

# Advances in Real-Time Airborne Molecular Contamination Monitoring

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## Abstract

The semiconductor industry is moving toward data on demand to monitor the levels of cleanroom contaminants. No single (or simple combination of) instrument(s) is available today that is sufficiently sensitive, absolutely selective and reliable to meet the requirements and provide the required on-line monitoring of all desired airborne molecular contamination (AMC) present in semiconductor fabs. However, on-line monitors are rapidly improving, and we present here a review of the monitoring requirements and the tools that can address these requirements.

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Airborne molecular contaminants (AMCs) at critical levels cause yield issues at all technology nodes in the semiconductor industry. Semiconductor fabs have long had monitoring programs that have taken advantage of grab or point sampling to understand the environmental load of these critical contaminants. While these sampling programs have been useful for determining the target levels of AMCs (see Table 1) and have been able to provide the ultimate in required sensitivity, this type of monitoring

only provides a snapshot of the diurnal or weekly changes in contaminant levels.

A large variety of techniques exist which may be utilized to provide continuous monitoring of AMC levels. These analytical tools need to be cost-effective, compact, require little operator intervention, be self-calibrating, and offer multipoint testing, which is a very tall list of requirements. The following provides a list of techniques that may begin to meet some of these requirements.

## Surface Acoustic Wave (SAW)

Acoustic wave sensors were used in the '50s as quartz crystal microbalances. Later, in the '70s, surface acoustic wave sensors were applied toward chemical sensing, and the latest SAW technologies can measure mass changes of less than  $0.02\text{ng}/\text{cm}^2/\text{Hz}$  with a 1-minute sampling interval. One advantage that SAW technology holds is its ability to provide data that is directly relatable to how AMC affects the surface of interest. SAW devices can be fabricated from  $\text{SiO}_2$  or copper and thus can be directly related to what is happening on the surface of the semiconductor product or photolithography optical components. This technique measures the gas-phase

contamination which accumulates on a surface, but cannot identify the adsorbing molecular species. SAW sensors provide a measurement of surface molecular contaminants (SMCs) and are utilized as a gross (although sensitive) measure of contaminant levels.

**Chemiluminescence (CL)**

Chemiluminescence has been promoted by several analytical companies as a sensitive and mature method for the *in-situ* analysis of NOx and many molecular bases (MB: NH<sub>3</sub>, NMP, amines). Indeed, this technique has been shown to provide low ppb DLs for these nitrogen-containing compounds by reacting their nitrogen into NO and then converting the nitric oxide with ozone into the “excited” NO<sub>2</sub>\* followed by collecting the subsequent luminescence radiation. The method is destructive and potentially generates ozone, which is undesirable in the cleanroom environment. This technique is restricted to nitrogen-containing molecules, and cannot be applied to most of the MC and MA compounds on the SEMI list, significantly diminishing the usefulness of CL techniques for real-time AMC monitoring.

**Ion Mobility Spectrometry (IMS)**

Ion mobility spectrometry is widely utilized, and its acceptance is growing as a portable analytical technique. In IMS, analyte vapors are ionized and the resulting ions are characterized using a drift tube at atmospheric pressure in the presence of a drift gas, typically air or nitrogen. One of the significant advantages of IMS is its capacity to operate at atmospheric pressure with no moving parts. This is unlike traditional mass spectrometry, which operates at reduced pressure and requires bulky and expensive vacuum pumps. As is the case in traditional mass spectrometry, the direct analysis of analyte mixtures using IMS leads to complex spectra which may be challenging to interpret either quantitatively or qualitatively. Some manufacturers have used mathematical algorithms and chemometric data-treatment methods to deconvolve mixture mass-spectra in real time. Other approaches involve the forfeit of real-time data in favor of “near-real-time” data by using “fast-GC” or by simply adding a GC to pre-fractionate the sample mixture and deliver analyte constituents individually to the ion mobility spectrometer. Thus, the fast-GC option for IMS serves to simplify the

Material Category	1 ppt	10 ppt	100 ppt	1,000 ppt	10,000 ppt
Acids	MA-1	MA-10	MA-100	MA-1,000	MA-10,000
Bases	MB-1	MB-10	MB-100	MB-1,000	MB-10,000
Condensables	MC-1	MC-10	MC-100	MC-1,000	MC-10,000
Dopants	MD-1	MD-10	MD-100	MD-1,000	MD-10,000

Table 1. SEMI F21-95 AMC Classification of Semiconductor Cleanroom Environments and Measurement Equipment Performance

complexity of the resulting ion mobility spectral data at the cost of increased analysis time and instrumental complexity.

Unfortunately, even though sensitive enough, this analytical technique is not selective for most of the tabulated molecules and is known to often generate spurious ghost signals, especially in the cases of complex mixtures. There have also been reported problems with analytical windows not sufficiently narrow to discriminate the signal from an overlapping compound. This technique has found a niche application for the analysis of ppb levels of ammonia in lithography areas.

