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Sampling and analysis procedure for calculating hydrogen sulphide leaving cooling towers in geothermal power stations

IGG/CNR-4 METHOD
(M4)

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Method: IGG/CNR -4 (M4)
Rev:0
Edition: 14.06.2018

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1. PURPOSE AND SCOPE OF APPLICATION

This method is an adaptation of the UNICHIM 634 method "Measurements at emission points, gaseous flows conveyed, determination of hydrogen sulphide using a volumetric method" [1] for the correct collection and analysis of hydrogen sulphide in the gaseous effluents emitted by cooling towers in geothermal power plants. This method extends the field of application to the emissions by geothermal power stations and the measurement range for the above-mentioned method to the following values:

1. Concentration of hydrogen sulphide between 0.2 and 18 mg/Nm^3 for an aeriform sample of 200L.
2. Concentration of hydrogen sulphide between 19 and 25 mg/Nm^3 for an aeriform sample of 100L.

The method is applicable a temperatures between 10 °C and 60 °C

2. REFERENCE DOCUMENTS

This method refers to dispositions contained in other publications. These references to standards with related updates in the text and are listed below.

[1] UNICHIM 634 “Measurements at emission points, gaseous flows conveyed, determination of hydrogen sulphide using a volumetric method"

[2] APAT / IRSA-CNR 2003 Manual Analytical methods for Water – Vol II – Sect. 4000 Inorganic non Metallic – Method 4160

[3] APHA Standard Methods, 21st ed., Method 4500-S2-D (2005) (EPA 376-2).

[4] HACH LANGE LCK 653 method Sulphides 0.1 - 2.0 mg/L

[5] UNI EN ISO 16911-1:2013 “Emissions from a stationary source, manual and automatic determination of flow speed in pipelines, part 1: manual reference method”.

[6] UNI EN 15259:2008 “Air Quality, Stationary Source Emission, requirements for measurement sections and sites and objectives, measuring plan and report”.

[7] UNI EN 13284-1: 2003 “Stationery source emissions - Calculation of mass concentration of powders at low concentrations - Manual gravimetric method".

3. TERMS AND DEFINITIONS

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

Hydrogen sulphide: hydrogen sulphide (H_2S) in gaseous form.

Sampling: sampling at constant or variable flow at the minimum number of sampling points indicated in the sampling plan, as specified in UNI EN 13284-1:2003. For the sampling a gas, iso-kineticism must not be guaranteed because the substance of interest is not present either as solid particulate or in droplets.

Absorber: IMPINGER type device in which gaseous hydrogen sulphide is absorbed by an absorption solution.

Drift: drops of water circulating in the cooling tower that become incorporated into the air flow from the tower and emitted into the atmosphere

Cell: portion of an forced draught cooling tower equipped with a fan and walls sending air out of the tower which can be considered as an elementary emitter. In the case of a natural draught tower, the cell is made up of the tower itself

4. PRINCIPLE

The fluid is sampled near the cooling tower outlet mouth using a probe connected to teflon pipes to convey the sampled gas to the absorbers. There is no dry solid particulate in the cooling tower effluent of geothermal plant, so that it is not necessary to use a filter in the sampling system. Three absorbers are used: the first is empty to collect the condensing vapour and *drift*; the second and third contain the hydrogen sulphide capture solution based on zinc [$Zn(CH_3COO)_2$].

A sample flow of gas effluent is extracted in a representative manner from the stack of one of the coolant tower cells for a given period of time at a controlled flow rate of no more than 2L/min and volume between 100L and 250L.

At the end of the sampling period, the absorption solution is collected and can be analysed immediately. Alternatively, the solution can be analysed in the laboratory after alkaline stabilization. In this case, the analytical determination must be performed within two weeks of taking the sample.

Sampling and analysis data are combined and the results are expressed in milligrams of hydrogen sulphide per harmonised cubic meter (mg/Nm^3) of dry gaseous effluent.

