VIRTUAL NO$_x^-$ — A MEASUREMENT ARTIFACT IN WET IMPINGER AIR SAMPLING

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Introduction

This application note describes a measurement artifact, which we named "virtual NO$_x^-$," its impact on semiconductor cleanroom operation and solutions to deal with it. We also define terminology and briefly describe the chemistry of the involved compounds.

Background

A measurement artifact has been discovered that produces positive nitrate and nitrite responses when using water-based impingers in air sampling to determine airborne molecular contamination (AMC) of acidic character (namely, dissolved nitrous and nitric acid) in semiconductor cleanroom environments (although the effect applies to all environments). Small amounts of nitrite and nitrate are occasionally observed downstream of filters, which are operated to remove acidic compounds. Concerns over the removal efficiency of such chemical filters for these compounds and over the accuracy of sampling techniques triggered this investigation.

Terminology and Chemistry

The terminology in this matter can be rather confusing, as similar definitions are commonly used for different, but similar, chemical species. The following listing shows the correct terminology and two new terms introduced here (ionic NO$_x^-$, virtual NO$_x^-$).

The gases NO, NO$_2$, HNO$_2$ and HNO$_3$ are commonly found in ambient air and stem mostly from combustion processes (car and smoke stack emissions, field burning, heating systems, etc.) and their following atmospheric reactions. These compounds also participate heavily in atmospheric photochemistry and some are part of what is commonly known as SMOG formation.

NO = Nitric oxide (or nitrogen oxide) (gas)

NO_2 = Nitrogen dioxide (gas)

NO_x = $NO + NO_2$ (sum of both gases)

NO_y = $NO_x + HNO_2 + HNO_3 + N_2O + N_2O_3 + N_2O_4 ...$ (gas - phase, inorganic nitrogen oxides)
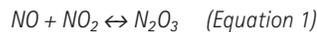
HNO_2 = Nitrous acid (gas)

NO_2^- = Nitrite, the salt of nitrous acid (dissolved)

HNO_3 = Nitric acid (gas)

NO_3^- = Nitrate, the salt of nitric acid (dissolved)

NO_x^- = "Ionic NO$_x^-$" – the sum of dissolved nitrite and nitrate

To complicate matters, some of these gas-phase compounds can also form dimers such as the equilibrium of NO and NO$_2$, for which the left side (monomer) in Equations 1 and 2 is favored at higher (room) temperatures:

$$NO + NO_2 \leftrightarrow N_2O_3 \quad \textit{(Equation 1)}$$

$$2NO_2 \leftrightarrow N_2O_4 \quad \textit{(Equation 2)}$$

Gas-phase NO and NO$_2$, even in very high concentrations, are not known to cause any problems in semiconductor cleanroom environments. The compounds of acidic character, most prominently nitrous acid (HNO$_2$) and nitric acid (HNO$_3$), can cause corrosion and are of most concern to the semiconductor community. We would like to point out, however, that detrimental effects of these acids at low ppb concentration levels have not yet been observed on cleanroom equipment. Nitric and nitrous acid are measured in their dissolved forms nitrite (NO$_2^-$) and nitrate (NO$_3^-$), both of which can potentially also form salt residues when dried (e.g., in conjunction with sodium or potassium). These ionic forms are typically reported in analytical data reports, as required by optics manufacturers.

Nitrous oxide, N$_2$O, is another common nitrogen oxide ("laughing gas", an anesthetic), but behaves much more conservatively in air. It is about as soluble as NO$_2$, but much less reactive. It is found at 320 ppb in the atmosphere, has a lifetime of about 150 years and we do not consider this gas here.

Ambient air NO is commonly found everywhere at concentrations of 20 ppb (parts-per-billion, 10^{-9} mols per mol) to several ppm (parts-per-million,

10^{-6} mols per mol), whereas NO$_2$ concentrations are more regulated for health and environmental reasons and are consequently lower. Both gases are considered toxic at ppm-level (with NO$_2$ being a reactive oxidant and a corrosive precursor).

Cleanroom concentrations of NO$_x$ have been observed with Extraction-brand TMB monitors to vary between 20 ppb and more than 700 ppb in some cleanrooms where ambient air intakes are impacted by field stubble burning, nearby busy highways or large parking lots or where fossil fuel heating systems are used. Concentrations vary naturally and largely from one day to the next and even within a day (for example, rush hour traffic on highways, employee shift changes, heating system cycles, etc.).

