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UNCERTAINTY DETERMINATION FOR ELECTROCHEMICAL PORTABLE EMISSION ANALYZERS USING REFERENCE MATERIALS AND STACK IN SITU VALIDATION (INTERCOLLABORATIVE TEST).

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AIMS OBJECTIVES AND WORKING METHODS

To determine contaminant emission levels emitted by industrial combustion processes, the equipment normally used by the inspection bodies, as standard practice, is the “portable gas analyser”.

These portable gas analysers determine contaminant concentrations by means of the electrochemical cell measurement technique.

Considering the widespread use of these potable gas analysers in the general market of combustion emissions analysis, (use ranging in the order of 80% of the combustion processes control), this universal and generally accepted conventional measurement technique, does not have, at European, nor international level, any form of specific recognition in the form of official industry standards.

At European Union level there are no actual valid and recognised criteria with respect to the accuracy of the measured levels against which such equipment should comply with.

Given this situation, the only alternative in terms of recognised industry standards available to the inspection teams are the following North American standards: US EPA CTM-030 or US EPA CTM- 034 (www.epa.gov/ttn).

Several official inspection bodies had joined together to develop and research the technical aspects of the accuracy of such equipment and have created a technical workin group in Spain.

This technical working group has been carrying out various research projects, both in the field (chimney real stack conditions) and simulated field conditions (in the laboratory).

The aim of these research projects is to investigate and therefore provide technical information for the future development of measurement accuracy criteria.

This criteria is intended to hopefully serve as a basis of the european standard (EN).

Principal goals to be achieved by the working groups are:

a) To establish a “criteria pack” to optimize calibration works for electrochemical portable analyzers, periodic verification fixed by the US EPA CTM-030, to be used as a reference standard. These criteria can provide traceability between the established known reference standard and the results of the measurements taken by this kind of gas analyzers.

b) To give sufficient guarantees regarding the quality of the obtained results during the measurements taken during the industrial combustion processes, in accordance with the criteria set by the EN-45004:1995 and EN-17025:2000 standards even of the point of view of the statistics like of the guarantees of the performance characteristics of the analyzer.

c) Calculate under "optimum laboratory conditions" the measurement uncertainty from the results obtained for each of the principal compounds stated in the US EPA CTM 030 standard (SO_2, NO_x, CO) and also in real plant conditions (stack emission conditions). This uncertainty will be calculated from two intercollaborative tests, in the lab and on site plant determinations.

Lab Intercolaborative Test from reference materials (july 2002)

This intercollaborative test was developed at the NW Spain in A Coruña city (Galicia Autonomous Region), during july of 2002 and was organized by the Galician Environmental Laboratory from the Autonomous Government (Xunta de Galicia).

At this test five inspection bodies has been involved, with different branch and model instruments and different configurations. In the test was involved electrochemical analyzers without any sample preparation, some of them with dry systems and another with dry system and heated gas line from the sampling duct to the moisture elimination system.

This approach, at the principle not homogeneous, can demonstrate, also, at laboratory conditions, which are the main influences at the results variation when several analyzers are measuring over the same gas matrix sample. Also it can be useful to test if the variations due to the sample preparation conditions are or not critical to achieve comparable results and correlated to the reference certified standard concentration.

The arrangement consists in a stainless steel tube with holes for all the analyzers. Continous flow are injected at this tube provided by a pressure bottle of certified material (binary mix) and passed over two calibrated traceable dinamic dilution systems with room air (with no contamination present) to provide the wanted gas concentration in the tube.

All the analyzers pump a gas sample and provide the concentration that is registered at the proper form sheets at the same time (sound warning every 30 seconds).

Two dilutors are required to guarantee enough flow to achieve a quantity superior to the sum of every pump flows of the analyzers fitted at the tube, for every concentration of every compound analyzed. Over all the test the flow was enough high to assure a little gas excess in order to assure that the results of the equipment will be not affected by the pressure variations over the electrochemical cell membrane.

The objective of the intercollaborative test was double:

a) comprobate the performance characteristics of the analyzers: zero calibration error, span calibration error, linearity and measuring stability.

b) Calculate the measurement uncertainty based on the obtained deviations from every equipment and the real certified concentration of the reference material and the dilution level.

At the first, all the analyzers that want to participate must demonstrate his ability to provide the correct concentration. The acceptance/discard criteria used to evaluate the results was the same stated at the US EPA CTM-030 standard.

From this demonstration all the approved analyzers were connected to the test tube and the first gas mix concentration was generated and measured for all the participants.

The above mentioned reference standard US EPA CTM-030 set that every span gas concentration is valid for the nominal range included between the 25% of the span conc. value to the 125% span concentration value.

Taking all the ranges that must been validated, four concentrations were calculated for every compound of the test. With the overlap of several ranges and concentrations full range of the analyzers has been validated for the three interest compounds.

The concentrations calculated and used for the evaluated compounds has been presented at the following figure.

Compound	NOx (ppm)	CO (ppm)	SO_2 (ppm)
Validated Range	25 – 3000	25 - 3000	25 – 2500
Applied values (concentrations)	100	100	100
	250	500	500
	500	1000	1000
	2400	2400	2000

The procedure consists on the introduction of the required concentration of every compound and, after the necessary reaching time for the equipment stabilization (according US EPA CTM 030) several readings was taked for every participant every 15 seconds over 2 minutes (8 readings every time).

