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Sampling and analysis of mercury in geothermal fluids by modified Giggenbach method

METHOD IGG-ICCOM/CNR-1

(M1)

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Sommario

Sampling and analysis of mercury in geothermal fluids by modified Giggenbach method

1. SCOPE AND APPICATION

Present document reports a method applicable to the determination of mercury mass concentration in endogenous fluids. The method is an extension of Giggenbach protocol [1] for sampling and analysis of endogenous fluids of volcanic and/or geothermal origin [2].
The method has been validated in a range of total mercury concentration between 0.02 and 0.1 mg/kg in geothermal fluids and it can be applied for the following kinds of fluids:

- Sampling of fluids in pressurized steam pipelines or well-head sampling in geothermal wells
- Sampling from open stationary sources in the soil with ambient pressure or mildly pressurized sources
- Gas sampling in other stationary sources from the soil or in pipelines

This method is alternative to the condensation/separation method applied in geothermal fluids deriving from Elliss e Mahon method [3]. In particular stainless steel equipment are avoided in order to prevent mercury absorption in the equipment used for sampling [4]

2. REFERENCES

The following referenced documents are the necessary document extension for the application of this document. Documents reported include methods, standard document, specifications, guidelines, scientific papers. For dated references, only the edition cited applies. Far undated references the latest edition of the referenced document (including any amendments) applies.

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[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)
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3. DEFINITIONS

In the present document the following definitions apply:

Analyte: element or chemical species undergoing mass or concentration measurement

Mercury: elemental mercury and mercury in irs compounds.

Total mercury: the sum of concentrations or the amounts of mercury in the gaseus effluent regrdless its physical state (solid, liquid, gas) or aggregation status present in sample (dissolved in droplets, adsorbed on solids or liquids etc.) and chemical species containing it (elemental mercury, mercury in its compounds).

Well-head: well-head is the interface of oil or gas well at the surface connected to casing. Typical components are the master valve (main closing valve) and other secondary valves suitable for throttling and flow rate regulation.

Representative sampling: sampling procedure performed at controlled flow rate conditions and equipment settings able to create chemical and physical conditions preventing alteration of sample composition or allowing quantitative transfer of analyte and its compounds in the absorbing solutions.

Absorbing device: specific collecting device suitable to quantitative transfer and stabilization of analyte in the absorption solution such as glass washing bottles or glass flasks.

Rotaflo® or screwcock valve: two-way valve equipped of screwed stopcock and PTFE conical stem. The valve connects the gas inlet tube (angel) and flask connector tube.

4. PRINCIPLE OF METHOD

The pressurized steam from transport pipes, wellhead or surface unpressurized vents is eventually drown to ambient pressure or directly collected at ambient pressure and collected in a flask containing absorption solution under vacuum.

The absorbing device is 250 ml glass flask equipped with a ROTAFLO® type valve of the syze and shape as specified in paragraph. In the flask is present the oxidizing agents in a 4M NaOH solution as described in paragraph 6.3.

At the end of sampling procedure, the absorption solution is kept in the flask with no further treatment, ready for the following laboratory analysis.

If the absorption solution is transferred from the flask, it can be poured in suitable bottles before analysis. In both cases, the storage time between sampling and analysis cannot exceed two weeks.

The absorption solutions are analyzed with two possible independent analytical methods. In the present method two alternatives are suggested:

(i) Cold Vapour Atomic Absorption Spectrometry according to EPA 7470 (1990) method [5]
(ii) CNR method with direct sample analysis in specific DMA-80 (Milestone) instrumentation and compliance to standard methods US EPA 7473 [6], ASTM D-6722-11 [7] and ASTM D-7623-10 methods [8].

Sampling and analysis data are then processed to calculate total mercury concentration expressed nanogram of total mercury per gram of steam (ng/g) or, equivalently, in mg/kg.

NOTE: Other analytical methods are possible after demonstrated equivalence with above-mentioned methods by positive results of ‘two average comparison FISHER test’ [15] (Student t test).

4.1 METHOD APPLICABILITY

The method can be applied in case of sampling fluids from stationary sources or with low concentration fluctuations. The types of fluids are practically two:

a. Steam pipes or wellhead carrying geothermal steam or endogenous gases
b. Spot vents from the soil or from bubbling ponds

In the presence of pressurized steam before sampling a depressurization line like the one shown in Fig. 1a is used. A pipe equipped with a 3-way 'T' connector equipped with a valve is connected to pipeline or wellhead by a valve. The fluid is delivered to atmosphere for pressure release and the absorber is connected to the 3-way in order to allow sampling at atmospheric pressure (fig. 1b).

The NaOH in absorption solution allows quantitative sampling of acid type gases in the non-condensable fraction of the fluid. This makes possible sampling of significant volumes of steam, typically in the range of 3-5 liter at standard conditions (273,15 K and 101,325 kPa).

The absorption solution contains a 4M NaOH matrix in which 0,3 M sodium hypochlorite is dissolved. This solution can perform mercury oxidation in its compounds in the steam. Other oxidizing agents are allowed like $KMnO_4$ and $(NH_4)_2S_2O_8$. The method has been tested and validated besides previous solutions also with 0,1 and 0,2 M hypochlorite.

