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## 1 Executive Summary

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.

### The Problem

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.

### The Solution

In response to this problem, the project set out 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, and the development of appropriate reference materials to provide traceability for the AMC measurements and sampling techniques.

### 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<sup>1</sup> 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

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<sup>1</sup> Note that ppb in this report quantifies an amount fraction and is equivalent to nmol mol<sup>-1</sup>. We use ppb in the following, because it is much more common in the industry than the SI-based unit nmol mol<sup>-1</sup>.

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>)

## 2 Project context, rationale and objectives

### 2.1 Context

Monitoring of AMC in clean rooms can be done using a variety of techniques which, in a first step, can be divided into online and offline techniques. “Offline” means that a delayed analysis in a laboratory is required after air is sampled or some measurement device has been exposed to air (e.g. environmental reactivity coupons, ERCs). Although measurement results from offline techniques can be helpful to reconstruct and analyse contamination events, they cannot help to directly prevent or mitigate such events. With “online” techniques we mean techniques which report AMC concentration at least every few minutes and which can be operated directly in the clean room. An online AMC monitor that provides prompt and reliable measurements would be valuable as it allows early detection of (higher than acceptable) contamination, determination of the contamination source, corrective actions before valuable data is lost or major losses in the yield occur, and to quickly assess the air quality in mini-environments.

Currently available instrumentation, typically based on mass spectrometry and environmental reactivity coupons (ERCs), is often not fit-for-purpose due to high costs, large size, limited reliability, or unacceptable long response time. Examples of online techniques which are also used in AMC monitoring (listed in the ITRS) are based on ion-mobility spectrometry, chemiluminescence, UV spectroscopy, cavity-enhanced spectroscopy, or photoacoustic spectroscopy. Laser techniques, such as the latter two examples, combine many properties sought in AMC monitoring and have the potential to become a preferred method in the industry. In these techniques, a laser is used to probe the wavelength-dependent interaction of gas and light at very high spectral resolution which enables low cross-sensitivity and rare false-alarms in well-designed systems. Laser spectra can be recorded with a time resolution well below a second. Through the use of cavity-enhancement or photoacoustic detection, sensitivities in the range of 0.1 ppb to a few ppb in a measurement interval of a few seconds to minutes are possible for some typical contaminants.

Laser-based techniques such as cavity ring-down spectroscopy (CRDS), cavity-enhanced absorption spectroscopy (CEAS), and photoacoustic spectroscopy (PAS) have reached technical maturity and many analysers based on these techniques are now commercially available, although they are commonly designed for different applications. Some of these instruments are advertised as AMC monitors, but there is a lack of accessible knowledge on field-performance in clean rooms, optimal handling, and reliability. Moreover, they usually lack traceability and metrologically sound uncertainty analysis. This calls for the development of a solid metrological infrastructure.

The current demand for online AMC analysers is clearly substantiated in the International Technology Roadmap for Semiconductors (ITRS, 2011)<sup>2</sup>, which states ‘There is clearly a need for better AMC monitoring instrumentation in the clean room to measure AMC at the part per trillion level (by volume) in real time.’ The ITRS also states ‘The impact of AMC on wafer processing can only be expected to become more deleterious as device dimensions decrease.’ Industrial sectors for which online monitoring and control of AMCs are crucial include in addition to semiconductor industry nanotechnology-, photovoltaic- as well as high brightness and organic LED industries, among others.

The high tendency of the common AMCs to adsorb on surfaces, combined with their ambient concentration being very low, makes sampling a challenge that has to be solved before a monitoring system will be fully functional. A further need from industry exists for reference materials for AMCs at appropriate amount of substance levels. For instance, for an important AMC like ammonia the lowest amount of substance level currently provided by national metrology institutes is one ppm, far above the limit set by the industry, which is

<sup>2</sup> The ITRS identifies the needs and technological challenges facing the semiconductor industry over the next 15 years and is sponsored by amongst others the European Semiconductor Industry Association ESIA.

closer to ppb. For many other AMC's like semi-Volatile Organic Compounds (sVOCs), the situation is markedly worse as reference materials are completely lacking. Current practice is to set up ad hoc systems for gas mixture generation using in particular permeation or diffusion sources of unknown performances, which are not traceable. Alternatively, gas standards in cylinders, often of unknown or even known poor quality, are used and diluted using mass-flow controllers. Reference gases at low concentrations and reliable sampling techniques are needed for validation and traceable calibration of the AMC monitoring instruments.

## 2.2 Objectives

The aim of this project was to provide reliable methods for monitoring AMC's 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 actions taken in this project to tackle the problems associated with AMC monitoring in clean rooms can be categorized in three central themes:

- **Measurement of AMC's:** Development of online AMC measurement capabilities based on optical detection techniques (well-established as well as novel) and improvement of conventional non-optical techniques
- **Sampling of AMC's:** Development of sampling methods to increase the practicability of AMC monitoring
- **Generation of AMC's:** Development of dynamic and portable methods to generate reference gas mixtures with trace AMC concentration for traceable instrument calibration

The project objectives are oriented towards these three prerequisites for practical and reliable AMC monitoring.

### Objective 1

Check the principle (laboratory tests) and practical usability (intercomparison & 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.

### Objective 2

Develop an advanced spectroscopic system (NICE-OHMS) for improved sensitivity (at least tenfold compared to PAS, CRDS and CEAS) and report on options both 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.

### Objective 3

Improve the applicability of gas chromatography (GC) to AMC monitoring by developing 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.

### Objective 4 & 5

Develop dynamic generation methods for trace level airborne molecular contaminants. A portable material generator will be evaluated in a comparison.

Develop suitable sampling techniques (materials, flow rate, number of sampling points) for practical AMC monitoring.

### 3 Research results

#### 3.1 Optical AMC detection based on cavity-enhancement spectroscopy and photoacoustic spectroscopy (Objective 1)

The outline of the research undertaken in this objective is as follows: Spectrometers for AMC detection were developed by PTB (PAS for  $\text{NH}_3$  detection), VSL (PAS and CEAS), and VTT MIKES (PAS for simultaneously detection of  $\text{NH}_3$  and HF). The developed systems, as well as a commercial CRDS system (PTB), were evaluated in laboratory tests and partially in field campaigns in clean rooms (PTB, VTT MIKES) and compared against each other in an intercomparison at VSL. The sensitivity and time resolution target for the systems was 1 ppb in 5 min, which is required in AMC monitoring. The developed systems surpassed the current state-of-the-art by novel sample handling, the use of novel light sources, or the combination of laser amplification and multi-pass configuration to extend sensitivity, for example. Some activities required close collaboration of participants: HCP developed a novel OPO laser, which was characterised and used to develop a CEAS spectrometer at VSL. The intercomparison of spectrometers made heavy use of reference gas generation capabilities at VSL.

In the following, the undertaken research is described in greater detail.

##### 3.1.1 Selection of analytes, absorption lines, and light sources

The development of new spectroscopic measurement systems was preceded by a stakeholder questionnaire to identify the most important AMCs. 14 Stakeholders from both industry and research institutions participated in the questionnaire which yielded that ammonia ( $\text{NH}_3$ , 9 votes), hydrogen fluoride (HF, 8 votes), and hydrogen chloride (HCl, 7 votes) should be the main target of the MetAMC project.

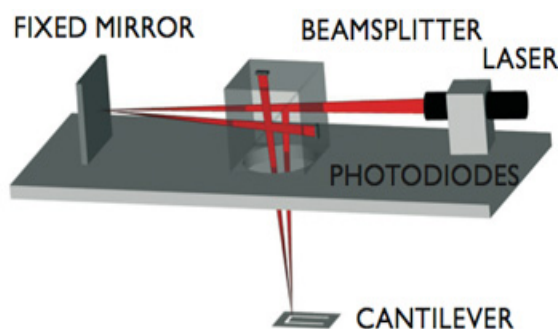
Spectral simulations of these and other important AMC in air were prepared jointly by NPL, PTB, VSL and VTT MIKES to identify optimal spectral regions with low potential cross-interference from other common air components and strong light absorption by the target compound. These simulations were the foundation to choose appropriate light sources (lasers) for the systems that were developed later in the project. The chosen wavelengths were partly located in the near-infrared (NIR) range where technically mature and robust diode lasers are available:  $6548\text{ cm}^{-1}$  for  $\text{NH}_3$  (used by NPL, PTB, VTT MIKES),  $7618\text{ cm}^{-1}$  for HF (used by VTT MIKES); Furthermore, optical parametric oscillators at  $2963\text{ cm}^{-1}$  for HCl and a quantum cascade laser operating at  $1053\text{ cm}^{-1}$  for  $\text{NH}_3$  were used by VSL.

