



## MEASUREMENT OF LOW MOLECULAR WEIGHT SILICON AMC TO PROTECT UV OPTICS IN PHOTOLITHOGRAPHY ENVIRONMENTS

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### Abstract

A new analytical method for semiconductor-specific applications is presented for the accurate measurement of low molecular weight, silicon-containing, organic compounds TMS, HMDSO and D3.

Low molecular weight/low boiling point silicon-containing compounds are not captured for extended periods of time by traditional chemical filters but have the same potential to degrade exposure tool optical surfaces as their high molecular weight counterparts. Likewise, we show that capturing these compounds on sample traps that are commonly used for organic AMC analysis does not work for various reasons.

Using the analytical method described here, TMS, HMDSO and D3 can be measured artifact-free, with at least a 50:1 peak-to-noise ratio at the method detection limit, determined through the Hubaux-Vos method and satisfying a conservative 99% statistical confidence. Method detection limits for the compounds are 1–6 ppt in air. We present calibration curve, capacity, capture efficiency, break-through and repeatability data to demonstrate robustness of method.

Seventy-one real-world samples from 26 projects taken in several fab environments show that TMS is found in concentrations 100 times higher than those of HMDSO and D3. All compounds are found in all environments in concentrations ranging from 0–12 ppm, but most concentrations were below 50 ppb. All compounds are noticeably higher in litho-bays than in sub-fabs and we found all three compounds inside of two exposure tools, suggesting cleanroom and/or tool-internal contamination sources.

### Introduction

Silicon containing hydrocarbons are a class of airborne molecular contamination (AMC) causing persistent degradation of UV exposure tool optical surfaces.<sup>1,2,3</sup> Silicon compounds are efficiently split into components by 193 nm UV light, commonly

used in photolithography applications. The resulting reactive silicon atoms can recombine with oxygen to create a layer of amorphous silicon dioxide on optical surfaces, which can be difficult to remove and may require lens exchange and polishing, potentially destroying optical coatings and creating substantial tool downtime and cost.

Many of these chemicals, such as cyclic siloxanes with three silicon atoms or more (high molecular weight or HMW) can be captured effectively by suitably designed chemical filters and can be conveniently measured by common grab sample methods employing sample traps such as Tenax® TA or Tenax GR. Exposure tool manufacturers (OEMs) have mandated measurement of these compounds starting with 193 nm lithography to protect optical systems worth millions of dollars.

More recently,<sup>4</sup> focus has shifted to silicon containing compounds of low molecular weight (LMW, less than six carbon atoms)/low boiling point, as these chemicals are not captured for extended periods of time by traditional chemical filters and they break through the filter system long before expiration of their predicted lifetime for high molecular weight (HMW, six or more carbon atoms) AMC. However, the potential of LMW silicon compounds to degrade optical surfaces is as high as that of HMW Si compounds. Fab-wide characterization, prediction (and control) of these chemicals is essential to protect equipment, reduce the maintenance time for and extend the life of optical surfaces.

### Compounds of Interest

Some high molecular weight Si compounds that are captured by chemical filters are also believed to be captured by common sampling methods because they fall within the range of exposure tool OEM requirements (about six carbon atoms and higher). Tests in our lab clearly show that two of these HMW compounds are not quantitatively captured by Tenax TA or GR sampling traps and

require a different analytical approach: hexamethyldisiloxane (HMDSO) and hexamethylcyclotrisiloxane (D3). Because of these effects, we consider these two compounds to belong to the LMW range. In addition to its low capture efficiency, D3 is also produced as an artifact when using silicon-containing separation columns.

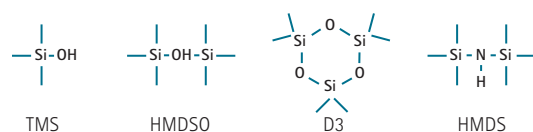


Figure 1. Molecular structure of the compounds of interest.