The analysis of hydrogen sulphide can be performed in accordance with the analytical protocols of the UNICHIM Method 634, integrated with APHA Standard Methods, 21st ed. Method 4500-S2-D (2005) (EPA 376-2).

The flow rate measured refers to the aeriform moisture at the temperature and pressure conditions of the tower at the sampling point; the dry to wet correction is calculated by assuming that the aeriform on output from the tower is in saturation conditions (the error introduced by this approximation is negligible compared to the flow measurement error). This correction is necessary because the analytical concentration measured in the field is related to dry gas.

5. SAMPLING EQUIPMENT

5.1 SAMPLING CONDITIONS

If a gas injection point different from the one sampled is present at the measuring cell (for example gas from the gas extractor outlet and from the AMIS plant outlet), sampling must be carried out at a sufficient distance from the gas inlet point in order to avoid interference with the amount of analyte taken. For samples taken from forced draught towers comprising several cells, sampling must be carried out in a cell not affected by the introduction of gas (by closing the valve on the gas supply pipe to the cell itself).

5.2 GENERAL REQUIREMENTS

The sampling equipment comprises:

1. A probe with Teflon tubes 10mm in diameter. For this application an uncontrolled and no-nozzle temperature probe is used. The probe is not thermostat-controlled because the temperature of the sampled gases is similar to ambient temperature.

2. Gas absorption line made up a series of absorbers (absorber 1 empty, absorbers 2 and 3 used for 100 ml of zinc acetate absorption solution).

3. Silica gel to eliminate residual moisture

4. A suction pump to ensure the required flow of sampled gas (2L/min). This pump must be fitted with a volumetric (positive displacement) meter to quantify the volume of sampled gas (150L - 250L).

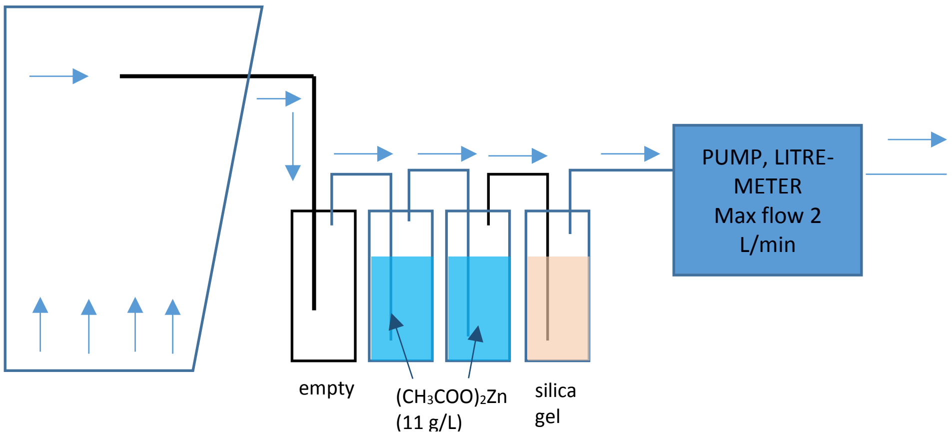


Figure 1 - Sampling system used for taking samples of hydrogen sulphide.

Figure 1 shows the layout of the system used for sampling hydrogen sulphide gas leaving the cooling towers of geothermal power plants. Figure 2 shows the same sampling system layout with the addition of traps containing sulphuric acid 1% vol (100mL) to absorb ammonia (NH_3). This latter configuration allows selective absorption of ammonia while the hydrogen sulphide, which is not very soluble in the ammonia absorption acid solution, is instead blocked in the downstream absorbers containing zinc acetate.

