

Development of a novel proton-transfer-reaction mass spectrometry (PTR-MS) instrument for monitoring and quantifying airborne molecular contaminations in cleanroom environments

J. Kames¹, H. Seehauser², S. Jürschik^{2,3}, E. Hartungen², A. Jordan², P. Sulzer², C. Lindinger², L. Märk², T.D. Märk^{2,3}

¹ artemis control AG, Seestraße 147, CH-8610 Uster, Switzerland

² IONICON Analytik GmbH, Eduard-Bodem-Gasse 3, 6020 Innsbruck, Austria

³ Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, 6020 Innsbruck, Austria



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Abstract

Airborne Molecular Contaminations (AMC) are, in contrast to particle contamination, gaseous traces of chemicals present in cleanroom environments due to unavoidable tiny process leakages and human operator presence. They are a **serious threat** in specific to microelectronic and **semiconductor production**, e.g. by irreversible hazing of deep UV optics and photomasks, wafer surface deposition and doping [1]. Here we present a **newly developed instrument** based on **proton-transfer-reaction mass spectrometry (PTR-MS)** for **real-time monitoring and quantification** of volatile organic AMC in the clean room air and mini-environment air.

In PTR-MS water vapor is converted to H_3O^+ in a hollow cathode ion source and subsequently introduced into a drift tube where proton transfer between the H_3O^+ and trace compounds possessing a higher proton affinity than water takes place. The resulting protonated molecules are afterwards analyzed in a mass spectrometer (e.g. quadrupole mass filter or time-of-flight mass analyzer). For the new instrument we further developed the PTR-MS technology for the special needs of continuous AMC monitoring, i.e. the **unambiguous on-line quantification** of jointly present substances with highly dynamic concentration profiles. We show results of calibrations with well defined samples introduced into the instrument via a novel direct aqueous injection system [2] as well as results from cleanroom environments in operation, proving an online detection capability of below 1 ppbv, response times of below 100 ms and real-time quantification without the need of standards.

AMC-Monitor C-1000



Experimental Setup

The AMC monitor is based on a PTR-QMS 300 instrument consisting of a hollow cathode ion source for the production of H_3O^+ , a drift tube where the proton transfer takes place and a quadrupole mass filter (range 1-300 amu) followed by a channel electron multiplier for the ion selection and detection. In the lower picture on the left a schematic overview of this setup is given. The upper picture represents a photograph of the final instrument.

The built-in vacuum system consists of two turbomolecular pumps and a membrane pre-vacuum pump. The sample air containing the contamination traces is continuously introduced (and analyzed) into the system via a heated inlet line with an adjustable flow between 50 and 500 sccm.

An embedded PC system installed in the AMC monitor controls and supervises the instrument's parameters (e.g. automatic shut-off of sensitive parts in case of a vacuum failure) and the measurement itself. It is connected to a touch-screen mounted on the front panel. Via this touch-screen the measurement can be followed and controlled without the need of an external computer.

The overall dimensions of the AMC monitor are 56x61x53 cm at a weight of approximately 70 kg. For operation only electric power and small amounts of distilled water (1 liter lasts for several months) are needed.

Semiconductor Processing - Monitoring

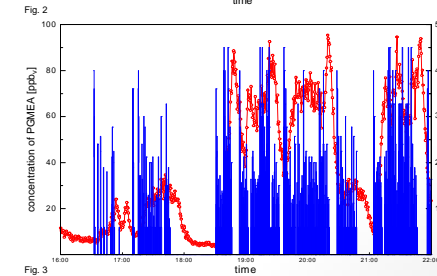
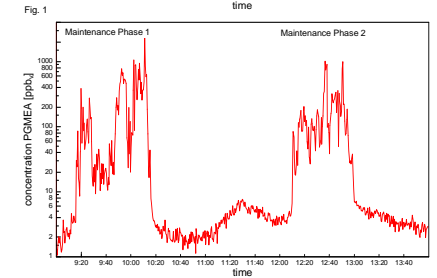
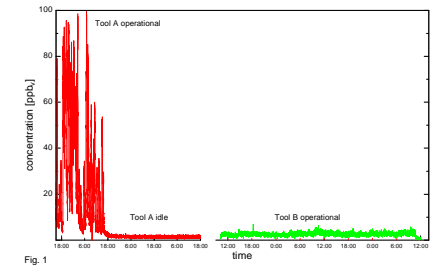
Measurements that are performed in semiconductor clean room environments are always strived to identify origins of process emissions to be able to minimize or stop contamination.

In the case described here PGMEA (propylene-glycol-monomethyl-ether-acetat) had been emitting constantly and unattended and had interacted with chemical filter devices meant to protect a high purity process step. This interaction produced acetic acid as unwanted by-product of the purification process. Acetic acid turned out to be a "killer" component for the DUV-photolithography process [1]. We could identify the PGMEA sources based on the capabilities of the AMC C-1000 monitor: unattended monitoring for 24 hours / 7 days a week and a response time (rise time one cycle, 45 seconds) to record the occurrence of peak emissions.