NOTE: In the case of high H_2S concentrations are present it is recommended the use of 0,3 M NaOCl solution in order to assure reliable measurements.

5. SAMPLING EQUIPMENT AND REQUIREMENTS

5.1 SAMPLING CONDITIONS

This method, considering the sampling is of batch type, cannot be applied in cases where Isokinetic sampling is required. Particulate matter should be removed with a filter at the inlet line or be derived from the results of the analysis using specific chemical markers

The method applies to steam under pressure in pipelines or in wellhead and to point gas emanations from the ground.

5.2 GENERAL REQUIREMENTS

The sampling equipment consists of:

- A high pressure fluid sampling probe and its depressurization line: **type A probe** (fig. 1a)
- A sampling probe for fluid at ambient pressure: **type B probe** (fig.2)
- A number of vials containing the absorption solution, previously placed under vacuum, for fluid collection (fig.3).
- A water/ice bath cooling system to refrigerate the vials.

The materials of the equipment making up the sampling system should follow the specifications reported in section 5.7.

5.3 SAMPLING PROBE

The sample probes are essentially of two types depending on whether the sample is drawn from equipment under pressure (type A probe) or ambient pressure (type B probe).
The probe of type A (fig. 1a) is a depressurization and withdrawal line composed of two lines of PTFE tube with an inside diameter of 20 mm. The hose is reinforced with a STAINLESS steel outer braid for limiting expansion due to high temperature and pressure. The two branches are joined by a three

way stainless steel connection of 'T' type (Figure 1b) equipped with a drain valve on the Middle branch, connected to a second stainless steel tube with silicone tubing fitting. The free end of the sampling probe discharges to atmosphere through a silencer. The probe is connected to steam pipe through a fitting with quick connector.

A brief description of the materials follows:

Inner tube diameter and tube material: 0,5” (1.27 cm) male/male THREADED CONICAL GAS (13 mm PTFE CORE COATED STAINLESS STEEL MESH)

Diameters of fittings and STAINLESS ‘T’ 3 way connector: FEMALE thread 0,5"(1.27 cm) GAS CONICAL THREADING, P=50 BAR

Valve diameters and Threading: STAINLESS BALL VALVE, MALE 0,5" (1.27 cm) TAPERED THREADED, P=50 BAR, with STAINLESS STEEL MALE/FEMALE THREADED CONICAL GAS NIPPLE

Type of fitting, OLIVE GRIP STAINLESS 0,5" MALE DN14 MALE 0,5" (1.27 cm) GAS TAPERED THREADED CONNECTOR

Quick connector: STAINLESS STEEL QUICK CONNECTOR (TYPE VR) female 1" (with GASKET)/female 0,5” (1.27 cm) TAPERED, THREADED GAS TYPE

The silencer (outer diameter 2"= 5,08 cm) is equipped with male quick coupling 1" (2.54 cm) to be connect to the end of the pipe (exhaust) on which a female quick connector is mounted.

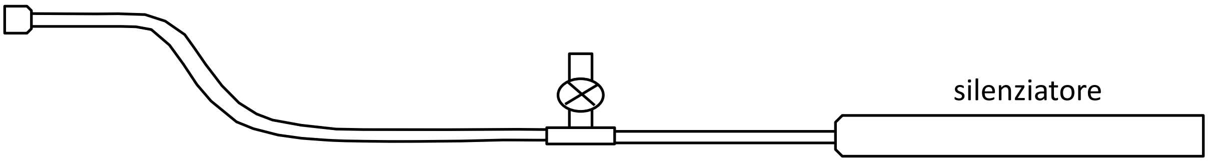


Figure 1a: sampling probe with T-type connector: type A probe

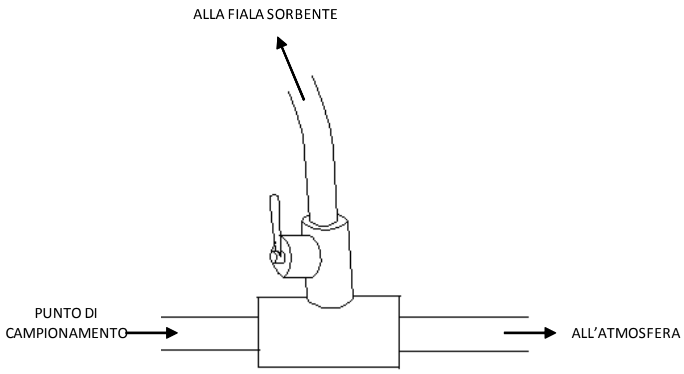


Figure 1b: 3 way 'T' connector

The probe of type B (fig. 2) requires a quartz pipe of suitable length introduced into the ground. Quartz is necessary to ensure a tight seal at high temperatures and to minimize any effects of mercury absorption on the line.

