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Settings for TD-GC-MS

Table 1 TD-GC-MS settings for Sorbent tube analysis

TD100-xr	Setting	Value
Tube desorption	Desorb time 1 (min)	10
	Desorb temp (C)	300
	Trap in line – Trap flow (ml/min)	50
Pre-desorption	Dry purge time (min)	3
	Purge flow (mL/min)	50
Desorb Trap	Trap Purge time (min)	1
	Trap purge flow (mL/min)	50
	Trap low temp (C)	-20
Elevated trap purge	Elevated trap purge temp (C)	5
	Trap heating rate (C/s)	MAX
	Trap high temp (C)	320
	Trap desorb time (min)	3
	Desorb split on (Split flow mL/min)	10
General	Flow path temp (C)	160
	Min. carrier pressure (psi)	5
PolarisQ	Ion source (C)	250
	Start time (min)	0.4
	Full Scan (*m/z*)	45-250
TraceGC 2000	Oven Temp program Initial (C) 32	Hold (min) 2
RAMP1	Rate C/s 8.0 Temp (C) 170	Hold (min) 0.50
RAMP2	Rate C/s 20.0 Temp(C) 290	Hold (min) 2
Injector settling	Inlet Temp (C)	110
Constant flow	Flow (mL/min)	1.2

Determining detection and quantitation limits pre and post instrument maintenance.

During the normal calibration routine, slopes are monitored for changes in sensitivity over time. Additionally, calibrations are done before and after instrument maintenance to assess the change in sensitivity after ion source cleaning in the PTR-ToF-MS. This was done in May 2024, since sampling at WWTPs have generally high concentrations of VOCs in their sampling locations, so fouling of the ion source can occur. Limits of detection limits (LOD) and quantification (LOQ) were determined using Equation 5 and Equation 6, respectively.[61] These numbers are highlighted in the Table 2 below. The standard deviation of the low concentration signals was decreased after cleaning indicating a steadier signal is achieved. The loss of sensitivity for some compounds may be due to the calibration generator (DynaCal 320, VICI Metronics, Washington, USA), as the zero air was supplied by the onboard scrubber and can fluctuate slightly effecting the blank-standard deviation.

$$LOQ = 10\ x\ \left(\frac{s_{a,zero}}{Slope_a}\right) \qquad (6)$$

Table 2 Limits of detection and quantification for Dimethyl sulfide, Methanethiol and ethyl benzene before and after ion source cleaning. Showing % change of LOD and LOQ from before to after cleaning. R# denotes the replicate number.

Dimethyl sulfide (*m/z* 63.02)	R1	R2	R3	Avg Slope	Stdev.$_{ZERO}$ $(s_{a,zero})$	Stdev. Normalized Signal$_{Low\ conc.}$	DL$_{ppbv}$	LOQ$_{ppbv}$
before cleaning	29.13	29.37	30.82	29.77	1.44	6.82	0.14	0.48
after cleaning	26.21	24.92	n/a	25.56	2.5	2.89	0.29	0.97
Methanethiol (*m/z* 49.01)								
before cleaning	19.99	20.18	21.09	20.42	1.19	7.96	0.17	0.57
after cleaning	17.72	16.91	n/a	17.31	1.33	6.46	0.23	0.78
Ethyl benzene (*m/z* 107.08)								
before cleaning	12.08	12.74	11.76	12.19	1.28	3.15	0.31	1.04
after cleaning	11.33	11.44	11.46	11.41	1.09	0.40	0.28	0.95

