21NRM04 BiometCAP

**A3.1.2: Identification of the performance characteristics of the selected industrial gas analysers and reference instrumentations**

**Partners:** PTB, NPL, TFS, GERG, DTU and VTT

**Description of the activity:**

Using input from A3.1.1, PTB, in collaboration with NPL, TFS, GERG, DTU, and VTT, will identify the performance characteristics (e.g. limit of detection, response time, limit of quantification, repeatability, reproducibility, linearity, quality control, cross interference , selectivity, matrix effects, uncertainty) of the selected industrial gas analysers that need to be assessed during the evaluation of the industrial gas analyser and reference instrumentations for biomethane conformity assessment. The output of this activity will be used in A2.1.4 to further inform the development of the protocol, should any additional considerations be found based on the instrument identification.

1. **Basic Instrument specifications**

In A3.1.1, the following measurement techniques/analysers have been selected:

For on-site measurements:

* MAXiR (FTIR analyser, multiple component)
* Agilent 990 Micro GC (with µTCD detector, multiple component)
* OFCEAS (laser-based, single component)

For laboratory measurement:

* OFCEAS (laser-based, single component)
* Agilent GC-FID (classical bench-top GC system, multiple component)

In the Table 1 below, a summary of the selected gas analysers is given. It should be noted that the Table reflects instrument supplier’s data sheets.

**Table 1**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Partner** | **Selected Analyser** | **Analyte(s)** | **LOD** | **Response time for 10%-90%** | **Measurements range** |
| TS | FTIR-  MAXiR | NH3, CO, HF, CO2, and siloxanes, etc. |  | -- | -- |
| DTU | Micro GC  Agilent 990 | C1-C6, CO, CO2, O2, SO2 and H2S | 0.5-2 ppm | 35s | Few ppm to few % |
| PTB | OFCEAS | NH3 | 0.05 ppm | < 160s (typical) | 0.05 – 50 ppm |
| VTT | AP2E | NH3 | 0.05 ppm | <180s | 0-100 ppm |

During the injection of biomethane into the existing natural gas distribution grid, the components such as NH3 (max 3 mg/Nm3, i.e. 4 mmol/mol), H2S (max 30 mg/Nm3 i.e. 21 mmol/mol), siloxanes (max 1mg/Nm3) and odorants for e.g. THT (min 10 mg/Nm3 i.e. 2.8 mmol/mol), mercaptans (min 4 mg/Nm3 i.e. 2 mmol/mol) at the consumer point need to be measured. Among the above-mentioned components, water dew point and H2S should be monitored continuously and O2, CO2, NH3 and siloxanes should be monitor periodically as per requirement of the individual biogas plant. Some additional components such as terpenes also need to be measured depending on the necessity of the local operator. Moreover, for the transmission gas grid, the biomethane should follow NH3, CO2 and other specifications given by grid operators. Therefore, all these issues need to be taken into account for characterization of the analyzer.

1. **Performance Characteristics**

The following performance parameters will be considered: Limit of detection, response time, linearity, cross interference, matrix effects, reproducibility, and uncertainty.

* 1. **Limit of detection (LOD)**

The minimum concentration of the analytes that can be measured with an analyzer is defined as limit of detection [[[1]](#endnote-1)]. It must be considerably lower than the threshold concentration of the analyte(s) in biomethane. The LOD also must be verified experimentally. For instance, the manufacturer specified LOD of NH3 is 50 ppb for the OF-CEAS spectrometer which is about 200 times lower than 10 ppm (lower range to be measured in the BiometCAP project).

* 1. **Response time**

Response time is an important for characterisation of an analyser. The Instrument manufacturers usually provide the response time of the analyser itself. For practical measurements the sampling line response also need to be known. Therefore, the response time here would typically be the response time of the whole system (sampling line and analyser). The response time of the instruments could be determined by instantaneously switching between a zero and a span gas.

* 1. **Linearity**

Linearity could be checked by recording the response of an analyser when interrogated with e.g. reference gas mixtures or gas standards at different amount fractions within the target measurement range of the instrument.

* 1. **Cross interference**

Selectivity of the instrument provides measurement of one or more components such that the values of each component are independent of other measurands being investigated. Interferences can either be treated on a hardware (GC-analysers: e.g. heating rate change) or software levels (e.g. FTIR spectrometers: chemometrics). For e.g. water vapor or other trace gases might influence the measurement of the concentration of NH3. Options to check such effects should be investigated.

* 1. **Matrix effects**

Alteration of matrix gas effectively changes the broadening of the probed absorption line. The broadening of the absorption line will be difference for different gas matrices e.g. N2, CH4, etc. Therefore, to achieve accurate concentration results, matrix effects on e.g. spectroscopic measurement must be corrected, when changing the matrix gas e.g. from N2/synthetic air to CH4

* 1. **Reproducibility**

The reproducibility could be evaluated from e.g. measurements done before and after the field comparison.

* 1. **Uncertainty**

The uncertainty of the measurement must be estimated. GUM principles are recommended for evaluating an uncertainty budget for Lab or field measurements [[[2]](#endnote-2)].

**References**

1. . Thompson M, Ramsey M, “Environmental and Agricultural Applications of Atomic Spectroscopy”, Encyclopedia of Spectroscopy and Spectrometry (Second Edition),

   Academic Press,1999, 494-501, https://doi.org/10.1016/B978-0-12-374413-5.00135-4. [↑](#endnote-ref-1)
2. . SO. ISO Guide 98-3, Guide to the Expression of Uncertainty in Measurement; International Organization for Standardization: Geneva, Switzerland, 2008; ISBN 9267101889. [↑](#endnote-ref-2)