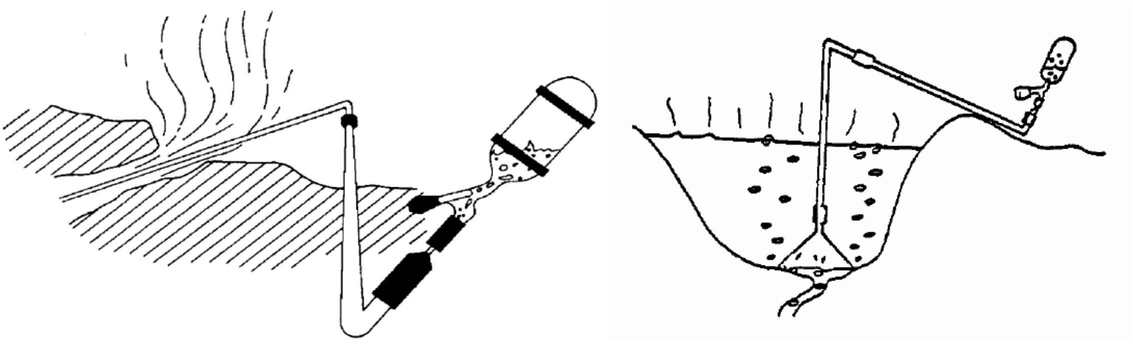


Figure 2: probe-vial arrangement for sampling from vents in the soil and in water/mud ponds: type B probe

5.4 THE SAMPLING VIALS

The vials required for sampling are of ' GIGGENBACH ' type with volumes between 100 and 250 ml equipped with ROTAFLO ® type needle valve (Figure 3)

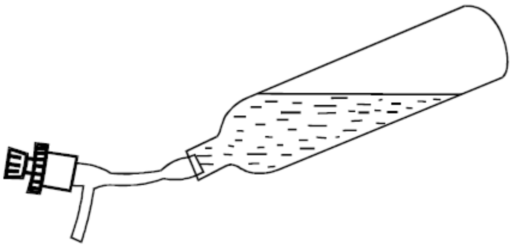


Figure 3: typical scheme of a vial of 'GIGGENBACH' type

5.5 CONNECTIONS

Connect the sampling probe (type A or type B) to the vial using a 10 mm inner diameter PTFE tubing. Silicone tubing connects PTFE tube to probe and vial. Silicone connections should not exceed 2 cm^2 inner surface in contact with sampled fluid.

The silicone connections will be replaced after each sampling in order to avoid absorption and subsequent releases of mercury from inner surface of silicone tubing.

In order to ensure the tightness of the silicone fitting on the PTFE tube the connection must be held by cable ties. Guidance for selecting materials for the connections between the different parts of the sampling equipment is provided in paragraph 5.7.

NOTE: minimizing contact surface with silicone to the technically possible limit is necessary because of its proven affinity for mercury [4]

5.6 BOTTLES AND STORAGE CONTAINERS

Bottle storage material for absorption solution is shown in 5.7 paragraph. Storage vials for solution of potassium permanganate must be obscured and stored away from light in order to prevent further formation of MnO_2.

5.7 SAMPLING EQUIPMENT MATERIALS

The sampling equipment parts in contact with gaseous discharges containing mercury or mercury containing liquids, must be made of the materials listed in Table 1

Table 1 — materials for sampling equipment.

Part of the equipment	Material	**Note**
Type A sampling probe	PTFE	
Type B sampling probe	QUARTZ	
GIGGENBACH vial	Boro-silicate glass	
Connectors	Silicone (with a maximum exposed inner surface < 2 cm^2)	
Tube connecting type A probe and GIGGENBACH vial	PTFE	
Storage containers	Low density Polyethylene (LDPE) High density Polyethylene (HDPE)	

6. REAGENTS

6.1 GENERAL REQUIREMENTS

Use only reagents of certified analytical grade, distilled or deionized water (Resistivity > 18,2 MΩ/cm), all of them with low mercury content.

WARNING: use reagents in accordance with appropriate regulations on health and safety.

6.2 REAGENTS UTILIZATION

Use reagents for absorption solutions and glassware cleaning as follows:

- Sodium Hydroxide, NaOH: high purity (i.e. pellets Fluka, ACS)
- Sodium hypochlorite solution (10% NaOCl) high purity chemicals (i.e. Fluka, or other analytical grade)
- Potassium permanganate with low mercury content (Hg max 0.000005 %)
- Ammonium persulfate $(NH_4)_2S_2O_8$ high purity chemicals (i.e. Carlo Erba, ACS, for analysis)
- Hydroxyil-ammonium chloride ($HONH_3Cl$), 12% m/v high purity
- Deionized water (Resistivity >18,2 MΩ/cm)

In any case, different choices will involve the use of high-purity reagents for analysis with minimum mercury content to. In this cases the content of mercury must be verified in the blank of reagents (see section 6.3.1)

6.3 PREPARATION OF ABSORPTION SOLUTIONS.

6.3.1 REQUIREMENTS

The absorption solutions can be of the following type:

0.3M di sodium hypochlorite solution in 4M NaOH:
Prepared by 180 ml of NaClO solution at 10% (Fluka Analytical, d = 1.25 g/ml) to which are added 160 g NaOH (Fluka, very pure analytical grade), adding deionized water (*) to 1 litre volume with. Over 0,3M NaClO solution also 0,1 and 0,2 M NaClO can be used.

Alternatively the following solutions can be used:

0.3M ammonium persulfate solution in 4M NaOH:
Prepared by 68.4 g $(NH_4)_2S_2O_8$ (Carlo Erba, ACS for analyses) to which are added 160 g NaOH (Fluka, pure for analysis, pellets), adding to 1 liter volume with deionized water (*).

