# Final Publishable JRP Summary for IND63 MetAMC Metrology for airborne molecular contamination in manufacturing environments

## Overview

Airborne molecular contamination (AMC) is chemical contamination in the form of gases, vapours or aerosols that has adverse effects on products, processes or instruments in clean room manufacturing environments. This project has developed field-deployable optical instruments for online measurement of AMCs in clean rooms and AMC reference materials for instrument calibration. High technology manufacturing industries such as semiconductor, nanotechnology and photovoltaics will now be able to define critical AMC sources, optimise microfabrication processes and enable fast corrective actions in production. As a result, product quality will be improved, yield losses and process shut down times will be decreased and competitiveness will be increased.

## Need for the project

Microfabrication processes are happening on an ever smaller scale, which brings new challenges for environmental control, especially cleanliness. The primary AMC source is the chemicals used in production processes, but the formation and behaviour of these contaminants in production environments are largely unknown because there is currently a lack of sensitive on-site measurement methods for air cleanliness. The relevant chemicals are very diverse in nature: acids, bases, condensables, dopants and metals, and are often reactive and highly adsorptive and thus difficult to measure. The relevant levels of these molecules are typically at the (sub) parts per billion level, making their detection extremely challenging.

There is a clear demand from high technology manufacturing for measurement methods that are capable of reliably detecting AMCs in real time. This means that the process phases where AMC concentrations have risen above normal background levels can be identified quickly and the contamination source identified. Early information on unacceptable contamination levels enable corrective actions to be taken before major process yield losses occur and before significant areas of the clean room have been contaminated.

Regulations, know-how and analytical capabilities in this field are much less well developed than in the field of contamination by particles. Currently available instrumentation is often not fit-for-purpose due to high costs, large size, limited reliability and unsuitably long response times. In addition, AMCs are often reactive or they easily condense, and so cannot be stored in a gas cylinder, which makes it hard to produce traceable reference materials for instrument calibration. The project addressed both these issues, and concentrated on the commonly found AMCs.

## Scientific and technical objectives

The aim of this project was to provide reliable methods for monitoring AMCs in clean room manufacturing environments. This required the development, improvement and assessment of a number of potential techniques for practical AMC monitoring (objectives 1, 2 and 3), and the development of appropriate reference materials to provide traceability for the AMC measurements (objective 4) and sampling techniques (objective 5). The project objectives were:

1. Check the principle (laboratory tests) and practical usability (inter-comparison & field tests) of photoacoustic spectroscopy (PAS), cavity ring-down spectroscopy (CRDS) and cavity-enhanced

absorption spectroscopy (CEAS) for AMC online detection with a time resolution and sensitivity better than 5 min and 1 ppb, respectively.

2. Develop an advanced spectroscopic system (noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy, NICE-OHMS) for improved sensitivity (at least tenfold compared to techniques studied in the first objective) and report on options both for extending the method to more complex molecules and alternative optical techniques such as femtosecond combs or Fourier transfer infrared spectroscopy (FTIR), for trace gas detection of multiple species.
3. Improve the applicability of gas chromatography (GC) to AMC monitoring by using a technique based on a negative temperature gradient. The developed method will not only improve the separation of analytes (e.g. volatile organic compounds, VOC), but also increase the sensitivity.
4. Develop dynamic generation methods for trace level airborne molecular contaminants. A portable material generator will be evaluated in a comparison.
5. Develop suitable sampling techniques (materials, flow rate, number of sampling points) for practical AMC monitoring.

## Results

*Principle and practical usability of PAS, CRDS and CEAS for AMC online detection*

Optical detection based on laser spectroscopy was chosen as the main detection technique, since it combines many properties sought in AMC monitoring, e.g. a short measurement interval, high chemical selectivity, which lowers the probability of costly false alarms and high dynamic range, such that high concentration peaks are not missed.

Successful spectroscopic detection of AMCs depends on the existence of strong and relatively isolated spectral windows specific to the AMCs that are identifiable using commercial off-the-shelf laser sources. Firstly, the spectral windows were identified for five pre-selected common analytes ($NH_3$, HCl, HCOH, HF and HBr), then a survey on the availability of suitable commercial lasers or frequency conversion-based light sources was carried out. $NH_3$, HF and HCl were selected for further studies.

