

## AN ANALYTICAL METHOD FOR THE MEASUREMENT OF TRACE LEVEL ACIDIC AND BASIC AMC USING LIQUID-FREE SAMPLE TRAPS

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# Abstract

The measurement of parts-per-trillion (ppt) level acidic and basic airborne molecular contamination (AMC) is essential for process protection and yield control in semiconductor photolithography and adjacent applications. Real-time monitoring solutions are highly desired, as they provide instantaneous and continuous measurement. However, even the most advanced monitors cannot achieve detection limits in the low parts-per-trillion (ppt) range and many restrictions apply for the detection of acidic AMC. High cost of ownership is another disadvantage.

Discontinuous sampling with sample traps is capable of achieving ppt-level measurement, but the currently accepted methods use sample traps filled with deionized water (impingers) to capture soluble acidic and basic AMC. Several inherent disadvantages of these methods result in inconsistent data and increased detection limits. Some proprietary solid state solutions have been reported, but involve complex preparation, have high background signals and require 24–72 hour sample duration, or they are protected trade secrets that are not available as an industry standard.

To eliminate these disadvantages, we developed a liquid-free sample trap that allows parts-perquadrillion level (ppq) measurement of acidic and basic AMC within one work shift, typically a 4-6 hour sample period. The traps can easily be manufactured and prepared in small lab operations, are sealed and protected from the outside and operator handling in the field, have months of shelf life and show high capture efficiencies while minimizing reactions and artifacts.

Capacity results for the liquid-free base trap using ammonia (NH<sub>3</sub>) as a test gas yielded more than 200 ppb-h at 100% capture efficiency without any moisture (simulating sampling of CDA or N<sub>2</sub>) and 350 ppb-h at 40% RH. The capacity results for sulfur dioxide (SO<sub>2</sub>) were highly dependent on moisture content of the sample gas and yielded 5 ppb-h at 90% capture efficiency and 0% RH, but increased exponentially to more than 1200 ppb-h at 40% RH. Performance testing indicates that the liquidfree trap provides both more precise and more accurate results for  $NH_3$ ,  $SO_2$  and HF in comparison to standard impinger in lab testing, with a relative standard deviation not exceeding 8% and capture efficiency greater than 95% for all three compounds. Acetic acid was the only compound that shows slightly decreased performance but still maintained a precision and accuracy comparable to the other compounds tested.

In-field validation deployment to external and internal customers in parallel with standard wet impingers resulted in less than 10% difference between the traps, providing the necessary evidence that liquid-free traps are suitable for replacement of and better than wet impingers.

## Introduction

Process and equipment issues related to airborne molecular acid and base contamination (AMC) in photolithography applications have been well documented, including reticle hazing,<sup>1</sup> reaction with photoresist and corrosion.<sup>2</sup> As the sensitivity of critical processes to AMC exposure in photolithography increases, the recommended allowable concentrations continue to decrease and AMC monitoring and concerns have expanded to areas outside of the litho bay, including electrochemical deposition, CMP, wafer handling and dry etch. The International Technology Roadmap for Semiconductors (ITRS) recommends a minimum detection limit of 10 ppt for both acids and bases at the 22 nm node and these detection limits are expected to decrease to parts per quadrillion (ppq) levels with the introduction of 14 and 10 nm technologies.3 AMC controls and specifications for the introduction of extreme ultra-violet (EUV) lithography are currently still based on those of DUV lithography, but may change to push those limits further down, as new process or equipment sensitivities may be discovered. All concentrations in this publication are in volumetric, molar units, not mass based.

Real-time AMC monitoring solutions are desirable because they provide instantaneous and continuous measurement. However, even the most advanced technologies, such as ion mobility spectrometry (IMS), continuous wave cavity ring-down spectroscopy (CW-CRDS), photo-acoustic spectrometry (PAS) and others can only achieve reliable detection limits in the ppb to high ppt range. In addition, sample transport, particularly of acidic compounds, is affected by line losses and reaction with bases. Finally, real-time monitors typically have substantial cost of ownership for maintenance, operation and calibration.

Traditionally, devices filled with deionized water, such as impingers (also known as bubblers) or open beakers have been the preferred sample trap method for the measurement of acidic and basic AMC. An impinger is a cylindrical container partially filled with liquid, (typically deionized water) that allows gas to be drawn through the liquid. As the gas passes through the liquid, soluble contaminants either react or dissolve into the liquid, dissociating into ionized species that can then be analyzed by ion chromatography. For example, hydrogen chloride gas (HCl) has a high dissociation constant and completely dissociates in water to form the chloride anion (Equation 1).

