 2.0 | 0.05 | 2.3 | 0.5 |  | 6.0 |  |
| 14. AA (2) B (Ni, Pb and Zn (1) B) |  | < 0.4 | < 0.8 | < 0.8 | 0.13 |  | < 0.2 | 0.7 | 5.5 |  |
| 15. AA (?) A | < 5 |  | 5 | < 0.5 | < 0.5 |  |  |  |  |  |
| 16. EC |  |  |  | 0.09 | 0.10 |  | 0.99 |  | 4.8 |  |

TABLE 4 (Continued)

| Institute and Method | Co | Fe | Ni | Pb | Cd | Cr | Cu | Mn | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| 17. EC | | | | 0.13 | 0.03 | | 1.0 | | | |
| 18. AA (2) C | | 1.1 | | | <0.05 | | 0.5 | 0.24 | 11 | |
| 19. AA (1) A | | | <0.2 | <0.4 | <0.05 | | 0.3 | | 2.9 | |
| 20. PE | | | 0.35 | | <0.07 | 0.63 | | | 5.6 | |
| 21. AA (2) B | | | | 0.15 | 0.053 | | 0.39 | | | |
| 22. AA (2) D | 0.13 | 1.05 | 0.80 | 0.71 | 0.099 | | 0.55 | 0.39 | 4.0 | |
| 23. AA (2) A | 0.17 | 8.1 | 0.28 | | 0.13 | | 0.76 | 1.5 | 10.8 | |
| 24. AA (?) B | | | | <1 | 0.04 | | 1.4 | | 11.6 | |
| 25. AA (?) A | | | 0.44 | | 0.023 | | 0.22 | | 5.5 | |
| 26. AA (2) C | | | | | | 0.40 | | | | |
| 27. AA (1) A | | | 6.4 | 1.4 | 0.2 | | 2.2 | | 2.1 | |
| 28. AA (2) A | | | 0.26 | | 0.020 | | 0.27 | | 7.55 | |
| $\overline{X}$ | | 3.51 | 1.63 | 1.04 | 0.12 | 0.93 | 0.70 | 0.99 | 7.36 | |
| S | | 2.48 | 2.34 | 1.37 | 0.12 | 0.92 | 0.44 | 0.75 | 4.59 | |
| V% | | 71 | 144 | 132 | 100 | 99 | 63 | 76 | 62 | |

<u>Key:</u>

AA = Atomic absorption
EC = Electrochemistry
PE = Plasma emission
(1) = Flame
(2) = Furnace
(3) = Cold vapour

A = Organic extraction
B = Ion exchange resin
C = Direct injection
D = Coprecipitation
* = Colorimetric

## TABLE 5

## THE ANALYSIS OF SAMPLE B ($\mu g\ l^{-1}$)

| Institute and Method | Co | Fe | Ni | Pb | Cd | Cr | Cu | Mn | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. AA (2) A |  | 1.2 |  | 0.12 | 0.17 |  | 0.63 | 9.8 | 7.6 |  |
| EC |  |  |  |  |  |  |  |  | 7.7 |  |
| 2. AA (1) A (Mn*) |  | <1.0 | <2.5 | <0.5 | 0.14 | 0.5 | 0.7 | <10 | 15.2 |  |
| 3. AA (1) A | 0.4 | 4.0 | 1.2 | 0.6 | 0.2 | 0.3 | 1.0 | 9.8 | 9.8 |  |
| 4. EC (Hg AA (3) |  |  |  | 0.32 | 0.11 |  | 0.90 |  | 7.92 | 27.5 |
| 5. AA (2) A | <0.5 | <1.0 | 1.8 | <0.5 | <0.1 | <10 | 0.8 | <20 | 10.5 |  |
| 6. EC |  |  |  | 5.0 | 0.3 |  | <1.0 |  | 6.6 |  |
| 7. AA (2) A (Zn (1) A) |  |  |  | 0.09 | 0.11 |  | 1.2 |  | 11.8 | 0.07 |
| 8. EC |  |  |  | 0.205 | 0.080 |  | 0.83 |  | 3.78 |  |
| 9. AA (2) B |  |  |  |  |  |  | 0.54 |  |  |  |
| 10. AA (1) A (Cd, Pb, Mn (2) A) |  | 2.6 |  | 0.51 | 0.13 |  | 0.6 | 10.6 | 10.5 |  |
| EC pH 8.1 |  |  |  | 0.26 | 0.12 |  | 0.3 |  | 4.65 |  |
| EC pH 1.85 |  |  |  | 2.2 | 0.09 |  | 0.9 |  |  |  |
| 11. AA (2) A |  | 2.2 | 1.0 |  | 0.10 |  | 0.5 | 13.8 | 8 |  |
| EC |  |  |  | 1.1 | 0.09 |  |  |  |  |  |
| 12. EC |  |  |  | 0.42 | 0.087 |  | 0.89 |  |  |  |
| 13. AA (1) A |  |  | 0.9 | 0.5 | 0.15 | 3.3 | 0.8 |  | 10.0 |  |
| 14. AA (2) B (Ni, Pb and Zn (1) B) |  | <0.4 | <0.8 | <0.8 | 0.09 |  | <0.2 | 9.8 | 10.4 |  |
| 15. AA (?) A | <5 |  | 16 | <5 | <5 |  |  |  |  |  |
| 16. EC |  |  |  | 0.11 | 0.09 |  | 1.10 |  | 11.0 |  |

TABLE 5 (Continued)

| Institute and Method | Co | Fe | Ni | Pb | Cd | Cr | Cu | Mn | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| 17. EC |  |  |  | 0.11 | 0.23 |  | 1.4 |  |  |  |
| 18. AA (2) C |  | 1.7 |  |  | 0.20 |  | 1.1 | 7.4 | 11 |  |
| 19. AA (1) A |  | 1.2 |  | <0.4 | 0.10 |  | 0.6 |  | 9.0 |  |
| 20 PE |  | 1.9 |  |  | 1.2 | 0.52 |  |  | 14 |  |
| 21. AA (2) B |  |  |  | 0.11 | 0.103 |  | 0.6 |  |  |  |
| 22. AA (2) D | 0.15 | 1.80 | 0.72 | 0.80 | 0.078 |  | 0.46 | 9.6 | 7.8 |  |
| 23. AA (2) A | 0.13 | 5.8 | 0.69 |  | 0.57 |  | 0.71 | 11.6 | 13.8 |  |
| 24. AA (?) B |  |  |  | <1 | 0.2 |  | 0.8 |  | 13.3 |  |
| 25. AA (?) A |  |  | 1.1 |  | 0.17 |  | 0.29 |  | 15 |  |
| 26. AA (2) C |  |  |  |  |  | 0.66 |  |  |  |  |
| 27. AA (1) A |  |  | 24.2 | 11.2 | 1.9 |  | 8.8 |  | 30.3 |  |
| 28. AA (2) A |  |  | 0.95 |  | 0.032 |  | 0.60 |  | 11.6 |  |
| $\overline{X}$ |  | 2.76 | 4.31 | 1.39 | 0.25 | 1.06 | 1.08 | 10.30 | 10.89 |  |
| S |  | 1.61 | 7.59 | 2.80 | 0.40 | 1.26 | 1.63 | 1.84 | 5.10 |  |
| V% |  | 58 | 176 | 201 | 160 | 119 | 151 | 18 | 47 |  |

Key:
AA = Atomic absorption
EC = Electrochemistry
PE = Plasma emission
(1) = Flame
(2) = Furnace
(3) = Cold vapour

A = Organic extraction
B = Ion exchange resin
C = Direct injection
D = Coprecipitation
* = Colorimetric

## TABLE 6

## A STATISTICAL ANALYSIS OF TRACE METAL DATA FROM INSTITUTES REPORTING MANGANESE VALUES

SAMPLE A

| | Fe | Ni | Pb | Cd | Cu | Mn | Zn |
|---|---|---|---|---|---|---|---|
| $\overline{X}$ µg/l | 3.51 | 0.55 | 0.56 | 0.16 | 0.62 | 0.99 | 7.80 |
| S | 2.48 | 0.22 | 0.27 | 0.08 | 0.16 | 0.75 | 2.97 |
| V% | 71 | 40 | 48 | 50 | 26 | 76 | 38 |

SAMPLE B

| | Fe | Ni | Pb | Cd | Cu | Mn | Zn |
|---|---|---|---|---|---|---|---|
| $\overline{X}$ µg/l | 2.76 | 0.90 | 0.51 | 0.19 | 0.71 | 10.30 | 10.13 |
| S | 1.61 | 0.24 | 0.29 | 0.16 | 0.25 | 1.84 | 2.10 |
| V% | 58 | 27 | 57 | 84 | 35 | 18 | 21 |

intercalibration after the completion of the first three rounds. However, the situation revealed by the second and third rounds invited a re-examination of the intercalibration program since planning for the multi-ship exercise appeared premature. ICES authorized the conduct of this intercalibration and the responsibility for its design and conduct was assumed by the author on behalf of the Bedford Institute of Oceanography, Canada. It should be stressed that the organizers made a determined effort to ensure that the metal levels in the samples used in this intercalibration be as close as possible to the ambient levels in the water mass sampled and, in particular, lower than those in samples used in previous intercalibrations of this series.

The experimental design involves sufficient replication (4 aliquots of a natural offshore water sample) to enable reliable estimates of precision to be made for each participant. A spiked sample was included in order to estimate low-level spike recovery. The magnitude of each metal spike was determined on the basis of the statistical probability that it could be discerned as different from the replicates by participants with precisions comparable with our own published estimates (Bewers et al, 1976). An additional sample, referred to herein as a 'dummy', was also introduced to the sample set in order to increase the 'blindness' of the experiment. This dummy sample was expected to contain significantly lower concentrations of most metals than either the spiked or replicate samples. Sufficient replication in the analysis of replicate samples had to be assured so that both within-sample and between-sample precisions could be determined. Comparable replication of the spiked and dummy sample analyses should permit both an additional check on precision and estimates of spike recovery to be made. Each participant thus received a total of six samples and was asked to analyze each sample in triplicate. Sample information provided to participants was restricted to the methods of collection and salinity range of the sample set. The replicate samples were collected from a depth of

180 metres on the Scotian Shelf some 100 km offshore while the dummy samples, and those subsequently spiked, were drawn from a depth of 150 metres in the Atlantic Slope Water.

Forty-three laboratories in fourteen countries participated in the experiment. The composite mean concentrations and standard deviations of the replicate, dummy and spiked samples for all elements analyzed by a large number of laboratories are shown in Table 7. Only outliers have been excluded. The ranges of reported values are quite large, although both the means and standard deviations are smaller than in the GEOSECS (Brewer and Spencer, 1970) and ICES 3rd Round (Jones, 1977) intercalibrations. Nevertheless, because of the large range of reported values, it is difficult to draw firm conclusions from the entire body of the data. It should be noted that whilst the levels of most metals are close to those expected in offshore shelf waters (Bewers et al 1976) the zinc and lead concentrations are very much elevated. This is suspected to have been a result of contamination of the bulk intercalibration samples by these elements during the homogenizing and aliquotting procedures.

One of the principal objectives of the intercalibration was to determine analytical precisions for each participant. These have been determined for all laboratories that have provided us with two or more independent analyses of each of the replicate samples or given us other information suitable for this purpose. If we subset, for each element in Table 7, in those laboratories with better analytical precisions we observed a marked improvement in the comparability of results (see Table 8). The limiting precision criterion is approximately equal to one-third of the currently established concentration for the metals in shelf waters with the obvious exceptions of lead and zinc for which arbitrary choices have been made based upon the intercalibration returns. As can be seen in Table 8 the average replicate and dummy sample values are lower than those in Table 7 and closer to real environmental levels for all elements except lead and zinc. The

# TABLE 7

## SUMMARY OF RESULTS FOR ALL LABORATORIES EXCLUDING OUTLIERS (µg/1 )

| | Cadmium | | Copper | | Iron | | Lead | | Manganese | | Nickel | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen |
| Number of labs* | 20 | 16 | 19 | 17 | 7 | 6 | 18 | 14 | 4 | 6 | 4 | 8 | 16 | 15 |
| Replicate $\bar{x}$ | 0.097 | 0.068 | 0.92 | 0.40 | 1.76 | 1.81 | 0.79 | 0.64 | 0.23 | 0.18 | 0.42 | 0.35 | 6.55 | 3.69 |
| s | 0.084 | 0.040 | 0.72 | 0.46 | 1.23 | 2.02 | 0.55 | 0.61 | 0.09 | 0.16 | 0.34 | 0.23 | 1.97 | 1.42 |
| Dummy $\bar{x}$ | 0.100 | 0.055 | 0.71 | 0.48 | 1.17 | 1.57 | 0.53 | 0.33 | 0.18 | 0.20 | 0.46 | 0.33 | 9.58 | 6.52 |
| s | 0.086 | 0.021 | 0.55 | 0.59 | 0.67 | 1.45 | 0.55 | 0.22 | 0.11 | 0.19 | 0.52 | 0.34 | 2.92 | 2.66 |
| Spike $\bar{x}$ | 0.244 | 0.186 | 2.58 | 1.67 | 3.79 | 3.07 | 0.60 | 0.41 | 0.52 | 0.39 | 1.11 | 0.94 | 8.86 | 5.59 |
| s | 0.094 | 0.055 | 1.34 | 0.52 | 1.72 | 1.48 | 0.47 | 0.19 | 0.17 | 0.21 | 0.76 | 0.56 | 2.42 | 2.31 |
| % Spike Recovery | 68 | 62 | 89 | 57 | 77 | 44 | 36 | 38 | 94 | 53 | 81 | 76 | - | - |

* Outliers excluded on the basis of Chauvenet's criterion.

