Publishable Summary for 17IND09 MetAMCII
Metrology for Airborne Molecular Contaminants II

Overview

Airborne Molecular Contamination (AMC) in the form of chemical vapours or aerosols has an adverse effect on products, processes or instruments. Technological progress is driven by the ability to operate at ever smaller scales and with greater complexity, thus increasing the demand for lower AMC concentration measurement. Real time online monitoring is critical to ensure that corrective action is taken before this impacts on production costs. Therefore, this project successfully worked on developing underpinning metrology focused on new ultra-sensitive spectroscopic techniques and high accuracy reference materials at extremely low concentrations for key AMCs. The project's achieved its aim to increase industrial competitiveness, reduce down time and remove barriers to efficient manufacturing.

Need

The European semiconductor industry supports ~200,000 European jobs directly and more than 1,000,000 jobs indirectly. The global turnover of the semiconductor sector was ~€230 billion in 2012, with micro and nano electronic components manufacturing having a turnover of around €1,250 billion in 2012. The manufacture of micro and nano electronics is estimated at 10 % of worldwide GDP (European Semiconductor Industry Association (ESIA) data). Europe currently has 9 % of the world share of the semiconductor manufacturing industry, representing $27 billion, with plans, outlined in a European Leaders Group report, to increase this to 20 % by 2025. In this high value business, the need is clearly demonstrated because a small increase in the yield can lead to savings/profits of hundreds of millions of euros. An initial assessment of the economic benefit to industry of our project outputs is given on our project website.

Adverse AMC-related effects can occur in electronics production including, for example, the corrosion of metal surfaces on the wafer, and the formation of contamination layers. These AMCs come from sources including process chemicals, filter breakthrough, building and cleanroom construction materials and operating personnel. Regulations and analytical capabilities in this field are much less well developed than in the field of contamination by particles. AMCs generated as part of the production process need to be detectable at very low concentrations as these are detrimental to the product. Prior to this project, there was a need to extend the findings of previous studies to other AMCs (e.g. HCl), to improve detection sensitivity, and to increase the range of dynamic reference standards.

Improved real time measurements of AMC are essential in order to enable corrective actions to be taken before production yields are affected and to demonstrate compliance with ISA Standard S71.04. Prior to this project, there were no NMI realised standards for HCl with which compliance can be verified. Available instrumentation is often not fit for purpose due to high costs, large size, measurement rate or limited reliability and this issue is specifically raised in the International Technology Roadmap for Semiconductors (ITRS).

Objectives

This project assessed the potential of state-of-the-art optical spectroscopic techniques for traceable AMC monitoring in cleanroom environments and how advanced optical techniques impact on the detection of smaller AMC quantities. Therefore, this project had the following objectives:

1. To develop ultra-sensitive and real-time spectroscopic methods for the detection of critical airborne molecular contaminants (AMCs) (e.g. NH_3, HCl and water vapour) with target detection values for HCl lower than 1 nmol/mol and in less than 1 minute. In addition, to determine the optimal spectral windows for such techniques based on High Resolution Transmission (HITRAN) calculations and component availability.

2. To develop traceable static and dynamic reference materials for use with real time monitoring for priority AMCs in a nitrogen matrix at less than 1 nmol/mol, specifically static and dynamic references and for HCl at 10 µmol/mol, using methods to produce dilutions higher than 10000:1 for AMCs with a target accuracy better than 0.5 % relative. In addition to develop instrumentation and novel passivation techniques to optimise the long-term stability of static reference materials for AMCs.
3. To compare and perform field tests of different spectroscopy techniques for real-time AMC detection, including an investigation of typical AMC monitoring scenarios (e.g. monitoring filter breakthrough and confined environments). The target time resolution for the spectroscopy techniques is better than 5 min and with a sensitivity lower than 1 nmol/mol for AMCs.
4. To develop traceable dynamic or static gas transfer standards for AMCs and opto-analytical transfer standards for the validation of measurement techniques commonly used in cleanrooms (e.g. ion-mobility spectrometry), including the use of in-situ calibration techniques.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. accredited laboratories and instrument manufacturers), standards developing organisations (e.g. ISO TC 158, CEN TC 264, International Society for Automation (ISA) Standard 71.04-1985 and standards bodies associated with European Waste Incineration Directive 2000/76/EC and the Ambient Air Quality Directive 2008/50/EC) and end users (e.g. the semiconductor and electronics industries).

