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NON-ORGANIC MICROPOLLUTANTS OF THE ENVIRONMENT

Volume 4

METHODS OF ANALYSIS

REPORT OF A WORKING GROUP OF EXPERTS

Prepared for the Commission of the European Communities

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NON-ORGANIC MICROPOLLUTANTS OF THE ENVIRONMENT

VOLUME 4 : Methods of analysis

S U M M A R Y

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Meetings n°1 - 7 December 1972

n°2 - 20-21 March 1973

n°3 - 14-15-16 November 1973

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NON - ORGANIC MICROPOLLUTANTS OF THE ENVIRONMENT

A. FOREWORD

This report has been prepared by the working group on the consequences for man and his environment, of environmental pollution due to non-organic micropollutants; it is part of the outline of actions that have to be undertaken at Community level in the domain of reduction of pollutions and nuisances. These actions are included in a comprehensive programme of the European Communities in the field of environment that has been accepted by the Council of Ministers on the 19th of July 1973.

Non-organic micropollutants are listed in the first category of pollutants of the environment which have to be considered primarily because of their toxicity and of the present state of knowledge concerning their sanitary and ecological importance.

The objective evaluation of risks being the aim of the general programme a knowledge is required of the level of these pollutants in the environment as well as a study and analysis of the undesirable effects which would result from exposure of the target to a given pollution or nuisance.

At a meeting held on December 7th 1972, the working group decided to prepare an inventory of the data available since 1968 on the levels of non-organic micropollutants in the environment. The report has been compiled by Mr BOUQUIAUX from information supplied by delegates of the various Member States. The list of micropollutants was examined at the meeting of December 7th, 1972. The final date agreed by the rapporteur for receipt of information was May 15th 1973.

A first draft of the report was examined at the meeting of March 20th and 21st 1973. The final text was discussed at the meeting on November 14th-16th 1973 and was agreed by the experts present except for Volume 4 which was written by Mr BOUQUIAUX after the last meeting.

It should be remembered that 2 important non-organic micropollutants were studied in depth at the Symposium "Problems of contamination of man and his environment by Mercury and Cadmium" organised by the Commission of the European Communities in Luxembourg on 3-5th July 1973.

The whole report appears in 4 volumes entitled:

Volume 1 - general presentation;
Volume 2 - detailed listing of levels present in the environment;
Volume 3 - synthesis of data;
Volume 4 - methods of analysis.

B. PRESENTATION OF THE DOCUMENT .

The methods used for the measurement of non-organic micropollutants of the environment are much varied .
Descriptions of the methods used have been sent by the delegations of different Member-Countries with the analytical results .
These descriptions are sometimes full of details or very brief or else, they refer to methods given in the litterature .

The submitted methods have been studied closely and a general scheme has been drawn that could be applied to each one . This study has in fact drawn the following general steps that can be found in all the methods (even if some them are sometimes omitted) :

1. Pre-treatment ;
2. Destruction of organic matter;
3. Separation ;
4. Measurement .

Many possibilities can be found in each separate step and, in some of them, such as pre-treatment and separation, several possibilities can be associated .
These possibilities are listed in table 1 (p.12) ,which can be considered as a table of contents for describing methods of analysis .

Table 2 (p.45) gives a summary of the different methods used in the different laboratories which have provided measurements . This summary is based upon the scheme of analysis which is used in this report .

The method for the determination of methyl-mercury in fish is given in an appendix (p.55) .

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TABLE 1.

ANALYSIS - POSSIBLE STEPS.

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C. DESCRIPTION OF METHODS

1. PRE-TREATMENT

A pre-treatment is generally needed to insure the conservation of the sample, to isolate the part of the sample that must be analysed, or to prepare the sample before analysis.

1.1 - WATER

Most authors have pointed out that surface water was filtered (or centrifuged) and / or acidified according to different methods before analysis .

1.1.1 FILTRATION

Several procedures have been used :
- Filtration alone (without any indicated acidification) (47);
- Centrifugation of sample when received in the laboratory , followed by further acidification (17,41,76) ;
- Filtration made on the sampling place (27) ;
- Filtration and acidification made on the sampling place(19);
- Filtration and analysis made on the sampling place (30.2, Cu , colorim.) ;
- Filtration following acidification (46).

The amount of suspended matter in water depends on many factors mainly related with the perturbations of the water : storms, floods, crossing of boats, velocity of the river,etc... In these conditions, bottom sludges are often put into suspension . These suspended matter strongly disturb the constancy or reproducibility of the analysis results, specially for non-organic micropollutants .
Moreover, they are in fact a phase quite different from the aqueous phase . It should then be necessary to separate them previously by centrifugation or filtration and to analyse them separately .

The separation of suspended matter should always be carried out on the sampling place so as to avoid the transformation of the suspended matter during transportation and conservation. However this method is subject to many difficulties which can only be dealt with on boats or in moving laboratories provided with a good equipment .

Centrifugation appears to be better than filtration because it has no effect on mechanical and electrical behaviour of colloïds . Moreover, centrifugation can deal with strongly charged waters .

Filtration, on the other hand, seems to be more adequate for treatment of large volumes of water with slight amount in suspended matter .

1.1.2 ACIDIFICATION

The sample is frequently preserved by acidification at pH 5 by means of hydrochloric acid (19) or, in a more general way , at pH 1 or 2 by means of hydrochloric or nitric acid (15,16, 27,41,45,46,50,76) .

The filtered or centrifuged sample has to be preserved by means of acidification so as to avoid precipitations and losses in metals due to deposition on the containers walls . These deposits can occur even in plastic bottles . According to Butterworth et al.(19), Martin (1968) has stated that plastic surfaces can develop ion exchange capacity with consequent plating out of trace metals . These authors have examined their plastic collecting vessels for plating from raw sea water and found that a considerable proportion of the zinc and lead were lost in this way . However, when the pH was adjusted to 5.0 with nitric acid on collection no loss in this way could be detected .

The vessels must of course and necessarily be washed with acid before they can be used .

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1.1.3 CONSERVATION AT LOW TEMPERATURE

Samples are sometimes kept at low temperature for preservation :
- in the freezer (27,between filtration made on the sampling place and acidification made at the laboratory);
- in the refrigerator (50) .

Conservation of water samples at low temperature is specially intended for avoiding the transformation of nitrogenous and organic compounds when their determination is carried out in the same sample as non organic micropollutants . But the acidification of water makes this way of proceeding purposeless where metals are concerned .

1.1.4 OXIDATION WITH PERSULPHATE

According to Fonds and Vanden Eshof (76), an oxidation step is necessary before the liquid -liquid extraction of a series of metals from water .

These authors use the following method :
- Add 0.5 ml 65% HNO_3 and 5 ml 50% $(NH_4)_2S_2O_8$ solution to 500 ml (centrifuged) surface water or drinking water and bring to boiling .
- Boil for 10 minutes,stop boiling and after 1 minute cooling add 25 ml 5% $(NH_4)_2S_2O_8$ solution .
- Boil down to 350 ml.
- Cool to 20°C and add 5 ml 10% ascorbic acid solution, mix and allow to stand for 10 minutes .

This method is followed by the liquid-liquid extraction described at paragraph 3.2.4.2.

Oxydation of the water sample is certainly useful in order to bring the metals to an ionic state suitable for extraction with organic complexing reagents.
However , this step is generally omitted,the sample being simply acidified .