## $HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$

Although impingers are generally effective, the capture efficiency for different species varies and is dependent on and limited by several factors including analyte solubility, dissociation constant of the dissolved species, evaporative losses, residence time of the gas within the mass transfer zone, bubble size and the potential for secondary reactions (formation of  $HNO_x$ , interference with dissolved  $CO_2$ , UV catalyzed reactions, disproportioning of species and conversion from one to another species).

The mass transfer zone for gas diffusion within the impinger trap can be considered at the gas/liquid interface of each bubble as it travels through the liquid column. The longer the gas is in contact with that interface the more gas can dissolve into the liquid. Bubble size and consistency has a significant impact on the capture efficiency of the trap since large bubbles may inhibit diffusion by preventing gas in the center of the bubble from reaching the mass transfer zone during its residence time in the water. A high density of very small bubbles, on the other hand, can also decrease transfer efficiency since many small bubbles can reduce the surface area of the mass transfer zone by effectively creating one large bubble. Combined, these factors limit the possible flow rate of the sample gas through the trap and trap size is limited by practical implementation considerations. This decreases detection capability by limiting the absolute amount of contaminant that can be collected during a given sample duration.

Impingers also undergo evaporative losses ranging from 0.1-0.5 mL/h depending on trap design, flow volume and moisture content of the sampled gas. This also limits sample time and decreases residence time of gas by reducing the height of the liquid column. Larger liquid volumes can be used to compensate for these evaporative losses, but that results in sample dilution and decreased detection capability, again, requiring longer sample times.

The standard analysis method for impinger trap solutions is ion chromatography with conductivity detectors. Quantitative measurement this way is dependent on full dissociation of the ionized species. As indicated in Equation 1, hydrogen chloride is a strong acid, resulting in full dissociation and a 1:1 ratio of captured to detected chloride anions. However, when attempting to detect weak acids and bases, we observe partial dissociation, resulting in non-linear response curves. This is another limitation of impingers as it may require secondary reactions (added chemicals) to produce the ionized species. For example, ammonia gas ( $NH_3$ ) is a weak base in solution and only partially dissociates to form the ammonium ion (Equation 2).

## $NH_{3(g)} + H_2O \leftrightarrow NH_{3(aq)} + NH_4^+ + OH^-$ (2)

The amount that does not dissociate and remains as aqueous ammonia in solution will not be detected by IC. That amount varies and depends on both temperature and total pH of the impinger solution, often resulting in measurement inconsistency.

Sulfur dioxide gas  $(SO_2)$  is technically an acidic gas acting as an electron acceptor (Lewis acid) and reacts with water through a complex mechanism producing a number of intermediate species in tautomeric equilibrium highly dependent on both pH and temperature.<sup>4</sup> Oxidation of the resulting species by excess water or dissolved oxygen, autoprotolysis and dimerization can further result in a number of secondary intermediate species, contributing to substantial variability and inconsistent measurement results. Finally, SO<sub>2</sub> was also found in an internal study to not quantitatively

(1)

dissolve in pure water at air concentrations above 1 ppb without the aid of added peroxide to fully convert it to the dissolved form.

One persistent artifact associated with water impingers is the formation of "virtual NO<sub>x</sub>," the ionic forms of nitrous and nitric acids from the dissolution of atmospheric NO<sub>x</sub> (the sum or NO and NO<sub>2</sub>), which cannot be distinguished in single impingers from actual HNO<sub>2</sub> or HNO<sub>3</sub> and which frequently get reported as false positives. In prior studies, we found that up to 1% of ambient NO<sub>x</sub> may get converted to HNO<sub>x</sub>.<sup>5</sup> At ambient concentration of several hundred ppb, that signal can be very substantial.

In addition to chemical limitations, impinger traps are also often subject to handling errors, inadvertent contamination and the potential for bacterial degradation, particularly if the liquid gets transferred between storage/transport and sampling vessels, a practice carried out by many labs (but not this lab). Water impingers have limited shelf life of a few weeks at the most, and are prone to bacterial contamination, particularly after being exposed to ambient air environments, and international shipping often causes customs delays based on the concern over the presence of liquid.