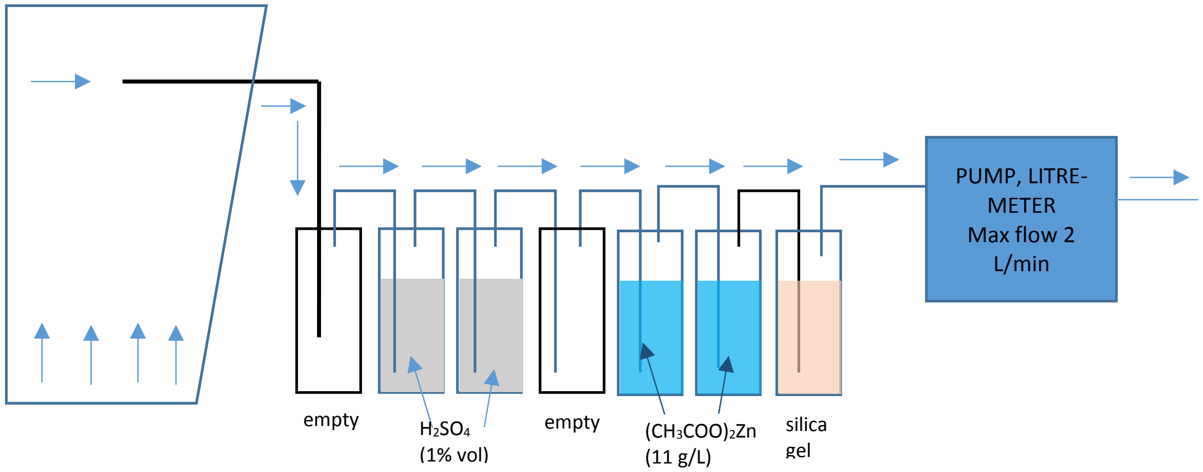


Figure 2 – Sampling system used for taking samples of ammonia (NH_3) and hydrogen sulphide (H_2S).

5.3 SAMPLING EQUIPMENT

The equipment includes a non-heated sampling probe in one of the materials listed in paragraph 5.7

5.4 ABSORBERS

To ensure efficient collection, absorbers must be positioned in series. An additional vacuum absorber (volume about 250ml) is used up-line of these absorbers as a condensation trap.

5.5 CONNECTIONS

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 hydrogen sulphide.

The silicon connections connecting the various traps should be short and the surface in contact with the fluid should be less than 2 cm^2 for each coupling.

5.6 STORAGE FLASKS AND CONTAINERS

The material used for bottle storing absorption solutions is indicated in para 5.7. If laboratory analysis is performed, storage bottles for the absorption solution (6.3.2) should be stored in a refrigerated area, protected from light to avoid oxidation of H_2S.

5.7 MATERIALS FOR SAMPLING EQUIPMENT

The parts of the sampling apparatus in contact with the gaseous effluent are made with the materials shown in Table 1.

Table 1 - Materials for sampling equipment.

Part of the equipment	Material	**Notes**
Sampling probe (suction tube)	PTFE (teflon)	
Absorbers (Impinger type)	Borosilicate glass	250 mL or 180 mL
Connection couplings between absorbers	Silicone (with a total internal surface <2 cm^2)	
Connection pipes (between the last absorber and silica gel and between the silica gel and the pump)	Silicone	
Storage flasks with cap.	Low density polyethylene (LDPE) for NH_3 High density polyethylene (HDPE) for NH_3 Glass for H_2S	

5.8 SUCTION UNIT

The suction unit must be gas-tight (see 7.3.2 for seal tests) and able extract at least the required gas flow rates from the duct (2L/min).

Non-return valves can also be used to stop gas flow or backflow caused by low pressure on the sampling line.

Flowmeters (variable section regulator, plate with orifice, etc.) are strongly recommended in order to monitor the flow rate. Flowmeters must be subjected to sealing tests and be calibrated at regular intervals.

5.9 GAS VOLUME MEASURING UNIT

Dry-base flow measurements must be used to measure gas volumes. The requirements for dry-base flow measurements are as follows:

1. Inclusion of a silica gel filter up-line of the pump
2. Gas-tight pump
3. Flow adjustment flowmeter
4. Dry gas volume meter (uncertainty <2% at required flow rate of 2L/min) with correction for the associated pressure and temperature measurement (measurement uncertainty <1%).