In addition, the partitioning between NO and NO$_2$ in the Fab environment can change considerably. This was demonstrated with some of the data of a TMB-193 system (Application note APN000010). To reiterate, NO slowly oxidizes to NO$_2$ in air over time, thus NO reflects air that is close to the source of nitrogen oxides and NO$_2$ reflects air that has been aged (oxidized). An outside world example would be the plume of an unfiltered power plant, which will exhibit very high NO and very low NO$_2$ concentrations at the stack, but will show gradual conversion from NO to NO$_2$ further downwind of the plant.
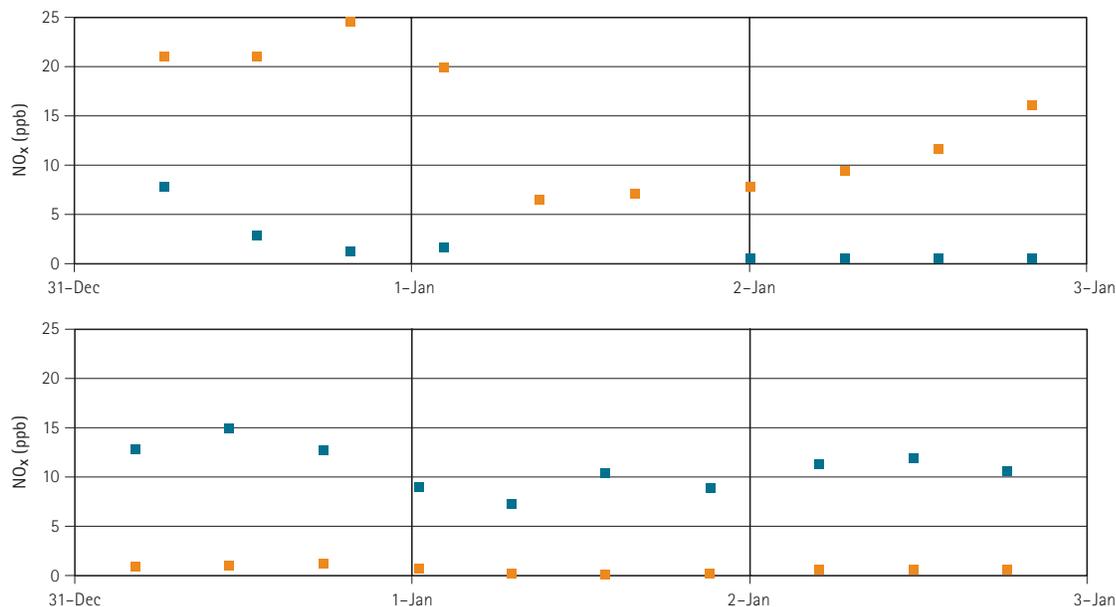

Figure 1. Levels of gas-phase NO (blue) and NO$_2$ (orange) in cleanroom ambient (top) and chemically filtered air (bottom). Note the conversion of NO$_2$ by chemical filters.

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In contrast to NO, NO$_2$ can be removed or converted by chemical filters. Activated carbon, as it is used in many cleanroom and equipment filters, can remove substantial amounts of NO$_2$. However, we also observed that chemical filters (which may contain treated carbon and various ion exchange media) can convert the NO$_2$ found in cleanroom ambient air back to NO.

Figure 1 shows a comparison of cleanroom ambient and exposure tool filtered air (taken from Entegris application note APN000010). Note the changed levels of NO$_2$ between the aged ambient air (5−25 ppb) and the filtered exposure tool air (0−2 ppb). This effect is important to understand some of the results found in impinger measurements discussed below.

Description of the Artifact

Measurement of nitrous acid, nitric acid, nitrite and nitrate are commonly done by using wet impingers (Figure 2), where air is bubbled through water to force water-soluble compounds, such as acids and bases, to dissolve in the water. Running such a setup for several hours accumulates and concentrates large amounts of the compounds of interest to attain low detection limits. The water is then analyzed for cations (acids) and anions (bases) on ion chromatography (IC) equipment and the air concentration is calculated by scaling the solution concentration to the entire volume of air drawn through the impinger.
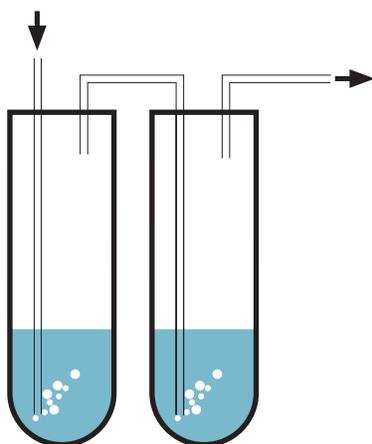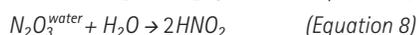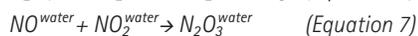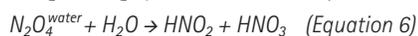

Figure 2. Concept of wet impingers configured for serial operation.

Soluble acidic compounds of interest here are HNO$_2$, HNO$_3$, as well as small particles containing nitrates and nitrites (NO$_2^-$ and NO$_3^-$). All of these compounds typically appear in cleanroom air at low (sub-) ppb levels; typical quantitation limit for reporting is 0.1 ppb.

