Deliverable 1.1.3:
2-4 analytes selected for further study

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

MIKES CMI INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA VSL

NPL National Physical Laboratory PTB Physikalisch-Technische Bundesanstalt Braunschweig und Berlin POLITECNICO DI TORINO 1859 1906 HCP

Document information

Owner

Lead Name:	Tuomas Hieta
Lead Organisation:	MIKES
E-mail:	Tuomas.hieta@mikes.fi

Context

Author(s):	Tuomas Hieta (MIKES) Anne Rausch (PTB) Stefan Persijn (VSL) Geoffrey Barwood (NPL) Mariapaola Sassi (INRIM)
Work Package:	WP1
Task:	Task 1.1
Deliverable Number	D1.1.3
Deliverable Name	2-4 analytes selected for further study

Contents

Summary 4
1 Background 4
2 Stakeholders contacts 5
3 Analyte selection 5
3.1 Overview of the detection techniques 5
3.2 Expected sensitivity 7
4 Conclusions 7
Acknowledgements 8
References 8

Summary

This report summarises on which airborne molecular contamination (AMC) analytes the online detection part of MetAMC project will focus on. The selection is based on industrial needs, availability of commercial laser or frequency conversion-based light sources and whether suitable spectral windows with strong absorption features and minimal interferences can be found. Spectral windows were identified in deliverable D1.1.1 for five preselected analytes (NH_3, HCl, HCOH, HF and HBr). The availability of suitable light sources enabling the detection of these analytes was investigated in deliverable D1.1.2. A questionnaire was sent to 19 stakeholders, out of which 14 answered. NH_3, HF and HCl were found to be the three most important AMCs based on the stakeholders' answers. Ultrasensitive optical techniques will be further developed for the detection of these three AMCs in the MetAMC project. This report will be used as a basis when a selection of AMCs for dynamic generation will be made later in work package 3.

1 Background

Technological progress in several high tech industries is enabled, if not driven, by the ability to operate at ever smaller scale. This introduces new challenges, also in the metrological realm. Airborne Molecular Contamination (AMC) is chemical contamination in the form of vapours or aerosols that has adverse effects on products, processes or instruments. Industrial sectors for which the control of AMC is crucial include the semiconductor-, nanotechnology-, photovoltaic- and high brightness and organic LED industries. Examples of possible adverse effects include the corrosion of metal surfaces on the wafer, and the formation of contamination layers on surfaces like optics and wafers after reaction/condensation.

The relevant chemicals are very diverse in nature and include acids, bases, condensables, dopants and metals. Yield Enhancement Technical Working of the International Technology Roadmap for Semiconductors (ITRS) provides a detailed description of the main critical impurities [1]. Important sources for AMC include process chemicals, filter breakthrough, building and clean room construction materials and operating personnel. The relevant levels of these analytes are typically at the (sub) parts per billion by volume (ppbv) level, making their detection extremely challenging.

MetAMC is focused on detection and generation of AMCs. One of the key goals is to review, develop, explore, and exploit current optical detection techniques suitable for online/real-time and on-site monitoring of AMCs. The techniques include photoacoustic spectroscopy (PAS) and cavity-enhanced techniques (CRDS). The target detectable amount fraction and time resolution using the techniques mentioned above for the selected analytes are 1 nmol/mol (ppbv) and 5 minutes, respectively. In addition, Noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS), which is generally thought to be the most sensitive optical detection method, will be tested and evaluated for AMC detection. Another key goal is to develop dynamic generation methods for trace level airborne molecular contaminants and to develop suitable sampling techniques for their monitoring. Traceable reference materials are essential for the validation and calibration of monitoring equipment but are currently virtually non-existent for AMCs.

2 Stakeholders contacts

A questionnaire was sent to 19 stakeholders in December 2013 inquiring which AMCs are most important for their applications or for their clients. The purpose of the questionnaire was to help this project to focus on the most important AMCs for the industry. 14 stakeholders representing both private companies (10) and research institutions (4) answered in time. Many of these stakeholders from six different countries are actively involved in clean room related contamination R&D. Due to requests from some of these stakeholders no detailed information on individual companies will be published.

Ammonia, HF and HCl were most often identified as the key AMCs having nine, eight and seven mentions in the stakeholders' answers, respectively. Other AMCs that were mentioned at least once were NMP, PGMEA, HBr, SO_2, H_2S and H_2O_2. In addition to single molecules, also volatile organic compound (VOC) and siloxane groups were mentioned.