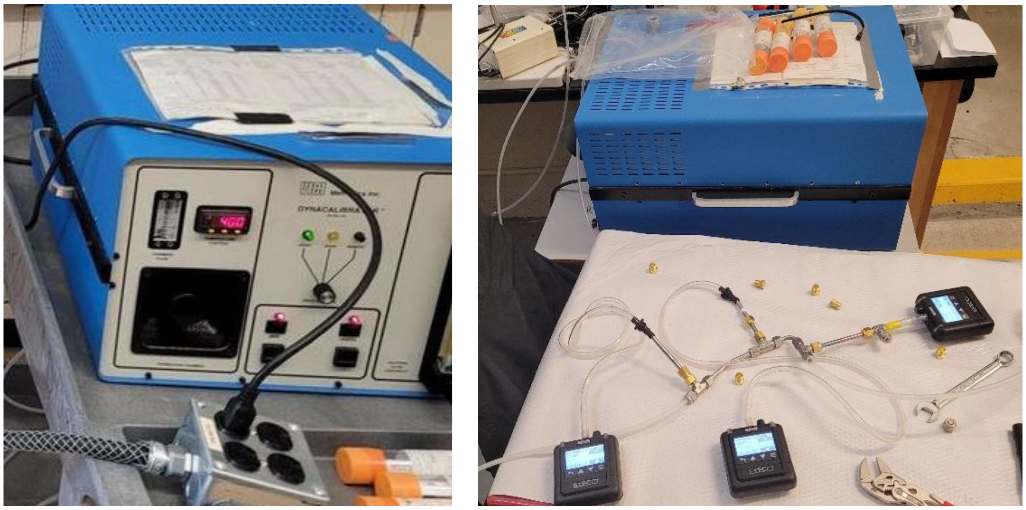

Figure 1 (Left) Photo of Dynacal 320 permeation tube calibration unit (VICI Metronics, Washington, USA). (Right) Dynacal 320 plumbed to Pocket pumps and sorbent tubes during calibration.

Investigation of humidity effects on sensitivity for organosulfur compounds using PTR-ToF-MS

Table 3 Proton affinities and humidity effects on calibration slopes using the PTR-ToF-MS for methanethiol, ethanethiol, dimethyl sulfide and dimethyl disulfide.

Compound	Mass to charge (*m/z*)	Proton affinity (kj/mol)[62]	Calibration slope Sensitivity ncps/ppbv	
			Normal <50%RH	Humid >99%RH
Water $(H_2O)H^+$	19.02	697		
Methanethiol *MeSH*$(CH_3S)H^+$	49.01	773	12.11	7.29 *(-40%)*
Ethanethiol *EtSH*$(C_2H_6S)H^+$	63.02	798	8.25	5.81 *(-29%)*
Water dimer $(H_3O^+ + H_2O)$	37.03	808		
Dimethyl disulfide *DMDS* $(C_2H_6S_2)H^+$	94.99	815	21.23	23.30 (+10%)
Dimethyl sulfide *DMS* $(C_2H_6S)H^+$	63.02	830	27.05	27.36 *(+1%)*

