REGIONAL SEAS

UNITED NATIONS ENVIRONMENT PROGRAMME

16 September 1983

Determination of total dissolved cadmium in sea-water by differential pulse anodic stripping voltammetry

Reference Methods For Marine Pollution Studies No. 18

Prepared in co-operation with

IOC

UNEP 1983

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The document has been reviewed by the IOC Group of Experts on Methods, Standards and Intercalibration (GEMSI) whose comments have been integrated into the text.

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PREFACE

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans. The Regional Seas Programme at present includes ten regions and has over 120 coastal States participating in it. (1), (2)

One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources, and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world-wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies are being developed and are recommended to be adopted by Governments participating in the Regional Seas Programme.

The methods and guidelines are prepared in co-operation with the relevant specialized bodies of the United Nations system as well as other organizations and are tested by a number of experts competent in the field relevant to the methods described.

In the description of the methods and guidelines the style used by the International Organization for Standardization (ISO) is followed as closely as possible.

The methods and guidelines, as published in UNEP's series of Reference Methods for Marine Pollution Studies, are not considered as final. They are planned to be periodically revised taking into account the development of our understanding of the problems, of analytical instrumentation and the actual need of the users. In order to facilitate these revisions the users are invited to convey their comments and suggestions to:

International Laboratory of Marine Radioactivity
International Atomic Energy Agency
c/o Musee Oceanographique
MC98000 MONACO

which is responsible for the technical co-ordination of the development, testing and intercalibration of Reference Methods.

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(1) UNEP: Achievements and planned development of the UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1 UNEP, 1982.

(2) P. HULM: A Strategy for the Seas. The Regional Seas Programme: Past and Future UNEP, 1983.

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DETERMINATION OF TOTAL DISSOLVED CADMIUM IN SEA-WATER BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMETRY

CONTENTS

1. SCOPE AND FIELD OF APPLICATION

This reference method describes an electrochemical technique for the determination of total dissolved cadmium in sea and estuarine waters. Detection limit is 1 ng of cadmium per kilogram of sea-water using a mercury film rotating electrode (MFE).

2. REFERENCES

MART, L. (1979) Prevention of Contamination and other Accuracy Risks in Voltametric Trace Metal Analysis of Natural Waters. Part 1 : Preparation steps, filtration and storage of water samples. Frezenius Z. Anal. Chem. 296, 350-357.

MART, L., NURNBERG, H. W. and VALENTA, P. (1980) Prevention of Contamination and other Accuracy Risks in Voltametric Trace Metal Analysis of Natural Waters. Part III : Voltametric ultratrace analysis with a multicell designed for clean bench working. Frezenius Z. Anal. Chem. 300 - 362.

SCHAULE and PATTERSON, C. C. (1980) Lead in the marine environment. Proceedings of the International Experts Discussion on Lead Occurrence, Fate and Pollution in the Marine Environment, Rovinj, Yugoslavia, 18 - 22 October 1977. M. Branica and Z. Konrad (eds.), Pergamon Press, Oxford. pp. 31-43.

EGG. PRINCETOWN APPLIED RESEARCH (1979) Model 303 static mercury drop electrode operating and service manual.

3. PRINCIPLES

After sampling and pretreatment, the sample is placed in the voltametric cell. Cadmium is concentrated in a thin mercury film by application of a sufficiently negative potential at the MFE. The stripping involves oxidation of cadmium into solution by application of an increasing potential with superimposed pulse and the resulting current is recorded.

4. REAGENTS

For the analysis, use only demineralized water and reagents of recognized analytical quality with as low as possible Cd concentrations.

4.1 Demineralized water supply from a MILLI-RO-MILLI Q device from MILLIPORE S.A. or tridistilled.

4.2 Nitric acid (distilled or Merck suprapur).

4.3 Nitric acid (analytical reagent grade).

4.4 Hydrochloric acid (distilled or Merck suprapur).

4.5 Hydrochloric acid (analytical reagent grade).

4.6 Saturated potassium chloride solution prepared from Merck suprapur potassium chloride.

4.7 Mercury (hexadistilled or Merck suprapur).

4.8 Mercuric nitrate solution. Prepare a $Hg(NO_3)_2$ solution containing 5 mg/l of Hg^{++}; weigh 5 mg of mercury (4.7); add HNO_3 (4.2) until complete dissolution and dilute with distilled water to 1 l.

4.9 Cadmium stock solution. 1 g/l Merck titrisol in 0.1 M HCl (4.4).

4.10 Cadmium standard solution. Prepare daily a series of working standard solutions by appropriate dilution of the cadmium stock solution (4.9) with demineralized water adding 10 ml of HCl (4.4) per litre.