Although the questionnaire was targeted to find out the most important AMCs, many stakeholders gave insightful answers concerning contamination as a whole. Many addressed the complexity of the AMC problem in general. While there are many fairly standard processes with known relations between specific AMCs and defects/failures, there are even more cases where the relations are largely unknown. Another practical issue that concerned some of the stakeholders was the response time of AMC monitoring devices. Since operational accidents are an important source of AMCs, the time response of AMC monitor devices should be preferably around one minute to guarantee fast spill detection capability.

3 Analyte selection

In this section, the optimal wavelength regions and the expected sensitivities for NH_3, HF and HCl will be briefly reviewed. The key to successful detection of these analytes is the existence of strong and relatively isolated transitions that are accessible using preferably commercial off-the-shelf laser sources. It is evident from D1.1.1 and D1.1.2 that fortunately these criteria are met for the three selected analytes.

3.1 Overview of the detection techniques

The measure of the minimum absorption coefficient when the signal-to-noise ratio (SNR) of the measurement reaches 1 is the normalized noise equivalent absorption coefficient (NNEA). NNEA is commonly used in laser spectroscopy to describe the quality of the instrument. Absorbance strength, optical power and averaging time is required to evaluate the achievable minimum detectable concentration for each analyte separately. More detailed information on various parameters required for determining the minimum detectable concentration can be found in refs [2, 3]. All the estimates for detectable amount fraction limits in this section are for 1-minute averaging time.

<u>MIKES PAS</u>

The implementation of cantilever enhanced PAS for online AMC detection is one of the main tasks of MIKES in this project. The target analytes for MIKES are NH_3 and HF. The measurement set-up consists of DFB lasers and an optical amplifier operating at telecom C-band suitable for NH_3 detection. HF detection is done using a DFB laser operating in the telecom O-band. The reported minimum detectable absorption limit for a MIKES PAS system is 1.1 x 10^{-9} cm^{-1} for 20 mW optical power [4]. The estimated detectable amount fraction for both NH_3 and HCl are expected to be below 2000 pmol/mol or in parts per billion by volume (pptv). The developed system will be used later in the project for field measurements.

PTB PAS

PTB`s PAS system consists of a commercially available cantilever-enhanced PAS detector. The main target analyte will be NH_3. According to spectral simulations (D1.1.1) the spectrometer will be equipped with a DFB laser source at a wavelength of 1520 nm. However, options to replace this low output power DFB (20mW) by a more powerful laser exist (D1.1.2). So PTB`s PA spectrometer has some flexibility for adapting the sensitivity if needed. The DFB laser-based minimum detectable amount fraction is currently estimated to be 4400 pmol/mol (pptv). The developed system will be used later in the project for field measurements.

VSL PAS

VSL has designed a novel photoacoustic cell made out of glass to reduce adsorption and reaction effects associated with commonly used cells made of (coated) stainless steel. In order to achieve high sensitivity a narrow resonator design was chosen. Different microphones have been purchased (opto-acoustic microphone and 2 standard microphones). The cell will be combined with a mid-infrared OPO and possibly also QCL's. It is expected that sensitivities in the 1×10^{-9} cm-1 range can be achieved. For the mid-infrared range this translates into pmol/mol (pptv) detectable amount fraction levels for many analytes including HCl and HCOH.

PTB CRDS

To complement PTB`s analytic capabilities to detect ammonia a commercial CRDS gas analyzer will be explored additionally. This spectrometer operates in the near infrared and will be used as turn-key device in a first run. Based on this device a minimum detectable NH_3 amount fraction of 45 pmol/mol (pptv) is estimated. A targeted metrological characterization within the MetAMC project will reveal whether the instrument`s settings and components may need an improvement, which in this case will then be implemented in the JRP. In particular the operation procedure will be adapted to metrological needs.

VSL CRDS

The output of a mid-infrared OPO is guided through an acousto-optic modulator, and via mode-matching optics coupled into the ring-down cavity. Length of the cell is modulated at several 10's of Hz using 3 piezoelectric transducers. Light emerging from the cell is focused with a lens on a fast photodetector. Typical sensitivities are 5×10^{-9} cm-1 (dependent on mirror reflectivity and hence wavelength).

