DETERMINATION OF THE TOTAL WEIGHT OF MERCURY IN THE ELECTROLYSIS CELLS BY RADIOISOTOPES

ANALYTICAL 10

2nd Edition

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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

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).*

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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.

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 Environmental 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	Curie and Rem (old units) are maintained with Becquerel and Sievert
3	Use of specific PE bottles of the same production charge is recommended.
9	Washing of samples is recommended
Appendix 4 section 2	"The preparation of the active sticksolution and the bottling of the doping samples has to be achieved in a laboratory fume hood" is added

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PREFACE

The mercury loss in a chlorine production plant working with mercury cells is to be determined by regular, in general annual, inventories of the total amount of mercury in the plant. As the consumption, which is relatively low in proportion to the total amount, is determined by the difference of two large numbers, viz. the two successive mercury inventories, they must be performed very accurately.

Instead of weighing the mercury, which was the only possibility in the past, the radioactive dilution method has now become an attractive procedure. It has two major benefits in that it requires considerably less working time and does not need the electrolysis to be interrupted. If possible, the measurement should be achieved after having a washing of cells and recovered mercury. Technical difficulties have to be considered however, as the operation of an electrolysis plant is not an ideal system for the application of this analytical method.

The dilution method is a simple means of determining the amount of liquid in a container. A small amount of a concentrated solution of a compound, not already present in the liquid, is added and, after thoroughly mixing, the final concentration of the added substance determined. The amount of liquid in the container can be calculated from the initial and final concentrations of the added compound.

The use of a radioactive tracer replaces the concentration determinations by activity measurements which are independent of the chemical quality of the liquid under test.

Radioactive mercury is the most suitable tracer to determine the amount of mercury present in electrolysis cells by the dilution method. The necessary mixing of the radioactive labelled mercury with the cell mercury is achieved by the continuous circulation of the mercury in the cell-decomposer assembly.

For the correct application of this method attention must be paid to a number of features, such as: chemical purity of the stable mercury to be irradiated, counting conditions and phial geometry, the method for dosing and sampling the cells, the choice of the mixing time, etc.

These different points are detailed in the procedure described hereafter.

1 CHOICE OF ISOTOPE

Hg 197 ($T_{1/2}$ = 65 hours) and Hg 203 ($T_{1/2}$ = 47 days) can be used but the choice is dependent upon the time required for complete mixing of the radioactive mercury with the mercury in the electrolysis cell (including thick mercury). If the mixing time is of the order of one week, Hg 203 must be used. When using Hg 197, correction factors for the decay rate must be applied. In addition, because of the short half life all the operations have to be carried out quickly and it requires the counting equipment to be installed near the electrolysis plant.

2 IRRADIATION OF MERCURY

Pure analytical grade mercury or mercuric oxide (spec. pure) is used for irradiation to minimise unwanted radioisotopes. Mercury or mercuric oxide is placed in a quartz ampoule of high purity and irradiated in an atomic pile. The total activity required is calculated on a basis of minimum 740 MBq/ton (20 mCi/ton) of cell mercury for Hg 197 and of 25 to 50 MBq/ton (0.67 – 1.35 mCi/ton) of cell mercury for Hg 203. When using Hg 203 the irradiated sample should be put aside for 2-3 weeks to allow short-lived mercury isotopes to decay.

When using HgO, the quartz ampoule is crushed after irradiation and the HgO dissolved in conc. HNO_3. The Hg^{++} is reduced to metallic mercury by adding zinc powder and formic acid. Excess zinc is dissolved with HCl.

A γ-spectrum is carried out on the radioactive mercury prior to the preparation for cell dosing to check that it is not contaminated with radioactive impurities.

3 CHOICE OF COUNTING PHIALS

Use only phials which give the same response on the counting equipment. To check for symmetry fill the counting phials with radioactive mercury whose activity is a few times higher than that of the cell mercury samples. Adjust the mercury level or its weight in each phial, remove air bubbles by tipping them several times and measure the activity as described in Section 10. Retain the phials which give counts within $\pm$ 0.2% (2 σ) and discard the others. Use of specific PE bottles of the same production charge is recommended.