0.2M potassium permanganate in 4M NaOH:
Prepared by 31.6 g KMnO4 (low in mercury Hg < 0.000005) to which 160 g NaOH (Fluka, pure for analysis, pellets)are added, adding deionized water (*) to 1 liter volume with.

NOTE: (*) = Resistivity >18,2 MΩ/cm)

The absorptions olutions are obtained by slow addition of 160 g NaOH pellets to about 600 ml of water. After cooling, 60 ml or 120 ml or 180 ml of 10% solution of reactive oxidizer NaOCl are added to obtain 0,1, 0,2 or 0,3 M NaOCl solutions respectively. All the solutions are then brought to 1 liter volume.

For alternative oxiding agents $(NH_4)_2S_2O_8$, $KMnO_4$ refer to the above prescriptions.

The maximum storage time of absorption solution prior to sampling is one week.

Mercury concentration in blank capture solutions
As an example the purity (Hg content) of some reagents are reported after direct measurement on a Milestone DMA-80 instrument.

It is appropriate that concentrations in blanks do not exceed by more than 30% from the following concentrations:

Reagents in 4M di NaOH	**Hg measured in the absorption solution (§) (μg/L)**
0.3M NaClO	< 0,1
0.3M $(NH_4)_2S_2O_8$	< 0,1
0.2M $KMnO_4$	< 0,1

(§) Mercury content in blank absorption solutions on a Milestone DMA-80 instrument, see Note 2 on paragraph 7.5.2

WARNING: solutions must be stored in the dark and in vials with Cap allowing venting of gases produced in the decomposition of the solutions (oxygen production).

6.3.2 PREPARATION OF VIALS FOR ABSORPTION

The vials, properly washed before in order to eliminate traces of mercury as indicated in Appendix A, are weighed under vacuum and the initial weight P_0 is recorded (the contribution to weight due to air is eliminated by weighing under vacuum). The vials under vacuum are connected to a Tygon ® tube (medical use type) using a silicone fitting to the outlet valve of vial. The void into vials is used to let in the absorption solutions. Through the ROTAFLO tap ® about 80 ml solution are transferred into the vial (1/3 of the volume of vial). Immediately after loading the vial is connected to vacuum again to facilitate the removal of dissolved gases in the absorbing solution. The minimum reachable void is about 20 mbar due to the vapour pressure of mounting solution. Afterwards the vial is again weighted and recorded the weight of vial + fixing solution: P1. The vial so prepared is kept protected from light until sampling time. In order to avoid leaks and decomposition of absorbing solutions, the vials should be used within 72 hours.

7. SAMPLING PROTOCOL

The following paragraphs describe the preliminary operations performed when sampling in the two possible cases of pressurized pipelines or from emitters at ambient pressure, respectively.

7.1 SAMPLING FROM PRESSURIZED WELL-HEAD OR PIPELINES

Sampling method here described can be carried out at well-head, downstream the master valve and on pressurized steam supply pipelines, at the steam side of water/steam separator or other parts of plant in contact with pressurized steam.

Sampling is performed by venting the fluid under pressure through an ASTM 1066 [9] type valves on the pipeline, equipped with taps or flanges.

Before each sampling, fully open the valves on the pipeline to warm the sampling point and let moisture and fouling out. Purge the steam at maximum flow rate for at least 5 minutes. At the end of the first conditioning, close the sampling valves on the pipeline

In order to facilitate all sampling operations consider to use quick connector valves.

7.1.1 PURGING AND STABILIZATION

Before sampling, connect the type A probe (three-way reinforced teflon tube) to the tubing. Open again and completely the sampling valve and let steam out across the probe for at least 15 min (stabilization time) in order to allow warming and line self-cleaning.

At the end of stabilization time the sampling valve on the 3-way connector is fully open and fluxed by steam for at least 10 min more. Slightly regulate the flow to start sampling.

7.1.2 SAMPLING

At the end of purging and conditioning the sampling vial is connected to the sampling line taking care to keep ROTAFLO tap ® beneath the valve body so that the gas can enter the vial (Figure 3) by crossing and bubbling in the liquid phase in the vial.

Sampling is performed by opening the ROTAFLO tap ® and lushing, at a flow rate that avoids excessive heating of the vial.

Overheating causes a slowing of exothermic reaction between CO_2 and H_2S with sodium hydroxide

It is suggested to perform sampling that practically lets to observe bubbling of about 5 gas bubbles per second. The sampling end time is usually chosen when a substantial decrease of gas flow inside the flaask is observed. During sample collection the vial must be kept cooled by wetting the flask with rags soaked in cold water (a container containing water and ice is necessary). In order to improve sampling ASTM D1066 [9] standard sampling probe is suggested. The procedure is applicable to the sampling from the well head and pipes with pressure from a few bars up to about 100 bar

7.2 SAMPLING FROM VENTS, AERAL SOURCES AND WATER SPRINGS

Sampling is performed from gas vents at surface or gas in surface springs or pools. In presence of water a funnel turned upside down is used to let gas flow and sampling. In other cases as a quartz probe is inserted in hot or cold gas vents.

Before sampling insert the probe (or probe funnel quartz) and drain the gas for 15 minutes to allow heating and probe self-cleaning.

