

## Determination of mercury leaving cooling towers in geothermal power stations instrumental method

## **IGG-CNR-5 METHOD**

(M5)

## Authors: Alessandro Lenzi<sup>1,2</sup>, Antonio Caprai<sup>1</sup>, Marco Paci<sup>2</sup>, Alessandro Bettini<sup>2</sup>, Antonio Ciompi<sup>2</sup>

<sup>1</sup>C.N.R.- National Research Council (CNR) Institute of Geo-Sciences and Geo-Resources, Via Giuseppe Moruzzi, 1-56124 Pisa (I)

<sup>2</sup>Enel Green Power, Via Andrea Pisano, 120 - 56122 Pisa (I)

Method:IGG/CNR-5Review:0Edition:08.01.2018

C	_			
Сс	n'	ΓP	n	LS.
u		<i>cc</i>		

1.	PURPOSE AND SCOPE OF APPLICATION
2.	REFERENCE DOCUMENTS
3.	TERMS AND DEFINITIONS
4.	PRINCIPLE
5.	MEASUREMENT EQUIPMENT
5.	1 MEASUREMENT CONDITIONS
5.	2 GENERAL REQUIREMENTS
5.	3 MEASUREMENT EQUIPMENT
5.	4 IMPINGER TO ELIMINATE MOISTURE FROM THE GAS
5.	5 CONNECTIONS
5.	6 LUMEX INSTRUMENT
5.	7 MATERIALS FOR SAMPLING EQUIPMENT
_	PROCEDURE
_	PROCEDURE
6.	PROCEDURE
6. 1.	PROCEDURE
6. 1. 6.	PROCEDURE       8         GENERAL REQUIREMENTS       8         2       PRE-CLEANING THE EQUIPMENT       8         3       PREPARING AND INSTALLING THE EQUIPMENT       9
6. 1. 6.	PROCEDURE       Seal tests         PROCEDURE       Seal tests
6. 1. 6. 6.	PROCEDURE       Seal tests         QENERAL REQUIREMENTS       Seal tests         2       PRE-CLEANING THE EQUIPMENT         3       PREPARING AND INSTALLING THE EQUIPMENT         4       Seal tests         5       Installing the equipment
<ol> <li>1.</li> <li>6.</li> <li>6.3.1</li> <li>6.3.2</li> </ol>	PROCEDURE       Separate Requirements       Separate Requirement       Separate
6. 1. 6. <b>6.3.1</b> <b>6.3.2</b> 6.	PROCEDURE       8         GENERAL REQUIREMENTS       8         2       PRE-CLEANING THE EQUIPMENT       8         3       PREPARING AND INSTALLING THE EQUIPMENT       9         1       Seal tests       9         2       Installing the equipment       9         4       TAKING MEASUREMENTS       10         5       DISMANTLING THE EQUIPMENT       10
6. 1. 6. <b>6.3.1</b> <b>6.3.2</b> 6. 6.	PROCEDURE       8         GENERAL REQUIREMENTS       8         2       PRE-CLEANING THE EQUIPMENT       8         3       PREPARING AND INSTALLING THE EQUIPMENT       9         1       Seal tests       9         2       Installing the equipment       9         4       TAKING MEASUREMENTS       10         5       DISMANTLING THE EQUIPMENT       10         1       Rinse the connection pipes on the first absorber       10
6. 1. 6. <b>6.3.1</b> <b>6.3.2</b> 6. 6. <b>6.5.1</b>	PROCEDURE       8         GENERAL REQUIREMENTS       8         2       PRE-CLEANING THE EQUIPMENT       8         3       PREPARING AND INSTALLING THE EQUIPMENT       9         1       Seal tests       9         2       Installing the equipment       9         4       TAKING MEASUREMENTS       10         5       DISMANTLING THE EQUIPMENT       10         1       Rinse the connection pipes on the first absorber       10         2       Rinsing the sampling equipment       10