To address the disadvantages of impinger traps, we have developed liquid-free adsorbent traps specific to both acidic and alkaline gas phase contamination that are intended to replace impingers for standard AMC sampling. The liquid-free traps consist of porous substrates coated with either a bicarbonate (NaHCO<sub>3</sub>) or phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) solution, resulting in ionic capture of the AMC species and eliminating several problems associated with the dissolution based capture mechanism of liquid impingers.

We propose to adopt that methodology as a new industry standard to overcome widespread inaccuracy and problems in the reporting of volatile acidic and alkaline AMC and false positive artifacts for acids.

# Methodology

The basic principle of a dry sample trap is to capture acidic and basic compounds on a solid state medium that is coated with a base (NaHCO<sub>3</sub> to capture acids) or acid ( $H_3PO_4$  to capture bases) and subsequent extraction of that medium in deionized water for analysis in ion chromatographs. This adds one logistical step to the sample processing (dissolution of the captured ions in water) compared to water impingers, but has many advantages.

Each sample trap type was evaluated with common contaminants for the respective AMC class. Ammonia (NH<sub>3</sub>) was selected as the alkaline test gas, since it is a weak base that remains a potential concern and is usually the highest concentrated or only base in most semiconductor environments. Hydrogen fluoride (HF), acetic acid (CH<sub>3</sub>COOH) and sulfur dioxide (SO<sub>2</sub>) were selected as acidic test gases. Hydrogen fluoride as a moderately acidic inorganic species commonly found (often as an artifact from using PFA impinger materials and tubing), acetic acid as the weakest common organic acid and sulfur dioxide for the reasons previously mentioned to evaluate trap performance for all potential chemical behaviors.

## Capacity

Absolute trap capacity describes how much mass of an AMC species can be trapped before chemical reaction is exhausted and the compound may break through the trap without being retained. Capacity is a potential limitation of the sampling time at a given concentration or a limitation of the maximum concentration that can be sampled at a given sample time. Because it is ultimately a function of both time and concentration, we express capacity in ppb-hours (ppb-h), which then enables to calculate either time or maximum concentration by using the other known amount.

Initial testing was done by performing a titration of the extract as a proof of concept that some capacity for the target AMC did exist. Once feasibility was established, the trap was subjected to a known challenge at varying relative humidity and the capture efficiency (CE) was monitored over time and calculated as:

$$CE = \left(1 - \left(\frac{Upstream}{Downstream}\right)\right) * 100 (\%)$$
(3)

Trap capacity (in ppb-h) was then calculated by multiplying the total hours of testing (above a specified CE) by the challenge concentration. This is essentially the same process as determining the capacity or lifetime of a chemical filter. Sample traps are miniaturized chemical filters and vice versa.

The NH<sub>3</sub> challenge was created using a NIST<sup>®</sup> traceable permeation device (122 ng/min NH<sub>3</sub>  $\pm 4.99\%$  at 30°C) and diluted to a concentration

of approximately 10 ppb using purified clean-dry air (Entegris GateKeeper® purifier CE700KF04RR). The stability of the upstream concentration was verified with a Total Molecular Base monitor (Extraction Systems Inc. TMB) prior to placing the sample trap in the gas stream. The TMB was then used to verify the downstream concentration at a measurement interval of 2 min. until the CE had decreased below 90%. Sample flow through the traps during testing was approximately 0.7 L/min, pulled by the vacuum pump of the monitor.

The SO<sub>2</sub> upstream challenge was created using a NIST traceable permeation device (473 ng/min  $\pm 2.77\%$  at 40°C and diluted to a concentration of approximately 16 ppb using purified clean-dry air (GateKeeper purifier CE700KF04RR). The stability of the upstream concentration was verified with a Thermo Model 43i-TLE SO<sub>2</sub> monitor prior to placing the sample trap in the gas stream. The monitor was then used to verify the downstream concentration at a measurement interval of 5 min. until the CE had decreased below 90%. Sample flow during testing was approximately 0.5 L/min, pulled by the vacuum pump of the monitor.

To create a variable humidity challenge, the purified clean-dry air dilution gas was split and a controlled percentage was bubbled through ultrapure water (UPW), and the humidified portion was used for the test. The downstream moisture level was verified by an in-line hygrometer (Cole-Parmer<sup>®</sup> 03313-66).

