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

ANALYTICAL 10

2nd Edition

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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

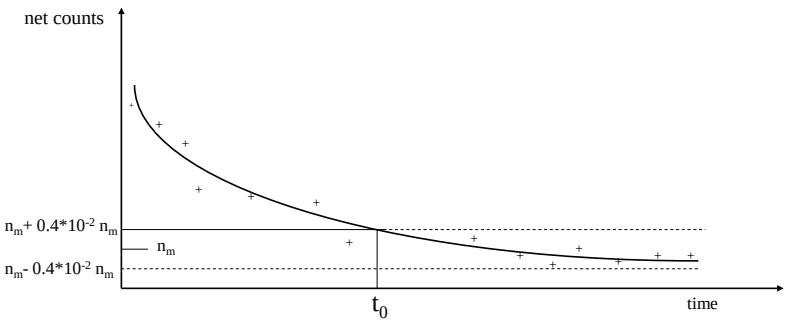
Determine the minimum time (t_o) for complete mixing of the cell mercury and the radioactive dose by taking samples from the decomposer at regular intervals (hours or days). Measure the γ-radiation of the samples on a scintillation counter, plot net counts (corrected for decay) against time.

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.

Figure 1



8 SAMPLING OF THE CELLS

Use clean containers for sampling.

Take the cell mercury samples after a time 1.25 T_o but at any rate after at least one day. A second sample may be taken after minimum 1.5 T_o , to confirm (within $\pm$ 0.4 %) the activity of the first sample.

This ensures that complete mixing is reached for each cell and that no sampling error has occurred.

9 PREPARATION OF SAMPLES FOR COUNTING

It is recommended to wash the samples in a separating funnel with HCl (2N) to remove sodium. Transfer the washed mercury into the phials in the same way as described in section 3.

Washing may be avoided if the activity measurements are not influenced by the density changes resulting from the amalgam present, that is when the sample has the saturation thickness towards the γ-rays emission.

10 MEASUREMENT OF ACTIVITY

Set up the counting equipment, e.g. scintillation counter with a sodium iodide crystal, as described in the manufacturers operating manual. Carry out a pulse height spectrum at the start of the counting series and maintain a suitable window, e.g. from 20 to 120 keV for Hg 197 and from 220 to 320 keV for Hg 203 (see Appendix Nr 1). Choose the counting time so that the cell mercury samples give a count of about 100,000 (2σ = 0.6 %) above the cell background samples. (With a count of 150,000, 2σ = 0.5 %).
(Note: when the individual cell mercury weight needs to be known with a better precision, the total counting time may be increased).

Use the same counting time to measure the activity of the cell mercury samples, the cell background samples, the mercury background samples and the standards.

To simplify calculations, standards are measured every two hours. The Hg 203 decay may then be ignored and the mean arithmetic value of the two standards enclosing cell mercury samples may be used to calculate the cell content.

In case the counts of the standards and the cell mercury samples are very different, correct them for dead-time losses.

Check the counts of standards and mercury background samples regularly over the whole counting period to ensure that the counting device remains in good working order.

Calculate the original amount of Hg, Q (kg) in each cell, by the following formula:

$$Q = (\frac{P}{r} X \frac{n_t}{n_c}) - P$$

in which :

P, kg,	is	the weight of radioactive mercury introduced into the cell
r,		the common rate of dilution of the standards (of the order of $10^{-4} – 10^{-3}$)
n_c, cps,		the net activity of the cell mercury sample
n_t, cps ,		the arithmetic mean of the net activity of the standards.

11 LIST OF ANNEXES

Appendix 1: Choice of a narrow window instead of using total counts conditions for the activity measurements comments the choice of a narrow window for the activity measurements

Appendix 2: Complete formula giving the amount Q when withdrawal and addition of mercury have occurred gives a complete formula for Q taking into account withdrawal and addition of mercury during the mixing period.

Appendix 3: Accuracy of the method analyses the accuracy of the method and Appendix 4: Handling of radioactive mercury details the material and the manipulations for a safe handling of radioactive mercury.

Appendix 5: Regulations to be followed by the factories gives the regulations to be followed by the factories for a correct application of the method.

Appendix 6: gives the list of the members of the Mercury Inventory Subcommittee.

1. Appendix 1: Choice of a Narrow Window

instead of using total counts conditions for the activity measurements

In the case of Hg 203 activity measurements, the total counting given by a very wide window of 10 to 4500 keV is only 30 % higher than that obtained with a narrow window of e.g. 220 to 320 keV.

As there is no significant difference in the standard deviation of the two countings, a narrow window is to be preferred so as to diminish background counts and to minimise any interference from possible radioactive impurities.

However, the choice of a narrow window requires counting equipment with low drift.

2. Appendix 2: Amount of Mercury to be Added

The objective of this appendix id to give the complete formula for the amount Q when withdrawal and addition of mercury have occurred: in the case of long mixing times it sometimes occurs that withdrawal of thick mercury followed by addition of natural mercury has to be done during the mixing period.

