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Sampling and analysis of Hg in geothermal fluids using vacuum sampling systems

IGG-ICCOM/CNR-2 METHOD
(M2)

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1. PURPOSE AND SCOPE

This document outlines a manual method for determining the mass concentration of mercury in endogenous fluids. The procedure is an extension of the EPA 29 [11] Method for sampling and analysis of fluids of volcanic and/or geothermal origin [2].

The method has been validated in the total mercury concentration range from 0.02 to 0.1 mg/kg in geothermal fluids. The method can be applied to:

- Sampling of fluids carried in a vapour manifold from the well-head of geothermal wells
- Sampling from sources at ambient pressure or slight overpressure
- Gaseous effluents from other sources.

The method is an alternative to the condensation/separation process based on the Elliss and Mahon method [3]; it eliminates the steel equipment required by the latter method, thereby minimizing the risk of adsorption of mercury by the materials used for sampling [4]

2. REFERENCE DOCUMENTS

This method refers to dispositions, scientific articles and methods contained in other publications. These references to standards are indicated at appropriate points in the text and are listed below. With regard to references with dates, amendments to these publications are only valid if included in this method as an update or review. For references that are not dated, the last edition of the publication to which it refers (including updates) applies.

[1] A Simple Method for the Collection and Analysis of Volcanic Gas Samples, Giggenbach, Bulletin Volcanologique, March 1975, Volume 39, Issue 1, pp 132-145

[2] 'Volcanic and Geothermal Gases and Low-enthalpy Natural Manifestations Methods of Sampling and Analysis by Gas Chromatography', Caprai A., Journal of Applied Sciences 5 (1): 85-92, 2005

[3] Chemistry and Geothermal Systems (Energy science and engineering), Feb 1978, by A.J. Ellis and W.A.J. Mahon

[4] Gas-phase adsorption losses of elemental mercury in cold-vapor atomic absorption spectrometry', R. Scott Daniels, Donald C. Wigfield, Analytica Chimica Acta, Volume 248, Issue 2, 1 August 1991, Pages 575-577

[5] EPA 7470A:1990 "Mercury in liquid waste (manual cold-vapor technique)"

[6] EPA. 1998. "Method 7473 (SW-846): Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry," Revision 0

[7] ASTM D-6722-11, Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis

[8] ASTM D-7623-10 (2015), Standard Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method

[9] ASTM D1066-11, "Standard Practice for Sampling Steam"

[10] EPA 6010C:2007 "Inductively Coupled Plasma - Atomic Emission Spectrometry"

[11] EPA 29: "Determination of metals emissions from stationary sources"

[12] EN 1483 "Water quality – Determination of mercury"

[13] JCGM 100:2008 "Evaluation of Measurement data – Guide to the expression of uncertainty in measurement (GUM)

[14] Student, 'The Probable Error of a Mean', Biometrika, Vol. 6, No. 1 (Mar., 1908), pp. 1-25

[15] R. A. Fisher, M. A., 'Application of Student's distribution', Metron, 5: 90-104 (1925)

[16] D'Ulivo Rapporto Tecnico prot. 3638 del 18/12/2014 "Determinazione del mercurio totale in N. 15 campioni liquidi provenienti dal campionamento su centrale geotermica", C.N.R.- Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici, S.S. di Pisa - Via Giuseppe Moruzzi, 1 - 56124 Pisa (I)

Caprai e D'Ulivo rapporto tecnico prot. 2572 del 05/11/2016 "Messa a punto di trappole chimiche per il campionamento e la determinazione del mercurio nel vapore geotermico, C.N.R. – Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse, C.N.R.- Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici, S.S. di Pisa - Via Giuseppe Moruzzi, 1 - 56124 Pisa (I)

[17] Compendium of Chemical Terminology, Gold Book, Version 2.3.3, 2014-02-24, http://goldbook.iupac.org/PDF/goldbook.pdf

3. DEFINITIONS

For the purposes of this method, the following definitions apply:

Analyte: chemical element or species whose quantity or concentration is measured

Mercury: elemental mercury and mercury in the chemical species that contain it.

Total mercury: sum total of the concentrations or amounts of mercury in the gaseous effluent, regardless of the physical state (solid, liquid, gas) or form of aggregation in which the compound is found (dissolved in drops, adsorbed in solid or liquid, etc.) and the chemical species that contains it (elemental mercury and mercury in the chemical species that contain it).

Well head: the well head is the interface between a mining well and the surface. It generally comprises a master valve (main valve for closing the shaft) and a series of rolling valves to regulate flow.

Typical sampling: Sampling at constant flow for which chemical-physical sampling conditions are create that do not alter the composition of the sample or in any case allow absorption of the analyte and its compounds into the fixing system.

Absorber: device to which the analyte (total mercury in this specific case) is transferred and stabilized in an absorption solution.

