



# **Determination of Mercury in Solids**

**Analytical 3**

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*This document can be obtained from:*  
**EURO CHLOR - Avenue E. Van Nieuwenhuyse 4, Box 2 - B-1160 BRUSSELS**  
*Telephone: 32-(0)2-676 72 65 - Telefax: 32-(0)2-676 72 41*

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- maintain open and timely dialogue with regulators, politicians, scientists, the media and other interested stakeholders in the debate on chlorine;
- ensure our industry contributes actively to any public, regulatory or scientific debate and provides balanced and objective science-based information to help answer questions about chlorine and its derivatives;
- promote the best safety, health and environmental practices in the manufacture, handling and use of chlor-alkali products in order to assist our members in achieving continuous improvements (*Responsible Care*).

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## RESPONSIBLE CARE IN ACTION

Chlorine is essential in the chemical industry and consequently there is a need for chlorine to be produced, stored, transported and used. The chlorine industry has co-operated over many years to ensure the well-being of its employees, local communities and the wider environment. This document is one in a series which the European producers, acting through Euro Chlor, have drawn up to promote continuous improvement in the general standards of health, safety and the environment associated with chlorine manufacture in the spirit of *Responsible Care*.

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This edition of the document has been drawn up by the Analytical Working Group to whom all suggestions concerning possible revision should be addressed through the offices of Euro Chlor.

## Summary of the Main Modifications in this version

Section	Nature
All	Complete review and update (from ANAL 03-07 and Env Prot 3); include the old Analytical 4

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## 1. INTRODUCTION

When decommissioning and demolishing mercury cell brine electrolysis plants, a lot of different types of solid materials, mainly inorganic in nature, contaminated with mercury have to be recycled or disposed of (see ***Env Prot 03 - Decommissioning of Mercury Chlor Alkali Plants***).

To classify these materials and decide if they can be directly recycled, disposed of in industrial or in special landfill, or if treatment is necessary, it is necessary to define a good analysis programme of their mercury concentration and the form of the mercury (speciation).

In the case of solids containing inorganic materials, these must be destroyed during a pre-treatment phase.

This recommendation describes the methods proposed by Euro Chlor, starting from the precautions to be taken for the sampling.

## 2. SCOPE

The objective is to determine concentrations above 0.1 mg Hg per kg of material, the level of contamination depending of the nature of the material (metal, brick and concrete, plastic, rubber, wood ...).

Unfortunately, as well as the wide range of types of materials involved, the nature of the mercury contamination and its homogeneity can also vary widely, from purely surface contamination to complete penetration of the mercury into the bulk of the material. From a true analytical standpoint therefore, the data generated is extremely sample dependent and these factors have to be taken into account both when the initial analytical requests are discussed and also in the interpretation of the final analytical data generated.

## 3. PRINCIPLES

The form in which the mercury is present is usually well known, and depends on the way the material was in contact with mercury (metallic mercury or dissolved mercury).

The basic principle adopted is to break down the sample as completely as possible by oxidation to produce a solution containing mercury in the ionic form which can be readily measured. Three methods are proposed here:

- combustion in a Wickbold burner (to avoid damage to the quartz burner with samples containing salts or alkali metals and phosphorous compounds, a stainless steel burner can be used, but chloride corrosion may become a problem)
- bomb digestion with nitric acid (not applicable to chlorinated compounds and if the sample contains substances that can form explosive compounds with nitric acid)

- wet oxidation under reflux with nitric-sulphuric acid (difficult to destroy fatty materials and acid insoluble residues can result in some mercury being retained)

All forms of mercury, including organic compounds, are pre-oxidised to ionic mercury. If necessary, final and complete oxidation can be achieved by adding an oxidising agent (see list below) and heating, if necessary, to maximum 80°C for 2 hours. After cooling, the excess of oxidant must be destroyed and the mercury reduced to metallic form. It is then either determined directly or concentrated on a gold film and then determined.