# Determination of mercury leaving cooling towers in geothermal power stations :instrumental method

#### 1. PURPOSE AND SCOPE OF APPLICATION

This method is an alternative instrumental approach to the current extraction method ([8]), that in turn is an adaptation of the UNI EN 13211:2003 standard "Air Quality, Stationary Source Emission, Manual Method for the Determination of Total Mercury" for the correct sampling and analysis of total mercury in gaseous effluents emitted by cooling towers in geothermal power stations. This method extends the field of application to emissions from geothermal power stations and the field of measurement of the above-mentioned extraction method to values of mercury concentration from 1 ng/Nm<sup>3</sup> to 500 µg/Nm<sup>3</sup> (the extraction method is validated for mercury concentrations between 20 ng/Nm<sup>3</sup> and 500 µg/Nm<sup>3</sup>).

#### 2. REFERENCE DOCUMENTS

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

- [1] UNI EN 1483:2008 "Water quality Determination of mercury"
- [2] UNI EN 13284-1:2003 "Stationary source emissions Determination of low range mass concentrations of dust Manual gravimetric method"
- [3] EPA 7470A:1994 "Mercury in liquid waste (manual cold-vapor technique)"
- [4] EPA 6010D:2014 "Inductively Coupled Plasma Atomic Emission Spectrometry"
- [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] EPA 29 "Determination of metal emissions from stationary sources".
- [8] IGG-ICCOM/CNR-3 METHOD "Sampling and analysis procedure for the determination of mercury leaving cooling towers in geothermal power stations".

#### 3. TERMS AND DEFINITIONS

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

Mercury: mercury and mercury in its compounds.

**Total mercury**: total amount of mercury in the gaseous effluent regardless of its physical state (gaseous, dissolved in drops, solid, absorbed into particles).

**Typical sampling**: sampling at constant flow at the minimum number of sampling points indicated in the sampling plan, as specified in UNI EN 13284-1:2003. Unlike European standard UNI EN 13211:2003, there is no need to ensure isokinetics for typical sampling since there is no solid particulate matter and/or droplets above  $1 \mu \text{ g/Nm}^3$ .

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

#### 4. PRINCIPLE

The fluid is sampled near the cooling tower outlet mouth using a probe connected to a teflon pipe to convey the sampled gas to the on-line measurement instrument. 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.

A sample flow of gaseous effluent is extracted in a representative manner from the stack of one of the coolant tower cells for a period of time (about 5-10 minutes) that assures stabilisation of the measurement at an instrumentally controlled flow rate of about 1L/min.

The results are expressed in micrograms of total mercury per each standard cubic metre  $(ng/Nm^3)$  of dry<sup>1</sup> gas effluent. The instrument expresses the results in  $ng/m^3$ , which are then harmonised with T and P measurements.

The measurement of the aeriform flow rate emitted by the cooling tower, which is needed in order to calculate the mass flow of mercury, is performed by means of a precise measurement of speed using a turbine gauge at points defined in accordance with UNI EN ISO 16911-1:2013 (assuming 4 iso-areas in the method [8] - IGG-ICCOM/CNR-3, "Sampling and analysis procedure for the determination of mercury leaving cooling towers in geothermal power stations").

The mass flow rate of Hg is calculated by multiplying the flow of dry air by the concentration of Hg which, in the calculation adopted, refers to a unit of dry volume. The aeriform flow rate from the tower is measured as moist at the temperature and pressure conditions in the tower. The flow rate must therefore be adjusted from wet to dry. This 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).

m<sup>3</sup> expressed in m<sup>3</sup> under dry conditions, harmonised at 0°C and 101.325 kPa.