Rotaflo® cock or screw cock: two-way cock with a conical seal needle valve having two sections converging on the cock: inlet tube (angel) and gas inlet tube.

4. PRINCIPLE OF THE METHOD

The fluid from a steam manifold, a well head under pressure or in-air or concentric emitters is brought to ambient pressure or sampled at ambient pressure and transferred to a vial. A glass ampoule with a volume of about 1000 ml is used as an absorber, fitted with a dual ROTAFLO® type cock (details of which are specified in paragraph 5.4.) Once sampling is complete, a fixing solution containing $KMnO_4/H_2SO_4$ is injected into the absorber as described in paragraph 6.3.

The fixing solution is collected in suitable storage containers as described in paragraph 5.7 without further processing and then analyzed in the laboratory. The total storage period should not exceed two weeks.

The fixing solutions obtained are analyzed in the laboratory using two independent analytical techniques. For this method, the following techniques were used:

(i) atomic absorption spectrophotometry coupled with the cold mercury vapour generation technique, in accordance with EPA 7470 (1990) [5]

(ii) CNR method with direct analysis of the sample using the DMA-80 (Milestone) instrument conforming to US EPA 7473 [6] and ASTM D-6722-11 [7] and ASTM D-7623-10 [8] standard methods.

Sampling and analysis data are combined and the results are expressed in nanograms of total mercury per gram of fluid (ng/g) or, in an equivalent manner, in milligrams of total mercury per kilogram of fluid (mg/kg).

NOTE: Other methods are allowed and their equivalence with the foregoing methods must be demonstrated by passing a FISHER test [15] (Student t-test) with two averages.

4.1 APPLICABILITY OF THE METHOD

The procedure is valid for sampling fluid from constant emission sources or with low fluctuations in concentration. There are essential two types of source:

a. Pipelines or well heads under pressure for transport of endogenous fluids
b. Regular sources of emanation from the ground and gaseous sources in pools of water

For a pressurized fluid, the sample is taken by means of a depressurization line such as the one shown in Figure 1a. The line is fitted with a 'T' joint allowing the absorbers to be connected to the fluid delivery point and sampling at atmospheric pressure (Fig. 1b).

The fixing solution comprises potassium permanganate ($KMnO_4$) in a sulphuric acid (H_2SO_4) environment. The solution oxidizes and fixes the mercury in the various forms which this element can take.

5. SAMPLING EQUIPMENT AND REQUIREMENTS

5.1 SAMPLING CONDITIONS

This method, given the type of sampling, cannot be applied to cases where isokinetic sampling is required. If particulate matter is present, it should be eliminated by a filter mounted on the head of the sampling line or be calculated from the results of analysis using specific chemical particulate markers.

5.2 GENERAL REQUIREMENTS

The sampling equipment comprises:

- A high-pressure fluid probe for sampling and depressurizing the fluid: **type A probe** (fig. 1a)
- A probe for sampling fluid at ambient pressure: **type B probe** (fig.2)
- A series of vials containing the fixing solution under vacuum for fluid sampling (fig.3).
- A water/ice bath cooling system to cool the absorbers.

The materials used for sampling system equipment should be those described in paragraph 5.7.

5.3 SAMPLING PROBE

There are essentially of two types sampling probe depending on whether sampling is performed at sampling points under pressure (**type A probe**) or at ambient pressure (**type B probe**)

The type A probe (Fig. 1a) forms a depressurization and sampling line comprising two sections of PTFE pipe (inside diameter 20 mm). The tube is reinforced by an external stainless steel mesh to contain expansion caused by high temperatures and pressure. The two sections are connected to a stainless steel three-way T-coupling (Figure 1b) fitted with an exhaust valve on the central branch, connected to an oval stainless steel tube for coupling the silicon pipe during sampling. The end of the sampling probe discharges into the atmosphere through a silencer. The probe is connected to the vapour transport pipe through a quick-fitting coupling. Brief description of materials:

Diameter of internal pipe and material MALE/MALE ½" (1.27 cm) TAPER GAS THREAD PIPES (PTFE CORE 13 mm LINED WITH STAINLESS STEEL)

Diameters of couplings and threads STAINLESS STEEL FEMALE T-COUPLING ½" (1.27 cm) TAPER GAS THREAD P 50 BAR

Diameters of valves and threads STAINLESS STEEL FEMALE BALL VALVE ½" (1.27 cm) TAPER GAS THREAD P 50 BAR + STAINLESS STEEL MALE/MALE NIPPLE TAPER GAS THREAD

Type of oval coupling DN14 STAINLESS STEEL OVAL MALE SOCKET ½" (1.27 cm) TAPER GAS THREAD

Type of quick-fitting coupling STAINLESS STEEL QUICK-FITTING COUPLING (VR TYPE) FEMALE 1" (C/W SPECIFIC GASKET) / FEMALE ½" (1.27 cm) TAPER GAS THREAD

The silencer (outer diameter 2"= 5.08 cm) is fitted with a 1" (2.54 cm) male quick-fitting coupling connecting to the end of the pipe (discharge) on which a quick-fitting female coupling is mounted.