7.2.1 PURGING AND STABILIZATION

Slightly open the sampling valve and regulate the flow rate to assure adequate sampling conditions.

7.2.2 SAMPLING

At the end of purging and conditioning the sampling vial is connected to the sampling line taking care to keep ROTAFLO® tap beneath the valve body so that the gas enters the vial (Figure 3) by crossing and bubbling in the liquid phase in the vial.

Sampling is performed by opening the ROTAFLO® tap and lushing, at a flow rate that avoids excessive heating of the vial.

Overheating causes a slowing of exothermic reaction between CO_2 and H_2S with sodium hydroxide

It is suggested to perform sampling that practically lets to observe bubbling of about 5 gas bubbles per second. The sampling end time is usually chosen when a substantial decrease of gas flow inside the ampoule is observed. During sample collection the vial must be kept cooled by wetting the flask with rags soaked in cold water (a container containing water and ice is necessary).

Sampling proceeds exactly as in the previous paragraph, taking particular care to avoid any hint of air and/or liquids (in case of gas from water springs).

7.3 PRE-CLEANING OF SAMPLING EQUIPMENT

All parts in contact with the mercury sampling equipment should be cleaned before sampling following the Protocol of Appendix A

The following parts must be cleaned:

- Sampling probe (internal parts);
- Silicone tubings;
- flasks;
- Storage bottles for reagents as listed in Chapter 6.

The washing procedure is applied to all equipment used.

In order to check the quality of the washing procedure solutions after equipment rinse are conserved to check, eventually or periodically, residual mercury content.

We recommend to prepare the washing solution at the beginning of each sampling campaign.

The quality of reagents must conform to the instructions in paragraph 6.2.

7.4 REQUIREMENTS FOR STORAGE

Keep samples away from light and analyze them as soon as possible, usually within two weeks from sampling.

The portion of tube in the sampling flask connected to the Rotaflo® valve is fluxed by the sampled fluid must be carefully rinsed with water (Resistivity >18,2 MΩ/cm) and kept isolated from external contamination by a plastic or *parafilm* cap.

7.5 REQUIREMENTS BEFORE STARTING ANALYSIS

The analyses can start only after weighing absorbers under the same conditions of the weighing carried out after the filling phase. For Giggenbach type absorbers remove protective sleeve on the sampling tube (see 7.4).

7.5.1 Analysis by CV-AAS

In case of use of $KMnO_4$ solutions/NaOH before analysis with CV-AAS, excess permanganate is reduced with hydroxylammonium chloride (solution to 12% m/v), by adding a few milliliters (1 ml at a time) until complete dissolution of the absorption solution and bleaching of the MnO_2.

7.5.2. Analysis with DMA-80 [16] equipment

Before extraction of the sample from the absorber (see 7.4) sampling tube shall be carefully rinsed with deionized water (Resistivity > 18.2 MΩ/cm) and a few ml of absorption solution are let out to deeply rinse the glass and discarded.

The absorption solution is then collected and transferred in a flask free from mercury contamination for the subsequent analysis. Use typically 0.1-0.2 ml for sample volumes and a quartz cell to minimize the value of blank of mercury.

It has been verified that NaOH interferes with the direct determination of Hg. In case sampling accomplished the requirements of sections 7.1.2 and 7.2.2 no pretreatment is required to direct analysis with DMA-80.

NOTE 1: mercury concentration assessment of the in blank solution (capture solutions formed by NaOH + oxidant) requires the addiction HCl prior to analysis to neutralize interfering NaOH

NOTE 2: The slope of the calibration solutions plot (NaOH + oxidant, referred to in paragraph 6.3.1) after acidification are comparable with that obtained from a mercury standard solution in water. This indicates that oxidants do not interfere in the determination of Hg.

7.6 ANALYSIS

The solution after treatment according to paragraph 7.5, can be analyzed according 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 MASS OF REACTANT IN THE SAMPLING FLASK

The amount of absorption solution loaded in the flask is calculate from the difference in weight after solution transfer (P_1) in comparison to the weight of the empty flask (P_0):

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

The amount of sampled fluid is calculated form the difference of final weight of flask after sampling in respect to weight of the flask including reactants:

$$m_{fluid} = P_2 - P_1$$

8.2 TOTAL MERCURY CONTENT

$$[Hg]_{in\ fluid} = [Hg]_{analysis} \times \frac{P_2 - P_0}{P_2 - P_1}$$

where:

$[Hg]_{in\ the\ fluid}$= mercury cncentration in the fluid; 3 samples average suggested (ng/g);

$[Hg]_{analysis}$ = mercury concentration in the absorption solution (ng/g);

P_0 = initial weight of flask (under vacuum) (g);

P_1 = flask + absorption solution weight (g);

P_2 = final flask weight after sampling (absorption solution + sampled fluid + empty flask) (g);

9. METHOD PERFORMANCE CHARACTERISTICS

Method validation has been performed by cohoperation between CNR and Enel Green Power with several sampling campaign on real geothermal fluids and by submission of results to statistical analysis alloweing to define the following parameters:

- Limit of Detection (LOD often reported as DL);
- Analytical range
- Repeatability uncertainty or type A uncertainty (JCGM 100:2008 “Evaluation of Measurement data – Guide to the expression of Uncertainty in Measurement (GUM) [13]), dealt in the present method as confidence interval (95% probability - IC95%)
- Accuracy estimate by comparison of independent sampling and analysis methods and validation by Fisher Test [15] (ANOVA)

The performance characteristics of the assay were carried out in the absence of reference samples due to the type of sampled fluid, consisting of endogenous high temperature and pressure steam or emanations from the ground. The ability to test samples within different methods and analysis with different analytical techniques has allowed the comparison of tests carried out on the same sample of fluid and application of above mentioned statistical methods.