TABLE 8

SUMMARY OF RESULTS FOR HIGH PRECISION LABORATORIES (µg/l )

| | Cadmium | | Copper | | Iron | | Lead | | Manganese | | Nickel | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen | Acidified | Frozen |
| Required Analytical Precision | 0.015 | 0.015 | 0.06 | 0.06 | 0.25 | 0.25 | 0.08 | 0.08 | 0.05 | 0.05 | 0.06 | 0.06 | 0.5 | 0.3 |
| Number of labs | 13 | 10 | 6 | 12 | 4 | 5 | 6 | 9 | 3 | 4 | 3 | 3 | 7 | 11 |
| Replicate $\bar{x}$ | 0.059 | 0.047 | 0.33 | 0.19 | 1.42 | 1.01 | 0.45 | 0.41 | 0.20 | 0.23 | 0.25 | 0.22 | 5.68 | 3.95 |
| s | 0.020 | 0.011 | 0.20 | 0.10 | 0.80 | 0.50 | 0.08 | 0.16 | 0.09 | 0.18 | 0.10 | 0.11 | 1.23 | 1.30 |
| Dummy $\bar{x}$ | 0.063 | 0.053 | 0.29 | 0.22 | 0.88 | 1.04 | 0.27 | 0.33 | 0.13 | 0.19 | 0.20 | 0.21 | 9.02 | 6.84 |
| s | 0.020 | 0.072 | 0.27 | 0.17 | 0.27 | 0.70 | 0.07 | 0.20 | 0.09 | 0.20 | 0.07 | 0.15 | 2.37 | 1.97 |
| Spike $\bar{x}$ | 0.207 | 0.195 | 1.84 | 1.50 | 3.71 | 2.51 | 0.39 | 0.40 | 0.48 | 0.45 | 0.74 | 0.86 | 9.21 | 5.73 |
| s | 0.076 | 0.062 | 0.37 | 0.32 | 1.03 | 0.66 | 0.09 | 0.16 | 0.19 | 0.24 | 0.25 | 0.31 | 1.35 | 1.82 |
| % Spike Recovery | 68 | 67 | 74 | 61 | 83 | 43 | 62 | 35 | 97 | 72 | 68 | 82 | - | - |

## TABLE 9

## COMPARISON OF SAMPLE STORAGE AND METHODOLOGY DIFFERENCES BASED UPON HIGH PRECISION RESULTS

| Element | Frozen Samples | | | | Acidified Samples | | | | Difference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SD | $N_r$ | $N_p$ | Mean | SD | $N_r$ | $N_p$ | Diff | T | Sig |
| Cd | 0.046 | 0.016 | 109 | 10 | 0.061 | 0.024 | 151 | 13 | -0.015 | -6.05 | Sig |
| Cu | 0.205 | 0.158 | 130 | 12 | 0.335 | 0.199 | 74 | 6 | -0.130 | -4.81 | Sig |
| Fe | 0.940 | 0.516 | 51 | 5 | 1.318 | 0.673 | 49 | 4 | -0.378 | -3.16 | Sig |
| Mn | 0.246 | 0.178 | 40 | 4 | 0.193 | 0.079 | 40 | 3 | 0.053 | 1.71 | NS |
| Ni | 0.226 | 0.118 | 30 | 3 | 0.235 | 0.088 | 35 | 3 | -0.009 | -0.35 | NS |
| Pb | 0.383 | 0.164 | 104 | 9 | 0.447 | 0.102 | 77 | 6 | -0.064 | -3.24 | Sig |
| Zn | 3.918 | 1.418 | 122 | 11 | 5.676 | 1.578 | 78 | 7 | -1.758 | -8.18 | Sig |

| Element | Atomic Absorption | | | | Electrochemistry | | | | Difference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SD | $N_r$ | $N_p$ | Mean | SD | $N_r$ | $N_p$ | Diff | T | Sig |
| Cd | 0.056 | 0.021 | 214 | 19 | 0.048 | 0.026 | 46 | 4 | 0.008 | 2.17 | Sig |
| Cu | 0.258 | 0.191 | 160 | 15 | 0.230 | 0.159 | 44 | 3 | 0.029 | 0.92 | NS |
| Pb | 0.446 | 0.155 | 112 | 10 | 0.352 | 0.101 | 69 | 5 | 0.093 | 4.91 | Sig |
| Zn | 4.601 | 1.202 | 129 | 12 | 4.797 | 2.574 | 59 | 5 | -0.195 | -0.56 | NS |

$N_r$ is the number of individual analyses.

$N_p$ is the number of laboratories from which data are drawn.

N.B. - Mean values will differ from those given in Table 2 since the number of individual analyses per laboratory varies.

replicate standard deviations are generally smaller, reflecting improved agreement between high precision participants. In most cases the dummy samples give lower results than the replicates. As in the case of the total data set, lower levels and lower spike recoveries are generally observed for frozen samples. The differences between acidified and frozen replicates are significant at the 95% level of confidence in all cases except manganese and nickel (Table 9). Lower concentrations in frozen samples could result from poorer preservation by this technique, contamination of acidified samples by the acid, or by increased leaching of the storage bottles at low pH. Generally inferior spike recoveries may, however, indicate poorer preservation of frozen samples.

We have also used the replicate sample results to test for differences between atomic absorption and anodic stripping analyses for cadmium, copper, lead and zinc. There exist small but significant (95%) differences between these two techniques for cadmium and lead but insignificant differences for copper and zinc (Table 9). Since the cadmium results were close to levels found in ambient seawater some caution should be exercised in directly equating cadmium analyses by these different techniques.

## 3. JMG ACTIVITIES

As a result of the ICES experience with trace metal intercalibrations the Joint Monitoring Group of the Oslo and Paris Commissions requested ICES to conduct for it low level intercalibrations for cadmium and mercury. These experiments were carried out during 1979 and recently reported (Thibaud 1980 and Olafsson 1980). Both of these experiments involved the distribution of natural and spiked seawater samples. Two sets of spikes were involved in both cases - one at about 5 times ambient seawater values and one at about 50 times ambient. The results of these experiments (Table 10 (Cd) and Tables 11 and 12 (Hg)) demonstrate that the proportion of laboratories obtaining good precisions and spike recoveries has increased dramatically since the commencement of intercalibration activities.

JMG is also conducting an intercalibration for trace metals in sediments. Its organizer is Dr. Chaussiepied of the Centre National de l'Exploration des Oceans (CNEXO) in France. No details of this intercalibration are, however, presently available.

## 4. IOC ACTIVITIES

The Global Investigation of Pollution of the Marine Environment (GIPME) program of IOC contains a Pilot Project Phase that includes intercalibration and training programs for laboratories within IOC member states that have expressed interest in the GIPME program. The Pilot Project includes three intercalibration steps for trace metals in seawater. These are a) a standards intercalibration, b) a low level seawater intercalibration and c) a sampling intercalibration. Due to the valuable work carried out within the various ICES intercalibrations, IOC was able to undertake the sampling intercalibration first rather than in sequence. It therefore took advantage of offers of laboratory facilities from the Bermuda Biological Station and of an oceanographic vessel from the US National Oceanographic and Atmospheric Administration (NOAA) to conduct an assessment of commonly used sampling devices for the collection of seawater samples for trace metal analysis.

This intercalibration experiment took place at the Bermuda Biological Station between January 10th and 25th 1980 as part of the IOC/UNEP/WMO Intercalibration of Sampling Procedures (PANCAL-80). Sampling operations were carried out on the National Oceanic and Atmospheric Administration vessel 'Kelez' temporarily based in St. George, Bermuda. The objectives of the experiment were to examine differences between commonly used procedures for seawater sampling. Therefore comparison of different sampling bottles (GO-FLO, Hyrdo-Bios and Niskin) and different methods of

TABLE 10

| | ALL LABORATORIES | | | | HIGH PRECISION LABORATORIES ABLE TO DETECT ± 30% OF THE CADMIUM ADDED | | | | HIGH PRECISION LABORATORIES ABLE TO DETECT ± 15% OF THE CADMIUM ADDED | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | n: | m: | S.D. | | n: | m: | S.D. | | n: | m: | S.D. |
| SAMPLES WITHOUT SPIKING | All Samples | 251 | 0.10 | 0.033 | All Samples | 105 | 0.10 | 0.029 | All Samples | 45 | 0.10 | 0.015 |
| | Frozen Samples | 89 | 0.10 | 0.036 | Frozen Samples | 36 | 0.12 | 0.026 | Frozen Samples | 18 | 0.11 | 0.008 |
| | Acidified Samples | 162 | 0.10 | 0.031 | Acidified Samples | 69 | 0.09 | 0.022 | Acidified Samples | 27 | 0.10 | 0.016 |
| | | n: | m: | S.D. | | n: | m: | S.D. | | n: | m: | S.D. |
| SAMPLES SPIKED WITH 0.65 µg Cd/l | All Samples | 282 | 0.81 | 0.158 | All Samples | 128 | 0.78 | 0.135 | All Samples | 62 | 0.76 | 0.083 |
| | Frozen Samples | 102 | 0.83 | 0.168 | Frozen Samples | 41 | 0.80 | 0.131 | Frozen Samples | 26 | 0.79 | 0.063 |
| | Acidified Samples | 180 | 0.80 | 0.151 | Acidified Samples | 87 | 0.77 | 0.137 | Acidified Samples | 36 | 0.75 | 0.092 |
| | | n: | m: | S.D. | | n: | m: | S.D. | | n: | m: | S.D. |
| SAMPLES SPIKED WITH 5.70 µg Cd/l | All Samples | 277 | 5.68 | 0.822 | All Samples | 140 | 5.68 | 0.670 | All Samples | 86 | 5.81 | 0.402 |
| | Frozen Samples | 94 | 5.75 | 0.834 | Frozen Samples | 62 | 5.84 | 0.738 | Frozen Samples | 41 | 5.80 | 0.424 |
| | Acidified Samples | 183 | 5.64 | 0.815 | Acidified Samples | 78 | 5.55 | 0.584 | Acidified Samples | 45 | 5.82 | 0.385 |

Reorganization of the results obtained for the frozen seawater samples and those obtained for the acidified seawater samples. (n = no. of analyses,
m = mean in µg Cd/l,
S.D. = Standard Deviation

## TABLE 11

## SUMMARY OF RESULTS WHEN OUTLIERS HAVE BEEN EXCLUDED

| Sea Water | Sea Water + Spike I | | Sea Water + Spike II | |
|---|---|---|---|---|
| ng/l | ng/l | % | ng/l | % |
| 9.5 ± 8.9 | 25 ± 9 | 109 ± 26 | 151 ± 34 | 98 ± 21 |
| n=24 | n=25 | n=22 | N=28 | N=26 |

