

Monitoring Airborne Molecular Contamination: a Quantitative and Qualitative Comparison of Real-time and Grab-sampling Techniques

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ABSTRACT

Monitoring and controlling Airborne Molecular Contamination (AMC) has become essential in deep ultraviolet (DUV) photolithography for both optimizing yields and protecting tool optics. A variety of technologies have been employed for both real-time and grab-sample monitoring. Real-time monitoring has the advantage of quickly identifying “spikes” and upset conditions, while 2 – 24 hour plus grab sampling allows for extremely low detection limits by concentrating the mass of the target contaminant over a period of time. Employing a combination of both monitoring techniques affords the highest degree of control, lowest detection limits, and the most detailed data possible in terms of speciation. As happens with many technologies, there can be concern regarding the accuracy and agreement between real-time and grab-sample methods. This study utilizes side by side comparisons of two different real-time monitors operating in parallel with both liquid impingers and dry sorbent tubes to measure NIST traceable gas standards as well as real world samples. By measuring in parallel, a truly valid comparison is made between methods while verifying the results against a certified standard. The final outcome for this investigation is that a dry sorbent tube grab-sample technique produced results that agreed in terms of accuracy with NIST traceable standards as well as the two real-time techniques Ion Mobility Spectrometry (IMS) and Pulsed Fluorescence Detection (PFD) while a traditional liquid impinger technique showed discrepancies.

Keywords: ammonia, sulfur dioxide, airborne, molecular, contamination, impinger, sorbent tube, real-time, AMC, IMS

1. INTRODUCTION

Liquid impingers have traditionally been considered the “gold standard” method for making sub-ppb_v measurements of AMC, specifically for airborne molecular acids and bases. As a variety of new measurement techniques have been introduced to the semiconductor industry, it is vital to understand the accuracy and agreement of the results obtained through different measurement techniques. While some degree of uncertainty is inherent in each technique, the ability to calibrate the entire method to a NIST traceable standard is essential to ensure an accurate result, regardless of the technique used.

In the case of liquid impingers, many laboratories will simply run a NIST traceable liquid standard of the desired analyte directly through their Ion Chromatography (IC) equipment and assume that the results from their entire technique are NIST traceable. While the IC response may then have a NIST traceable calibration, there are additional parts of the technique that have been neglected. To properly validate the entire technique, a humidity and temperature controlled, gas-phase, NIST traceable standard must be bubbled through the impinger and then the resulting liquid solution must be run through the calibrated IC analysis. If the technique is done properly, a 100 ng/ml liquid standard run directly through the IC analysis should agree 1:1 with an equivalent theoretical mass concentration run in gas phase through the liquid impinger and then analyzed with the same IC. Unfortunately, phenomena such as evaporative losses, analyte solubility, and sample gas and liquid-phase contacting can drastically affect trapping efficiency within a liquid impinger. Consequently, many impinger results turn out to be lower than expected when compared to properly executed NIST traceable standards.

Real-time monitors, on the other hand, have a major advantage over grab-sample techniques in terms of calibration. Since real-time monitors give instantaneous results, they can be calibrated directly against a humidity and temperature controlled, gas-phase, NIST traceable standard. For this same reason, real-time monitors can be validated as NIST traceable as soon as a NIST traceable standard is applied.

In this study, two grab-sample and two real-time AMC analysis techniques were investigated. The two grab-sample techniques both utilize IC analysis with one technique employing liquid impingers and the other dry sorbent tubes. One of the real-time techniques applies Ion Mobility Spectrometry (IMS) and the other Pulsed Fluorescence Detection (PFD).

1.1 Grab-sample technique – liquid impingers

An impinger is simply a sealed container partially filled with liquid (typically DI water) through which gas is forced or drawn. A typical impinger setup can be seen in Fig. 1. as ambient air is drawn in through the inlet tube to the bottom of the vial where the gas escapes as bubbles that float to the surface of the liquid and exit through the outlet fitting at the top of the vial. The flow is driven by a small vacuum pump plumbed to the outlet fitting. The basic theory is that airborne molecular acids and bases present in the incoming sample air will transfer from the gas phase (inside of the individual bubbles) into the liquid phase in the surrounding solution. The solution is then analyzed using IC to determine the average concentration of a given analyte present in the sample air over the period of time that the sample was collected.

1.2 Grab-sample technique – dry sorbent tubes

The dry sorbent tube technique is very similar to the impinger technique. The main difference is that the sample air is drawn through a tube containing dry sorbent media instead of a liquid-filled impinger as illustrated in Fig. 2. The dry sorbent media is coated with a counter-ion so that an ionic bond can be formed with the target analyte. For this reason, there are different media for trapping molecular acids versus bases as different chemistries are required for the counter-ion coating. The sorbent media particles also have a specially designed size, shape, and porosity to allow optimum surface area for surface chemistry and contacting of the flow-through sample air.

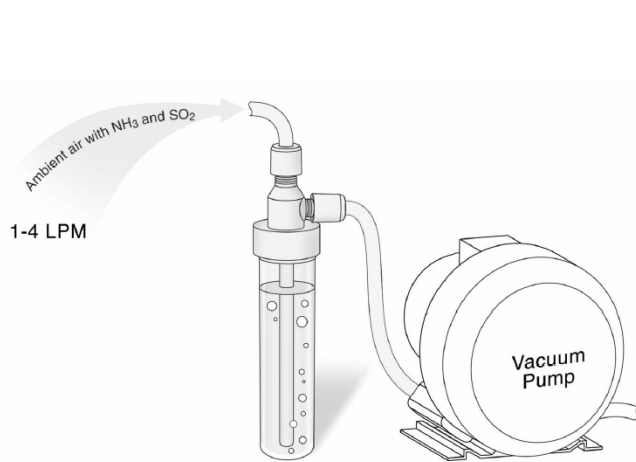


Fig. 1. Basic impinger setup.

