

Environmental Applications

Whole Air Canister Sampling and Preconcentration GC-MS Analysis for pptv Levels of Trimethylsilanol in Semiconductor Cleanroom Air

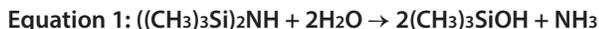
By Jason S. Herrington, Ph.D.

Abstract

The costly damage trimethylsilanol (TMS) in cleanrooms exacts on scanner lenses in the semiconductor industry has resulted in the demand for accurate and reliable methods for measuring TMS at trace levels (i.e., parts-per-trillion, volume-per-volume of air [pptv] [$\sim\text{ng}/\text{m}^3$]). This study developed a whole air canister-based approach for field sampling trimethylsilanol in air, as well as a preconcentration gas chromatography–mass spectrometry (GC-MS) laboratory method for analysis. Results demonstrate clean canister blanks (0.06 pptv [$0.24\text{ ng}/\text{m}^3$], which is below detection limit [BDL]); excellent linearity (a calibration relative response factor [RRF] relative standard deviation [RSD] of 9.8%) over a wide dynamic mass range (1.0 to 100 pptv); recovery/accuracy of 93%; a low selected ion monitoring (SIM) method detection limit (MDL) of 0.12 pptv ($0.48\text{ ng}/\text{m}^3$); replicate precision of 6.8% RSD; and stability (84% recovery) out to four days of storage at room temperature. These performance levels should meet the demands of the semiconductor industry for monitoring trace levels of trimethylsilanol in cleanrooms.

Introduction

Volatile methylsiloxane (VMS) compounds are low molecular weight organosilicon species with relatively high vapor pressures under ambient conditions. VMS species are directly emitted to the environment from cosmetics and other personal care products (e.g., shampoos, skin creams, toothpaste, deodorants), and during the degradation of polydimethylsiloxane (PDMS), which is used in a broad range of applications (e.g., industrial, personal care, and household) [1,2]. Historically, VMS compounds were of concern due to their ubiquitous presence in biogas emitted from landfills and wastewater treatment plants [1-3]. However, this is not due to human health concerns, as siloxanes are considered safe to the general public [2]. Rather, VMS compounds receive considerable attention due to the combustion of biogas containing siloxanes, which results in the formation of microcrystalline silicon dioxide. The silicon dioxide acts as a corrosive and/or abrasive agent in combustion chambers, thereby resulting in premature failure and/or required maintenance of engines [4]. More recently, VMS species such as trimethylsilanol (TMS, CAS 1066-40-6) have been gaining attention in the semiconductor industry due to concern about trimethylsilanol optics haze. TMS is a silanol (although it is considered to belong to the siloxane group) that forms from the reaction of hexamethyldisilazane and water vapor during silicon wafer production (Equation 1) [5,6].



Trimethylsilanol in air at trace (i.e., pptv [$\sim\text{ng}/\text{m}^3$]) concentrations may accumulate on photolithography tools (e.g., UV scanners), resulting in costly and irreversible trimethylsilanol optics haze [5]. Therefore, analysis of TMS at trace levels is necessary to help prevent damage to UV scanner lenses, masks, reticles, lasers, and optics. Field sampling and analytical methods have historically focused on TMS and several linear and cyclical siloxanes at concentrations in the ppmv ($\sim\text{mg}/\text{m}^3$) to ppbv ($\sim\mu\text{g}/\text{m}^3$) range. These methods include the use of organic solvents [7,8], Tedlar® (polyvinyl fluoride) bags [9], canisters [3], and solid sorbents including, but not limited to, activated carbon/charcoal [7], Tenax® (poly 2,6-diphenylene oxide) [2,10], XAD and polyurethane foam (PUF) [11]. To date, it appears that only one study has targeted siloxanes in the low pptv ($\sim\text{ng}/\text{m}^3$) range, with the use of a tube packed with Tenax® TA and Carboxen® [2]. The Tenax® TA and Carboxen® sampling approach coupled with thermal

desorption GC-MS was able to provide trace-level TMS concentrations. Although solid sorbent sampling methods may be small, thereby easy to ship and store, they are prone to sample breakthrough, relative humidity (RH) sensitivities, sampling/analytical artifacts, and only single sample analyses. Therefore, for the current study a whole air canister-based approach, which avoids many of these issues, was utilized for the sampling and analysis of trace levels of trimethylsilanol in air.

The canister-based approach was chosen based on the following: the ability to provide relatively quick (i.e., ~10 seconds) grab samples, the flexibility to sample for long-term (i.e., a few hours to days) sampling durations with the use of a passive sampler, the ability to sample without a pump, and the capability for multiple sample analyses. Previous studies have already demonstrated whole air canister sampling for siloxanes; however, this was conducted for siloxanes in the ppmv (~mg/m³) to ppbv (~µg/m³) range. Whole air canister-based methods for trace levels (i.e., parts-per-trillion, volume-per-volume of air [pptv] [~ng/m³]) of TMS do not exist. The current study develops a preconcentration gas chromatography–mass spectrometry (GC-MS) method for trace levels of TMS, which will be of benefit to the semiconductor industry as a potential approach for quantifying trimethylsilanol in cleanrooms.