## TABLE 12

## RESULTS FROM LABORATORIES REPORTING LESS THAN 10 ng/l IN SEA WATER

| Lab No. | Sea Water | Sea Water + Spike I | | Sea Water + Spike II | |
|---|---|---|---|---|---|
| | ng/l | ng/l | % Rec. | ng/l | % Rec. |
| 1 | 5.3 ± 0.8 | 21 ± 0 | 102 | 108 ± 4 | 72 |
| 4 | 7.2 ± 1.5 | 20.7 ± 0.6 | 87 | 133 ± 1.5 | 88 |
| 11 | 2.9 ± 0.7 | 17.9 ± 3.3 | 97 | 146 ± 7 | 102 |
| 12 | 7.1 ± 1.9 | 26.5 ± 2.5 | 126 | 110 ± 5 | 72 |
| 18 | 2.2 ± 0 | 17.5 ± 0.6 | 100 | 130 ± 2 | 89 |
| 20 | 2.4 ± 0.4 | 17.2 ± 2.9 | 96 | 145 ± 5 | 100 |
| 24 | 2.5 ± 0.4 | 18.1 ± 0.8 | 102 | 143 ± 4 | 98 |
| 26 | 3 ± 0 | 17.5 ± 1.9 | 94 | 153 ± 11 | 105 |
| 27 | 7.2 ± 2.5 | 25.3 ± 1.5 | 118 | 181 ± 19 | 121 |
| 28 | 7.5 ± 0.9 | 25.2 ± 3.2 | 115 | 137 ± 11 | 91 |
| 29 | 2.9 ± 1.1 | 16.9 ± 1.6 | 91 | 141 ± 7 | 96 |
| 30 | 2.4 ± 0.3 | 19.6 ± 1.0 | 112 | 143 ± 3 | 98 |
| 32 | 3.8 ± 0.5 | 19.0 ± 0.5 | 98 | 138 ± 8 | 94 |
| 34 | 2.1 ± 0.2 | 19.4 ± 0.9 | 112 | 150 ± 3 | 104 |
| 35 | 3.9 ± 0.4 | 24.5 ± 0.9 | 134 | 176 ± 5 | 121 |
| 36 | 8.2 ± 1.3 | 26.2 ± 1.2 | 117 | 164 ± 8 | 109 |
| N=16 | 4.4 ± 2.3 | 20.8 ± 3.5 | 106 ± 13 | 144 ± 20 | 98 ± 14 |

deployment (on stainless steel, Kevlar and plastic-coated galvanized steel hydrowire) was conducted. The experimental design consisted of deployment of the three types of sampling bottle together on a single hydrowire within a homogeneous body of water on Panulirus Station (Ocean Station S). Each participant was required to recover four duplicate samples from each type of sampling bottle in order to examine differences in the quality of samples recovered from them. Subsequent deployments of the same sampling devices on the other hydrowires in the same water mass were then used to examine relative hydrowire influences through the collection of additional samples.

The chosen experimental design contained considerable inherent redundancy to allow for reductions in the available ship-time, equipment failure or other constraints. The design was in fact modified during the course of the program by reducing this redundancy whilst maintaining the validity of the intercomparisons. The actual sampling procedure carried out involves individual comparisons as outlined in figure 2 below:

Figure 2

| | Bottle Type | | | |
|---|---|---|---|---|
| | Hydro-Bios | Modified GO-FLO | Niskin | GO FLO |
| Hydrowire Type | | | | |
| Stainless Steel | | X---------------- | X | |
| Kevlar | | X---------------- | X | |
| Plastic-coated Galvanized Steel | X-------------- | X | | |
| Stainless Steel | | X---------------------------- | | X |

Because of limitations in the winch handling capability aboard the 'Kelez' the original intention to deploy the sampling bottles at depths between 1500 and 2000 metres, where temporal and spatial gradients in temperature and salinity are small, had to be abandoned. As a result the bottles were deployed in depths of 1200-1300 metres and it became desirable to check the assumption of homogeneity over depth and time scales utilized in the above comparison. A set of duplicate samples were therefore collected at spatial and temporal extremities of a set of hydrowire casts to test the homogeneity assumption.

In addition, an examination of the effects of storage within sampling bottles was also carried out. A large volume of nearshore surface water was collected and used to fill different sampler types. Samples were then withdrawn from the sampling bottles at intervals up to 12 hours to see what influences on sample composition result from storage. Each participant was also encouraged to take samples of this surface water to provide additional intercalibration samples.

In most cases the participants took their samples to their home laboratories for analysis. They are expected to report their analytical data to the organizers by May 31st, 1980. The analytical facilities provided by the Bermuda Biological Station and by Perkin Elmer and Varian were extremely good and as a result a few participants carried out preliminary analyses or extractions on site.

Participants were drawn from Canada, the Federal Republic of Germany, the German Democratic Republic, Iceland, Japan, Korea, Malaysia, the Netherlands and the United States. Seven of these participants had previously participated in the ICES Fourth Round Intercalibration for Trace Metals in seawater.

## 5. PLANNED INTERNATIONAL ACTIVITIES

ICES - As the next step in its trace metal intercalibration series, ICES intends to carry out its own comparison of sampling devices. This exercise is known as the "ICES 5th Round Intercalibration for Trace Metals in Seawater"

First designed in 1977 this intercalibration will probably be modified on the basis of the results of the IOC's PANCAL-80 experiment. The ICES Working Group on Marine Chemistry which has overall responsibility for the ICES intercalibrations is presently considering introducing multi-ship and training aspects into the original 5th Round design. It is hoped that the experiment can be carried out in 1982, probably in a shelf or regional sea environment, and that it will examine comparability of samples collected by various sampling devices on various vessels.

ICES is also starting to invest in intercalibrations of other analytes in other media. It intends to commence a program of intercalibration for metals in marine sediments. The design of these experiments will await a review of the results of the JMG sediment intercalibration, but will probably be based upon the use of both sediment standards, such as MAG-1, and homogenized regional sediment reference materials such as those being prepared by the NRC Chemistry Division as part of the Canadian Marine Analytical Standards Program.

ICES is presently conducting an intercomparison exercise for petroleum hydrocarbons in crude oil fractions biota and sediments. This exercise, being coordinated by Dr. J. Portmann of the Ministry of Agriculture, Fisheries and Food, Burnham-on-Crouch, UK, will probably be followed by a series of intercalibrations, each designed to answer specific questions related to petroleum hydrocarbon analyses in marine materials.

IOC - The IOC is expected to proceed with both its high level standards and low-level seawater intercalibrations for trace metals in the next two or three years. It is unlikely that this organization will conduct further exercises unless the United Nations Environmental Program requests IOC to carry out intercalibration/training exercises within future Regional-Seas programs of this agency.

I have purposely not dealt with IOC activities related to other analytes. However the IOC will continue to expand on its activities during the PANCAL-80 exercise to improve the reliability and comparability of organohalogen analyses of seawater and sediments. A great deal was achieved during PANCAL-80 with regard to methods of sampling, extraction and analyses for organohalogen compounds in seawater. The interested reader is referred to the report of this exercise which should be available in late 1980.

## 6. SUMMARY

Considerable improvement in the intercomparability of marine analyses has been demonstrated through various international intercalibrations. It is to be hoped that future exercises will only be conducted to answer specific questions and wherever possible they will be carried out collaboratively by the various organizations interested in assessing and improving the quality of marine analytical data. It is equally beneficial to seek as wide a participation as possible to reduce costs and to increase the value of such exercises. As the refinement of these experiments and the performance of participants improves we should expect more universal use of better sampling and analytical procedures for the determination of contaminants in the marine environment.

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# THE OCEAN DUMPING CONTROL ACT IN THE ATLANTIC REGION

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In 1972 Canada signed with 44 other countries "The Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter", better known as the London Dumping Convention. The agreement specifies that signatory countries should regulate by means of a permit system the disposal of wastes in national marine waters and upon the high seas. In 1975 the Ocean Dumping Control Act was passed by the Parliament of Canada to control the disposal of wastes in waters and from vessels under Canadian jurisdiction, thereby fulfilling Canada's international obligations under the London Dumping Convention. The Department of the Environment, through the Environmental Protection Service is responsible for the administration of the Act by the mechanisms defined in the Ocean Dumping Control Regulations.

Ocean dumping as defined in the Act, "means any deliberate disposal from ships, aircraft, platforms or other man-made structures at sea of any substance", but does not include any disposal that is incidental in the normal operations of a ship or aircraft or is incidental or derived from the exploration and/or exploitation of the mineral resources of the sea bed, activities which are regulated by such legislation as the Canada Shipping Act and the Oil and Gas Production and Conservation Act. General prohibitions under the Ocean Dumping Control Act are:

1. No person shall dump except in accordance with the terms and conditions of a permit.
2. No person shall load a ship or aircraft in Canada for the purpose of dumping except in accordance with the terms and conditions of a permit.

3. No person shall dispose of any substance at sea by placing it on ice.
4. No person shall dispose of any ship, aircraft, platform or other man-made structure at sea except in accordance with the terms and conditions of the permit.
5. A person may dump, without a permit, if the dumping is necessary to avert danger to human life at sea or to any ship or aircraft.
6. Incineration at sea is deemed to be Ocean Dumping under the terms of the Act.

Substances considered to be harmful to the marine environment are listed in what is known as Schedule I of the Act. The disposal of Schedule 1 substances in concentrations greater than those listed in the following table is prohibited except in exceptional circumstances.

TABLE 1

SCHEDULE 1 (PROHIBITED) SUBSTANCES AND THEIR REGULATED LIMITS

| SUBSTANCE | MAXIMUM QUANTITY OR CONCENTRATION |
|---|---|
| 1. Organohalogen Compounds | .01 Parts of a Concentration shown to be toxic to Marine Animals and Plant sensitive organisms |
| 2. Mercury and Mercury Compounds | Solid Phase - 0.75 mg/kg<br>Liquid phase - 1.5 mg/kg |
| 3. Cadmium and Cadmium Compounds | Solid phase - 0.6 mg/kg<br>Liquid phase - 3.0 mg/kg |
| 4. Persistent Plastics and other Persistent Synthetic Materials | 4% by Volume in a suitably comminuted form |
| 5. Crude Oil, Fuel Oil, Heavy Diesel Oil and Lubricating Oil, Hydraulic Fluids and any Mixtures containing any of them. | 10.0 mg/kg of n-Hexane soluble substances |

| | | |
|---|---|---|
| 6. | High Level Radioactive waste or Other High Level radioactive Matter | - 10 Ci/t $\alpha$ - Active<br>- 10 Ci/t $\beta/\gamma$-Active |
| 7. | Substances Produced for Biological or Chemical Warfare | No Prescribed Limit |

The signatories to the London Convention recognized that special care should be exercised in releasing certain other substances to the marine environment. These substances are listed in Schedule II of the Act as outlined in Table 2. Acceptable levels of contamination of material to be dumped, containing these substances, have not been established as yet, although they are currently under review.

## TABLE 2

## SCHEDULE II (RESTRICTED) SUBSTANCES*

1. Arsenic and its compounds
2. Lead and its compounds
3. Copper and its compounds
4. Zinc and its compounds
5. Organosilicon compounds
6. Cyanides
7. Fluorides
8. Pesticides and their by-products not included in Schedule I
9. Beryllium and its compounds
10. Chromium and its compounds
11. Nickel and its compounds
12. Vanadium and its compounds
13. Containers and Scrap Metal
14. Radioactive Wastes or other Radioactive Matter not included in Schedule I
15. Substances that by reason of their bulk would interfere with fishing

*NOTE: No prescribed limits are given for these substances in the Act.

Control over ocean disposal is maintained by means of a permit system as depicted in Figure 1 and outlined below:

1. Application is made by a proponent on one of the five prescribed forms. Data regarding various parameters describing the type and origin of the material to be disposed of and the location of the dumpsite as listed in Schedule III of the Act are required on these forms. The application must be accompanied by supporting analytical documentation characterizing the material and determination of Schedule I and II substance concentrations. The proponent must, if necessary, be able to defend the analytical procedures and results in a court of law.
2. When permit applications are received by the Environmental Protection Service they are screened to ensure that all relevant information is present. The information is then entered into a computer where it is constantly updated as the applications pass through the review system.
3. After screening the applications are distributed to the appropriate agencies for review as indicated in Figure 1.
4. The comments on each application, when received from the reviewing agencies, (time limit of 3 weeks) are incorporated by EPS into the terms and conditions of a permit.
5. The permit, with its terms and conditions, is reviewed by the Regional Ocean Dumping Advisory Committee (RODAC), which is composed of representatives from the Department of Fisheries and Oceans as well as the Environmental Protection Service, (EPS), and makes a final recommendation on approval to the Regional Director General of EPS. The terms of reference for RODAC are outlined in Appendix I.