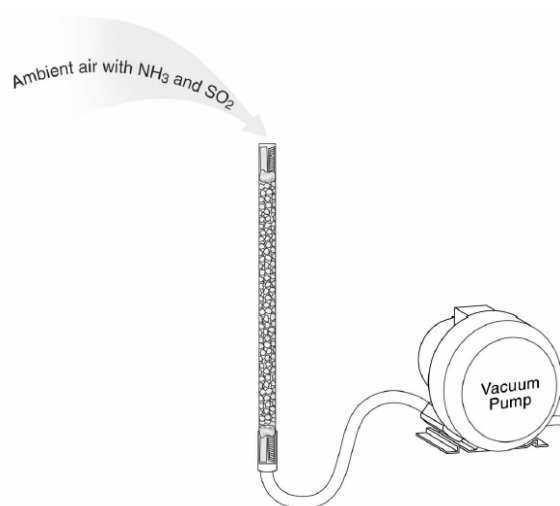


Fig. 2. Basic sorbent tube setup.

The dry sorbent tube technique investigated in this study utilized the Particle Measuring Systems AirSentry Surveyor as depicted in Fig. 3. This device is a fully automated sampler designed to take grab samples of ambient air or purge gas using Particle Measuring Systems AccuSorb Technology. AccuSorb Technology is a proprietary sorbent tube and analysis method for measuring airborne molecular acids, bases, and organics. There is a specific AccuSorb sorbent tube designated for each of the three aforementioned classifications of airborne molecular contaminants; each tube is cleaned and packaged for extremely low background levels, and formulated with media designed for maximum trapping and recovery efficiency for its appropriate family of target compounds.



AccuSorb Technology

Fig. 3. AirSentry Surveyor and AccuSorb Technology sorbent tubes.

Inside the enclosure (Fig. 4.), there is a Teflon® sorbent tube manifold that allows three different tubes to be loaded in parallel. On either side of each tube, there is an electronic solenoid valve that seals off and isolates each tube from the outside environment when the sampler is not running. On the downstream side of the manifold (bottom), there are three orifices (one for each tube) that control the flow through each sorbent tube driven by a single vacuum pump further downstream. Finally, a built-in timing circuit controls the sample collection time by automatically starting the pump and opening the solenoid valves when the power switch is turned on. An air sample from a single point is drawn in through the sample inlet and then into the top of the manifold where it enters the three sorbent tubes. After 24 hours (or any other factory-settable preset time), the timing circuit cuts power to the pump and the solenoid valves leaving the three sorbent tubes independently sealed until they are removed for laboratory analysis. A “blank” tube for each family of airborne molecular contaminants is also placed unopened inside the AirSentry Surveyor. The blank serves to establish if any background contamination is present from the tube media or from the shipping and handling of the tubes.

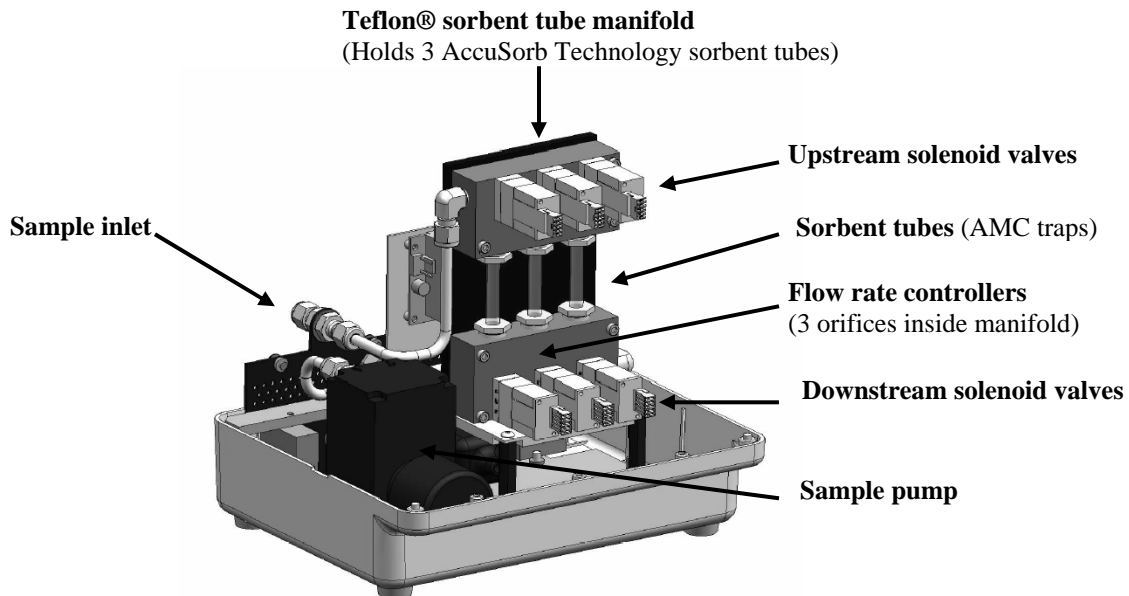


Fig. 4. AirSentry Surveyor - internal diagram.