Experimental

Materials

Trimethylsilanol (≥98.5%) was obtained from Sigma Aldrich (St. Louis, MO, U.S.). Hexane (95%) was obtained from J.T. Baker (Phillipsburg, NJ, U.S.).

Analytical System

For all of the experiments, the following analytical system was utilized: a Nutech 8900DS preconcentrator (GD Environmental Supplies, Inc., Richardson, TX, U.S.) paired with an Agilent 6890 gas chromatograph (GC) (Agilent Technologies, Santa Clara, CA, U.S.) coupled with an Agilent 5973 mass spectrometer (MS) detector. The Nutech 8900DS preconcentrator utilizes three cryogenically cooled traps to concentrate/focus target analytes (often referred to as “micro-scale purge-and-trap”) for delivery to the GC-MS system. In order of sample flow: Trap 1 consists of Siltek®-treated borosilicate beads (40/60 mesh) used to remove water vapor, nitrogen, oxygen, and carbon dioxide (CO₂) from the sample stream; Trap 2 consists of Tenax® GR (80/100 mesh) material used to focus the VOCs and remove any residual water vapor and CO₂; and Trap 3 is a proprietary trap used for final analyte focusing and transfer of analytes to the GC column (via a Vici® [Vici Valco Instruments, Houston, TX, U.S.] zero volume union [i.e., direct injection]). All samples were analyzed by preconcentrating 400 mL of sample with the addition of 100 mL of TO-14A internal standard/tuning mix (Restek, Bellefonte, PA, U.S., cat.# 34408) (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₅, and 4-bromofluorobenzene) prepared at 20 ppbv concentrations. TMS was analyzed in selected ion monitoring (SIM) mode with the target ion 75 m/z and qualifier ions 45, 47, and 59 m/z. The remainder of the preconcentrator and GC-MS parameters may be found in Tables I and II, respectively.

Analytical System Blanks/Detection Limit (ADL)

Due to the ubiquitous nature of silicon-containing materials, seven analytical system blanks (a 100 mL injection of internal standards via the preconcentrator GC-MS system) were analyzed to determine if there was any background TMS in the preconcentrator GC-MS system. From these results, an analytical detection limit (ADL) was calculated as the standard deviation of the seven replicate measurements multiplied by 3.14 (i.e., the Student’s *t* value for 99 percent confidence for seven values) (Equation 2).

$$\text{Equation 2: ADL} = s \times t_{(n-1, 1-\alpha = 0.99)}$$

n = Number of replicate measurements

s = Standard deviation of *n* measurements

t = Student’s *t* value at *n* - 1 degrees of freedom

α = Significance level

Canister Cleaning/Blanks

The canisters were cleaned with a TO-Clean canister cleaning system (Restek, Bellefonte, PA, U.S., cat.# 22916), as per the recommended procedures outlined in section 8.4.1 of Method TO-15 [12]. Briefly, at 100 °C all canisters were evacuated down to 500 mTorr and held under vacuum for 60 minutes; the canisters were then filled with humidified (45% RH) nitrogen to 30 psig. All RH values were verified by an EXTECH hygro-thermometer/datalogger (Model SDL500) (Extech Instruments Corporation, NH, U.S.). This cycle was completed two additional times for a total of three cycles (Table III). All vacuums/pressures were controlled by the TO-Clean canister cleaning system’s internal gauge; however, vacuums/pressures were periodically verified using an Ashcroft® digital test gauge (Stratford, CT, U.S., Restek cat.# 24268).

Blank canisters were generated by pressurizing clean evacuated canisters with humidified (45% RH) nitrogen to 30 psig, storing them for three days at room temperature (this was done to simulate sample handling/shipping times), and then analyzing them for cleanliness. Nitrogen was humidified (45% RH) by sparging the nitrogen through a humidification chamber (Restek, Bellefonte, PA, U.S., cat.# 24282) filled with deionized (DI) water. This was done so as to best replicate the RH in semiconductor cleanrooms, which, among several environmental conditions, is controlled at 30 to 50% RH [13].

Table I: Nutech 8900DS preconcentrator settings. Default preconcentration volume = 400 mL.