TMS, the only low molecular weight silicon-containing compound investigated here, is found in litho-bays, the most common source being the moisture-induced breakdown of hexamethyldisilazane (HMDS), a common process chemical. However, ambient (atmospheric) air can also contain substantial amounts of TMS, particularly in the vicinity of landfills. Even though new, more effective filtration solutions are becoming available,<sup>7</sup> TMS is not filtered out as efficiently as HMW compounds on existing, chemical tool or HVAC filters. For the same reason, TMS cannot be collected quantitatively with Tenax TA or GR sample traps due to its low retention.

To exacerbate the analytical challenge, TMS also produces erratic results when using carbon-containing sample traps and thermal desorption (TD) analysis, for which we found that TMS recovery and results are not reproducible. Multiple uses of the same traps over time (Figure 2) were found to produce diminishing concentrations of TMS, whereas results are more consistent for Tenax TA,

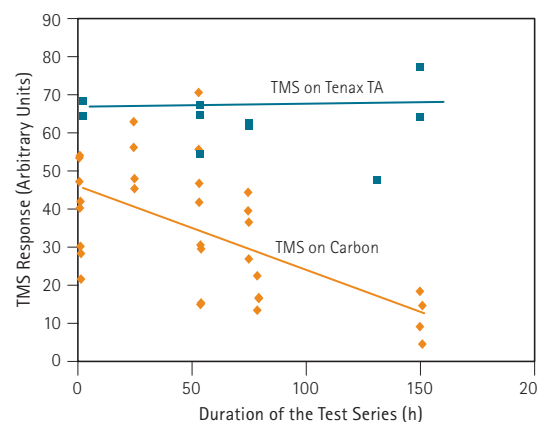


Figure 2. TMS recovery from thermal desorption of Tenax TA and carbon traps.

suggesting that quantitative TMS recovery is not possible from carbon-containing traps through thermal desorption. This effect was also observed on Tenax GR traps, which contain about 30% carbon. We used short sampling times for these tests to avoid sample break-through on Tenax TA.

On Tenax TA sample traps, TMS and HMDSO break through after about 5–15 minutes (depending on the amount of Tenax adsorbent in the trap) of air sampling at common sample flows. For longer sample times that are required for low detection limits (typically 2–4 hours), resulting data are incomplete and underestimate cleanroom concentrations by as much as 90% for TMS and HMDSO, and 50% for D3 (Figure 3).

Summarizing our findings on retention of silicon-containing AMC, Figure 3 shows a linear trend of capture efficiency as a function of compound boiling point. All three compounds included in our method described here have substantially insufficient capture efficiencies on Tenax TA.

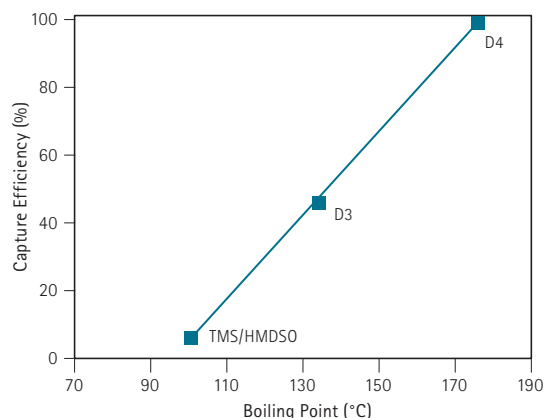


Figure 3. Capture efficiency on Tenax TA (350 mg, 36 l volume) for some compounds found in semiconductor cleanrooms.

Two special relationships exist for the compounds mentioned above. HMDS, the source for much of the TMS found in litho-bays, immediately breaks down to TMS in the presence of moisture, to form one molecule of ammonia and two molecules of TMS (Eq. 1).



The 40% relative humidity found in litho-bays is enough to ensure that this reaction is quantitative, essentially losing control over the formation of TMS. Once HMDS is emitted into the cleanroom air, conversion to TMS is so fast that it makes efficient filtration difficult. It may be possible to capture

HMDS if filtration is applied directly at the source (the dry track chamber). Because of the unstable nature of HMDS, this compound was not considered for our analytical method.