Progress beyond the state of the art

In this project, sensitive spectroscopic methods developed within the first EMRP “MetAMC” project were further developed specifically to address HCl and progress towards industrial take-up of the novel technologies being developed – the first project primarily targeted ammonia detection, with some additional work on HF. Prior to the start of this project, there were no NMI realised standards for HCl with which compliance can be verified. Available instrumentation was often not fit-for purpose due to high costs, large size, measurement rate or limited reliability.

1. The consortium developed ultra-sensitive and real-time spectroscopic methods for the detection of critical airborne molecular contaminants (AMCs) (e.g. NH_3, HCl and water vapour) with target detection values for HCl lower than 1 nmol/mol and in less than 1 minute. Spectroscopic methods to be investigated included cantilever-based photo-acoustics and noise immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). The project went beyond the state of the art by extending the range of AMC detection, improving measurement traceability, and improving system robustness and transportability.
2. The consortium developed traceable static and dynamic reference materials for use with real time monitoring for priority AMCs in a nitrogen matrix at less than 1 nmol/mol.
3. The consortium compared and performed field tests of our different spectroscopy techniques for real-time AMC detection, including an investigation of typical AMC monitoring scenarios.
4. To develop traceable dynamic or static gas transfer standards for AMCs and opto-analytical transfer standards for the validation of the measurement techniques that are commonly used in cleanrooms (e.g. ion-mobility spectrometry), including the use of in-situ calibration techniques.

Results

Objective 1. *To develop ultra sensitive and real time spectroscopic methods for the detection of critical airborne molecular contaminants (AMCs) (e.g. NH3, HCl and water vapour) with target detection values for HCl lower than 1 nmol/mol and in less than 1 minute.*

Static reference materials have been prepared in cylinders with traceability provided through gravimetric preparation. The stability of the gas standards in time has been determined. NPL developed HCl gas standards at 10 µmol/mol with a provisional expanded uncertainty of 4 % and a stability of 12 months. VSL developed HCl gas standards at 10 µmol/mol with an expanded uncertainty of 2 % and a stability of at least 12 months. Gas standards at 1 µmol/mol proved to be less stable. A guide to the use of static reference materials has been written highlighting the use of the correct materials and a proper flushing procedure.

NPL has extended its development of an ammonia NICE-OHMS-based optical spectroscopy device with the aim to provide detection of HCl (at 1742 nm) and water vapour (at 1854 nm) within the same instrument. A SilcoNert-coated cavity enclosure houses the SilcoNert-coated cavity spacer, which, with the addition of dual-wavelength high-reflectivity mirrors, are used to create an open cavity through which the test gas can flow for real-time detection by NICE-OHMS. Bespoke electronics for the NICE-OHMS system were designed and tested to produce a (DeVoe-Brewer) error signal for stabilisation of the rf modulation frequency to the cavity free spectral range frequency with improved signal-to-noise ratio and baseline stability. The new electronics were also used on the ammonia cavity system to produce a NICE-OHMS output signal with a signal-to-noise ratio of 20 at the maximum of the output signal (at a frequency corresponding to the side of a water vapour feature). Software modelling of the expected NICE-OHMS signal was performed for HCl concentrations in the region between 1 ppb and 1 ppm, which required implementation of extended theories for correct results.

A unique laser source at 1742 nm to enable the detection of even sub-ppb level concentrations of HCl was developed and characterized by VTT and Optoseven. The new laser source was combined with previous laser sources from EMRP JRP IND63 MetAMC to enable the simultaneous sensing of HCl with NH3 and HF. Material testing was performed specifically for highly reactive and corrosive HCl including. The test included evaluation of the influence of 2 - 4 different materials, continuing the work undertaken in EMRP JRP IND63 MetAMC for base and acid gases (NH3 and HF), in order to optimise the response time (< 1 minute) and to minimise sampling losses. The most favourable material for these chemicals turned out to be PFA and SilcoNert coated stainless steel.

Having these results, this objective was successfully achieved.

Objective 2. To develop traceable static and dynamic reference materials for use with real time monitoring for priority AMCs in a nitrogen matrix at less than 1 nmol/mol, specifically static and dynamic references and for HCl at 10 µmol/mol, using methods to produce dilutions higher than 10000:1 for AMCs with a target accuracy better than 0.5 % relative.

