REGIONAL SEAS

UNITED NATIONS ENVIRONMENT PROGRAMME

17 July 1985

Determination of total chromium in marine sediments by flameless atomic absorption spectrophotometry

Reference Methods For Marine Pollution Studies No. 31

Prepared in co-operation with

IAEA

UNEP 1985

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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.

This draft issue of the Reference Method for Marine Pollution Studies No. 31 was prepared in co-operation with the International Atomic Energy Agency (IAEA). It includes comments received from a number of scientists who reviewed and tested the method. The assistance of all those who contributed to the preparation of the draft issue of this reference method is gratefully acknowledged.

CONTENTS

1. SCOPE AND FIELD OF APPLICATION

This reference method describes the determination of total chromium in marine sediments by flameless atomic absorption spectrophotometry after the extraction of chromium by acid leaching. The sensitivity of the method is about 5$\mu g kg^{-1}$ Cr.

2. REFERENCE

OREGIONI, B and ASTON, S.R. (1984) The determination of selected trace metals in marine sediments by flameless atomic absorption spectrophotometry. IAEA Monaco Laboratory Internal Report.

3. PRINCIPLES

An aliquot of sample is digested in a nitric/perchloric/hydrofluoric acid mixture in a teflon beaker and the total chromium determined by flameless atomic absorption at 357.9 nm wavelength using a deutrium background corrector.

4. REAGENTS

All reagents, including deionised double distilled water must be as low in chromium concentration as possible. All reagents must be checked for chromium contamination by analyzing blanks.

4.1 Deionised Double Distilled Water (DDDW). Water is deionised with a mixed-bed resin and double distilled.

4.2 $HNO_3/HClO_4/HF$ acid mixture. Mix 300 ml of AnalaR (or equivalent) HNO_3 (d_{20^oC}=1.42) with 200 ml AnalaR (or equivalent) $HClO_4$ (sp.gr 1.54) and 100 ml of AnalaR (or equivalent) HF (sp.gr. 1.13) in a teflon bottle.

4.3 Hydrochloric acid, AnalaR (or equivalent), d_{20^oC}=1.17.

4.4 Hydrochloric acid, AnalaR (or equivalent), 0.1.M.

4.5 Nitric acid, AnalaR (or equivalent), d_{20^oC}=1.42.

4.6 Chromium Standard Solutions.

4.6.1 Stock chromium solution: Prepare a solution containing

0.7470 g K_2CrO_4 in 200 ml of deionised double distilled water (4.1). This stock solution, which contains 1 mg ml^{-1} Cr, is stable indefinitely when stored in a teflon bottle (5.2).

4.6.2 Chromium standard solution: From the stock solution (4.6.1) prepare, by appropriate dilutions using micropipettes (5.8), chromium standard solutions. Prepare these solutions at least weekly using as dilutant 1 ml nitric acid (4.5) diluted in 250 ml of deionised double distilled water (4.1).

4.7 Working matrix: Prepare the working matrix by homogenizing a sufficiently large sample (e.g. 300 g of fresh weight) of the same type of sediment which will be analyzed. Test the homogenity of the working matrix by analyzing 5 subsamples for their chromium content (6), including digestion. If the coefficient of variation of the five analyses is less than 5% the working matrix is ready for use. Otherwise homogenize the working matrix until the above coefficient of variation is obtained or prepare a new working matrix.

5. APPARATUS

5.1 Twenty or more 50 ml teflon beakers and 25 ml glass volumetric flasks.

5.2 One litre teflon bottle.

5.3 Clean cabinet for air drying sediment samples.

5.4 Oven for drying glassware at 105°C.

5.5 Pestle and mortar for homogenizing samples.

5.6 Polyethylene screw-cap bottles for storing sediments.

5.7 Electronic balance, preferably "top-load" variety, capable of weighing to $\pm$ 0.001 g.

5.8 Micropipettes for standard chromium solution preparations.

5.9 Hotplate, thermostatically controlled, to accomodate the 50 ml teflon beakers.

5.10 Plastic seive with 63 µm screen.

5.11 Atomic absorption spectrophotometer (AAS), double beam with deuterium background corrector and chromium hollow-cathode lamp. Flameless carbon furnace attachment. Optimum operating conditions will depend on the actual instrument available (see manufacturer's manual).