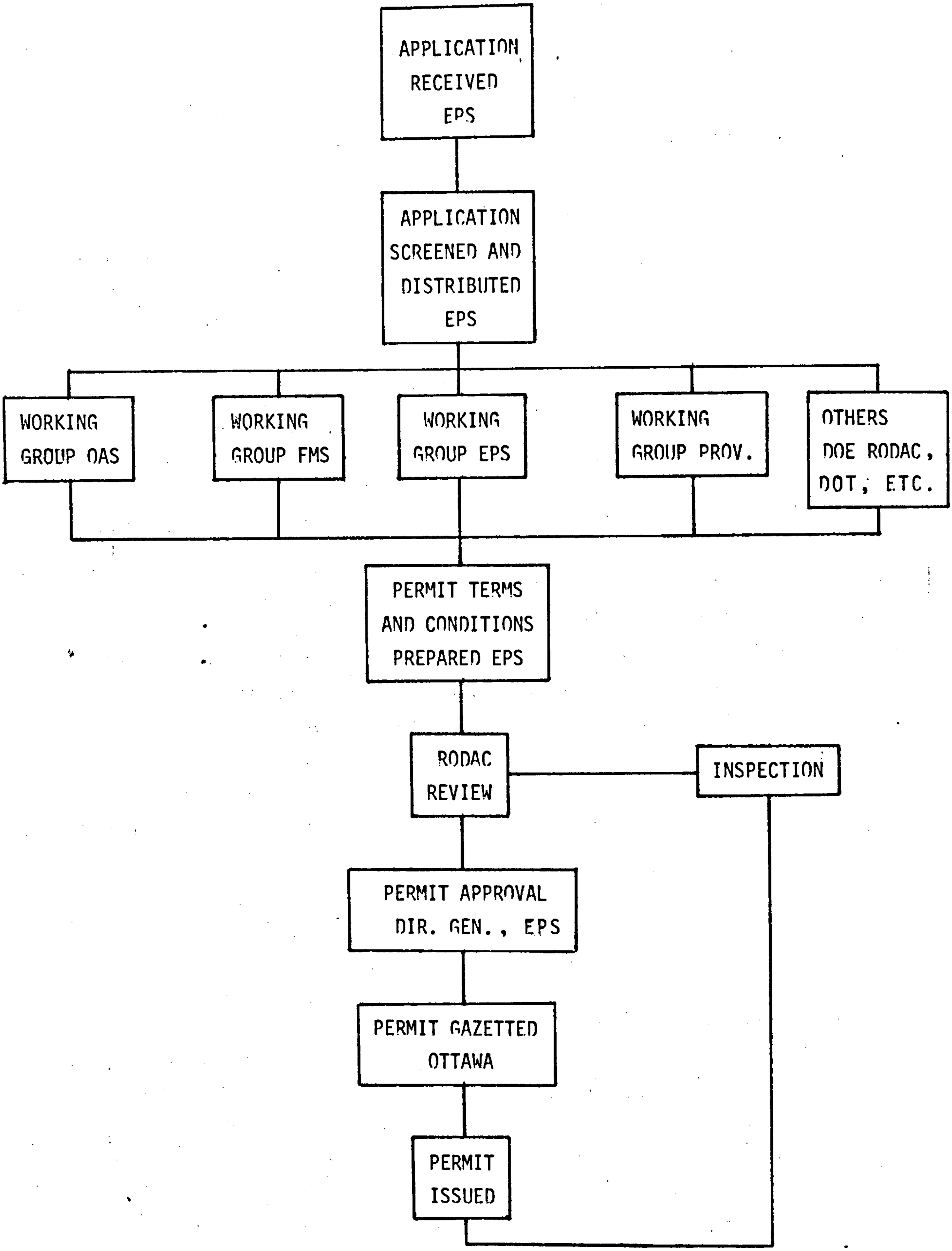

FIGURE 1: PROCEDURE FOR OCEAN DUMPING PERMIT APPLICATION REVIEW IN THE ATLANTIC REGION

6. If a permit is approved it must then be published in the Canada Gazette prior to being issued to the proponent. Permits are generally valid for one year. Restrictions of time, quantity and manner of disposal, if required, are incorporated in the text of the permit.

The permit processing system has been streamlined by the incorporation of a series of guidelines for the pre-screening of applications for the disposal of dredging spoils, which are repeated annually, and involve clean material only. Through this system if a permit application complies with the guidelines as outlined in Appendix II, and if no other concerns are expressed, it will be referred directly to RODAC members by phone and a permit with recommendation for approval by RODAC is immediately drafted for signature.

To date, in the Atlantic Region, 491 permit applications have been reviewed as follows: 99 in 1976; 116 in 1977; 142 in 1978; and 134 in 1979. The vast majority of these relate to the dredging of ports, harbours and channels. Other less frequent applications involve vessel disposal, fish gurry disposal and oil spill experiments, to name the predominant types.

Of the 491 applications for disposal 387 (79%) were approved on first review by RODAC while of the remaining 104, 78 were approved after further investigation. Fifteen permits have been denied, with alternate disposal methods suggested, and 9 remain under review.

Fifty of the applications which presented problems to RODAC involved reported high levels of the Schedule I substance, Cadmium. Of these, 38 permits were granted after further analysis and review, 6 were refused, 2 withdrawn and 4 are still pending.

Mercury levels above those specified in Schedule I accounted for 11 first round rejections with an ultimate refusal of 2 permit applications. Organohalogens were implicated in 17 cases resulting in 6 refusals. The foregoing summary is, however, an oversimplification of the actual circumstances since in many cases more than one contaminant was implicated.

From the foregoing description of the Ocean Dumping Permit issuing system it is readily apparent that accurate, standardized analyses are the foundation upon which the system rests. Permits are, in many cases, approved or denied on the basis of measured concentrations of Schedule I substances in the material to be disposed of. Also the effects of ocean disposal upon the sediment geochemistry and concentrations of contaminants in biota at the disposal site can only be monitored by carrying out accurate, repeatable chemical analyses. Hopefully this "Round Robin" process and similar workshops in the future will help to assure accurate analyses which are comparable between laboratories, thereby insuring a fair and dependable measure of environmental contamination and a reliable tool for environmental protection.

# APPENDIX I

## REGIONAL OCEAN DUMPING ADVISORY COMMITTEE
## (Atlantic)

TERMS OF REFERENCE:

1. To ensure the technical review of applications is received pursuant to the administrative requirements of the Ocean Dumping Control Act and to recommend to the Regional Director of the Environmental Protection Service (a) terms and conditions to be incorporated with the permits issued; (b) denial of permit because of unacceptable damage to the marine environment.

2. To advise the Regional Director of the Environmental Protection Service on technical and scientific matters pertaining to the Ocean Dumping Control Act.

3. To develop and coordinate regional methods of achieving the operational requirements of inspection, assessment, monitoring and investigation for the effective implementation of the Ocean Dumping Control Act.

4. To recommend the appointment of inspectors and analysts and the nomination of members for the Board of Review.

5. To review and assess reports pursuant to Section 8(4) of the Ocean Dumping Control Act and to recommend action.

6. To ensure that appropriate consultation with other federal government departments and provincial agencies is being carried out.

7. The membership of the Committee is to be composed of one member from each of the following: EPS Atlantic (Chairman), Fisheries Management (Maritimes) and Ocean and Aquatic

Sciences (Atlantic); in matters pertaining to Fisheries Management in Newfoundland and Labrador, there will be a standing member of Fisheries Management (Newfoundland) who will be the voting representative instead of the Maritime Region representative.

8. Environmental Protection Service will provide the Secretariat functions for RODAC and ensure that ocean dumping requests are registered, screened and adequate information accompanies each application.

9. Develop and monitor the effectiveness of pre-screening guidelines for ocean dumping requests.

10. RODAC reports to the Regional Director, Environmental Protection Service, with respect to recommendations on approval or denial of ocean dumping requests. RODAC members are responsible to respective Service Directors regarding the quality of technical review of applications received for ocean dumping.

11. Recommendations made to the Regional Director of the Environmental Protection Service re Permit conditions, including amendments, shall contain the signature of each RODAC member.

# APPENDIX II

## PRESCREENING GUIDELINES

## OCEAN DUMPING APPLICATIONS

If an ODCA application meets all the requirements listed below, it will be referred directly to RODAC members by phone. If no additional concerns are expressed, a permit and a recommendation for approval will be drafted for signature by RODAC members.

GUIDELINES:

1. If the operation is identical to a past operation.

2. If the operation is similar to a past operation but with small changes*, e.g. amount of dredged spoils less than 50% increase of previous quantity to a maximum of 75,000 cubic metres.

3. Past chemical reports indicate the dredged site is not contaminated by Scheduled Substances. New chemical and physical data is required every four years.

4. No major concerns were expressed by Federal or Provincial agencies following the same operation in the past.

5. No newly developed industrial sites in the area.

6. No complaints from the public.

7. Dumping of fish offal.

* Changes include dredging within 1/2 kilometre from previous dredging site. Changes do not include changes in dredging equipment, timing of dredging and disposal operations, and changes in dump site.

# THE MARINE ANALYTICAL CHEMISTRY STANDARDS PROGRAM

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## ABSTRACT

The purpose of this National Research Council program is to help improve the accuracy of analytical chemistry data produced in response to needs in marine science and engineering and for the management of marine resources. Work at the Atlantic Regional Laboratory and the Division of Chemistry is aided by advice from a Committee on Marine Analytical Chemistry, representative of marine science and analytical chemistry interests. Development of reference materials is emphasized. Analytical methods are also studied and developed. Much is done through cooperative projects and by contracts. Some results will be presented.

Note: The details pertaining to this Abstract are presented in the following paper by Berman and Sturgeon.

# NRC REFERENCE MATERIALS PROGRAM

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## ABSTRACT

As part of the Marine Analytical Chemistry Standards Program, the Chemistry Division, National Research Council, Ottawa is carrying out a program of inorganic analysis aimed at improving analytical data in marine science. Problems associated with the determination of heavy metals in both seawater and marine sediments are currently being examined.

Progress in the preparation of two marine sediment standard reference materials for trace metal analysis as well as the intralaboratory analysis of seawater samples is discussed.

As part of the Marine Analytical Chemistry Standards Program (cf. W.D. Jamieson), the Division of Chemistry, National Research Council, Ottawa, is carrying out a program of inorganic analysis aimed at improving analytical data in marine science. Problems associated with the determination of heavy metals in both seawater and marine sediments are currently being examined. In this connection we report here on progress in the preparation of two marine sediment standard reference materials for trace metal analysis as well as the intralaboratory analysis of seawater samples.

Analytical facilities available in the Division of Chemistry are well suited to meet the demands of the marine program. Table 1 outlines the instrumental techniques that have been used for the analysis of both marine sediments and seawater following the chemical and/or physical conversion of the sample into a form compatible with the selected instrumentation. It is felt that such facilities will be adequate for the in-house certification of a wide range of trace metals in marine matrices.

Prior to the Marine Standards Program the laboratory had no experience in the analysis of marine samples. An intensive program of internal self-calibration and participation in a number of interlaboratory analyses of trace elements in marine materials was therefore undertaken. Table 2 lists the interlaboratory analytical programs in which this laboratory participated.

With the experience gained through participation in such programs and the already proven capability in inorganic trace analysis it was felt that production of a marine Standard Reference Material (marine sediment) was a feasible task. In this connection two marine sediments were collected and freeze dried for NRC through private contract. Grab samples were taken from the Mirimichi Estuary and the Baie de Chaleur in the Gulf of St. Lawrence. Following freeze drying 388 lb of Mirimichi sediment (hereafter designated as MESS-1, Mirimichi Estuary Sediment Sample-1) and 334 lb of Baie de Chaleur (BCSS-1) were available for processing in this laboratory. Table 3 outlines the sequence of operations used to process the sediments. The major debris (stones, wood, shells, etc.) were first removed by hand from the freeze dried material and the larger aggregates rolled. Fine crushing of the material was avoided in an effort to preserve the mineralogical integrity of the samples. Following screening at -120 mesh (stainless steel screens) 45% of the MESS-1 and 83% of BCSS-1 by weight were recovered for blending and bottling. Homogenization was carried out in a steel blender large enough to accommodate the entire weight of each sample. Following tests for homogeneity (analysis by XRF and ICPES), the sample was bottled in 60-75 gram lots in 4 oz glass bottles with polypropylene screw caps. The samples were then $\gamma$-irradiated (2.5 x 10 Rads) in order to arrest bacteriological action and a further group of bottled samples was randomly selected for further homogeneity analysis.

We are presently completing the homogeneity testing of the bottled samples and are preparing for an in-house certification of the materials. An in-house certification will be carried out primarily because of the time factor and because we feel that we have the necessary expertise for most elements of interest for such a certification. A limited number of other laboratories will be invited to participate in the project.