##### 3.1.2 Spectrometer development and characterization

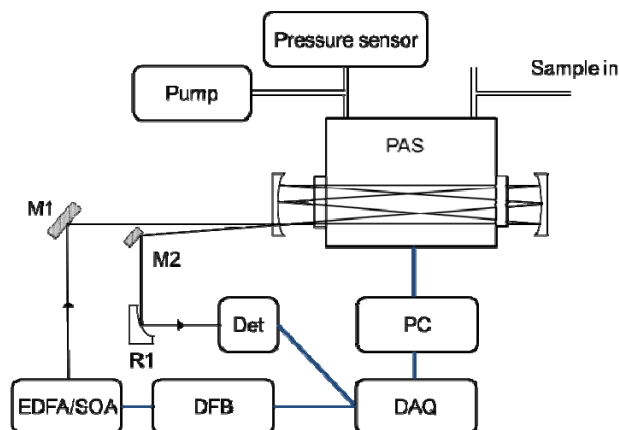
A photoacoustic spectrometer (PAS) based on an optical cantilever-microphone was developed for the *simultaneous detection of ammonia and hydrogen fluoride* based on cantilever-enhancement. Cantilever-based photoacoustic spectroscopy (CEPAS) has the advantage of high sensitivity. An optical cantilever-microphone platform from a commercial PAS spectrometer was used as a starting point for constructing the device. Optimal wavelengths for  $\text{NH}_3$  and HF were selected according to simulations and laboratory test results (see above). To enhance sensitivity, optical amplification was used both for  $\text{NH}_3$  and HF lasers (erbium-doped fibre amplifier (EDFA) and a semiconductor optical amplifier (SOA), respectively). This showed increased photoacoustic signal levels without significant increase in noise and accordingly improved the sensitivity by a factor of 5 to 10. Also an optical multipass scheme (Herriot-type) was implemented to further enhance the sensitivity of the analyser by a factor of 4 to 8. Sensitivity (RMS) of the analyser for  $\text{NH}_3$  is approximately 1 ppb and for HF 0.2 ppb using one-minute averaging time.



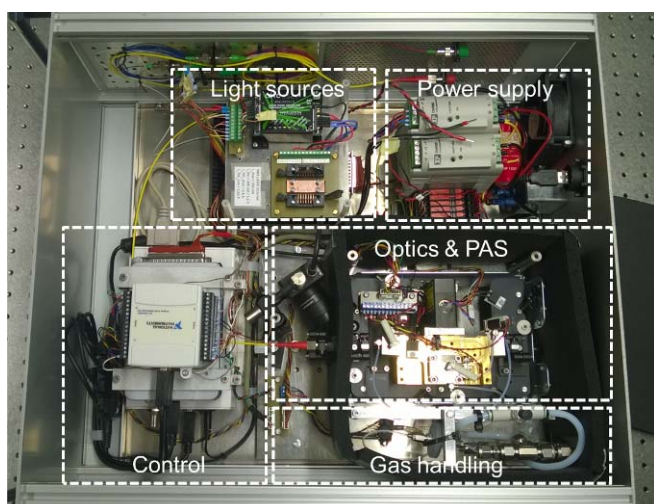
## IDEA



## DESIGN



## PROTOTYPE



## MEASUREMENTS

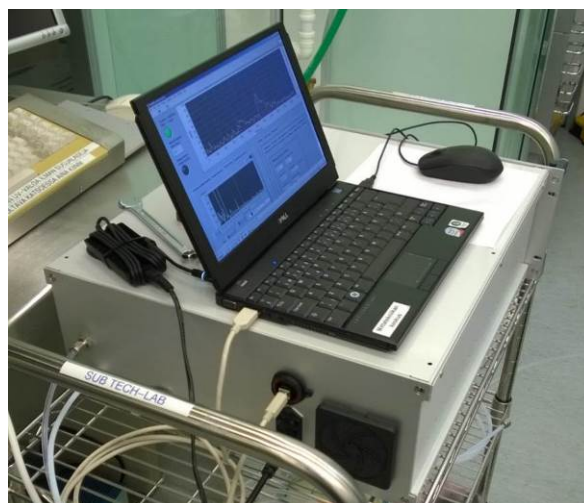


Figure 1. Principle of photoacoustic spectroscopy (PAS) with optical cantilever microphone (top left); design for PAS analyser (top right); prototype analyser with 19" rack enclosure cover open (bottom left); analyser measuring  $\text{NH}_3$  and HF in a clean room.

To enable simultaneous continuous measurement of acid and base gases HF and  $\text{NH}_3$  by using the developed photoacoustic analyser, a novel sampling system was developed. This included evaluation and optimisation of sample pump types and configurations, line lengths, sample-wetted part materials, sample gas filtering, and flow rates. The response time depends on the sampling scheme. On standard operation the response time (10 %  $\leftrightarrow$  90 %) is below 180 s for  $\text{NH}_3$  and below 360 s for HF. The whole system is controlled and automatically run by proprietary software developed with LabVIEW. The instrument performance was tested in VTT's clean room facilities. The device was capable of autonomous operation over long periods (several weeks) and the testing in clean rooms was done during a total of several months' period. It was possible to detect the background level of about 3 ppb to 6 ppb for  $\text{NH}_3$  in different clean room spaces. For HF the background level was below the minimum detection limit of about 0.5 ppb for the analyser.



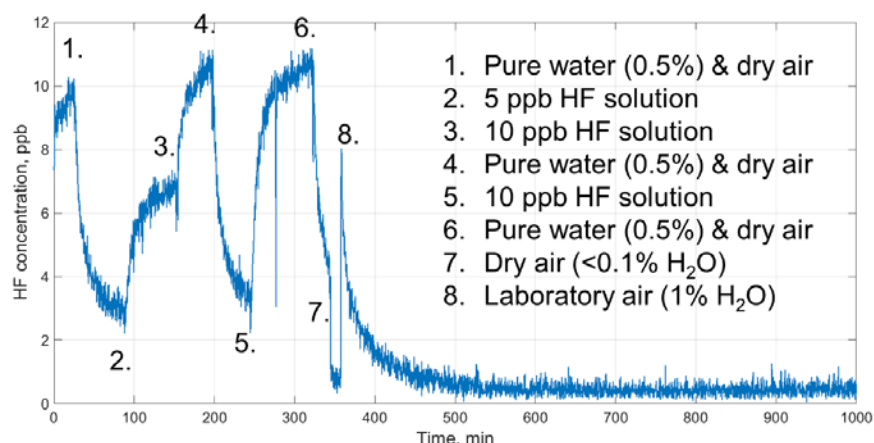


Figure 2. Laboratory tests for the analyser. Sub-ppb performance achieved when measuring HF.  $\text{NH}_3$  was measured with close to 1 ppb level (not shown in figure).

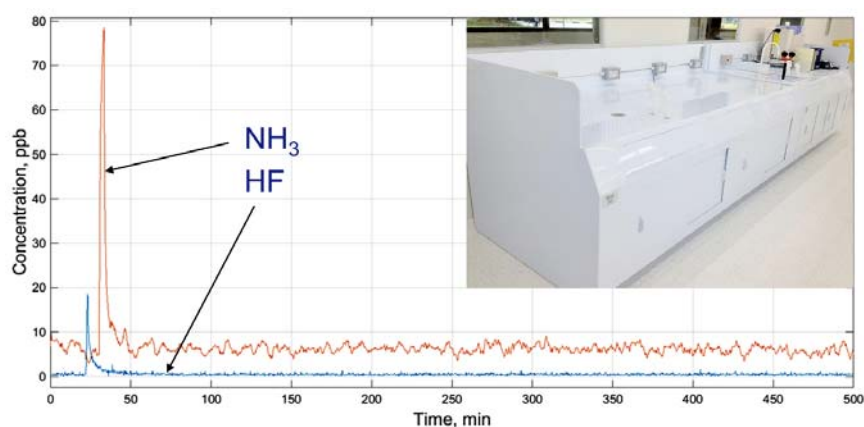


Figure 3. Test measurements near wet benches containing both HF and  $\text{NH}_3$  solutions. Elevated  $\text{NH}_3$  background level observed in less clean area.

A second CEPAS spectrometer was developed for ammonia detection, leveraging a commercial photoacoustic cell equipped with an optical cantilever microphone. The focus of the development of the second CEPAS instrument was on a new measurement procedure. CEPAS measurements are usually done using static gas samples, whereas gases that adsorb strongly on surfaces require measurements in flow. Measuring a flow of sample gas requires that the sample cell stays open during the measurement of the acoustic signal, which leads to rather strong pick-up of noise, typically cancelling the advantage of high sensitivity of the optical microphone. To overcome this limitation and to enable measurement of strongly adsorbing ammonia, the new measurement procedure was developed: a spectrum is scanned while the gas is rapidly exchanged, i.e. each spectral point is measured from a fresh gas sample with the sample cell being closed during the actual photoacoustic signal measurement. This procedure allows a high gas throughput and a short retention time of the gas sample in the measurement cell without sacrificing sensitivity due to flow-noise. Laser and gas exchange control, as well as signal processing and logging are realized by proprietary software developed with LabVIEW.

Ammonia amount fraction results are retrieved from spectra by linear correlation to a spectrum measured from a gas sample with known concentration. The use of a laser amplifier allowed for a detection limit ( $3\sigma$ ) of about 20 ppb (see Figure 4). The shortest measurement interval which was realised was 3 minutes. The measurement interval was limited by the speed with which the cantilever position is sampled and the width of the photoacoustic spectrum that is measured. The PAS spectrometer could thus not compete with the cavity ring-down system that was also used by PTB (see below).