### ***Fourier Transform Infrared Spectroscopy (FTIR)***

The majority of the molecular airborne compounds of interest exhibit large infrared absorption cross sections, and this technique is one of the most commonly used real-time monitoring techniques for molecular air pollutants with abundant commercial equipment available. The high quality of modern multipass closed cells (ranging in path length from 10 to 100 m), along with substantial progress in the design of low-noise near and mid-IR detectors, allows many of the cutting-edge FTIR systems to be sensitive to the low ppb level, sufficient for continuous AMC monitoring. These sensitive measurements typically require cryogenic or thermo-mechanical cooling of the detector. Several manufacturers (MIDAC, Thermo Nicolet, MKS, Horiba, Bruker, Varian) offer instruments that could deliver real-time performance sufficient for the individual on-line analysis of many MA, MB and MC compounds.

Among the major disadvantages of FTIR, besides the low sensitivity to a limited number of compounds, is the

difficulty of quantification of similar compounds (e.g., amines), because of their similar IR spectra. In a real-world air matrix, overlapping bands from different species produce interferences in various spectral intervals. In order to identify the compound, extensive and reliable reference spectral libraries and specialized software are required to deconvolute the spectra.

Open-path FTIR (OP-FTIR) leverages massive path lengths to achieve high sensitivity, and is mainly utilized for fenceline analysis of airborne pollutants around plants and factories. The use of OP-FTIR for AMC analysis in the cleanroom does not appear to yield a significant advantage over the state-of-the-art closed-cell instruments. OP-FTIR use in cleanrooms is hampered by the fab layout itself (closed mini-environments with limited path lengths), moving optical obstructions, ceiling-to-floor airflow and air recirculation, high humidity and instrument calibration challenges.

### ***Resonance-Enhanced (Multiphoton) Ionization Combined with Time-of-Flight Mass Spectrometry REI-TOF***

REI-TOF is another potentially extremely sensitive technique to measure various volatile organics in air. It adds the high-efficiency resonant photo-ionization, with an appropriately tuned laser source, to the mass discrimination of TOF MS. Trace aromatic and chlorinated polycyclic air pollutants have been monitored *in-situ* at sub-ppb (and low ppt) range by several groups. However, much work needs to be done to utilize this technique as a rugged, portable on-line monitoring technique, and the very high equipment costs may inhibit widespread adoption.

## Atmospheric Pressure (Chemical) Ionization Mass Spectrometry

(AP(C)I-MS) has been the most sensitive and advanced analytical technique used by Air Liquide Electronics US (ALEUS) for on-line analysis of bulk and inert gases. ALEUS, in collaboration with VG (currently a part of Thermo Electron Corporation) has successfully developed commercial products (Trace+™, APIX™) allowing automatic continuous monitoring of such critical impurities as CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, etc., down to single ppt limits of detection, in different UHP matrixes: N, Ar, He and H. As early as 1980, AP(C)I-MS techniques were applied to ambient analysis for sub-ppb detection of inorganic and organic acids

and volatile organic solvents (including amines). These results, along with the fact that the first ionization potential of most of the targeted molecules is lower than that of N and O, suggest AP(C)I-MS methods could be considered for the on-line AMC monitoring in the cleanroom. The major foreseeable difficulties, such as mass interference ensuing from the potential complex composition of AMC mixtures or various competing charge-transfer reactions, could be resolved by such standard remedies as switchblade multichamber ionization sources with appropriate inlet membranes, and makeup reactants. Current APIMS technology is mechanically complex and quite expensive.