Then, Q, at the time of dosing, is given by the following formula :

$$Q = \frac{G - M + A + \sqrt{(G - M + A)^2 - 4\ AG}}{2} - P$$

In which: $A = \frac{p}{r} x \frac{n_t}{n_c}$ (see Section 10)

G, kg, the weight of thick mercury withdrawn from the cell
M, kg, the weight of mercury added.

This formula may be applied only when a total weight of G kg thick mercury has been withdrawn from the cell before being replaced by M kg of fresh mercury.

After this correction, only withdrawals of thick mercury are allowed.

3. Appendix 3: Accuracy of the Method

1) Random errors cause positive and negative deviations from a true value m in a statistical manner resulting in a "normal distribution" with a mean value $\bar{m}$ and a standard deviation σ. The interval $m \pm \sigma$ involves 68.3 % and the interval $m \pm 2\sigma$, 95.5 % of the obtained values. The relative standard deviation of a product or quotient is equal to the Pythagorean sum of the single relative standard deviations.

   Consequently, the standard deviation σ_{QC} of the amount of mercury in the cell $Q_c = (P x n_t / r x n_c) - P$ becomes (neglecting the error in the subtractive term P):

$$\sigma_{Q_c} = \left[\sigma_r^2 + \sigma_p^2 + \sigma_{n_t}^2 + \sigma_{n_c}^2\right]^{1/2}$$

   For a dilution rate r obtained by double dilution, calculation shows σ_r is $\pm$ 0.02 % for an individual weighing error of $\pm$ 0.005 %.

   The following table gives the amounts of the single relative standard deviations.

σ_i	Origin of Error	Symbol
$\sigma_r = \pm\ 0.02\%$	dilution rate of standards	r
$\sigma_P = \pm\ 0.05\%$	weight of dosing	P
$\sigma_{n_t} = \pm\ 0.1\%$	counting of standard (statistical error, geometry of phials and homogeneity of the stock solution)	n_t
$\sigma_{n_c} = \pm\ 0.3\%$	counting of cell sample (statistical error and geometry of phials)	n_c

   The standard deviation of Qc becomes by applying the given formula to the above listed
   single standard deviations

$$\sigma_{Q_c} = \pm 0.32\%$$

   The standard deviation of the total amount of mercury in n cells becomes

$$\sigma_Q = \pm 0.32\% / \sqrt{n}$$

   Note that the latter formula is only reliable if the mercury content of all the cells in the cell-room follows a Gaussian distribution.

2) Systematic errors cause either positive or negative deviations from the true value by a systematic failure of the method or the quality of the cell and the mixing process. They are expressed as relative errors in Q_c, in the concerned order of magnitude, to be added algebrically.

The following table lists up the systematic errors.

Systematic error in Q_c sign and max. estimated amount	**Origin of error**	**Symbol of affected value**	**Effect on**
+ or – 0.005 %	dilution factor	r	all cells
+ 0.1 %	active impurities in dose mercury removed by electrolysis or sole extraction	n_c	all cells
+ 0.1 %	tracer loss on dosing	n_c	single cell
- 1 %	uncomplete mixing, resp. dead corners, kept below 1% by mixing time control	n_c	majority of cells depending on cell quality

The negative deviation from the true value of Q by uncomplete mixing or dead corners is the biggest of the errors taken into consideration. It. is related to the quality of the cell and should therefore remain unchanged between two subsequent inventories if the same mixing time (the time between dosing and sampling) is chosen. This systematic error cancels for the annual loss, determined as a difference of two subsequent inventories.

3) Random errors related to the annual loss of mercury

Let us assume a total weight Q of 200 t Hg for n cells, known at $\pm$ 2 σ_Q = $\pm$ 0. 2 t Hg $\left(\sigma_Q = \sigma_{Q_c} / \sqrt{n} = 0.05\%\right)$ and a total annual consumption of 3 t Hg.

The error of ca. 0.3 t Hg ($\sqrt{2}$ x 0.2 t Hg) which affects the difference of two successive annual inventories represents only 10 % of the total loss.

In that case, σ_{Q_c}, equal to 0.05 % x $\sqrt{n}$, may be equivalent to $\pm$ 0.5 % for a plant of 100 cells having a Gaussian distribution of weights.

For such a plant, the accuracy of the determination of the annual consumption will even be better than 10 % when the value of σ_{Q_c} equals $\pm$ 0.32 % as calculated in paragraph 1.

4. Appendix 4: Handling of Radioactive Mercury

Local and national safety regulations must be strictly observed by the operators to whom adequate training must be given.

The following working procedure is given as an example.

1) Protection of the operator

When handling radioactive mercury, the operator will wear:

- laboratory coat
- pair of rubber gloves
- two film tests (chest and wrist).

The operator will have at his disposal a contamination control device and a radiation monitor or an equivalent type of Dosimeter. This latter instrument allows continuous measurement of the dose of radiations emitted by the radioactive product.

The manipulations are performed mostly behind a lead wall (see below).

2) Materials

The preparation of the active sticksolution and the bottling of the doping samples has to be achieved in a laboratory fume hood.