1.3 Real-time Monitoring Technique – IMS

IMS is an ionization-based time of flight technique, performed at atmospheric pressure. The heart of IMS is the sample cell. A continuous ambient air sample is drawn into the sample cell where it is mixed with a purified dry doped-gas stream, before being delivered to the reaction region. There, the sample is ionized by low-level beta energy emitted by a sealed nickel-63 radiation source. The ionized sample drifts through the cell under the influence of an electrostatic field. A shutter grid is biased electrically to either block the ions, or allow them to pass through. This shutter grid is pulsed to periodically allow the ions into the drift region. There, they begin to separate based on their size, shape and charge while flowing counter to a drift gas flow, which is introduced at the end of the drift tube (the opposite flow aids in separation of the molecules). The smaller ions move faster than larger ions through the drift tube and arrive at the detector. A collector (Faraday plate) located at the end of the tube detects the arrival of the ions and produces a current. This current is amplified to produce a time of flight spectrum and a microprocessor evaluates the spectrum for the target compound, determining the concentration based on the peak height. Because of the specificity of the dopant gas, enhanced ionization, and time-of-flight, there is the highest degree of certainty that the analyzer is measuring only the compound of interest, even in the presence of other potential interferents.

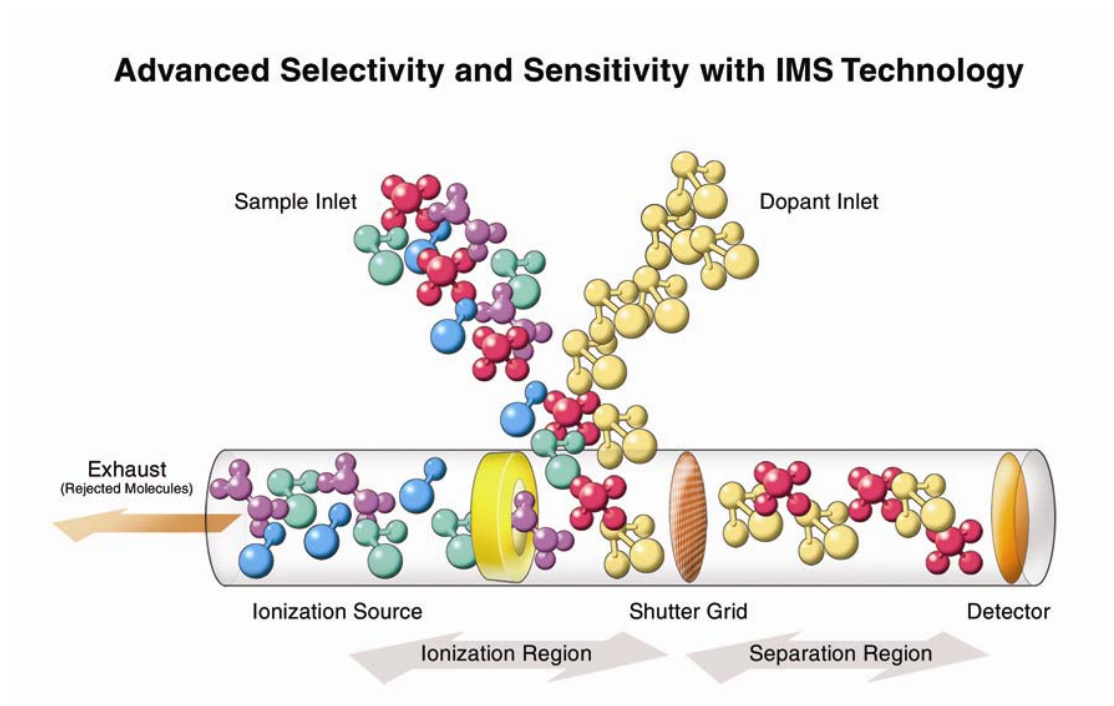
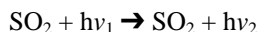


Figure 5: IMS Cell Detection Methodology

1.4 Real-time Monitoring Technique – PFD

Pulsed Fluorescent Detectors utilize the UV absorption and decay characteristics of Sulfur Dioxide in order to quantitatively identify this contaminant. When a sample stream is exposed to UV light at a wavelength known to be strongly absorbent by SO₂ molecules, the UV excites the SO₂ molecules into a higher energy state. When the UV light is pulsed (turned off from an on state), the excited SO₂ molecules decay to a lower energy state by emitting UV light of another wavelength.



Precision mirrors and optical filters control the light entering the chamber and pass the emitted light to the photomultiplier tube. Output from the photomultiplier is proportional to the SO₂ concentration in the sample. A hydrocarbon scrubber removes any hydrocarbons in the sample, while allowing SO₂ molecules to pass through unaffected.

2. METHODOLOGY

This study was done in two phases. The first phase consisted of measuring NIST traceable standards in controlled laboratory conditions. Ammonia, an airborne molecular base, and sulfur dioxide, an airborne molecular acid, were selected due to their ubiquity and deleterious effects to product yield as well as processing equipment in the semiconductor industry, such as ammonium sulfate hazing of 193 nm photolithography optics. The second phase of the study focused on measuring ammonia in situ inside a production fab environment in Japan.