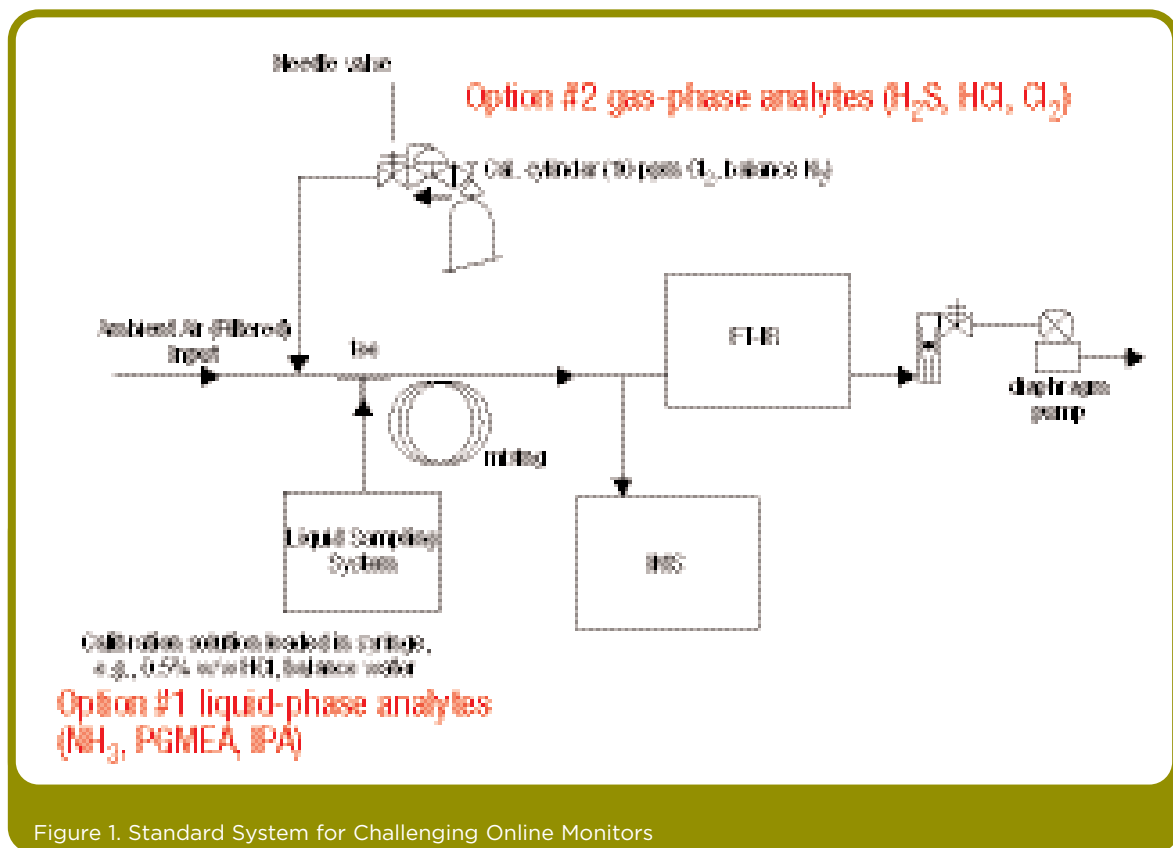


Figure 1. Standard System for Challenging Online Monitors

## **Thermal-Desorption Gas Chromatography (TDGC)**

TDGC is often the preferred method for environmental samples, where high sensitivity is desired. In the context of AMCs, TDGC requires that a metered volume of air is impinged and concentrated directly onto an adsorbent trap. The trap is subsequently heated in a relatively short amount of time and purged with an inert gas, so that the analytes are desorbed onto the head of the GC column. Analyte separation occurs on the GC column and is detected by flame ionization, mass spectrometry or other means, including a detection method called mini argon ionization detection (MAID) that incorporates argon as a carrier gas and a tritium source for ionization. This method works with most organic analytes because their ionization potential falls below that of argon.

## **Guaranteeing System Calibration**

Each system installed at semiconductor fabs should be challenged with a series of MA, MB, MC and MD compounds at a concentration at the lower limits of the operating levels. A typical system for challenging online instrumentation is shown in Figure 1.

## **Conclusions/ Recommendations**

### **Acids/oxidizers:**

- FT-IR appears best to achieve targets for HF, HCl, HBr, Acetic acid and ozone.
- Cl<sub>2</sub> must be done by IMS or other dedicated monitor.
- Other acids (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and organic acids) are best done by IC (grab sampling for now with on-line IC being developed).

### **Bases:**

- FT-IR appears to provide same or better sensitivity in comparison with IMS.
- Must use IC (via grab sampling) to achieve sub-ppb DLs.

### **Molecular Condensables:**

- FT-IR appears to provide sensitivities comparable to IMS. However, FT-IR calibration stability and speciation ability are generally far superior to IMS. Either method will detect low-molecular-wt organics, and will complement TD-GC-MS.
- Must use TD-GC-MS (off-site) to achieve 0.1 ng/liter-air DLs, or to provide speciation of similar compounds.

### **Refractories:**

- FT-IR appears to provide same or better sensitivity in comparison with IMS.
- Must use TD-GC-MS-based method (via grab sampling) to achieve sub-ppb DLs. ■

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## **About the Authors**

### **Dr. Dan Cowles**

Dr. Dan Cowles is the gas lab manager for Air Liquide Balazs in Dallas, Texas. He has been with Air Liquide for 13 years, including three years in Air Liquide's Tsukuba, Japan R&D Center. His work has focused on reactive gas sampling and analysis, process tool exhaust characterization and sampling methods for trace contaminants in air. Currently he is working on a variety of applied R&D projects in Air Liquide's Dallas Chemical Center. Cowles received a Ph.D. in physical chemistry from the University of Colorado-Boulder, Boulder, Colo., and a B.A. in chemistry from the University of Oregon, Eugene.

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### ***Dr. Hugh Gotts***

Dr. Hugh Gotts is the Director of Research and Development for Air Liquide – Balazs Analytical Services, and is responsible for the development of analytical methods for lab-based as well as on-line analyses. He has worked for Philips Semiconductors developing the measurement of on-line thin film analysis and established Analytical Services Group, LLC, which provided consulting and analysis services to major Silicon Valley companies. Hugh has been a member of the Technical Advisory Board, MicroBar, Inc. He has a Ph.D. in physical chemistry from UC Santa Cruz, where he studied excimer laser-induced nucleation of metal cluster in the gas phase.

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