



## 17IND09 MetAMCII

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# Metrology for Airborne Molecular Contaminants II

An airborne molecular contaminant (AMC) monitor that provides analysis and feedback within approximately one minute would enable the timely detection of (higher than acceptable) contamination and it would allow the cause of the contamination to be determined, enabling corrective actions that would make a significant impact on industrial competitiveness. AMC is known to be one of the major components affecting product yield in the microscale manufacturing processes of semiconductors and this can lead to increased electronics defects and subsequently to higher production costs. AMC is a major factor affecting product yield in nanoscale semiconductor manufacturing. Reliable AMC monitoring and control schemes are essential for the success of this industry. Improved state-of-the-art techniques are needed for industrially-relevant and -identified AMCs such as HCl and NH<sub>3</sub> and new solutions are needed for monitoring, sampling, and reference gas generation.

One of the aims of the EMPIR MetAMCII Joint Research Project is to explore the different spectroscopic methods for measuring trace amounts of various industrially-relevant atmospheric contaminants, namely hydrogen chloride (HCl), ammonia (NH<sub>3</sub>), and water vapour (H<sub>2</sub>O). The focus is on developing “online” spectroscopy instruments that are capable of detecting HCl with a targeted measurement sensitivity better than 1 nmol mol<sup>-1</sup> on the timescale of one minute. This work will culminate in the testing and development of the spectroscopic instruments for HCl detection, and then in performing comparisons, tests, and measurements using the spectroscopic instruments with the gas reference standards that are also being developed in this research project. As the key industrial need is for reliable AMC monitoring and control schemes to ensure the increasing success of the semiconductor industry and cleanroom user community, one main task in the MetAMCII project is to take this realised instrumentation into industrial environments for testing.

To that end, the aim of this Specification Document is to deliver a “Specification for the laboratory tests and field studies of the optical measurement methods (different spectroscopy techniques) for AMC monitoring.” This includes recommendations on the measurement system device calibration methodology and an explanation of the tests to be applied to the measurement system that will be used in a cleanroom environment to verify it is working to specification.

This Specification Document has been drawn together from review of industrial requirements, including the industrial questionnaire developed by the consortium, a literature review of requirements, datasheet standards and existing monitoring methods, engaging directly with our stakeholders at consortium meetings, and through discussion and interaction of the consortium partners in preparing the document.

Quoting from the “Guide to the expression of uncertainty in measurement” (GUM) [1], “*When reporting the result of a measurement of a physical quantity, it is obligatory that some quantitative indication of the quality of the result be given so that those who use it can assess its reliability. Without such an indication, measurement results cannot be compared, either among themselves or with reference values given in a specification or standard. It is therefore necessary that there be a readily implemented, easily understood, and generally accepted procedure for characterizing the quality of a result of a measurement, that is, for evaluating and expressing its uncertainty.*” This statement will be our guide when documenting the specification of each measurement device.

## Performance characteristics to assess and specify

In this section we list the specifications we will explore and establish when testing our measurement devices.