NOTE: The concentration of the Cd standard solutions depends on the Cd levels anticipated in the samples to be analysed.

4.11 Ultrapure nitrogen.

4.12 Al_2O_3 (0.3u) available from Methrom, OSI, etc.

5. APPARATUS

5.1 Sampling equipment

5.1.1 Sampling bottles without rubber or metallic parts. Modified GOFLO can be used (SCHAULE and PATTERSON 9180).

5.1.2 500 ml high pressure polyethylene bottles.

5.1.3 Polyethylene bags.

5.2 Filtration equipment

5.2.1 A laminar air flow bench.

5.2.2 A filtration set. The polycarbonate 600 ml MILLIPORE under pressure filtration set can be used. Glass and pyrex are prohibited.

5.2.3 0.45 u membrane filters (Millipore or Nuclepore).

5.2.4 Micropipettes.

5.3 Analysis equipment

5.3.1 A vertical laminar air flow bench.

5.3.2 A balance (200 g with a precision of ± 0.001 g).

5.3.3 Plastic gloves.

5.3.4 Micropipettes.

5.3.5 Quartz and teflon beakers.

5.3.6 An electrochemical analyser equipped with differential pulse mode (e.g. the P.A.R.) 174 A from PRINCETOWN APPLIED RESEARCH, METHROM analyser).

5.3.7 A 50 ml teflon polargraphic cell.

5.3.8 A working electrode. A rotating mercury film on glassy carbon electrode (MFE) (e.g. the METHROM E 628 has proved to give acceptable results). This electrode can be constructed in the laboratory (MART et al. 1980).

5.3.9 An Ag/AgCl reference electrode (e.g. METHROM EA 427).

5.3.10 A Pt counter electrode (e.g. METHROM EA 202).

5.3.11 An X-Y recorder.

5.3.12 Ultrapure nitrogen. Nitrogen N 60 from l'AIR LIQUIDE containing less than 0.1 ppm of O_2 can be used without column for removing O_2 traces. In this case only a scrubbing bottle containing water acidified to pH1 with HCl (4.4) is used. If another type of nitrogen is used an oxygen scrubbing system is necessary. It is constituted of Vanadium II solution and zinc amalgam for Vanadium II regeneration. For the preparation of this solution see EGG PRINCETOWN APPLIED RESEARCH (1979).

5.3.13 A chronometer.

5.3.14 A high pressure UV lamp (e.g. HANAU 150 W).

6. CLEANING PROCEDURE

All quartzware, bottles, teflon, beakers and cells must be cleaned before being used.

Use only demineralized water. All manipulations have to be carried out by hands covered with plastic gloves.

6.1 Polyethylene bottles and filtration sets

Fill the bottles with 10% HCl (4.5) and heat to 70 C for 2 days. Repeat this operation twice. The procedure is then repeated with 2% HCl (4.4). The bottles are transferred to the laminar air flow bench and filled with 1% HCl (4.4) and heated to 70 C for 4 days. After that time, the acid is decanted and the bottle filled with demineralized water acidified by adding 1 ml HCl (4.4) to 1 l of water. Each capped bottle is placed in a polyethylene bag (5.13).

6.2 Teflon beakers and quartz items

The same procedure as 6.1 can be used, but replace HCl with HNO_3.

6.3 Filters

The filters are soaked in cold 50% HCl (4.5) for 2 days. The acid is changed and the filters are left in a fresh solution of the same acid for 2 days. After this, they are rinsed several times with demineralized water and soaked in 10% HCl (4.4) for a week. After a repeated rinsing with ultrapure water, the filters are kept in 1% HCl (4.4) for longer storage. Several days before use the filters are rinsed with demineralized water and conditioned (i.e. soaked with sea-water).

6.4 Pipette tips

Several hundred pipette tips are heated to 80 C in 20% HCl (4.5) for two days in a 2 l Erlenmeyer flask. This procedure is repeated twice, each time followed by a careful rinsing with ultrapure water. A final cleaning and heating is performed in 10% HCl (4.4). After rinsing several times, the pipette tips are dried and sealed into cleaned polyethylene bags (20 per bag).

6.5 Polyethylene bags

Polyethylene bags are first rinsed with normal tap water, then they are filled with 10% HCl (4.5) and immersed into the same acid in a polyethylene container for one half day. After rinsing with dermineralized water, the procedure is repeated, with 10% HCl (4.4) for 1 day. The bags are rinsed with demineralized water and dried in the laminar air flow bench.