6. REAGENTS

6.1 GENERAL INFORMATION

Only use recognized analytical reagents and distilled or deionized water:

1.	Sulphuric acid (H_2SO_4)	Solution 95-97% m/m analytical grade
2.	Zinc Acetate $CH_3COO)_2Zn)$	Crystalline
3.	Iodine (I_2) 0.05 M (0.1 N)	Commercially available solution
4.	Sodium thiosulphate ($Na_2S_2O_3$) 0.05 M (0.1 N)	Commercially available solution
5.	Hydrochloric acid (HCl)	Solution 37% (w/w), d=1.186 g/cm^3
6.	Soluble starch	Powder
7.	Potassium hydroxide (KOH)	Tablets
8.	Sodium Hydroxide (NaOH)	Tablets
9.	Pure acetic acid (CH_3COOH)	Solution 100% (p/p), d=1.050 g/cm^3
10.	Ultrapure water	(Resistivity >18.2 MΩ/cm)

CAUTION Use reagents in accordance with applicable health and safety regulations.

6.2 REAGENTS FOR PRE-CLEANING OF SAMPLING EQUIPMENT

Use appropriate reagents for pre-cleaning the sampling equipment; see point 7.2.

6.3 SELECTING ABSORPTION SOLUTIONS

6.3.1 General Information

The absorption solution comprises a 0.1N solution of zinc acetate prepared from anhydrous salt or with crystallization water. In the latter case, the concentrations must always refer to zinc acetate as $(CH_3COO)_2Zn$.

Note: if the sampling line is complete and also includes an ammonia absorption line, the other reagents used must also be characterized by analytical grade purity.

6.3.2 Zinc acetate absorption solution 0.1N

Take 11g of $(CH3COO)_2Zn.2H_2O$ or 10g of anhydrous $(CH_3COO)_2Zn$, bring up to a volume of 1L by adding extremely pure deionised water and mix completely. Store in dark glass bottles (the solution is stable up to a seventh standard solution I_2 0.1N: ready to use.

6.3.3 Standard solution I_2 0.1N

Standard solution I_2 0.1N :ready to use.

6.3.4 Standard solution $Na_2S_2O_3$ 0.1N

Standard solution $Na_2S_2O_3$ 0.1N :ready to use.

6.3.5 HCl solution 1:1

Add 100mL of concentrated HCl to 100 mL of water, while stirring. Store in a glass bottle (the solution is stable for at least one year).

6.3.6 Starch solution

Method: dissolve 1g of soluble starch in about 5mL of water and pour into 200mL of boiling water. Boil for 2 or 3 minutes, leave to rest for a few hours and then filter. Add 0.25g of salicylic acid or a few drops of toluene to prevent fermentation (point 4.5 Unichim Method 634)

Method B: prepare a paste comprising 6 g of soluble starch in a little cold water. Place the paste in 1L of boiling water and add 20 g of KOH while stirring. Leave to rest for two hours and then add 6 mL of pure acetic acid. Mix and add concentrated HCl to reach pH 4. Store in a dark glass bottle (the solution is stable for at least one year).

6.3.7 NaOH 6 M solution

Take 24g of NaOH in tablets, make up to a volume of 100mL with ultrapure water and mix completely. Allow the solution to cool, then place it in a polyethylene bottle of suitable capacity.

6.3.8 H2SO4 solution for NH3 absorption

10mL concentrated H2SO4 to one litre of ultrapure H_2O. Some drops of methyl orange are added.

6.4 REAGENTS FOR RINSING THE SAMPLING LINE AFTER SAMPLING

6.4.1 HNO_3 solution, 10% m/m

Prepare a solution of $HN0_3$ 10%m/m by adding 150mL of HNO_3 (d=1,41kg/L 65% m/m) to 1L of ultrapure water.

6.4.2 Washing with detergent (‘decontamin’ type) and rinsing with ultrapure water.

7. PROCEDURE

7.1 GENERAL REQUIREMENTS

The sample analysed must be taken from a sample of at least 200L of gas.