**Highlighted regions showing calibration slopes are from experimental data. Data shown is same data as in Figure 2.*

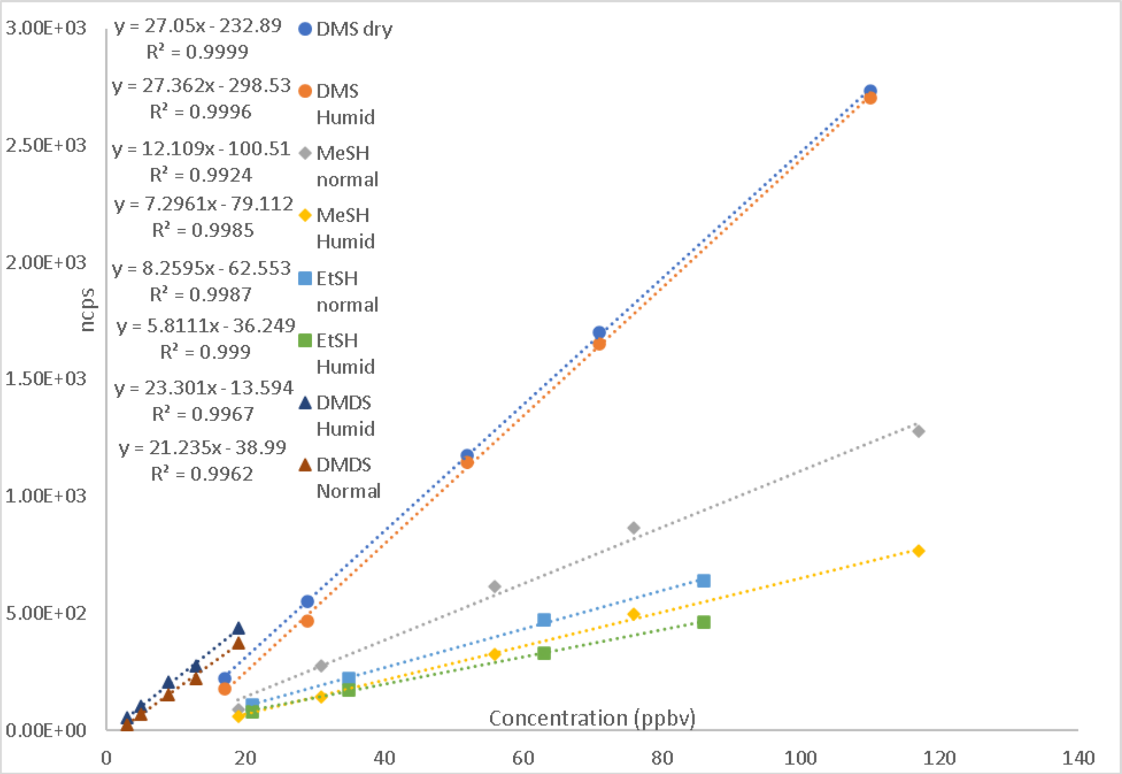

*Figure 2 Calibration data for humidity experiments using PTR-ToF-MS, from Table 2. *Dry <35% RH, normal 35-50% RH, Humid >99% RH. Calibration ranges were limited by permeation tubes concentrations.*

Investigation of used sorbents from WWTP3 (1C)

The dynamic headspace investigation of the used sorbents from the activated carbon scrubber was done using 40 mL TOC vials, containing 10 g of used sorbent (Sulfasorb-XL, Azzuro, AZ, USA) from the primary odour control (1C). An inlet line was setup going into the top of the sealed vial from an ultra-zero air cylinder (Linde, Canada) and a sample line out of the vial, with flows of 300 ml/min in and out of the vial and to the PTR-ToF-MS, where measurements were made of the VOCs coming from the headspace of the TOC vial. The configuration of the scrubber towers flows foul air in through the middle of the tower and out on the peripheries, so the sorbents in the middle of the tower are in more contact with the VOCs then the peripheries of the tower. Therefore, the sorbents should become spent in the mid-tower first. This is seen in the sampling of the sorbents, with the sample taken from mid-scrubber having very high concentrations of reduced sulfur compounds (5500 ppb$_v$ DMDS) compared to near the bottom of the scrubber (350 ppb$_v$ DMDS), which is further away from the injection point (Figure 3). This sampling was interesting as the input concentrations of methanethiol to the scrubbers is on average 500 ppb$_v$ while DMDS is about 20 ppb$_v$ (Main document, Figure 29). This suggests that sorbed methanethiol may be converting to dimethyl disulfide on the sorbent over time, increasing the concentrations seen of DMDS and lowering the concentrations of MeSH. Finding higher concentrations of DMDS post-treatment could be an indication of sorbents becoming spent and in need of replenishing.