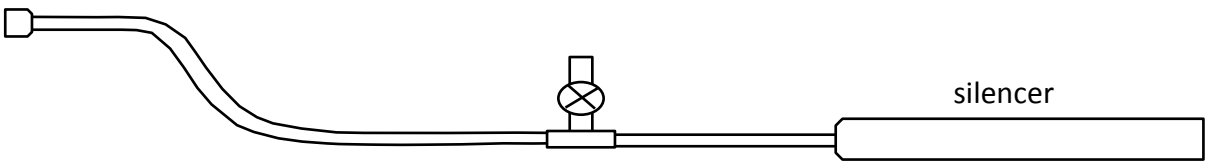


Figure 1a: sampling probe fitted with T-coupling: type A probe

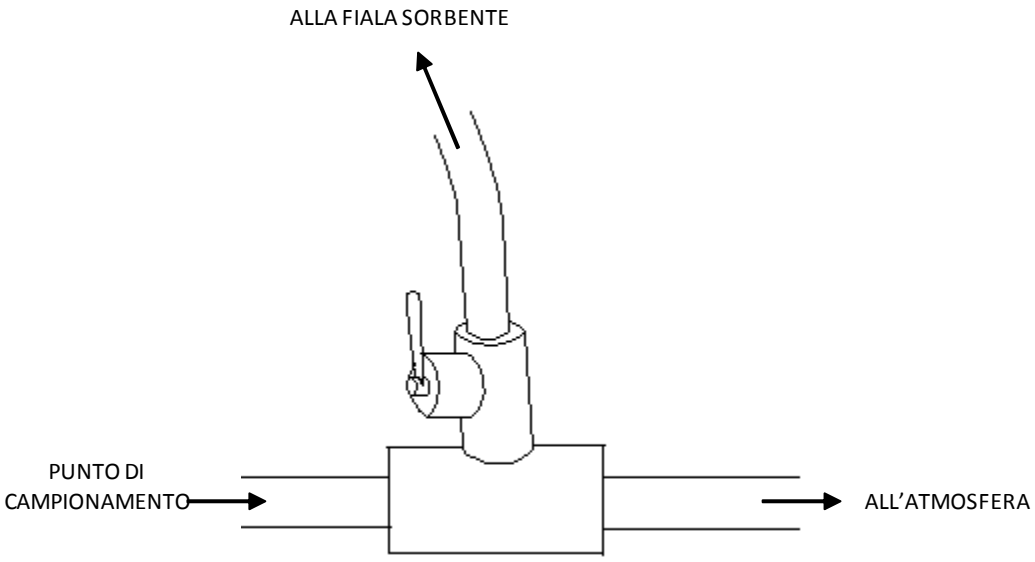


Figure 1b: T-coupling

The type B probe (fig.2) comprises a quartz tube long enough to be inserted into the ground or a upside-down glass funnel to be placed, in the case of water pools, above the gas bubble point. The quartz in the first case and the glass in the second are required to ensure sealing at high temperatures and to minimize any absorption effects.

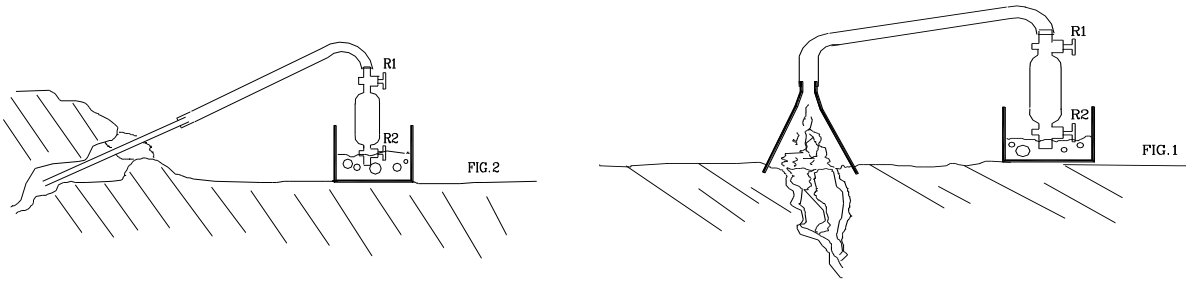


Figure 2: arrangement sampling from the well head in the ground or the pool: type B probe

5.4 SAMPLING VIAL

ROTAFLO® 1000 ml dual cock vials are used (figure 3)