7.2 PRE-CLEANING THE EQUIPMENT

All parts of the sampling equipment (Table 1, section 5.7) and reagent storage containers (point 6) that may come into contact with the sampled fluids and reagents used must be cleaned before taking samples.

Cleaning will be performed using the procedure described in paragraph 6.4 for the probe and connecting pipes.

It is advisable to prepare washing solutions as required and in any case at the beginning of each experimental sequence.

The quality of the reagents used must comply with paragraph 6.1.

7.3 PREPARING AND INSTALLING THE EQUIPMENT

7.3.1 Installing the absorbers

Three absorbers are used: the first is empty to collect the condensing vapour and *drift* carried; the second and third contain:

1. 100mL of absorption solution, as per paragraph 6.3.2.

The above-mentioned absorbers must be installed in a cooler or water/ice bath to ensure a constant temperature of the sampled gas throughout the sampling procedure.

WARNING: Take appropriate safety measures to prevent personal injury and/or damage to the equipment in the event of breakage or leaks affecting the absorbers.

7.3.2 Seal tests

It is advisable to perform a seal test before each sampling. The seal test is carried out by sealing the nozzle and starting up the suction unit. Once the minimum pressure has been reached, the leak flow rate must be less than 2% of the rated sampling flow rate.

7.3.3 Installing the equipment in the sampling position

Install the assembled and complete sampling equipment in the sampling position on the walkway and place the sampling probe in the sampling aperture of the cooling tower cell selected for measurements. All sampling equipment installed on the walkway must comply with applicable safety regulations. Avoid any unintentional gas flow through the sampling equipment before taking samples if there is low pressure in the cell. The sampling probe comprises one or more teflon tubes (10mm diameter) secured to a rigid beam that can be fitted inside the cell through a flanged pipe located about 2m from the walkway.

1. Place 1 empty 250mL glass absorber as a moisture trap
2. Place and connect the second and third absorbers containing the absorption solution
3. Place and connect the silica gel trap
4. Place and connect the sampling line to the gas suction system (adjustable flow pump equipped with volumetric meter, thermometer and silica gel tower for gas drying)
5. Connect the sampling line to the absorber set.

7.4 SAMPLING

Assemble the equipment and check whether there are any leaks. Note the readings shown on the gas and ambient pressure measuring device. Start the sampling pumps, set the sampling rate and extract gaseous effluent from the duct. Note the temperature and pressure readings shown on the gas measuring device at the outset and for every plunge.

Take samples in conformity with UNI EN ISO 16911-1:2013 and UNI EN 15259:2008. Three repetitions must be performed in parallel for each sampling session. Once the sampling time has elapsed, stop extracting gaseous effluent. Record the readings (volume taken from the sampling device or calculated as the difference of the volumes recorded by the volumetric meter at the end and beginning of sampling) of the gas measuring device, the ambient pressure and the temperature of the sampled gas. Details of the sampling operations are shown below:

1. Sample the gas by setting a suction flow rate not higher than 2L/min (visually check the gas bubbling inside the absorbers filled with absorption solutions) for the time required to reach about 200 L of dry gas.
2. About halfway through the sampling time, measure the temperature at the pump outlet and the barometric pressure. It is assumed that the aeriform temperature may be considered as constant.
3. At the end of sampling: transfer the contents of the impinger used to determine NH_3 into two 100 mL plastic bottles. Transfer the solutions in the last H_2S absorbers into two 250mL transparent glass bottles, always taking care to wash any deposits attached to the walls of the absorbers with a little ultrapure water; Then perform chemical analysis, as described in the next paragraph. The washing solutions must be combined with the corresponding absorption solutions for subsequent analysis.

7.5 DISMANTLING THE EQUIPMENT

7.5.1 Collecting absorption solutions from absorbers

Use new and separate flasks to collect the absorption solution for each labelled and identified absorber.

