



Determination of Mercury in Liquids

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Euro Chlor

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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 from ex-ANAL 03-07 with simplification to refer to existing standardised method

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1. INTRODUCTION

Within the framework of all the technical and organisational prevention measures taken in the chlor-alkali industry to further reduce the mercury emissions (see **Env. Prot. 11- Code of Practice - Mercury Housekeeping**), it is necessary to define and implement a good monitoring programme to determine the mercury concentration in liquids.

This recommendation describes the methods developed for this monitoring, including precautions to be taken during sampling.

2. SCOPE

The methods given are applicable for water, waste water, brine, brine purification mud, sodium hydroxide solutions and sodium hypochlorite.

The objective is to determine concentrations down to 0.1 µg Hg per kg or litre, depending on the analytical technique used and the sample matrix.

CVAAS (Cold Vapour Atomic Absorption Spectroscopy): 3 - 200 ng of total mercury in a maximum of 50 ml of (waste) water solution, a maximum of 50 ml of brine at ≤ 300 g NaCl/l, 1 g of NaOH 50 % or 10 g of bleaching liquor at 160 g active chlorine per litre.

CVAFS (Cold Vapour Atomic Fluorescence Spectroscopy): 7 – 100 ng of total mercury in a maximum of 50 ml of (waste) water solution, a maximum of 50 ml of brine at ≤ 300 g NaCl/l, 1 g of NaOH 50 % or 10 g of bleaching liquor at 160 g active chlorine per litre.

The quantification limits that can be obtained with the above sample sizes are stated in the next table as an example.

	CVAFS	CVAAS
(Waste) water	0.2 µg Hg/l	0.1 µg Hg/l
Brine, ≤ 300 g NaCl/l	0.2 µg Hg/kg	0.1 µg Hg/kg
Bleaching liquor, 160 g act. Cl ₂ /l	3.5 µg Hg/kg	1.5 µg Hg/kg
NaOH-solutions 50 %	6 µg Hg/kg	3 µg Hg/kg
Brine mud	7 µg Hg/kg	3 µg Hg/kg

These limits also depend, amongst other things, on the level of the instrument noise and the amount of mercury in the reagent blank, and should be locally determined.

3. PRINCIPLES

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

This can be achieved 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 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 references in chapter 7).

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:

- Aqua regia (HCl/HNO₃)
- Oxidising agent (nitric acid / sodium chlorate and hydrochloric acid, potassium dichromate, potassium permanganate, etc)
- Sulphuric acid
- Phenolphthalein indicator
- 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 nitric acid to permanently remove the need for pipettes. It is also essential that all the glassware used should be retained exclusively for this determination in order to minimise the risk of cross-contamination.

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 can also be used.

5. SAMPLING AND PREPARATION BEFORE ANALYSIS

If total mercury has to be determined, cover the beaker with a watch glass and place on a hotplate at a tested temperature and duration to ensure all mercury is transformed to the ionic form

5.1 Water and Waste Samples

There are a number of published protocols for determining mercury in water and it is recommended that one of these is followed. These include EN 1483, EN 13506 and ISO 17852 (see detailed references in Chapter 7).

The principles of these methods involve oxidising any mercury present to ensure that all the mercury is present as soluble mercury (II) ions. The mercury ions are then reduced to elemental mercury by the addition of one of the reducing agents given in the Reagent list above, before being analysed by CVAAS or CVAFS.

It is recommended that where samples cannot be analysed immediately, their integrity is preserved by the addition of 10 ml of concentrated nitric acid and 5 ml of potassium permanganate or dichromate solution.

5.2 Brine Samples

If the brine samples cannot be analysed straight away, immediately after sampling add 10 ml of concentrated nitric acid and 5 ml of potassium permanganate or dichromate solution (40 g/l) for each litre of sample for preservation.

The size of sample to be taken for the analysis depends on the expected mercury concentration) and on the analytical technique used, but for an expected concentration of up to 15 µg/l the following method is proposed.

Into a 250 ml beaker, add 50 ml of sample by pipette, followed by approximately 10 ml of deionised water. Add 2 ml of potassium permanganate solution and then add carefully, by autopipette, 5 ml of the 10% w/v sulphuric acid solution. Add, by dispenser, 2 ml of hydroxylamine hydrochloride solution. Transfer the solution to a 100 ml volumetric flask and make up to the mark with deionised water and mix well.