Estimates for the minimum detectable amount were performed for each analyte. It was found that the three most important AMCs defined by the stakeholders were within the measurement capabilities of the project partners in the MetAMC project.

Several instruments based on different spectroscopic methods (PAS, CEAS and CRDS) were developed for online detection of the selected AMCs. All instruments met the targeted time resolution and sensitivity; and their practical applicability for online monitoring was successfully demonstrated in clean room measurement trials. Moreover, two mid-IR light sources based on PPXX technology were developed to provide new practical high power light source alternatives for CRDS and PAS spectroscopy.

This objective demonstrated that the performance of the optical techniques developed in the project meets the current needs of clean room operators for AMC detection at part-per-billion (ppb) levels, both in terms of measurement sensitivity (better than 1 ppb) and time resolution (better than 5 minutes) even for very reactive compounds like HF. The time resolution achieved allows for real-time monitoring and timely corrective actions, in case of unacceptably high AMC concentration in the clean room air. The sensitivity ensures that very low concentrations — which are still relevant for clean room manufacturing processes — can be detected. The techniques developed have the potential for commercialisation for industrial use.

*Developing NICE-OHMS system for improved sensitivity and studying options for extending the method to more complex molecules and alternative optical techniques such as femtosecond combs or FTIR for trace gas detection of multiple species.*

NICE-OHMS offers much greater measurement sensitivity than the other spectroscopic methods investigated, and thus has the potential to make accurate measurements at even lower concentration levels. A prototype NICE-OHMS spectrometer was successfully developed by NPL and used to measure different concentrations of ammonia in nitrogen. The project also outlined methods for multi-species detection, particularly using femtosecond combs. The objective was completed and the spectrometer calibrated in the ~100 nmol/mol to 10 µmol/mol range at different ammonia concentrations prepared using a high accuracy, self-referencing dilution device developed at NPL as part of this project. The NICE-OHMS device has the potential to be further developed for commercial applications, and a company is in the early stages of discussions about using this technology.

*Improving the applicability of GC to AMC monitoring by using a technique based on a negative temperature gradient*

Gas chromatography is a commonly used technique for measuring AMCs, although the conventional techniques cannot detect low concentrations. A gas chromatography method based on the use of a negative temperature gradient for off-line analysis of AMC was developed and tested so that the capabilities of GC could be improved.

The method enhanced the signal-to-noise ratio when analysing AMC, and makes it possible to use the GC technique with flame-ionisation detector (FID), which is often used for elementary AMC analysis. The improved separation of target components prevents co-elution (where compounds do not separate chromatographically) with other components in the sample, which would happen in conventional GC. Therefore, the developed technique allows analysing AMC components that have a very low concentration and thus are difficult to determine by conventional GC.

*Dynamic generation methods for trace level airborne molecular contaminants*

A review of existing dynamic methods for generating reference standards for several key airborne molecular contaminants in manufacturing environments at trace amount fractions was made. This provided the basis for the development of several new dynamic reference standards of key airborne molecular contaminants.

Two dynamic facilities for generation of $NH_3$ and HCl based on permeation tubes were designed and constructed to cover a broad range between a few nmol/mol up to one µmol/mol with an uncertainty of typically 2 % ($k$=2) or better. In parallel two self-referencing portable dilutors were constructed. A generation system based on two-stage dilution was constructed and validated for the preparation of standard atmospheres of semi-VOCs at levels of 10 ppb down to ~100 ppt. A portable dynamic generation system for methanol was designed and built making use of computational fluid dynamics modelling. The reproducibility (3 % at 80 nmol/mol level) and stability (better than 1 % per hour,) of the prototype generator was demonstrated to fulfil stakeholders' needs in calibration of AMC monitoring devices.

Traceable dynamic reference methods and generators were established for trace amounts of a number of molecules, ranging from small reactive compounds to large semi-VOCs. This successfully provided the metrology infrastructure as set out in the objective. The methods and devices allowed calibration of instrumentation to monitor AMCs at trace levels. This will enable better monitoring of individual clean room conditions and enable better comparisons between different clean room facilities.

*Suitable sampling techniques for practical AMC monitoring*

Proper sampling is crucial to get the AMC from the point of sampling to the analyser in a short period of time without affecting the concentration of the sample. The high reactivity and adsorptivity of the common AMCs combined with their very low concentration make this challenging. Different sampling lines were tested for the monitoring of ammonia and a multi-point sampling system was designed, constructed and optimised for simultaneous detection of HF and $NH_3$. Detailed tests were done to optimise response time.