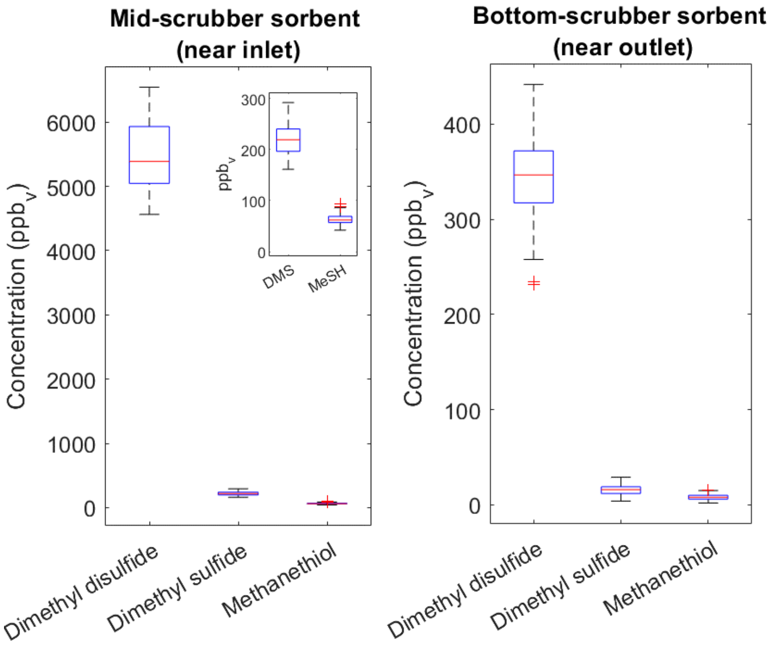

Figure 3 Dynamic headspace sampling of spent sorbents from WWTP3, showing boxplots of DMDS, DMS and MeSH. Foul air flows through the middle of the tower and out of the top and bottom of the tower.

Bench scale experiment investigating transformation of methanethiol to dimethyl disulfide

A bench scale flow through experiment was done to confirm that conversion of methanethiol to dimethyl disulfide was possible under the conditions at WWTP3. The experiment was setup using the DynaCal 320 calibration gas generator to provide a constant amount of methanethiol to a flow tube filled with fresh sorbent (CPS-12, Trane) obtained from WWTP3, to simulate conditions in their secondary treatment media scrubber system (Figure 4). The gas flow was passed through the sorbent, then to the PTR-ToF-MS for monitoring VOCs. The setup included an inline vessel containing clean water to increase humidity in the gas flow and was monitored by the GHG analyzer to assess humidity levels (>70%). During the experiment, sample gas containing only methanethiol was flowed into a flow tube containing packed clean sorbent and was monitored for breakthrough of methanethiol and for dimethyl disulfide production. The sorbent packed flow tube was provided methanethiol at 50 $\mathrm{ppb_v}$ for about 20 minutes then was switched to 240 $\mathrm{ppb_v}$ methanethiol, to help expedite the process (Figure 5). Once at 240 $\mathrm{ppb_v}$ it was held constant at this concentration until the final step where clean zero air was flushed through the flow tube. During the experiment the flow tube was heated externally up to 40-50°C three times throughout, twice while under humid conditions and once while under dry conditions (<50% RH) and finally clean zero air was flowed through the sorbent flow tube. After increasing the concentration of methanethiol to 240 $\mathrm{ppb_v}$ it was seen that breakthrough of methanethiol (>0.5 $\mathrm{ppb_v}$) began and some indication of DMDS (0.5 $\mathrm{ppb_v}$) was apparent (Figure 5). After 15 minutes of flowing the methanethiol at 240 $\mathrm{ppb_v}$ through the flow system it was at a relatively stable level from minute 30-45 (Figure 5), then the flow tube was heated and an elevated concentration of DMDS (2.5 $\mathrm{ppb_v}$) was observed in conjunction with a decrease of methanethiol signal, indicating conversion of MeSH to DMDS. To investigate the influence of temperature on this reaction, the flow tube was heated to 40°C and held for 25 minutes. At this temperature the DMDS concentrations were slowly rising (0.5 →1 $\mathrm{ppb_v}$) during this process (Figure 5). At approximately minute 70 the humidity was reduced (<50%) and DMDS concentrations went down, and MeSH was again apparent (>0.5 $\mathrm{ppb_v}$). The flow tube was left to cool for a few minutes then the system was heated back up to 50°C and then left to cool to room temp (20°C), where a spike of DMDS (>1 $\mathrm{ppb_v}$) was seen then it decreased as it cooled (Figure 5). Finally, zero air was introduced into the flow tube and the signal for both compounds were observed to drop below detection limits. The observations here using sorbents from WWTP3 are consistent with the results reported by Hayashi *et al.* 2010.[36] These findings also suggest a link between humidity and temperature for conversion of methanethiol to dimethyl disulfide in this media scrubber system, which could be influenced by ambient temperatures, humidity in the gas stream and by sorption processes which may release heat.