2.1 Ammonia Laboratory Test

First, a NIST traceable 1.50 ppb_v ammonia in air standard is prepared. The standard begins with a gravimetrically certified permeation device maintained at a specific temperature within a certification oven. A clean dry air (CDA) flow is sustained through the oven to provide a primary dilution. The outflow of the oven is combined with a secondary dilution flow of CDA bubbled through DI water. All dilution flows are set using a NIST traceable primary standard flow meter and maintained by digital mass flow controllers. The total dilution, temperature, and humidity are precisely controlled to ensure the delivered ammonia standard is 1.50 ± 0.03 ppb_v, 22.0 ± 0.2°C, and 45 ± 2% RH. The standard is then delivered to the AMC measurement devices via conditioned ¼ inch PFA tubing.

For the ammonia laboratory test, two independent liquid impingers (filled with DI water) are plumbed to the 1.50 ppb_v NIST traceable ammonia standard in parallel with three independent AccuSorb sorbent tubes (all loaded into one AirSentry Surveyor). A Particle Measuring Systems AirSentry-IMS Ammonia in Air Analyzer is also plumbed in parallel to provide a real-time measurement. The results are shown in Sec. 3.

2.2 Sulfur Dioxide Laboratory Test

The sulfur dioxide laboratory test is carried out in an identical manner as the ammonia laboratory test in Section 2.1. The only differences are that the delivered standard is 10.0 ± 0.15 ppb_v of sulfur dioxide in air, 22.0 ± 0.2°C, and 45 ± 2% RH; and the real-time monitor is a Particle Measuring Systems AirSentry Sulfur Dioxide in Air analyzer. The results are shown in Sec. 3.

2.3 Ammonia test in real fab environment

For this test, one AirSentry Surveyor (loaded with three independent AccuSorb Technology sorbent tubes), an AirSentry-IMS Ammonia in Air real-time analyzer, and three independent DI water impingers were set up to sample the same ambient air location within a fab in Japan simultaneously for 24 hours. Upon completion of sample collection, the entire AirSentry Surveyor was shipped back to Particle Measuring Systems in Boulder, Colorado with the sorbent tubes still intact for analysis. Meanwhile, the three impingers were shipped to a third-party lab in Japan for analysis. Finally, the data from the AirSentry-IMS system were downloaded from its onboard PC. All results for this test are documented in Sec. 3.

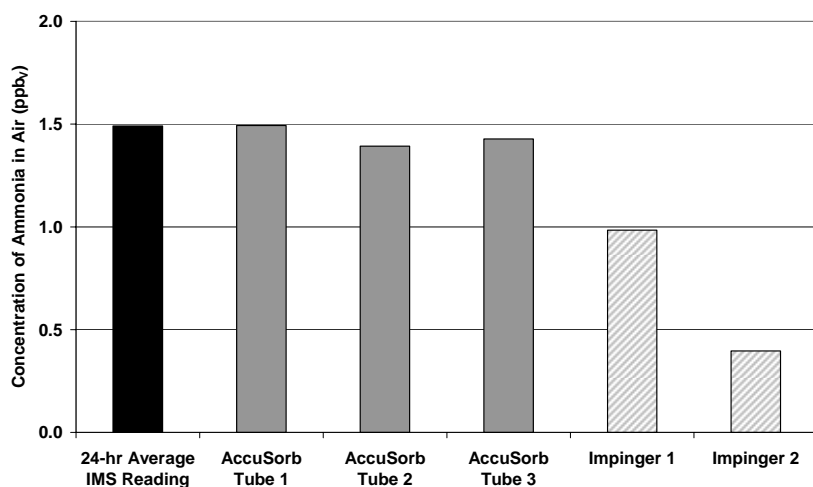
2.4 Sample Analysis

To calculate the concentration of ammonia trapped on the sorbent tubes or in the impingers' liquid phases, the total sample air volume (integrating flow) that was drawn through each device must be known. The total air sample volume is calculated from the sampling flow rate (measured by a precision flow meter) and the time duration. The air sample volume for each impinger and sorbent tube collected is recorded. The samples are each analyzed separately using the same IC with a conductivity detector and an auto suppressor.

3. RESULTS

3.1 Results from ammonia laboratory test

The data for the ammonia laboratory test are illustrated below in Fig. 6. and Fig. 7. Fig. 6. shows the average concentration as detected by the real-time AirSentry-IMS analyzer, the AccuSorb Technology sorbent tubes (using the AirSentry Surveyor), and two DI water impingers all simultaneously measuring in parallel the delivered ammonia standard at 1.50 ± 0.03 ppb_v, $22.0 \pm 0.2^{\circ}\text{C}$, and $45 \pm 2\%$ RH. Fig. 7. shows the real-time data collected by the AirSentry-IMS analyzer and averaged over the 24-hour sample collection period.