Following total decomposition with a HCl, $HNO_3$, $HClO_4$ and HF mixture, the samples will be certified for as many trace elements as feasible with special attention being given to Cu, Pb, Zn, Cr, Co, Cd, As, Ni, V, Mn, Hg, Se, U, Mo, Ag, Sb, Fe and Be as recommended by S. MacKnight and R. Guevremont in their Report to the Marine Standards Group of the National Research Council of Canada on the Preparation of a Marine Sediment Reference Material for Trace Metal Analysis (March, 1979). We will also attempt to characterize the materials with regard to a number of major and minor constituents.

It is intended that certification of these samples be completed by the end of 1980. Approximately 1000 bottles of MESS-1, each containing 60 g of material, will be available. Approximately 1400 bottles of BCSS-1, containing 75 g sediment per bottle, have been processed. These materials will be marketed through NRC at a cost that is yet to be determined.

Should these two marine sediments prove useful to the marine analytical community, preparation and certification of additional sediments will be undertaken in the future.

In addition to the preparation of the above sediments, work is continuing with the analysis of seawater for trace metals. Table 4 lists the analytical techniques currently applied to this problem. Filtered, acidified coastal seawater samples are analyzed for Fe, Zn, Cd and Mn by graphite furnace atomic absorption using direct injection of the sample and for Fe, Zn, Cd, Mn, Pb, Cu, Ni, Cr, and Co following matrix separation and preconcentration using chelation-solvent extraction (APDC-MIBK) and ion-exchange (on Chelex-100) techniques. Additionally, such preconcentrates (by ion-exchange) are also analyzed by isotope dilution spark source mass spectrometry and by inductively coupled argon plasma atomic emission.

These techniques have been successfully applied to a number of seawater samples. Results for a typical filtered coastal seawater are given in Table 5 wherein it is evident that good agreement has been obtained for the concentrations of trace elements by the different techniques. Intralaboratory studies such as these provide a practical means of testing the validity of different analytical methods, give increased confidence in the results obtained and are especially valuable when standard reference materials are unavailable.

This laboratory is now in a position to begin an intensive study of the long term storage characteristics of seawater, eventually leading to the production of a trace metal standard reference material for seawater.

## TABLE 1. NRC - ANALYTICAL FACILITIES

Flame Atomic Absorption Spectrometry
Electrothermal Atomic Absorption Spectrometry
Inductively Coupled Plasma Atomic Emission Spectrometry
Isotope Dilution Spark Source Mass Spectrometry
X-ray Fluorescence Spectrometry
Photon Activation Analysis
D.C. Arc Emission Spectrography
Ion Selective Electrodes
UV-Vis Spectrophotometry
Classical Wet Chemical Methods

## TABLE 2. NRC - PARTICIPATION

ICES 4th Round Trace Elements in Seawater
ICES Cd in Seawater
ICES Pb and Cd in Fish Tissue
NBS Oyster Tissue SRM Certification

## TABLE 3. SEDIMENT PROCESSING

Collection - grab samples
Freeze dried
Rolled, debris removed
Screened at 120 mesh
Blended for 10 hours
Homogeneity analysis
Bottling: 60-75 g/bottle
Irradiated
Homogeneity analysis
Certification in-house

# TABLE 4. SEAWATER ANALYSIS

Electrothermal Atomic Absorption - direct
- preconcentrates

Isotope Dilution Spark Source Mass Spectrometry
- preconcentrates

Inductively Coupled Plasma Atomic Emission
- preconcentrates

## TABLE 5. ANALYSIS OF SEAWATER

CONCENTRATION, ng/mL

| | GFAAS | | | ICPES | IDSSMS |
|---|---|---|---|---|---|
| Element | Direct | Chelation-Extraction | Ion-Exchange | Ion-Exchange | Ion-Exchange |
| Fe | 3.7 ± 0.3[a] | 3.2 ± 0.2 | 3.4 ± 0.4 | 3.2 ± 0.2 | 3.3 ± 0.3 |
| Mn | 2.5 ± 0.2 | 1.9 ± 0.2 | 2.2 ± 0.3 | 2.3 ± 0.1 | ND |
| Cd | 0.05 ± 0.01 | 0.06 ± 0.01 | 0.053 ± 0.007 | ND | 0.07 ± 0.01 |
| Zn | 1.8 ± 0.3 | 1.8 ± 0.1 | 2.0 ± 0.1 | 1.6 ± 0.2 | 1.9 ± 0.1 |
| Cu | ND[b] | 0.5 ± 0.1 | 0.51 ± 0.03 | 0.73 ± 0.06 | 0.61 ± 0.04 |
| Ni | ND | 0.46 ± 0.03 | 0.45 ± 0.05 | 0.38 ± 0.02 | 0.43 ± 0.03 |
| Pb | ND | 0.06 ± 0.02 | 0.10 ± 0.01 | ND | 0.11 ± 0.02 |
| Cr | ND | 0.29 ± 0.03 | 0.25 ± 0.02 | ND | ND |
| Co | ND | 0.015 ± 0.003 | 0.018[c] ± 0.008 | ND | 0.028[d] ± 0.001 |

[a] Precision expressed as standard deviation

[b] Not determined

[c] Preconcentrated 100-fold

[d] Spark source mass spectrometry-internal standard method

# SAMPLING AND ANALYSIS OF SEDIMENTS FOR THE PURPOSES OF THE OCEAN DUMPING CONTROL ACT. PROBLEMS AND SUGGESTIONS FOR SOLUTIONS

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## ABSTRACT

Sample collection, analysis, and data interpretation are discussed with an emphasis on chemical, statistical, and regulatory problems. The current practice is quite unsatisfactory. Analytical data for some of the trace elements are questionable and the situation is much worse for PCB's and organochlorine pesticides. For the latter, not only the quantitative data, but even the identification poses problems. Literature data are reviewed to obtain some estimates of analytical variance. Few data on variance between samples are available. Probability distributions and their effects on confidence limits are considered. It is recommended to use statistical methods in determining compliance with regulations.

## 1. INTRODUCTION

Sampling and analysis of sediments under ODCA include the design and execution of a sampling scheme, handling of the samples prior to analyses, analytical operations such as preparation of samples for analyses, extraction, cleanup, quantitation, calculations, preparation of a report and interpretation of the results.

As a rule, all steps of this sequence are not performed by the same staff, and in many cases not even by the same organization. For example, analyses may be performed by commercial laboratories and the results interpreted by various government agencies. Consequently, it is important for all participants to be aware of the precision and accuracy of the data and of possible pitfalls.

The error of the final data consists basically of the sum of the sampling error (how representative of the sampled area is the analyzed sample) and the analytical error (how accurate are our analyses of the collected samples). Although the latter appears to be the main topic of this workshop, this paper will discuss both types.

## 2. SAMPLING

Sampling methods and instruments have been discussed in detail by Walton (1978) and will not be mentioned here. Instead, I will address the question of the sampling error. It seems that most dredging permits are based on one or on just a few analyses. It would be obviously too expensive to set up a detailed sampling grid in each and every case, and we have to use judgement and live with some uncertainty. At the same time we should have an estimate of the magnitude of this uncertainty.

In the case of trace elements, the upper limit of the variations likely encountered in sediments may be obtained from a study of soils by Shaclette et al. (1971). A part of the data is reproduced in Table 1.

TABLE 1

MEAN COMPOSITION OF SOIL (EASTERN U.S.)

AFTER SHACLETTE ET AL. (1971)

| Element | Geometric<br>Mean (mg/kg) | Coefficient of variation (%) |
|---|---|---|
| Copper | 14 | 18 |
| Iron | 15000 | 0.02 |
| Manganese | 285 | 1.3 |
| Nickel | 13 | 20 |
| Lead | 14 | 14 |
| Zinc | 36 | 5.3 |

The distribution of the results was lognormal; consequently, the standard deviation is multiplicative. For example, for lead, 68% of the values is in the interval 7-41 mg/kg. It is clear that the variations are considerable. Unfortunately, cadmium was not measured in this study.

It is likely that similar, possibly somewhat smaller variations may be encountered for contaminants such as PCB's and organochlorine pesticides, particularly in areas subject to dredging, such as harbours.

The data are very sketchy. For PCB's in Victoria, B.C. harbour, the variation between samples from the same barge was 25%, between samples from different barges 35%, but unfortunately, it was 40% between subsamples (MacDonald 1979). For hydrocarbons, the coefficients of variation were 8, 18.5, and 26.3% for duplicate analyses, subsamples, and grab samples, respectively (Boehm and Quinn 1978).

It is possible to design a statistically optimal sampling program, as demonstrated for instance by Kleiber et al. (1978) for water samples. The first and most important step in the procedure is to determine the variance between replicate subsamples and between samples. This alone would give some idea about the errors associated with attempts to characterize a dredge spoil by a single sample.

The intrinsic heterogeneity of sediments may play a significant role in determining the confidence intervals of minor constituents. This aspect was considered in detail in geological analyses and it has been established that the results depend on subsample size (Ingamells 1974), with accuracy decreasing with decreasing size of the sample. Theoretical considerations of this problem are based on the assumption that trace components tend to have a Poisson rather than a normal distribution. There are indications that this may be the case for oil droplets in water (Ahmed et al. 1974). It would not be surprising to find that under some circumstances contaminants in sediments have a Poisson distribution as well. Poisson distribution is frequently positively skewed and its variance equals the mean. An example is given in Fig. 1.

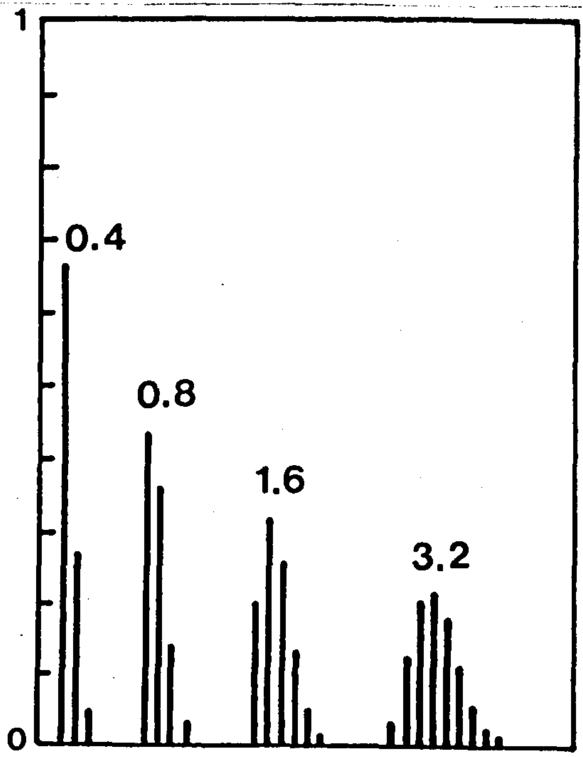

FIG. 1. Poisson distribution. Bars indicate probability of 0, 1, 2, etc. occurrences for expectations indicated in the figure.

Until better data on the degree of variation between sediment samples are obtained it may be assumed for PCB's and organochlorine compounds that variance is equal to the mean. Data of Table 1 could be used as maximum estimates of variance for trace elements.

In many permit applications containing more than one sediment analysis it is often impossible to identify the origin of the samples. All too often the applications have attached analytical data on Sample 1, 2, 3, etc. without any indications as to where these had been obtained.

Contamination is a continuing hazard from the collection, through handling and workup of samples up to quantitation, where it may, in addition, take on the form of interference or mis-identification.

## 3. SAMPLE HANDLING AND PHYSICAL ANALYSIS

Sample handling, including taking subsamples from samples, the choice of containers, storage and physical analysis have been discussed in detail in Walton (1978). It may be interesting to estimate the variability due to the heterogeneity of samples as taken by various samplers.

The commonly used wet sieving through a 2-mm sieve should be used with caution on samples containing organic materials such as bark, wood chips and wood fiber. Considerable quantities of organic contaminants, for example PCB's, may be adsorbed on this material and might escape detection.

The exposure of anaerobic sediments to air should be limited as much as possible to avoid oxidation. Oxidation may modify the distribution of trace elements as determined by selective leaching techniques.

## 4. CHEMICAL ANALYSIS OF SAMPLES

The digestion of samples or selective extraction for the determination of trace elements, and extraction of organic contaminants have been described elsewhere (see for example Förstner 1979; Zitko 1980).

Analytical errors associated with these steps have been evaluated only occasionally. In the determination of hydrocarbons in sediments, the coefficient of variation between chromatographic runs was 5% as compared to the coefficient of variation between duplicate analyses of 9% (Boehm and Quinn 1978).