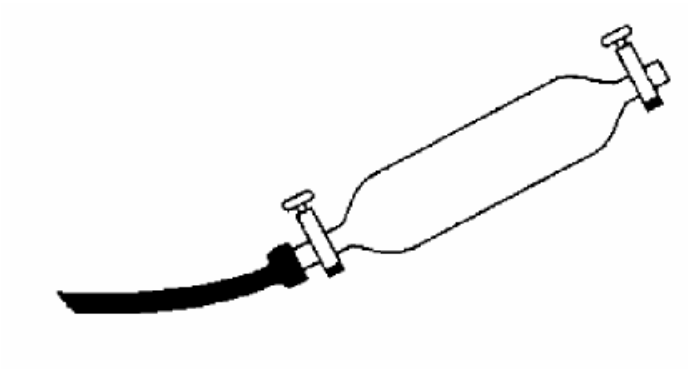


Figure 3: typical layout of a 1000 ml sampling vial fitted with a double cock

5.5 CONNECTIONS

The vial is connected to the sampling probe (type A or type B) through a PTFE coupling having a 10 mm inside diameter. The connections are made using silicon pipe sections. The silicon connections connecting the vial to the sampling probe should be short and the surface in contact with the fluid should be less than 2 cm^2. These silicone connections must be replaced downline of each sampling to avoid absorption and subsequent release of sampled mercury.

It is advisable to secure the silicone seal on the PTFE hose by tightening the connection with plastic hose clamps. Guidance concerning the choice of materials for connections between the different parts of the sampling equipment is provided in paragraph 5.7 and must be applied for parts in contact with the gaseous effluent containing mercury.

NOTE: reduction of the contact surface with silicone to the technically minimal values is necessary in view of its proven affinity for mercury [4]

5.6 STORAGE FLASKS AND CONTAINERS

The material used for bottle storing absorption solutions is indicated in para 5.7. Storage flasks for the permanganate solution must be darkened and kept away from sunlight to prevent the formation of MnO_2.

NOTE: the solutions must be kept in the dark and in flasks fitted with a cap that allows venting of the gas produced by the decomposition of the solutions themselves (oxygen)

5.7 MATERIALS FOR SAMPLING EQUIPMENT

The parts of the sampling equipment in contact with the gaseous effluent containing mercury, or liquids containing mercury, must be in the materials listed in **Errore. L'origine riferimento non è stata trovata.**.

Table 1 - Materials for sampling equipment.

Part of the equipment	Material	**Notes**
Type A sampling probe	PTFE	
Type B sampling probe	QUARTZ/GLASS	
1000 ml vial absorber with dual ROTAFLO® cock and septum	Borosilicate glass	
Connecting couplings	Silicone (with a total internal surface <2 cm^2)	
Connection pipes between sampling probe and sampling vial	PTFE	
Storage flasks with cap	Low Density Polyethylene (LDPE) High density polyethylene (HDPE)	

6. REAGENTS

6.1 GENERAL INFORMATION

The solution used for absorption of gaseous mercury comprises a potassium permanganate / sulphuric acid solution ($KMn0_4$ 2% m/m H_2SO_4 10% m/m).

WARNING: Use reagents in accordance with the applicable health and safety regulations.

6.2 REAGENTS USED

Use reagents for fixing solutions and pre-cleaning of the sampling equipment list below:

- Potassium permanganate ($KMnO_4$) with low Hg content (max 0.000005%)
- Sulphuric acid (H_2SO_4) 95-97% with low Hg content (max 0.005 ppm)
- Nitric acid (HNO_3) 65% with low Hg content
- Hydroxylammonium chloride ($NH_2OH{\cdot}HCl$), 10% m/m

In any case, alternative choices will envisage the use of high purity reagents for analysis, with the lowest mercury content among those available. Mercury content must also be verified in the reagent whites.

NOTE: (*) = Resistance >18.2 MΩ/cm)

6.3 PROCEDURE FOR PREPARATION OF CAPTURE SOLUTIONS.

6.3.1 INTERMEDIATE SOLUTION H_2SO_4 5.4M - SOLUTION A

1. Carefully transfer while shaking 300 ml of concentrated H_2SO_4 (96% p/p) into a graduated 1000 ml flask containing about 500 ml of deionized water (Resistance >18.2 MΩ/cm).

2. Top up to the required volume and mix completely. The mixture prepared in this way with an approximate concentration of **5.4 M of H_2SO_4** (528.5 g/l) is identified as ***solution A***. This solution will then be used to prepare the **final solution of $KMnO_4/H_2SO_4$**.

6.3.2 INTERMEDIATE SOLUTION OF $KMnO_4$ 64 g/l – SOLUTION B

3. Dissolve up to saturation while continually agitating, 70 g of crystalline $KMnO_4$ in a graduated 1000 ml flask containing about 950 ml of H_2O.

4. Top up to volume with H_2O leaving the base body in the flask.

5. Filter using fibre glass filters to prevent the degradation of the mixture because of the autocatalytic reduction of $KMnO_4$ in the presence of MnO_2 and store in dark glass bottles.