Different types of dilution systems have been developed at CMI, VSL and NPL based on either thermal mass flow controllers or sonic nozzles. For the dilution system a selection of materials and coatings was made based on their physical and chemical properties and availability. The dilution system at NPL is a 2-step dilution system that has been tested down to 5 nmol/mol HCl in nitrogen.

VTT and Optoseven employed a dynamic reference gas generation system based on evaporation of a liquid HCl solution to generate HCl at 1 nmol/mol - 1 µmol / mol concentration range. At 1 µmol/mol the system has an uncertainty of 1.6 %. The system was applied to generate nmol/mol levels of HCl to validate a new analyser system developed within this project. The uncertainties of the dilution devices developed could generate dynamic mixtures with uncertainties of ~0.5 %. However, the uncertainty achieved in the static standards (2 %) limited the uncertainty of the HCl dynamic mixtures.

Having these results, this objective was successfully achieved.

Objective 3. To compare and perform field tests of different spectroscopy techniques for real time AMC detection, including an investigation of typical AMC monitoring scenarios (e.g. monitoring filter breakthrough and confined environments).

The developed photoacoustic trace gas analyser (PAS) was compared and validated by VTT and Optoseven in ambient air conditions using reference materials for HCl, NH3 and HF obtained using the evaporative methods developed in EMRP JRP IND63 MetAMC for NH3 and HF and optimised during this project for HCl as well. In parallel with this, two other analysers based on other optical laser spectroscopic techniques, i.e. tailored direct laser absorption spectrometer (DLAS) and commercial cavity ring-down spectrometer (CRDS) by Tiger Optics, were characterized as well in order to test the systems applicability for reliable online monitoring of HCl in cleanroom environment. The work was done according to the specifications given in a report available on the project website All three analysers operated linearly in wide concentration range and the PAS and especially the CRDS detected low concentrations down to sub-ppb level. For long 5-minute averaging time, the LOD were less than 10 ppb for all three analysers and again the PAS and especially the CRDS were able to achieve even much lower LODs in sub-ppb level. According to the results obtained by the project, CRDS seems to outperform the PAS and DLAS analysers. However, by considering the measurement uncertainty sources of the PAS and DLAS, several possible improvements were identified and all are potential techniques to be used at cleanroom monitoring of studied AMCs.

VSL upgraded for the present project its OPO-based CRDS system used to determine HCl at trace levels as observed in clean rooms. It operates in the mid-IR region (2.4-5.1 µm wavelength range) enabling access to all strong HCl absorption lines of the v_1 fundamental band. By extending the cell length and making use of high-quality mirrors and careful alignment, a very long effective path length of 7 km was obtained. To handle the highly reactive HCl gas, all parts of the flow system (tubing, pressure regulator and mass flow controller) and measurement cell have been coated with SilcoNert 2000. This system has been validated using both a magnetic suspension balance (MSB) containing a HCl permeation tube and via dilution of static HCl gas standards using thermal mass flow controllers.

GASERA developed a prototype HCl PAS sensor using a 3375 nm ICL as the light source. A dual-pass multipass configuration was used to get the detection limit (1xRMS) of the system to a level of ~1 ppb using 60-sec sample time. Response time of the developed system was verified by generating sample of zero air and 7.5 ppm HCl samples periodically in a stepwise manner. The response time of the developed prototype (10/90) is in the order of 2 minutes. GASERA's prototype unit was used in continuous cleanroom measurement for 14 days. The unit was able to detect when there was activity at the wet bench, which is a known source of HCl. The tests showed good stability over time and potential in continuous clean room monitoring activities e.g. near known sources of contaminants.

Having these results, this objective was successfully achieved.

Objective 4. To develop traceable dynamic or static gas transfer standards for AMCs and opto analytical transfer standards for the validation of measurement techniques commonly used in cleanrooms (e.g. ion mobility spectrometry), including the use of in situ calibration techniques.