Secondly, HMDSO and TMS exist in an equilibrium state,<sup>5</sup> also governed by the presence of moisture (Eq. 2).



This equilibrium is shifted to the right side (in favor of TMS) either in aqueous solution or with significant air moisture (40% RH). However, this equilibrium could be used to prevent the formation of TMS by filtering out the HMDSO present in air (e.g. through recirculation and advanced chemical filters), essentially shifting the equilibrium and forcing the reaction to the left.

The initiation of the HMDSO breakdown in Eq. 2 also takes place in hybrid adsorption media containing acidic layers or acid-coated carbon, and forms TMS, which propagates through the filter array much faster than HMDSO. Although observations on high concentration systems<sup>6</sup> find the contrary, the conversion of HMDSO to TMS on acidic media is consistent at low concentrations (less than 1000 parts per billion, ppb,  $10^{-9}$  mols per mol) as found in semiconductor cleanrooms (typically much less than 100 ppb, see Section 4.3). In fact, our lab uses the near-quantitative conversion of HMDSO on acidic media to create a the TMS challenge gas<sup>7</sup> used for filter tests and for the comparison in Section 3.4.3.

As a result of the above limitations on sampling and capturing, current OEM requirements are rarely fulfilled with respect to LMW silicon-containing AMC and there are very few labs worldwide with a suitable method for TMS analysis. In this paper, we demonstrate a new method that measures all three compounds reliably at the low parts per trillion level (ppt,  $10^{-12}$  mole per mole) by employing a 4-hour sampling period and optimized analytical equipment.

## Experimental

All concentrations in this publication are expressed in volumetric, not mass-based, molar ratios.

### Air sampling

Sampling of AMC is carried out using small, battery operated sample pumps that are accurate to within 2% and calibrated before and after deployment.

Sampling traps are one-use devices filled with activated carbon that is split into a larger upstream bed and a half-size downstream carbon bed. The downstream bed serves as a control blank for the sample, undergoing the exact same procedure as the sample itself.

Air is drawn through the trap for about four hours, effectively trapping and pre-concentrating AMC of interest. This type of trap was shown to quantitatively retain organic compounds of boiling points 70°C and higher. Carbon sampling traps are sealed with plastic caps after sampling for transport. The caps were tested to not contain or contaminate the compounds of interest.

### Sample Analysis

Because thermal desorption analysis of carbon traps does not work for TMS, we apply a solvent micro-extraction (SME) to the trap adsorbent. Traps are uncapped and the carbon content is transferred to two sample vials, one for the main trap, another for the back-bed (control blank). Each vial with adsorbent is then filled with an extraction solvent and agitated to ensure proper transfer of organic compounds to the solvent. One microliter of solvent is then analyzed with a gas chromatography/mass spectrometry system (Autosystems XL, Turbomass Gold, Perkin Elmer). The mixture is separated on a non-polar column and followed by mass spectrometric detection in single ion mode, monitoring the most common ions of each compound.

Compounds were identified and validated with pure chemicals, suitably diluted, as well as by monitoring several mass fragments. Figure 4 shows the three compounds (scaled to each peak's maximum); analyzed masses of the compounds for this chromatogram were near the detection limit.

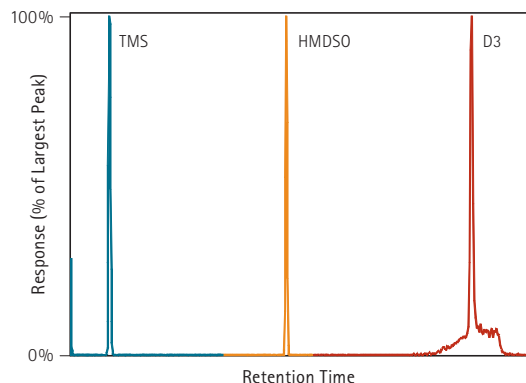


Figure 4. Typical chromatogram of a mixture of LMW Si near the detection limits.

Signal response areas obtained from the chromatography software are integrated and compared to calibration standard responses. Results are reported either in absolute  $\mu\text{g}/\text{sample}$  or in ppb or  $\mu\text{g}/\text{m}^3$  in air, as the compound, which is a more accurate method than reporting AMC "as toluene."