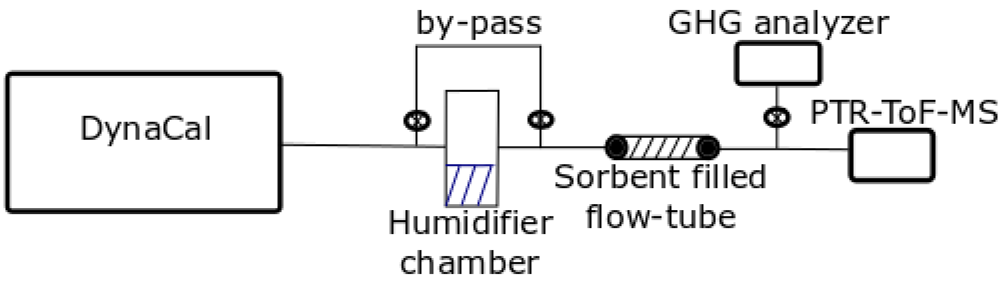

Figure 4 Bench scale flow tube sampling setup, small circles with an x denote switches to redirect flow.

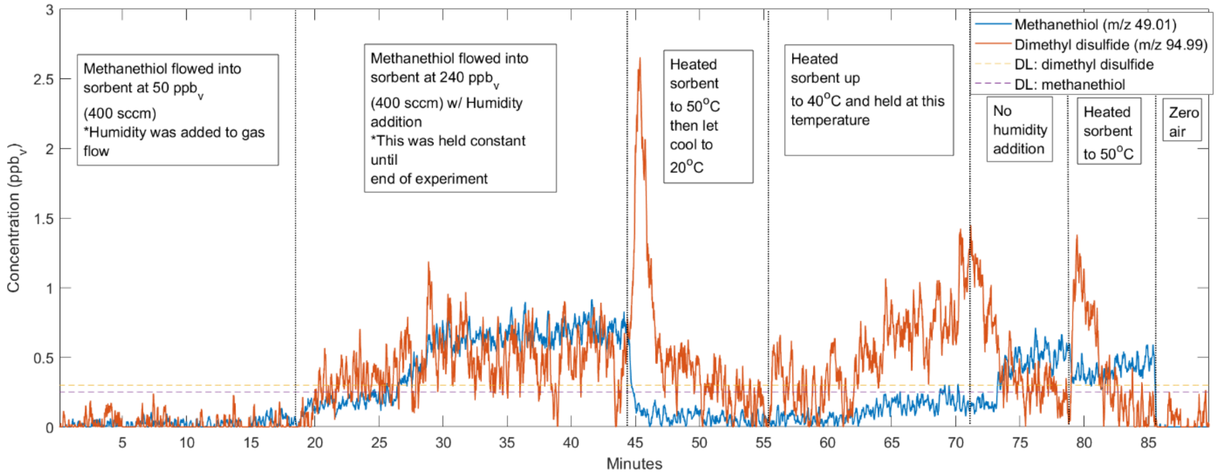

Figure 5 Timeseries from bench scale flow-tube experiment for dimethyl disulfide generation from methanethiol. Detection limits are shown by horizontal dashed lines. Methanethiol in blue, dimethyl disulfide in orange.