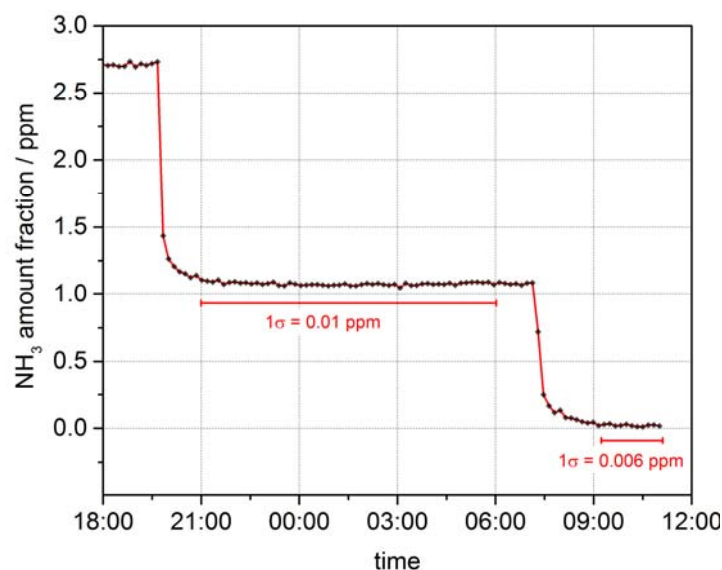


Figure 4. Time series of test measurement of ammonia gas mixtures with the second photoacoustic spectrometer to characterize sensitivity and response time (1 ppm = 1000 ppb).

Note that the two CEPAS instruments described above have a slightly different focus. The first instrument uses a multi-pass configuration to increase the sensitivity and two lasers to simultaneously detect  $\text{NH}_3$  and HF. The second instrument lacks a multi-pass configuration and measures only  $\text{NH}_3$  with a single laser. However, it scans the ammonia spectra in a wider spectral range and derives the concentration from a correlation with a reference spectrum, while the first instrument measures the photoacoustic signal at fewer, selected wavelengths. The first allows for a higher time-resolution and a better sensitivity, but it is more prone to measurement bias due to changes in the gas matrix. The second instrument will indicate those by an increased measurement uncertainty. Therefore, the first instrument is optimised for best sensitivity, while the second instrument makes a compromise to get an indication for unusual measurement conditions.

A commercial cavity ring-down system for ammonia was characterized in laboratory measurements and clean room performance tests. Laboratory measurements confirmed detection limits well below 1 ppb ( $3\sigma = 0.35$  ppb with shortest measurement interval of about 1.7 s,  $3\sigma = 0.03$  ppb for averaging five minutes). Measurements of the instrument's 10 % to 90 % rise time<sup>3</sup> yielded values between 40 s (0 to 200 ppb) and 90 s (0 to 50 ppb) while the 90 % to 10 % fall time was found to be shorter, between 10 s (200 to 0 ppb) and 60 s (50 to 0 ppb). This allows for measuring with a time resolution of better than 5 minutes, as required by objective 1. Measurements of ammonia reference gas mixtures yielded deviations of measurement results to reference values, which were smaller than their expanded ( $k = 2$ ) uncertainties, i.e. the measurement results were compatible with reference values (expanded  $k = 2$  uncertainties of reference values and measurement results were both between 5 % to 6 %). In general, a low uncertainty enhances the comparability of measurement results and thus facilitates reproducing process conditions from site to site. Especially important for industrial applications is the detection of alarm conditions (AMC concentrations beyond individually set upper limits), which may have less stringent requirements regarding the measurement uncertainty. The uncertainty stated above should be adequate for such applications where the analyser is used to detect accidental release of AMC.

<sup>3</sup>The 10 % to 90 % rise time and 90 % to 10 % fall time are used to indicate how quickly the instrument can detect changes in the amount fraction of the target analyte in the sampled gas. They are quantified by measuring the instrument response to a step change in the amount fraction of the sampled gas, e.g. by using two reference gases and a switching valve. The signal that the instrument provides in response to the step change is delayed due to the time it takes to exchange the gas in the instrument's measurement cell, analyte ad/desorption on wetted surfaces, etc. The time it takes for the signal to increase from 10 % to 90 % relative to the change of the amount fraction of the sample (reference) gas is denoted the '10 % to 90 % rise time'. The time it takes for the signal to drop from 90 % to 10 % when the sample gas amount fraction is abruptly decreased is denoted the '90 % to 10 % fall time'.

Performance tests in PTB's clean room demonstrated the observation of small and slow variations in the ammonia ambient concentration in the sub-ppb range, which may be attributed to clean room staff activity (exhaled ammonia, ammonia emission from skin). These variations were superimposed on a background level of about from 4 ppb to 5 ppb. Observation of a wafer etch process using hydrogen fluoride buffered in ammonium fluoride solution demonstrated that the response and recovery of the CRDS instrument is fast enough to detect ammonia amount fraction changes in the ppb range, which happen on the time scale of a few seconds up to a few minutes.

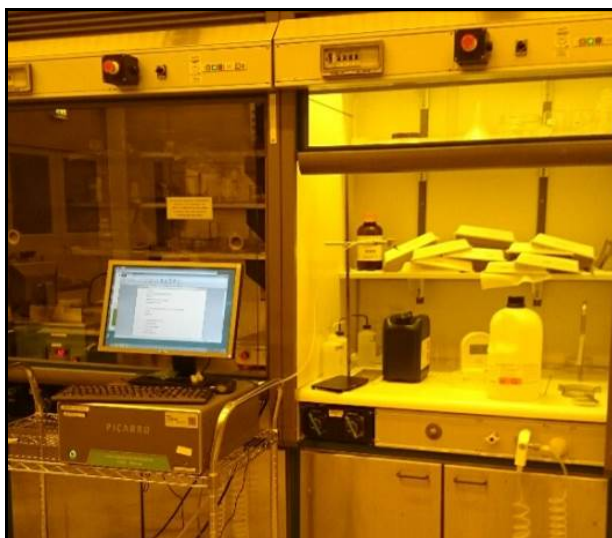


Figure 5. Cavity ring-down instrument next to fume hood in PTB's clean room, monitoring a wafer etch process.

A cavity ring-down spectrometer for detection of hydrogen chloride was developed using an optical parametric oscillator (OPO) system that is based on PPXX (periodically poling lithium niobate/tantalate) technology developed by HCP. VSL and HCP worked together on the design of the compact OPO and the spectrometer. HCP constructed the compact OPO, which provides mid-infrared light with an output power of 10...~100 mW, linewidth of <100 MHz, and a wavelength range from 2800 nm to 3700 nm. VSL and HCP will work together continuously towards commercialization of the instrument e.g. by improving its stability and integrated feedback control.

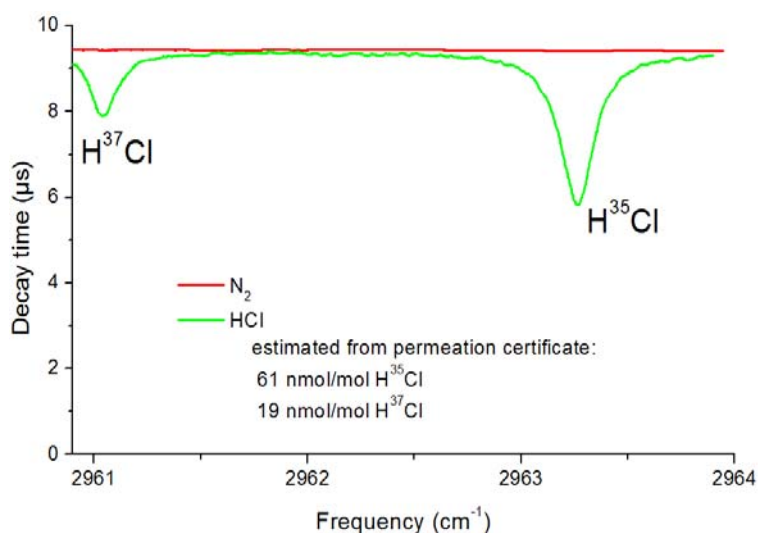


Figure 6. Measurement result of low amount fractions of HCl using CRDS. Both major isotopes can be recorded in a signal scan of the OPO. The sensitivity for HCl of the system is around 100 pmol/mol (ppt).

PTB, VSL, and VTT performed an intercomparison between three ammonia spectrometers based on cavity ring-down spectroscopy (PTB), cavity-enhanced absorption spectroscopy (VSL) and photoacoustic spectroscopy (VTT). The three systems measured simultaneously ammonia in the ppb range generated via dynamic dilution of static reference mixtures. Typical relative uncertainty in the measurements was 1 % for the CRDS system and about 5 % for both other systems. In addition, the effect of low (~100 ppm) water levels was investigated. It was shown that addition of water led to a release of previously adsorbed ammonia and that this effect lasted for a prolonged period of time (>1 hour). The time responses of the instruments were fast but difficult to quantify as there was a notable ammonia adsorption/desorption in the gas flow system even though only polymer tubings and a SilcoNert coated mass flow controller were used. Moreover, the photoacoustic experiment had a strong, unexpected dependence on the matrix gas (air vs nitrogen).

### 3.2 Develop an advanced spectroscopic system (NICE-OHMS) for improved sensitivity (Objective 2)

The selected technique is a variant of cavity enhanced spectroscopy that also incorporates the advantage of excellent signal to noise ratio obtained by detecting signals at high frequencies (~GHz) where the laser shot noise is low. The gas sample is contained within a very high finesse optical cavity (the measured optical finesse of our cavity was  $F \sim 171,000$ ) and the laser is frequency modulated at the cavity free spectral range. For our 10 cm cavity, this frequency is ~1.5 GHz; electronics were developed and tested to servo this frequency to the exact free spectral range. When the laser is modulated at this frequency, the carrier and two sidebands all resonate within the cavity and the device behaves as if we were performing frequency-modulation (optical heterodyne) spectroscopy on a sample of length  $2F/\pi$  times the cavity spacer length of 10 cm. In our system this effective path length is therefore approximately 11 km. The combination of this long effective path length and the low laser noise at a high modulation frequency gives the method its very high sensitivity. A further advantage of the method is that the output signal is also largely independent of laser frequency noise induced by a non-ideal lock of the laser to the cavity. This method is therefore termed “noise-immune cavity-enhanced optical heterodyne molecular spectroscopy” or “NICE-OHMS”.