7.6 SAMPLE STORAGE REQUIREMENTS

Samples in glass bottles, stabilized with NaOH, must be stored at a temperature of less than 6 °C (refrigerator) and in the dark. The samples should be analysed within two weeks of sampling.

7.7 ANALYSIS

This section describes the analytical procedure to be followed for solutions intended for immediate field analysis (protocol 1) and for stabilized solutions intended for subsequent analysis in the laboratory (protocol 2). For titration with 0.1N thiosulphate using 2mL of acidified $I_2$0.1N, special care must be taken to ensure that the sample is added to the I2 acid solution and not vice versa. Make sure that the pH of the solution remains acid, otherwise add more HCL 1:1.

7.7.1 Field analysis procedure - protocol 1

Separately analyse the portions from the absorption hydrogen sulphide (contents of the 2nd and 3rd absorbers (5th and 6th absorbers in the event of simultaneous sampling of NH_3) using the following method:

1. Pour 2 ml of Iodine 0.1N and about 20mL of ultrapure water into a flask.
2. Acidify with approximately 2mL of HCl 1:1 and then add the first portion (2nd impinger), making sure that the final pH of the solution is acid (with litmus paper).
3. Titrate any excess iodine with 0.1N sodium thiosulphate by adding about 0.3mL of starch solution just before the colour change (pale straw yellow).
4. Perform the same measurement on the second portion (3rd impinger) and on 100mL of the solution used for fixing (white).

NOTE: it is essential, in order to ensure that the iodine solution does not undergo non-acidic pH variations and therefore generate iodide and hypoiodous acid, that the analysis solution is added to the iodine solution.

7.7.2 Laboratory analysis procedure - protocol 2

If it is not possible to carry out titration immediately after sampling, each of the two portions containing absorption solution as per 6.3.2 should be stabilized with 2 mL of NaOH 6 M (240 g/L). Then proceed as described below:

1. Pour 2 ml of Iodine 0.1N and about 20mL of ultrapure water into a flask.
2. Acidify with approximately 5mL of HCl 1:1 and then add the first portion (2nd impinger), making sure that the final pH of the solution is acid (with litmus paper).
3. Titrate any excess iodine with 0.1N sodium thiosulphate by adding about 0.3mL of starch solution just before the colour change (pale straw yellow).
4. Perform the same measurement on the second portion (3rd impinger) and on 100mL of the solution used for fixing (white).

NOTE: it is essential, in order to ensure that the iodine solution does not undergo non-acidic pH variations and therefore generate iodide and hypoiodous acid, that the analysis solution is added to the iodine solution.

7.7.3 Calculating the amount of H_2S in the absorption solution

To calculate the amount of H_2S in the absorption solutions, proceed as follows:

$$H_2S_{al1} = (V_{tios.-white} - V_{tios.al1}) * 0.1 \times 17.04$$

$$H_2S_{al2} = (V_{tios.-white} - V_{tios.al2}) * 0.1 \times 17.04$$

$$H_2S_{tot.} = H_2S_{al1} + H_2S_{al2}$$

where:

H_2S_{al1}: amount of hydrogen sulphide in the first absorption solution (mg)

H_2S_{al2}: amount of hydrogen sulphide in the second absorption solution (mg)

$H_2S_{tot.}$: total amount of hydrogen sulphide (mg)

$V_{tios.-white}$: volume of thiosulphate solution used to titrate the fixing solution (white) (mL)

$V_{tios.al1}$. : volume of thiosulphate solution used to titrate the first absorption solution (mL)

$V_{tios.al2}$: volume of thiosulphate solution used to titrate the second absorption (sample) (mL)

8. EXPRESSION OF RESULTS

8.1 HYDROGEN SULPHIDE CONTENT16

The concentration of hydrogen sulphide in the gaseous effluent is calculated using the following formula:

$$C_{H_2S} = \frac{H_2S_{tot.}}{V_{gas}} \cdot 1000 \qquad (1)$$

where:

C_{H_2S} = concentration of hydrogen sulphide measured in the tower aeriform (mg/Nm^3 - dry); Mean value for three samples replicated in parallel

$H_2S_{tot.}$ = mass of hydrogen sulphide collected in absorbers (mg);

V_{gas} = volume of dry aeriform sampled under normal conditions (L).