### **Accuracy and Precision**

The precision and accuracy of solid state traps, standard liquid impingers (containing deionized water) and impingers spiked with 0.005M phosphoric acid were determined for comparison by taking multiple samples of a known  $NH_3$  challenge. Acidification of impinger was done to maximize ionization of  $NH_3$  for comparison to pure DI water devices.

The  $NH_3$  challenge was created using the same NIST traceable permeation device as above and output was diluted to a concentration of approximately 8 ppb using purified clean-dry air adjusted to 40% RH. The stability of the upstream concentration was verified with the TMB prior to and during sampling.

The SO<sub>2</sub> capability of solid state traps, standard liquid impingers and impingers spiked with 3%  $H_2O_2$  as an oxidative catalyst were determined for comparison by taking multiple samples of a known SO<sub>2</sub> challenge. The challenge was created using the same NIST traceable permeation device as above and diluted to a concentration of approximately 16 ppb using purified clean-dry air adjusted to 35% RH. The stability of the upstream concentration was verified with the Thermo Model 43i-TLE SO<sub>2</sub> monitor prior to and during sampling.

The HF testing of solid state traps and standard liquid impingers were compared by taking multiple samples of a known HF challenge, which was created using a NIST traceable permeation device (1971 ng/min  $\pm 15\%$  at 50°C) and diluted to a concentration of 248 ppb  $\pm 15\%$  using purified clean-dry air adjusted to 40% RH.

The CH<sub>3</sub>COOH testing was done with solid state traps and standard liquid impingers for comparison by taking multiple samples of a known CH<sub>3</sub>COOH challenge. The challenge was created using a NIST traceable permeation device (327 ng/min  $\pm 2\%$  at 35°C) and diluted to a concentration of 13.3 ppb  $\pm 2\%$  using purified clean-dry air adjusted to 25% RH.

The sample flow of all traps was controlled by pulling through a #14 orifice directly upstream of the trap with a vacuum pump (<15 Torr) resulting in a flow rate of 1.07 L/min.

The capture efficiency of the solid state trap also includes the extraction efficiency or recovery of the measured AMC from the media. A second series of testing was included as part of the initial testing to determine the extraction efficiency as a function of time and extraction conditions for NH<sub>3</sub>.

### **In-field Evaluation**

The performance of sample traps in controlled laboratory conditions is an indication of optimal performance. However, when sampling in the field the control of external conditions may not be ideal and the performance of the sample trap under less controlled conditions needed to be evaluated. For method validation, the liquid-free traps were deployed to the field for both semiconductor environments and internal support, in parallel with standard impingers for comparison.

### **Sample Analysis**

After sampling, the trap media were transferred to a 30 mL HDPE container and extracted with deionized water and sonication. The extraction solution was then analyzed using a Thermo Fisher<sup>®</sup> Dionex<sup>®</sup> ICS3000 ion chromatography system equipped with electrolytic suppression and conductivity detection. The anion channel of the system uses a potassium hydroxide eluent gradient with an AS19 250 × 2 mm analytical column and CRD200 carbonate removal device. The cation channel uses a methane sulfonic acid eluent gradient and CS19  $250 \times 2$  mm analytical column.

## Results

#### **Media Selection**

There is a number of solutions for the solid state material itself, such as packed beds of granulates or inert glass or plastic spheres (similar to organics traps and used in some existing, but proprietary solid state trap designs), coated hollow tubes (typically known as denuders) in single or multiple parallel implementation, etc. We selected a single, porous, solid-state device over the other designs for practicality, handling and preparation as well as for coating with the capturing chemical and efficiency in capturing the AMC of concern in a single pass at the flow rates needed for detecting low concentrations. The actual solid-state material for the base trap is a low-cost, one-use device that is discarded after extraction.

Likewise, we investigated a number of chemicals that could potentially be used for coating the solidstate media and concluded that the bicarbonate and phosphoric acid are the most suitable for a number of reasons associated with ion chromatography handling, degradation of columns, interference with detected compounds and speed of analysis as well as coating of the media.

To prepare the solid-state substrate for deployment, it is treated in the chemical coating and then dried in a purified clean-dry air (XCDA<sup>®</sup>) purged oven. The coated substrate is then stored in chemically clean containers and inserted into a trap housing for sample collection. To extract the captured AMC from the solid state media, that substrate is immersed in deionized water and sonicated for solvent penetration into the pore structure of the substrate. The liquid is then directly used for IC analysis.