In common with other methods involving laser spectroscopy, NICE-OHMS requires lasers to be commercially available at frequencies where there are strong and well-resolved linear absorption features. From the results of a survey of clean-room users in the first few months of the project, it was decided that ammonia was of significant industrial interest and also had the advantage of laser and optical component availability in the ~1530 nm region, where there were strong linear absorptions. Whilst this technique has previously been published, this was the first time that this method was applied to AMCs of importance to the clean-room community. Previous published results were often (but not always) limited to molecules such as acetylene that allowed use of narrow-linewidth 1550 nm fibre lasers. Our system required the frequency stabilisation of DFB laser diodes (linewidth typically 1 MHz) to optical cavities that had <10 kHz linewidths; this was a significantly more challenging undertaking than using fibre lasers. Also, we needed to flow gas samples through the cavity, typically at 1–2 l/min. At the start of the project, it was unclear whether a combination of the resulting air turbulence within the cavity and the noisy lasers would make frequency locking impossible. Fortunately, NPL has significant experience in locking of lasers to high finesse cavities in connection with work in optical frequency metrology which we were able to adapt for this application. Nevertheless, it was realised that this would be a particularly challenging aspect of the overall project.

Optical cavities designed for narrow linewidth laser development are generally based around a cylindrical (or similarly shaped) cavity spacer that is held within a vacuum chamber. The spacer is mounted in an evacuated chamber and the spacer is completely closed except for a small vent-hole to allow air to escape during the initial pump-down process. This situation is very different from the AMC detection requirement, where the cavity spacer needs to be as open as possible and operated at atmospheric pressure, with a significant gas-flow (around 1–2 l/min). There was also a concern that the materials used for cavity spacers (Corning ULE or Invar) might also adsorb AMCs, therefore significantly increasing the required gas flow. Finally, it was unclear at the project outset whether prolonged low exposure to ammonia could degraded optical mirror surfaces although discussions with manufacturers indicated that this was unlikely. Initial feasibility tests allowed NPL to design a cavity that has proved to meet these different apparently conflicting requirements.



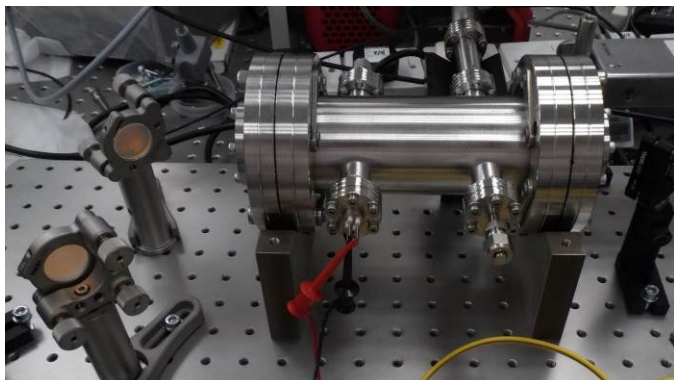


Figure 7. Left: Photograph of the vacuum system containing the optical cavity (two similar cavities in identical vacuum housings were manufactured with different finesses). Right: Lasers at different wavelengths were purchased for the detection of AMCs. In the photo is a 1527-nm laser mounted in a TEC cooling mount.

With the cavity and electronics design finalised, the full system was developed and the NPL time and frequency group (that developed the NICE-OHMS system) worked with the NPL gas metrology team who have developed the capability to generate known concentrations of ammonia in nitrogen down to the ~100 ppb level. At the time of project completion, this system is still being optimised and evaluated; the prototype is easily capable of rapidly detecting this concentration of ammonia and the signal has demonstrated a dependency on ammonia concentration. Also, the system has demonstrated significant robustness by being transported between NPL laboratories without requiring realignment. It has also operated in a gas metrology laboratory that has significantly higher acoustic noise levels and higher temperature instability than the optical laboratories. Part of the requirement of this project was to develop a robust system that could be offered for development into a commercial product and the overall robustness of the prototype device has shown that this has been achieved.

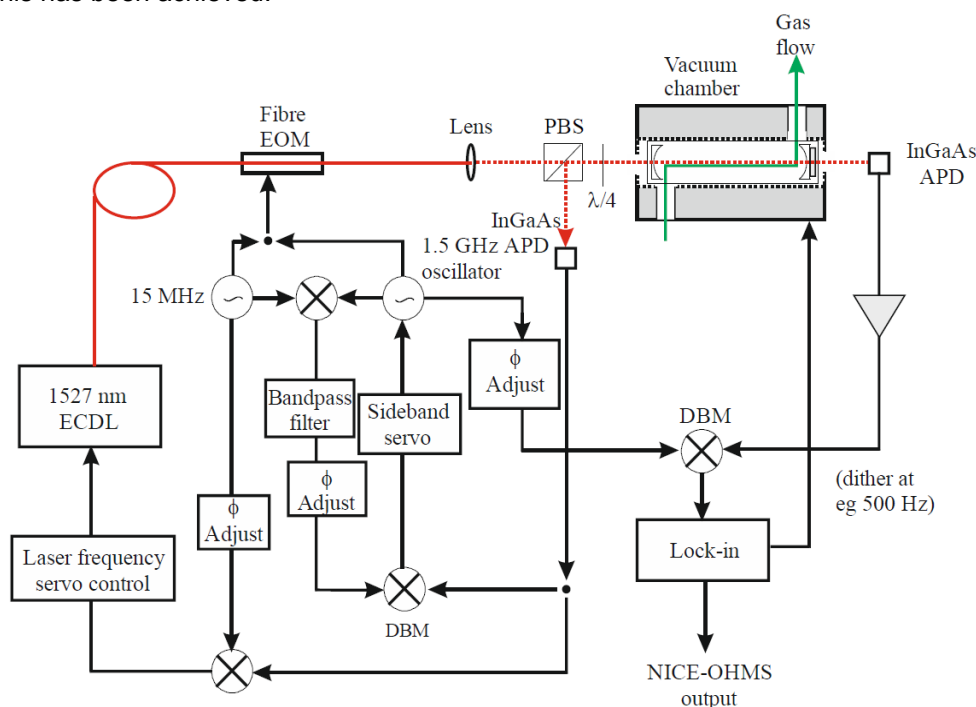


Figure 8. Schematic of the overall NICE-OHMS system, including the optical cavity in its housing, the laser and electronics for the cavity and free spectral range lock. Free-space optical outputs are shown as dotted red lines. Fibre connections are shown as solid red lines.

Finally, within MetAMC, we planned to demonstrate the feasibility of NICE-OHMS with other molecules. There are water vapour lines that overlap with ammonia in the ~1530 nm region and these were easily observed using the NICE-OHMS instrument. However, attempts to detect formaldehyde using weak linear absorption features at 1512 nm were not successful. At the time of the project completion, it is not clear why this was and the issue will continue to be investigated. Possible reasons for not observing the formaldehyde was the higher uncertainty in the formaldehyde concentration than the ammonia samples provided by the NPL gas metrology team; also the 1512 nm laser had a larger linewidth and the resulting cavity lock was noisier. It is also possible that there were unexpected adsorption issues with the materials selected for the optical cavity, although this is considered unlikely. For the best sensitivities, it is also note that it would be better to operate further into the infrared (~3  $\mu\text{m}$ ) although some key optical components are not commercially available at this longer wavelength. Good Practice Guides have been produced to indicate how this system might be developed in the future both in preparation for commercial exploitation and for the detection of other molecules. Methods for multi-species detection, particularly comb spectroscopy are also discussed in these reports.

### **3.3 Improve the applicability of GC to AMC monitoring by using a technique based on a negative temperature gradient (Objective 3)**

Volatile Organic Compounds (including sub-classes) in cleanroom environments have usually too low concentrations for analysis via gas chromatography without pre-concentration and sample treatment techniques. Compounds can be accumulated by using a suitable adsorbent. Desorption of the compounds from adsorbents will unfortunately broaden peaks in the subsequent GC analysis. Before injection onto the capillary column, it is thus necessary to focus the analyte band to narrow the peak widths and to have a high signal-to-noise ratio. Bandwidth decreases significantly causing the analyte to concentrate in a small area of the capillary column. Such a technique has been applied in commercially available instruments for some time. In practice, the focusing often causes a severe drop in temperature which on the one side traps quantitatively all compounds but on the other side mixes them together though they were initially released off the sorbent consecutively. This can be improved by using smart focusing, i.e. by cooling a selected area of the column. The cooling causes the analyte to spend more time in the stationary phase, which slows it down. The leading edge of the sample band will then travel more slowly compared to the trailing edge. Hence, the trailing edge starts catching the beginning of the peak.

In this project, a method based on the use of negative temperature gradient for off-line AMC monitoring of a selected analyte. An enriching trap and a cryo-focussing column are the foundation of the system. The temperature of the enriching trap and cryo-focussing column are controlled by dipping them into a liquid nitrogen reservoir and electrical heating while pulling the columns from the liquid nitrogen. Subsequently, the gas sample is analysed on GC with a flame ionization detector (FID).

Controlled desorption helps to improve the separation of the VOC components and subsequent analysis on GC. Separation of the target compounds already begins during desorption from the cryo-focussing column. This pre-separation in turn leads to a better separation of components based on their boiling point. The lower boiling point VOCs have slightly narrower peaks than without the use of controlled desorption.