Name of Sample	Ammonia in Air (ppb _v)
IMS – 24 hr. Avg.	1.49
AccuSorb Tube 1	1.49
AccuSorb Tube 2	1.39
AccuSorb Tube 3	1.43
Impinger 1	0.98
Impinger 2	0.40

Fig. 6. 24-hour average measurement of NIST traceable 1.50 ppb_v ammonia in air standard

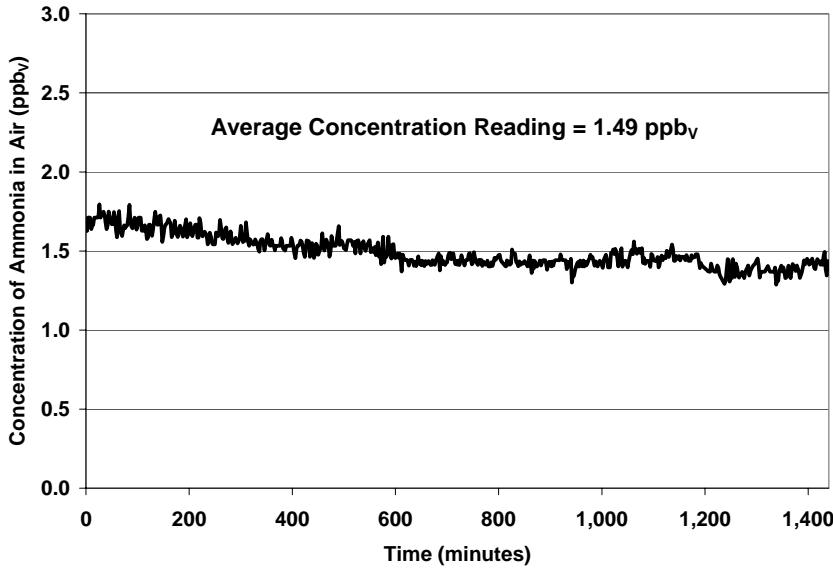
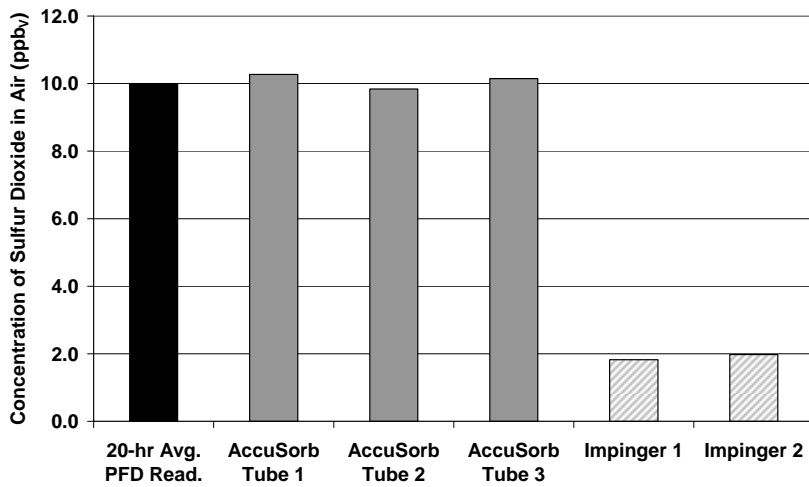


Fig. 7. 24-hour real-time data collected by Particle Measuring Systems AirSentry-IMS Ammonia in Air Analyzer

3.2 Data from sulfur dioxide laboratory test

The data for the sulfur dioxide laboratory test are illustrated below in Fig. 8. and Fig. 9. Fig. 8. shows the average concentration as detected by the real-time AirSentry Sulfur Dioxide analyzer, the AccuSorb Technology sorbent tubes (using the AirSentry Surveyor), and two DI water impingers all simultaneously measuring in parallel the delivered sulfur dioxide standard at 10.0 ± 0.15 ppbv, $22.0 \pm 0.2^\circ\text{C}$, and $45 \pm 2\%$ RH. Fig. 9. shows the real-time data collected by the AirSentry-PFD analyzer and averaged over the 20-hour sample collection period.



Name of Sample	Sulfur Dioxide in Air (ppbv)
PFD – 20 hr. Avg.	10.0
AccuSorb Tube 1	10.3
AccuSorb Tube 2	9.8
AccuSorb Tube 3	10.1
Impinger 1	1.8
Impinger 2	2.0

Fig. 8. 20-hour average measurement of NIST traceable 10.0 ppbv sulfur dioxide in air standard

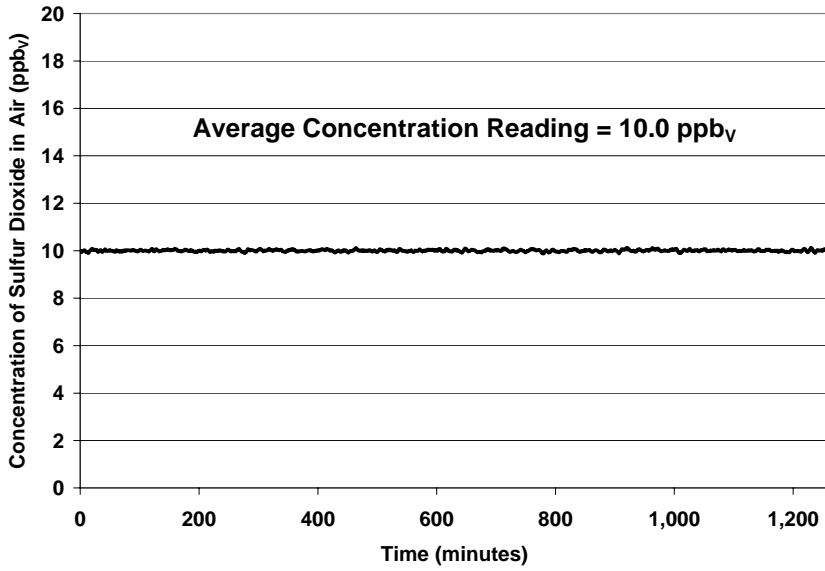
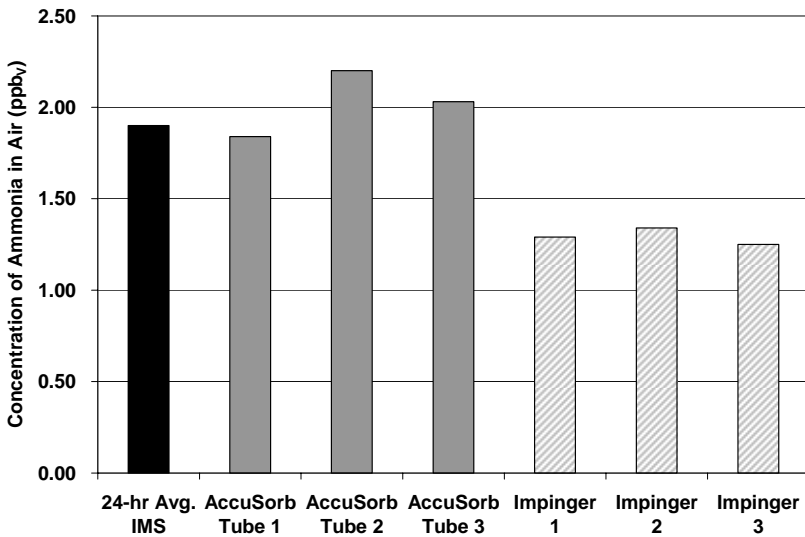


