



Determination of Mercury in Gasses

Analytical 6

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EURO CHLOR PUBLICATION

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

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, in 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 and update (from ANAL 03-07)

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1. INTRODUCTION

In the frame 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**) and protect the health of the workers (see **HEALTH 2 - Code of Practice: Control of Worker Exposure to Mercury in the Chlor-Alkali Industry**), it is necessary to define and organise a good monitoring programme of the mercury concentration in the air.

This recommendation describes the methods developed for this monitoring, starting from the precautions to be taken for the sampling. Mercury analysis in gaseous chlorine is treated in a separate document (**Analytical 5 – Determination of Mercury in Chlorine**).

2. SCOPE

The objective is to determine concentrations ranging between 0.1 and 10 000 ng Hg per m³ of gas, depending on the instrument used.

The method is applicable for air (in cell room or ducts/chimneys or personal monitoring), hydrogen ...

It must be reminded that in the case of hydrogen (or other possible explosive mixture), intrinsically safe equipment are required.

3. PRINCIPLES

All forms of mercury, including organic compounds, are pre-oxidised to ionic mercury. If necessary, the final and complete oxidation can be achieved by adding potassium persulphate and heating to about 100°C for 2 h. 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/HNO₃)

- Oxidising agent (nitric acid / sodium chlorate and hydrochloric acid, potassium dichromate, potassium permanganate, 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 can also be used.

5. SAMPLING

There are basically four sampling and preparation methods (see also **EN17733**):

- a) Washing the air sample with acidified potassium permanganate (KMnO_4) solution (BITC Standardisation of Methods for the Determination of Traces of Mercury-Part 1 Determination of total inorganic mercury in inorganic samples, Anal. Chim. Acta **72** (1974), 37-38).
- b) Adsorption of mercury on cellulose powder and activated charcoal; the contents of the sampler are burnt in an oxy-hydrogen flame (W. Dürr, K. Hausmann, Determination of Mercury and Mercury Compounds in Air and other Non-Corrosive Gases, Z. Anal. Chem. **283**, (1977), 337-341)
- c) Adsorption of mercury on hopcalite (mixture of manganese and copper oxides); the sample is then oxidised by dissolution in aqua regia (BITC, Standardisation of methods for the Determination of Traces of Mercury-Part 4. Determination of Total Mercury in Gasses by AAS, Anal. Chim. Acta, **108**, (1979), 1-11)
- d) Adsorption of metallic mercury on gold wool; after sampling the adsorption tube is heated and the mercury is transported by a nitrogen-stream into an acidified KMnO_4 solution for oxidation/dissolution (P. Schierling, K.H. Schaller, Atomic Spectroscopy, Vol 2, (1981), 91 ff.)

Methods b) and c) have been developed to provide more comprehensive analysis than method a) by measuring not only mercury vapour but also mercury aerosols.

6. PREPARATION BEFORE ANALYSIS

6.1. Liquid sample

This preparation procedure applies after sampling methods a), c), and d).

The size of the aliquot to be taken for the analysis depends on the expected mercury concentration and on the analytical technique used.

Weigh a quantity of sample between 0.5 and 5 g into a 100 ml beaker. Add distilled water to a volume of 40 ml. Cover the beaker with a watch glass, boil for a few seconds if necessary, and cool. Decolourize the solution by the dropwise addition of hydroxylammonium chloride solution. If necessary, transfer the solution to an aeration flask or cylinder, bring to volume and measure the mercury content.

6.2. Gaseous sample

After the sampling method b), the adsorption material is burnt in a Wickbold apparatus. Hg is analysed in the absorption liquid of the Wickbold apparatus (see 6.1. here above).

7. ANALYSIS

The analysis is performed after mercury reduction into metallic form.

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.