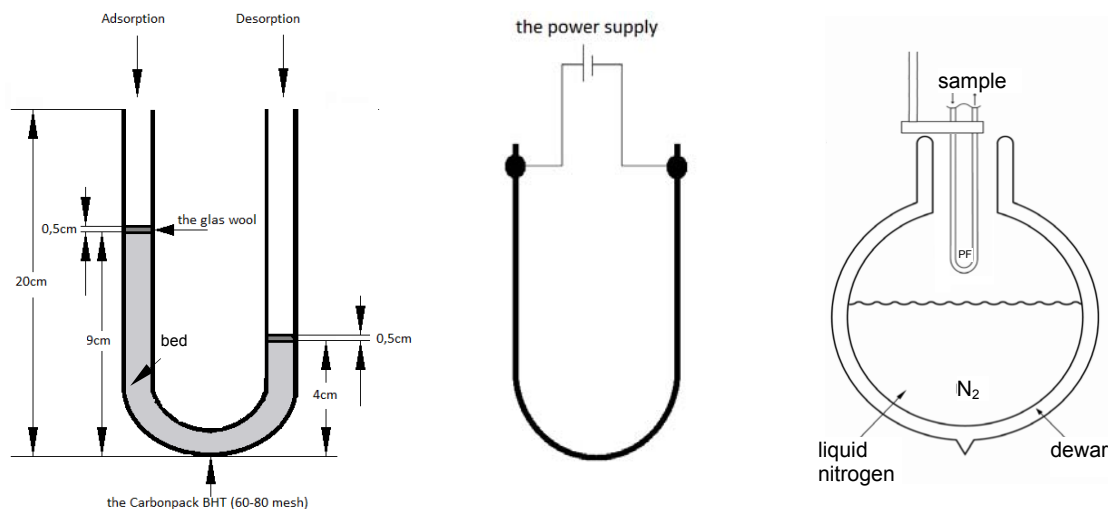


Figure 9. Left: Scheme of the enrichment trap (ET). Geometry of the bed corresponds to the adsorption vs. desorption stream. The bed is held using glass wool plugs. Centre: Cryo-focussing column. Right: Positioning of ET in the Dewar. The enrichment trap is always above the level of liquid nitrogen.

The developed method combines several steps, which are important for the correct determination of VOCs in its entirety. Samples with VOC content can be in the same format as usual (e.g. in canisters). Before GC analysis it is necessary to concentrate the sample as the VOC content is typically very low in the gas sample. The developed device uses a gradual drop in temperature and desorption takes place at a defined temperature and flow and thus prevents a severe drop in temperature that takes place in most of the commercial cryo-focussing equipment. The gradual decrease in temperature also allows each component to be captured in a slightly different location of the column.

The developed method improves the resolution and the signal-to-noise ratio and allows the use of a flame ionization detector in the gas chromatograph for determining VOC content. In figure 10 is shown chromatographs from analysis of hydrocarbon without focus and after focussing. By using an FID instead of a mass spectrometer, an almost equal carbon atom response can be achieved for all hydrocarbons except ethyne. Consequently, even compounds that have not been calibrated can be quantified.

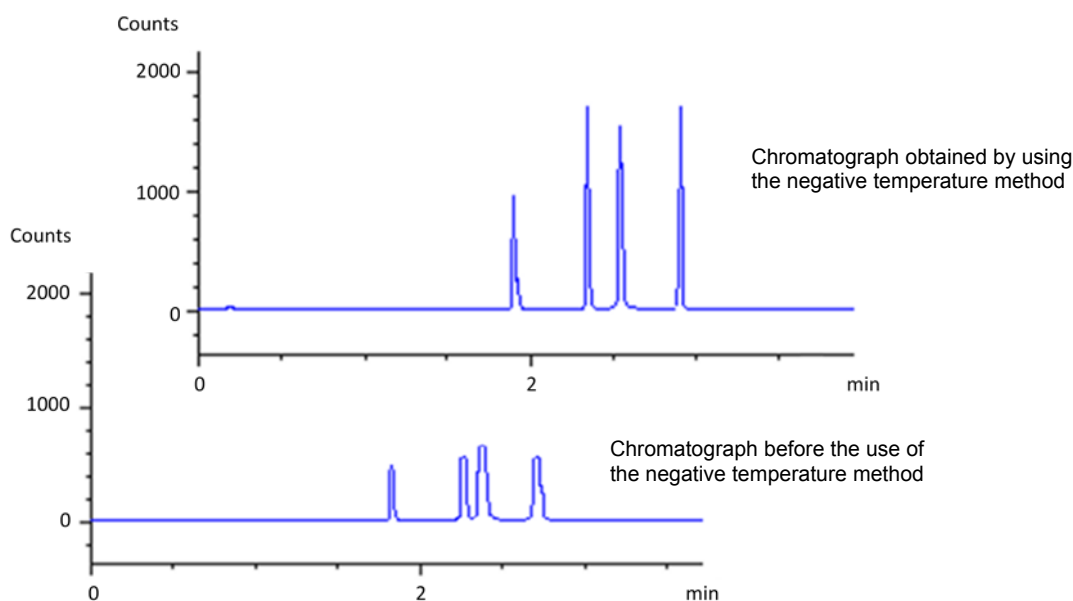


Figure 10. Chromatographs showing improvement in resolution and signal-to-noise ratio achieved by using the negative temperature gradient method. The second and third peaks are clearly resolved in the upper curve.

### 3.4 Develop suitable sampling techniques for practical AMC monitoring (Objective 4)

Proper sampling is crucial to get the AMC from point of sampling to the analyser in a short period of time without affecting the concentration of the sample. Several materials have been tested for their suitability for the monitoring of AMCs and in particular ammonia. The polymer PVDF (polyvinylene difluoride) was found to be the best tubing at low humidity levels, while at high humidity PTFE (polytetrafluoroethylene), a polymer typically used for tubing in analytical laboratories, performed better. All metallic tubing tested had far higher ammonia adsorption (a couple orders of magnitude higher).

Table 1. Summary adsorption data; ammonia on PVDF and PTFE tubing (average of three measurements).

Material	Molecules adsorbed $\text{cm}^{-2}$	Nominal amount fraction $\mu\text{mol/mol}$ (ppm)	Pressure (mbar)
PVDF	$(3.3 \pm 0.6) \times 10^{11}$	0.5	500
PTFE	$(2.2 \pm 1.4) \times 10^{12}$	0.5	500
PTFE	$(4.3 \pm 1.8) \times 10^{12}$	1.5	500

A novel sampling system was developed for the developed photoacoustic analyser to enable simultaneous continuous measurement of acid and base gases HF and  $\text{NH}_3$  by using. This included evaluation and optimisation of sample pump types and configurations, line lengths, sample-wetted part materials, sample gas filtering, and flow rates.

A multi-point sampling system reduces the cost of AMC monitoring but it may have several disadvantages. Longer tubing of a multi-point sampling system may increase the response time. A spectrometer using multi-point sampling provides less usable data for a single measurement point than a point-of-use device: Each sampling point can only be measured for a fraction of the day, and because AMC from the measurement of the previous sampling point might be trapped in the sampling system, the user has to purge when switching between sampling points, which may lead to extended dead time. During this project an automatic multi-point sampling system was constructed and demonstrated for  $\text{NH}_3$  and HF in clean room environment. Its performance was characterised in real-time using a photoacoustic spectroscopy analyser developed within this project and a commercial CRDS analyser. With different configurations for the multi-point sampling system there was no significant difference compared to single-point operation. Response times of the two analysers were comparable with and without multipoint sampling. This result also indicates that the most essential points in sampling system design are proper tubing materials, high enough sample flow rate (several litres per minute) and continuous sample line flushing.

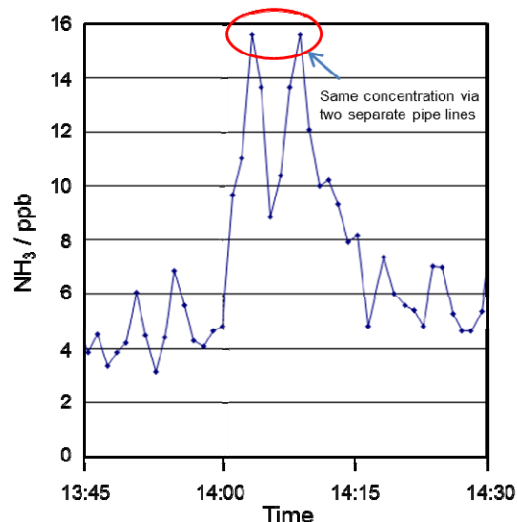
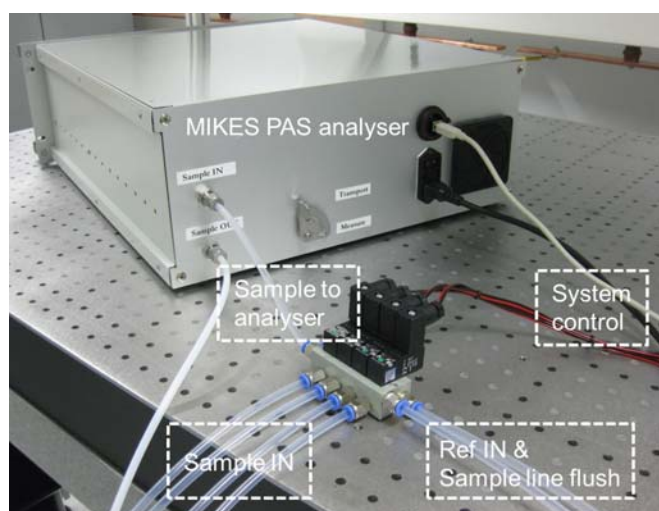


Figure 11. MIKES PAS analyser equipped with multipoint sampling system (left). Multi-point sampling system showed no difference in concentration, when measuring  $\text{NH}_3$  with two separate pipe lines (right).