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1.1.5 ADDITION OF A TRACER

A radioactive tracer can be added to check the yield of the chemical separations . Ex. : ^{203}Hg (16).

The addition of a radioactive tracer can be useful to check the yield of a new method . However it is seldom necessary in routine methods and only when the methods used for separation cannot be reproduced easely.

1.1.6 EVAPORATION

Water samples can be evaporated at 110°C and calcinated at a temperature of < 450°C . This procedure has been used before UV-spectrography (32).

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The elaborated pre-treatment used by Preston et al.(27) is given here as an example :

" Surface samples were collected using a polypropylene bucket and rope; subsurface collections were made by drawing the water through a2.5cm diameter PVC hose (reinforced with braided terylene) with the aid of an electrically-driven pump,constructed entirely from polypropylene and PTFE except for a small carbon shaft-seal. No significant variation between the methods of sampling has been detected.

" It was decided that some form of separation of the sample into 'mainly solid' and 'mainly liquid' phases was essential- the chief reason being the considerable variation in suspended load due to weather conditions; Millipore cellulose acetate filter papers (142mm diameter, 0.2 µm pore size)mounted in a PTFE filter press were used to effect this separation rapididly in preference to centrifuging, because of the

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difficulty in carrying out the latter operation on board ship . The contamination problem from the Millipore filters is well known (Robertson,1968) and much work has been carried out at this laboratory on the problems of the leaching of impurities from the paper . The filtrate was collected in a polythene container ,rapidly frozen and stored at -20°C until required for analysis - this procedure has been shown to be satisfactory and does not require the use of concentrated acids at sea . The samples were left frozen until the start of the analysis, when they were thawed and acidified to pH 2 with redistilled hydrochloric acid to ensure that iron was in a form suitable for subsequent analysis . The filter membrane and filter were stored in a 5 in (approx.13 cm) polystyrene petri dish until required for analysis".

1.2 - BIOLOGICAL SAMPLES AND SEDIMENTS.

1.2.1 GRANULOMETRIC SEPARATION (SEDIMENTS).

As heavy metals of sediments are met preferentially in small particles (6.2) , many authors operate a granulometric separation and express their results only for a given size of particles considered as being the most representative one .

Ex. : fraction <16 µm (6.2,30.1) ;
fraction < 2 µm (44);
fraction 80-mesh(26).

Other authors don't operate this granulometric separation and express their results on dry matter (9, 15,19, 22, 47, 53,62) or on wet matter (16) .

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1.2.2 CONSERVATION AT LOW TEMPERATURE

When biological samples are not analysed directly , they are always kept at low temperature, either in a freezer at -15°C to -20°C (11,19,20,22,27,32,59) or in the refrigerator. The same procedure is sometimes used for sediments (45, 53) .

1.2.3 SAMPLED PART (biological samples,food products)

For food and biological samples, the analysis has nearly always been made on the edible portion of the sample as presented or sold in shop.

Only the muscle part (edible part) of fish was in general analysed.

Cooking of whole fish in a microwave oven until flesh is tender, allows an easy separation of edible portion from bone and other tissue . This method has been used in ref.75 in special cases for the determination of mercury . Fish was cooked with its skin intact to prevent loss of moisture .

1.2.4 DRYING

Drying of samples containing water (at 90 to 105°C) is obviously necessary before calcination (30.3 ,32,61) .

However ,some samples of biological material (19,20,27) and of sediments or soil have also been dried at 70 to 105°C (generally for 24h) before wet decomposition (19,53,62,64) or before UV-spectrography or X-ray fluorescence (32). In one case (6.2) ,samples of sediments have been dried at 40°C before determination of mercury by neutron activation . In some cases, freeze-drying has been used for biological samples and sediments before determination of mercury by neutron activation (16) or before UV-spectrography or X-ray fluorescence on biological samples (32) .

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1.2.5 HOMOGENISATION

It is obviously necessary to take the part that has to be analysed from an homogenized sample (1,28,31,50,59).

Homogeneity of biological samples can be attained with the help of a mixer (11,61) or by crushing (75) .
Dried samples of biological material or sediments can be grinded (64) or crushed (32,61,62) .

Contamination of samples by the material of the apparatus must be avoided(knives of the mixers, grinders,...).

1.2.6 NEUTRON ACTIVATION

Some elements can be measured by neutron activation .
This technique has been used for :
- mercury in biological material and in sediments (6.2,6.3,6.5 to 6.9, 16,22,23,33,59,74) ;
- manganese and zinc in butter (34);
- several metals in air particulates (43).

The neutron activation method includes the following steps (6.2, 6.3,6.5 to 6.9, 33,34,74) :
- introduction of 0.1 to 1 g of sample into a quatz tube; sealing of the tube ;
- irradiation in a flux of slow neutrons produced by a nuclear reactor ;
- radioactive " cooling " for a lapse of time which depends on the element that is to be measured ;
- cooling of the tube in liquid nitrogen(74) , to reduce the internal pressure from gases produced by radiolysis and prevent any loss of sample when opening the tube ; opening of the tube ;
- addition of an inactive carrier , before or during the destruction of organic matter .

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The neutron activation method is a very sensitive and reliable one . It can be used for a large variety of samples and in a very large range of concentrations .

2. DESTRUCTION OF ORGANE MATTER.

2.1 - WATER

Except for the determination of mercury, no destruction of organic matter is performed on water samples(river or sea water), whatever the element to be measured .

However, the sample is nearly always acidified during the pre-treatment (see 1.1.2 above) . In one case oxidation with persulphate has been carried out during the pre-treatment (see 1.1.4 above).

2.1.1 NO DESTRUCTION

Even for mercury, destruction of organic matter has been omitted by one author (16), but the 20-40 l sample was acidified . Mercury was then separated as a chloro-complex on anion exchange resin (see 3.1.2. below) .

2.1.2 DESTRUCTION WITH POTASSIUM PERMAGANATE

Destruction of organic matter in water samples with potassium permanganate has been used by four authors at least (on six) (15,17,45,47) for the determination of mercury .

In the method of David Smith et al.(17), the sample is made normal in sulphuric acid by adding 50% v/v H_2SO_4, and 0.05 normal in permanganate by adding 5% w/v KMnO4 in water; the sample is then shaken for 1 h. Excess of permanganate and any amount of MnO_2 formed are reduced by adding 30% H_2O_2 solution .

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According to the authors, this treatment dissolves elemental mercury, mercury salts, and organo-mercury compounds as Hg^{2+} . Mercury is then separated by deposition on an Ag coil (sec 3.6 below).

The other procedures are as follows :
- destruction with H_2SO_4 , HNO_3 and $KMnO_4$ (45) ;
- oxidation with $KMnO_4$ alone (without acidification) for 2 days at room temperature (47);
- oxidation of acidified sample with permanganate to obtension of a stable rose (15) .

2.1.3 DESTRUCTION WITH BROMINE

In one case, water samples have been treated with bromine before the determination of mercury by flameless atomic absorption spectrophotometry (41).

2.2 - BIOLOGICAL SAMPLES AND SEDIMENTS

Very good descriptions of methods for the destruction of organic matter are given in The Analyst by the Analytical Methods Committee (80,81,82) . Each method is commented regarding its applicability, advantages, disadvantages and hazards .
The methods of the A.M.C. will serve as a guide for this report .