The coefficients of variation are, as one would expect, higher in interlaboratory comparisons than in analyses performed in the same laboratory (Table 2, 3).

TABLE 2

RESULTS OF INTERLABORATORY SEDIMENT ANALYSES

| Component | Sediment 1 Mean | Sediment 1 C.V. | Sediment 2 Mean | Sediment 2 C.V. | Method | Reference |
|---|---|---|---|---|---|---|
| Organic carbon | 2.28 | 3.2 | 61.2 | 1.5 | S | Zink-Nielsen |
| | 2.96 | 50.5 | 43.1 | 23.6 | D | |
| Copper | 6.7 | 17.8 | 69 | 16.2 | S | " |
| | 6.7 | 33.8 | 75 | 5.4 | D | |
| Lead | 7.2 | 88.0 | 74 | 19.7 | S | " |
| | 6.3 | 51.5 | 64 | 18.7 | D | |
| Cadmium | 0.8 | 68.5 | 2.2 | 45.5 | D | " |
| Mercury | 0.047 | 34.1 | 0.759 | 8.0 | D | " |
| Hydrocarbons | 0.187 | 135 | 1.84 | 110 | D | Hilpert et al. (1978) |
| Total extractable hydrocarbons | 6.4 | 114 | 31.0 | 122 | D | " |
| Polynuclear aromatic hydrocarbons | | 1-30 | | | S | Heit & Tan (1979) |
| PCB's | 0.583 | 26 | | | | Pavlov & Hom (1976) |
| DDT | 0.03 | 86 | | | | " |

mg/g for organic carbon, mg/kg for other components
C.V. = coefficient of variation, %
S = same; D = different

## TABLE 3
## RESULTS OF INTRALABORATORY SEDIMENT ANALYSES

| Compound | Mean, mg/kg | C.V., % | Reference |
|---|---|---|---|
| Oil and grease | 329 | 13 | Fulk et al. (1975) |
| PCB's | 0.120 | 6.5 | Shimokawa et al. (1978) |
| Aliphatic hydrocarbons | 20 | 37 | Farrington et al. (1977) |
| Hydrocarbons | 0.418 | 30 | Hilpert et al. (1978) |
|  | 0.910 | 25 | " |
| Copper | 7-122 | 4 | Loring and Rantala (1977) |
| Lead | 12-40 | 4-15 | " |

It can be seen from Tables 2 and 3 that the coefficients of variation increase by a factor of about 4 when analyses are performed by several laboratories.

Detailed studies of coefficients of variation of organochlorine pesticides in sediments are not available to my knowledge. The results of an OECD intercalibration study (Table 4) may give some indication of the interlaboratory variability.

## TABLE 4
## ORGANOCHLORINE COMPOUNDS, RESULTS OF INTERCALIBRATION BETWEEN 24 LABORATORIES. SUBSTRATE: AMENDED CORN OIL (OECD 1978)

| Compound | Mean (ng/g) | Coefficient of variation (%) |
|---|---|---|
| Hexachlorobenzene | 50.5 | 19.7 |
| α-HCH | 41.0 | 24.6 |
| β-HCH | 45.4 | 28.1 |
| γ-HCH | 46.4 | 19.4 |
| Dieldrin | 102.4 | 10.3 |
| p,p'-DDE | 97.9 | 24.2 |
| p,p'-DDD | 184.7 | 18.7 |
| p,p'-DDT | 192.3 | 17.8 |
| PCB (1254) | 1070 | 15.4 |

The substrate was homogeneous. Consequently, one would expect that for sediments the coefficients may be 2-5 times higher.

Polycyclic aromatic hydrocarbons (PAH's) are not, as such, one of the scheduled substances under ODCA, but it is only a question of time before the rather imprecise definitions of oil or oil and grease will be changed. The new definition will almost certainly include the term polycyclic aromatic hydrocarbons.

No data on the interlaboratory variability of analyses of PAH's in sediments are available and, to provide some bench marks, some results of a study of PAH-amended minced meat is given in Table 5. Fluoranthene and pyrene are usually the most abundant PAH's in sediments, but have not been included in this intercalibration.

TABLE 5

POLYCYCLIC AROMATIC HYDROCARBONS, RESULTS OF INTERCALIBRATION BETWEEN FIVE LABORATORIES, SUBSTRATE: AMENDED MINCED MEAT (HAENNI 1978)

| Hydrocarbon | Mean (ng/g) | Variation coefficient (%) |
|---|---|---|
| Chrysene | 13.3 | 9.2 |
| Benzo b fluoranthene | 12.1 | 3.1 |
| Benzo b pyrene | 7.65 | 27.0 |
| Benzo a pyrene | 11.1 | 23.7 |
| Perylene | 8.89 | 22.7 |
| Dibenzo[a,j]anthracene | 11.8 | 7.1 |

Again, due to the heterogeneity of sediments, the variation coefficients of PAH's are likely to be higher than those in Table 5.

On homogeneous samples and with laboratories experienced in analyses, the coefficients of variation may be kept quite low, as illustrated in Table 6 for trace elements.

## TABLE 6

## RESULTS OF AN INTERLABORATORY STUDY OF TRACE ELEMENTS IN OYSTER TISSUE (FUKAI ET AL. 1978)

| | Overall | | | Selected | | |
|---|---|---|---|---|---|---|
| Element | No. | Mean (mg/kg) | C.V. (%) | No. | Mean (mg/kg) | C.V. (%) |
| Copper | 66 | 311 | 2.9 | 37 | 335 | 1.2 |
| Zinc | 77 | 2700 | 3.7 | 37 | 2870 | 1.1 |
| Cadmium | 50 | 2.7 | 15 | 37 | 2.3 | 4.4 |
| Mercury | 44 | 0.27 | 15 | 31 | 0.20 | 5 |
| Lead | 34 | 3.0 | 17 | | | |

As the data in Table 6 indicate with some polishing of the results using statistical criteria, the coefficient of variation for most trace elements can be kept at 5% or lower and at about 15% or better using "raw" data.

Comparing the data of Table 6 with those of Tables 2 and 3 one may conclude that there is considerable room for improvement in the performance of sediment analyses. On the other hand, before going too far in this direction, we should know the amount of variation inherent in the heterogeneity of the sediments. In other words, there is not much point in striving, at all costs, for a coefficient of analytical variation of 1% when the between-samples variation is 100%.

There are still problems with the determination of trace elements, particularly cadmium in sediments, but those encountered with PCB's and organochlorine pesticides are much worse. In this case, not only the precision and accuracy but even the identification is questionable. Since laboratories report regularly o,p'-DDE, p,p'-DDE, and p,p'-DDT (Table 7), others report DDE, DDD, and DDT, presumably all p,p' (Table 8).

## TABLE 7

## CONCENTRATIONS OF ORGANOCHLORINE PESTICIDES AND PCB'S IN SEDIMENTS AS REPORTED BY SOME LABORATORIES.

CONCENTRATION (ng/g)

| o,p'-DDE | p,p'-DDE | p,p'-DDT | PCB |
|---|---|---|---|
| 0.4 | 0.3 | - | 0.3 |
| 1.5 | 1.1 | 5.6 | 1.4 |

It is not clear from the application for dredging, but these appear to be duplicate samples.

## TABLE 8

## CONCENTRATION OF ORGANOCHLORINE PESTICIDES AND PCB'S IN SEDIMENTS, AS REPORTED BY SOME LABORATORIES

| | Concentration (ng/g) | | | |
|---|---|---|---|---|
| Depth (cm) | DDE | DDD | DDT | "Arochlor" 1254[1] |
| 0-12 | <0.2 | 58.5 | 151 | 1000 |
| 12-23 | 1.8 | 3.7 | 7 | 1800 |
| 0-12 | 42.0 | 96.0 | 126 | 3700 |
| 12-28 | 21.4 | 93.7 | 453 | <5 |

[1] At least they could learn to spell Aroclor.

The samples in Table 8 came from the same general area, and it is difficult to believe that the variations are real.

GC records of sediment analyses for organochlorine compounds, together with records of standards, should accompany routinely analytical reports. It would also be helpful to have a better description of the method used. A reference to Walton (1978) is not sufficient, since the report contains several methods. A description quoted in Table 9 is not very illuminative either, except perhaps on the competence of the laboratory.

TABLE 9

EXAMPLE OF A POOR DESCRIPTION OF AN ANALYTICAL TECHNIQUE

"RESIDUES WERE EXTRACTED FROM THE SEDIMENT WITH A SOXHLET EXTRACTOR, ELUTED THROUGH A FLORISIL COLUMN AND QUANTITATED WITH THE ELECTRON CAPTURE DETECTOR OF A GAS CHROMATOGRAPH"

PAH's may interfere with the quantitation of organochlorine compounds and to assess the potential for interference one must know the cleanup conditions, the type of the EC detector and its operating temperature (Zitko 1980).

In ODCA, organochlorine compounds are regulated on the basis of toxic effects ("0.01 of a concentration shown to be toxic"). There is a lack of data for converting effects into concentration. From the work of McLeese and Metcalfe (1980) on the toxicity of organochlorine pesticides in water and in sediment to *Crangon septemspinosa*, one may attempt to derive the toxic concentration (Table 10).

TABLE 10

TOXIC CONCENTRATIONS AND REGULATED LEVELS OF ORGANOCHLORINE PESTICIDES IN SEDIMENTS (BASED ON MCLEESE AND METCALFE 1980). IT IS ASSUMED THAT SEDIMENT CONTAINS 6% OF ORGANIC CARBON.

| | ng/g | |
|---|---|---|
| Pesticide | Lethal concn. | 0.01 x lethal concn. |
| Dieldrin | 60 | 0.6 |
| Endosulfan | 280 | 2.8 |
| DDT | 650 | 6.5 |
| Endrin | 1460 | 15 |
| Chlordane | 3110 | 31 |

McLeese and Metcalfe (1980) concluded that the toxicity of pesticides incorporated in sediments is determined by their concentration in water that is in equilibrium with the contaminated sediment. The equilibrium concentration is given by the adsorption coefficient, which in turn, depends on the organic carbon content of the sediment. The data in Table 10 were calculated by assuming arbitrarily an organic carbon content of 6%. For other values, the concentration would be proportionally different.

In any case, if the provisions of ODCA were applied, we would need the detection capability for organochlorine pesticides in the neighborhood of 1 ng/g. Unfortunately one cannot have much confidence in the currently reported data.

PCB's are not lethal in concentrations comparable to those of organochlorine pesticides. The hazard of PCB's lies in their accumulation and chronic effects. One may attempt to estimate the needed detection limit in sediments on this basis.

Assuming that the 'no effect' level in fish tissues is at a PCB concentration of 10 ng/g, and assuming further that these PCB's are best represented as pentachlorobiphenyls with a water solubility of 0.007 mg/L, then from equations given by Kenaga and Goring (1978), the bioconcentration factor is 10,000 and the adsorption coefficient is 67,000 on an organic carbon basis, or 4,000 for a sediment containing 6% organic carbon. This corresponds to a PCB concentration in sediment of 4 ng/g.

This is obviously a very rough estimate, but it may be considered a useful benchmark, indicating that the detection limit for PCB's in sediments should be in the low ng/g range. The estimated general range of PCB concentration in Atlantic coastal sediments is 10-40 ng/g (Environmental Studies Board 1979). Consequently, the regulated level must be higher to be realistic.

## 5. INTERPRETATION OF RESULTS

The present regulations specify single, not be exceeded concentrations, 0.75 mg/kg for mercury, 0.6 mg/kg for cadmium, 4% by volume for persistent plastics and other persistent synthetic materials, and 10 mg/kg of hexane-soluble substances, in addition to the toxicity criterium for organohalogens, discussed above.

Obviously, the "hexane-soluble substances" category should be better defined and the concentration reconsidered, and a similar process is awaiting "persistent plastics and other persistent synthetic materials".

It should be pointed out that in these, as well as in practically all other regulations, no consideration is given to the errors of measurement and sampling.

The data on the analytical error, expressed as coefficient of variation, have been reviewed above. It may be concluded that for most minor constituents of sediments the coefficients of variation are at least 20-30%, based on the standard deviation of the data. This assumes that the data belong to a normally distributed population.

It is well recognized that determinations of trace elements of many matrices usually result in a lognormal distribution of the data (Eckschlager 1978) and, in addition, the distribution may be shifted because of the impossibility to measure below detection limits (Eckschlager and Stepanek 1978). The well known normal and a few shifted lognormal distributions are depicted in Fig. 2 and 3.