### 3.5 Develop dynamic generation methods for trace level airborne molecular contaminants (Objective 5)

Reference materials are required for calibration of analytical instruments and quality control. For many AMCs reference materials are lacking as they are reactive or they easily condensate (the latter in particular holds for semi-VOCs) and therefore cannot be stored in a gas cylinder. A solution to this is the use of a dynamic generation system.

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. The review provided the basis for the development of dynamic reference standards of key airborne molecular contaminants.

Two dynamic facilities for generation of  $\text{NH}_3$  and  $\text{HCl}$  based on permeation tubes were designed and constructed. Using split vents, the dynamic range of the setups were optimised to cover a broad range between a few ppb up to one ppm. The uncertainty of these systems is typically 2 % relative ( $k=2$ ) or better. In parallel two self-referencing portable dilutors were constructed. They are based on arrays of critical flow orifices allowing for highly stable and repeatable flows. The prototype was validated and is used as a standard generator for the NICE-OHMS system at NPL using ammonia and formaldehyde static standards. The second portable dilutor is used to validate the permeation tube systems.

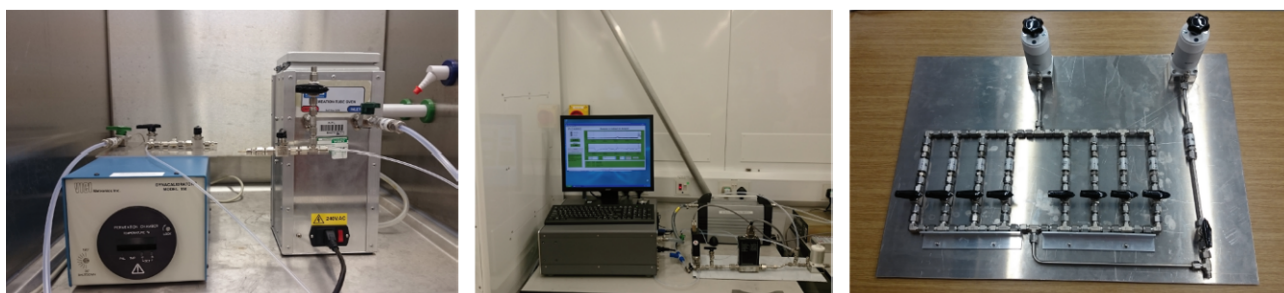


Figure 12. Permeation tube ovens for  $\text{NH}_3$  and  $\text{HCl}$  (top left),  $\text{NH}_3$  analyser and dilution module (top middle), portable self-referencing dilutor prototype (top right)

A generation system (see Figure 13) 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 circa 100 ppt. Semi-VOCs have boiling points between 240–260 °C and 380–400 °C (ISO 16000-61) and low vapour pressure.

Presence of semi-VOCs is a major problem in the semi-conductor industry as it can lead to the development of haze on optical elements. A robust metrological underpinning of semi-VOCs measurements can help to better quantify the semi-VOCs in the industry.

The working principle is based on continuous syringe injection as described in ISO standard 6145-4. The principle is that a liquid mixture is led into an oven to evaporate, and then is diluted with purified air, homogenized and led to the sampling ports.

The system features include:

- Reliable generation of reference gas mixtures containing semi-VOCs due to a unique design preventing cold spots
- Wide range of compounds can be generated including toluene, 1,4-dichlorobenzene, n-methylpyrrolidone, dimethyl phthalate, dibutyl phthalate and n-C10 up to n-C20
- Wide range of concentrations by using either 1 or 2 stage dilution
- Production of transfer standards in thermal desorption tubes

The novelty of the developed system lies in:

- Enclosing the entire generation system in an oven kept at 80 °C to avoid condensation of the semi-VOCs at cold spots.
- Possibility to switch between 1 or 2 stage dilution to cover a wide range of concentrations.
- The new generation system for semi-VOCs at VSL will enable a more reliable generation of high-boiling point VOCs which was not possible previously with existing systems at NMIs.

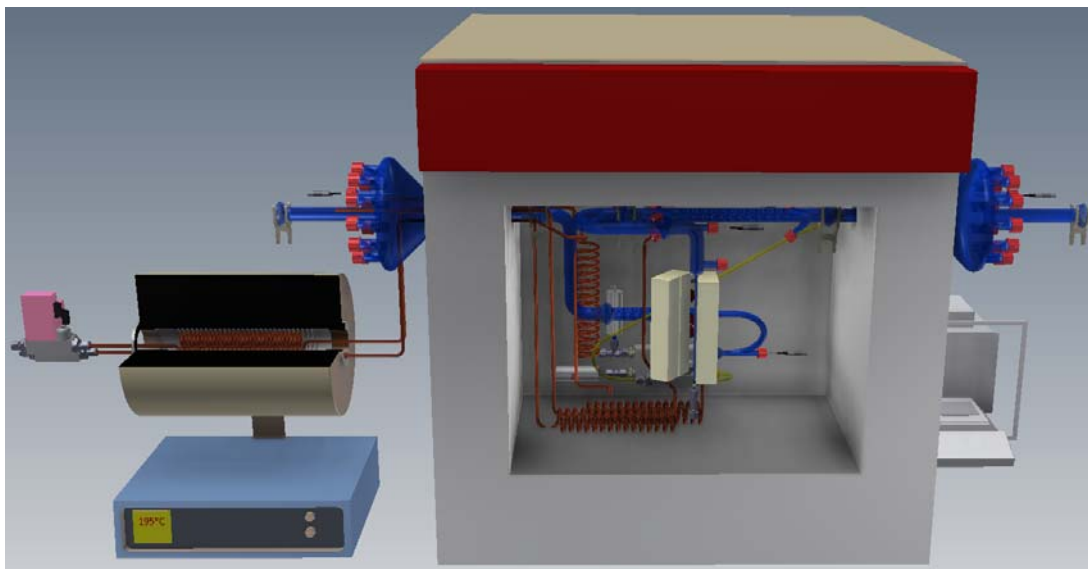
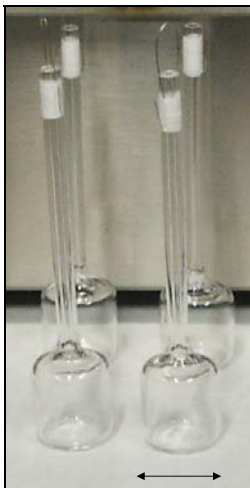


Figure 13. Two stage generation/dilution system for semi-VOCs

A second dynamic generation system was developed as a result of CFD modelling and experimental studies. This system is a portable generator for VOCs. The prototype is dimensioned for preparation of methanol/air mixtures in the range 50–200 ppb. The accuracy of the prepared mixtures is limited by calibrated transportable diffusion vials. MetAMC proposed vials as a transportable standard material for dynamic generation of VOC mixtures by diffusion, INRIM carried out the realization of the transportable vials with calibrated diffusion rates, and together with VSL showed their potential in an interlaboratory comparison.



standard name	VOC	Nominal neck lenght [cm]	Nominal neck i.d. [mm]	nominal DR @ 25°C [ug/min]
IND63_L_Me	methanol	10	0,6	0,5
IND63_L_Ac	acetone	10	0,6	1
IND63_H_Me	methanol	10	2,2	10
IND63_H_Ac	acetone	10	2,2	20

Vial reservoir: 8 g

Figure 14. Standard vials for VOC mixture generation by diffusion. i.d. = inner diameter, DR = diffusion rate.



The prepared methanol mixtures were measured with gas chromatography technique. In addition, during a one-week research visit from INRIM and POLITO researchers to VSL, a mid-infrared CRDS spectrometer developed by VSL was used to establish the short term stability (made possible by the high time resolution of the measurement system). The generator presents a short term stability better than 1 % per hour, a reproducibility of 3 % at the 80 ppb level and a linearity in the molar fraction range 50–200 ppb of 99.6 %. The comparability of primary INRIM and VSL air/methanol mixtures at 50–200 ppb was found to range ranging from 2 % to 17 %. Methanol is one of the chemicals used for wafer cleaning in the semi-conductor industry. In addition, it is the most prevalent VOC in exhaled human breath and thus clean room personnel are an important source of contamination. The 'ITRS 2012 Yield Tables' state an upper limit of several 10's of ppb for VOCs (limits dependent on the process area). Therefore, stability, reproducibility and linearity of the molar fraction the portable system presented are fully in line with the industry requirements. However, the obtained value for comparability highlights the need of further work to improve the accuracy of primary standards at very low concentrations (under 100 ppb).

