

Analysis of Vehicle Interior Air Quality (VIAQ) using SIFT-MS

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Introduction

Vehicle interior air quality (VIAQ) has been of concern to both car manufacturers and the public for some time, along with the possible health impact of this “new car smell”. This has led to several countries imposing concentration limits on a range of volatile organic compounds (VOCs), an example of which can be seen in Table 1. The current analytical methodologies are centered on either GC-MS or HPLC based technologies, which are relatively slow and can be expensive to run. They also suffer from potential discrimination of difficult compounds, such as small polar compounds like formaldehyde or acrolein.

Compound ($\mu\text{g}/\text{m}^3$)	China	Japan	Korea
Formaldehyde	100	100	250
Acetaldehyde	50	48	No set limit
Acrolein	50	No set limit	No set limit
Benzene	110	No set limit	30
Ethylbenzene	1500	3800	1600
Xylene	1500	870	870
Styrene	260	220	300
Toluene	1100	260	1000
Tetradecane	No set limit	330	No set limit

Table 1 – Maximum permissible concentrations ($\mu\text{g}/\text{m}^3$) for the Chinese, Japanese and Korean VIAQ Standards.

This application note demonstrates the use of SIFT-MS to analyse the interior air quality of a vehicle over 5 hours of ambient heating in a carpark, followed by a continuous measurement of a 15 minute vent cycle. As well as demonstrating the ease of analysis that SIFT-MS offers, the final vent cycle shows some unusual behavior that could be missed using the standard tube sampling chromatography methods.

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is a form of direct mass spectrometry that uses precisely controlled soft ionisation to enable real-time, quantitative analysis of volatile organic compounds (VOCs) in air, typically at detection limits of parts-per-trillion level (by volume; pptv). This eliminates the need for sample preparation, pre-concentration and chromatography. Figure 1 shows a schematic of the instrumentation.

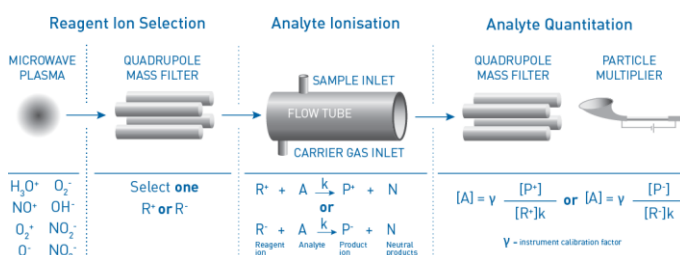


Figure 1: Schematic representation of the SIFT-MS technique.

Reagent ion selection – A microwave discharge through moist air forms the standard SIFT-MS positive and negative ions; H_3O^+ , NO^+ , O_2^+ , OH^- , O_2^- , O^- , NO_2^- and NO_3^- and these are then selected using a quadrupole mass filter.

Analyte ionization – The selected reagent ion is injected into the flow tube and excess energy is removed through collisions with the carrier gas (either nitrogen or helium). The sample is then introduced and an ion-molecule reaction takes place to form well-characterised product ions.

Analyte quantitation – Product ions and unreacted reagent ions pass into a second quadrupole mass analyser and the analyte concentration is calculated as a ratio of product ions to reagent ions multiplied by a rate constant, k , unique to that ion-molecule reaction.

The use of eight, selectable reagent ions, coupled with a library of known reaction products and reaction rates enables SIFT-MS to quantify multiple analytes, in real-time, without the need for prior chromatographic separation.

Instrumentation

Syft Technologies' Voice 200ultra running LabSyft software (version 1.6.2). Helium carrier gas, HPI inlet, pumped flow-pass method at 1L/min.

Method

The vehicle to be tested was a small 4-door hatchback, less than one year old. It was parked in the carpark outside the laboratory in early summer in sunshine (ambient temperature approx. 20°C). A 20m length of ¼" Teflon tubing was attached at head height to the driver's seat headrest and run out of the rear door, taking care not to compress the tubing, and back to the laboratory (see figure 2 – the tubing is exiting the rear door). The car doors and windows were closed and the car was allowed to heat, as the prevailing weather conditions allowed.



Figure 2 – Vehicle under test conditions. Note the tubing exiting from the rear door on the left of the picture.

In order to transfer the interior air, to the SIFT-MS, with the minimum of residence time in the tubing, a flow-passed approach was used. The tubing was attached to a Swagelok T-piece fixed to the SIFT-MS HPI inlet and a pump was attached downstream from the T-piece. The pump was set to pump at 1L/min, which led to a residence time of less than 5 seconds in the tubing.

The SIFT-MS sampled the analyte stream at 25 mL/min with the remainder going to waste. The inlet set-up is shown in figure 3.