The means of lognormal distributions tend to compensate for skewness and standard deviations are smaller than those calculated from original (not transformed) data. At the same time, the standard deviations are multiplicative, which results in considerably broader confidence intervals of lognormally distributed data.

A statistical study of the determination of compliance as measured by sediment analysis should be carried out.

A similar problem has been considered by Russell and Tiede (1978). These authors evaluated the effect of measurement uncertainties on compliance with pollutant discharge permits. To adopt such a system one would have to know the analytical variance, the between-samples variance, and the distribution of the data.

It is apparent, from just a very simple statistical calculation, that a measured value may be considerably higher than the concentration specified in the regulations without being significantly different. From elementary statistics the difference between the measured and the specified concentration, D, will be statistically significant if it is larger than $2S/\sqrt{N}$ (S = standard deviation, N = number of analyses).

For example, assuming somewhat optimistically, that S = 30%, N = 1, and measured value is 0.9, D = 0.54. If the specified concentration is 0.6, measured concentrations of up to 1.1 may not be significantly different (P = 95%). If the sampled population had a lognormal distribution, then measured concentrations of up to 2.1 may not be significantly different.

This example underlines the importance to consider the uncertainties involved in the evaluation of compliance with regulations.

## 6. OTHER ORGANIC CHEMICALS

There is obviously a lot to be done in improving the analytical capability, intercalibration and characterization of sampling uncertainties in respect to trace elements, PCB's, organochlorine pesticides and hydrocarbons. The need for the determination of other chemicals may arise as time goes by.

The analysis of sediments for organic compounds is a very complicated task, partly because of the presence of a variety of natural organic compounds in considerable concentrations (Simoneit 1978).

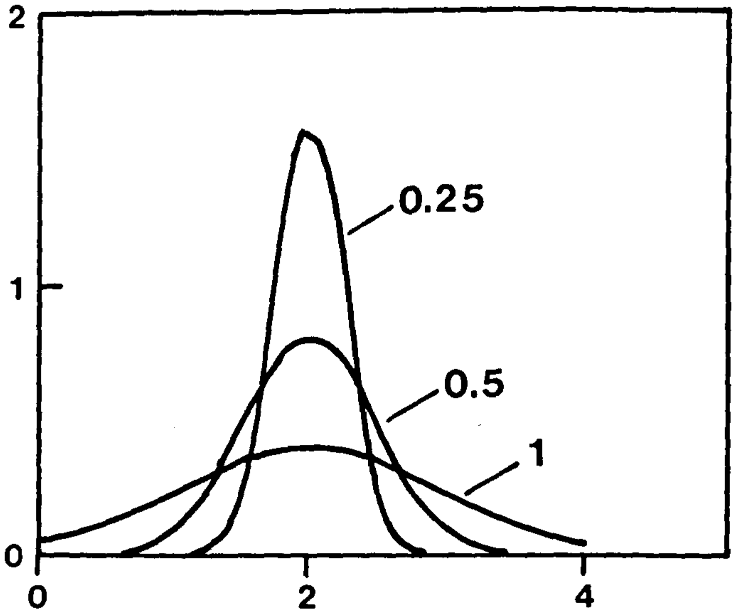

Fig. 2. Normal distribution. Standard deviations indicated in the figure.

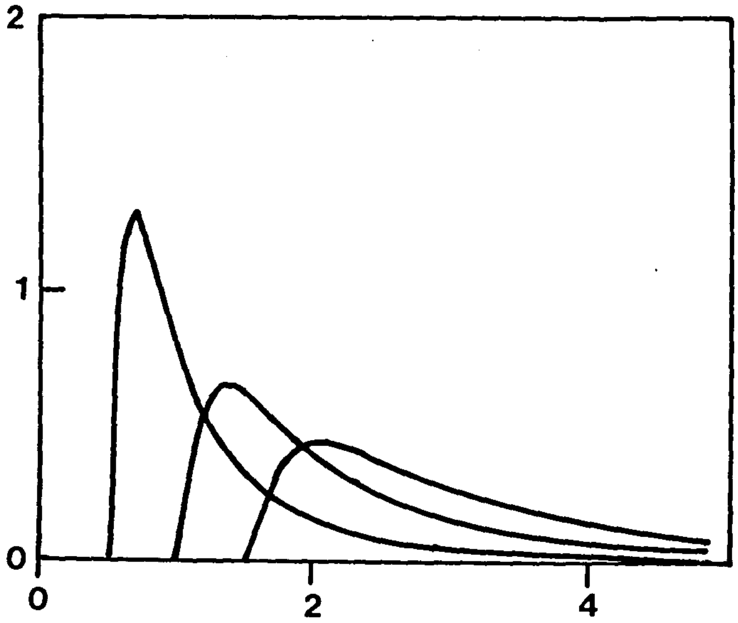

Fig. 3. Shifted lognormal distribution. From left to right: threshold 0.5, 1.0, and 1.5; standard deviation 0.5, K = 1 (Eckschlager and Stepanek 1978).

Some of the additional contaminants that may require future attention are listed in Table 11 (Zitko 1980). These originated in relatively highly industrialized areas, but some of our major harbours may not be much different in this respect.

TABLE 11

COMPOUNDS DETECTED IN A SURVEY OF SEDIMENTS IN JAPAN

| | No. of detections | No. of samples | Concentration (mg/g dry wt.) |
|---|---|---|---|
| Polyoxyethylene alkylphenyl ether | 6 | 15 | 7-30 |
| P-octylphenol | 2 | 6 | 0.004 |
| Nonylphenol | 3 | 3 | 0.05-0.07 |
| LAS | 21 | 51 | 1-260 |
| Nitrobenzene | 19 | 117 | |
| Tributyl phosphate | 48 | 117 | |

## 7. CONCLUSIONS

It appears that there are six priority areas in respect to sediment analyses under ODCA:

1) Intercalibration for PCB's and organochlorine compounds, with further exploration of the interference by some hydrocarbons in the quantitation;
2) Better definition of oil in terms of groups of hydrocarbons and natural hexane-soluble compounds in sediments, and intercalibration of methods;
3) Further improvement and intercalibration of trace element determinations. Adoption of techniques more closely related to the biological availability of trace elements (selective leaching);
4) Development and verification of statistical protocols and their application to the interpretation of data;
5) Development of a data storage and retrieval system that would lead eventually to a "contaminants in sediments" map of our coastal areas;
6) Preparation of "standard reference sediments" for intercalibration and method development.

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# THE ROLE OF THE ENVIRONMENTAL EMERGENCIES DIVISION

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## ABSTRACT

This presentation deals with the mandate given by cabinet in 1973 to the Environmental Emergencies Division. The mandate provides for leadership and guidance in such areas as contingency planning, response to emergencies, prevention of spills of hazardous materials and the research and development of pollution abatement equipment. The presentation also discusses the roles and responsibilities of other response orientated agencies in the Atlantic Region.

On November 29, 1973 the Cabinet of the Government of Canada approved a directive defining the mandate of the Environmental Protection Service (EPS) of Environment Canada with respect to environmental emergencies. The mandate generally outlines that the Department take a lead role in ensuring that the environment is adequately protected in the event of a spill of oil or hazardous materials. Aspects of this role include co-ordination with other government departments and agencies, leadership and guidance in development of contingency plans, maintenance of a national reporting system and data base, development and testing of new emergency equipment, encouragement of good prevention practices, conducting training programs and, in the event of an emergency, ensuring that appropriate and efficient cleanup is carried out.

In the Atlantic provinces agreements are presently in place between EPS, the Canadian Coast Guard (CCG) and the appropriate provincial departments of Environment with respect to emergency response. All reports of spills are directed to a single telephone number reporting system (Maritime Provinces - Zenith 49000, Newfoundland Zenith 07021) which is monitored 24 hours a day by CCG personnel. After receiving a call the CCG operators in turn notify the other appropriate government agencies. In terms of responding to spills CCG investigates those originating from ships (based on the Canada Shipping Act), the Provincial Department of Environment responds to land based spills (using the appropriate Provincial Environmental Protection legislation), and EPS is responsible for spills from federal facilities and mystery spills (using the Fisheries Act).

As a part of the EPS response capability our laboratory at the Bedford Institute of Oceanography carries out a variety of analyses and tests which assist in identification of the source of a spill and its possible effects on the receiving environment. A test called an "oil match" can be carried out to determine the similarities of one sample of oil with another, using gas chromatography, spectroscopy and fluorescence. Bioassays can also be carried out on oils and other chemicals, such as oil dispersants, to assist in assessing their possible environmental effects.

A summary of information has been collected and compiled by EPS which documents areas of environmental sensitivity in the Atlantic Provinces such as bird colonies and nesting areas, fishing grounds, shellfish areas, bird and fish migration routes, seaweed harvesting areas etc. These documents have been developed so that in the event of a marine spill protection and cleanup priorities can be quickly established.

Research projects which the EPS emergency staff are presently involved in include:

(1) A dispersant testing program which evaluates toxicity and effectiveness.

(2) A dispersant field testing study which is scheduled for St. John's, Newfoundland this Fall.

(3) An Arctic Marine Oil Spill Program (AMOP) which tests cleanup equipment and spill countermeasures in ice infested waters.

(4) A Baffin Island Oil Spill Study (BIOSS) involving a controlled release of oil into Arctic marine waters and followup studies which will examine oil weathering, the effectiveness of dispersants, the effects on local plants and animals, etc.

Further information on any of the above programs can be obtained by contacting the EPS Dartmouth office.

# DIRECT DETERMINATION OF CADMIUM IN SILICATES FROM A FLUOBORIC-BORIC ACID MATRIX BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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## ABSTRACT

An analytical method for the determination of cadmium in silicates using graphite furnace atomic absorption is described. The samples are decomposed in Teflon bombs with an acid mixture of HF: Aqua Regia. The resulting fluoboric-boric acid solution is injected in the furnace without further pretreatment and atomized at a low temperature (950$^{\circ}$C). Percent recovery was determined by the method of standard additions. Precision and relative accuracy were evaluated by analyzing marine mud and rock standards.

# SIMULTANEOUS MULTI-ELEMENT ANALYSIS OF MARINE SEDIMENTS WITH INDUCTIVELY COUPLED ARGON PLASMA EMISSION SPECTROSCOPY

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## ABSTRACT

The use of Inductively Coupled Argon Plasma Emission Spectroscopy for simultaneous multi-element determination of fifteen elements in marine sediments and plant tissue samples has been investigated. Several sample preparation procedures have been used. Strong interference of iron at the emission line 226.5 nm used for cadmium measurement elevates the results. Sample preparation techniques affect the dissolution of metals. In marine sediment the lead line, 220.3 nm, is suppressed and concentration is not measured. The analytical results obtained by this method for Ba, Co, Cr, Cu, Li, Ni, V and Zn in the U.S.G.S. Standard Reference Material MAG-1 agree with the literature values.

## 1. INTRODUCTION

Inter-element and spectral interferences have been noted in the spectrometric methods of chemical analysis (1-3). In soil and rock samples where the concentrations of metals vary from percentages to sub-ppm levels (4) the matrix effects can rigorously affect the simultaneous multi-element analysis. Easily ionizable metals in samples have also been reported to change the properties of dc plasma (5,6) and flame (7). These effects alter the operational characteristics of an instrument and affect their performance. In this work the use of Inductively Coupled Argon Plasma Atomic Emission Spectrometer was evaluated as a tool for (simultaneous multi-element) analysis of marine sediments.

"Methods for Sampling and Analysis of Sediments and Dredging Materials" (8) recommends two alternative procedures for sample preparation. The results can vary (by the two methods) depending on the nature of the sample. The metals bound to organic and inorganic components of the sediment are leached by acids; metals in phytoplantonic components are released after oxidation of organic matter and the metals in the crystalline matrix after the destruction of crystalline structure. For total sediment analysis use of nitric, hydrofluoric and perchloric acids has been recommended (9). Use of perchloric acid requires special procedures to avoid laboratory hazards (10) and is not followed in many laboratories.

## 2. METHODS AND MATERIALS

Reagents:

Nitric Acid, Reagent grade (Baker Analyzed Reagent)
Hydrochloric Acid, Reagent grade (Baker Analyzed Reagent)
Hydrofluoric Acid (Baker Analyzed Reagent)
Hydrogen Peroxide (Baker Analyzed Reagent)
Distilled Deionized Water: (Glass Distilled Deionized)

Standard stock solutions 1000 mg/l were prepared by dissolving 1 g of the metal (99.9% purity) in minimum amount of nitric acid. Standard test solutions were prepared by diluting the stock solutions and checked with the Environmental Research Associates Reference standard TM (Trace Metals Wastewater Lot #A1876).