Fig. 9. 20-hour real-time data collected by Particle Measuring Systems AirSentry-PFD Sulfur Dioxide in Air Analyzer

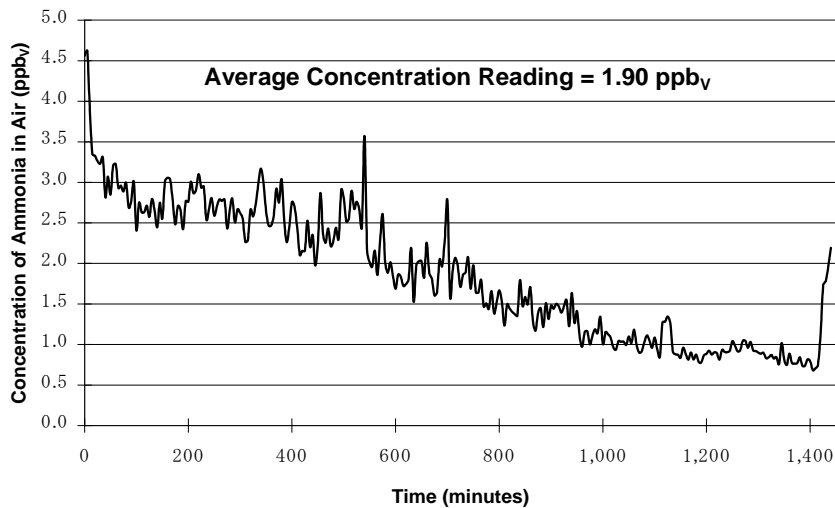
3.3 Data from ammonia test in real fab environment

The data for the ammonia test in the real fab environment are illustrated below in Fig. 10. and Fig. 11. Fig. 10. shows the average concentration as detected by the real-time AirSentry-IMS, the three AccuSorb Technology sorbent tubes (using the AirSentry Surveyor), and three independent DI water impingers all simultaneously measuring in parallel the same ambient air point within the fab in Japan. Fig. 11. shows the real-time data collected by the AirSentry-IMS analyzer and averaged over the 24-hour sample collection period.



Name of Sample	Ammonia in Air (ppbv)
IMS – 24 hr. Avg.	1.90
AccuSorb Tube 1	1.84
AccuSorb Tube 2	2.20
AccuSorb Tube 3	2.03
Impinger 1	1.29
Impinger 2	1.34
Impinger 3	1.25

Fig. 10. 24-hour average measurement of ammonia in air in real fab environment



24-hr Sample	Ammonia in Air (ppb _V)
Maximum	4.62
Minimum	0.70
Average	1.90

Fig. 11. 24-hour real-time data collected by Particle Measuring Systems AirSentry-IMS Ammonia in Air Analyzer

4. ANALYSIS

4.1 Ammonia and sulfur dioxide laboratory tests

In both the ammonia and the sulfur dioxide laboratory tests where both real-time and grab-sample methods were challenged with NIST traceable standards, it was clear that the IMS, PFD, and AccuSorb Technology sorbent tube techniques all agreed well with the NIST traceable standard. On the other hand, the DI water impinger technique read significantly below the correct values in all cases. Sec. 4.3. makes an attempt to qualitatively explain why these impinger readings came up so low.

4.2 Ammonia real fab environment test

The results produced using the AirSentry-IMS Ammonia in Air real-time analyzer showed an average concentration reading of 1.90 ppb_V while the AirSentry Surveyor with AccuSorb Technology showed an average concentration of 2.02 ppb_V between the three sorbent tubes. The three impingers, on the other hand, yielded an average of 1.30 ppb_V of ammonia in air. Particle Measuring Systems AirSentry-IMS real-time analyzer as well as the AccuSorb Technology are verified against NIST traceable gas standards and redundantly checked with real-time monitoring equipment. As such, it is believed that their approximately 30% higher readings are more accurate values for the true concentration of ammonia at the real fab environment's sample point than are those produced by the three DI water impingers.