#### 5. MEASUREMENT EQUIPMENT

#### 5.1 MEASUREMENT CONDITIONS

As highlighted in sections 3 and 4, the measurement is taken in a non-isokinetic manner. Sampling can in fact be carried out in non-isokinetic mode since no powders are present and the concentration of mercury in the drift<sup>2</sup> is always less than  $1\mu g/Nm^3$  (section 5.1 UNI EN 13211:2003)

#### 5.2 GENERAL REQUIREMENTS

The measurement 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. An empty impinger immersed in an ice bath for partial elimination of the humidity contained in the sampled gas.
- 3. The online tool is the LUMEX.

**Errore. L'argomento parametro è sconosciuto.** Illustrates the layout of the sampling and measurement system used to determine mercury in gaseous form leaving the cooling towers of geo-thermoelectric power stations.

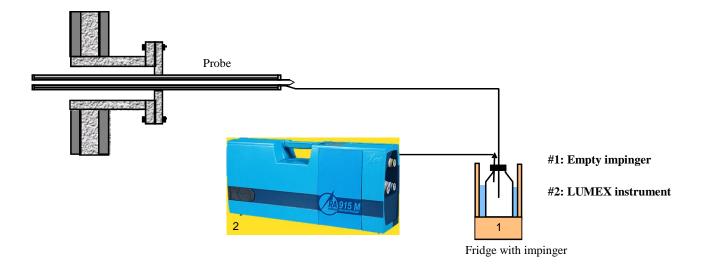


Figure 1 – Sampling system used to sample and measure mercury.

<sup>2</sup> A small amount of geothermal fluid droplets carried out of the cooling towers and which can fall in the area around the plant

#### 5.3 MEASUREMENT EQUIPMENT

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

#### 5.4 IMPINGER TO ELIMINATE MOISTURE FROM THE GAS

Guidance for the choice of materials for the impinger to be used to eliminate moisture from the sampled gas are provided in paragraph 5.7. This impinger must be kept inside a water/ice bath in order to ensure better elimination of the humidity in the sampled gas. Before sampling, this impinger must be washed in accordance with the procedure given in [8] to ensure the absence of mercury contamination (see section 6.2). The condensate accumulated in the impinger during gas sampling must be collected and stored in a labelled and identified HDPE or LDPE storage bottle for possible subsequent analysis in order to verify the absence of mercury.

#### 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 mercury.

#### 5.6 LUMEX INSTRUMENT

The Ohio Lumex instrument exploits Zeeman-effect atomic absorption spectrometry with high-frequency modulation of Zaas-HFM light polarization. The mercury discharge lamp is placed in a magnetic field and the radiation is polarized. A series of mirrors passes the radiation over an optical path of about 10 metres which isolates only the band of interest and eliminates all diffused light. In this analytical technique, the signal depends exclusively on the concentration of mercury and not on powders, aerosols or other contaminants that may be found in the gaseous matrix. These expedients make it possible to obtain an on-line measurement with a detection limit of **1 ng/Nm<sup>3</sup>** (the detection limit for the Lumex device is more than one order of magnitude lower than that indicated in the method [8]) and is consequently in line with the mercury concentration values in the gas leaving the cooling towers of the geothermal power stations.

#### 5.7 MATERIALS FOR SAMPLING EQUIPMENT

The parts of the sampling equipment in contact with the gaseous effluent containing mercury must be in the materials listed in Table 1.

Part of the equipment	Material	Notes
Sampling probe (suction tube)	PTFE (teflon)	
Impinger for eliminating moisture	Borosilicate glass	250ml
Connecting couplings	Silicone (with a total internal area <2 cm <sup>2</sup> )	
Storage bottles for washing solutions	Low Density Polyethylene (LDPE) High Density Polyethylene (HDPE)	See section 6.6

Table 1 – Material	s for	sampling	equipment.
		Samping.	equipment

#### 6. **PROCEDURE**

#### 1. GENERAL REQUIREMENTS

Four sampling and measuring apertures arranged at 90° to each other having two diameters at about 0.90m above the fans of the cell in question. The probe is inserted into the cell and placed in contact with the gas through these above-mentioned apertures. The average radius of these cells is about 4.50 m and there must be at least four sampling points along each radius, positioned as identified according to the UNI EN ISO 16911-1:2013 standard. At least three adjacent radii in the cell must be surveyed for this type of tower. Measurements must be repeated at least twice on the same day (indicatively, one measurement on three radii in the morning repeated in the afternoon).