Using the SME method allows analysis of many aliquots of the same sample, if necessary or desired. This is an advantage over analyzing samples from traps such as Tenax or Carbotraps, which typically allow only for one analysis. On the other hand, the fact that only a fraction of the liquid and, hence, the sample, is analyzed causes a loss of response for any one compound. Using the most sensitive mode of the GCMS system regains some of that response loss.

### Calibration

Calibration is carried out using pure chemicals and diluting them with the same solvent that is used for sample extraction. Note that there are no standard reference materials (SRM) traceable to the National Institute of Standards and Technology (NIST) or similar standards organizations for any of these compounds of interest. Calibration standards are created using volumetric or gravimetric methods, with equipment calibrated to ISO 17025 standards.

A calibration curve of instrument response versus analyte concentration at five to nine concentration levels with five to seven replicates each are used

to create a calibration reference (Figure 5). This laboratory uses the Hubaux-Vos (H-V) method<sup>8,9</sup> to determine detection limits. In short, this method is a statistical evaluation of measurement uncertainty and uses a pre-determined confidence interval (99% for all of this lab's methods).

Using statistical uncertainty intervals around the calibration curve, the method allows the determination of two types of detection limits by graphical interpolation:

1. The instrument detection limit (IDL), which is the lowest concentration that can be considered different from zero. All concentrations below this level should be reported as zero.
2. The method detection limit (MDL), which is the lowest amount that should be reported with 99% confidence. In some cases, exposure tool OEM guidelines require a reporting limit (RL, e.g. 0.1 ppb or  $\mu\text{g}/\text{m}^3$ ), which is not related to and may be different from the MDL, but should never be lower. The MDL is typically about  $2 \times \text{IDL}$ .

One limitation of this method should be noted: the statistical approach does not consider artifacts. If there is a persistent background contamination, the calibration curve would shift up vertically (positive intercept), but the DL methodology would yield the same numeric values. However, a built-in control of this method is to ensure that the zero intercept is within the two uncertainty intervals (Figure 5 inset). If that is the case, the intercept is considered zero and does not show any artifact with 99% certainty).

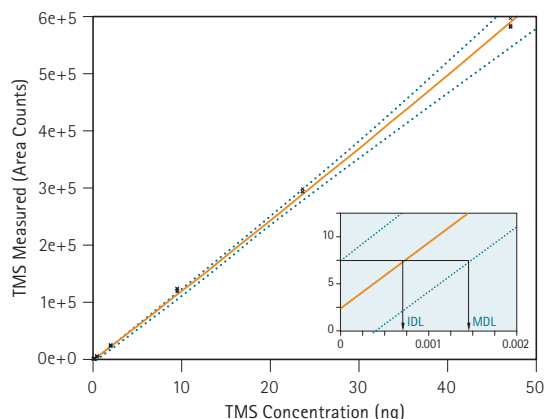


Figure 5. Calibration curve for TMS. The inset shows the low end of the curve used to determine the detection limits through graphical interpolation (arrows). Dashed lines are the 99% confidence intervals.

### Accuracy and Method Validation

Precision or repeatability of this method is considered within the statistical H-V approach described above. Typical  $1\sigma$  precision is less than 5% at the detection limit, about 1% at higher concentrations.

Accuracy can be gauged in different ways, the most common approach being a comparison to standard reference materials (SRM) published or made available by organizations such as NIST or TÜV and others. As mentioned, there are no such SRMs available for the compounds of interest and accuracy needs to be described by addressing the following issues.

### Sample Trap Capacity and Capture Efficiency

Carbon traps used for this method are manufactured with two carbon beds back to back, the upstream bed containing twice as much carbon as the downstream bed. The downstream bed is an excellent internal diagnostic and was used to study break-through.

In all of our tests, the back-bed of carbon did not show significant amounts of the compounds of interest. In some cases, we observed a persistent, but low background for TMS and D3 in all measurements, which was caused by separation column breakdown and disappeared when we switched to a different analytical column. Having no break-through from the first to the second carbon bed means that capture efficiency was 100% in all cases.