Detection of mercury vapour is usually performed with CVAAS (Cold Vapour Atomic Absorption Spectroscopy) or CVAFS (Cold Vapour Atomic Fluorescence Spectroscopy).

## 4. REAGENTS

Some laboratory suppliers now offer a range of reagents of guaranteed low mercury content especially for trace mercury analysis, and certified mercury standards (concentrations are given as example):

- Aqua regia (HCl/HNO<sub>3</sub>)
- Oxidising agent (nitric acid / sodium chlorate and hydrochloric acid, potassium dichromate, potassium permanganate, potassium persulphate, etc)
- Hydroxylamine hydrochloride 100 g/l or ascorbic acid (solid or in solution)
- Reducing agent (Tin II chloride 25% in hydrochloric acid, 20% w/v, or 7 g/l sodium borohydride in 4 g/l caustic soda)
- Standard mercury solution 1000 ± 5 mg/l

Note 1: All reagents must be used within 1 year of opening unless otherwise stated.

Note 2: To minimise contamination, use auto-dispensers for the stannous chloride and the oxidising agent or only nitric acid to permanently remove the need for pipettes. It is also required that all the glassware used should be retained exclusively for this determination.

Other equipment includes a glass wash bottle (about 500 ml capacity), separating funnels (capacity 250 ml and 500 ml), and a bulb (volume ≥ 1000 ml) with two PTFE-taps. Volumetric flasks may also be required.

## 5. SAMPLING

A wide range of mercury concentrations will be encountered during any sampling exercises involving these types of material. In order to minimise cross-contamination of the samples, and thereby minimise errors, it is important that scrupulously clean sampling equipment and sample containers are used for each individual sample and sample storage.

## 5.1. Metals

All types of metals, (plates, girders or pipework), can be sampled either by cutting, sawing or drilling. Unfortunately all of these procedures generate high levels of heat during the sampling process which, if not controlled, can lead to loss of mercury from the sample due to volatilisation. Consequently, it is recommended that only the initial (large) sampling be carried out in situ or on site and the analytical sampling subsequently performed in the laboratory where the necessary cooling precautions, water cooling, freezing etc., can be taken.

Slow drilling of water-cooled samples is currently the best technique to obtain analytical samples. This operation be carried out very slowly, thereby generating little heat, and the analytical sample produced is in the form of easily dissolvable metal turnings.

If a profile of the mercury contamination through the thickness of the original metal is required, samples of the turnings can be taken at prescribed depths of the metal.

## 5.2. Bricks, Mortar and Concrete

Initial sampling of these types of materials can be performed simply with a hammer and chisel but a more controlled procedure is to use a drill, (preferably water cooled), to obtain core samples. After drying at ambient temperature portions of these samples can then be ground to a coarse powder, again being careful not to generate too much heat during the grinding. The analytical (test) samples can be obtained from these coarse powders by taking appropriately sized portions, usually about 1 g.

## 5.3. Plastic, Rubber & Wood

Initial sampling of these types of material can be carried out either by cutting, (knife, shears etc.) or sawing. Shavings or drillings of these initial samples can be used to obtain appropriate analytical (test) samples; again these operations are best carried out under laboratory conditions.

## 5.4. Grass and vegetation

Care is necessary in sampling vegetation since the mercury content may vary with the rate of growth and different results may be obtained at different times of the year. The water content of vegetation is also high and variable and trace metal analysis is normally carried out on material dried at 80 °C. However, there is evidence that mercury losses may occur at this temperature with some species of plants and it is advisable to analyse the undried specimens and then correct the results to a dry basis after measuring the loss on drying of another sample. The following sampling procedure is recommended: chop up the vegetation into short pieces 1-2 cm long immediately on collection, mix thoroughly and take a representative sample of approximately 200 g; store in a refrigerator in a polythene bag until required for analysis.