" When organic matter is to be destroyed as a preliminary to the determination of metallic traces, the choice of method will depend (a) on the nature of the organic material and of any inorganic constituent and (b) on the metal that is subsequently to be determined and the method to be used for its determination " (80).

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2.2.1 WET DECOMPOSITION

2.2.1.1- Destruction with nitric and sulphuric acids, with or without the aid of perchloric acid or hydrogen peroxide.

The methods using sulphuric acid " are not recommended in the presence of appreciable amounts of alkaline -earth metals, which give insoluble sulphates, since the insoluble sulphates absorb a considerable proportion of trace metals, particularly lead. In such instances decomposition with nitric and perchloric acid should be employed " (80) .

2.2.1.1.1- Sulpho-nitric destruction -Apparatus 1

Four different methods are given by the A.M.C.(80),depending on the reactivity of the material that is to be destroyed. These methods are frequently the first step prior to a treatment with perchloric acid (2.2.1.1.3) or hydrogen peroxide (2.2.1.1.4) .

2.2.1.1.2- Sulpho-nitric destruction. Special method for mercury (81). -Apparatus 2.

" The proposed method (a) affords a more convenient means of adding nitric acid to maintain oxidising conditions during the decomposition, and (b) avoids losses of mercury through distillation " (81).

However, when the determination of mercury is to be carried out on a routine basis, a method such as 2.2.1.4 (destruction with potassium permanganate) or 2.2.1.5 (destruction with hydrogen peroxide) would certainly be more convenient .

Remark : At the end of the destruction, the digestate is treated with hydroxylamine hydrochloride to remove oxides of nitrogen .

Methods very similar to 2.2.1.1.2 have been used for the determination of mercury in biological material by some of

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the authors of the papers received, with (1,41) or without (28) addition of hydroxylamine hydrochloride .

Methods similar to 2.2.1.1.1 or 2.2.1.1.2 have been used for the determination of mercury by other authors as well (12,50,58).

2.2.1.1.3 - Sulpho-nitric destruction (2.2.1.1.1), followed by the addition of perchloric acid (80).-Apparatus 1.

The use of a method involving oxidation with perchloric acid is to be avoided for mercury determinations . Hydrochloric acid produced during wet oxydations with perchloric acid leads to enhanced volatility of mercury .

2.2.1.1.4 - Sulpho-nitric destruction(2.2.1.1.1), followed by the addition of hydrogen peroxide (80).-Apparatus 1.

A method of that type has been used for the determination of Cd and Pb in biological material(41), but as a continuation of method 2.2.1.1.2 (with apparatus 2) : the whole digestate is transfered in an open flask, where it is heated with 0,5ml - portions of 30% hydrogen peroxide added several times to the hot solution .

2.2.1.1.5 - Destruction with nitric, perchloric and sulphuric acids.

Two different methods are given by the A.M.C.(80), one of them using apparatus 3, the other using apparatus 1.

Methods of that type have been used for the determination of Cd,Pb,Zn, in biological material (19) , of Cu in sediments (30.1) and of Mn in neutron activated butter after addition of inactive Mn as a carrier (34).

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2.2.1.2- Destruction with nitric and sulphuric acids,with the aid of a catalyst.

That method is not mentioned by the A.M.C. but has been used by Cumont et al.(31) for the determination of Hg in fish. The catalyst was vanadium oxide, and the destruction was carried out under a refrigerated atmosphere.

2.2.1.3- Destruction with nitric and perchloric acids.

Three different methods are described by the A.M.C. (80) (Apparatus 1,4 or 5).

A method of that type has been used for the determination of metals (Ag,Cd,Cu,Fe,Mn,Ni,Pb,Zn) in oven-dried biological material (27).

2.2.1.4- Destruction with potassium permanganate and sulphuric acid, with or without the aid of nitric acid.

Those methods are specially used for the determination of mercury in biological material.

2.2.1.4.1 - The A.M.C.(80) describes a special method for mercury where, as a first step, the destruction is carried out by boiling with nitric acid and potassium permanganate (Apparatus 6).
Sulphuric acid and an ammoniacal hydroxylamine solution are added afterwards and the mixture is allowed to stand at room temperature for at least 3 hours.
The method leads to a partial oxidation of liquids containing relatively small amounts of organic matter (urine and other finely minced biological materials).

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2.2.1.4.2 - The A.M.C. (80) also describes a variation of the former method intended for stronger biological material, where sulphuric acid is added before the digestion under reflux condenser (Apparatus 6) .

2.2.1.4.3 - Jeffus et al.(75) give a method where, after a sulpho-nitric digestion (as desbribed in 2.2.1.1.1 but with apparatus 6), potassium permanganate is added, and the solution is brought to momentary boiling . Hydroxylamine hydrochoride solution is then added to destroy the excess of oxidants.

2.2.1.4.4 - Thibaut(11) gives a very smooth method where 0,4 to 0,7 g of finely minced fish are digested during 2 hours at 50-60°C in an open long neck flask with 6 ml sulpho-nitric acid (1 part conc. H_2SO_4 + 1 part conc.HNO_3).
A supernatant greasy layer doesn't disturb. After cooling, 16 ml of a 6% potassium permanganate solution are added and the flask is allowed to stand at room temperature for at least 3 hours . Hydrogen peroxide is then added dropwise until decoloration.

2.2.1.4.5 - Fouassin (18) doesn't use nitric acid for the digestion .
One gram of fish is digested with 30 ml of concentrated sulphuric acid at room temperature during 15 minutes, then put in a water bath at 58°C during 2 hours . After cooling, the solution is diluted with 50 ml bidistilled water, and oxidized overnight at room temperature with 20 ml of saturated potassium permanganate solution (7%) . Excess of oxidant is then destroyed with 5 ml of a 15% hydroxylamine hydrochloride solution .

The same procedure is used by the Gemeinsamen Komitee Flensburger Förde (62) for the destruction of organic matter in sediments (1g wet sediment

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+ 4 ml conc.H_2SO_4 , 2h at 58°C ; + 15 ml 5% $KMnO_4$, overnight at room temperature ; + hydroxylamine hydrochl.sol. ; filtration) .

2.2.1.4.6 - Quentin (45) operates a wet digestion of river sediments by heating with $KMnO_4$ and $K_2S_2O_8$ in sulpho-nitric medium under reflux .

2.2.1.5- Destruction with hydrogen peroxide and sulphuric acid.

2.2.1.5.1 - Destruction with 50% hydrogen peroxide .

The A.M.C.(82) gives 5 possible variations (depending on the material to be destroyed) of a new method using 50% hydrogen peroxide and sulphuric acid . The method seems full of promise .

2.2.1.5.2 - Destruction with 30% hydrogen peroxide .

Heating with 30% hydrogen peroxide and concentrated sulphuric acid in a flask fitted with a reflux condenser (Apparatus 6) has been used for the destruction of biological material (16,47,61,74) and of sediments (74) for samples in which mercury had to be measured.

2.2.1.5.3 - Destruction with 30% hydrogen peroxide .Quick method.

Herman(32) uses a very quick method for the destruction of fish in which Hg and Cu have to be measured .
Three to ten gram of fish are introduced in a 250 ml - conical flask fitted to a water-cooled reflux condenser by means of a standard ground joint (apparatus 6).
Five ml of concentrated sulphuric acid are added through the top of the condenser, and are followed by 2.5 ml 30% hydrogen peroxide . The content of the flask is heated lightly during 3 to 4 minutes (for decomposition of H_2O_2). The cooled solution is brought to 100 ml with water in a 100 ml flask .
(At this stage, an aliquot is taken for determination of copper by direct atomic absorption) .