To determine the capacity of these traps for the compounds of interest, we created a challenge of TMS and HMDSO in air, sampled this source gas through a carbon trap and measured the outlet of the trap. The breakthrough curves for TMS and HMDSO in Figure 6 show a maximum sample time of 15 hours for TMS and 25 hours for HMDSO before the compound can be measured at the outlet.

The challenges for this test were 0.5–0.8 ppm, which translates to a capacity of 6–11 mg of compound per trap. Flow rate and sampling temperature will heavily influence the breakthrough volume (but not necessarily the capacity). Operating this trap type at our standard flow rate and sample time at lithography cleanroom temperatures, capacity is sufficient to capture ppm level concentrations quantitatively.

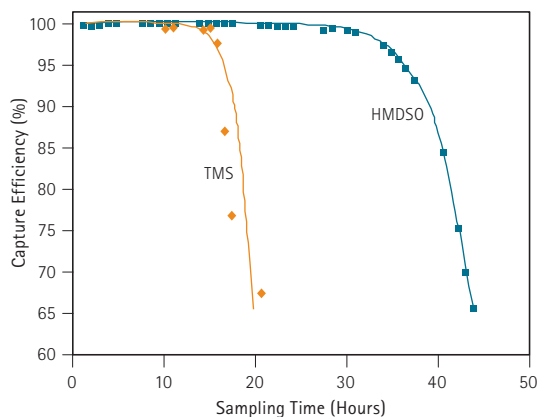


Figure 6. Capture efficiency as a function of time for TMS and HMDSO.

For D3, a solid compound, it is safe to assume that it is retained better than TMS and HMDSO on almost any adsorbent, based on its molecular weight and structure, boiling point and elution on common separation columns. If capture efficiency on carbon traps is sufficient for TMS and HMDSO, it will be higher for D3.

### Compound recovery

Aside from capture efficiency, the recovery upon solvent extraction, i.e. the fraction of compound that is released by the adsorbent, is an important metric for this trap sampling method. Recovery was studied by spiking the traps with 10 µl of gravimetrically prepared standards of known concentration. Results in Table 1 suggest that recovery is within 2% of the spiked amount and well within overall measurement uncertainty.

TABLE 1. COMPOUND RECOVERY FROM CARBON SAMPLING TRAPS USING SME

Test #	TMS			HMDSO			D3		
	Challenge	Measured	Recovery	Challenge	Measured	Recovery	Challenge	Measured	Recovery
	ng	ng	%	ng	ng	%	ng	ng	\$
1	0.95	0.94	99%	0.414	0.424	102%	0.035	0.033	94%
2	0.95	0.94	99%	0.414	0.425	103%	0.035	0.038	109%
3	0.95	0.94	99%	0.414	0.423	102%	0.035	0.037	106%
4	0.95	0.93	98%	0.414	0.419	101%	0.35	0.365	104%
5	1.9	1.83	96%	0.83	0.796	96%	0.35	0.342	98%
6	1.9	1.81	95%	0.83	0.802	97%	0.35	0.346	99%
7	1.9	1.82	96%	0.83	0.788	95%			
8	1.9	1.88	99%	0.83	0.797	96%			
Averages			98%			99%			102%

### Comparison to a Gas-phase Source

Another validation test was used to confirm absolute accuracy. A challenge gas of TMS and HMDSO in air was created from an independent dynamic dilution system (DDS). Concentrations were calculated based on the evaporation rate of the liquids and the flow rates of air used for the two-step dilution.

TABLE 2. COMPOUND RECOVERY FROM CARBON SAMPLING TRAPS USING SME

Test #	TMS			HMDSO		
	Source Concentration	Measurement	Agreement	Source Concentration	Measurement	Agreement
	ppb	ppb		ppb	ppb	
1	177	199	113%	960	1069	111%
2	177	175	99%	960	1155	120%
3	177	214	121%	960	1029	107%
4	177	200	113%	960	916	95%
Averages			111%			109%

Variability of the source gas was 40% between extreme excursions for TMS and 14% for HMDSO (standard deviations were 10% and 4%, respectively). Within the variability of this source gas, agreement of the measurements (11% and 9%) with calculated source gas concentrations was sufficient and close to the respective standard deviations.