7. SAMPLING AND PRETREATMENT

7.1 Sampling

If possible use a small boat. The best technique is to move the boat upstream and sample in front of the boat. The sample is transferred to a 500 ml polyethylene bottle (5.12) which in turn is placed in a clean polyethylene bag (5.13).

7.2 Pretreatment

The samples must be filtered as soon as possible on 0.45 um filters in a laminar air flow bench in the laboratory. After filtration, the samples are acidified to 1% with HCl (4.4).

NOTE: Problems could arise with water samples from polluted coastal areas with high organic content. In this case, the samples must be UV irradiated prior to analysis. The procedure is described by MART et al. 1980. The UV irradiation device is represented in figure 1.

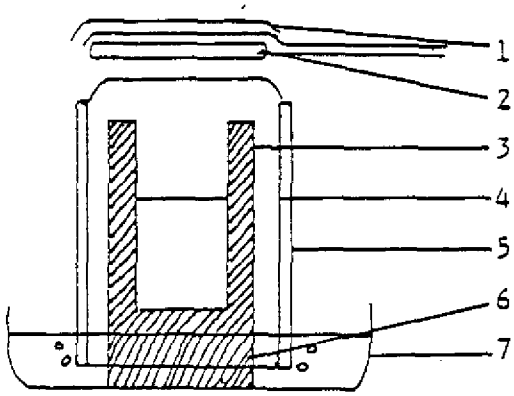

FIGURE 1 : UV IRRADIATION DEVICE

Depending on its origin and its dissolved organic matter content the sample is irradiated for 1 to 12 hours.

8. ANALYSIS

Weigh 50 g of the sample directly in the voltametric cell on the balance placed in the laminar air flow bench. Add 20 ul of HCl (4.4); 50 ul of a solution of $HgNO_3$ (4.8). The sample is purged with ultrapure nitrogen (4.10) for at least 10 minutes.

Working conditions: Electrolysis time 6, 10, 12 minutes. Electrolysis time depends on Cd concentration of the sample to be analysed. For unknown samples an exploratory run with a deposition time of 5 minutes has to be performed. From this run the appropriate deposition time from 3 to 12 minutes can be deduced.

Initial potential = -1 V vs Af/AgCl. This rather negative potential is chosen to obtain homogeneous mercury film.

At least two standard additions must be made because of possible matrix effects.

Between each measurement the MFE has to be polished with Al_2O_3 (0.3u). Aluminium powder (4.12) is spread over a wet filter paper and the polish is obtained by rotating the electrode in contact with the powder. After polishing, rinse the MFE with demineralized water. A final rinsing step is performed by rotating the electrode for several minutes in demineralized water acidified to pH 1 with HNO_3 (4.2), followed by a second rinse with demineralized water.

Then a blank must be run. For this purpose demineralized water spiked with 20 ul HCl (4.4), 50 ul of $HgNO_3$ (4.8), 100 ul of KCl (4.6) is placed in the voltametric cell. The deposition time is 6 minutes. The voltamogram is registered. If the blank value is below 1 to 5 ng/kg the demineralized water can be replaced by the sample after having allowed the electrode to rotate during 1 minute at 0.5 V vs Af/AgCl in order to remove the film. Between the standard addition let also the electrode rotate at the same potential.

Another alternative to this procedure is proposed by MART et al. (1980): if working conditions are good, no background signal is measured and there is no need to compensate it.

9. REPORTING OF RESULTS

h_1 = height of the peak corresponding to the sample.

h_2 = height of the peak corresponding to the sample spiked with A ng of Cd.

h_3 = height of the peak corresponding to the sample spiked with 2A ng of Cd.

$h_2 - h_1$ and $h_3 - h_2$ should be equal. If there is a slight difference, take:

$$= \frac{1 + 2}{2}$$ to calculate the cadmium content (Xng) of the sample.

The Cd content is:

$$X_{ng} = \frac{A}{\quad} \times h_1$$

The Cd concentration (ng/kg) of the sample is:

$$C = \frac{Xng}{M}$$

Where M is the weight (kg) of sample placed in the voltametric cell.

NOTE: This calculation is only for linear calibration curves.

10. ESTIMATION OF PRECISION AND ACCURACY

10.1 Precision

Estimate precision (C.V. = coefficient of variation) of the analytical procedure by taking 7 different subsamples from the original sample. The precision must be estimated for different ranges of concentrations, e.g. 1 ng/kg to 10 ng/kg, 10 ng/kg to 100 ng/kg, 100 ng/kg to 1000 ng/kg.

10.2 Accuracy

Participate to intercalibration exercises and/or analyse a known certified standard of a matrix similar to the material under study.