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A few drops (~ 10) of a 5% potassium permanganate solution are then added until a rose coloration develops (destruction of the remaining organic matter and of H_2O_2) .

2.2.1.6 - No destruction of organic matter .Acid solubilisation.

2.2.1.6.1 - Acid digestion

No destruction (or only a partial destruction) of organic matter has been carried out in some cases . A simple acid digestion has been used instead , especially for samples of sediments .
Boiling with nitric acid has been used (Hg in sediments :50 ; Cd, Cr, Cu, Pb, Zn in sediments : 62), or boiling with hydrochloric acid (fluorine in soil :64) or with hydrochloric acid and hydrogen peroxide (metals in suspended matter : 27) .

In one case (20) ,concentrated nitric acid only has been used to dissolve dried biological samples (determination of Cd, Pb,Zn).

2.2.1.6.2 - Hydrofluoric -perchloric acids digestion.

This procedure has been used for the analysis of metals in sediments in only two cases (19,53) .

2.2.1.6.3 - Hydrofluoric digestion

This procedure has been used for the destruction of mineral samples containing silicates ,before UV-spectrography or X-ray fluorescence (32) .

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2.2.2 DRY DECOMPOSITION

The Analytical Methods Committee (80) gives a good description of six methods of dry ashing of organic matter (with or without ashing aids) .

" Dry ashing is applicable to the determination of most common metals, usually with the exception of mercury and arsenic, in organic matter " . (80)

" The dry-ashing procedure is of particular advantage when the use of sulphuric acid is objectionable ; for instance, for the determination of lead in materials containing appreciable quantities of alkaline earths , whose sulphates occlude lead sulphate " . (80)

In general , the temperature of 420°C should not be exceeded. After ashing, ashes are dissolved in an acid .

Dry ashing has been used in some of the received papers, for the determination of lead (1,58), of lead and zinc (32) , of Cu,Fe,Mn,Ni,Pb,Zn (32,61) in biological material, and of Cd, Cu, Fe, Mn, Pb , V , Zn in air particulates (63).

In one occasion(30.3) a Low Temperature Asher has been used at a maximum temperature of 60°C for the determination of copper .

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3. SEPARATION .

3.1 - SOLID - LIQUID EXTRACTION

Resins are useful when separation of heavy metals from alkali salts is needed as well as a concentration effect.

Moreover, the volume of water that can be treated may be very important (10 to 40 ℓ) .

3.1.1 CATIONIC RESINS

Cationic chelating resins have been used for the separation of Cd, Cu, Pb, Zn from sea or river water (10 ℓ) , the measurement being made by pulse polarography(24,25) or atomic absorption (25).
Cationic resins have also been used to separate Cd, Pb, Zn from estuary water (19); a 2 ℓ sample was acidified to pH 5 , adsorbed on an acid resin , and eluted with 2 N nitric acid; the measurement was made by polarography .

3.1.2 ANIONIC RESINS

Anionic exchange resin has been used for the adsorption of mercury as a chloro-complex from a 20-40 ℓ sample of estuary water, acidified to 0,1 N with sulphuric or hydrochloric acid (16). ^{203}Hg is added as a tracer during the pre-treatment (see 1.1.4 before).
Mercury is eluted in a solution of perchloric acid and ethyl acetate . After removal of ethyl acetate , mercury is extracted with dithizone (see 3.2.5.below) and measured colorimetrically.

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3.2 - LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction has been mainly used for separation and concentration of (heavy) metals from water or destructed biological samples, prior to a colorimetric determination or an atomic absorption spectrophotometry.

3.2.1 EXTRACTION OF LEAD

3.2.1.1 - Dithizone extraction .

A very good description of the determination of lead in organic matter is given by the Analytical Methods Committee in The Analyst (77) . Lead is extracted from the digestate or acid dissolved ash by means of dithizone at pH 9.0 to 9.5, after the addition of citrate , and in the presence of sodium hexametaphosphate so as to prevent the precipitation of magnesium or calcium phosphates. For samples with a high content in calcium, magnesium and phosphate , a preliminary extraction from acid solution with diethylammonium diethyldithiocarbamate (D.A.D.D.T.C.) is substituted for the hexametaphosphate procedure .

Lead is dissolved again in diluted nitric acid, and re-extracted with dithizone after addition of an ammoniacal sulphito-cyanide solution . The optical density of the dithizone extract is measured .

When considerable bismuth interference is indicated, a given modified procedure should be used.

The method recommended by the A.M.C. has been used by one author (1) .

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3.2.1.2 - A.P.D.C. extraction

Another author (58) has separated lead with ammonium pyrollidine dithiocarbamate (A.P.D.C.) , the measurement being made by atomic absorption spectrophotometry .

3.2.2 EXTRACTION OF CADMIUM

The Analytical Methods Committee gives a very good description of methods for the determination of small amounts of cadmium in organic matter(83) .
A first method is based on a double-extraction with dithizone followed by a colorimetric determination .
A second method, based on another procedure of double extraction with dithizone , is followed by a polarographic determination .

Another method can be found in the Official Standardized and Recommended Methods of Analysis of the Society for Analytical Chemistry (1963) and has been used in reference 1.

3.2.3 EXTRACTION AF CADMIUM AND LEAD

Extraction with sodium diethyldithiocarbamate (Na D.D.T.C) and methyl-isobutyl-keton (M.I.B.K.) has been used by the Rijksinstituut voor de Volksgezondheid (41) for the determination of Cd and Pb in destructed biological samples . After back-extraction with diluted nitric acid, the metals are measured by atomic absorption .

3.2.4 EXTRACTION OF METALS (from water)

3.2.4.1 - A.P.D.C.extraction

For sea water, Preston et al. (27) have used an extraction in chloroform at pH 6 of the ammonium pyrollidine dithiocarbamate (A.P.D.C.) complexes . Atomic absorption spectrophoto-

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metry is then carried out on a small portion of the extract using the tantalum boat technique (Kahn et al., 1968) for Cd, Pb and Ag ; the remaining portion of the chloroform extract is converted into a methanolic solution and aspirated directly into an A.A. instrument (for Cu,Fe,Mn,Ni, Zn). For an initial sea water volume of 1 litre and 2 X 25 ml chloroform extracts, the listed elements are extracted with yields superior to 95% , and the use of methanol as aspirant means that the extracted samples can be directly compared with a mixed element standard of the metal chlorides dissolved in methanol.

Extraction in methyl-isobutyl-ketone (M.I.B.K.) of the A.P.D.C complexes has also been used for river water (15) , the MIBK extract being measured directly by atomic absorption spectrophotometry for Cd, Co, Cr, Cu, Fe,Ni, Pb . Yields of 100% are attained by adapting the APDC concentration to each element .

3.2.4.2 - A.P.D.C.-D.A.D.D.T.C. extraction

A very elaborated method is used at the Rijksinstituut voor de Volksgezondheid in Utrecht (41) and is described by Fonds and Van den Eshof (76) . The yield of the extraction for Cd, Co, Cu, Mn, Ni, Pb, Zn from drinking or river water is 100 % .

An APDC/MIBK extraction at pH 2 to 2.5 is followed by an extraction with diethylammonium-diethyldithiocarbamate (D.A.D.D.T.C.) in chloroform, first at pH 3.5, then at pH 6 to 7 . The combined extracts are back-extracted with diluted nitric acid . This last solution is measured by atomic absorption spectrophotometry.