9.1 Detection Limit

The limit of detection (LOD) was estimated by instrumental absolute limit (LOD 1 pg Hg, in the case of analytical determination with DMA 80 "tri-cells") and related to the amount endogenous fluid normally sampled, considering an average 50% dilution due to capture solution. A standard value for analytical volumes is around 0.1 ml solution. This value leads to calculated LOD of 0.02 µg/kg. Lower values of LOD can be achieved by increasing the volume of solution being analyzed. The analytical LOD value calculated according to the IUPAC definition [17] is reported in reference [16].

9.2 Analytical Range

Analytical range assignment followed a conservative criteria by assessing, as the lower limit, the detection limit (LOD) reported on paragraph 8.2.1 and as the upper limit, the one corresponding to samples at highest concentration analyzed during the setup of experimental method. The analytical range is so included between 0.02 to 0.1 mg/kg in case of use of 0.1 ml solution for analysis with DMA80 "tri-cells".

9.3 Confidence interval and type A uncertainty

The confidence interval is defined as the range of possible values around the observed avergae that corresponds to a default likely probability (usually the required percentage is of 95%. A typical range covers a 95% probability but different ranges can be take in to account (64%, 90% etc.).

In this method the uncertainty is calculated as repeatability uncertainty (type A uncertainty according to JCGM 100:2008 "Evaluation of Measurement data – Guide to the expression of Uncertainty in Measurement (GUM) [13]) and the distribution function of the average is assumed to follow a distribution function of type ‘Student’ [14]. In this study several samplings have been performed form pressurized steam pipes at two geothermal power plants using sampling tasks of Giggenbach type with three different absorption solutions in NaOH carrying different oxidation agents and a different method used by EGP/CNR, which involves sampling with vials of 1 L preemptively placed under vacuum and subsequent absorption by injection of acidic $KMnO_4$ solution. The several type of sampling system are summarized below:

1. Giggenbach flask/NaOH with $KMnO_4$ 0,2 M as oxidizing agent
2. Giggenbach flask /NaOH with $NH_4S_2O_8$ 0,3 M as oxidizing agent
3. Giggenbach flask /NaOH with NaClO (01, 0,2 e 0,3 M) as oxidizing agent
4. Fiala sotto vuoto e aggiunta di $KMnO_4$ (0.21 M $KMnO_4$)/H_2SO_4(1.8 M H_2SO_4) as oxidizing agent introduced after sampling

For each of the above mentioned solution types 6 sampling hav been performed and confidence interval calculated form repeatability uncertainty (type A uncertainty according to JCGM 100:2008 "Evaluation of Measurement data – Guide to the expression of uncertainty in measurement (GUM) [13]) with the following definitions:

TYPE A UNCERTAINTY $U = t_{95\%}\frac{s}{\sqrt{n}}$

With a coverage factor corresponding to $t_{95\%}$ of a Student type distribution with n-1 degrees of freedom (n number of samplings and hence number of measurements). By this definition the calculated confidence interval is:

CONFIDENCE INTERVAL $IC_{95\%} = 2t_{95\%}\frac{s}{\sqrt{n}}$

The $t_{95\%}$ is the auxiliary t variable parameter of a Student distribution of a mean corresponding to a probable range $[-t_{95\%}; +t_{95\%}]$ with a 95% probability. The s and n parameters are the experimental standard deviation of the sample and the number of measurements:

EXPERIMENTAL STANDARD DEVIATION $s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}}$

The parameter $\overline{x}$ is the arithmetic average of the sample:

ARITHMETIC AVERAGE: $\overline{x} = \frac{\sum_{i=1}^{n} x_i}{n}$

The confidence interval has been calculated with a mean following a *Student* type distribution [14]

Table D.1 shows the absolute value and percentage value of teh $IC_{95}\%$ (the latter obtained by dividing the $IC_{95\%}$ by the mean value of measurements (EGP/CNR measurement campaigns)

TEST 18/03/2016	Absorption solution $KMnO_4/H_2SO_4$ EGP	Absorption solution hypoclhorite 0.1 M CNR	Absorption solution hypoclhorite 0.2 M CNR	Absorption solution hypoclhorite 0.3 M CNR
LE PRATA PLANT	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
arithmetic mean (ng/g)	22,5	22,5	33,3	20,9
madian (ng/g)	22,6	21,7	32,7	20,4
experimental standard deviation (ng/g)	1,6	1,5	3,7	2,5
$IC_{95\%}/2$ (ng/g)	2,6	1,8	6,0	4,0
result (ng/g)	22,5	22,5	33,3	20,9
$IC_{95\%}/2$	11,5%	8,0%	17,9%	19,1%
$IC_{99\%}/2$	21,1%	13,3%	32,8%	35,0%

Table D.1 – Statistical analysis and calculation of the confidential interval. The IC95% is necessary for acceptance of analysis replicates in case of 3 sample measurement (see paragraph. 9.5).