### Error Evaluation

For the overall error evaluation, we considered the following error sources:

- Chemical purity as per vendor's certificate (0.1-2%)
- Flask and syringe tolerances in the volumetric dilution sequence (<2% for the sequence)
- Analytical precision from H-V calibration curve (1.0 - 4.5%, depending on concentration and compound)
- Instrument response drift during analysis (15% max allowance)

We calculated the overall, worst-case (cumulative) error for any one measurement to be  $\leq 25\%$  of result at the method detection limit,  $\leq 20\%$  at concentrations higher than 100 ppt in air.

## Results

### Detection Limits

Following the H-V approach, we determined the method detection limits shown in Table 3, all of which are in the single-digit ppt range in air for this sampling approach and may be extended down by a factor of 10–30 by using longer sample times and higher sample flows and/or larger traps.

TABLE 3. DETECTION LIMIT PARAMETERS FOR THE COMPOUNDS OF INTEREST

	MDL 99% Confidence (ppt)	MDL 99% Confidence (pg)	Peak:Noise Ratio at the MDL
TMS	1	1.5	200
HMDSO	1	3.7	500
D3	6	29	60

Note that the peak-to-noise ratios of these compounds are between 60 and 500 at the MDL (Table 3). Very often, detection limits are defined as the level where peak:noise ratio is 3 or higher. This is a

suitable definition for online monitors, where high frequency of measurement increases confidence, but is woefully inadequate for any chromatographic method representing spot-measurements. Applying the peak-to-noise approach to the TMS method shown here, detection limits would become 0.015 pptV (15 parts per quadrillion). However, as outlined above, any measurement less than 1 ppt needs to be considered zero within the chosen confidence, as the measurement uncertainty does not allow to distinguish lower levels. Confidence at the 3:1 peak:noise level is probably less than 20%, which means that the probability for false positive reporting is 80%! This point is very important for OEM exposure tool compliance reporting, because an inadequately chosen DL will substantially increase the number of false positives.

Detection limits achieved with this method are suitable to satisfy the most demanding exposure tool OEM requirements.

### Comparison to Tenax TA Traps

We carried out tests with Tenax TA sample traps/TD in parallel with the carbon trap/SME approach to compare the results from the two sampling methods. Tenax TA sampling requires several adjustment factors, depending on the exact method parameters used. If, for example, TMS is measured using single ion mode of the GCMS system, and scan mode for toluene calibration (to report the compound "as toluene"), at least three factors need to be considered: a factor to adjust for the break-through volume, a factor to scale single ions up to full response and a factor to convert from single ion mode to scan mode response.

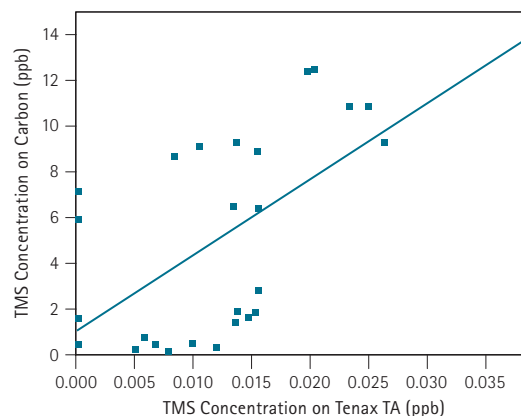


Figure 7. Comparison of side-by-side results of Tenax TA/TD and carbon traps/SME.

Using our best-estimate for breakthrough volume on Tenax TA traps and an empirically established conversion factor from single ion mode to scan mode and published NIST results for the ion fragment yield for ion 75, we calculated the concentration of TMS in about 40 samples taken over the course of five months in different semiconductor environments. Results from this comparison (Figure 7) show a factor of about 300 between carbon/SME and Tenax TA/TD sampling as well as a poor correlation with a variance  $r^2 = 0.35$ .