Trap 1 Settings		Internal Standard	
Cooling Temp.	-155 °C	Purge Flow	100 mL/min
Preheat Temp.	5 °C	Purge Time	6 sec
Preheat Time	0 sec	Volume	100 mL
Timeout	10 min	ISTD Flow	100 mL/min
Desorb Temp.	20 °C		
Desorb Flow	5 mL/min	Sample	
Desorb Time	360 sec	Purge Flow	100 mL/min
Bakeout Temp.	200 °C	Purge Time	6 sec
Flush Flow	120 mL/min	Sample Flow	100 mL/min
Flush Time	60 sec		
Sweep Flow	120 mL/min	GC Control	
Sweep Time	60 sec	Remote Start	Yes
Temp. Target Range	2 °C	GC Run Time	3 min
Stable Time	60 sec	Flush Sample Line	No
Cooling w/He	No	GC Ready Required	Yes
		GC Ready Timeout	1 min
Trap 2 Settings		Idle State Configuration	
Cooling Temp.	-35 °C	Cryotrap1	150 °C
Desorb Temp.	190 °C	Transfer Line	125 °C
Desorb Time	30 sec	Valve Oven	125 °C
Timeout	10 min	Cryotrap2	150 °C
Bakeout Temp.	200 °C	Sampler Line	125 °C
Bakeout Time	10 sec	Sampler Oven	125 °C
Temp. Target Range	2 °C	Auxiliary	125 °C
Stable Time	10 sec		
Cooling w/He	No		
Cryofocus Settings			
Cooling Temp.	-160 °C		
Inject1 Time	140 sec		
Timeout	10 min		
Temp. Target Range	3 °C		
Stable Time	10 sec		

Table II: Agilent 6890-5973 GC-MS parameters.

GC Parameters			
Oven	32 °C (hold 1 min) to 150 °C at 8 °C/min to 230 °C at 33 °C/min		
Carrier Gas	He, constant flow		
Flow Rate	1.2 mL/min		
MS Parameters			
Transfer Line Temp.	230 °C		
Source Temp.	230 °C		
Quad Temp.	150 °C		
Electron Energy	70 eV		
Solvent Delay Time	1.00 min		
Tune Type	BFB		
Ionization Mode	EI		
SIM Program			
Group	Start Time (min)	Ions (m/z)	Dwell (ms)
1	0.00	49, 130, 128, 51, 75, 45, 47, 59, 147, 73, 148, 66	25
2	6.25	114, 63, 88, 57	50
3	7.00	207, 208, 96, 191	50
4	10.00	117, 82, 52, 54	50
5	12.00	50, 75, 95, 96, 173, 174, 175, 176, 177	25

Calibration

A seven-point calibration curve was generated by analyzing a series of volumes of a 47.6 pptv (192 ng/m³) primary standard (Table IV). The default preconcentration volume for samples was 400 mL. The 47.6 pptv primary standard was generated by injecting 5 µL of neat TMS into an evacuated 6 L canister and pressurizing that canister with 45% RH nitrogen to 45 psig. The resulting standard was 42.1 ppmv (170 mg/m³) TMS. The standard was allowed to age for at least 24 hours, but was no older than 30 days at the time of use. The standard was then dynamically diluted down to 47.6 pptv. A calibration criterion of 30% (i.e., the percent relative standard deviation [%RSD] for the relative response factor [RRF]) was adopted from U.S. Environmental Protection Agency (EPA) Compendium Method TO-15 [12].

Table III: Canister cleaning procedures conducted at 100 °C with humidified nitrogen (45% RH).

Cycle	Evacuation (mTorr)	Pressurization Pressure (psig)
1	500 (Hold for 60 min)	30
2	500 (Hold for 60 min)	30
3	500 (Hold for 60 min)	30
Final	50	30 (only for blanks)

Table IV: Calibration curve.

Standard (pptv)	Injection Volume (mL)	Calibration Concentration (pptv)
47.6	800	95.2
47.6	400	47.6
47.6	200	23.8
47.6	80	9.52
47.6	40	4.76
47.6	20	2.38
47.6	8	0.95

Recovery/Accuracy

It was imperative to assess how efficient the Nutech 8900DS preconcentrator was at recovering TMS from a canister and injecting it onto the GC-MS, and also how accurate the preconcentrator GC-MS system was as a whole at relevant concentrations. The recovery/accuracy of the preconcentrator GC-MS system was determined by comparison to audit standards. A 1 µL aliquot of TMS diluted in *n*-hexane (802 pg/µL TMS) was analyzed via direct injection and the same GC-MS conditions used for canister analysis (with the exception that a 9:1 split was used, resulting in 80.2 pg of TMS on column). This audit standard was compared to seven 400 mL injections of the aforementioned 47.6 pptv (192 ng/m³) standard via the preconcentrator GC-MS, resulting in 76.6 pg of TMS on column. In addition, a five-point calibration curve was generated from direct liquid injections for comparison purposes.

A recovery/accuracy criterion of 30 percent was adopted from Method TO-15 [12]. Recovery/accuracy was calculated as the difference between the response of the audit standard and the response of the preconcentrator GC-MS value divided by the response of the audit standard, expressed as a percentage as shown in Equation 3.

$$\text{Equation 3: Recovery/Accuracy (\%)} = (\text{Audit Value} - \text{Measured Value}) / \text{Audit Value} \times 100$$

Method Detection Limit (MDL)

The method detection limit (MDL) was determined as prescribed in the Code of Federal Regulations (40 CFR 136 Appendix B). Specifically, the MDL was determined from seven replicate measurements of a low-level standard containing TMS at a concentration near (within a factor of five) the expected detection limit. In this case, it was deemed that the blank canister concentrations were near the expected MDL; therefore, seven blank canisters were analyzed. The MDL was also determined by direct liquid injection of 1 µL of 0.802 pg/µL TMS (0.8 pg on column) repeated seven times. The MDL was calculated as the standard deviation of the seven replicate measurements multiplied by 3.14 (i.e., the Student's *t* value for 99 percent confidence for seven values) (Equation 4).

$$\text{Equation 4: MDL} = s \times t_{(n-1, 1-\alpha=0.99)}$$

- n* = Number of replicate measurements
- s* = Standard deviation of *n* measurements
- t* = Student's *t* value at *n*-1 degrees of freedom
- α = Significance level

An MDL criterion of 10.0 pptv was adopted, based on what was deemed appropriate for aiding the semiconductor industry.

