Viability of using the spectroscopic methods developed in MetAMCII project in other continuous trace gas monitoring applications

INTRODUCTION

As part of the MetAMCII project several measurement techniques, i.e. NICE-OHMS, cantilever enhanced photoacoustic spectroscopy, CRDS and dTDLAS/WMS for ultra-sensitive continuous detection of HCl gas are being developed. The target measurement sensitivity of the systems is better than 1 nmol/mol in 1 minute and the target application is clean room measurements. In this review, the applicability of these techniques in other fields is evaluated for increasing our understanding about the potential usability of the project results.

Continuous and sensitive measurement of trace gases is a common need. Depending on the application, the competitive advantage of the developed techniques versus currently used devices may be one or a combination of these: better sensitivity or selectivity, faster response time, lower price or operating costs, portability, reliability or ease of use. Besides the replacement of present analysis techniques in existing applications, it is also possible that new applications can be brought out when new kind of measurement devices are introduced. In this review, the focus is in reviewing existing trace gas applications where there is potential for the application of existing MetAMCII techniques, or following device modification, to cover new target gases.

AIR QUALITY MEASUREMENTS

The harmfulness of several toxic gases for the climate have been known for decades, and plenty of work has been done in measuring and reducing their amounts in the air. However, as our knowledge increases and technology advances, new pollutants are recognized all the time creating a need for even better measurement techniques and devices. At the same time, the pollution sources and relative amounts of pollutants are changing. For example, the amount of SO2 emissions has decreased remarkably in Europe thanks to the strict legislation, but in the same time emissions of volatile organic compounds (VOC) have increased. This is mainly caused by increased used of biofuels. [1]

The United States Environmental Protection Agency (EPA) has acknowledged 187 hazardous air pollutants that require control. From this list, 30 compounds are stated as urban air toxic pollutants, that pose the greatest potential health threat in urban areas. Most of these are VOCs. [2] These 30 compounds are shown in Table 1.

Table 1. EPA's list of 30 most potential health thread compounds in urban areas [2].

List of 30 Urban Air Toxics		
Acetaldehyde	Dioxin	Mercury compounds
Acrolein	Propylene dichloride	Methylene chloride (dichloromethane)
Acrylonitrile	1,3-dichloropropene	Nickel compounds
Arsenic compounds	Ethylene dichloride (1,2-dichloroethane)	Polychlorinated biphenyls (PCBs)
Benzene	Ethylene oxide	Polycyclic organic matter (POM)
Beryllium compounds	Formaldehyde	Quinoline
1,3-butadiene	Hexachlorobenzene	1,1,2,2-tetrachloroethane
Cadmium compounds	Hydrazine	Tetrachloroethylene (perchloroethylene)
Chloroform	Lead compounds	Trichloroethylene
Chromium compounds	Manganese compounds	Vinyl chloride

VOCs are problematic in several ways. First, some are toxic by themselves (e.g. benzene and formaldehyde) and secondly, in the presence of sunlight they can react and produce ozone, one of the main climate pollutants [3]. Besides the biofuels, major sources of VOC emissions are also glues, paints, cleaning chemicals, furniture and interior decoration materials, meaning that VOC levels are usually even higher in indoor air compared to outdoor levels.

Total VOC concentration (i.e. sum of all VOCs) can be measured with, for example, relatively affordable and portable photoionization detectors [e.g. 4, 5]. However, selective and sensitive measurements of VOC compounds need chromatographic techniques, which are laborious, expensive and need sampling for laboratory analysis. Thus, a need for portable and easy-to-use continuous VOC-analyzers capable for selective and sensitive measurements is evident and growing all the time.

When individual VOC compounds are measured, averaging over hours and sometimes days can be required, because of a lack of a continuous measurement techniques. Moreover, measurement locations are few because of the complexity and price of accurate measurement devices. For example, in Helsinki, the capital of Finland, there are only eight urban air quality measurement stations and common carcinogenic compounds, for example formaldehyde and benzene, are not measured in these stations. [6]

In future, it is probable that besides stationary measurement stations, the emissions of individual vehicles will be tracked for SO2 and NOx emissions as is done today for ship plumes [7]. For that purpose, portable and relatively fast and accurate gas measurement devices are needed for target gases such as formaldehyde, benzene, NOx, CO and acetaldehyde. Currently, these measurement systems are being investigated within European Union's Horizon 2020 project called CARES [8].