### Required:

- (1) Working range
- (2) Limit of detection (LOD)
- (3) Measurement uncertainty

### Optional, but recommended:

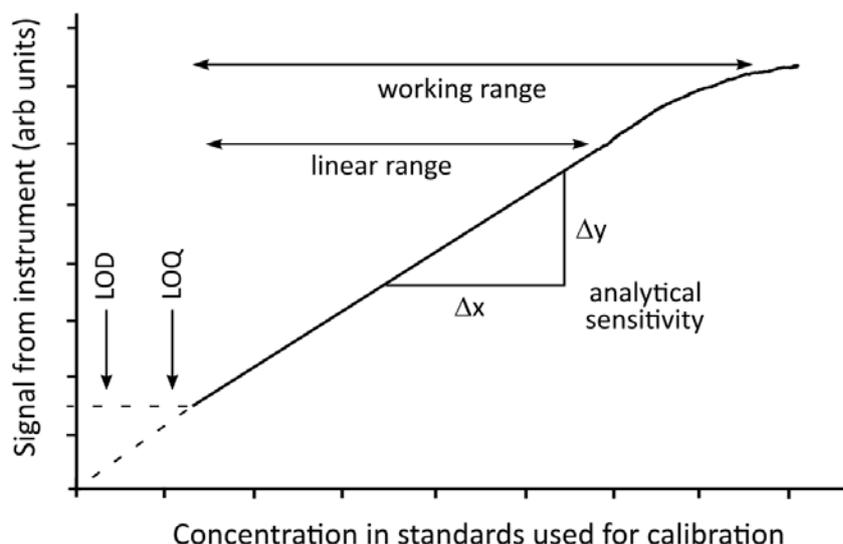
- (a) Response and recovery time
- (b) Effects of other gas species on measurement
- (c) Zero drift
- (d) Span drift
- (e) Effects on measurement when changing temperature and/or humidity and/or pressure and/or flow rate through the analyser

## Detailed description of required specifications

An initial description of the analyser will be given, including the spectroscopic method utilised (including measurement wavelength), and the method of sampling used for laboratory-based test and calibration, as well as for cleanroom use, if different.

### (1) Working range

For each device a “working range” should be given, which describes the measurement capability of the device in terms of concentrations of HCl it can accurately measure. The relationship between the LOD (or LOQ - limit of quantification) and the upper end of the working range should be described - linear, curvilinear, etc. - and plotted (similar to the example in figure 1). The entirety of the working range should be modelled (if possible) and confirmed experimentally. It is expected that the working range could be quite different in practice between the devices being developed for this project.



**Figure 1.** Representation of working range of a measurement device - including limit of detection (LOD), limit of quantification (LOQ), and analytical sensitivity (S). (Image derived from reference [2])

(2) Limit of detection (LOD) - including measurement (averaging) time

LOD of the device should be given such that it contains both concentration and averaging time information: HCl concentration level measured (measurement or averaging time). This should be given for one or more HCl concentrations, as applicable, e.g. 1 ppb (5 sec), 0.5 ppb (30 sec). For these purposes we will define LOD as follows [3]:

$$LOD > \frac{3\sigma}{S}$$

where  $\sigma$  is the standard deviation of the noise of the instrument and  $S$  is the sensitivity, which can be derived from the gradient of the calibration or “working range” plot (see Figure 1).

Note: it would be useful for the collaboration in MetAMCII that all partners when possible provide path length and time normalized absorbance ( $3\sigma$ ) in the unit of  $\text{cm}^{-1} \cdot \text{Hz}^{-1/2}$ , for comparability between the devices.

(3) Measurement uncertainty

Each device will have a description of known contributors to measurement uncertainty, e.g. baseline drift (give timescale), signal-to-noise effects, etc. This will include an explanation of if and how this might differ at different HCl concentrations, and uncertainty should be estimated for all concentrations in the “working range”.

In addition, for each instrument we will provide a description of the environment under which device was tested, specifying the type of testing space (cleanroom, research laboratory, etc.), the temperature and humidity control specification of that space, and other relevant details of the testing environment, e.g. quiet and isolated vs. acoustically/vibrationally noisy.<sup>1</sup>

Finally, a description of the method(s) used to calibrate the measurement instrument, including advice on when recalibration is necessary, must be given.

#### **To summarise:**

A model equation will be provided for each instrument, including the working range under which this model equation is valid. Information on corrections that need to be applied to the output must be provided, along with a list of systematic components of uncertainty associated with these corrections, as well as the uncorrected uncertainties of the measurement device system.