The mercury concentration value is determined by applying the following formula (1):

$$C_{HG} = \frac{\sum_{i}^{n} C_{i} v_{i}}{\sum_{i}^{n} v_{i}} \quad (1)$$

Where:

- 1.  $C_i$  is the mercury concentration measured (in ng/Nm<sup>3</sup>), in the i-th iso-area.
- 2.  $V_i$  is the aeriform velocity measured (in m/s) in the i-th area (see section 4 for the methods used to measure the aeriform flow rate on output from the cell).

The value for mercury emitted by the sampling cell is calculated using the following formula (2):

$$E_{HG} = \sum_{i}^{n} C_{i} v_{i} A_{i}$$
 (2)

#### Where:

3.  $A_i$  is the extension (in m<sup>2</sup>) of the i-th iso-area. Since the output section of the cell where measurements were taken is divided into iso-areas in accordance with UNI EN ISO 16911-1:2013, the outcome will be  $A_1=A_2=A_3=A_4$ .

On the total emission, the  $E_{HG}$  value must then be multiplied by the number of cells in the cooling towers in the geothermal power plant, assuming virtually identical air flow rates on each cell. Before taking measurements of mercury emissions, check that the fan motor for the cell being measured has absorption within  $\pm 10\%$  of the maximum absorption value of the fan motors for the emission cells. If these limits are not met, the measurement of the mercury emitted is carried out nonetheless and the results will subsequently be harmonised by a correction factor as envisaged in DGR 1743 dated 8/5/2014.

#### 6.2 PRE-CLEANING THE EQUIPMENT

All parts of the sampling equipment (Table 1, section 5.7) that may come into contact with mercury must be cleaned before taking samples.

Cleaning should be performed using the procedure indicated in [8] (Appendix A.2 for the probe and the connection pipes and Appendix A.3 impinger eliminating moisture from the sampled gas).

Check the quality of the washing procedure by keeping the washing solutions used to wash the absorbers in order to determine the content of mercury whenever necessary in the event that non-conforming measurements are taken.

#### 6.3 PREPARING AND INSTALLING THE EQUIPMENT

#### 6.3.1 Seal tests

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

#### 6.3.2 Installing the equipment

Install the assembled and complete sampling and measurement 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 and measurement equipment installed on the walkway must comply with applicable safety regulations. Avoid any unintended gas flow through the measuring equipment. The sampling probe comprises a teflon tube 10mm in diameter secured to a rigid beam that can be fitted inside the cell through a flanged pipe located about 2m from the walkway. Four flanged couplings are provided to allow sampling along 4 radii at right angles to each other.

#### 6.4 TAKING MEASUREMENTS

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

Measure the mercury for a suitable time (about 5-10 minutes) to obtain a stable mercury concentration value (expressed in ng/Nm<sup>3</sup>). Three repetitions must be performed in parallel for each sampling session. After the required sampling time, stop extraction of gaseous effluent and move the probe to next plunge

#### 6.5 DISMANTLING THE EQUIPMENT

#### 6.5.1 Rinse the connection pipes on the first absorber

See Appendix A.2 to [8].

#### 6.5.2 Rinsing the sampling equipment

For the washing procedure after each measurement, refer to Appendix A.2 to [8]. The washing solutions as per paragraph 6.5.1 and this paragraph must be combined stored in labelled, identified bottles for subsequent analysis.

#### 6.7 SAMPLE STORAGE REQUIREMENTS

Samples in HDPE or LDPE storage flasks should be stored at a temperature of less than 6 °C (refrigerator) in the dark. The samples should be analysed within two weeks of sampling.