Even though dissolution of NO and NO$_2$ on thin water films on cleanroom surfaces according to Equations 3 and 4 could be part of the source for the acidic compounds of interest, the resulting amounts of nitrous and nitric acid would be small compared to their gas-phase counterparts from combustion sources.

$$NO^{gas} \rightarrow NO^{water} \qquad \text{(Equation 3)}$$
$$NO_2^{gas} \rightarrow NO_2^{water} \qquad \text{(Equation 4)}$$
$$2NO_2^{water} \rightarrow N_2O_4^{water} \qquad \text{(Equation 5)}$$
$$N_2O_4^{water} + H_2O \rightarrow HNO_2 + HNO_3 \qquad \text{(Equation 6)}$$
$$NO^{water} + NO_2^{water} \rightarrow N_2O_3^{water} \qquad \text{(Equation 7)}$$
$$N_2O_3^{water} + H_2O \rightarrow 2HNO_2 \qquad \text{(Equation 8)}$$

On the other hand, impingers contain a large amount of liquid water and physical dissolution of gases can take place immediately, only governed by their solubility in water at the given temperature and the contact time with water. It was found that the dissolution of gas-phase NO and NO$_2$ in the impinger water can form measurable amounts of nitrate and nitrite. Dissolution of NO$_x$ in water, of course, is dependent also on its gas-phase, ambient air concentration, as described in Henry's law.

Solubility of NO and NO$_2$ in water is low, Henry's law coefficients are 1.9×10^{-3} and 2.6×10^{-2} mol l^{-1} atm^{-1}, respectively. However, reactions along the lines of Equations 5−8 continuously remove dissolved NO and NO$_2$ from the aqueous phase, allowing far more NO and NO$_2$ to be dissolved than what is expected based on Henry's law. Indeed, we find around 2000 times more nitrite and nitrate than we would expect from NO and NO$_2$ solubility alone.

Test Data

To study the formation of ionic NO$_x^-$ from dissolution of gas-phase NO and NO$_2$, we sampled the outlet of a dynamic dilution calibration system that provided a steady gas stream of a programmed mix of NO and NO$_2$. We varied the concentration mix both ways between zero and ~ 300 ppb each to evaluate the formation of ionic NO$_x^-$.

The amount of ionic NO$_x^-$ varied substantially, but was expectedly a low percentage of the input gas-phase NO$_x$. Equations 5 and 7 show that NO$_2$ is required in order to form ionic NO$_x^-$, regardless of the amount of gas-phase NO. The results found from this test confirm that prediction. Ionic NO$_x^-$ was mostly zero and only small amounts of nitrate were found at high gas-phase NO (Figure 3).
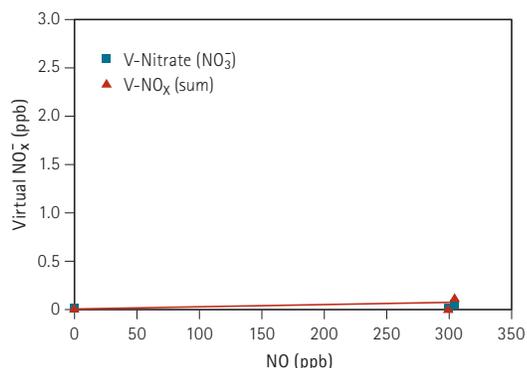

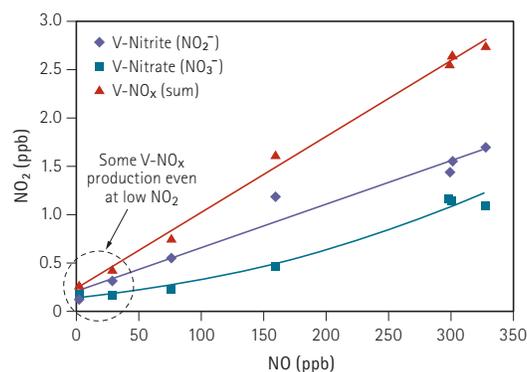*Figure 3. Virtual NO$_x^-$ formation as a function of gas-phase NO concentration.*

Figure 4. Virtual NO$_x^-$ formation as a function of the gas-phase NO$_2$ concentration. A clear, near-linear relationship exists.

However, a good correlation was found when varying gas-phase NO$_2$ concentrations. Higher NO$_2$ produced more ionic NO$_x^-$ (Figure 4). It is unclear if the correlation of NO$_3^-$ formation is linear or consistently curved (as shown), but it appears that some ionic NO$_x^-$ is formed even at low concentrations of NO$_2$. A few ppb of NO$_2$ in the air seem to be enough to form measurable amounts of nitrite and nitrate. Note that all low NO$_2$ measurements have high NO in the background (Table 1).