LIST OF REFERENCE METHODS FOR MARINE POLLUTION STUDIES

LISTE DES METHODES DE REFERENCE POUR LES ETUDES DE POLLUTION MARINE

UNEP/WHO : Guidelines for monitoring the quality of coastal recreational and shellfish-growing waters. (Draft) Reference Methods for Marine Pollution Studies No. 1, UNEP 1984.

UNEP/WHO : Determination of total coliforms in sea-water by the membrane filtration culture method. Reference Methods for Marine Pollution Studies No. 2 Rev. 1, UNEP 1983.

PNUE/OMS : Détermination des coliformes totaux dans l'eau de mer par la méthode de culture sur membranes filtrantes. Méthodes de Références pour les Etudes de Pollution Marine No 2, Rév. 1, PNUE 1983.

UNEP/WHO : Determination of faecal coliforms in sea-water by the membrane filtration culture method. Reference Methods for Marine Pollution Studies No. 3 Rev. 1, UNEP 1983.

PNUE/OMS : Détermination des coliformes fécaux dans l'eau de mer par la méthode de culture sur membranes filtrantes. Méthodes de Références pour les Etudes de Pollution Marine No 3, Rév. 1, PNUE 1983.

UNEP/WHO : Determination of faecal streptococci in sea-water by the membrane filtration culture method. Reference Methods for Marine Pollution Studies No. 4 Rev. 1, UNEP 1983.

PNUE/OMS : Détermination des streptocoques fécaux dans l'eau de mer par la méthode de culture sur membranes filtrantes. Méthodes de Références pour les Etudes de Pollution Marine No 4, Rév. 1, PNUE 1983.

UNEP/WHO : Determination of faecal coliforms in bivalves by multiple test tube method. Reference Methods for Marine Pollution Studies No. 5 Rev. 1, UNEP 1983.

PNUE/OMS : Détermination des coliformes fécaux dans les bivalves par le test des tubes multiples. Méthodes de Références pour les Etudes de Pollution Marine No 5, Rév. 1, PNUE 1983.

UNEP/FAO/IAEA : Guidelines for monitoring chemical contaminants in marine organisms. Reference Methods for Marine Pollution Studies No. 6, UNEP. (in preparation)

UNEP/FAO/IOC/IAEA : Sampling of selected marine organisms and sample preparation for trace metal analysis. Reference Methods for Marine Pollution Studies No. 7 Rev. 2, UNEP 1984.

UNEP/FAO/IOC/IAEA : Determination of total mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry. Reference Methods for Marine Pollution Studies No. 8 Rev. 1, UNEP 1984.

UNEP/FAO/IAEA : Determination of total arsenic in selected marine organisms by hydride generation atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 9, UNEP 1985.

UNEP/FAO/IAEA : Determination of total selenium in selected marine organisms by hydride generation atomic absorption spectrophotometry. Reference Methods for Marine Pollution Studies No. 10, UNEP 1984.

UNEP/FAO/IOC/IAEA : Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry. Reference Methods for Marine Pollution Studies No. 11 Rev. 1, UNEP 1984.

UNEP/FAO/IAEA : Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons. Reference Methods for Marine Pollution Studies No. 12 Rev. 1, UNEP 1984.

UNEP/FAO/IAEA : Determination of methylmercury in selected marine organisms by gas chromatography. Reference Methods for Marine Pollution Studies No. 13, UNEP 1984.

UNEP/FAO/IOC/IAEA : Determination of CDTs and PCBs in selected marine organisms by packed column gas chromatography. Reference Methods for Marine Pollution Studies No. 14 Rev. 1, UNEP 1985.

UNEP/IOC/IAEA : Monitoring of tar on marine beaches. (Draft) Reference Methods for Marine Pollution Studies No. 15, UNEP 1985.

UNEP/IAEA : Determination of DDTs, PCBs, PCCs and other hydrocarbons in sea-water by gas chromatography. (Draft) Reference Methods for Marine Pollution Studies No. 16, UNEP 1982.

UNEP/IAEA : Determination of DDTs, PCBs and other hydrocarbons in marine sediments by gas-liquid chromatography. (Draft) Reference Methods for Marine Pollution Studies No. 17, UNEP 1982.

UNEP/IOC : Determination of total dissolved cadmium in sea-water by differential pulse anodic stripping voltammetry. (Draft) Reference Methods for Marine Pollution Studies No. 18, UNEP 1983.

UNEP/IOC/IAEA : Determination of mercury in estuarine waters and suspended sediment by cold vapour atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 19, UNEP 1985.