It is necessary to use a work bench whose covering is non absorbent not liable to amalgamation.

The operator must use adequate materials, examples of which are given the following list :

- a plate (50 x 30 cm) of stainless steel or PVC with a raised edge of about 1 cm
- bricks made of lead 5 cm thick, for building a wall (30 x 30 cm) in front of the table
- the lead wall is surmounted by a lead glass sheet 5 cm thick
- a 500 cm^3 beaker of stainless steel, or PVC, containing about 3 kg stable mercury
- materials and equipment for distance manipulation, including an ampoule breaker.

3) Manipulation

Check the dose at the surface of the cardboard delivery box.

After opening the cardboard box, all manipulations will be performed on the

recessed table arranged behind the lead wall.
Check the dose at the surface or the can.

Place the can on the table.

Extract the aluminium container using ordinary tongs at least 20 cm long.

Unscrew the lid using the tongs, keeping the container stationary with another pair of similar tongs.

Extract the ampoules containing the radioactive mercury using a pair of small tweezers with long jaws and immediately place them in the beaker clean mercury.

Break open the ampoules using an ampoule breaker, keeping it at extreme arm's length.

Remove the large pieces of broken quartz after rinsing them by dipping them several times into the mercury using the small tweezers and put them back into the aluminium container.

Following this initial dilution the radiation emitted should not be more than a few hundreds of µSv/h (a few tens of mR/h, so that further manipulation does not require lead shielding.

Filter the mercury on cotton-wool, placed in the bottom of a funnel, to remove the smaller pieces of quartz from the mercury.

Gently pour the 3 kg of radioactive mercury into the vat containing the whole amount of mercury to be labelled and homogenized for several hours.

Fill the polyethylene containers.

4) <u>Decontamination</u>

Screw on the lid of the aluminium container, in which are the quartz pieces.

Reconstruct the original package and keep it locked away until complete loss of activity or removal by a specialist service.

Check for any contamination of all materials and of the work bench using the contamination control device.

Clean contaminated areas using nitric acid or a detergent paste and abrasive until completely decontaminated.

Check the cleaning materials and rinse generously with water.

5. Appendix 5: Regulations to be Followed by the Factories

1) Mercury inventory of cells

- To minimise the cleaning of cells and to favour the mixing of radioactive mercury with cell mercury, cells suspected of containing abnormal quantities of thick mercury should be cleaned prior to the dosing.

- Mercury lutes should be cleaned directly before dosing as to prevent blockages of mercury circulation.

- During 48 hours after dosing no mercury should be withdrawn from the cell. After 48 hours of mixing a withdrawal of mercury will not influence the concentration of radioactive mercury.

- No fresh mercury may be added to cells during 48 hours before sampling. Added mercury always influences the concentration of radioactive mercury.

- Mercury movements, especially additions, should be restricted to a minimum and be recorded with precision for each individual cell (weights and dates). It is important to note if mercury has been withdrawn first and added later or vice versa.

- Big quantities of mercury can better be handled in a single than in several operations in order to improve and facilitate the corrections.

- Withdrawn mercury being radioactive may never be added to another cell and must be stocked apart or added to the cell from which it has been taken.

- When the mixing is assured by a circulating mercury pump, cells may be shut down for long periods.

- A complete shut down of the unit for long periods for example in case of strikes, will make a correct inventory difficult. However if the mercury pump keeps running and no excessive leakages of mercury occur, the inventory will be correct.

2) Mercury inventory of factory

A certain part of the mercury of a factory will not be measured by the radioactive tracer technique as this mercury is present outside the cell-denuder circuit. Recoverable mercury is present in:

- the stocks of the cell rooms
- the mains of hydrogen, caustic, wash water, waste hydrogen and possibly brine circuit
- reservoirs of the above mentioned circuits
- sumps and drains of the cell rooms
- muds of caustic filtration and waste water sumps and all other mercury containing mud.

For a good mercury inventory of the factory, it is necessary to know the stocks at the date of inventory or the changes in the stocks compared to the last made inventory.

A complete cleaning of mains and reservoirs before inventory is extremely difficult. Cleaning of caustic, hydrogen and brine mains and reservoirs needs a complete shut down of the plant. The cleaning of waste hydrogen and wash water mains and reservoirs is possible at low loads.

However, a high pressure spray unit available for this kind of work emulsifies the mercury and makes recovery extremely difficult and unhealthy. The best solution will be the adoption during construction of the highest possible slope for the mains and the fixing of purgers at the lowest points. This enables mercury to be taken away at least just before the date of inventory.

To prepare a correct inventory:

Drain all purges of the mains and reservoirs and clean the sumps and drains of waste water before the date of the inventory, separate the mud present on the date of the inventory from the mud produced later on, recover all mercury of the mud by decantation and/or distillation add or book all recovered mercury to the mercury stock of the cell rooms on the date of the inventory.

Industrial consumers of chlorine, engineering and equipment supply companies worldwide and chlorine producers outside Europe may establish a permanent relationship with Euro Chlor by becoming Associate Members or Technical Correspondents.

Details of membership categories and fees are available from:

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