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3.2.5 EXTRACTION OF MERCURY

Extraction of mercury from the digestate of organic matter diluted to 0,1 N acidity with dithizone in carbon tetrachloride is given by the Analytical Methods Committee in The Analyst (81) . After a back-extraction with 0,1 N hydrochloric acid, mercury is re-extracted with dithizone and measured by colorimetry .

A similar method has been used in ref.16.

3.3 - CHROMATOGRAPHY

The method of Woidich et al.(84) has been used for the determination of mercury in biological material (12) . Mercury is extracted from the digestate with dithizone . The dithizone complex is purified by thin layer chromatography, and the mercury band is extracted with methanol . The measurement is made by colorimetry .

3.4 - DISTILLATION

Distillation has been used for the separation of mercury chloride or bromide , when neutron activation method was used (16, 22, 59,74) .

3.5 - ISOTOPIC EXCHANGE

Isotopic exchange has been used after distillation of the mercury chloride or bromide .

Isotopic exchange of ^{203}Hg on an amalgamated copper foil has been used in ref.59.

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The procedure used by de Goeij (74) , after the wet destruction of organic matter , is the following :

" The mercury is volatilized at 200°C by adding hydrogen bromide and trapped in a sodium acetate solution . An inactive mercury droplet is added to this solution and the mixture vigorously stirred for 1 hour, braking the elemental mercury into hundreds of droplets thus ensuring a good isotopic exchange . The mercury metal is then collected on a sintered glass filter and washed with water and with acetone . Finally it is dissolved in nitric acid and counted".

3.6 - DEPOSITION ON METAL

For the separation and concentration of mercury , David Smith et al. (17) use a procedure which leads to a very sensitive method for the determination of mercury in water . After the oxydation of the sample with $KMnO_4$ (see 2.1.2 above), the procedure is as follows :

" A silver coil freed of mercury by heating was added to each bottle and the bottles shaken overnight .
Up to this stage the samples remained in their collecting bottles, thus minimizing contamination and losses of mercury.
Each coil was removed from the solution, washed with water and acetone and dried in air . Optimum conditions for the recovery of mercury were determined using ^{203}Hg tracer.
Mercury amalgamated with the silver was driven off by heating the coil to roughly 250°C in a silica tube . The mercury vapour was passed in a stream of nitrogen through a cell of 15 cm light path, in an atomic absorption spectrophotometer.

For 1 kg samples ..... the coefficient of variation at the 0,050 ug/kg level was 1,8 % . "

This method is the only case of concentration prior to flameless atomic absorption spectrophotometry of mercury .

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3.7 - PRECIPITATION

In two cases, precipitation has been used for separation .

3.7.1 PRECIPITATION OF ARSENIC

Arsenic is precipitated from water samples with thionalide(41). The precipitate is filtered and destructed and AsH_3 is formed (see 3.9. below).

3.7.2 PRECIPITATION OF MANGANESE

In this procedure (34) , manganese is separated from the digestate of neutron activated butter, after addition of a Mn carrier (see 2.2.1.1.5. above).
The dry rest of the digestate is dissolved in 150 ml water and 30 g potassium chlorate is added . The solution is boiled a few minutes, then left 45 to 60 minutes at room temperature to allow the formation of a precipitate of manganese dioxide . The precipitate is filtered, dried and counted in a gamma spectrometer .

3.8 - REDUCTION-MERCURY

The determination of mercury by flameless atomic absorption spectrophotometry follows the principles of the Hatch and Ott method . Mercury compounds are reduced to elemental mercury , the vapors of which are evolved through a silica cell where it is measured .

The method is composed of the following steps :

a. The exces of oxidants in the digestate is destroyed (if not abready done at the end of the destruction of organic matter step) by addition of a solution of hydroxylamine hydrochloride . This treatment may be done separately (18,62,75) or in combination with the next step (11,41) .

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b. The reduction of the mercury compounds to elemental mercury is obtained by addition of a 5 to 20 % solution of stannous chloride or suplhate , combined (11, 41) or not with the hydroxylamine hydrochloride solution .
The quantity of reagent added varies largely according to the authors (0,1 to 3 g of dry reagent per gram of original biological sample).

The reduction can also be obtained by addition of 2 ml of a 1% sodium borohydride ($NaBH_4$) solution in 0,005 N NaOH (32).

Borohydride leads to a more constant reduction and is purer than tin salts .

c. The elemental mercury vapours are conducted to the measuring cell with the aid of a flow of air or nitrogen.

3.9 - REDUCTION -ARSENIC.

Inorganic arsenic is reduced into arsine,AsH_3 , by zinc in acid solution . The arsine is then passed through a scrubber containing glass wool impregnated with lead acetate solution and into an absorber tube containing silver diethyldithiocarbamate dissolved in pyridine . In the absorber, arsenic reacts with the silver salt and forms a soluble red complex which is suitable for photometric measurement .

The method has been used for the determination of arsenic in water, after precipitation with thionalide (41) , in biological material, after digestion (1, 41), and in dry sediments (62).

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4. MEASUREMENT .

Table 3 (p. 54) shows the approximate percentages of samples analysed by the different techniques available .

4.1 - ATOMIC ABSORPTION SPECTROPHOTOMETRY

Wherever it was possible to use it, atomic absorption was the method most frequently employed . It has been used for more than 80% of the results transmitted. This recent technique, allowing a quick and sensitive measurement of metals , is probably the ground for the development of most researches in the field of non-organic micropollutants .

The detection limit that can be achieved on water ranges from 1 to 100 µg/l , according to the metal measured (for instance Ag, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn) and the apparatus employed . After an extraction by means of a complexing reagent in a combustible solvant (f.i. M.I.B.K) a further sensitivity factor from 1 to 50 can still be gained according to the element taken into account , the final detection limit being then 1 to 5 µg/l or even better .

Different accessories, especially at the level of the element excitation (graphit oven, tantalum boat) , lead to detection limits ranging from 0,001 to 0,1 µg/l for some metals .

Biological samples and solid samples must inevitably be destroyed and put in solution before injection in the flame ; this nearly always produces a dilution from 10 to 100 with a reducing effect on sensitivity which is still very good for that kind of samples (detection limit ranging from 0,01 to 5 mg/kg according to the metal) .

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4.2 - FLAMELESS ATOMIC ABSORPTION.

This technique is presently the best one for mercury measurement. It is quick and easy and can be carried out by means of a traditional atomic absorption spectrophotometer fitted with a special measurement cell, or by means of special apparatus conceived for mercury measurement .
The detection limit reached in water is about 0,02 µg/l.

Reduction in metallic Hg with stannous chloride or sulfate or sodium borohydride (see 3.8 above) is preceded by an oxidation which is usually carried out with acid permanganate when water is concerned (see 2.1.2 above) , or by a more or less elaborated destruction of organic matter for biological samples or sediments (see 2.2.1 above) .

One author only (17) proceded to a previous concentration of water, by setting down mercury on a silver coil . In these conditions, the coefficient of variation at the 0,050 µg/kg level was 1,8 % for 1 kg sample .

4.3 - SPECTROPHOTOMETRY (COLORIMETRY)

Colorimetry has been used for the measurement of metals by different laboratories before they could be equipped with atomic absorption spectrophotometers , or in particular circonstances .