UNEP/IOC/IAEA : Monitoring of petroleum hydrocarbons in sediments. Reference Methods for Marine Pollution Studies No. 20, UNEP. (in preparation)

UNEP/WHO/IAEA : Determination of total coliforms in sea-water by multiple test tube (MPN) method. (Draft) Reference Methods for Marine Pollution Studies No. 21, UNEP 1985.

UNEP/WHO/IAEA : Determination of faecal coliforms in sea-water by multiple test tube (MPN) method. (Draft) Reference Methods for Marine Pollution Studies No. 22, UNEP 1985.

UNEP/WHO/IAEA : Determination of faecal streptococci in sea-water by multiple test tube (MPN) method. (Draft) Reference Methods for Marine Pollution Studies No. 23, UNEP 1985.

UNEP/WMO/IAEA : Sampling of aerosols and wet precipitation for analysis of chemical pollutants. (Draft) Reference Methods for Marine Pollution Studies No. 24, UNEP 1985.

SPC/UNEP : Coral reef monitoring handbook. Reference Methods for Marine Pollution Studies No. 25, UNEP 1984.

UNEP/IAEA : Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 26, UNEP 1985.

UNEP/IAEA : Determination of total cadmium in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 27, UNEP 1985.

UNEP/WHO/IAEA : Determination of staphylococcus aureus in sea-water and sewage by the membrane filtration culture method. Reference Methods for Marine Pollution Studies No. 28, UNEP. (in preparation)

UNEP/WHO/IAEA : Determination of pseudomonas aeruginosa in sea-water and sewage by the membrane filtration culture method. Reference Methods for Marine Pollution Studies No. 29, UNEP. (in preparation)

UNEP/WHO/IAEA : Isolation/Enumeration of salmonella from sea-water and sewage. Reference Methods for Marine Pollution Studies No. 30, UNEP. (in preparation)

UNEP/IAEA : Determination of total chromium in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 31, UNEP 1985.

UNEP/IAEA : Determination of total cobalt in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 32, UNEP 1985.

UNEP/IAEA : Determination of total copper in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 33, UNEP 1985.

UNEP/IAEA : Determination of total lead in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 34, UNEP 1985.

UNEP/IAEA : Determination of total nickel in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 35, UNEP 1985.

UNEP/IAEA : Determination of total vanadium in marine sediments by flameless atomic absorption spectrophotometry. (Draft) Reference Methods for Marine Pollution Studies No. 36, UNEP 1985.

UNEP : Sampling and identification of common Mediterranean Scyphomedusae and evaluation of their occurrence. (in preparation)

UNEP/IOC/IAEA : Monitoring of petroleum hydrocarbons in sea-water. (in preparation)

UNEP/IAEA : Guidelines for monitoring of estuarine waters and suspended matter. (in preparation)

UNEP/WHO/IAEA : Determination of faecal coliforms in estuarine waters, suspended matter and sediments. (in preparation)

UNEP/WHO/IAEA : Determination of phosphorus in suspended matter and sediments. (in preparation)

UNEP/WHO/IAEA : Determination of nitrogen in suspended matter and sediments. (in preparation)

UNEP/WHO/IAEA : Determination of BOD_5 and COD in estuarine waters. (in preparation)

UNEP/FAO/IAEA : Acute toxicity tests. (in preparation)

UNEP/IOC/IAEA : Determination of total cadmium in estuarine waters and suspended matter. (in preparation)

UNEP/FAO/IAEA : Biological non-acute toxicity tests. (in preparation)

UNEP/IOC/IAEA : Determination of basic oceanographic and meteorological conditions. (in preparation)

UNEP/IOC/IAEA : Determination of standard physical and chemical parameters. (in preparation)

UNEP/WHO/IAEA : Statistical methods for the evaluation of results from monitoring the quality of coastal recreational and shellfish-growing waters. (in preparation)

UNEP/FAO/IOC/IAEA : Determination of DDTs and PCBs in selected marine organisms by capillary column gas chromatography. (in preparation)

UNEP/IAEA : Determination of selected trace metals in aerosol and in wet precipitation. (in preparation)

UNEP/IAEA : Determination of halogenated hydrocarbons in aerosol and in wet precipitation. (in preparation)

UNEP/WMO/IAEA : Sampling of dry deposition. (in preparation)

UNEP/WHO/IAEA : Determination of methylmercury, total mercury and selenium in human hair. (in preparation)

UNEP/WHO/IAEA : Guidelines for monitoring and epidemiological studies on health effects of methylmercury. (in preparation)

UNEP/IOC/IAEA : Guidelines for the determination of riverine inputs of contaminants to estuaries. (in preparation)

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