The results indicate that the most essential points in sampling system design are proper tubing materials, high enough sample flow rate and continuous sample line flushing. The polymer PVDF was found to be the best tubing at low humidity levels while at high humidity PTFE performs better. The sampling system developed for simultaneous continuous measurement of HF and $NH_3$ showed high enough sensitivity and fast response time to enable its use on forthcoming customer projects and even in production situations.

## Actual and potential impact

This project established new AMC monitoring and reference gas generation methods, which meet the current requirements of industry to control manufacturing conditions in clean rooms. Industry can benefit from new reference materials for AMC analyser calibration, availability of new optical real-time AMC analysers with ppb sensitivity, availability of new light sources for custom optical AMC analysers, as well as consultation regarding optical detection and GC-based AMC analysis.

The outputs of the project are already being commercialised by NMIs and instrumentation companies. This will ensure the new AMC measurement capabilities will be available to users of clean rooms in high performance manufacturing and research environments:

- The high-tech start-up company Optoseven Oy (www.optoseven.com) has been founded, and will use the project results in commercial gas analyser products for ammonia and hydrogen fluoride.
- The dynamic facility developed within the project for the generation of semi-VOCs has already been used at VSL to provide quality control/transfer standards in sorbent tubes to customers.
- HCP, an instrumentation manufacturer, developed a compact mid-infrared (MIR) laser suitable for AMC detection and for several other MIR applications. The laser will be released to the market after product reliability and long term performance has been verified.
- VSL and HCP are working together towards commercialisation of the cavity ring-down spectrometer.
- NPL will pursue commercial interest with a view to licencing the NICE-OHMS technology.

### *Standards*

The knowledge gained from the development of dynamic capabilities for HCl, $NH_3$ and formaldehyde at NPL has helped to shape the revisions of ISO6142 (Preparation of calibration gas mixtures – Gravimetric method) and ISO6145 (Preparation of calibration gas mixtures using dynamic methods), which are currently addressed by ISO/TC158 (Gas Analysis).

### *Potential impact*

AMC monitoring, and therefore reduction, has a direct financial benefit, through higher product yields and better process reproducibility from site to site. The techniques developed in this project for trace level detection and generation of reactive gases are not restricted to AMC monitoring in clean rooms, but applicable to many fields of research and industry, e.g. breath analysis used in the medical sector and indoor/outdoor air quality monitoring. Due to the hazardous nature of the AMC analytes, the output of this project may also improve the safety of personnel by quantifying specific analytes more reliably. In the longer-term, improving the quality of the produced semiconductor devices, light emitting sources (e.g. LEDs) and photovoltaic units would have a huge potential impact on energy efficiency. For example, simple photovoltaic cells have conversion efficiency around or below ~20 %. Using more sophisticated designs and complex structures could increase efficiency, but they would be more prone to AMC related defects. The results make better control of AMCs possible.

### *Dissemination*

To reach a large audience and stimulate uptake, the project results were disseminated widely, including regular newsletters and the project website (http://www.ptb.de/emrp/metamc.html).Results from the project were presented in eleven papers, twelve posters and fourteen oral presentations, including one invited talk. The project was showcased at three trade fairs to reach the relevant audience from the industry. A stakeholder workshop was organised at the Cleanzone 2015 trade fair to attract clean room technology experts. The workshop provided new insights for the participants regarding measurement capabilities of optical systems, and stakeholders were positive about considering optical detection of AMCs in future planning of AMC monitoring and control in their clean room facilities. The Good Practice Guides addressing the issues of online AMC monitoring techniques and generation of reference gases at trace levels were drawn up for stakeholders and will enhance knowledge on optical detection, sampling, and generation of AMCs The Good Practice Guides will be available on the project website until the end of 2019. (http://www.ptb.de/emrp/metamc.html)

## List of publications

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N. Lüttschwager, A. Pogány, J. Grodde, O. Werhahn, V. Ebert, “Cantilever-enhanced Photoacoustic Spectroscopy of Ammonia with Accelerated Gas Exchange”, *Laser Applications to Chemical, Security and Environmental Analysis (LACSEA)*, (25–28 July 2016, Heidelberg, Germany).

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