Precision

Precision determinations were made from seven replicate measurements of a standard containing TMS at 9.51 pptv (38.3 ng/m³), which is near expected field sample concentrations and close to the desired detection limit for this method. A precision criterion of 25% was adopted from Method TO-15 [14]. Precision for each analyte was calculated as the standard deviation of the seven replicate measurements divided by the average value of the seven replicate measurements and expressed as a percentage (Equation 5).

$$\text{Equation 5: Relative Standard Deviation (RSD[\%])} = \sigma/\mu \times 100$$

σ = Standard deviation of an array

μ = Average of an array

Sample Stability

Silanol, in particular TMS, are considered unstable species due to: the ease at which they undergo condensation [1,5,6]; their reaction with the alkali in glass [13]; and their propensity for oxidative degradation by reactions with the hydroxyl or nitrate radical, and ozone [14]. Therefore, the following experiment was designed to evaluate the stability of TMS in electropolished and silica lined canisters, in the presence of variable RH, over time. Two electropolished TO-Can® air sampling canisters (Restek, Bellefonte, PA, U.S., cat.# 24178) and two silica-lined SilcoCan® air sampling canisters (Restek, Bellefonte, PA, U.S., cat.# 24142-650) were spiked with TMS and pressurized with 20% RH nitrogen to 30 psig, resulting in a final TMS concentration of ~5 pptv. In addition, two more electropolished and two more silica-lined canisters were spiked with TMS and pressurized with 93% RH nitrogen to 30 psig, resulting in a final TMS concentration of ~5 pptv. All eight canisters were analyzed periodically over a two-week period.

Although 20% and 93% RH levels were chosen to represent the extreme ends of the RH spectrum, a final optimized stability experiment was conducted by spiking two electropolished canisters with TMS and pressurizing them with 45% RH nitrogen to 30 psig, resulting in a final TMS concentration of ~5 pptv. This was done to mimic the conditions most likely encountered in a semiconductor cleanroom. The same recovery/accuracy criterion of 30 percent adopted from Method TO-15 [14] was applied to all sample stability experiments.

Results and Discussion

Analytical System Blanks/Detection Limit (ADL)

The ubiquitous presence of silicon-containing materials in laboratory equipment produced a background level of TMS. The average TMS concentration from seven analytical system blank analyses was 0.11±0.03 pptv, which corresponds to an ADL of 0.09 pptv (0.36 ng/m³). This background level was reproducible and, therefore, could be subtracted from all measurements. During several additional system blank analyses, the various components of the preconcentrator GC-MS system were individually isolated in order to locate the origin of the background TMS. Results indicate the single strongest source of TMS is often the canister, which can contribute ~20% or more of the total background TMS. In particular, the internal standards (ISTD) used for every analysis are generated in and delivered from a canister. Therefore, the presence of any TMS in the ISTD canister strongly dictates the background TMS concentration. However, the background TMS concentrations may easily be kept to a minimum with the use of proper canister cleaning procedures (as outlined in the Experimental section). It is important to note that humidifying the canister cleaning N₂ is imperative for generating the lowest TMS concentration in blank canisters.

It is also important to note that several analytical system blanks were evaluated immediately following the analysis of standards containing up to ~500 pptv TMS. Results from this evaluation indicate that there was no observable TMS carryover between analyses. However, analysis of several analytical system blanks immediately following the analysis of standards containing up to ~5 ppbv TMS did result in carryover on the order of ~10 pptv, which was immediately cleared on a subsequent run.

Calibration

The seven-point calibration curve demonstrated excellent linearity with a relative response factor (RRF) relative standard deviation (RSD) of 9.8% for 1.0 to 100 pptv TMS. The calibration curve was generated by preconcentrating varying volumes of the same primary standard, which indicates the preconcentrator GC-MS system was able to effectively preconcentrate gas-phase TMS from an evacuated canister over a wide linear range (i.e., 8–800 mL) of volumes.

Recovery/Accuracy

The seven analyses of a 400 mL injection of 47.6 pptv (192 ng/m³) TMS via the preconcentrator GC-MS were compared to a five-point calibration curve generated from direct liquid injections of TMS into the GC-MS. The recovery was 93±10% at this 76.6 pg on-column loading level. These results indicate the preconcentrator is efficiently trapping and delivering trace levels of TMS to the GC-MS. These results also demonstrate that the gaseous standard generation technique used for this study was appropriate. As shown in Figure 1, the preconcentrator GC-MS system was able to chromatograph TMS quite well.