4.3 Why impinger readings are low

There are a number of reasons why impingers read lower than expected. Looking a little closer at the impinger, it becomes apparent that trapping gases in a liquid is never 100% efficient; only partial trapping is possible. Fig. 12. below illustrates this phenomenon. While gases inside each individual bubble continuously dissolve into the liquid phase (including molecular bases like ammonia along with nitrogen and oxygen in the ambient air), already dissolved molecular contaminants come out of solution back into the gas phase and enter back into the bubble. In essence, there is a continuous bidirectional flow of gases into and out of the liquid phase. The result is an equilibrium where a certain portion of the airborne molecular contaminants are left in the gas phase and only the remaining portion is trapped into the liquid phase. Furthermore, as the bubbles rise to the surface of the impinger's liquid phase and burst, the undissolved

gases are drawn away through the outlet by the vacuum pump; thus, escaping entrapment and further reducing the overall trapping efficiency.

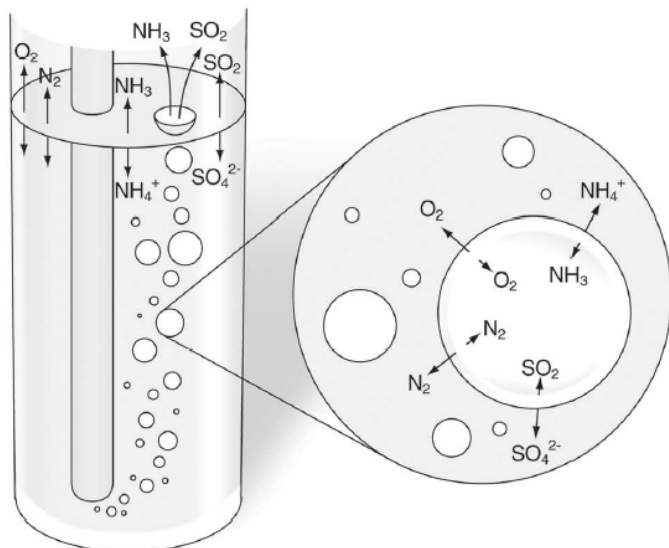


Fig. 12. Reduced trapping efficiency and losses within an impinger.

In addition to the gas exchange within each bubble, the same phenomenon occurs at the surface of the liquid phase at the top of the impinger. Here, molecular acids and bases also go into and out of solution. This effect is especially important during the time after sampling until the liquid is run on the chromatography column. The end result is that trapping efficiency with an impinger is never 100%. In fact, it may be less than 50% for less water-soluble compounds such as sulfur dioxide.

Nevertheless, techniques have been explored to improve trapping efficiency. As Figure 13 illustrates, multiple impingers can be "trained" together in series so that the airborne molecular contaminants that escape entrapment in (or breakthrough) the first impinger have another chance to be captured by the next impinger. While a greater overall trapping can be achieved, training still fails to get 100% of any given contaminant for the same reasons depicted in Figure 12. Furthermore, an impinger train causes greater dilution of the target ion. For example, instead of having 50 ng of ammonium ion in 100 ml of DI water with one impinger, a train of three impingers disperses that same mass over 300 ml of DI water. The end result is a reduction in the concentration of target ion supplied to the IC, which directly impacts detection limit by at least factor of three. While trapping efficiency can be improved by the train technique, the final concentration reading will still be lower than a truly accurate reading.

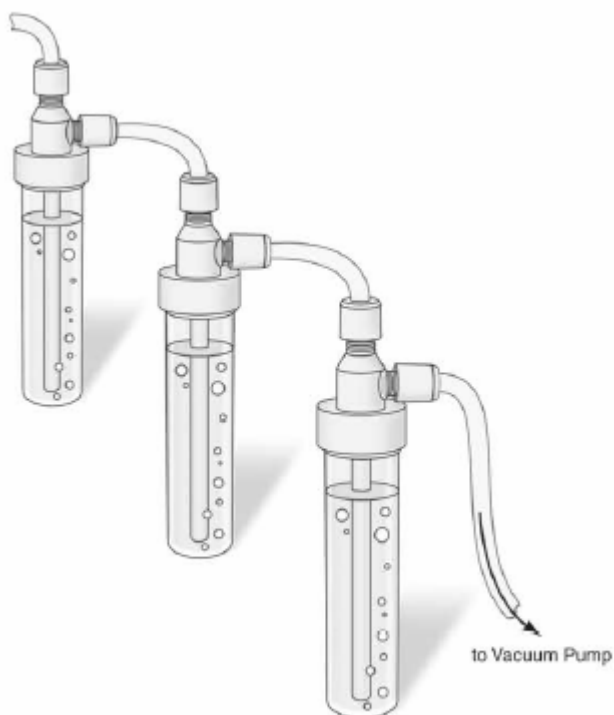


Figure 13. Impinger Train to Improve Trapping Efficiency

Particle Measuring Systems AccuSorb Technology sorbent tubes do not experience the same problems as liquid impingers. AccuSorb Technology takes advantage of solid-state media that is specially formulated to chemically trap ammonia (as well as numerous other AMC species) using the strength of ionic bonds to lock target compounds into specifically shaped pores as shown in Figure 14.