The sample trap housing is a proprietary design of Entegris, Inc. and is made from PEEK material (Figure 1), which is known to be chemically much cleaner than PFA materials, hence, more suitable for the application. It is a three piece design to ensure complete sealing and secure retention of the substrate, optimized internal flow channeling and easy preparation and handling. The tube ends have a 6.4 mm OD and can be capped with standard tube fittings for transport and storage. Length of the trap has been chosen to match that of commercially available organic traps made from stainless steel or glass. Internal design is optimized for flow, handling and minimized contamination.



Figure 1. Liquid-free sample trap.

### **Ammonia Capacity**

With diffusion and dissolution of the sample gas to a liquid eliminated, ammonia capture is based on a simple acid/base reaction and capacity in solidstate traps is primarily determined by the number of active sites for ionic bonding, i.e., the amount of acid used to coat the porous material, where the  $NH_3$  forms a combination of the mono-ammonium and diammonium salts on the surface of the substrate (Equation 4). The tri-ammonium salt is unstable.

$$NH_{3(a)} + H_3PO_4 \leftrightarrow (NH_4)H_2PO_4 + (NH_4)_2HPO_4$$
<sup>(4)</sup>



Figure 2. NH<sub>3</sub> capacity as a function of capture efficiency at 0% and 40% relative humidity.

Trap capacity for  $NH_3$  was determined to be 200 ppb-h at 0% relative humidity. For typical 0% RH applications, such as supply and process gas lines, trap capacity is more than one hundred times what is required for typical tool OEM specifications and ITRS recommendations for allowable AMC concentrations. Entegris Analytical Services typically finds less than 1 ppb of AMC in CDA and  $N_2$  lines, but process gases may contain higher levels.

The addition of moisture at 40% relative humidity increased trap capacity to 350 ppb-h. The increase in capacity by adding moisture results from the ability of water to lower the free energy of formation for the reaction and as a secondary consequence may provide a means for ion mobility within the media. Capacity for  $NH_3$  was determined at the 99% capture efficiency level, i.e. less than 1% break-through.

Given modern supply gas concentrations of less than 1 ppb and typical cleanroom concentrations of less than 10 ppb of  $NH_3$ , the measured capacity translates to a quantitative capture of  $NH_3$  for 20-35 hours of sampling at 3.5 L/min, much in excess of what is required for ppq-level analysis. This allows for the sampling of AMC within one work shift and without the need for sampling 12–72 hour sampling typically done by most laboratories.

As mentioned, alkaline capacity is a function of the number of acidic active sites for ionic bonding (in this case the first and second protons of  $H_3PO_4$ ) and can be predicted for other compounds with similar chemical behavior, like amines (Equation 5).

$$Capacity (Mol Eq.) = \left(\frac{Number of Active Sites}{|Net Ionic Charge|}\right)$$

This should provide a rough estimate for amine capacity. However,  $pK_b$  of the alkaline species and steric hindrance due to larger molecule size must be considered. As an approximation, we estimate the same capacity for amines or any combination of ammonia and amines collected. Verification for specific amines is still outstanding research to be done.

### **Sulfur Dioxide Capacity**

Trap capacity for  $SO_2$  was determined to be only 5 ppb-h at 0% relative humidity and 90% capture efficiency. The addition of moisture at 22% relative humidity increased trap capacity to 60 ppb-h for 90% CE and at 35% relative humidity trap capacity increased to more than 400 ppb-h for 99% (Figure 3).

For typical dry applications like process gas lines, trap capacity is sufficient to meet requirements for common tool OEM specifications and ITRS recommendations (these are typically in the ppt range). Entegris Analytical Services does not find  $SO_2$  to be elevated above 1 ppb even in fairly outdated semiconductor environments, hence, the capacity is considered sufficient and not a limitation for sample time.

The proposed mechanisms to describe the capture of  $SO_2$  on the dry media involves an initial reaction of  $SO_2$  with excess water to produce the intermediate bisulfite ion (Equation 6), the primary reaction product in a pH range of 2 to 8.

$$SO_{2(g)} + H_2 O \leftrightarrow HSO_3^- + H^+$$
 (6)

The resulting bisulfate ion is then free to react with the NaHCO<sub>3</sub> on the surface of the media to form the sodium sulfate salt (Equation 7).