Method Detection Limit (MDL)

The average TMS concentration from seven blank canisters (four electropolished and three silica-lined) was 0.06±0.04 pptv, which corresponds to an MDL of 0.12 pptv (0.48 ng/m³). The ADL and MDL are virtually indistinguishable because, as discussed earlier, the system background levels were strongly dictated by the TMS concentration in the ISTD canister utilized by the preconcentrator GC-MS system.

The MDL was also determined to be 0.65 pg of TMS on-column by direct liquid injection onto the GC-MS, which corresponds to a 6 L canister concentration of 0.40 pptv (1.63 ng/m³) TMS. The two different modes of generating MDLs gave values (0.12 and 0.40 pptv) that were very close in magnitude, which strengthens the confidence in the MDL. It also further validates the system's recovery/accuracy, even at concentrations near the detection limit.

It is important to note that the MDL is simply a statistical number and may not have any practical application. Therefore, it is recommended that a practical quantitation limit (PQL) of five times the MDL be adopted. Based on this, the PQL is 0.60 pptv (2.42 ng/m³) TMS, which is consistent with the lowest observed calibration level (0.95 pptv) that could be confidently distinguished from background noise. The current TMS PQL is ~5x lower than Lee et al.'s, 2012 [5] MDL (9.5 ng/m³) for a 6 L sample collected on a thermal desorption (TD) tube. However, the current PQL can be achieved with a ~10-second grab sample, something not previously demonstrated with TD tubes.

Precision

The precision experiment data demonstrate that the preconcentrator GC-MS system had a 6.8% RSD for seven replicate analyses of a 9.51 pptv (38.3 ng/m³) TMS standard.

Sample Stability

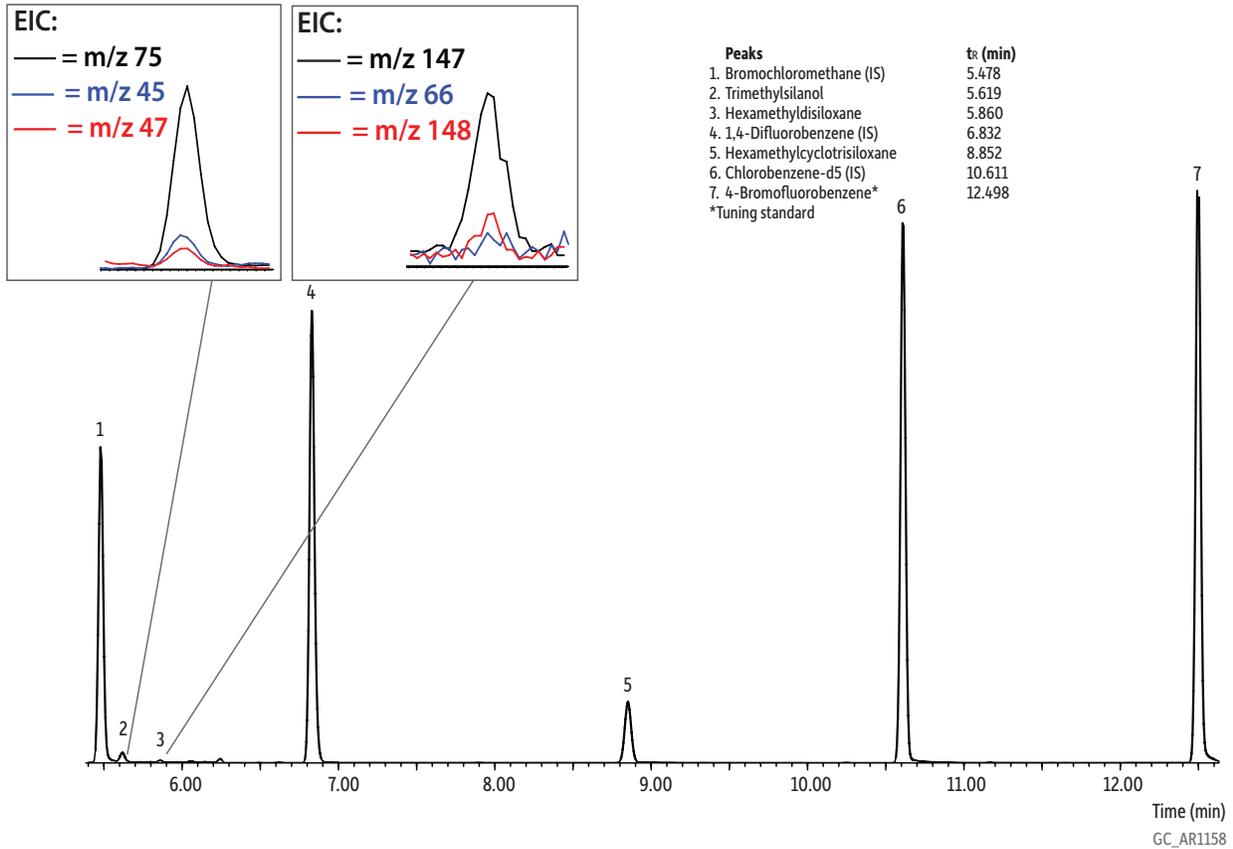
As shown in Figure 2, TMS was stable in canisters for up to three days (73% recovered). Beyond three days of storage, sample recovery dropped off to ~20–30% recovery and then appeared to stabilize. This apparent stabilization of TMS after one week of storage is consistent with Lee et al.'s [2] observation for TMS on solid sorbents.