NOTE: All glassware used for the first time must be washed with nitric acid (4.5) and several times with deionised double distilled water (4.1).

6. METHOD

6.1 Sample collection and storage

The collection, transport and storage of sediment samples constitute critical stages in the determination of trace metals. For optimum accuracy in the determination of chromium in environmental samples, a full consideration must be given to these factors, and the final accuracy and precision of the result should be assessed from this broad point of view. Several points in connection with these pre-analysis stages must be taken into account:

a) methods of sampling;
b) container material and methods of cleaning;
c) transport to the laboratory
d) storage before analysis.

6.1.1 Surface Sediment Samples

A 20 cm length teflon spatula may be used as a sampling tool for accessible (e.g. intertidal) sediments, and sediments should be scraped from the top 0.5cm over an area of approximately 10cm radius for each sample. Suitable sample containers are polyethylene screw-cap bottles precleaned with nitric acid (4.5) and rinsed with DDDW (4.1). Samples are then transported in plastic bags containing solid carbon dioxide, or at ambient temperature when the transport time is less than 30 minutes. On arrival at the laboratory the samples should be dried and analysed as soon as possible or stored at 5°C.

6.1.2 Core and Grab Samples

Core samples may be collected using gravity or piston devices with P.V.C. core-liners. During transport, the cores should be sealed at their top and bottom ends using polythene bungs. Extrusion of the cores should be performed immediately on shipboard or on arrival at the laboratory after storing at 5°C.

6.2 Sample preparation

Air dry sediment or filter samples in Petri dishes in the clean cabinet (5.4) at room temperature. This will usually take one night. Weigh the samples after drying and check constant weight before analysis. Homogenize dried sediment with a pestle and mortar. In order to normalize for variations in grain-size distributions, the dried sediment samples should be sieved through a 63 µm screen (5.10) for the analysis of the silt size fraction (< 63 µm). Weigh out accurately between 0.25 - 0.5 g of dried sediment into a teflon beaker (5.1) cleaned with concentrated nitric acid (4.5) and deionised double distilled water (4.1) and dried at 105°C (5.4).

6.3 Digestion

Add 2 ml of concentrated HNO_3 (4.5) to the teflon beaker (5.1),

evaporate to dryness at 80°C. Add 5 ml of $HNO_3/HClO_4/HF$ mixture (4.2) and evaporate to dryness, gradually increasing the temperature to 120°C to remove the $HClO_4$ residue.

IMPORTANT: Digestions with perchloric acid are potentially EXPLOSIVE. It is most important that the FIRST DIGESTION WITH NITRIC ACID is used to remove most organic matter in the sample.

Cool to room temperature and use 5 ml of dilute HCl (4.4) to rinse and transfer the residue to a 25 ml volumetric flask (5.1). Add another 5 ml of HCl to the beaker and transfer to the flask. Make up the volume with a dilution of HCl (4.4).

6.4 Atomic Absorption Measurement

The optimum conditions will vary depending on the actual instruments in use. Refer to the manufacturer's manual for guidance on operation of the AAS (5.11), flameless attachment and deuterium background corrector. Measurements should be made at 357.9 nm. Using standard solutions, determine the optimum atomisation temperature and time, repeat this for the ashing step also. Most systems use 5-10 µl for sample injection, but this may vary with the equipment in use.

6.5 Calibration and blanks

The atomic absorption spectrophotometer should be calibrated with a series of standard solutions representing the linear range of the absorption curve. These are prepared by dilutions using the stock chromium solution (4.6.1, 4.6.2). Aliquots of the solution are analysed in the same manner as samples, commencing at step 6.3. Calibration should be performed on a daily basis at least. Perform blanks (in triplicate), using the procedure from step 6.3 with no sample in the test-tube.