4 PREPARATION OF RADIOACTIVE MERCURY FOR CELL DOSING

Place very clean, dry, low activity mercury in a suitable container (decantation and filtration on cotton-wool is normally sufficient to obtain satisfactory mercury) and carefully add the radioactive mercury.

Mix thoroughly using a slowly rotating stirrer or a rolling mixer. This mixture is

called the stock mercury. Transfer known quantities (by weight or volume) of this stock mercury to clean containers for individual cell doping. The aliquots are called doses. Weigh the doses to an accuracy of 0.05 % using 100 g as a minimum dose size. Take at least three samples at regular intervals during the dispensing, to check for complete mixing and to prepare standards for counting purposes.

5 CHECK OF COMPLETE MIXING AND PREPARATION OF STANDARDS AND MERCURY BACKGROUND SAMPLES

Mix thoroughly a part of each of the above at least three samples, called the standards, with the quantity of clean, dry, non radioactive mercury to give an activity similar to that expected when the doses are diluted within the cell. Carry out the weighing to 0.005 % . Measure their γ-radiation on a scintillation counter. The counts of each of the standards must be within $\pm$ 0.2 % (2σ) to make sure that the stock mercury is homogeneous.

Take samples from the stock of non radioactive mercury used to prepare the standards which will be called mercury background samples and use them to take into account extra pulses arising from the radioactivity of surroundings, electronics noise, etc.

6 DOSING THE CELLS

When using Hg 197, after one year no residual detectable activity remains even from the small amount of Hg 203 impurity. Therefore there is no need to take samples, called cell background samples, from the cells prior to dosing.

When using either isotope, take cell background samples from all the cells if the time between two inventories is less than 12 months.

In the case of Hg 203 labelling, if an inventory is made every 18 months or more, no sampling is necessary.

Nevertheless, it must be kept in mind that contamination of the cells may occur, e.g. by using contaminated mercury bought from an electrolysis plant or a mud distillation plant. It is therefore of good practice to keep a sample of external plant mercury and to check its radioactivity.

Carefully add the doses to the cells, ensuring that they mix with the moving bed of mercury (avoid splashing). This addition may be instantaneous or spread over a period of time.

Make sure that the radioactivity is transferred quantitatively into the cell:

- by measuring the residual activity, or
- by rinsing the container either with water or mercury (specially for polyethylene containers), or

- by weighing.

The method must be checked in advance for efficiency.

In any case, do not use the empty dose containers to sample the cells.
During the mixing period the addition and removal of mercury from the cells should be avoided. If, exceptionally, mercury has to be added or removed, the quantities must be measured and recorded.

Transfer of mercury from one cell to another is not permitted before the cells have been sampled.

7 DETERMINATION OF MINIMUM MIXING TIME

Determine the minimum time (t_o) for complete mixing of the cell mercury and the radioactive dose by taking samples from the decomposer at regular intervals (hours or days). Measure the γ-radiation of the samples on a scintillation counter, plot net counts (corrected for decay) against time.

The following figure shows an example of such a graph which reaches a plateau when the number of counts is minimum (n_m). This indicates that homogeneity is reached.

For a given cell, the minimum mixing time t_o is given by the intersection of the plot with a horizontal line corresponding to ($n_m + 0.4 \times 10^{-2} n_m$) as shown in the figure. The value ($n_m + 0.4 \times 10^{-2} n_m$) takes into account the repeatability $\pm$ 0.4 % (2σ) of a routine counting of a sample. This work has to be carried out only once for each type of cell by checking 5 % of the total number of cells installed in every cell room.

For each given type of cell the mixing time T_o to be chosen is the highest t_o value found
The determination of T_o has to be repeated if major changes of the mercury inventory, cell construction, etc., have been made.