It has also been used for the measurement of elements which are not adapted, or were not adapted at the time of measurement, for atomic absorption : arsenic , boron, molybdene,selenium .

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Arsenic has always been measured by means of silver -diethyl-dithiocarbamate dissolved in pyridine (1,41,62).
A colorimetric method by means of zinc - dibenzyl - dithiocarbamate has been used for direct and continuous measurement of copper in water from a boat (30.2) and for measurement in digested sediments (30.1) and (low t° -) ashed biological material (30.3) .
Colorimetry has also been used for the measurement of the Hg-dithizone complex separated by thin-layer chromatography and dissolved in methanol (12,see 3.3 above) , and for the measurement of the Hg-dithizone complex dissolved in chloroform, after separation of the chloro-Hg-complex on anionic resin (16, see 3.1.2 above) .

Usually, previous concentrations or extractions are necessary when detection limits similar to those achieved by atomic absorption have to be performed in colorimetry .

4.4 - RADIOACTIVE COUNTING (AFTER NEUTRON ACTIVATION)

Neutron activation is a sensitive and reliable technique for the measurement of many elements . It can be applied to a variety of samples with a wide range of concentration levels. However, in many cases , a chemical separation is required to separate the formed radioisotopes . Moreover a nuclear reactor is necessay !

Measurement of the formed radioisotopes is carried out mainly by gamma spectrometry . Mercury has been measured that way (as Hg 197) in biological samples and sediments after destruction of organic matter , separation by distillation and isotopic exchange (see 3.5 above) (6.2,6.3,6.5 to 6.8, 74) and in biological samples (22,59) .

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In that way also, manganese has been measured in butter as Mn 56, after separation of the MnO_2 precipatate (34, see 3.7.2 above) and zinc in butter, as Zn 65, without any separation (34) .

Beta counting of Hg 203 has been used for measurement of Hg in biological samples and sediments, after destruction of organic matter, distillation as the chloride, and further radiochemical purification (16) .
A sensitivity from 0,1 to 1 µg /kg can be achieved for mercury for samples of 1 g of wet matter .

4.5 - POLAROGRAPHY

Polarography has been used by five authors for work on river and sea waters(13,19,24,25,50) and by one (55) for measuring Cu in fruit .
Pulse polarography has been used by two of them (24,25) for measurement of Cd,Cu,Pb,Zn on river and sea water, after concentration on cationic resin (see 3.1.1 above) .

Pulse polarography is a sensitive method, but requiring skilful technicians .

4.6 - U.V-SPECTROGRAPHY

U.V-spectrography was used by one author for work on river and sea sediments, soils and plants (15,32) .

The material to be analysed is first brought up in dry powder form :

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- for biological samples , bu lyophilisation (fruit,fish) or drying at <70°C or ashing at <450°C.
- for mineral samples, by drying at <105°C or, for siliceous material , by treatment with hydrofluoric acid (see 2.2.1.6.2 above) , drying and ashing at <450°C .
- for water samples, by evaporation to dryness, and ashing at <450°C (previous possible concentration on resin) .

The ground residue is introduced in a graphite electrode . The excitation is given by means of a continuous arc, the spectrum is photographed .

This method is a delicate one; the making of standards in matrixes similar to those of the sample is usually required and the staff must be well trained . Its application is advantageous only for large series of samples .
When these conditions are fulfilled, this method allows the measurement of a series of elements on the same sample, with detection limits ranging from 1 to 100 µg per g of analysed product . Another advantage is that the sample is concentrated (drying or ashing) while in wet methods, the sample is usually diluted .
However , the accuracy, which is about 10% in the most effective cases, is usually not so good as in the other methods .

4.7 - X-RAY FLUORESCENCE

X-ray fluorescence was used by only two authors for measuring Fe, Ti , and Sr in soils and plants (32) and for Cd, Pb, Ni in air particulates and in rain (43) .

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The samples is prepared as in U.V-spectrography [32 , see 4.6 above] then set on a cellulose tablet or any other convenient support .
Air filters can be analysed directly .

X-ray fluorescence is more accurate and reproducible than U.V-spectrography ; the sensitivity is similar and both methods have the same problems with matrixes .
One advantage is that the method is a non-destructive one .

A P P A R A T U S .

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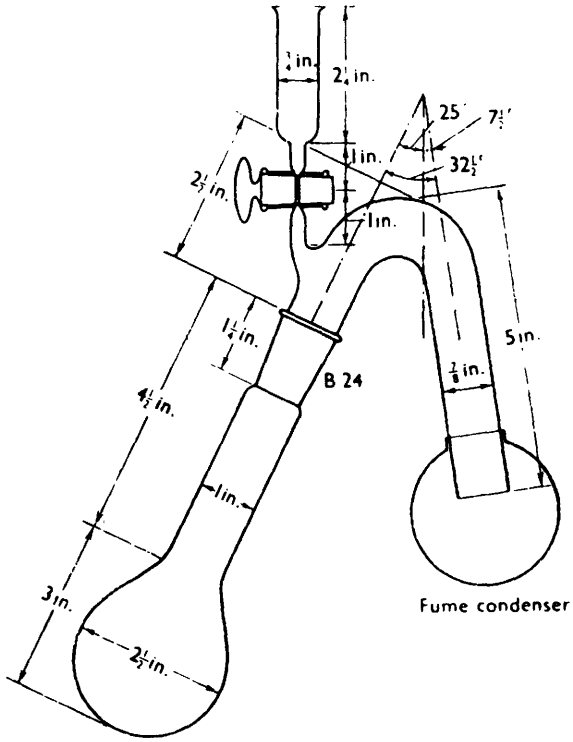

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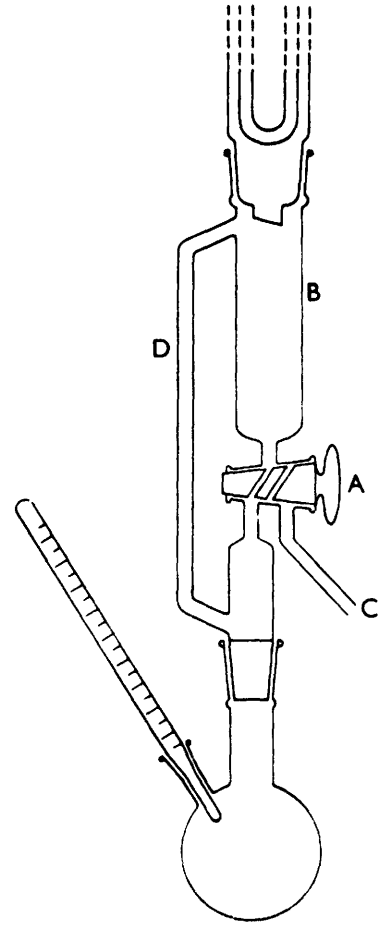

3. Conical flask with short reflux tube extension, electrical hot plate ;

4. Conical flask, electrical hot plate ;

5. Large boiling tube (40 mm X 230 mm) ;

6. Round - bottommed flask or conical flask fitted by means of a standard ground joint to a long water - cooled reflux condenser .

TABLE 2.

ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT		DESTRUCTION		SEPARATION		MEASUREMENT	
Hg	Estuary water	17	Filtr. Acid.	1.1.1. 1.1.2.	H_2SO_4 + $KMnO_4$	2.1.2.	Deposition on Ag coil	3.6.	F.ℓ.A.A.	4.2.
Hg	River water	15	Acid.	1.1.2.	$KMnO_4$	2.1.2.	Reduc.$SnCℓ_2$	3.8.	F.ℓ.A.A.	4.2.
Hg	Drinking water	45	Acid.	1.1.2.	H_2SO_4+HNO_3 + $KMnO_4$	2.1.2.	Reduc.?	3.8.?	F.ℓ.A.A.	4.2.
Hg	River water	46	Acid. Filtr.	1.1.2. 1.1.1.	?		Reduc.?	3.8.?	F.ℓ.A.A.	4.2.
Hg	Water	47	Filtr.	1.1.1.	$KMnO_4$	2.1.2.	Reduc.?	3.8.?	F.ℓ.A.A.	4.2.
Hg	River water	50	Acid. or low t°	1.1.2. 1.1.3.	?		Reduc.?	3.8.?	F.ℓ.A.A.	4.2.
Hg	River water	41	Filtr. Acid.	1.1.1. 1.1.2.	Br_2	2.1.4.	Reduc.$SnCℓ_2$	3.8.	F.ℓ.A.A.	4.2.
Hg	Biol.	1	Homog.	1.2.5.	Sulpho-nitric	2.2.1.1.2.	Reduc.$SnSO_4$	3.8.	F.ℓ.A.A.	4.2.
Hg	Biol.	28	Homog.	1.2.5.	Sulpho-nitric	2.2.1.1.2.	Reduc.$SnCℓ_2$	3.8.	F.ℓ.A.A.	4.2.
Hg	Biol.	41	?		Sulpho-nitric	2.2.1.1.2.	Reduc.$SnCℓ_2$	3.8.	F.ℓ.A.A.	4.2.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT	DESTRUCTION	SEPARATION	MEASUREMENT
Hg	Biol.	50	Drying 1.2.4. Homog. 1.2.5.	Sulpho-nitric 2.2.1.1.1. or 2.2.1.1.2.	Reduc.? 3.8.?	F.l.A.A. 4.2.
Hg	Biol.	58	?	Sulpho-nitric 2.2.1.1.1. or 2.2.1.1.2.	Reduc. $SnCl_2$ 3.8.	F.l.A.A. 4.2.
Hg	Biol.	31	Homog. 1.2.5.	H_2SO_4 +V ox. 2.2.1.2.	Reduc. $SnCl_2$ 3.8.	F.l.A.A. 4.2.
Hg	Biol.	11	Freezing 1.2.2. Homog. 1.2.5.	Sulpho-nitric, $KMnO_4$ 2.2.1.4.4.	Reduc. $SnSO_4$ 3.8.	F.l.A.A. 4.2.
Hg	Biol.	75	Homog. 1.2.5.	Sulpho-nitric, $KMnO_4$ 2.2.1.4.4.	Reduc. $SnSO_4$ 3.8.	F.l.A.A. 4.2.
Hg	Biol.	18	?	H_2SO_4, $KMnO_4$ 2.2.1.4.5.	Reduc. $SnCl_2$ 3.8.	F.l.A.A. 4.2.
Hg	Sedim. (river)	62	?	H_2SO_4 , $KMnO_4$ 2.2.1.4.5.	Reduc. $SnCl_2$ 3.8.	F.l.A.A. 4.2.
Hg	Sedim. (river)	45	Low $t°$ 1.2.2.	Sulpho-nitric, $KMnO_4$, $K_2S_2O_8$ 2.2.1.4.6.	Reduc.? 3.8.?	F.l.A.A. 4.2.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT		DESTRUCTION		SEPARATION		MEASUREMENT	
Hg	Biol.	47	?		H_2SO_4 + H_2O_2	2.2.1.5.2.	Reduc.?	3.8.?	F.l.A.A.	4.2.
Hg	Biol.	61	?		H_2SO_4 + H_2O_2	2.2.1.5.2.	Reduc.?	3.8.?	F.l.A.A.	4.2.
Hg	Biol.	32	Freezing	1.2.2.	H_2SO_4 + H_2O_2	2.2.1.5.3.	Reduc.$NaBH_4$	3.8.	F.l.A.A.	4.2.
Hg	Sedim.	50	Drying Homog.	1.2.4. 1.2.5.	HNO_3	2.2.1.6.1.	Reduc.?	3.8.?	F.l.A.A.	4.2.
Hg	River and sea water	16	Acid. Tracer	1.1.2. 1.1.4.			Anion resin Dithizone	3.1.2. 3.2.5.	Colorim.	4.3.
Hg	Biol.	81	Homog.	1.2.5.	Sulpho-nitric	2.2.1.1.2.	Dithizone	3.2.5.	Colorim.	4.3.
Hg	Biol.	12	?		Sulpho-nitric	2.2.1.1.1. or 2.2.1.1.2.	Chromato. dithizonate	3.3.	Colorim.	4.3.
Hg	Biol., sedim.	74	Neutron act.	1.2.6.	H_2SO_4 + H_2O_2	2.2.1.5.2.	Distill.brom. Isotopic.exch.	3.4. 3.5.	γ-spectrom.	4.4.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT	DESTRUCTION	SEPARATION	MEASUREMENT
Hg	Biol., sedim.	6.2 ,6.3, 6.5 to 6.8	Neutron act. 1.2.6.	?	Distill.brom. 3.4. Isotopic exch. 3.5.	γ -spectrom. 4.4.
Hg	Biol.	59	Freezing 1.2.2. Homog. 1.2.5. Neutron act. 1.2.6.	Wet ashing ?	Distill. 3.4. Isotopic exch. 3.5.	γ -spectrom. 4.4.
Hg	Biol.	22	Freezing 1.2.2. Neutron act. 1.2.6.	Wet ashing ?	Distill. 3.4.	γ -spectrom. 4.4.
Hg	Biol., sedim.	16	Drying 1.2.4. Neutron act. 1.2.6.	H_2SO_4 + H_2O_2 2.2.1.5.2.	Distill. chlor. 3.4.	β - country 4.4.
As	Water	41	Filtr. 1.1.1. Acid. 1.1.2.		Precipit. 3.7.1. Reduc.AsH_3 3.9.	Colorim. 4.3.
As	Biol.	1	Low t° 1.2.2.	Sulpho-nitric 2.2.1.1.2.	Reduc.AsH_3 3.9.	Colorim. 4.3.
As	Biol., sedim.	41	?	?	Reduc.AsH_3 3.9.	Colorim. 4.3.
As	Sedim.	62	Drying 1.2.4. Homog. 1.2.5.		Reduc.AsH_3 3.9.	Colorim. 4.3.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT		DESTRUCTION		SEPARATION		MEASUREMENT	
Cu	Biol.	1	Low t°	1.2.2.	Sulpho-nitric	2.2.1.1.2.			A.A.	4.1.
Cu	Biol.	32	Low t°	1.2.2.	H_2SO_4 + H_2O_2	2.2.1.5.3.			A.A.	4.1.
Cu	River water	30.2.	Filtr.	1.1.1.					Colorim.	4.3.
Cu	Sedim(river)	30.1.	Drying	1.2.4.	HNO_3 + H_2SO_4 + $HClO_4$	2.2.1.1.5.	?		A.A. or colorim.	4.1. 4.3.
Cu	Biol.	30.3.	Drying	1.2.4.	Low t° ashing	2.2.2.	?		Colorim.	4.3.
F	Soil	64	?		Acid.	2.2.1.6.1.	?		Specific electrod	
Mn	Butter	34	Neutron act.	1.2.6.	HNO_3 + $HClO_4$ + H_2SO_4	2.2.1.1.5.	Precipit.MnO_2	3.7.2.	γ-spectrom.	4.4.
Pb	Biol.	32	Low t°	1.2.2.	Calc.	2.2.2.	?		A.A.	4.1.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT	DESTRUCTION	SEPARATION	MEASUREMENT
Pb	Biol.	58	?	Calc. 2.2.2.	Liquid-liquid extraction 3.2.1.2.	A.A. 4.1.
Pb	Biol.	1	Low t° 1.2.2.	Sulphonitric or calcin. 2.2.1.1.2. 2.2.2.	Liq.-Liq.extract. 3.2.1.1.	Colorim. 4.3.
Zn	Biol.	32	Low t° 1.2.2.	Calc. 2.2.2.	?	A.A. 4.1.
Zn	Butter	34	Neutron act. 1.2.6.			γ-spectrom. 4.4.
Mn,Zn	Riv.water	15	Acid. 1.1.2.			A.A. 4.1.
Cd,Pb	Biol.	41	?	Sulphonitric + H_2O_2 2.2.1.1.2. 2.2.1.1.4.	Liq.-Liq.extrac. 3.2.3.	A.A. 4.1.
Cu,Fe,Mn, Ni, Pb	Sea water	27	Filtr. 1.1.1. Low t° 1.1.3. Acid. 1.1.2.		Liq.-Liq.extrac. 3.2.4.1.	A.A. 4.1.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT	DESTRUCTION	SEPARATION	MEASUREMENT
Ag, Cd,Zn	Sea water	27	Filtr. 1.1.1. Low t° 1.1.3. Acid. 1.1.2.		Liq.-liq.extrac. 3.2.4.1.	A.A. (Ta boat) 4.1.
Cd,Co,Cr,Cu, Fe,Ni,Pb	Riv.water	15	Acid. 1.1.2.		Liq.-Liq.extrac. 3.2.4.1.	A.A. 4.1.
Cd,Co,Cu,Fe, Mn,Ni,Pb,Zn	Water	41, 76	Centrif. 1.1.1. Acid. 1.1.2. Oxidation 1.1.4.		Liq.-liq.extrac. 3.2.4.2.	A.A. 4.1.
Cd,Pb,Zn	Biol.	19	Low t° 1.2.2. Drying 1.2.4.	HNO_3 + $HClO_4$ + H_2SO_4 2.2.1.1.5.	?	A.A. 4.1.
Cd,Pb,Zn	Biol.	20	Low t° 1.2.2. Drying 1.2.4.	HNO_3 2.2.1.6.1.	?	A.A. 4.1.
Cd,Cr,Cu, Pb,Zn	Sedim.	62	Drying 1.2.4. Homog. 1.2.5.	HNO_3 2.2.1.6.1.	?	A.A. 4.1.
Cu,Fe,Mn, Ni, Zn	Susp.matter	27	?	HCl + H_2O_2 2.2.1.6.1.	?	A.A. 4.1.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT	DESTRUCTION	SEPARATION	MEASUREMENT
Ag,Cd,Pb	Susp.matter	27	?	$HCl + H_2O_2$ 2.2.1.6.1.	?	A.A. (Ta boat) 4.1.
Cd,Pb,Zn	Sedim.	19	Drying 1.2.4.	$HF+HClO_4$ 2.2.1.6.2.	?	A.A. 4.1.
Metals	Sedim.	53	Low t° 1.2.2. Drying 1.2.4.	$HF+HClO_4$ 2.2.1.6.2.	?	A.A. 4.1.
Heavy metals	Biol.	27	Low t° 1.2.2. Drying 1.2.4.	HNO_3 + $HClO_4$ 2.2.1.3.	?	A.A. 4.1.
Cu,Fe,Mn, Ni,Pb,Zn	Biol.	61	Drying 1.2.4. Homog. 1.2.5.	Calc. 2.2.2.	?	A.A. 4.1.
Cd,Cu,Fe,Mn, Pb,V ,Zn	Air partic.	63	?	Calc. 2.2.2.	?	A.A. 4.1.
Metals (other than Cd,Ni,Pb)	Air partic.	43	Neutron act. 1.2.6.	?	?	γ-spectrom. 4.4.