6. The final solution obtained, saturated with di $KMnO_4$ (63.9 g/l), is identified as ***solution B***.

6.3.3 ABSORPTION SOLUTION ($KMn0_4$ 2% M/M H_2S0_4 10% M/M)

Mix 335 ml of solution A (H_2SO_4) with 625 ml of solution B ($KMnO_4$) and top up to a volume of 1 l. The mixture thereby obtained is a solution with 0.253M of $KMnO_4$ and 1.8M of H_2SO_4

NOTE 1: Store in a dark place.

NOTE 2: The solution must be prepared within three days prior to sampling.

WARNING: the solutions must be kept in the dark and in flasks fitted with a cap that allows venting of the gas produced by the decomposition of the solutions themselves (oxygen)

6.4 REAGENTS FOR RINSING THE SAMPLING EQUIPMENT AFTER SAMPLING

Use a solution of hydroxylammonium chloride ($NH_2OH{\cdot}HCl$) 10% m/m to rinse the absorbers.

WARNING: Observe health and safety requirements when using hydroxylammonium chloride.

For the washing procedure, refer to Appendix A.

7. SAMPLING PROCEDURE

The following paragraphs describe the operations to be carried out before and during sampling in two cases, respectively, of sampling from equipment under pressure or from emitters at ambient pressure.

7.1 SAMPLING FROM A WELL HEAD AND PIPES UNDER PRESSURE

The samplings described in this chapter are carried out at the head of production wells near the equipment located downline of the shut-off and manoeuvring valves and on the steam discharge pipes, water/steam separators (vapour part) and the like.

Sampling is performed by pouring the fluid under pressure from valves mounted on couplings meeting the ASTM 1066 standard [9] fitted with cocks or flanges. Before each operation, completely open the valves on the pipeline in order to condition the sampling point by clearing any deposits from it. To achieve this, drain the steam/vapour at the maximum permitted flow for at least 5 minutes. At the end of this initial conditioning stage, close the valves on the sampling pipe.

It is advisable to mount a quick-fitting connector in series with the valve in order to facilitate sampling.

7.1.1 BLEED AND REGULATION

Before proceeding with the sampling procedure, connect the A-type probe (three-way reinforced teflon tube) to the pipeline. Fully open the steam/vapour valve again and allow the steam/vapour to flow into the probe for at least 15 minutes so that the probe is heated and self-cleaned.

When the stabilization time has elapsed, the sampling valve on the 'T' fitting is opened fully and flushed with steam/vapour for at least 10 minutes.

Slightly roll the flow with the second cock on the 'T' fitting to adapt it to sampling requirements.

7.1.2 SAMPLING

At the end of the bleed and regulation operations, the sampling vial is connected to the 'T' coupling so that the gas enters the vial. The sample is taken by alternately opening/closing the ROTAFLO ® cock, flushing at flow rate that avoids an excessive overheating of the vial. While the sample is being taken, the vial must be cooled (a container with water and ice must be available).

It is advisable to mount sampling sockets on steam/vapour pipelines in accordance with the ASTM D1066 standard [9]. In this manual consequently makes reference to them.

The sampling procedure is applicable to samples taken from the well head and from piping at pressures from a few bar up to about 100 bar.

WARNING: the use of a type A probe (Fig. 1a) and 'T' coupling (Fig. 1b) is absolutely compulsory.

7.2 TAKING SAMPLES FROM APERTURES IN THE GROUND, AIR-BORNE EMISSION SOURCES AND POOLS OF WATER

Sampling envisages identifying a point on the ground or, at pool level, where an overturned funnel can be inserted to regulate the gas or a quartz probe for samples taken from fumaroles or high temperature sources. Before taking the sample, insert the probe (quartz probe or funnel) and allow the gas to flow out for 15 minutes to allow heating and self-cleaning of the devices.

7.2.1 BLEED AND REGULATION

Slightly roll the flow with a cock, if there is a strong flow of gas, and adapt it to sampling requirements.

7.2.2 SAMPLING

At the end of the bleed and regulation operations, the sampling vial is connected to the sampling probe so that the gas enters the vial. The sample is taken by alternately opening/closing the ROTAFLO ® cock, flushing at flow rate that avoids an excessive overheating of the vial. While the sample is being taken, the vial must be cooled (a container with water and ice must be available).

Sampling proceeds exactly as described in the previous paragraph, paying special attention to prevent any air and/or liquid returns (in the case of pools).

7.3 COLLECTING ABSORPTION SOLUTIONS FROM ABSORBERS

1. The vials should be fitted with thermostats. Note the ambient temperature (T_{vial}) where they are located.
2. Note the pressure (P_{vial}) inside the vials with a piezo-transducer measurement device, making sure there is a minimum "dead volume" between the cock on the vial and the measuring probe. The amount of gas exchanged must not exceed 1‰.
3. Pour 18 ml of 0.253M $KMnO_4$ - 1.8M H_2SO_4 (§ 6.3.3) solution for every 1000 ml of gas sampled.