#### 7. TEST REPORT

The test report must contain at least the following information:

- a) reference to this method;
- b) reference to the sampling report
- c) identification and number of sample(s) of condensate and washing solutions;
- d) description on the plant and process;
- e) plant operating conditions;
- f) position of sampling points;
- g) number of sampling points and identification of the sampled cell;
- h) sampling time;
- j) sampling date and time;

k) total content of mercury as concentration in mass;

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

#### APPENDIX A:

#### Statistical test for validation of the instrumental method

CNR-IGG in collaboration with Enel Green Power's chemical laboratory carried out experimental campaigns designed to verify effective reproducibility between measurements obtained with the current CNR-M3 method (which modifies and integrates UNI EN 13211:2003) and those obtained with the instrumental method described above.

Experimental campaigns were therefore carried out in three different power plants in order to verify the reproducibility of measurements obtained using the above-mentioned two methods for different concentrations of mercury in gas emitted by cooling towers.

The power plants where measurements were taken are:

- 4. Selva geothermal power plant characterized by a low concentration of mercury (<100 ng / Nm3) in the gas from the cooling towers. An experimental campaign was carried out in the power plant on 5 October 2017.
- 5. Piancastagnaio 5 geothermal power plant characterized by a mercury concentration between 300 ng/Nm<sup>3</sup> and 700 ng/Nm<sup>3</sup> in the gas from the cooling towers. An experimental campaign was carried out in the power plant on 12 October 2017.
- 6. Piancastagnaio 4 geothermal power plant characterized by a high mercury concentration (>800 ng/Nm<sup>3</sup>) in the gas from the cooling towers. An experimental campaign was carried out in the power plant on 10 October 2017.

Each experimental campaign involved the following tasks:

- five measurements repeated with the CNR-M3 method. For each repetition, sampling was carried out in four plunges.

- three repetitions for each plunge using the instrumental method. For each plunge, the three repetitions were performed respectively at the start, mid-point and end of sampling carried out using the CNR-M3 method.

The plunges are the same for both methods and are those listed in section 7.1 of the CNR-M3 method for forced draft towers. All the above-mentioned repetitions were carried out along a single measurement radius.

There follow the results for measurements carried out using the two methods (CNR-M3 method and instrumental method) in the three power plants indicated above:

	initial stage			inter	mediate s	stage		final stage	9	AVERAGE
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 1
PLUNGE 1 3.20 m	53	51	50	39	41	40	45	45	46	45
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 2
PLUNGE 2 2.00 m	51	46	48	40	43	41	46	44	46	45
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 3
PLUNGE 3 1.20 m	35	35	35				38	37	37	36
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 4
PLUNGE 4 0.5 m	40	37	37	40	41	40	40	40	40	39
						тот	41			
							5			

Table A.1 - Mercury-gas measurements from the tower at the Selva power plant using the Lumex instrument (ng/Nm<sup>3</sup>)

Table A.2 - Mercury-gas measurements from the tower at the Selva power plant using the CNR-M3 method (ng/Nm<sup>3</sup>).

Repetitions	Hg concentration (ng/Nm³)
Repetition 1	52
Repetition 2	39
Repetition 3	43
Repetition 4	42
Repetition 5	54
AVERAGE	46
STD DV	6.6

	initial stage			inter	mediate s	tage	1	final stage		AVERAGE
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 1
PLUNGE 1 3.20 m	696	657	703	608	671	633	658	645	615	654
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 2
PLUNGE 2 2.00 m	696	632	660	629	687	670	649	659	668	661
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 3
PLUNGE 3 1.20 m	656	611	621				647	649	709	649
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 4
PLUNGE 4 0.5 m	420	409	437	409	432	402	396	387	412	412
						тот	594			
							113			

Table A.3 - Mercury-gas measurements from the tower at the Piancastagnaio 5 power plant using the Lumex instrument (ng/Nm<sup>3</sup>)

**Table A.1** - Mercury-gas measurements from the tower at the Piancastagnaio 5 power plant using the CNR-M3 method(ng/Nm³).