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ELEMENT	MEDIUM	REFERENCE	PRE-TREATMENT	DESTRUCTION	SEPARATION	MEASUREMENT
Cu,Pb,Zn	Riv.water	25	?	?	Cat.resin 3.1.1.	A.A. 4.1 or Pulse Polar. 4.5.
Cd,Pb,Zn	Water	19	Filtr. 1.1.1. Acid. 1.1.2.		Cat.resin. 3.1.1.	Polaro. 4.5.
Cd,Cu,Pb,Zn	Sea water	24	?	?	Cat.resin. 3.1.1.	Pulse polaro. 4.5.
Metals	Water	32	Evapor. 1.1.6.	Calcin. 2.2.2.		UV-spectr. 4.6. or X-ray fl. 4.7.
Metals	Biol.	32	Drying 1.2.4. Homog. 1.2.5.	or Calcin. 2.2.2. Homog. 1.2.5.		UV-spectr. 4.6. or X-ray fl. 4.7.
Metals	Sedim.	32	Drying 1.2.4. Homog. 1.2.5.			UV-spectr. 4.6. or X-ray fl. 4.7.
Metals	Minerals, Silicates	32		HF 2.2.1.6.3. Calcin. 2.2.2.		UV-spectr. 4.6. or X-ray fl. 4.7.
Cd,Ni,Pb	Air part.	43	?	?	?	X-ray fl. 4.7.

TABLE 3.

Approximate percentages of samples measured by the different methods .

Method	Total of samples	Sb	As	Ba	Be	Bi	B	Br	Cd	Cr	Co	Cu	F	Fe	Pb	Mn	Hg	Mo	Ni	Se	Ag	Sr	Sn	Ti	V	Zn	Zr
AA	81				100	100			88	84	80	83		67	93	90	92		93		100	100			3.5	84	
Col	8.5		98				85		2.5			6		25	0.5		0.1	87.5		75					91		
NA	7	100	2	100				100	2.5	8	11	2.5		7			8	12.5		25			90			6	
Pol	2								6			6			4											5	
UV	1.5						15		0.7	8	9	2.5		0.25	2.5	10	0.1		7				10		5.5	5	100
X									<0.1					0.1	<0.1				0.1					100			

TABLE 3.

A P P E N D I X

METHYL- MERCURY IN FISH .

The methods used for the determination of methyl-mercury in fish are derivations of the Westöö method (85) . The method has been standardized by the Nordic Committee on Food Analysis (86) .

" The methylmercury in the homogenized sample is liberated from the proteins by hydrochloric acid,and the methylmercury chloride formed is extracted with benzene. Fats, phospholipids, and lipoproteins are co-extracted into the benzene phase . The methylmercury is further isolated by extraction with a water solution of cysteine slightly acidified with acetic acid . Excess of hydrochloric acid is added and methylmercury chloride is re-extracted into benzene. The benzene extract is dried and analysed using a gas chromatograph with electron capture detector " .

The sensitivity is of the order of 0,02 mg methylmercury per kg fish.

Results have been given for methyl-mercury by four authors only (6.4, 6.7, 6.8, 69).

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