The boxplots in Figure 3 suggest canister type has an effect on TMS recovery. Although not significantly different ($p = 0.059$ from Kruskal-Wallis test), results indicate electropolished canisters may be associated with higher TMS recoveries. The relatively lower recoveries from silica-lined canister may be explained by the loss of silanols via their reaction with the alkali in glass [13]. Therefore, electropolished canisters are recommended for the sampling, transportation, and storage of trace levels of TMS.

It is important to note that TMS may undergo acid catalyzed dimerization into hexamethyldisiloxane (HMDSO) [5,6]; therefore, HMDSO was monitored (Figure 1, peak 3) during the stability studies to see if the aforementioned mechanism explained the loss of TMS. Although HMDSO was observed in all of the stability samples, the concentration of HMDSO did not change with time, suggesting the TMS loss mechanism was not associated with HMDSO formation. The presence of HMDSO in all of the stability samples was attributed to the formation of HMDSO in the neat TMS standard used to prepare the samples.

The boxplots in Figure 4 suggest RH has an effect on TMS recovery. Results indicate higher RH is associated with higher TMS recoveries ($p = 0.007$ from Kruskal-Wallis test). The relatively lower recoveries associated with low RH have been reported previously for other VOCs [15]; however, it is not clear as to whether the low RH is causing lower recoveries due to losses during storage or perhaps an inefficiency during preconcentration. Regardless, the sampling and transportation/storage of TMS in canisters is not likely to be done in 20% RH based on semiconductor cleanroom environments that range from 30-50% RH [13]. Evaluating 20 and 93% RH was done only to examine TMS stability in canisters at the more extreme ends of the RH spectrum. Considering the aforementioned and that TMS exhibited slightly better stability in electropolished canisters, the stability of TMS was evaluated in electropolished canisters at 45% RH. Results indicate 84% of TMS could be recovered after four days of storage in electropolished canisters at 45% RH.

Figure 1: Chromatogram of 400 mL of 47.6 pptv TMS and 100 mL of 20.0 ppbv internal standard mix.



Column Rtx®-VMS, 30 m, 0.25 mm ID, 1.40 µm (cat.# 19915)
Sample Trimethylsilanol
 TO-14A internal standard/tuning mix (cat.# 34408)
Diluent: Nitrogen
Conc.: See notes
Injection Direct
Oven
 Oven Temp.: 32 °C (hold 1 min) to 150 °C at 8 °C/min to 230 °C at 33 °C/min
Carrier Gas He, constant flow
 Flow Rate: 1.2 mL/min
 Linear Velocity: 40 cm/sec @ 32 °C
Detector MS
 Mode: SIM
 SIM Program:

Group	Start Time (min)	Ion(s) (m/z)	Dwell (ms)
1	0.00	49, 130, 128, 51, 75, 45, 47, 59, 147, 73, 148, 66	25
2	6.25	114, 63, 88, 57	50
3	7.00	207, 208, 96, 191	50
4	10.00	117, 82, 52, 54	50
5	12.00	50, 75, 95, 96, 173, 174, 175, 176, 177	25

Transfer Line Temp.: 230 °C
 Analyzer Type: Quadrupole
 Source Temp.: 230 °C
 Quad Temp.: 150 °C
 Solvent Delay Time: 1.00 min
 Tune Type: BFB
 Ionization Mode: EI
Preconcentrator Nutech 8900DS
Trap 1 Settings
 Type/Sorbent: Siltek®-treated glass beads
 Cooling temp: -155 °C
 Preheat temp: 5 °C
 Preheat time: 0 sec
 Desorb temp: 20 °C
 Desorb flow: 5 mL/min
 Desorb time: 360 sec
 Bakeout temp: 200 °C

Flush flow: 120 mL/min
 Flush time: 60 sec
 Sweep flow: 120 mL/min
 Sweep time: 60 sec
Trap 2 Settings
 Type/Sorbent: Tenax® GR
 Cooling temp: -35 °C
 Desorb temp: 190 °C
 Desorb time: 30 sec
 Bakeout temp: 200 °C
 Bakeout time: 10 sec
Cryofocuser
 Cooling temp: -160 °C
 Inject time: 140 sec

Internal Standard
 Purge flow: 100 mL/min
 Purge time: 6 sec
 Vol.: 100 mL
 ISTD flow: 100 mL/min

Standard
 Size: 200 mL
 Purge flow: 100 mL/min
 Purge time: 6 sec
 Sample flow: 100 mL/min

Instrument Notes
 HP6890 GC & 5973 MSD
 400 mL of 47.6 pptv trimethylsilanol and 100 mL of 20 ppbv internal standards prepared at 45% relative humidity (RH).