4. Place the vials in a swivelling mixer or shake by hand at 10-minute intervals for at least 2 hours
5. pour into a 100 ml flask (sampling of 1 lvial) the contents of the vial for Hg analysis
6. Resume with 1-2 parts of H_2O of 2-3 cm^3 each
7. Pour into the vial 2-3 drops of 15% hydroxylamine solution + 2 cm^3 H_2O, wash the inside of the vial and transfer to the flask as described in the previous point.
8. Resume with 1-2 parts of H_2O of 2-3 cm^3 each or repeat point 7 if brown traces of MnO_2 remain in the vial
9. Proceed with pre-treatment and analysis as per paragraph 7.5

7.4 PRE-CLEANING THE EQUIPMENT

All parts of the sampling equipment in contact with mercury must be cleaned before taking samples by following the protocol indicated in Appendix A.

The following parts must be cleaned:

- Probe (inside tube);
- Connections pipes;
- Absorbers;
- Reagent storage containers as per section 6.

The washing procedure is applied to all the equipment used.

Check the quality of the washing procedure by keeping the washing solutions and periodically checking the residual content of mercury.

It is advisable to prepare washing solutions at the beginning of each experimental sequence.

The quality of the reagents used must comply with the dispositions indicated in paragraph 6.2.

7.5 SAMPLE STORAGE REQUIREMENTS

The samples taken should be kept in a dark place and analyzed as soon as possible, usually within two weeks of sampling.

7.6 PRE-TREATMENT PRIOR TO ANALYSIS

7.6.1 DETERMINATION WITH CV-AAS

Prior to determination with CV-AAS, excess residual permanganate is reduced with hydroxylammonium chloride (12% m/m solution), adding several millilitres (1 ml at a time) until complete decolouring of the absorption solution and dissolution of the MnO_2 precipitate.

The solution thereby obtained is topped up to a volume of 100 ml

7.6.2. DIRECT DETERMINATION WITH DMA-80

The solution obtained from the transfer of the absorption solution is then treated with hydroxylammonium chloride ($NH_2OH \cdot HCL$) until it is decolourized, **topped up to a volume of 100 ml** and immediately analyzed.

The sample volumes taken for analysis typically range from 0.1 to 0.2 ml and a quartz rather than a nickel cell is used to minimize the value of Hg whites.

NOTE 1: The gradients of the calibration curves of the capture solutions ($KMnO_4$/ H_2SO_4 referred to in paragraph 6.3.1) are comparable to those obtained from standard solutions of mercury in water. This indicates that the oxidants used do not interfere with the determination of Hg.

7.7 ANALYSIS

Analysis of the solutions pre-treated in accordance with paragraph 7.8 may be performed using the following methods:

- EN 1483 “Water quality – Determination of mercury” [12]
- EPA 7470A:1990 “Mercury in liquid waste (manual cold-vapour technique)” [5]
- EPA 6010C:2007 “Inductively Coupled Plasma - Atomic Emission Spectrometry” [10]
- EPA 29: “Determination of metals emissions from stationary sources” [11]

8. EXPRESSION OF RESULTS

8.1 CALCULATION OF THE REACTIVE MASS AND SAMPLED FLUIDS

The amount of fluid sampled is calculated from the difference in weight of the vial at the end of sampling (P_1) compared to the weight of the empty vial (P_0):

$$m_{fluid} = P_1 - P_0$$

8.2 TOTAL MERCURY CONTENT

The solution resulting from the analyses performed as per 7.6.1. or 7.6.2 has a final volume of 100ml. The concentration of mercury in the fluid is therefore:

$$[Hg]_{in\ the\ fluid} = 100 \times [Hg]_{analysis} \times \frac{1}{P_2 - P_1}$$

where:

$[Hg]_{in\ the\ fluid}$= concentration of Hg measured in the fluid; Mena value for three replicated samplings (ng/g);

$[Hg]_{analysis}$ = concentration of mercury determined in the fixation solution (100 ml) (ng/g or ng/µl);

P_0 = initial weight of the vial under vacuum (g);

P_1 = weight of the vial with reactives under vacuum (g);

9. PERFORMANCE CHARACTERISTICS

Statistical tests were carried out in collaboration between CNR and Enel Green Power in order to validate this method. These inter-calibration tests made it possible to identify reference values for the quantification of:

- Lower Detection Limit (LOD or DL);
- Analytical range
- Uncertainty of repeatability or type A uncertainty A (JCGM 100:2008 “Evaluation of Measurement data – Guide to the expression of Uncertainty in Measurement (GUM) [13]), indicated in this method as 95% Confidence Interval (CI95%)
- Estimate of accuracy by comparing methods and validation with Fisher test [15] (ANOVA)

The performance characteristics of the method were measured in the absence of reference samples given the type of sample used, i.e. endogenous fluids at high temperatures and pressures or deriving from emanations from the ground. The possibility of testing samples taken using different methods and analyzed with different analytical techniques nevertheless allowed comparisons between tests carried out on the same sample of fluid.