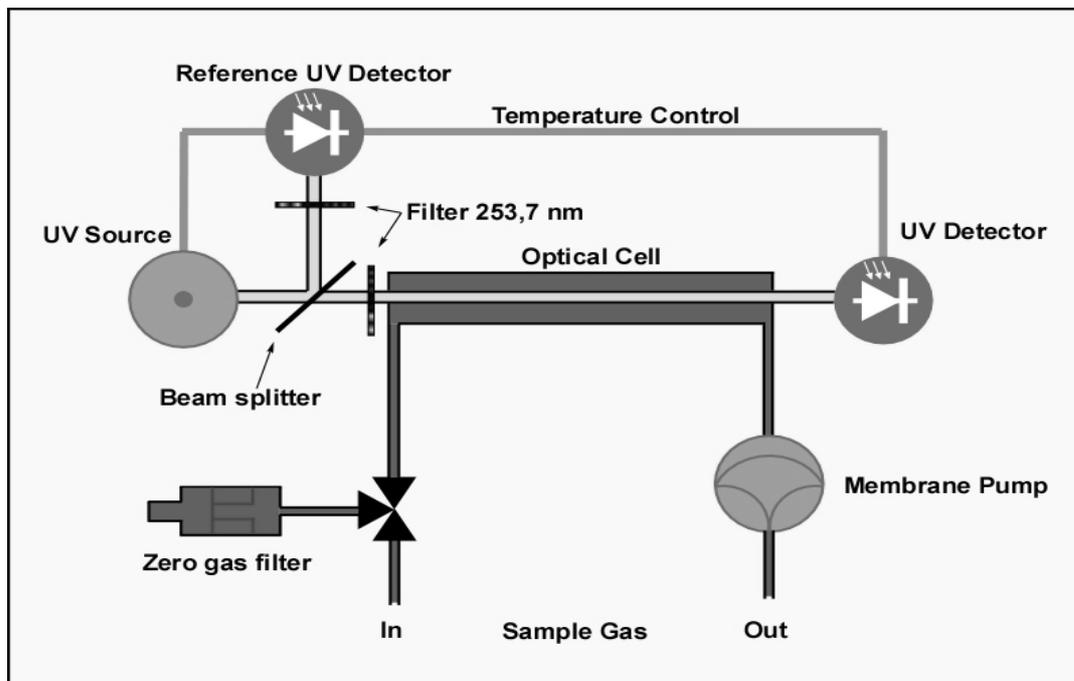
7.1. Measuring equipment

Detection of mercury vapour is performed with FAAS (Flameless Atomic Absorption Spectrophotometry), CVAAS (Cold Vapour Atomic Absorption Spectroscopy) or CVAFS (Cold Vapour Atomic Fluorescence Spectroscopy).

The equipment used only measures metallic mercury and not the mercury compounds (usually present in very small quantities).

For very low values, it is possible to pre-concentrate the mercury by absorption on a gold film.

In general a Mercury Vapour Detector is based upon the CVAAS technique given in the next Figure (schematic diagram of a quasi dual beam configuration):



The sample gas is (after removal of water vapour using a membrane) led through an optical cell. A mercury vapour discharge lamp is mounted on one side of the cell, the detector on the other side. The light source produces UV-light which passes through a band pass filter and/or a beam splitter. In this way only the spectral line of 253.7 nm, which is specific for mercury, passes through the cell where it is partially absorbed by the mercury atoms in the sample gas. Most instruments use a dual beam (2 cuvettes & 2 detectors) or a quasi dual beam (beam splitter, 2 filters, 1 cuvette and 2 detectors) to provide better long term stability.

7.2. Calibration

A full calibration is 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.

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 (0.1mg/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 $\mu\text{g Hg/l}$).
- 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 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**

The 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 from painting the cell room floor, 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 ₂	Disturbs due to HgCl ₂ -formation the measurements based on absorption on gold film

8. PORTABLE MERCURY ANALYSER

For portable instruments, the sampling recommendation included in the supplier's documentation shall be followed.

Adsorption of mercury on a gold film is quite cheap, but the mercury concentration is dependent on the changes in the electrical properties of the gold film that need to be systematically regenerated.

Calibration and verification can be done with a commercially available mercury vapour calibrator, e.g. EPM model 793-005 or similar. Even after periodic calibration by the supplier, the linearity in the range of practical interest must be checked before being returned to use. A periodic check should also be done at the concentration corresponding to the middle of the required range to check that the instrument has not drifted (if yes, recalibration is needed).

9. MERCURY ANALYSIS IN DUCTS AND CHIMNEYS

Euro Chlor recommends the use of published European Standards for the determination of total mercury in exhaust gases from ducts or chimneys.

For sampling duct or chimney emissions, it is recommended that procedure **EN 13211 "Air Quality – Stationary Source Emissions – Manual Method of Determination of the Concentration of Total Mercury"** is followed. This document describes the procedure for determining mercury in dust and droplet form, as well as the gaseous phase by isokinetic sampling. In situations where there are no droplets or dust particles present, the document describes the procedure for determining gaseous phase mercury by non-isokinetic sampling.

However, as most isokinetic sampling equipment is not intrinsically safe, the non-isokinetic method will have to be used in areas where there are likely to be flammable gases (hydrogen for example), irrespective of the presence of dust particles or droplets. In this case, the measurement uncertainty is likely to be higher and validation of the technique must be carried out by each company.

It must be reminded that intrinsically safe equipment is required for explosive gasses or mixture (hydrogen...).

Procedure **EN 13211** recommends the use of **EN 1483 "Water Quality – Determination of Mercury"** to analyse the samples collected above. This procedure details analysis using an atomic absorption spectrometer or a radiation source (hollow cathode or electrodeless discharge lamp). However, it is also possible to analyse the samples by atomic fluorescence spectrometer.

10. INDIVIDUAL WORKERS MONITORING

For individual monitoring, Euro Chlor recommends to use the standard **EN 17733** (Workplace air - Determination of mercury and inorganic mercury compounds - Method by cold-vapour atomic absorption spectrometry or atomic fluorescence spectrometry).

11. REFERENCES

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

HEALTH 2 – Code of Practice: Control of Worker Exposure to Mercury in the Chlor-Alkali Industry

Analytical 5 – Determination of Mercury in Chlorine

EN 1483 – Water Quality – Determination of Mercury

EN 13211 – Air Quality – Stationary Source Emissions – Manual Method of Determination of the Concentration of Total Mercury

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

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