A large part of this poor correlation was a common solvent that co-elutes with TMS and that diminishes – and randomizes – the TMS response through a quenching effect. These data confirm that Tenax TA cannot be considered a suitable trapping method for TMS and that break-through may occur earlier than we estimated. Results for HMDSO were substantially better (a factor of about 4 between trap types), but still require the mentioned factors.

### Real-world Data

Finally, we present data that were taken with the above carbon trap/solvent micro extraction method from different environments or sources within semiconductor fabs. Data presented here are from 26 projects with 80 samples taken in four countries at eight customer sites (Figure 8).

Most samples were taken in subfabs, a category that also includes all inlets for chemical filter cabinets feeding exposure tools with chemically clean air. Ambient means outside air, usually taken on the rooftop near the air handler intake. Purified air is cleanroom air filtered for KrF tool optics purge (and is different from CDA supplies typically used for ArF tools). Most cleanroom samples were taken in the vicinity of exposure tools.

Out of 71 samples, we found TMS in 65, HMDSO in 27 and D3 in 15 samples. High concentrations (larger than 10 ppb) were found 15 times for TMS, HMDSO was always below 1.7 ppb and D3 below 0.7 ppb. Only in two fabs did we find extreme TMS contamination in excess of 1000 ppb, one of which was caused by sampling fab exhaust; the source for the other occasion is unknown and may well represent normal cleanroom concentration of that particular fab.

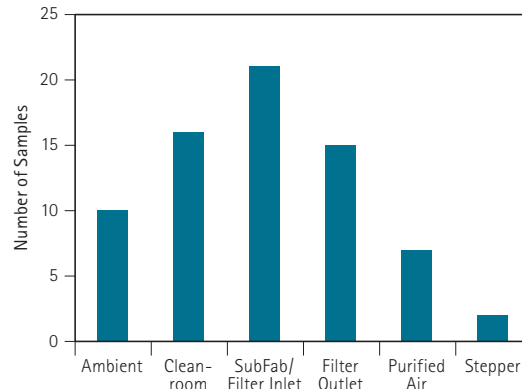


Figure 8. Type of samples taken in different semiconductor fab environments.

Overall, results were highly variable and data do not paint many clear trends or patterns, in part based on the limited number of samples taken. More data points as well as a further breakdown into sub-categories, such as regions, lithography technologies etc. will reveal more insight into LMW Si contamination.

Tables 4-6 summarize concentrations for TMS, HMDSO and D3 for the different sample types from Figure 8. Based on the high variability of data, we present both mean and median values as well as maximum and minimum concentrations observed. N is the number of total measurements, not the number of non-zero observations. Standard deviations were often higher than the mean and were found to be of little meaning in this limited data set.

Whereas it is not surprising that ambient, cleanroom and subfab environments contain silicon-containing AMC, the first significant conclusion from these data is that low molecular weight silicon compounds vary highly from fab to fab and even between cleanroom and subfab of the same facility.



TABLE 4. TMS RESULTS BY SAMPLE TYPE, EXCLUDING EXTREME CONTAMINATION &gt;1 PPM (N=4)

	Ambient	Cleanroom	SubFab/ Filter inlet	Filter Outlet	Purified Air	Scanner
Mean	4.5	12	4.4	2.6	0.6	12
Median	0.2	12	1.8	0.4	0.4	12
Max	14	33	14	20	1.9	12
Min	0	0.04	0.05	0	0	12
N	9	13	21	15	7	2

Excluding four extreme contamination events (>1 ppm) that we found in one Fab and one outside air event, TMS concentrations were found to be similar in outside ambient and subfab air, whereas cleanrooms showed substantially more TMS (Table 4). This is contrary to the notion that cleanrooms are less contaminated than subfabs and may indicate that sources of TMS are primarily located at the cleanroom level (where HMDS process chemical use occurs as well as its breakdown and some track venting). This may also mean that laminar flow schemes in cleanrooms may not remove AMC or diminish concentration gradients as efficiently as expected.