Repetitions	Hg concentration (ng/Nm <sup>3</sup> )
Repetition 1	657
Repetition 2	654
Repetition 3	615
Repetition 4	634
Repetition 5	548
AVERAGE	622
STD DV	44.5

	initial stage			inter	mediate s	tage	1	final stage	2	AVERAGE
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 1
PLUNGE 1 3.20 m	1177	1159	1146	1117	1113	1138	1113	1109	1068	1127
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 2
PLUNGE 2 2.00 m	1154	1103	1129	1070	1083	1108	1079	1052	1026	1089
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 3
PLUNGE 3 1.20 m	1001	1006	1081				993	977	929	998
	Hg 1	Hg 2	Hg 3	Hg 4	Hg 5	Hg 6	Hg 7	Hg 8	Hg 9	AVERAGE 4
PLUNGE 4 0.5 m	819	769	828	796	814	824	856	891	904	833
						тот	1012			
							126			

**Table A.5** - Mercury-gas measurements from the tower at the Piancastagnaio 4 power plant using the Lumex instrument (ng/Nm<sup>3</sup>)

**Table A.6** - Mercury-gas measurements from the tower at the Piancastagnaio 4 power plant using the CNR-M3 method (ng/Nm<sup>3</sup>).

Repetitions	Hg concentration (ng/Nm <sup>3</sup> )
Repetition 1	963
Repetition 2	957
Repetition 3	941
Repetition 4	1016
Repetition 5	942
AVERAGE	964
STD DV	30.6

In order to evaluate the equivalence of measurements taken by the two methods, the "Two-medium Student Test t" statistical method was used.

Table A.7 presents the results of statistical analysis carried out, where:

- 1.  $\langle X \rangle_{M3}$  is the average value of the measurements taken using the CNR-M3 method.
- 2. <X>LUMEX is the average value of the measurements taken using the instrumental method.
- 3.  $s_{M3}$  is the standard deviation of measurements carried out using the CNR-M3 method.
- 4. s<sub>LUMEX</sub> is the standard deviation of measurements carried out using the instrumental method.
- 5. tcalc is the auxiliary Student distribution variable t obtained from the measurements taken by the two methods. This variable is obtained using the following formula:

$$t_{calc} = \frac{(_{M3} - _{LUMEX})}{s_p \sqrt{\frac{1}{n_{M3}} + \frac{1}{n_{LUMEX}}}}$$

$$s_p = \sqrt{\frac{(n_{M3} - 1)s_{M3}^2 + (n_{LUMEX} - 1)s_{LUMEX}^2}{n_{M3} + n_{LUMEX} - 2}}$$

Where:  $n_{M3}$  and  $n_{LUMEX}$  are respectively the number of repetitions performed using the CNR-M3 method and the instrumental method.

6.  $t_{ref}$  auxiliary Student distribution variable t calculated at a confidence level of 95% on the total number of degrees of freedom  $n_{GL}$  for the system, equal to:

$$n_{GL} = n_{M3} + n_{LUMEX} - 2$$

The static test is passed if  $t_{calc} < t_{ref.}$ 

Table A.7 - Statistical comparison of CNR-M3 and Lumex methods using Student t Test with two averages.

PLANT	<x><sub>M3</sub></x>	<x>LUMEX</x>	Sмз	SLUMEX	tcalc	tref.	Test t passed?
SELVA	46	41	7	5	1.84	2.03	ОК
PC-4	964	1012	31	126	0.84	2.03	ОК
PC-5	622	594	45	113	0.54	2.03	ОК

The foregoing statistical analysis shows that t test is passed for each mercury concentration interval investigated, so it can be said that the two methods are reproducible and provide equivalent measurements. Inasmuch, the instrumental method using the Lumex instrument can be considered validated and applicable for the measurements in question as an alternative to the CNR-M3 method.