The spectrometer developed at PTB is based on time division multiplexed wavelength modulation spectroscopy (WMS) and direct tuneable diode laser absorption spectroscopy (dTDLAS). PTB has coined the term optical gas standard which is able to do calibration-free absolute amount fractions measurements and has the potential to replace primary gas reference standards. The dTDLAS based HCl optical gas standard spectrometer is calibration-free and can provide accurate absolute amount fraction measurements traceable to the SI The underlying model equation is based on the Beer-Lambert-law and an amount fraction is directly computed from the spectroscopic measurements involving traceable influence quantities. Harmonic WMS detection usually allows higher sensitivity due to reduced 1/f noise but requires calibration. The normalized 2f/1f WMS signal is calibrated against the absolute concentration gained from dTDLAS with a sufficient SNR. To take advantage of the calibration-free approach of dTDLAS and the effective noise suppression of WMS without sacrificing the calibration free capabilities a spectrometer was built by combining both techniques. The detection limit of <1 ppb at 1 min was achieved.

Having these results, this objective was successfully achieved.

Impact

The project outputs have been disseminated via six scientific conferences (CLEO 2020, CLEO 2021, OSA Laser Congress, HRMS 2021, SMSI 2021 and Photon 2020), two peer reviewed open access publications on leading-edge journals (Measurement Science & Technology and the International Journal of Hydrogen Energy), and one publication in a trade journal (Cleanroom Technology).

To promote the project impact, we set up a website at http://empir.npl.co.uk/metamcii/ that details the partners and describes the main aims of the project. We had uploaded abridged versions of the reports produced here as follows:

- "Summary Report describing the results of the study into current state-of-the-art spectroscopy methods, materials research for the effects on physical instrumentation in the presence of HCl, and investigations into determining the optimal spectral windows for HCl and water detection, including the availability of laser sources"
- "Report describing the potential and capability of the developed spectroscopic instruments for HCl detection"
- "Good practice guide on the handling and use of static HCl materials"; this report has an introductory YouTube video introductory YouTube video.
- "Specification for the Metrology of Airborne Molecular Contaminants"

Additionally, our website provides further reports on HCl detection and other applications for the technology developed within our project, as follows:

- Sampling Lines for HCl (VSL)
- Other applications for the present project spectroscopy methods (GASERA)

The consortium organized three major online workshops/training courses and lead one round table discussion which was part of the Cleanzone 2020 event. Key stakeholders from industry and academia participated as presenters/speakers in these three activities. Talks from the consortium members are available on YouTube and the project website. The popularity of the workshops greatly exceeded the expectations of the consortium. The total number of participants in the three major workshops was approximately 220. The consortium estimates that half of the participants were from industry and half from academia.

These meetings organised by the consortium were:

- Workshop on Advanced Optical Spectroscopy for Gas Detection, co-hosted by GASERA and NPL 2020
- Workshop on Airborne Chemical Contamination, hosted by GASERA 2020
- Workshop on Generation and Handling of Reactive Gases, hosted by VSL and GASERA 2021

A YouTube channel was set up which has four public presentations available. The above-mentioned material was advertised via direct emails to stakeholders (100 recipients) and workshop attendees and members of the consortium also communicated via Facebook and LinkedIn to a broader audience.

A final questionnaire was sent via email to 100 stakeholders and attendees to our events; feedback from stakeholders was also received directly during the events, which resulted in a very good response rate. The feedback highlighted that a) several stakeholders would be interested to be part of similar projects in the future (funded or unfunded) and b) those interested were mostly from industry.

Impact on industrial and other user communities

Europe has 9 % of the world share of the semiconductor manufacturing industry, representing $27 billion, with plans to increase this to 20 % by 2025. An AMC monitor, providing analysis and feedback within ~1 minute, would enable the timely detection of higher-than-acceptable contamination and determination of the cause, enabling corrective actions that would make a significant impact on industrial competitiveness. AMC is one of the major components affecting product yield in the microscale manufacturing processes of semiconductors and it can lead to increased electronics defects and to higher production costs. This project will create impact by providing improved instrumentation with better sensitivity and a reduced measurement time and also better static and dynamic reference standards. The work on the static gas standards will provide the specialty gas industry with information on the suitability of the tested cylinder treatments for HCl gas standards at low amount fractions. These instruments will be field tested and transfer standards will be improved to enhance traceability from national measurement institutes to industrial environments. To date, the consortium have signed a collaboration agreement with one company that is interested in exploiting the technology being developed within this project. An example of early uptake of the project output is in the use of field tests results of online real-time monitoring of sources of key contaminants and control of their flow in air circulation and purification systems to significantly improve manufacturing processes.