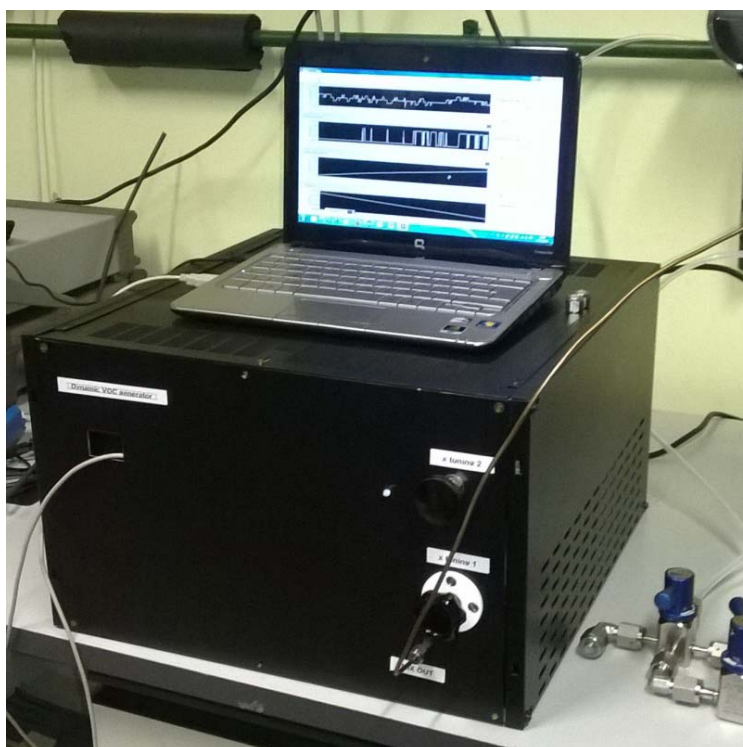


Figure 15. A portable device for producing stable mixtures of VOC in zero-gas was realized as prototype to act as a reference material for instrument calibration. The prototype was used in an interlaboratory comparison.

### 3.6 Summary

#### *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 time, 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 lines specific to the AMCs that are accessible using commercial off-the-shelf laser sources. Firstly, the spectral windows were identified for five pre-selected common analytes ( $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{HCOH}$ ,  $\text{HF}$  and  $\text{HBr}$ ), then a survey on the availability of suitable commercial lasers or frequency conversion-based light sources was carried out.  $\text{NH}_3$ ,  $\text{HF}$  and  $\text{HCl}$  were selected for further studies.

Estimates for the minimum detectable amount were performed for each analyte. It was found that the three most important AMC definitions 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  $\mu$ mol/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. 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  $\text{NH}_3$  and  $\text{HCl}$  based on permeation tubes were designed and constructed to cover a broad range between a few ppb up to one ppm 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<sub>3</sub>. 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<sub>3</sub> showed high enough sensitivity and fast response time to enable its use on forthcoming customer projects and even in production situations.

## 4 Actual and potential impact

### 4.1 Metrological achievements

The MetAMC project has significantly contributed to the promotion of optical techniques for continuous detection of airborne molecular contamination (AMC) in clean rooms. The project has provided field-deployable instruments for online and offline measurement of AMCs and reference material generators for *reliable and traceable* calibration of AMC equipment. Some of the tools are already in use to provide services for customers of NMIs.

Results obtained with different metrologically sound traceable optical instruments provide a solid basis for the uptake of *optical methods* for AMC monitoring in clean rooms and answer for the urgent demand of semiconductor industry to improve clean room AMC monitoring. The outcomes of this project will help in convincing the stakeholders of the measurement capabilities of optical systems, since most current AMC detection techniques are not based on optical technology, but rather on ion mobility spectrometry, mass spectrometry or gas chromatography.

For many AMCs, reference materials were lacking as they are reactive or they easily condensate and hence cannot be stored in a gas cylinder. The project made pioneering work on generation of reference materials by developing traceable *dynamic* gas generation methods. As a result, several NMIs have now knowledge and facilities to handle, sample and generate highly-reactive and adsorptive reference gases at trace levels. The developed equipment has already been used in the MetNH<sub>3</sub> EMPIR project and are planned to be used in possible forthcoming EMPIR projects (e.g. Metrology for biomethane). The dynamic facility developed within the project for the generation of semi-VOCs has already been used to provide services for customers.

### 4.2 Early impact

#### User uptake

The high-tech start-up company Optoseven Oy ([www.optoseven.com](http://www.optoseven.com)) has been founded. Foreground intellectual property (IP) obtained by VTT MIKES (at the time MIKES) in the course of the MetAMC project was transferred to Optoseven Oy. The foreground IP is being exploited in commercial gas analyser products for ammonia and hydrogen fluoride. (<http://optoseven.com/data/documents/Optoseven-HF-and-NH3-Gas-Analyser-Brochure-2015.pdf>)

HCP 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. Depending on the options the laser can deliver MIR wavelength from 2800 nm to 3700 nm, with >200 mW/100 mW MIR power for broadband/single frequency output.

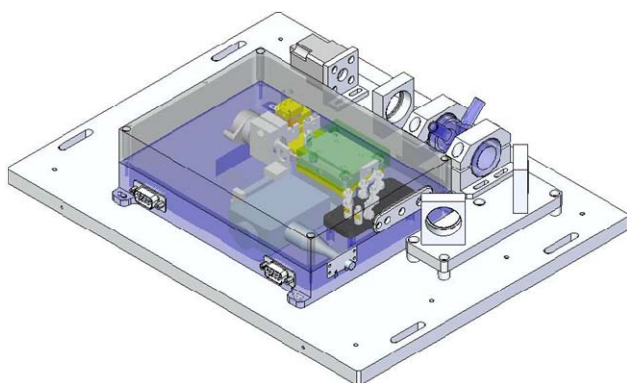


Figure 16. HCP developed a compact mid-infrared (MIR) laser suitable for AMC detection that will soon enter the market.

VSL and HCP are working together towards commercialization of the cavity ring-down spectrometer.

The dynamic facility developed within the project for the generation of semi-VOCs has already been used at VSL to provide services to customers.

The gas sampling and generation methods developed have been utilised in other EMPIR projects (e.g. MetNH<sub>3</sub>).

Now that NPL have an operational NICE-OHMS device, they will pursue commercial interest with a view to licencing the technology. They also plan to continue the collaboration between the NPL time & frequency and gas metrology teams to develop this system for other AMCs and will actively seek further funding opportunities. NPL have also continued activities with UOXF concerning the NICE-OHMS system. This cooperation is a further partnership developed within MetAMC that could continue beyond the end of the project.

PTB was invited to present the project to representatives from the photonics, optics, and semiconductor industry at an expert meeting on clean room technology organized by the expertise network *bayern photonics*. The presentation was well-received and well placed on this event, which focussed on airborne molecular contamination and clean room cleanliness requirements.

#### Standards

Knowledge gained from the development of dynamic capabilities for HCl, NH<sub>3</sub> 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).

### **4.3 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.

### **4.4 Dissemination activities**

#### **4.4.1 Publications**

The project has generated 10 publications in distinguished journals. A list of open access publications is provided in Section 6. Further publications will be prepared at least by PTB (photoacoustic spectrometer and clean room tests) and NPL (NICE-OHMS system, after it is fully characterized).

#### **4.4.2 Conferences & Workshops**

The project was presented on numerous occasions. A wider audience both from science and industry was reached at the *Pittcon* (New Orleans, 2015) and the *17th International Congress of Metrology* (Paris, 2015). The gas analysis community was addressed specifically at the *International Gas Analysis Symposium & Exhibition* (GAS2015), where the project was presented with two posters. The project was also presented on conferences specialized on optics and photonics, for example the *Photon14* (London, 2014) and the 2014

annual conference of the *Deutsche Gesellschaft für angewandte Optik* (DGaO). Overall, project results were addressed in twelve posters and fourteen oral presentations, including one invited talk.

#### 4.4.3 Stakeholder engagement

Stakeholders from the semiconductor industry and other relevant fields were consulted in the early planning phase of the project to select key AMC (see Section 3) and kept up-to-date *via* regular circulation of a newsletter and the project website (<http://www.ptb.de/emrp/metamc.html>). Further contact to industry was sought through the publication of a press release<sup>4</sup>, and by participating in the trade fairs *Laser World of Photonics* 2013 (5000+ visitors), *Optatec* 2014 (5000+ visitors), and *Cleanzone* 2015 (700+ visitors specialized to clean room technology).

The Cleanzone 2015 trade fair was used in particular to present the project to the relevant audience from the industry. Cleanzone is a growing international two-day trade fair and congress on clean room technology with around 730 visitors and 90 exhibitors. Cleanzone 2015, held in Frankfurt am Main, Germany, is a key event on clean room technology in Europe.

The MetAMC presence at the Cleanzone trade fair was widely advertised on the Cleanzone website as well as Twitter and Youtube. MetAMC was featured in the editorial text of the program, and in cleanroom magazine (04/2015). The project was showcased on an open lecture area with two oral presentations and had a separate stand with a demo model of a mid-infrared laser from HCP and posters offering detailed information on project results (Figure 17).

The MetAMC consortium was engaged in dozens of discussions with clean room consultants, clean room equipment manufacturers and advanced clean room operators. Some consultants used the project rationale to justify the need for AMC control for their customers. Visitors expressed their interest in AMC related measurements and it is anticipated that a number of these contacts will lead to an actual consultant service and/or long term collaboration in the future.



Figure 17. At the CleanZone 2015 trade fair, MetAMC had a booth with numerous posters and presentations, offering detailed information on the project results. In addition, MetAMC was showcased by two oral presentations on the CleanZone plaza, which is an open lecture area at the heart of the trade fair.