The sum of nitrite and nitrate found in wet impingers was about 1% of the gas-phase NO$_2$ concentration and absolute values were between zero and 1.8 ppb of nitrite (Table 1); nitrate was found up to 1 ppb. The data indicate that some ionic NO$_x^-$ formation occurs even at low NO$_2$ present in the gas stream.

TABLE 1. GAS–PHASE CONCENTRATIONS FROM A DYNAMIC DILUTION CALIBRATOR FOR THIS TEST SERIES. TEST #8 WAS DONE IN 2004.

Test Number	NO (ppb)	NO$_2$ (ppb)	Ionic NO$_2^-$ (ppb)	Ionic NO$_3^-$ (ppb)	Ionic NO$_x^-$ sum (ppb)	Ionic NO$_x^-$ sum (% of NO$_2$)
1	296	159	1.17	0.44	1.61	1.0
2	297	75	0.54	0.19	0.73	1.0
3	305	28	0.28	0.12	0.41	1.4
4	304	0	0.08	0.15	0.23	NAN
5	144	329	1.70	1.08	2.78	0.8
6	64	302	1.55	1.14	2.68	0.9
7	26	300	1.44	1.15	2.59	0.9
8	300	0	0.0	0.0	0.0	NAN

The chosen gas-phase concentrations for NO and NO_2 are very common for cleanroom environments. Even ambient air concentrations of only 20 ppb NO_x (the lower end of what should be expected) still resulted in 0.2 ppb of ionic NO_x^- in the impingers.

Due to the artificial nature of this effect, we named the dissolved amount of gas-phase NO_x^- "virtual NO_x^-" (note the minus sign to distinguish it from the term "NO_x" used for the sum of gas-phase NO and NO_2).

How Does This Apply to Chemical Filters?

Given the above, virtual NO_x^- formation can also be found downstream of chemical filters. Whereas gas-phase NO_2 can be both adsorbed and converted to NO by activated carbon filters (Figure 1), gas-phase NO is typically not withheld at all, hence the full amount of ambient NO is also found inside exposure tools and tracks. In addition, aged filters may lose their ability to retain or convert NO_2, hence, some of the reactions described in Equation 7 and 8 can commence involving residual NO_2. Table 1 and Figure 4 confirm that some virtual NO_x^- is formed even at near-zero NO_2 concentrations.

This situation is a challenge when evaluating filter removal efficiency for acidic gases. The user is cautioned to carefully interpret reported data for nitrate and nitrite, as they may not represent actual gas-phase nitric and nitrous acid. In addition, data over time cannot necessarily be compared, because of the high variability of ambient, gas-phase NO_x in cleanrooms. As mentioned, cleanroom NO_x may vary between 20 and more than 1000 ppb during a single day as well as from day to day, hence formation of virtual NO_x^- will vary accordingly (possibly also that of actual nitric and nitrous acids).

Solutions

There are several solutions to address the artifact of virtual NO_x^- formation.

1. The reporting of nitrate and nitrite (nitric and nitrous acids) could be ignored. Neither compound has been found in large quantities in the cleanrooms and, to-date, no publication is known that describes any impact of the two acids at sub-ppb levels on cleanroom equipment. Plus, virtual NO_x^- does not degrade a filter's acid capacity, because it is formed in the impinger water after the filter.

2. Virtual NO_x^- can be quantified by using two impingers in series, as shown in Figure 2. The amount of gas-phase NO_x that is captured by impingers is on the order of 1% of the gas-phase NO_x concentration, thus both serial impingers would capture about the same amount of virtual NO_x^-, because the amount of gas-phase NO_x is not appreciably diminished by the first impinger. Real, gas-phase nitric and nitrous acids, however, are very soluble, hence would be quantitatively captured in the first impinger and would not be found in the second impinger. A simple subtraction of the ionic NO_x^- found in impinger #2 from that of impinger #1 will yield the actual amounts of cleanroom ionic species. The drawback is that in-field assembly of serial impingers is prone to contamination, and work load for analysis doubles.

3. The use of a dry capturing media instead of wet impingers will strongly diminish the formation of virtual NO_x^-, as such a device would not use liquid water. The use of a water-free, dry sample trap greatly reduces the formation of Virtual NO_x^-. Entegris developed a dry acid and base trapping technique published elsewhere.[1]

[1] Tyler M. Moulton, Emily C. Zaloga, Katherine M. Chase, Jürgen M. Lobert. Analytical Sampling Method for the Measurement of Trace Level Acidic and Basic AMC using Water-Free Sample Traps in: Metrology, Inspection, and Process Control for Microlithography XXVIII edited by Jason P. Cain, Proceedings of SPIE Volume 9050 (SPIE, Bellingham, WA), 905081, 2014. ISBN: 9780819499738.

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