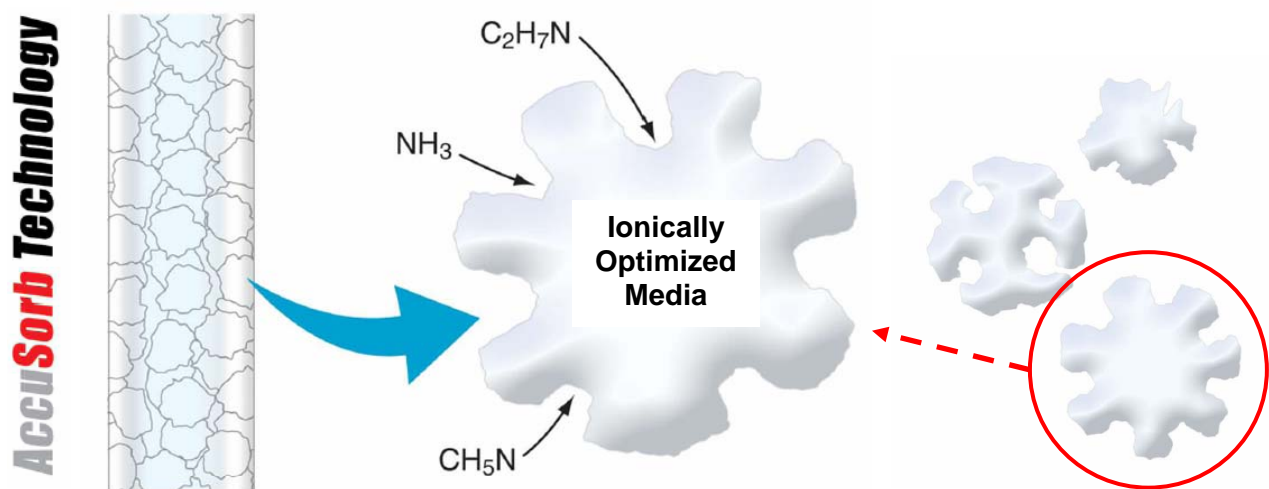


Figure 14. AccuSorb Technology Media for Trapping Molecular Bases

Trapping efficiency is further optimized by selecting appropriate flow rates through the sorbent tubes as well as sizing media particles appropriately as illustrated in figure 15 below.

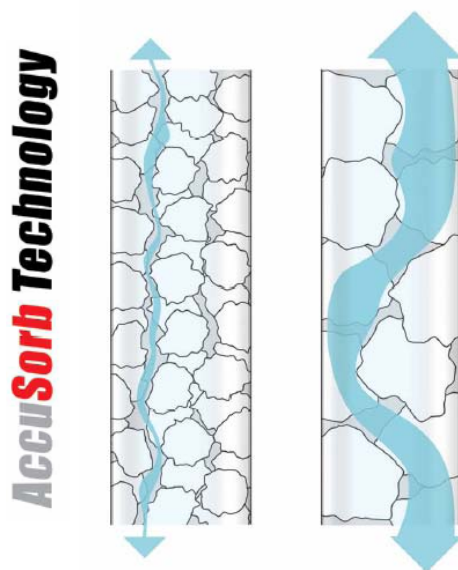


Figure 15. Optimizing Flow Rate and Media Particle Size for Maximum Trapping Efficiency

Finally, AccuSorb Technology provides a much higher concentration of raw extract for IC analysis than is achieved with impinger techniques. After collecting sample, AccuSorb Technology sorbent tubes are ultrasonically extracted using only 3 ml of liquid (instead of approximately 100 ml used in impingers) as illustrated in Figure 16 below.



Figure 16. AccuSorb Technology Ultrasonic Extraction with 3 ml of solvent

The result is that a much higher solvent concentration is achieved; thus allowing for enhanced detection limits and superior accuracy. As revealed in Table 1, the sorbent tubes have over a magnitude larger sample extraction when compared to impinger testing, allowing for a better sample analysis.

Name of Sample	Solvent or Raw Extract Concentration (ppb _w)
Impinger 1	30.7
Impinger 2	29.4
Impinger 3	28.6
Sorbent Tube 1	455
Sorbent Tube 2	576
Sorbent Tube 3	548

Table 1. Solvent or Raw Extract Concentration Before IC Analysis

5. CONCLUSIONS

As this investigation began, it was understood that there may be different reported results when analyzing AMC using different monitoring techniques. Through both laboratory and production cleanroom testing, the accuracy, magnitude and probable causes have been determined. Major items to note when choosing suitable monitoring equipment, or comparing monitoring techniques include:

- Proper Calibration – Techniques and equipment that measure gas phase analytes need to be calibrated by supplying NIST traceable gas standards.
- Evaluation and Understanding of Technique Error - The magnitude of error has been shown to be 50-100% in laboratory and production cleanroom environments when Ammonia is sampled and analyzed with impinger and IC technology. Primary causes for this include trapping efficiency, increased dilution, and evaporative losses. For SO₂, laboratory results indicate 430% error with impinger and IC methods, again due to significantly decreased trapping efficiency due to the low solubility of SO₂ in water, as well as the dilution needed for acceptable analysis.
- Equipment complexity – It can be generally stated that the more complex the sampling and analysis system, the greater the potential error that can be induced. As multiple sample collection systems are placed in sequence with one another, detection limits suffer.

This paper has also shown that significant benefits can be captured by utilizing sorbent tube media as a means to capture both acid and base contaminants for accurate quantitative analysis, as well as speciation. Real-time monitoring techniques provide advantages in that instant results allow decisions to be made in a timely manner. Proper monitoring schemes undoubtedly use both real-time and grab sampling methods in order to maximize real-time and speciation data available for analysis.