## **Detailed description of optional specifications**

(a) Response and recovery time

Due to the reactive nature of HCl gas, it would be relevant to establish the “response and recovery time” for each measurement apparatus. As a consortium we have already explored how the use of various materials (coated and uncoated) changes the detection response time in simple experimental setups, which is informing our choices in the final device build. Therefore it is recommended that each device provide information on both *response time* - how long it takes the measurement system to

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<sup>1</sup> For reference, temperature and relative humidity of cleanrooms have to be controlled to ensure process stability. For example, temperature control at 20°-22°C (+/- 1° C) and humidity control at 45 % (+/- 5 %), as well as control of particulate size and number, given in the classification of the cleanroom [4].

come to equilibrium measurement value (decided by the partners, e.g. time to 90% full value) when a fixed concentration of HCl is introduced into the system, and *recovery time* - how long it takes for the system to register below LOD once the HCl concentration is reduced below the LOD.

(b) Effects of other gas species on measurement

Depending on how the device acquires and analyses data, there is a concern that measurements of HCl may be affected by the presence of other gas species. It is recommended that modelling is performed of the overlap of spectroscopic lines of other gases with the HCl lines used by each spectroscopic measurement device under development (specifically at 1742 nm, and 3.3 and 3.6 microns). Then each device can quantify what effect these additional spectral line contributions would make on the HCl measurement process. Recommendations for gas species to investigate include water vapour (9000 - 14000 ppm) [4], CO<sub>2</sub> (400 - 2000 ppm), CH<sub>4</sub> (2 - 5 ppm), CH<sub>2</sub>O (1 - 100 ppb) [5,6], and others as found relevant. In addition to competing absorption cross section between gas mixtures, the composition of the carrier gas, particularly at variable humidity, can cause solvation interactions and perturb the molecular HCl concentration vs solvated HCl. Experimental verification could be performed by comparing the measurement of HCl at a certain concentration in dry nitrogen vs HCl in a laboratory air matrix (with known humidity), or with test gases of known quantities added to the matrix.

(c) Zero drift measurement

It would be useful to quantify the measurement stability of the baseline of the device when flowing "air" through the system (HCl concentration lower than LOD), which we refer to here as a "Zero drift" measurement. This could be done with room air, dry nitrogen, and/or humid air. Measurements of baseline stability at different timescales can be performed (e.g. shortest given averaging time for the device, or at 1000 s, or at 1 day).

(d) Span drift measurement

It would be useful to quantify the stability of measurement of a fixed HCl concentration over different time scales, which we refer to here as a "Span drift" measurement. This does not need to be a continuous, long-term measurement, although that would be ideal. Measurements of baseline stability at different timescales can be performed (e.g. shortest given averaging time for the device/ 1000 s/ 1 day).

(e) Effects on measurement when changing temperature and/or humidity and/or pressure and/or flow rate through the analyser

Ideally, controlled tests of changes in measurement characteristics would be performed using test gas from ambient air or gas cylinders over a range of laboratory/device temperatures, humidity levels, air pressures, and gas flow rates through the analyser. Any information gathered on these parameters would be useful to the end user.

**References:**

[1] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML, "Guide to the Expression of Uncertainty in Measurement", JCGM 100:2008 (GUM 1995 with minor corrections), 2008. [https://www.bipm.org/utils/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf)

[2] "The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics," [https://www.eurachem.org/images/stories/Guides/pdf/MV\\_guide\\_2nd\\_ed\\_EN.pdf](https://www.eurachem.org/images/stories/Guides/pdf/MV_guide_2nd_ed_EN.pdf)

[3] Analytical Methods Committee, "Recommendations for the definition, estimation and use of the detection limit," Analyst 112, 199-204, 1987.

[4] Fact Sheet: Cleanroom

[https://www.zurich.ibm.com/pdf/nanocenter/Factstheet\\_Cleanroom\\_EN\\_2.pdf](https://www.zurich.ibm.com/pdf/nanocenter/Factstheet_Cleanroom_EN_2.pdf)

[5] <https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/air-quality/formaldehyde-indoor-air-environment-workplace-health.html>

[6] "Formaldehyde in the Ambient Atmosphere: From an Indoor Pollutant to an Outdoor Pollutant?" T. Salthammer, Angew. Chem. Int. Ed., 52: 3320-3327 (2013). doi:[10.1002/anie.201205984](https://doi.org/10.1002/anie.201205984)