## 5.5. Atmospheric dust deposits

Collect deposits by exposing 2 litre narrow-necked bottles with 20 cm diameter funnels in the necks. To avoid losses of mercury during collection, add to each container 200 ml of water containing 20 ml of concentrated nitric acid and 10 ml of an oxidising agent such as potassium permanganate solution (40 g/l). Expose for one month or until the containers are almost full of rain water.

Remark: if potassium permanganate is used, decolourise the sample in the original container by the dropwise addition of hydroxylammonium chloride solution (100 g/l) and allow standing for a short while in order to solubilise manganese oxide.

Filter the contents of the container through a 47 mm cellulose acetate membrane filter, pore diameter 5 µm, into a 2 litre standard flask, dilute to volume with water and mix. Carry out an oxidation of this membrane filter, preferably by Wickbold combustion, but if apparatus for this is not available, by either of the other two methods, and determine the mercury content of the filtrate by the analytical method selected.

## 5.6. Soil and river mud

Soil samples should be taken as small cores 10 cm in diameter and 10 cm deep. Split each one into 3 sections each 3 cm thick and store separately. Mud samples vary widely both in depth and liquidity and it may not be possible to sample in this way. The sampling technique adopted should depend on the circumstances and will vary from coring as above to merely scraping up sufficient mud to provide a sample.

Thoroughly mix each sample and determine the loss on drying at 105 °C. Discard this sample weight and use a second one for mercury analysis. Express the results as mg Hg / kg on a dry basis.

# 6. PREPARATION BEFORE ANALYSIS

## 6.1. Metals

The sample preparation of metal samples will depend on the type of samples available for analysis, (flat pieces, drillings, pipe, etc.), and the information required, (surface or bulk analysis).

Where the sample consists of very small pieces or metal drillings an appropriate weight can be totally dissolved using a suitable oxidising agent with an acid digest.

General details of this type of sample dissolution are described in *Analytical Chimica Acta* 72 (1974), part 1.

When the sample consists of larger pieces of metal or when only surface contamination is required and it is inappropriate to dissolve the whole of the



sample, a regime must be employed which both removes (dissolves) the mercury contamination and also gives some idea of the amount of associated metal, e.g. measurement of the dissolved iron would give some indication of the amount of iron removed during the mercury dissolution. Accordingly, the metal should have several sequential short periods of time immersed in acid and each extract individually measured for both mercury and iron.

## 6.2. Bricks, Mortar & Concrete

A suitable portion of the ground sample is digested in a suitable oxidising agent with an acid digest and an aliquot of this solution used for the measurement of mercury.

## 6.3. Plastic, Rubber & Wood

Samples of material types containing organic matter must be subjected to complete oxidative decomposition in order to enable the total mercury content to be determined. This can be achieved using the techniques described in *Analytical Chimica Acta* 84 (1976), part 2, which include wet oxidation under reflux with nitric and sulphuric acids and digestion with nitric acid in a PTFE lined pressure digestion bomb.

# 7. ANALYSIS

All forms of mercury, including organic compounds, are pre-oxidised to ionic mercury (II).

This can be obtained by boiling the sample for 5 - 10 minutes with one of the oxidising reagents.

After cooling, the excess of oxidant is destroyed with hydroxyl ammonium or ascorbic acid and the mercury reduced to its metallic form by tin (II) chloride.

The mercury is either determined directly or concentrated into a smaller volume and then determined.

Mercury determination is usually performed by CVAAS (Cold Vapour Atomic Absorption Spectroscopy) or CVAFS (Cold Vapour Atomic Fluorescence Spectroscopy).

Detailed information on procedures can be found in EN 1483, EN 13506, ISO 5666, ISO 5993 and ISO 17852 (see detailed references in chapter 8).

### 7.1. *Measuring equipment*

For CVAFS, argon is usually used as carrier gas as it gives a higher sensitivity than nitrogen. The moisture from the gas is removed, usually via a membrane, to avoid condensation on the detector's windows.

The equipment used only measures metallic mercury in the treated sample, and not the mercury compounds.