NPL NICE-OHMS

A NICE-OHMS system comprises a phase-modulated laser and high finesse optical cavity. The analyte flows through the optical cavity and the high detection sensitivity arises from the long detection path within the cavity. The laser is phase modulated at two frequencies; the lower frequency (e.g. ~10 MHz) is used for Pound-Drever-Hall stabilisation of the laser to the cavity. The higher frequency is set to the cavity free spectral range and the resulting sidebands are transmitted though the cavity. Interference between the carrier and sidebands gives rise to a signal which is demodulated using a double-balanced mixer. Any differential frequency noise between the cavity resonance and the carrier affects the transmitted sidebands in the same way, and so there is a high degree of common mode noise cancellation. This "noise immune" character is the principal advantage of the NICE-OHMS technique. Recent results suggest a minimum detectable absorption limit using NICE-OHMS of $\sim 3 \times 10^{-12}$ cm-1 [5].

As part of MetAMC, we are investigating the adsorption of ammonia on different surfaces (e.g. invar or Corning ULE) that are likely to be used in the manufacture of a high finesse optical cavity. Low-loss mirrors for the ~1550 nm spectral region are available with finesses up to ~200,000; typical observed transmissions for an empty cavity are ~50%. It is straightforward to show that this transmission corresponds to a loss of ~4 ppm at the mirrors. A high cavity finesse (F) is important in order to detect low gas concentrations as the signal is then enhanced via the effective increase in path length by a factor of 2F/π. For the high cavity finesse planned to be used in NICE-OHMS, NPL should expect lower sensitivities than published for a 1-minute averaging time. Whilst issues with the use of acids such as HCl or HF are expected, the mirror supplier does not anticipate problems with low levels of ammonia. Detection of formaldehyde should also be achievable with the same mirror set as planned for ammonia but with reduced sensitivity.

3.2 Expected sensitivity

The estimated detectable amount fraction limits using different detection techniques for the analytes are evaluated by comparing simulated peak absorbance values with expected minimum detectable absorption limits. The peak absorbance values are adopted from D1.1.1, where the absorbance was evaluated for the analytes at 350 hPa and at 20 °C using a 100 cm path length. 350 hPa is a good estimate for optimal gas pressure, since it increases the separation of overlapping spectral components without significantly decreasing peak absorption (pressure broadening is the dominating broadening effect) when using NIR light sources. Table 1 shows the estimated minimum detectable amount fraction for each analyte and technique in pmol/mol.

Minimum detectable concentration, pmol/mol , 60-s, S/N = 1							
		MIKES	PTB	VSL	PTB	VSL	NPL
Analyte	Wavelength region	PAS	PAS	PAS	CRDS	CRDS	NICE-OHMS
NH3	Telecom C-band	**1900**	**4400**		**45**		**12**
HF	Telecom O-band	**1400**					
HCl	3500 nm			**100**		**200**	

Table 1: Estimated minimum detectable amount fraction limits for the three chose analytes.

In short, the sensitivity of the cavity enhanced technique (here also including NICE-OHMS) is not generally dependent on optical power while in PAS, the sensitivity is proportional to optical power. Therefore, comparison of these techniques is not straightforward, because the output powers of the lasers vary considerably at different wavelength regions. A common telecom C-band DFB laser (~50 mW) can have an order of magnitude higher output power than e.g. a DFB near 1740 nm (< 5 mW) designed for HCl detection. In addition, it is possible to use optical amplification at telecom C-band region, which further complicates the comparison. One should also note at this stage of the project, the report does not address any issue related to the estimated response times, which depend strongly on the selected analytes, used sampling system and on the structure of the analyser itself. The full assessment of the applicability of optical techniques for AMC detection will be reported as a part of this project in 2016.

4 Conclusions

We conclude that the three most important AMCs (NH_3, HF and HCl) defined by the stakeholders are within the measurement capability of national metrology institutes (NMI) in the MetAMC project. By using a combination of each NMI's expertise, we expect to measure the concentration of all these three analytes with detectable amount fraction limit better than 1 nmol/mol (ppbv) for 5-minute averaging time. Two good practice guides will be published in 2016 evaluating the applicability of commercially available optical techniques (PAS, CRDS) and more experimental techniques (NICE-OHMS) for practical AMC monitoring.

Acknowledgements

We gratefully acknowledge funding from the European Metrology Research Program (EMRP). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

References

[1] http://www.itrs.net/

[2] HITRAN paper describing 1996 edition available from http://www.cfa.harvard.edu/hitran/

[3] O. Werhahn and J. C. Petersen, Eds., "TILSAM technical protocol V1_2010-09-29," http://www.euramet.org/fileadmin/docs/projects/934_METCHEM_Interim_Report.pdf.

[4] V. Koskinen, J. Fonsen, K. Roth, and J. Kauppinen, Appl. Phys. B 86 451 (2007).

[5] A. Foltynowicz, I. Silander, and O Axner, J. Opt. Soc. Am. B 28, 2797 (2011).