Acknowledgement Nutech Instruments/EST Analytical

Figure 2: TMS stability in silica-lined and electropolished canisters at 20 and 93% RH. Each data point represents the mean recovery from eight canisters and errors bars represent standard deviation.

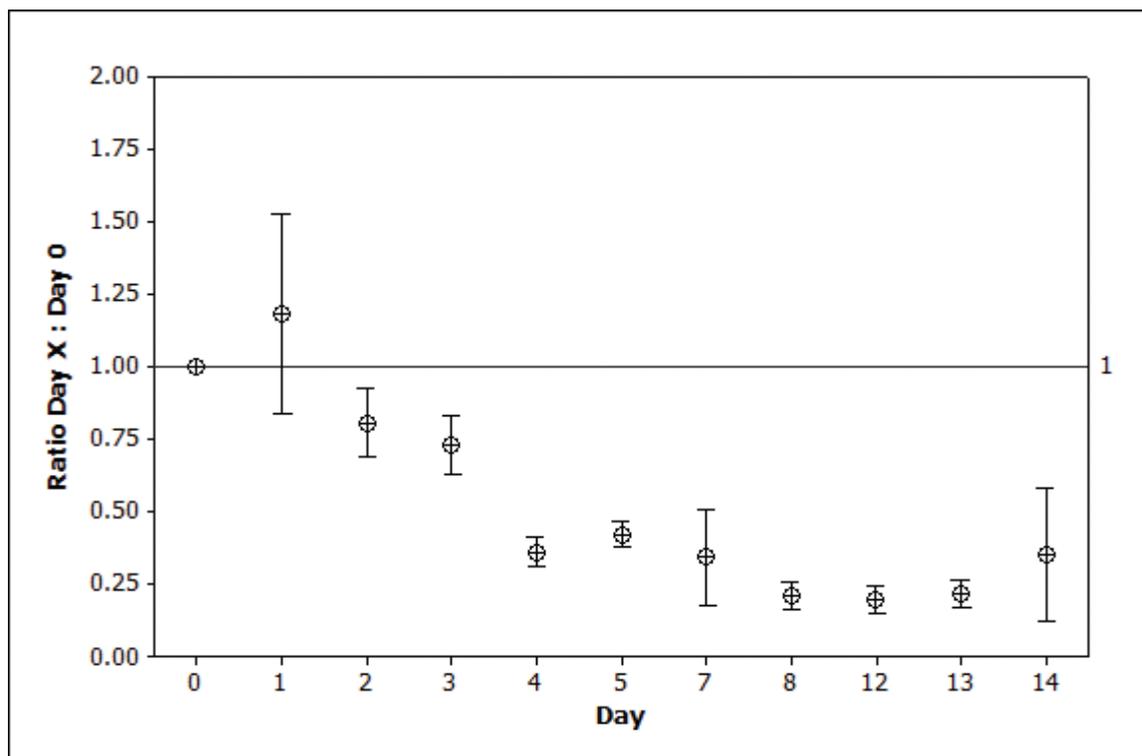


Figure 3: Boxplots comparing TMS recovery on day 14 in silica-lined and electropolished canisters spiked with 5 pptv TMS. * Represents outlier.