On the other hand, one possibility for creating a dense air quality measurement network in a city is to implement a large number of moving low-cost measurement devices, which are calibrated by a few high-accuracy analyzers, such as those being developed within MetAMCII. This kind of Smart City -related concept is currently investigated and is being demonstrated in Finland in the co-innovation project MegaSense, where 5G and artificial intelligence are utilized for calibrating the portable low-cost sensor outputs in real time against a stationary high-accuracy gas analyzer [9].

The European Parliament passed a resolution "A Europe that protects: Clean air for all" on March 2019, within which it "calls on the Member States to ensure adequate, representative, accurate and continuous measuring and monitoring of air quality" [10]. It is expected that more and more accurate, selectable and portable ambient air quality measurements will be a hot topic in the future and new market possibilities are opened also for MetAMCII results, related to, for example, VOC detection both from indoor and outdoor air.

To summarize, we have described the ambient air quality aspects in general. However, while the knowledge of hazardous compounds and their effects are growing all the time, it is possible that new regulations will be introduced for continuous control of concentration levels of individual chemicals not only in the cities or homes, but also at possible pollution hot spots, such as stack gas, fence lines of industry sites or inside the manufacturing plants. This would open new markets for gas measuring devices capable of accurate continuous and on-field measurements of individual gases. Even though existing allowed chemical levels are already being tightened, there may be need for more sensitive detection compared to that achievable by current monitoring devices.

AEROSPACE

One interesting application for MetAMCII based trace gas analyzers could be atmosphere composition measurements done from airplanes and satellites. Both individual measurement campaigns and more regular and continuous measurements have been already performed. In these applications, the interesting gases are, e.g. HCl, SO2, formaldehyde and VOCs, such as acetone, acetonitrile and methanol. [11, 12, 13, 14]

In principle, measurement devices of MetAMCII could be sent into space and we could thereby investigate the compositions of atmospheres of planets other than the Earth. Comparable measurements are already done within ESA's ExoMars 2016 Mission, where ExoMars Trace Gas Orbiter investigates gas concentrations of Martian atmosphere. [15]

MANUFACTURING INDUSTRY

Controlled AMC monitoring could enhance the yield and even security in several industrial fields, including semiconductor, pharmaceuticals and aerospace and astronomical component manufacturing. In each of these examples, even a small amount of an unwanted chemical can reduce the quality of the end products remarkably. For food and pharmaceuticals AMCs can be potentially dangerous, while in the case of semiconductor products this is a question of energy efficiency. As the semiconductor products are parts of electrical devices, poorer quality usually means less efficiency, i.e. more energy is needed to achieve the same result than with better quality component. This is also related to the price of the products and production failures.

It is expected that manufacturers will be more and more interested to control AMC levels during the manufacturing process when the knowledge of its capabilities increase, and devices are more affordable and easier to use. The standardization work done also during the MetAMCII project is one way to promote this topic.

Besides monitoring unwanted chemical components, trace gas detection can be used also in other ways. In the packaging industry, the airtightness of, for example, food and medical device packages can be investigated by filling them with a trace gas and measuring its concentration outside, telling us about leakage through the packaging material or holes in the package. [16]

HEALTHCARE

Gas composition of exhaled breath tells us about the health of the person, and there are research papers showing how analysis of respiratory air can be used as a diagnostic tool. This research is mainly in a laboratory state where markers for diseases are searched. As soon as markers are acknowledged, the portable and easy to use gas analysis devices with low detection limits will be needed for field use. The changes in gas concentrations caused by a disease are typically small, and thus the measurement technique used must be extremely sensitive. Breath analysis is an interesting method for diagnosis as it is non-invasive and potentially cheap, easy and doable outside the laboratory. [17, 18]

An example is chronical kidney diseases, which can be detected as raised level of ammonia in exhaled breath [19]. NH3 is one of the target gases of MetAMC projects, and thus this example is extremely interesting from our point of view.

The similar kind of approach is to diagnose plant diseases based on the VOC emissions from the plant material, e.g. trees. Electronic noses consisting of sensor arrays have been developed for this application, but they lack sensitivity. [20] Measurement techniques developed in MetAMCII are potentially capable for measuring simultaneously several gas compounds with high sensitivity.

CONCLUSION

In this review, several possible future applications for measurement techniques develop in the MetAMCII project are listed and speculated. As a whole, the market of trace gas monitoring applications is vast, and demands for measurement devices and their properties differ considerably even within one application. Thus, the content of this review only gives a broad overview, but still offers an insight into how diverse the utilization possibilities are of the project results. The spectroscopic techniques developed in the project could be used in the future for example as a diagnosis tool for diseases as well as mapping atmospheric composition of planets, and many other applications between these two extremes.

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