### $HSO_3^- + 2NaHCO_{3(s)} \leftrightarrow Na_2SO_{4(s)} + H_2O + 2CO_2 + H^+$ (7)

Even at 0% RH, there is some capacity for  $SO_2$  due to direct ionic bonding and the presence of crystalline water bound to the NaHCO<sub>3</sub> as the decahydrate salt (NaHCO<sub>3</sub> · 10 H<sub>2</sub>O). The resulting sodium sulfate salt completely dissociates in the extraction solution and was quantified as  $SO_4^{2^-}$  using established ion chromatography methods. It is expected that acidic species, that directly interact with NaHCO<sub>3</sub> to form immediate ionic bonds and do not depend heavily on the presence of moisture, will have significantly improved capacity at lower relative humidity.

(5)



Figure 3.  $SO_2$  capacity as a function of capture efficiency at 0%, 22% and 36% relative humidity.



Figure 4. Formation of the primary reaction products of  $SO_2$  and water as a function of  $pH_4$ .

## **Ammonia Accuracy and Precision**

The standard water impinger had an average capture efficiency of 88% for NH<sub>3</sub> at 40% RH in relation to the calculated and monitor-verified challenge concentration of 8.0 ppb (Table 1, Figure 5). The decreased capture efficiency likely results from the partial dissociation of ammonia in solution (Equation 2) and/or incomplete diffusion from the air bubbles into the water column. A decrease of pH of the solution results from either a decreasing ammonia concentration or the presence of an acidic species and has a direct effect on the ionization of ammonia, shifting the equilibrium increasingly towards ammonium formation. This results in the characteristic non-linear calibration curve for ammonia and amines in ion chromatography analysis.



Figure 5. NH<sub>3</sub> capture efficiency data for three trap types.

This assumption is corroborated by the test results from the pH adjusted impinger, which was spiked with 0.005M phosphoric acid, and which had an average capture efficiency of 95.1% for NH<sub>3</sub> at 40% RH, the remaining 5% likely attributed to inadequate capture efficiency. The increased concentration of phosphate counter-ions in the pH adjusted solution facilitates better conversion of the dissolved ammonia to the fully dissociated ammonium ion. Based on this, it can be predicted that the NH<sub>3</sub> capture efficiency of the impinger will continue to decrease with increasing ammonia when sampling with water impingers. That is particularly important for semiconductor fabs with older technology nodes, where concentrations above 10 ppb are found, or non-lithobay process areas with increased ammonia levels.

The liquid free trap had an average capture efficiency of 99.8% for  $NH_3$  at 40% RH with the lowest trap-to-trap variability (standard deviation of 7.6%). The chemical mechanism of the liquid-free trap media is based on the formation of ionic bonds (Equation 4) and is not subject to the limitations of dissolution based capture. Instead, the only limitations result from its capacity, which was shown to be sufficient.

# TABLE 1. AVERAGE $\rm NH_3$ CAPTURE RESULTS FOR VARIOUS TRAP TYPES.

Sample Trap	Average Measured NH <sub>3</sub> Concentration (ppb)	Relative Standard Deviation	Capture Efficiency
Standard imping	jer 7.02	8.3%	87.8%
pH-adjusted impinger	7.61	10.3%	95.1%
Entegris liquid-free trap	7.99	7.6%	99.8%
TMB monitor	8.00	2.3%	100%

#### **Sulfur Dioxide Performance**

Standard water impingers had an average capture efficiency of 91% for SO<sub>2</sub> at 36% RH for a challenge concentration of 16.8 ppb (Table 2). However, this average is skewed heavily by the presence of one outlying data point (manifested in a high standard deviation), which, if excluded, would reduce the capture efficiency to 86%. The low capture efficiency results from the formation of multiple intermediate species in solution and the decreased ionization with increasing concentration of those intermediate species. This would indicate that the capture efficiency is inversely proportional to concentration and will decrease as the total SO<sub>2</sub> concentration increases. The formation of sulfite and sulfate anions will also act to acidify the impinger shifting the equilibrium increasingly towards the gas phase as the pH of the solution continues to decrease.