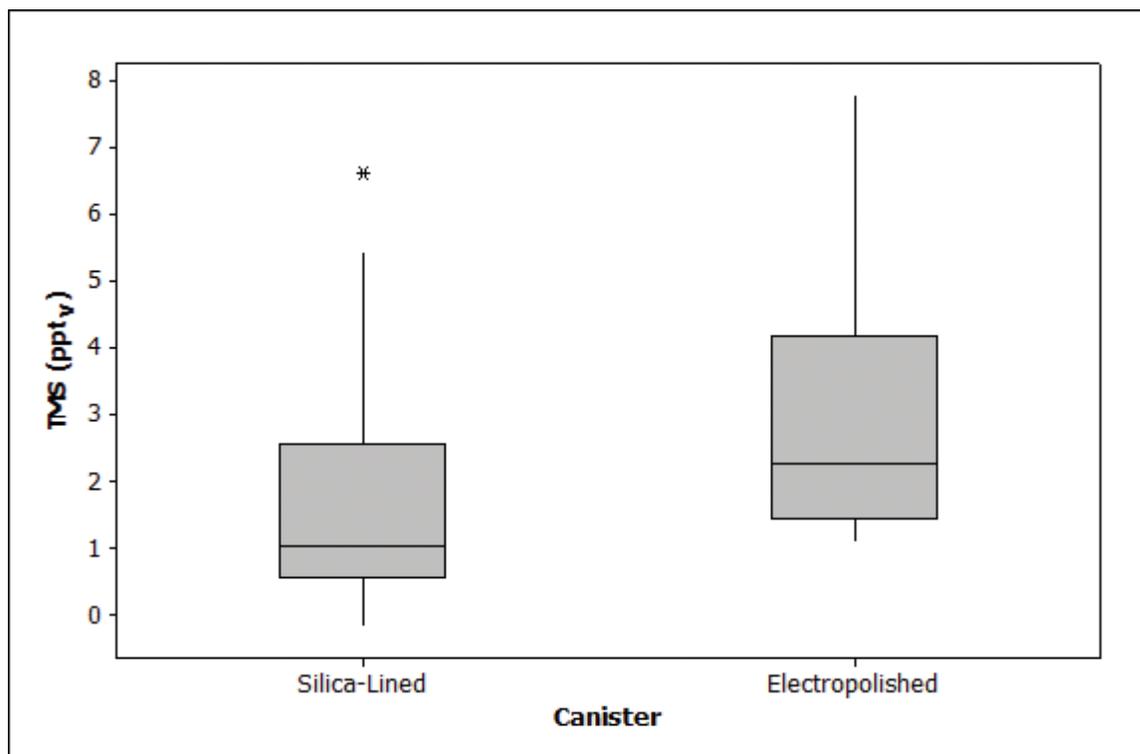
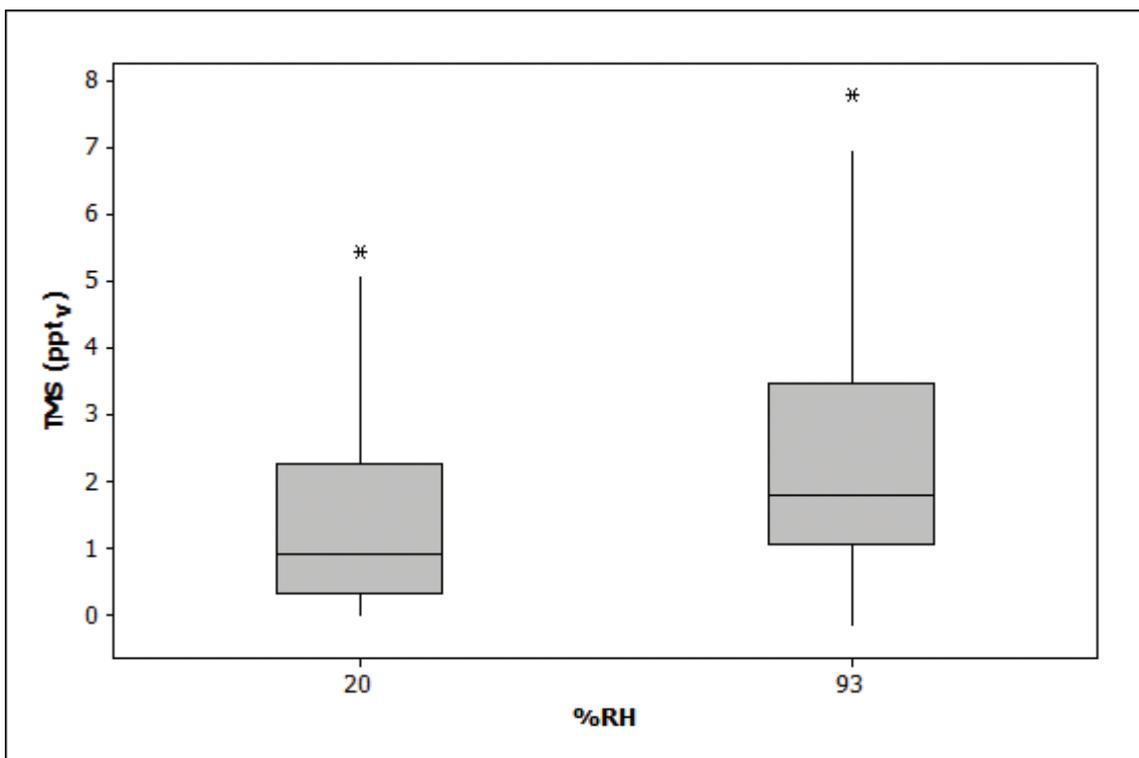


Figure 4: Boxplots comparing TMS recovery at 20% and 93% RH on day 14 in canisters spiked with 5 pptv TMS.
* Represents outlier.



Conclusion

Issues with trimethylsilanol optics haze have created a need for TMS methods in the semiconductor industry. A whole air canister-based method has been developed for TMS at trace levels (i.e., pptv [$\sim\text{ng}/\text{m}^3$]). This is the first method of its kind capable of such sensitivities and, when coupled with near instant (i.e., ~ 10 seconds) grab samples, it allows for the rapid screening of cleanrooms. Results demonstrate clean canister blanks (0.06 pptv, which is below detection limit [BDL]); excellent linearity (a calibration relative response factor [RRF] relative standard deviation [RSD] of 9.8%) over a wide dynamic mass range (1.0 to 100 pptv); recovery/accuracy of 93%; a low selected ion monitoring (SIM) method detection limit (MDL) of 0.12 pptv; replicate precision of 6.8% RSD; and stability out to four days of storage at room temperature. These performance levels will meet the demands of the semiconductor industry for monitoring traces levels of trimethylsilanol in cleanrooms.

Acknowledgments

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