## **7.2. Calibration**

A full calibration should be performed at a frequency appropriate to the analysis (prior to performing the analysis of a series of samples), prepared as below.

The Linear Correlation Coefficient obtained should be about  $1.00 \pm 0.01$ .

An example is shown below.

### 7.2.1. Calibration standards

- To five 250 ml volumetric flasks, containing approximately 50 ml of water, add 25.0 ml of the oxidising agent using the auto-dispenser, followed by 0 (blank), 5.0, 10.0, 15.0 and 20.0 ml of diluted standard solution (0.1 mg/l Hg) by high precision pipette.
- The flasks are then made up to the mark with deionised water, mixed well and marked (respectively 0, 2, 4, 6 and 8 µg Hg/l).
- Wash out a sample vessel with the standard, then fill it up and place it on the auto-sampler turntable. Repeat for each standard.
- Analyse according to the analysis procedure outlined in the instrument manual.
- A copy of the calibration curve/data must be stored in a records system for future reference.

### 7.2.2. Quality controls checks

It is highly recommended that quality control checks are included in the method of analysis, for example:

- Participation in a round-robin scheme
- Analysis of a sample with a known concentration of mercury (calibration sample) with each batch of analysis
- An instrument drift check
- Repeat analysis of a sample as a precision check
- Analysis of a spiked sample

## **7.3. Procedure**

Set the apparatus according to the equipment supplier's manual and analyse according to the analysis procedure outlined in the instrument manual, taking into account the aliquot of sample taken (normally 5 ml) and the final volume.

For analysers equipped with an autosampler, the instrument must be flushed with 10 % nitric acid blank by running it as a sample, after all analysis operation of the day are complete. This is done to prevent mercury contamination of the system.

The system must then be flushed clear of acid with water by running it as a sample. This is done to prevent excess wear on the tubing.

#### 7.4. Expression of results

- Read the concentration from the display and report the result with the appropriate decimal places, taking into account any dilution.
- The statistical specification data depend on the technology used in the analyser, but the accuracy is usually not better than 2 %.

#### 7.5. Interferences

Some potential interferences are indicated here below (selectivity and specificity), but the specific equipment characteristics have to be checked for possible compensation. Care must be taken for solvents used in painting floors or walls, in silicon sealants ...: they can influence the measure for several days.

Water	To be removed using a membrane
Ethanol	Disturb the measurements based on CVAAS; do not disturb using absorption on gold film
Benzene	
Ammonia	
Cl <sub>2</sub>	Disturbs due to HgCl <sub>2</sub> -formation the measurements based on absorption on gold film
Copper, nickel	Influence lowered when SnCl <sub>2</sub> is used as reducing agent
Iodide	Influence lowered when diluted NaBH <sub>4</sub> is used as reducing agent

## 8. REFERENCES

- **Env Prot 03 - Decommissioning of Mercury Chlor Alkali Plants**
- EN 1483: Water Quality – Determination of Mercury – Method using atomic absorption spectrometry.
- EN 13506: “Water Quality. Determination of mercury by atomic fluorescence spectrometry.”
- ISO 5666: Water Quality – Determination of total mercury by flameless atomic absorption spectrometry. Part 2: Method after pre-treatment with ultraviolet radiation.
- ISO 5993: “Sodium Hydroxide for Industrial Use; Determination of mercury content; Flameless atomic absorption spectrometric method.”
- ISO 17852: Water Quality – Determination of mercury – Method using atomic fluorescence spectrometry.
- Analytica Chimica Acta, 84, (1976), pp. 231-257 “Part 2 : Determination of Total Mercury in Materials Containing Organic Matter”

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Details of membership categories and fees are available from:

Euro Chlor  
Avenue E Van Nieuwenhuyse 4  
Box 2  
B-1160 Brussels  
Belgium

Tel: +32 2 676 7211  
Fax: +32 2 676 7241  
e-mail: [eurochlor@cefic.be](mailto:eurochlor@cefic.be)  
Internet: <http://www.eurochlor.org>