9.4 Estimate of method accuracy in absence of reference samples by comparison of results from different methods and ANOVA statistical analysis (Fisher test [15])

In the absence of standard samples the results obtained with 4 types of sampling method, different absorption solution and analytical methods have compared as discussed in section 8.2.1.d. The values obtained on multiple replicate within the same sampling/analysis method allowed calculation of the main statistical parameters including the mean, standard deviation, the 95% confidence interval. By the mean value measured for each method, the ricovery percentage was calculated. The obtained value is a first estimate of accuracy. The values reported in table D. 2 have enabled the calculation of following estimate of the percentage accuracy:

TEST 28/10/2015		Absorption solution $KMnO_4/H_2SO_4$ (ng/g)	Absorption solution persulfate/NaOH (ng/g)	Absorption solution hypochlorite 0,1M/NaOH (ng/g)	Absorption solution $KMnO_4$/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
arithmetic mean (ng/g) (A)		28,9	18,2	21,4	21,1
median (ng/g)		28,7	18,8	22,1	20,8
experimental standard deviation (ng/g)		1,2	2,5	1,8	2,0
$IC_{95\%}/2$ (ng/g)		2,0	3,9	2,9	3,2
Result (ng/g)		28,9	18,2	21,4	21,1
totael average(ng/g) (B)		22,4			
Recovery% (A/B X 100)		129	81	96	94

Tabella D.2 – Satistical analysis of data and calculation of percentage recovery as an estimate of accuracy

The results have allowed calculation of an estimate of accuracy below 30%

Comparison between methods

Data obtained from each method has been compared by Fisher test [15] (ANOVA). Before data comparison an OUTLIER assessment has benne performed. The values above the confidence interval in respect to the average values have been discarded. The OUTLIERS satisfied the following criteria:

$$OUTLIER\ if\ |x - med| > \frac{IC_{95}}{2}$$

The confidence interval has been calculated as:

$$IC_{95} = 2\ t_{95}\frac{s}{\sqrt{n}}$$

Where s and n are the standard deviation and the number of data respectively:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}}; \quad n = \text{number of samples}$$

Fisher test [15] has shown a mutual coherence between the various variants of Giggenbach type samplings (NaOCl, $(NH_4)_2S_2O_8$, $KMnO_4$ as oxidizing agents) (positive ANOVA test) and a significant difference in respect to the $KMnO_4/H_2SO_4$ sampling. This is due to differences in accuracy between methods (see the reported graph)

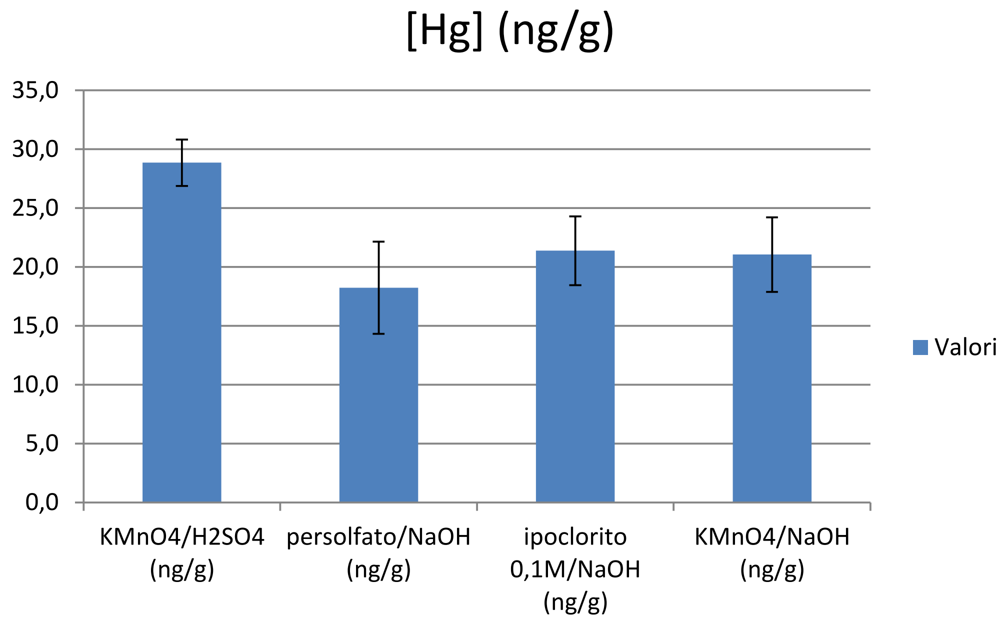


Fig. 4*: Comparison of mercury content observed with different sampling/analysis methods. In the first case sampling with evacuated flask followed by* $KMnO_4/H_2SO_4$ *treatment is significantly different (non passed test Fisher) form other methods with modified Giggenbach method and axydizing agents NOCl,* $(NH_4)_2S_2O_8$, $KMnO_4$.

9.5 REPLICA’S ACCEPTANCE RANGE

This paragraph shows the suggested criteria for the evaluation of the measurements obtained in the case of three replicates. A method considered appropriate by the working group of the present method for accepting three replicates and identification of outliers is based on comparison of measurements in respect to interval of confidence at 99% level evaluated in specific measurement runs.