The values obtained are listed in the IGG/CNR-1 METHOD

9.1 detection limit or lower detection limit

The detection limit (LOD) was calculated from the absolute instrumental limit (1 pg Hg for determination with DMA 80 "tri-cells") and related to the amounts of endogenous fluid usually sampled, taking an arbitrary dilution of 50% caused by the capture solution into account. Using 0.1 ml of capture solution. The LOD value calculated was 0.02 at µg/kg. Lower LOD values may be achieved by increasing the volume of the solution being analyzed.

9.2 analytical range

A conservative criterion was adopted by assigning as the lower limit of the range the detection limit (LOD) indicated in paragraph 8.2.1 and the upper limit as the one found for samples with higher concentrations analyzed during the experimental trials to finalise the method. The analytical range proved to be between 0.02 at 0.1 µg/kg for analysis of 0.1 ml capture solutions with DMA80 “tri-cells”

9.3 confidence interval and type A UNCERTAINTY

Table D.1 shows the CI (95%) as absolute and percentage values (the latter obtained by dividing the absolute CI by the mean value) derived from the foregoing samplings by EGP / CNR.

TEST DATED 18/03/2016 LE PRATA	KMnO4/H2SO4	hypochlorite 0.1 M CNR	hypochlorite 0.2 M CNR	hypochlorite 0.3 M CNR
	20.9	21.7	31.6	19.7
	23.9	24.7	33.8	18.5
		21.7	38.2	21.1
	24.0			
	21.3	21.1	29.5	
		23.3		24.3
mean	22.5	22.5	33.3	20.9
standard deviation	1.6	1.5	3.7	2.5
CI (95%)	**2.6**	**1.8**	**6.0**	**4.0**
CI_{99}%	**21.1%**	**13.3%**	**32.8%**	**35.0%**

Table D.1 – Statistical analysis to identify the Confidence Interval for replication acceptability.

9.4 Estimate of the accuracy of the method in the absence of reference samples with methods of comparison between methods and ANOVA statistical analysis (fisher test [15])

In the absence of reference samples, the results obtained with 4 types of sampling were compared in-house as described in paragraph 8.2.1. The values obtained from several replications of the same sampling and analysis method were used to compute the main statistical parameters including the mean, the experimental standard deviation and the 95% confidence interval. The average value measured for each method was used to calculate the percentage recovery used as an initial estimate of accuracy (Table D.2).

TEST DEL 28/10/2015	Soluzione di assorbimento $KMnO_4/H_2SO_4$ (ng/g)	Soluzione di assorbimento persolfato/NaOH (ng/g)	Soluzione di assorbimento ipoclorito 0,1M/NaOH (ng/g)	Soluzione di assorbimento $KMnO_4$/NaOH (ng/g)
RADICONDOLI	30,4	18,3		
		14,8	22,6	20,6
	29,4		21,9	23,7
	27,7	19,3	18,7	18,9
	28,0	20,6	22,3	21,0
media (ng/g) (A)	28,9	18,2	21,4	21,1
mediana (ng/g)	28,7	18,8	22,1	20,8
deviazione standard sperimentale (ng/g)	1,2	2,5	1,8	2,0
$IC_{95\%}/2$ (ng/g)	2,0	3,9	2,9	3,2
Espressione del risultato (ng/g)	28,9	18,2	21,4	21,1
media totale (ng/g) (B)	22,4			
Recovery% (A/B X 100)	129	81	96	94

Table D.2 – Statistical analysis to identify the percentage recovery as an estimate of accuracy

The results allow an estimated accuracy of less than 30% to be assumed

Comparison between methods

The data obtained were compared with the Fisher test [15] (ANOVA) listed in the IGG / CNR-1 METHOD

9.5 Acceptability of replications

This paragraph outlines the suggested evaluation criteria for the measurements obtained for three replications. A method deemed appropriate by the workgroup in charge of this method for accepting the three replications and identifying outliers is the one based on the 99% Confidence Interval calculated during specific measurement series. It should be noted that, in this way, the CI99% confidence interval can be evaluated at regular intervals by using a 'statistically' consistent number of replications (at least 6 replications are suggested) and, based on this confidence interval, evaluate the acceptability of measurements conducted with a smaller number of replications (typically 3).