7. EXPRESSION OF RESULTS

From the height of the absorption peaks in the calibration procedure (6.5) construct a calibration curve. Subtract any blank peak height and plot the height of peak versus ug chromium employed. Using the calibration curve, read off the weights of chromium found in the sample determinations and divide these by the known weights of samples used to calculate the final results in $\mu g kg^{-1}$ Cr (dry weight). An analytical report form is presented in Annex 1.

8. ESTIMATION OF PRECISION, ACCURACY AND QUALITY CONTROL

8.1 Precision

Estimate the precision of the entire analytical procedure (6 through

7) by digesting ten sub-samples of homogenized sample and analysing them seperately. Calculate the standard deviation (S) and the coefficient of variation (CV) where CV=S.100/mean value. If the CV is greater than 10% check the whole procedure for possible errors and/or contamination. The precision of the method is normally better than ± 5% at the 95% confidence level.

8.2 Accuracy

Using this Reference Method, analyse a certified standard, with a matrix similar to the material under study, together with your own working matrix chosen from among your samples (4.7). Calculate the mean and the standard deviation for the certified standard and the working matrix. If the value given for the certified standard is within the interval of your mean ± standard deviation, your method has the required accuracy and the working matrix can be used as a standard for checking the accuracy of your procedure. If not, check the whole procedure for errors.

NOTE: In addition, by participating in intercalibration exercises involving several analytical laboratories, the accuracy of the method as used by the analyst can be checked and compared with the accuracy obtained by other participants in the exercise.

8.3 Quality Control

Analyse periodically, at least once a week or whenever the routine has been interrupted for more than a week, the working matrix, in order to guarantee the precision and accuracy of your results. If, on any occasion, the calibration curve is found to be altered by more than 5% from the previous ones, check your routine for possible errors.

9. ANALYTICAL REPORT

Fill in the Analytical report (table 1) giving full details in every column.

Table 1: Analytical Report on Total Chromium Concentration in Marine Sediment

1. Sample code: _____

2. Determination of dry weight in oven: _____

   2.1 Duration of drying: _____ hours

   2.2 Date of drying: _____ day; _____ month; _____ year

3. Digestion

   3.1 Duration of digestion: _____ hours

   3.2 Temperature used for digestion: _____ °C

   3.3 Date of digestion: _____ day; _____ month; _____ year

   3.4 Anomalies observed which may influence results:

_____

_____

_____

4. Standardization (calibration)

   4.1 Date: _____ day; _____ month; _____ year

   4.2 Result:

digestion vessel	1	2	3	4	5	6	7	8
								(blanks)
added stand.sol.(ml)	-	0.1	0.2	0.3	0.4	-	-	-

mass of Cr (ng)

---

units of recorded signal

µg Cr kg^{-1}

---

5. Analytical result and estimation of precision using subsamples of same sample.

5.1 Date: _____day; _____month; _____year

5.2 Result:

digestion vessel	1	2	3	4	5	6	7	8	9	10
sample mass (g)										
units of recorded signal										
µg Cr kg^{-1}										

mean_____µg Cr kg^{-1}; Stand. deviation_____

coeff. of variation_____%

6. Estimation of accuracy

6.1 Date: _____day; _____month; _____year

6.2 Type of certified standard used: _____

6.3 Declared µg Cr kg^{-1} certified standard: _____

6.4 Results:

digestion vessel	1	2	3	4	5	6	7	8
mass certified standard (g)					-	-	-	-
mass working matrix (g)	-	-	-	-				
units of recorded signal								
µg Cr kg^{-1}								

mean_____µg Cr kg^{-1}; Stand. deviation_____

coeff. of variation_____%

certified standard identity

working matrix identity

7. Anomalies observed during analysis and other remarks relevant to the interpretation of results:

8. Intercalibration exercise (give details):_____

9. Full address of the institution which carried out the analysis:

_____

_____

_____

10. Name(s) and signature(s) of the person(s) who carried out the analysis:

_____

_____

_____

Date:_____

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. Reference Methods for Marine Pollution Studies No. 21, UNEP 1985. (in preparation)

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

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

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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