



Determination of Mercury in Gasses

Analytical 6

3rd Edition

June 2008

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

Euro Chlor is the European federation which represents the producers of chlorine and its primary derivatives.

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*).

This document has been produced by the members of Euro Chlor and should not be reproduced in whole or in part without the authorisation of Euro Chlor.

This reference manual is intended to give only guidelines and recommendations. The information is provided in good faith and has been based on the best information currently available. The information is to be relied upon at the user's own risk. Euro Chlor and its members make no guarantee and assume no liability whatsoever for the use and the interpretation of or the reliance on any of the information in this document.

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.

It has been assumed in the preparation of these publications that the users will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance they have been prepared. The contents are based on the most authoritative information available at the time of writing and on good engineering, medical or technical practice but it is essential to take account of appropriate subsequent developments or legislation. As a result, the text may be modified in the future to incorporate evolution of these and other factors.

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) |

TABLE OF CONTENTS

| | |
|--|-----------|
| 1. INTRODUCTION | 5 |
| 2. SCOPE | 5 |
| 3. PRINCIPLES | 5 |
| 4. REAGENTS | 5 |
| 5. SAMPLING | 6 |
| 6. PREPARATION BEFORE ANALYSIS | 6 |
| 6.1. Liquid sample | 6 |
| 6.2. Gaseous sample | 7 |
| 7. ANALYSIS | 7 |
| 7.1. Measuring equipment | 7 |
| 7.2. Calibration | 8 |
| 7.2.1. Calibration standards | 8 |
| 7.2.2. Quality controls checks | 9 |
| 7.3. Procedure | 9 |
| 7.4. Expression of results | 9 |
| 7.5. Interferences | 9 |
| 8. PORTABLE MERCURY ANALYSER | 10 |
| 9. MERCURY ANALYSIS IN DUCTS AND CHIMNEYS | 10 |
| 10. INDIVIDUAL WORKERS MONITORING | 10 |
| 11. REFERENCES | 11 |

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.

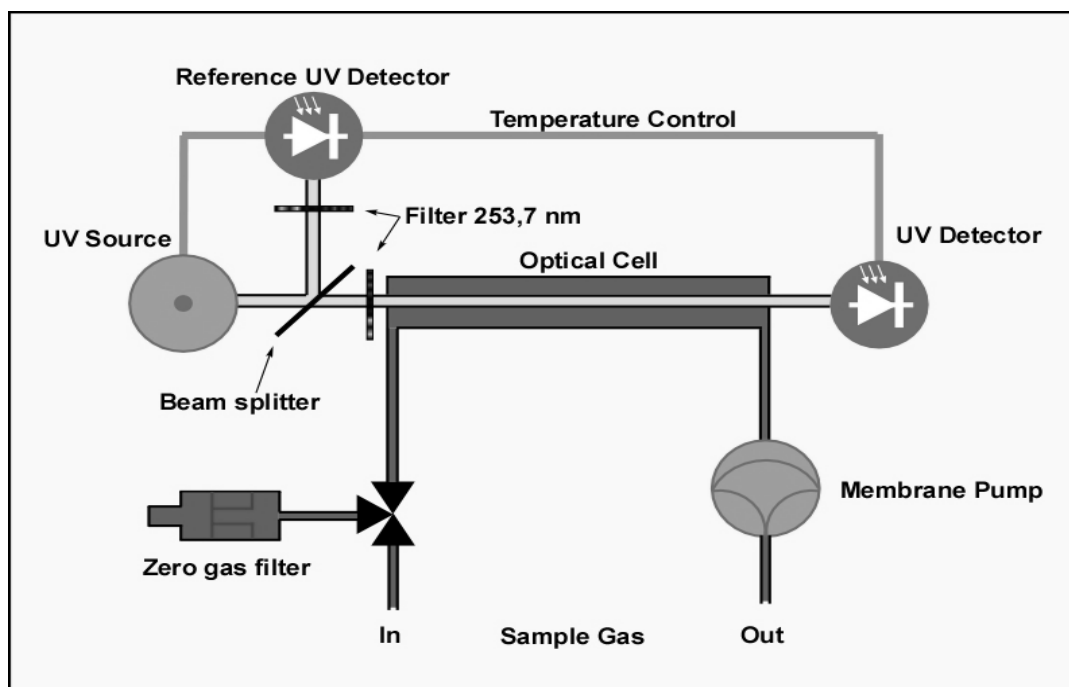
7.1. Measuring equipment

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

预览已结束，完整报告链接和二维码如下：

https://www.yunbaogao.cn/report/index/report?reportId=5_14053