On average, chemical filter outlets, which were a mix of cabinet styles and vendors, showed lower, but still significant TMS contamination, which

confirms that chemical filters do not retain TMS efficiently or for extended times. About one third of the investigated systems, those with new filter sets, showed zero TMS at the outlet. The filters that showed TMS in the outlet, however, were less than 2 years old, the targeted lifetime for most exposure tool applications.

Another important result is that purified cleanroom air and the inside of exposure tools can contain substantial amounts of silicon AMC. The latter may be an indication of tool-internal TMS sources, including outgassing from the wafer surface or airborne cross-contamination from the interface between exposure tool and the coater-developer chamber where HMDS or similar compounds may be used in track process steps.

TABLE 5. HMDSO RESULTS BY SAMPLE TYPE, EXCLUDING EXTREME CONTAMINATION &gt;10 PPB (N=4)

	Ambient	Cleanroom	SubFab/ Filter inlet	Filter Outlet	Purified Air	Scanner
Mean	0.1	0.36	0.1	0.02	0	0.12
Median	0.03	0.10	0.04	0	0	0.12
Max	0.5	1.6	0.5	0.2	0	0.2
Min	0	0	0	0	0	0.04
N	9	13	21	15	7	2

TABLE 6. D3 RESULTS BY SAMPLE TYPE, EXCLUDING EXTREME CONTAMINATION &gt;10 PPB. (N=3)

	Ambient	Cleanroom	SubFab/ Filter inlet	Filter Outlet	Purified Air	Scanner
Mean	0.1	0.04	0.06	0.01	0	0.3
Median	0	0	0	0	0	0.3
Max	0.7	0.4	0.4	0.1	0	0.5
Min	0	0	0	0	0	0
N	9	13	21	15	7	2

HMDSO concentrations were, on average, much lower than those of TMS (Table 7). Like TMS, HMDSO also shows highest average concentrations in the cleanrooms, not in the subfabs or outside air, second highest in the two exposure tools we investigated. Purified air sources were clean of HMDSO and D3.

**TABLE 7. RELATIVE RATIOS OF THE COMPOUND TO EACH OTHER.**

	TMS: HMDSO Ratio	TMS: D3 Ratio	HMDSO: D3 Ratio
Mean	91	99	3
Median	47	62	1
Max	667	500	22
Min	3	18	0
N	32	19	19

## Conclusions

We described a new method for the measurement of low molecular weight silicon containing AMC, including TMS, HMDSO and D3. Our tests clearly showed that Tenax TA adsorbent is unsuitable to trap any of these three compounds with standard 3.5" Tenax TA traps and sample times longer than a few minutes (1.5 hours for D3). The most important conclusion is that exposure tool OEM requirements are not met when using Tenax TA sampling traps.

We also found that carbon traps, which have a significantly higher capture efficiency for these compounds, cannot be used in conjunction with thermal desorption to recover TMS. Explaining the erratic results with this method require further investigation.

Solvent micro-extraction, on the other hand, produces very good, repeatable results for the capturing as well as the recovery from carbon traps of the compounds described here. Method detection limits are in the single digit ppt range and suitable for all OEM exposure tool measurement and compliance requirements.

Very few labs are known to apply a similarly suited method and we are not aware of any lab that is ISO 17025 accredited for this method.

In semiconductor environments, we found a very wide range of concentrations for TMS; concentrations varied within the same fab, within the same cleanroom and from day to day. Very high concentrations (ppm level) have been found in some outside ambient air but also a few cleanroom samples. TMS concentrations are always higher than those of HMDSO and D3 by 50–100×. HMDSO and D3 are found in roughly equal amounts, although D3 less often than HMDSO. The compounds were found in all fab environments, including places thought to be chemically clean such as exposure tools and purified air supplies.

The method described here is the only known, suitable method that produces repeatable, artifact-free results with single-digit ppt-level detection limits that allows a short sampling approach for semiconductor industry needs. Overall measurement uncertainty was estimated to be within 25% for any one compound.

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