



Determination of Mercury in Liquids

Analytical 7

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Euro Chlor

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Euro Chlor is working to:

- improve awareness and understanding of the contribution that chlorine chemistry has made to the thousands of products, which have improved our health, nutrition, standard of living and quality of life;
- 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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Prior to 1990, Euro Chlor's technical activities took place under the name BITC (Bureau International Technique du Chlore). References to BITC documents may be assumed to be to Euro Chlor documents.

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*.

The voluntary recommendations, techniques and standards presented in these documents are based on the experiences and best practices adopted by member companies of Euro Chlor at their date of issue. They can be taken into account in full or partly, whenever companies decide it individually, the operation of existing processes and in the design of new installations. They are in no way intended as a substitute for the relevant national or international regulations which should be fully complied with.

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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 |

TABLE OF CONTENTS

| | |
|----------------------------------------------------|-----------|
| 1. INTRODUCTION | 5 |
| 2. SCOPE | 5 |
| 3. PRINCIPLES | 6 |
| 4. REAGENTS | 6 |
| 5. SAMPLING AND PREPARATION BEFORE ANALYSIS | 7 |
| 5.1 Water and Waste Samples | 7 |
| 5.2 Brine Samples | 7 |
| 5.3 Sodium Hydroxide Solutions | 7 |
| 5.4 Sodium Hypochlorite | 8 |
| 5.5 Brine Purification Mud | 8 |
| 6. ANALYSIS | 8 |
| 6.1 Measuring equipment | 9 |
| 6.2 Calibration | 9 |
| 6.2.1 Calibration standards | 9 |
| 6.2.2 Quality controls checks | 9 |
| 6.3 Procedure | 10 |
| 6.4 Expression of results | 10 |
| 6.5 Interferences | 10 |
| 7. REFERENCES | 10 |

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.

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