<sup>4</sup> [http://www.gitverlag.com/media/issue/3651/blaetterkatalog\\_rtt0413.pdf](http://www.gitverlag.com/media/issue/3651/blaetterkatalog_rtt0413.pdf) (2016-06-06)

#### 4.4.4 Stakeholder Workshop

To use synergy with the Cleanzone trade fair and attract experts from the clean room industry, a stakeholder workshop was held at the trade fair site one day prior to the event. About 25 people from 9 different countries attended the full-day event including AMC experts from the industry. The workshop featured twelve oral presentations including a key talk on AMC issues in microelectronic manufacturing from stakeholder CEA-Leti.



*Figure 18. The project held a workshop titled "Airborne Molecular Contamination: Sampling, generation & measurement" as a pre-congress workshop of the Cleanzone 2015 trade fair.*

Since most AMC detection techniques are not based on optical technology, but rather on ion mobility spectrometry, mass spectrometry or gas chromatography based techniques, the workshop provided new insights for many stakeholders regarding measurement capabilities of optical systems and spawned a lively discussion. Stakeholders were positive about considering optical detection of AMCs in future planning of AMC monitoring and control in their clean room facilities. The workshop was very well received by workshop participants.

#### 4.4.5 Good Practice Guides

The Good Practice Guides addressing the issues of online AMC monitoring techniques ("Guidance in spectroscopy techniques others than PAS and CES applied to AMC monitoring" and "AMC monitoring by laser spectroscopy: Introduction and Recommendations") and generation of reference gases at trace levels ("Good Practice Guide addressing the issues of generating trace level AMCs") drawn up in the project for stakeholders will enhance knowledge on optical detection, sampling, and generation of AMCs, which turned out to be a new concept at least for most of the Cleanzone 2015 participants.

#### 4.4.6 Standards

The project was presented to relevant standardisation bodies. Members of the consortium participated in ISO/TC158 (Gas Analysis), CCQM GAWG, EURAMET TC-MC SCGA, and DIN NA 062-05-73 AA meetings. The ISO/TC158 focuses on the revision of ISO6142 (Preparation of calibration gas mixtures -- Gravimetric method) and ISO6145 (Preparation of calibration gas mixtures using dynamic methods). Both are relevant to preparation of reference standards for this project. The project was introduced in the 2014 DIN NA 062-05-



73 AA meeting. The project fits to this community very well since representatives from industrial users of gas analytical methods as well as specialty gas producers are attending.

#### 4.5 Effective cooperation between partners

The project united six national metrology institutes, one unfunded partner from the photonics industry (HCP Photonics) and three academic partners (Research Excellent Grant researchers) in a combined effort to lay the foundation for a European metrological infrastructure for AMC monitoring in clean rooms. The partners contribute with experience in reference gas generation and handling (VSL, NPL, INRIM), computer fluid dynamics simulations (Polytechnic University of Turin), spectroscopy (VSL, NPL, PTB, VTT MIKES, Aalto University, University of Oxford), gas chromatography (CMI) and mid-infrared lasers (HCP Photonics).

*There has been a fruitful collaboration between several partners during the course of the project:*

A researcher from PTB visited VTT MIKES and VSL to exchange know-how on spectroscopy and support spectrometer development. PTB provided its knowledge and helped VTT MIKES with test measurements specially regarding the optimal wavelength-modulation settings while VTT MIKES shared its expertise on different aspects of wavelength modulation spectroscopy and provided some publications relevant to this project.

PTB, VTT MIKES and VSL collaborated to pursue a spectrometer comparison at VSL laboratories. This work greatly profited from VSL gas generation capabilities. VSL provided gravimetrically prepared gas standards in cylinders which were diluted using mass flow controllers to prepare ammonia gas mixture samples at relevant concentration.

VSL and HCP worked together on the design of a compact OPO and a spectrometer. HCP constructed the OPO, which provides narrow line width light at about 3  $\mu\text{m}$ . A researcher from HCP visited VSL in order to perform joint tests with the compact OPO and to verify by spectroscopic measurements using the VSL gas facilities that the OPO is applicable to CRDS/PAS applications.

The development of a dynamic generation system has been a joint work of INRIM and POLITO. INRIM has in particular experimental experience with the generation of VOCs while POLITO has a strong background in modelling using computer fluid dynamics and other methods. Their combined experience enabled the development of the generation system. For the testing of the system the generator was brought by car to the VSL facilities. During a 1-week research visit the performance of the generator was tested using a mid-infrared CRDS spectrometer developed by VSL. The fast time response of the CRDS system enabled to establish the short term stability of the generator.

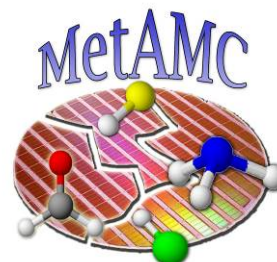
At the end of the project, partners jointly wrote several Good Practice Guides, which benefited from the combined expertise.



## 5 Website address and contact details

**Project website address** <http://www.ptb.de/emrp/metamc.html>

Information on the project (project description, events, publications, newsletters, reports, etc.) for partners and stakeholders.



### Contact details

For further information on the project, contact Kaj Nyholm, VTT, [kaj.nyholm\(at\)vtt.fi](mailto:kaj.nyholm@vtt.fi).

For information on AMC monitoring using a field-deployable photoacoustic spectrometer, contact Timo Rajamäki, Aalto University, [timo.rajamaki\(at\)aalto.fi](mailto:timo.rajamaki@aalto.fi) or Kaj Nyholm, VTT, [kaj.nyholm\(at\)vtt.fi](mailto:kaj.nyholm@vtt.fi).

For information on detection of AMCs using a commercial cavity ringdown spectrometer, contact Nils Lüttschwager, [nils.luttschwager\(at\)ptb.de](mailto:nils.luttschwager@ptb.de).

For information on AMC monitoring using cavity-enhanced absorption spectrometer, contact Stefan Persijn, VSL, [spersijn\(at\)vsl.nl](mailto:spersijn@vsl.nl).

For information on NICE-OHMS system for ultra-sensitive AMC detection, contact Geoffrey Barwood, [Geoffrey.barwood\(at\)npl.co.uk](mailto:Geoffrey.barwood@npl.co.uk).

For information on tunable mid-IR light sources for gas sensing applications, contact M. H. Chou, [choumh\(at\)hcphotonics.com](mailto:choumh@hcphotonics.com)

For information on generating and sampling reactive gases, contact Stefan Persijn, VSL, [spersijn\(at\)vsl.nl](mailto:spersijn@vsl.nl).

For information on portable diffusion generator for VOCs, contact, Guido Sassi, [g.sassi\(at\)inrim.it](mailto:g.sassi@inrim.it).

For information on using negative temperature gradient technique to improve AMC analysis for gas chromatography, contact M. Bárta, [mbarta\(at\)cmi.cz](mailto:mbarta@cmi.cz)

## 6 List of publications

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- A. Demichelis, G. Sassi, M. Lecuna, M. Sassi, "Molar fraction stability in dynamic preparation of reference trace gas mixtures", *IET Science, Measurement and Technology* **10**, 414–419 (2016), DOI: 10.1049/iet-smt.2015.0051.
- G. Sassi, A. Demichelis, M. Lecuna, and M. Sassi, "Preparation of standard VOC mixtures for climate monitoring", *Intern. J. Environ. Anal. Chem.* **95**, 1195–1207 (2015), DOI: 10.1080/03067319.2015.1016015.
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- A. Demichelis, G. Sassi, and M. Sassi, "Diffusion vials for low and accurate release of key-VOC in atmospheric chemistry and clean room industries", *XXI IMEKO World Congress Measurement in Research and Industry* (30 August – 4 September 2015, Prague, Czech Republic).
- M. Lecuna, G. Sassi, A. Demichelis, and M. Sassi, "Modelling of a VOC gas mixtures generator by computational fluid dynamics", *XXI IMEKO World Congress Measurement in Research and Industry*, (30 August – 4 September 2015, Prague, Czech Republic).
- Nils Lüttschwager, Andrea Pogány, Jarvis Nwaboh, Alexander Klein, Bernhard Buchholz, Olav Werhahn, and Volker Ebert, "Traceable amount of substance fraction measurements in gases through infrared spectroscopy at PTB", *17th International Congress of Metrology* (September 2015, Paris, France), paper 07005, DOI: 10.1051/metrology/20150007005.
- K. M. Manfred, L. Ciaffoni, and G. A. D. Ritchie, "Optical feedback cavity-enhanced absorption spectroscopy in a linear cavity: model and experiments", *Applied Physics B* **120**, 329–339 (2015). DOI 10.1007/s00340-015-6140-y.
- K. M. Manfred, G. A. D. Ritchie, N. Lang, J. Röpcke, and J. H. van Helden, "Optical feedback cavity-enhanced absorption spectroscopy with a 3.24  $\mu\text{m}$  interband cascade laser", *Applied Physics Letters* **106**, 221106 (2015). DOI: 10.1063/1.4922149.
- K. M. Manfred, J. M. R. Kirkbride, L. Ciaffoni, R. Peverall, and G. A. D. Ritchie, "Enhancing the sensitivity of mid-IR quantum cascade laser-based cavity-enhanced absorption spectroscopy using RF current perturbation", *Optics Letters* **39**, 6811–6814 (2014), DOI: 10.1364/OL.39.00681.
- S. O'Hagan, T. Pinto, P. Ewart, G. A. D. Ritchie, "Multi-mode absorption spectroscopy using a quantum cascade laser for simultaneous detection of NO and H<sub>2</sub>O", *Applied Physics B* (2016) **122**:226, doi:10.1007/s00340-016-6499-4.
- 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).