As can be seen in Fig. 2 maintenance processes of the solvent delivery system are contributing for short time intervals with extremely high emissions to the PGMEA challenge of the clean room air. As the air is predominantly re-circulated the quantity of solvent emitted in short time remains in the air for a long period.

We found out that even the standard manufacturing processes can lead to clean room contaminations in case of a unrecognized small defect on a machine part (see Fig. 1). On two nearly identical machines operated side by side a variation in the quality of an air extraction hose resulted in an unacceptable emission (red lines) compared to standard emissions (green line).

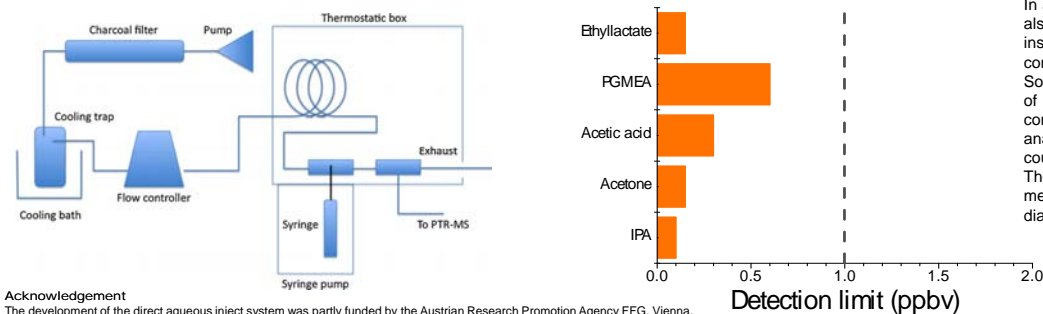
As the AMC C-1000 monitor is recording the data in real time we have been able to identify the underlying critical operation using the production- and machine log-files (Fig. 3).



Direct aqueous injection – calibration

The DAI system [2] (see left picture below for a schematic view) used for the calibration of the AMC monitor consists of a diaphragm pump generating an air stream which passes a charcoal filter and a cooling trap. This clean and dry "carrier" air stream is regulated by a mass flow controller and subsequently heated up to about 70°C. The liquid to be analyzed is filled into a syringe, which is controlled by a high-precision syringe pump. The tip of the syringe is pierced through a septum and thus reaches directly into the heated carrier stream, which is finally sampled with the PTR-MS instrument.

The graph on the right represents the obtained detection limits for five common contamination compounds.

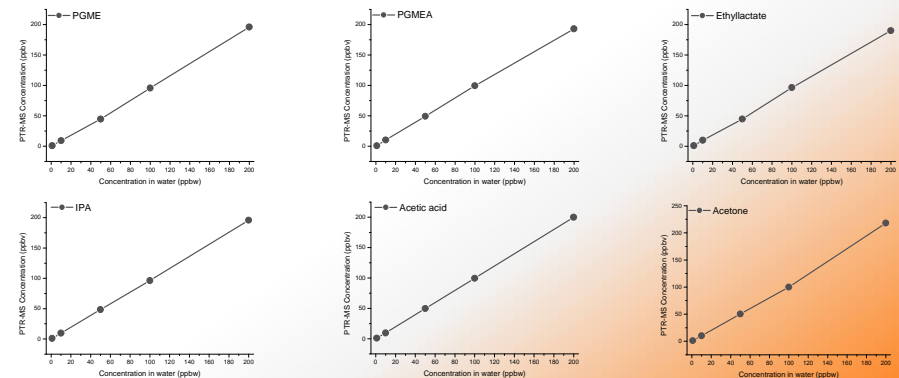


Linearity

In addition to the detection limits we also checked the linearity of the instrument's response to different concentrations.

Solutions with well-defined dilutions of six common contamination compounds were prepared and analyzed with the DAI system coupled to the AMC monitor.

The results of these linearity measurements are displayed in the diagrams on the right.



References

- [1] Pic, N., Martin, C., Vitalis, M., Calamou, T., Camlay, D., Grosjean, C., Lanier, A., Kames, J., Acksel, A., Galvez, C., Metrology, Inspection, and Process Control for Microlithography XXIV, edited by Christopher J. Raymond, Proceedings of SPIE Vol. 7638 (SPIE, Bellingham, WA 2010) 76380M.
- [2] S. Jürschik, A. Tani, P. Sulzer, S. Haidacher, A. Jordan, R. Schottkowsky, E. Hartungen, G. Hanel, H. Seehauser, L. Märk, T.D. Märk, International Journal of Mass Spectrometry 289 (2010), 173–176.

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