Finally, analyse the sample by CVAAS or CVAFS.

5.3 Sodium Hydroxide Solutions

Collect the sample in a polyethylene bottle containing a suitable amount of the oxidising agent (e.g. solid potassium permanganate to give a final concentration of 0.5 g KMnO_4 /100 g of sample). Shake vigorously to dissolve, then mix the sample and oxidising agent well, and allow to stand for at least 30 min before removing an aliquot for analysis.

Transfer the required aliquot of sample to a 100 ml beaker - the size of the aliquot to be taken for the analysis depends on the expected mercury concentration and on the analytical technique used. Where necessary, the sample can be diluted

with deionised water to bring it into the calibration range of the method being used.

Then, add carefully, by dispenser, 10 ml of 50% sulphuric acid (w/v) solution or a suitably tested alternative to acidify the solution.. Cool and add, by dispenser, the reducing agent (e.g. 2 ml of hydroxylamine hydrochloride solution). Transfer the solution to a 100 ml stoppered measuring cylinder, make up to the mark with deionised water and mix well. Then analyse by CVAAS or CVAFS.

Alternatively, there is a published method for the analysis of mercury in sodium hydroxide by flameless atomic absorption spectroscopy (ISO 5993).

5.4 Sodium Hypochlorite

Weigh 10 g of sodium hypochlorite into a 250 ml beaker and dilute to 50 ml with deionised water. Add carefully 20 ml of 50% sulphuric acid, cover the beaker with a watch glass and boil on a hotplate in a fume cupboard to remove most of the chlorine. (The solution changes from yellow/green to colourless).

After cooling, add the oxidizing agent (e.g. 5 ml of 5% potassium permanganate solution), and heat the solution at 80°C for approximately 60 minutes in order to remove any residual chlorine and complete the oxidation process. Chlorine will interfere with analysis by CVAFS, hence it is important to remove it all.

After cooling, add a suitable amount of the reducing agent (e.g. 2 ml of hydroxylamine hydrochloride solution) and transfer to a 100 ml standard flask. Make up to the mark with deionised water and analyse by CVAAS or CVAFS.

5.5 Brine Purification Mud

Weigh 5 g of mud into a 250 ml beaker. Add 20 ml of "aqua regia" (mixture of 1 part concentrated hydrochloric acid with 3 parts concentrated nitric acid). Cover the beaker with a watch glass, heat to boiling, boil for a few seconds and cool. Dilute to a suitable volume with water depending on the expected mercury concentration. Into an aeration flask, pipette a 25 ml aliquot of the clear liquid. Add 1 ml of 20% sulphuric acid, followed by a suitable amount of oxidising agent (for example 1 ml of potassium permanganate solution at 40 g/l).

After cooling, add a suitable amount of the reducing agent (e.g. 2 ml of hydroxylamine hydrochloride solution) and transfer to a 100 ml standard flask. Make up to the mark with deionised water and analyse by CVAAS or CVAFS.

6. ANALYSIS

The principles of these methods involve oxidising any mercury present to ensure that all the mercury is present as soluble mercury (II) ions. The mercury ions are then reduced to elemental mercury by the addition of one of the reducing agents given in the reagent list above, before being analysed by CVAAS or CVAFS. In some equipment, this reduction is performed automatically by the apparatus (injection of stannous chloride or sodium borohydride).

If manual reduction is necessary, the reducing agent is introduced into the aeration cylinder directly before the analysis.

6.1 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.

6.2 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 ± 0.01 .

An example is shown below.

6.2.1 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 (0.1mg/l Hg) by high precision pipette.
- The flasks are then made up to the mark with deionised water and mixed well. The flasks should be labelled 0 (blank), 2, 4, 6 and 8 μg Hg/l respectively.
- 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 must be stored in a records system for future reference.

6.2.2 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

6.3 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 autosamplers, the instrument must be flushed with 10 % nitric acid blank by running it as a sample, after all analysis for the day is 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.

6.4 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%.

6.5 Interferences

For CVAFS, possible interferents include oxidising gases, such as chlorine.

7. REFERENCES

- ***Env. Prot. 11 – Code of Practice - Mercury Housekeeping***
- 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.

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