WARNING The volume expressed in Nm^3 is considered to be dry gas, harmonised at 0 °C (273.15K) and 1013.25mBar.

8.2 VOLUME OF GAS UNDER REFERENCE CONDITIONS

The volume of gas under reference conditions is calculated as follows:

$$V_{gas} = V_{meas} \cdot \frac{273.15}{273.15+T_{meas}} \cdot \frac{P_{meas}}{1013.25} \qquad (2)$$

where:

V = volume of dry gas (L);

V_{meas} = volume of dry gas in litres, under effective conditions; in the event of moist gas measurement devices, recalculate the volume of moist gas in dry conditions;

T_{meas} = mean temperature of the gas volume measurement device in °C;

P_{meas} = mean pressure in the gas volume measurement device in mbar (hPa).

8.3 CALCULATING THE GAS FLOW FROM THE COOLING TOWERS

To obtain the flow rate value under different conditions, the following calculations are required:

calculating the dry aeriform flow rate

$$Q_{\mathrm{dry}} = \frac{Q_{\mathrm{moist}} \cdot (P_{\mathrm{amb}} - P_{H_2O})}{P_{\mathrm{amb}}} \qquad (3)$$

calculating the dry aeriform flow rate under normal conditions

$$\mathrm{QN}_{\mathrm{dry}} = \frac{P_{\mathrm{amb}} \cdot Q_{\mathrm{dry}}}{1013{,}25 \cdot (T_{\mathrm{tower}} + 273{,}15)} \cdot 273{,}15 \qquad (4)$$

calculating the moist aeriform flow rate under normal conditions

$$\mathrm{QN}_{\mathrm{moist}} = \frac{P_{\mathrm{amb}} \cdot Q_{\mathrm{moist}}}{1013{,}25 \cdot (T_{\mathrm{tower}} + 273{,}15)} \cdot 273{,}15 \qquad (5)$$

Where:

Q_{dry} = tower flow rate - dry aeriform (m^3/h)

Q_{moist} = measured flow rate of the tower - moist aeriform (m^3/h)

P_{amb} = atmospheric pressure at the time of sampling (mbar)

$P_{H}2_{O}$ = water vapour tension at sampling point (mbar)

T_{tower} = temperature of the tower at the sampling point (°C)

QN_{dry} = flow rate of the tower - dry aeriform under normal conditions (Nm^3/h)

QN_{moist} = flow rate of the tower - moist aeriform under normal conditions (Nm^3/h)

8.4 ACCEPTANCE OF REPETITIONS

See appendix A

8.5 PERFORMANCE CHARACTERISTICS

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

1. Estimated lower detection limit of 0.2 mg / Nm^3;
2. standard experimental deviation equal to 0,7 ng/Nm^3 for a mean concentration of 5.2 ng/Nm^3.

Table B.1 lists the measurements taken and the values of the CI_{99}% confidence interval calculated on the basis of measurements taken by Arpat at the Enel Green Power geothermal power plant in Chiusdino.

ARPAT CGTE Test Chiusdino 14.02.2017	4.57
	5.72
	3.77
	5.08
	5.85
	6.03
	5.34
	5.23
sum	41.59
mean	5.20
median	5.29
experimental standard deviation (s)	0.74
CV% (s/mean*100)	14.28
number of data	8.00
IC_{95}(%)	23.9
IC_{99}(%)	35.3

Table B.1 - Statistical analysis to identify the main statistical indicators and the Confidence Interval for repeatability acceptability.