After the data recording zero value were putted at the test tube introducing only room air (filtered with active coal) and the operation was repeated four times for every concentration (to see about the repeatibility).

The main results and conclusions are very hopeful and can be summarised as follows:

1. From the obtained results we have the opportunity to demonstrate that the analyzers shown a lineal behaviour over full validated range over all the test. This is a very important key because some criteria can be fitted for the verification and calibration processes of this kind of analyzers.

2. The levels of uncertainty of every inspection body participant can be calculated from the results compared against the certified reference material generated with traceable calibrated dynamic dilluters.

Anyway, the conclusions from the test report shown critical limitations of the test against a real routinely stack determinations like:

i. The effect of the moisture at the sample was not evaluated and can be important at routinely measures.

ii. Cross interferences between contaminants can exist at real measurements.

iii. Lab test was developed at ambient temperatures. Real stack determinations at hugh temperatures compared with ambient levels can have effects on the results accuracy.

In order to assure the reliability of the measurements at real stack conditions it is neccesary to make an intercollaborative test in an industrial stack during real burning combustion.

Real Stack conditions intercollaborative test (february, 2004)

The real stack conditions intercollaborative test was performed at february 2004 in a fuel (low sulphuf index fuel) industrial high capacity steam generation boiler.

The industrial source was provide by the "Cooperativa Agrícola de Guissona" (Lleida – Catalonia - Spain). The boiler objective is the steam generation for the animal cleaning process for food production. The characteristics of the process and the boiler make impossible any activity to modify the emission compound concentrations, that depend on the steam process demand in every process step.

This test was organized by the "Servei de Vigilancia i Control de l'Aire" of the Environmental and house Department of the Catalonian Autonomous Authority.

In this occasion Thirteen inspection bodies were participate at the test. As in the lab tests the configurations of the analyzers were different because every participant want to test his own equipment with his configuration. Even, some of them, do not achieve the minimum requirements of the US EPA CTM-030 standard.

At the second test, 3 different comprobations was made:

- Sampling plane points representativity (no stratification, no cyclonic flow present, hydraulic diameter criteria, ...).

- Previous tests in order to guarantee the performance characteristics of every analyzer to be used to the intercollaborative test.

- The stack test itself, with simultaneous readings for every participant were readings had been taked for the uncertainty calculation from all of the data obtained (maximun uncertainty derived from repeatibility and reproducibility).

The representativity of the sampling plane selected was performed with all of the participants on site (stack) by means of the stratification tests at the duct. This test shown that all of the sampling ports have a difference against the average concentration less than 5%. This average is hugh less than the general criteria for CEM (continous emission monitoring) so the sampling plane must be considered valid for this kind of tests.

Performance Characteristics tests in order to assure that every analyzer were maked but there is not an acceptance/reject criteria and we assume that every quality assurance system of every inspection body was enough guarantee (ENAC – European Accreditation recognition of technical capacity under EN – 45004 and EN ISO 17025:2000).

Even as an informative tool, a performance characteristics test was performed in order to assure the analyzers stability according the US EPA CTM-030 standard. This informative test give some technical information about the stabilization rise times and shown that this times are clearly superior that the times stated by the analyzers manufacturers and even superior that the times declared by the technical managers of every inspection body.

Furthermore, some participants propose a value of stabilization time that is timeless to achieve the cell stabilization. This is specially critical in the case of SO_2, but is also important at the case of CO and NO readings.

This observation must be taking in consideration for future technical procedures for emission measurements with this kind of analyzers for technical and quality reasons and, even for maintenance costs reasons.

Finally the simultaneous test readings in the stack for the thirteen company involved at the boiler were performed over 3 reading series. 2 of them of 30 minutes and the third of 60 minutes of total time to comply with the spanish legal rules (Order of Environental Ministry of 18^{th} october 1.976).

From the results obtained the z-score criteria was calculated and the inspection bodies with a z-score more than 2 were eliminated for the final calculations.

Main results of the intercollaborative test were:

- The absence at the stack gases of CO (good combustion control by the industry) and NO_2 (controled air excess) gives a no satisfactory result for this two compounds in order to calculate the uncertainty level associated to this two compounds.

- Only one inspection body shown a z-score more than 2 for the NO and one more for the case of SO_2 and was rejected.

- For the Oxygen level, all of the inspection bodies shown values useful for the uncertainty calculation.

- The obtained results can be used to fit some criteria for the sampling works at combustion emission processes, according to the US EPA CTM-030 standard, and also to calculate the measurement uncertainty for the compounds analyzed.

Future goals

For the next future the working group are preparing, always into the quality assurance goal and criteria setted at EN-45004 and EN ISO 17025:2000 for the inspection bodies results at emission measurements, a new intercollaborative test for the determination of CO, even the determination of the uncertainty level for the Organic Volatile Compounds (VOC) according the EN-12619:1999 european standard and following the rules of the 1999/13/CE European Directive (Spanish Royal Decree 217/2003).