As already pointed out, the parameter to be considered in order to identify outliers is $CI_{99}\%$ calculated as follows:

$$CI_{99} = 2t_{99}\frac{s}{\sqrt{n}}$$

Where:

- CI_{99} is the 99% confidence interval for the measurements performed by ARPAT used for statistical analysis (Table D.1)
- s is the typical deviation of measurements:

$$s = \sqrt{\frac{\sum_1^n (x_i - \bar{x})^2}{n-1}}$$

- x_i is the i-nth measurement performed by ARPAT
- $\bar{x}$ is the arithmetic mean of the measurements
- n is the number of measurements performed by ARPAT (n = 6 in Table D.1)
- CI99% is calculated from the following formula:

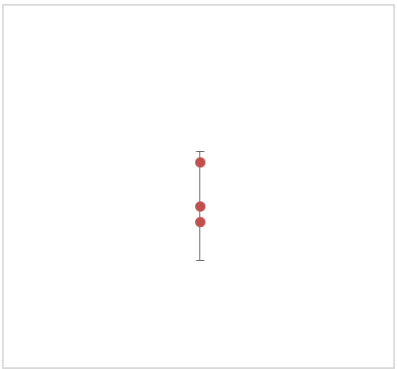
$$CI_{99}\% = \frac{IC_{99}}{\bar{x}}100$$

Any outliers are identified if the following condition is met:

$$|x_i - med| > \frac{CI_{99}}{2}$$

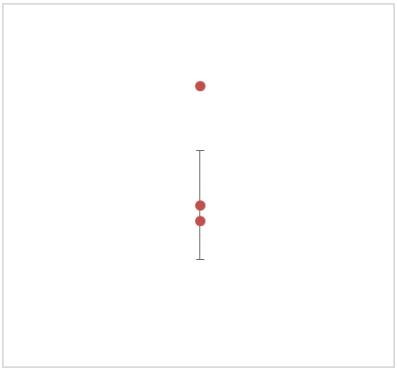
Where med is the median of the three replications. In accordance with the selection criteria for samples considered to acceptable as per the foregoing discussion and section 5.5, the following cases may arise:

Case 1: the three replications demonstrate comparable capture efficiency (no outlier). In this case, the three results are statistically evaluated using the above-mentioned method and, if the

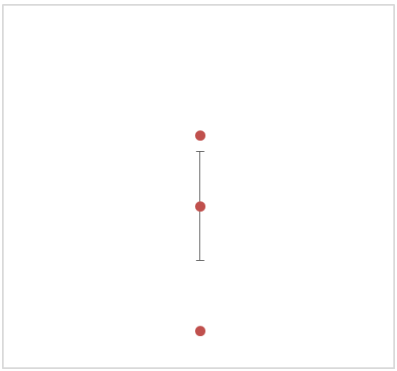


evaluation is positive, the result (concentration) is expressed as the average of the three replications.

Case 2: two replications alone demonstrate positive capture efficiency (only one outlier): the result will be expressed as the average of the two normal results remaining.



Case 3: where there are 2 outliers. In this case, the result will be expressed by the only value remaining.



10. TEST REPORT

The test report must contain at least the following information:

a) Reference to this method;
b) Identification and number of sample(s);
c) Description of plant and process;
d) Plant operating conditions;
e) Position of sampling points;
f) Number of sampling points, number of replications and identification of sampling points;
g) Sampling time and operating conditions for sampling;
h) Sampling volume(s);
i) Type of absorbers;
j) Type of absorption solution;

k) Analysis procedure (reduction agent, manual injection or flow);
l) Total content of mercury as concentration in mass;
m) Any deviation from this standard.

APPENDIX A: SAMPLING EQUIPMENT CLEANING PROCEDURE

A.1 General Information

Cleaning must be carried out in the laboratory in accordance with good laboratory practice. This appendix provides a number of options for cleaning equipment, absorbers and vials.

A.2 Sampling line

After each measurement, rinse the sampling line, connection pipes and absorbers (vial) with a solution of HNO_3 at 10% m/m.

WARNING The amount of mercury present in the wash solution can be used to verify sampling quality. If preliminary sampling suggests that this level does not absorb detectable amounts of mercury, the solution in question may be ignored.

A.3 Absorbers and storage containers for reagents and samples

The washing procedure for sampling vials (absorbers) and reagent storage containers can be divided into 5 consecutive steps:

1. Pre-wash with 50 ml of a solution of HNO_3 at 10% (b.t. Hg), agitating for about 5 minutes.
2. Rinse with demineralised water as required.
3. Rinse with 50 ml of an absorpion solution of (2% $KMnO_4$ (b.t. Hg, 10% H_2SO_4 b.t. Hg), agitating for about 10 minutes.
4. If cleaning solutions are stored in P.E. bottles, make sure to identify the air-locks and their washing (for possible analytical checks).
5. Rinse the absorbers with 2 ml of hydroxylammonium chloride solution ($HONH_3Cl$), 10% m/m.
6. Rinse several times with deionized H_2O (Resistance> 18.2 MΩ/ cm)