9. TEST REPORT

The test report must contain at least the following information:

1. reference to this method;
2. reference to the sampling report
3. identification and number of sample(s);
4. description of plant and process;
5. plant operating conditions;
6. position of sampling points;
7. number of sampling points and identification of the sampled cell;
8. sampling time;
9. sampling volume(s);
10. type of absorbers;
11. total Hydrogen Sulphide content as a mass concentration;

Certain information may be recorded in the sampling report referenced by the test report.

APPENDIX A: ACCEPTABLE OF REPLICATED DATA (THREE REPLICATIONS IN PARALLEL)

Once the acceptability of the single sample has been evaluated in accordance with the procedure highlighted in paragraph 5.4 of this method, the most appropriate statistical method for the acceptance of the three replicates and identification of outliers is based on the Confidence Interval (IC) 99% (assessed in advance on at least 6 replicates) using the following formulas

$$IC_{99} = t_{99} \cdot \frac{s}{\sqrt{n}} \qquad \text{eq. 1}$$

Where:

1. IC_{99} - 99% confidence interval calculated through at least 6 replications
2. t_{99} - *Student t (α 0.01; n. tests)*
3. s - experimental standard deviation:

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

1. x_i is the i-nth measurement
2. $\bar{x}$ is the arithmetic mean of the measurements

3. n. is the number of measurements performed
4. $CI_{99}\%$ is given by the following formula:

$$IC_{99}\% = \frac{IC_{99}}{\bar{x}} 100 \qquad \text{eq. 3}$$

The results obtained from the three replications carried out in the sampling stage must be evaluated in order to identify any outliers using the following condition:

$$|x_i - x_{median}| > \frac{IC_{99}\%}{100} * x_{median} \qquad \text{eq. 4}$$

That may be transcribed as:

$$x_{median} - \frac{IC_{99}\%}{100} * x_{median} < x_i < x_{median} + \frac{IC_{99}\%}{100} * x_{median} \qquad \text{eq. 4 bis}$$

Where:

x_{median} is the median of the three replications.

$CI_{99}\%$ is defined in accordance with equation 3

x_i Is the i-nth reading

In accordance with the selection criteria for samples considered to acceptable as per the foregoing discussion and section 5.4, the following cases may arise:

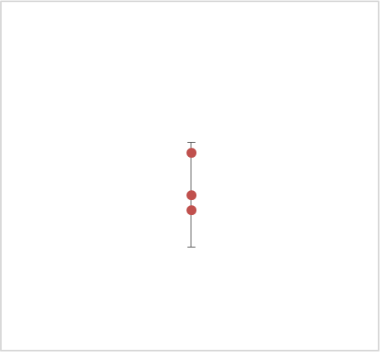
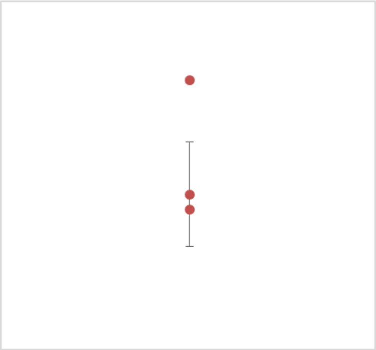
In the light of the data obtained, equation (4) becomes:

$$|x_i - x_{median}| < 0.559 * x_{median} \qquad \text{= data acceptability condition}$$

This is the acceptability condition for values found in the field.

Ed. Note :the median was considered rather than the mean because the median is a statistically more robust parameter; moreover, if the mean had been used, a combination might have occurred whereby none of the three samples would be acceptable, thereby invalidating the entire sampling process.

On the basis of the foregoing, the following cases may occur:

Case 1: **no sample discarded for abnormal distribution of H_2S between the absorbers as specified at para 5.4 and no outlier:** The result (in concentration) is expressed as the mean of three replications.	
Case 2: **one sample discarded for abnormal distribution of H_2S between the absorbers as specified at para 5.4 or because there is an outlier:** The result will be expressed as the average of the two normal results remaining.	
Case 3: **there are** 2 **outliers or 2 discarded samples because of abnormal distribution pf H_2S between the absorbers as specified at para 5.4**. In this case, the result will be expressed by the only value remaining