# TABLE 2. SO<sub>2</sub> CAPABILITY RESULTS FOR DIFFERENT TRAP TYPES.

Sample Trap	Average Measured SO <sub>2</sub> Concentration (ppb)	Relative Standard Deviation	Capture Efficiency
Standard imping	jer 15.3	16.7%	91.1%
Impinger with 1% H <sub>2</sub> O <sub>2</sub>	16.7	5.1%	99.4%
Liquid-free trap	16.3	4.9%	96.5%
SO <sub>2</sub> monitor	16.8	3.7%	100%

Water impingers spiked with 1% H<sub>2</sub>O<sub>2</sub> performed substantially better with an average and more consistent capture efficiency of 99.4%. The improved performance is a result of the peroxide fully oxidizing both undissociated SO<sub>2</sub> and partially oxidized species in solution, to facilitate complete conversion to the sulfate ion (Equation 8).

### $SO_2 + H_2O \leftrightarrow 2H^+ + SO_4^{2-}$

The liquid-free trap had an average capture efficiency of 96.5% for SO<sub>2</sub> at 36% RH with the smallest amount of trap-to-trap variability of 4.9% relative standard deviation. Although the 1% H<sub>2</sub>O<sub>2</sub> impinger had higher capture efficiency, the added peroxide is an additional process step and can be detrimental to the ion exchange resin used in the analytical columns of the IC system, posing a disadvantage for routine analysis. In addition, the presence of peroxide can also oxidize atmospheric gases, including NO and CO<sub>2</sub>, to create artifacts and altering the impinger chemistry.<sup>5</sup>

$$2NO + 3H_2O_2 \to 2H^+ + 2NO_3^- + 2H_2O \tag{9}$$

$$CO_2 + 2H_2O_2 \rightarrow H^+ + HCO_4^- + 2H_2O$$
 (10)

These reactions are minimized by the liquid-free trap due to the absence of a source for further oxidation.

### **Performance for HF**

For the capture of HF, the water impinger had a capture efficiency of 98.2% and the liquid trap 100.2% for air sampled at 40% RH (Table 3). The liquid-free trap had a slightly better precision than the impinger with a 3.5% standard deviation. The high capture efficiency of the impinger is expected since HF is fully miscible with water in all proportions and interacts through hydrogen bonding, unlike other hydrogen halides. The primary mechanism of capture on the liquid-free trap is purely an ionic reaction (Equation 11).

# TABLE 3. HF PERFORMANCE RESULTS FOR STANDARD IMPINGERS AND LIQUID-FREE TRAPS.

Sample Trap	Average Measured HF Concentration (ppb)	Relative Standard Deviation	Capture Efficiency
Standard impir	iger 244	5.5%	98.2%
Entegris liquid-free trap	249	3.5%	100.2%
Permeation device (calculated)	248	15.0%	N/A

## $NaHCO_{3(s)} + HF_{(g)} \rightarrow NaF_{(s)} + CO_{2(g)} + H_2O_{(l)}$ (11)

These results somewhat contradict previously reported results for both impingers and solid state trap technology, which indicated significantly lower capture efficiencies for both.<sup>6</sup> This may be a result of the moisture content of the sample gas, as this is the only clearly indicated difference between the tests, with this test being performed at 40% RH and is supported by the behavior of HF at low concentrations in the presence of water. It has been shown that the primary solute species is the H-H bonded ion pair  $[H_3O+\cdot F^-]$  which facilitates dissociation and increases HF solubility.

## **Acetic Acid Performance**

For the capture of acetic acid, the standard impingers had an average capture efficiency of 98.2% at 36% RH and a 4.1% relative standard deviation (Table 4). The liquid-free trap had about the same capture efficiency of 96.1% and slightly higher variability when compared to the standard impinger.

(8)

There is no reason to expect a decreased performance specifically for  $CH_3COOH$  since it is captured primarily through ionic bonding (Equation 12) but the fairly high pK<sub>a</sub> (weak acidity) of acetic acid may contribute to the capture efficiency being less than 100%. Nevertheless, we consider this to be a sufficient result.

 $NaHCO_3 + CH_3COOH \leftrightarrow NaCH_3COO^- + CO_2 + H_2O$  (12)

TABLE 4. ACETIC ACID PERFORMANCE RESULTS FOR STANDARD IMPINGERS AND ENTEGRIS LIQUID-FREE TRAPS.