Impact on the metrology and scientific communities

The partners in this consortium were actively involved in the CCQM Gas Analysis Working Group (GAWG) which met twice a year, usually April and October and the outputs from this project were presented to global experts. The development of reference materials for NH_3 and HCl will support future Key Comparisons organised by the GAWG and new calibration and measurement capability claims for amount fraction. Specifically, at the April 2020 meeting, the CCQM agreed to hold a key comparison on HCl / N_2 at 20 – 100 μmol/mol. Although originally planned for 2021, this comparison will now take place in 2022 as CCQM-GAWG members were concerned that the original proposed timescale was too short. Participants will now receive the travelling standards in January 2022 with reporting of results expected to extend into 2023. This decision endorses the critical importance and timeliness of the project aims.

Impact on relevant standards

The technical committees that the consortium interacted with were CCQM, ISO TC/158, Euramet (TC-MC; Sub-committee on Gases (SCGA)) and DIN (NA 062-05-73 AA Gas analysis and gas quality). The partners that were members of these committees ensured that the knowledge developed within the project was fed into the committee meetings. As an example, the knowhow gained in this project and some related EMPIR projects is used for the revision of ISO 6143 “Gas analysis – comparison methods for determining and checking the composition of calibration gas mixtures” of ISO TC/158.

In static gas mixtures (i.e. cylinders) some loss of HCl is currently unavoidable due to the high reactivity of HCl causing adsorption or reactions with water. The work carried out in by the project on this topic is of importance for future revisions of ISO 6142 “Gas analysis – Preparation of calibration gas mixtures” regarding the class of reactive molecules. Specifically, the EURAMET TC-MC (Metrology in Chemistry) committee meeting in

February 2020 to which NPL, PTB and VSL all contributed.

Longer-term economic, social and environmental impacts
The impact of this project will not be limited to the semiconductor industry; within 5-10 years, other industries that will benefit will include aerospace, pharmaceuticals, medical devices (e.g. breath analysis for health monitoring), food, indoor/outdoor air quality monitoring, healthcare and energy efficiency. These industries will benefit from the improved spectroscopic instrumentation and traceability developed within this project. This could result in, for example, improved production efficiency in the aerospace industry or more reliable diagnoses for some medical conditions. For example, checking for ammonia in breath is used in the diagnosis of renal failure; if our instrumentation were extended to HCN detection, this could be used for the diagnosis of bacterial lung infections. Environmental applications include the detection of CO_2 and methane; this would require lasers at ~2.05 μm and 1.6 μm or alternative bands further into the infrared. Other potential application areas include the detection of contaminants in background gases such as hydrogen (for fuel in hydrogen cars) and methane (including bio-methane).

The potential impact on energy efficiency will be huge in the longer-term when the quality of the semiconductor devices produced (light emitting sources (e.g. LEDs) and photovoltaic units) is improved. For example, even small improvements in solar panel efficiency could have a huge impact on global renewable energy production schemes. Simple photovoltaic cells have a conversion efficiency of around or below ~20%. More sophisticated designs use complex structures to obtain better efficiency, but these are more prone to AMC related defects.

As AMC is expected to affect product yield even more in the future, the demand for practical AMC monitoring devices will be high. An effective implementation of AMC monitoring equipment by European industry would give them a competitive edge over global competitors. However, it is expected that every company will adopt AMC monitoring systems when their worth has been proven. A summary of the economic impact of the results of this project is available on the project website here.

List of publications

- Heleen Meuzelaar *et al*, "Trace level analysis of reactive ISO 14687 impurities in hydrogen fuel using laser-based spectroscopic detection methods", International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.09.046
- Panu Hildén *et al*, "Real-time HCl gas detection at parts-per-billion level concentrations utilising a diode laser and a bismuth-doped fibre amplifier", Measurement Science and Technology, https://doi.org/10.1088/1361-6501/abd651

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Coordinator: Geoffrey Barwood, NPL Tel: +44 208 943 6032 E-mail: geoffrey.barwood@npl.co.uk Project website address: http://empir.npl.co.uk/metamcii/		
Internal Funded Partners: 1. NPL, UK 2. CMI, Czech Republic 3. PTB, Germany 4. VSL, Netherlands 5. VTT, Finland	External Funded Partners: 6. GASERA, Finland 7. Optoseven, Finland	Unfunded Partners: 8. POLITO, Italy
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