It can be assumed that the IC99% confidence interval can be evaluated on a periodic basis using a number of replicated ' statistically significant ' (suggested at least 6 replicated) measurements and on the basis of this confidence interval to judge the acceptability of measurements conducted with a small number samples (typically 3).

As mentioned above the parameter to be considered to identify outliers is the IC99% obtained according to the following relationships:

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

where:

- IC_{99} is the 99% confidence interval of measurements used for statistical analysis of data (see tab. D.1)
- s is experimental standard deviation:

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

- x_i is the measure of index I among the n measured samples
- $\bar{x}$ is the average of measurements
- n is the number of samples analyzed (n=6 in table D.1)
- $IC_{99\%}$% is given by the following:

$$IC_{99}\% = \frac{IC_{99}}{\bar{x}} X100$$

By this definition the confidence interval is calculated in specifically dedicated measurements runs, periodically repeated, while the value is used for the next measurements. In the specific case the relative confidence interval is used to estimate the absolute confidence interval of the median value of a group of measurements (e.g. the case of 3 replica):

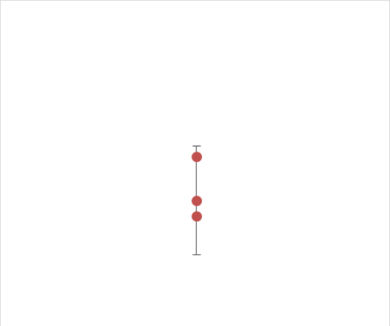
$$IC_{99} = \frac{IC_{99}\%}{100} med$$

The outliers are lined out when their value satisfies the following rule:

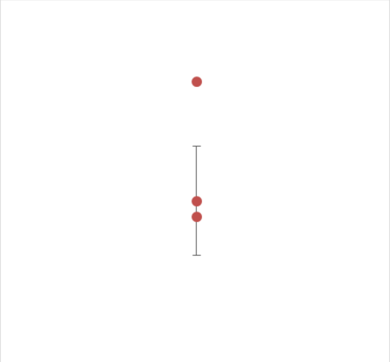
$$|x_i - med| > \frac{IC_{99}}{2}$$

Where the median value is over 3 replica. According to this criteria some cases can appen:

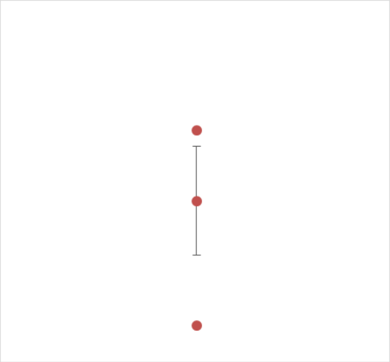
Caso 1: the 3 replica have not been discarded in the analytical phase. If all the data satisfy the above-mentioned criteria, the result is the median value of the 3 replica.



Caso 2: Only two data a responding to the above mentioned criteria and the result is the mean value of the two remainingg measurements.



Caso 3: 2 outliers are observed and value assigned to measurement is the third remaining.



10. REPORT CONTENT

The final report must contain at least the following information:

a) Reference to present method;
b) Identification and ID of samples;
c) Description of plant and process in the sampling area;
d) Operating conditions of plant during sampling;
e) Sampling point identification and position in the plant;
f) Number of sampling points, number of replica and identification of sampling points;
g) Sampling time and description of operating conditions during sampling;
h) Volume of sampled gas;
i) Type of absorbers;

j) Type of absorption solution;
k) Analytic procedure (reducing agent, manual/automatic injection in the flux of carrier gas etc.);
l) Mercury contenta as mass concentration;
m) Eventual exceptions from the present method adopted in sampling and analysis.

ANNEX A: CLEANING PROCEDURE OF SAMPLING EQUIPMENT

A.1 Generality

The cleaning of equipment is carried out in the laboratory in accordance to good laboratory practice. This appendix suggests some options for cleaning equipment, storage bottles and absorbers are provided.

A.2 Sapling line

After each measurement, rinse the sampling line, connecting pipes and absorbers (vials) with a solution of HNO_3 to 10% m/m

WARNING: The amount of mercury present in washing solution can be used to verify the quality of sampling. In case that preliminary sampling runs have shown no detectable amounts of mercury, the analysis of this solution may be neglected in further similar samplings.

A.3 Absorbers and bottles for samples and reagent solutions

The washing procedure of absorbers and reagents storage containers has a five step is divided in a 5 step process:

1. Rinse all bottles with 50 ml 10% HNO_3 al solution (low mercury content or mercury depleted), shaking bottles and absorbers for 5 min.
2. Rinse with demineralized water (*).
3. Rinse with 50 ml absorption solution (2% $KMnO_4$ low mercury content, 10% H_2SO_4 low mercury content), shaking bottles and absorbers for 10 min.
4. Store rinse solution in P.E. bottles by identifying absorbers and wash run for eventually necessary further analytical controls.
5. Rinse absorbers with 2 ml di solution hydroxyl-ammonium ($HONH_3Cl$), 10% m/m.
6. Rinse several times with water demineralized (*)

NOTE: (*) = Resistivity >18,2 MΩ/cm)