Sample Trap	Average Measured Acetic Acid Concentration (ppb)	Relative Standard Deviation	Capture Efficiency
Standard imping	ger 13.1	4.1%	98.2%
Entegris liquid-free trap	12.8	5.7%	96.1%
Permeation device (calculated)	13.3	2.0%	N/A

### **In-field Evaluation**

The performance of sample traps in controlled laboratory conditions is an indication of optimal performance. However, when sampling in the field, the external conditions may not be ideal and involves sample operator handling, shipping, etc. The performance of the liquid-free trap under less controlled conditions was evaluated for  $NH_3$  and is still in progress for acids. The liquid-free traps were deployed to the field for both external customers and internal support sampled in parallel with standard impinger traps resulting in an average 10.2% difference (impinger being generally lower) between the traps in more than 100 real-world data points with a concentration range spanning five orders of magnitude, between <10 ppt and 0.1 ppm.



Figure 6. Correlation plot of the captured NH<sub>3</sub> concentration for Entegris liquid-free traps and standard impingers.

The correlation of the two trap types is 0.98, hence, the data sets for the two traps are statistically not significantly different. An ANOVA analysis of the data produced a  $M_{\text{Measured}} = 0.0094$ ,  $F_{\text{Crit}} = 3.9$  and P-value = 0.92, also indicating a confirmation of the null hypothesis, that data are not statistically different. Nevertheless, the 7.6% difference indicated by the slope of the line likely reflects the approximately 10% increase in measured capture efficiency of the liquid-free trap compared to the standard impinger (Table 1).

## Shelf Life

Shelf life has been studied with this type of solid state trap by preparing a number of coated substrates and then storing these over a period of three months, analyzing redundant samples every week to observe potential trends. Our findings suggest that solid-state traps of this type can be stored in chemically clean containers and refrigerated for up to three months without impact above the detection level. A plot of the data indicates no increasing trend in the  $NH_3$  concentration during storage. This shelf life matches that of organic AMC traps and enables quicker dispatch and onsite storage for immediate deployment.



Figure 7. Trend line plot of ammonia as a function of storage time.

### **Disadvantages of Liquid-free Sample Traps**

When considering both trap types, the liquid-free trap does have some disadvantages compared to standard wet impingers. Sample preparation is more complex than simply filling an impinger with deionized water and involves substrate coating, drying and assembly steps. Likewise, sample extraction after sampling is more involved and requires the same considerations as the preparation. These additional steps increase analytical time.

Also, because we were unable to find any commercially available solutions that are clean enough, the liquid-free trap is a proprietary design, but the details will be shared to implement this as a new industry-wide standard for acidic and alkaline AMC sampling. Overall, we believe that this new solution is a substantial improvement over existing sampling techniques.

# Conclusions

To address the disadvantages of water-filled impinger traps, we developed liquid-free adsorbent traps specific to both acidic and alkaline gas phase contamination to replace water impingers for standard AMC analysis.

Capacity results for the liquid-free base trap for ammonia (NH<sub>3</sub>) yielded more than 200 ppb-h at 100% capture efficiency without any moisture (simulating sampling of CDA or N<sub>2</sub>) and 350 ppb-h at 40% RH. Capacity results for sulfur dioxide (SO<sub>2</sub>) were highly dependent on the moisture content of the sampled gas. At 0% relative humidity, capacity yielded only 5 ppb-h at 90% capture efficiency, but increased exponentially to more than 1200 ppb-h at 40% relative humidity. HF and acetic acid performance was satisfactory and matches that of impingers.

Given modern supply gas concentrations of less than 1 ppb and cleanroom concentrations of less than 10 ppb, both acid and base capacity significantly exceeds what is found in environments and required for low-level analysis. Trap performance allows for the sampling and analysis of ppq-level AMC within one work shift and without the need for 12-72 hour sampling typically applied by most labs in the industry.

Performance testing indicates that the liquid-free trap provides both more precise and more accurate results for  $NH_3$ ,  $SO_2$  and HF in comparison to the standard impinger in lab testing, with a relative standard deviation not exceeding 8% and capture efficiency greater than 95% for all three compounds. Acetic acid was the only compound that shows slightly decreased performance but still maintained a precision and accuracy fully suitable for the application.

Deployment to the field at both external customer sites and internal support applications in parallel with standard impinger traps resulted in up to 10% difference between the trap types, providing the necessary evidence that liquid-free traps are suitable for impinger replacement.

We believe that this new solution is a substantial improvement over existing sample techniques based on easier in-field handling, reduced contamination through handling, extended shelf life and eliminated concerns over shipping liquids.

We recommend to establish this new methodology as a new industry standard. Please contact the authors for details.

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