MAG-1, a marine sediment, was obtained from U.S. Geological Survey, top 972 Reston, Va.

N.B.S. Standard Reference Materials 1951 Orchard leaves and 1645 River Sediment were obtained from the National Bureau of Standards, Washington, D.C.

Apparatus:

A Jarrell-Ash Model 975 ICAP AtomComp direct reading spectrometer with 24 element channels and background correction was used. Operating conditions were in accordance with the manufacturers operational procedures.

Digestion Procedures:

$HNO_3$: About .5 g oven dried (110° C) sediment was slurried with .5 ml water in a 150 ml beaker. 10 ml of conc. $HNO_3$ were added to the beaker covered with watch glass and heated to boiling on a hot plate. The slow heating was then continued to near dryness. The slurry was washed with 5 ml of 5% hydrochloric acid (v/v) and deionized water. Final volume of the solution was made to 50 ml. The suspended material was allowed to settle down. The clear solution was aspirated for analysis.

$HNO_3$-HCl (1:3 v/v): About .5 g of the dried sediment was slurried with .5 ml water in a 150 ml beaker. 2 ml conc. $HNO_3$ and 6 ml conc. HCl were added. The beaker was covered with the watch glass and heated to boiling. The heating was then continued to near dryness. The digestate was washed with hydrochloric acid and deionized water to 50 ml as described above.

$HNO_3$-$H_2O_2$: About .5 g dry sediment was slurried with .5 ml water and 10 ml conc. $HNO_3$ were added and the mixture was boiled for 5 min. After cooling for 15 mins. 3 ml $H_2O_2$ (30%) were added drop-wise. The mixture was heated to near dryness. The slurry was washed with 5 ml hydrochloric acid (v/v) and deionized water to 50 ml.

Combustion-$HNO_3$ Digestion: About .5 g dried sediment was heated in a pyrex glass beaker at 450°C for two hours in a muffle furnace. After cooling, the sediment was digested with nitric acid as reported above.

Dry Ashing: About .5 g of dried sample (dried at 60°C for 24 hours) in a pyrex glass beaker was heated at 450°C for 2 hrs in a muffle furnace. After cooling the residue was digested with 10 ml conc. nitric acid to near dryness. The slurry was dissolved in 5 ml of 5% hydrochloric acid (v/v). The solution was made to 50 ml with distilled deionized water.

Wet Ashing: To about .5 g of the dried sample 10 ml conc. nitric acid were added in a pyrex glass beaker. The mixture was covered and left overnight. The mixture was boiled for 15 mins. after cooling for 15 mins. 3 ml of hydrogen peroxide (30%) were added drop-wise. The heating was then resumed and the process was repeated until the color of the solution disappeared. The solution was heated to near dryness and final volume (50 ml) was made up with 5 ml of 5% hydrochloric acid and distilled deionized water.

HF Digestion: About .5 g of sample was slurried with 5 ml water in a teflon bomb and 10 ml HF was added drop-wise. The bomb was capped and heated at 100°C for 2 hrs. After cooling, the bomb was opened and HF evaporated to dryness. The dry residue was transferred to a glass beaker and heated with 10 ml of aqua regia until complete dissolution.

## 3. RESULTS AND DISCUSSION

Hydrogen peroxide oxidation and dry ashing have been recommended for oxidizing organic matter in marine sediments (8). The methods were used to oxidize NBS orchard leaves and the samples analyzed by simultaneous multi-element analysis. The results are reported in Table 1.

TABLE 1. ICAP - ATOMIC EMISSION DETERMINATION OF METALS IN NBS SRM 1571 ORCHARD LEAVES

| ELEMENT | DRY ASHING ug/g | WET ASHING $HNO_3$ $H_2O_2$ ug/g | HNO DIGESTION DRY ASHING ug/g | CERTIFIED VALUES ug/g |
|---|---|---|---|---|
| As | 5.7 | 8.0 | 9.6 | 10 ± 2 |
| Ba | 47 | 43 | 46 | 44* |
| Co | 0.25 | 0.2 | 0.2 | 0.2* |
| Cr | 1.9 | 1.3 | 2.3 | 2.6 ± 0.3 |
| Cu | 11.4 | 10.7 | 12.0 | 12 ± 1 |
| Fe | 269 | 214 | 230 | 300 ± 20 |
| Mg | 5210 | 4734 | 5003 | .62% ± .02 |
| Mn | 88 | 76 | 91 | 91 ± 4 |
| Ni | 1.4 | .7 | 1.4 | 1.3 ± 0.2 |
| Pb | 39 | 35 | 43 | 45 ± 3 |
| Sr | 33 | 32 | 34 | 37 ± 1 |
| Zn | 27 | 22 | 36 | 25 ± 3 |

*Non-Certified Values.

As can be seen from this Table the dry ashing gave good recovery for all metals within the certified range except for arsenic and chromium where the recoveries were poor. These latter metals appeared to have been lost during ashing. A collaborative study has shown that dry and wet ashing with nitric and perchloric acids give similar recoveries for K, Ca, Cu, Mg, Mn, Fe and Zn. As and Cr were not analyzed in this study (11).

In the present investigation wet digestion with hydrogen peroxide did not oxidize the sample completely. The yellow solution contained solid residue and gave lower results. Analysis of the sample prepared by digesting it with nitric acid before dry ashing agreed with the certified assay for all the metals except Zn. The higher Zn concentration perhaps is attributable to contamination during sample preparation. Inter-elemental interferences in these investigations did not seem to be of any significance.

Aqua regia and hydrofluoric acid mixture was used to digest NBS - River sediment. Simultaneous multi-element analysis of this sample is compared with the certified composition in Table 2.

TABLE 2. ICAP - ATOMIC EMISSION DETERMINATION OF METALS IN NBS SRM 1645 RIVER SEDIMENT

| ELEMENT | CONCENTRATION (ug/g) | |
|---|---|---|
| | FOUND | CERTIFIED VALUES |
| Cd. | 21.0 | 10.2 ± 1.5 |
| Cu. | 111 | 109 ± 19 |
| Cr | 29153 | 2.9% |
| Mn | 785 | 727 ± 97 |
| Ni | 41 | 45.8 ± 2.9 |
| Pb | 618 | 714 ± 28 |
| V | 20.8 | 23.5 ± 6.9 |
| Zn | 1751 | 1720 ± 169 |

Concentrations of Cu, Cr, Mn, Ni, V and Zn as determined by ICAP agreed with the certified values. However, cadmium and lead measurements deviated from the certified concentrations. The higher concentration of cadmium was found to be due to a spectral overlap from the iron emission which interfered with the cadmium analysis (at 226.5 nm). An interelemental correction (3) improved cadmium results for this reference material, but for natural environment sediment samples containing .1-.5 ug/g Cd the results were poor.

The above sample preparation procedures were used to analyze the marine sediment MAG-1. This sediment has been analyzed for heavy metals in several laboratories (13-19) but its assay has not been certified. Sample preparations by digesting with aqua regia, nitric acid, and oxidation with hydrogen peroxide and combustion at 450°C followed by acid digestion solubilize the leachate fraction of metals bound to organic and inorganic fractions of the sediment. For total analysis hydrofluoric acid was used. Hydrofluoric acid and aqua regia did not dissolve the MAG-1 completely. A clear and complete solution was obtained through the following steps:

(1) Digesting the sediment with nitric acid.
(2) Burning the organic matter at 450°C for 2 hrs.
(3) Followed by hydrofluoric acid and aqua regia treatment.

The results of the analysis along with some of the metals analyzed by AA are given in Table 3.

The analytical data show that in this sediment concentrations of Al, Ba, Ca, Cr, Cu, Mg, Sr and V were influenced by the sample preparation procedures whereas with Co, Cu, Ni, and Zn the change was unnoticeable. The results depend on the relative distribution of metals in various sediment fractions and it can vary widely.

For total analysis the combustion of the sediment at 450°C did not change the results. For the two sample preparation procedures the respective atomic emission and atomic absorbance analysis data were similar, indicating that the black residue left after the hydrofluoric acid treatment did not significantly hold the metals.

The atomic absorption analyses showed slightly higher concentrations for Cu, Mn, Ni, and Zn. This may be due to

# TABLE 3

## ICAP - ATOMIC EMISSION DETERMINATION OF METALS IN U.S.G.S. SRM MAG-1 MARINE SEDIMENT

| ELEMENT | $HNO_3HCL$ ug/g | | $HNO_3-H_2O_2$ ug/g | | 450°C-$HNO_3$ ug/g | | HF-$HNO_3$ ug/g | | $HNO_3$-450°C HF-$HNO_3$/HCL ug/g | | LITERATURE VALUES ug/g |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | AE | AA | AE | AA | AE | AA | AE | AA | AE | AA | |
| Al | 23641 | | 24007 | | 29202 | | 59432 | | 69303 | | 8.4% |
| Ba | 122 | | 126 | | 125 | | 421 | | 448 | | 211,476,513 |
| Ca | 7217 | | 7857 | | 7997 | | 8652 | | 8380 | | 1.32% |
| Co | 17.4 | | 18.6 | | 19.1 | | 25 | | 21 | | 18.8 |
| Cr | 51 | 54 | 53 | 67 | 55 | 54 | 92 | 94 | 86 | 94 | 103 |
| Cu | 23 | 27 | 36 | 30 | 17 | 46 | 23 | 32 | 24 | 33 | 27.9 |
| Fe | 36175 | 38532 | 38703 | 40787 | 37885 | 38315 | 41209 | | 40475 | | 4.5%, 5.2% |
| Li | 56 | | 55 | | 63 | | 55 | | 67 | | 72 |
| Mg | 14176 | | 15180 | | 15538 | | 15338 | | 15838 | | 2.6% |
| Mn | 618 | 637 | 640 | 685 | 622 | 715 | 660 | 743 | 645 | 743 | 713, .102% |
| Ni | 36 | 49 | 44 | 52 | 47 | 50 | 44 | 67 | 48 | 67 | 54 |
| Pb | ND | 33 | ND | 33 | ND | 34 | ND | 37 | ND | 34 | 20.4 |
| Sr | 57 | | 59 | | 60 | | 106 | | 112 | | 167,179 |
| V | 69 | 91 | 75 | 96 | 74 | 92 | 143 | 157 | 134 | 146 | 142 |
| Sn | 117 | 121 | 124 | 123 | 126 | 133 | 122 | 128 | 119 | 132 | 106,148 |

ND = Not Detected

increased background emission of the salt in this sediment. The background corrections were not applied during analyses. Comparison of the atomic emission data with the literature also shows that this method produced similar results for Co, Cr, Cu, Li, Ni, V and Zn as reported by other laboratories (13-19). Spectrographic data reported in the literature (18) was not used for comparison.

Lead was not detected during the atomic emission analyses of this sediment. Atomic absorption showed 34, and 37 ug/g Pb. A value of 27 ug/g Pb has been reported by Rantala and co-workers (19). The nondetectability of lead by atomic emission method may be due to the presence of salt which may be affecting the 220.3 nm lead analyses wavelengths. Nygaard (20) has reported the optimum wavelength for lead analyses in sea water at 405 nm.

Thus with the exception of lead and cadmium simultaneous multi-element analysis by the atomic emission spectrometric method was found to give satisfactory results for the metals studied in marine sediment.

## 4. CONCLUSIONS

Digestion of sediment samples with nitric acid before dry ashing helps retain volatile metals which otherwise may be lost (during ashing of organic matter in the sediment).

The atomic emission spectrometric method can be used for the analyses of Co, Cr, Cu, Li, Ni, V and Zn metals in marine sediments when the levels of these trace metals are high.

Problems were experienced in analyzing cadmium at low levels and lead in marine sediments by the atomic emission method.

Thus with the exception of lead and cadmium atomic emission was found to give acceptable results for most of the heavy metals studied.

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# CATALYTIC SPECTROPHOTOMETRIC APPROACH IN TRACE ANALYSIS OF HEAVY METALS IN AQUEOUS SAMPLES

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## ABSTRACT

Reactions of substituted and non-substituted cyanometallates with organic ligands have been investigated under normal laboratory conditions. Some heavy metal ions have been found to catalyse ligand exchange with $CN^-$ in cyano compounds under controlled conditions. The formation of colored mixed ligand species, monitored spectrophotometrically, in the case of $Hg^{2+}$, $Pd^{2+}$, $Fe^{3+}$, $Ag^+$ and $Au^{3+}$ show linear responses even at sub ppm concentration levels. Some applications of these reactions toward trace analysis of such ions in potable and surface waters have been explored.

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