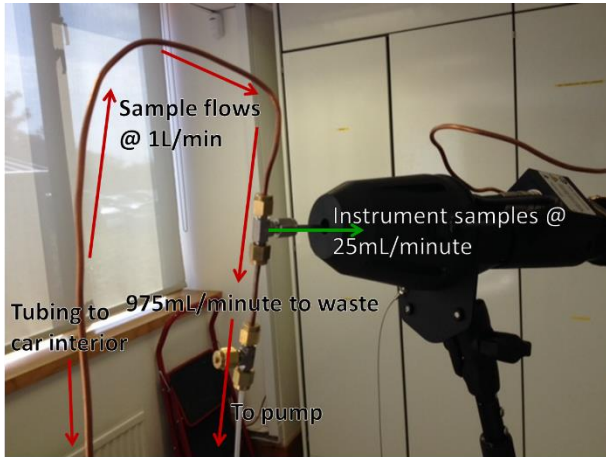


Figure 3 – Flow-passed inlet system used to sample the interior air of the vehicle.

A method was created to analyse the compounds listed in Table 1 (with the exception of tetradecane), as well as acetone, methanol, propanal, butanal and pentanal. Both H_3O^+ and NO^+ were used as reagent ions and the dwell time for detection was 100 ms per product ion. In order to minimise the extraction of air from the vehicle cabin (continuous sampling for 5 hours would remove 300 L of air), the method was run every 15 minutes for 60 seconds and the measured concentrations taken as the mean across the 60 second measurement.

For the final 15 minute vent cycle, the car windows were opened, the car started and the air conditioning run at full power. The SIFT-MS then sampled continuously using the above conditions for the full 15 minutes.

Results

Table 2 shows the analyte concentrations, in $\mu g/m^3$, at the beginning of the test and after 5 hours of ambient heating. Figures 4 and 5 show the SIFT-MS plots for both of these analyses. Figures 6a and 6b show the progress of the analysis over 5 hours, with the prevailing weather conditions shown. Figure 6b has the two highest VOC concentrations removed to more clearly show the lower concentration analytes.

Compound ($\mu g/m^3$)	Time = 0 hours	Time = 5 hours
Formaldehyde	17	51
Acetaldehyde	27	125
Acrolein	3	19
Benzene	17	15
Ethylbenzene + xylenes	11	59
Toluene	9	69
Styrene	22	35
Acetone	12	576
Methanol	18	935
Propanal	8	65
Butanal	8	61
Pentanal	8	117

Table 2 – Concentrations ($\mu g/m^3$) of analytes at start of analysis and after 5 hours of ambient heating.

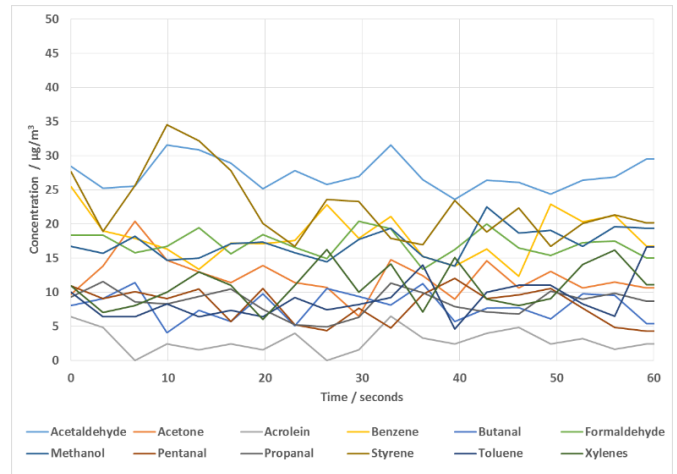


Figure 4 – Plot of 60 second measurement of car interior at start of analysis.

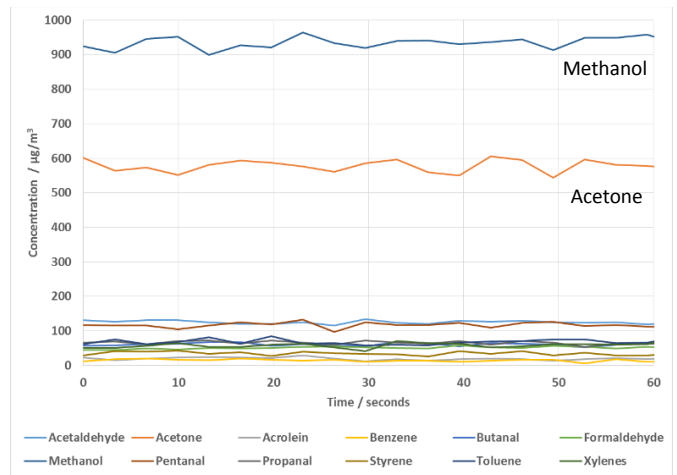


Figure 5 – Plot of 60 second measurement of car interior after 5 hours of ambient heating.

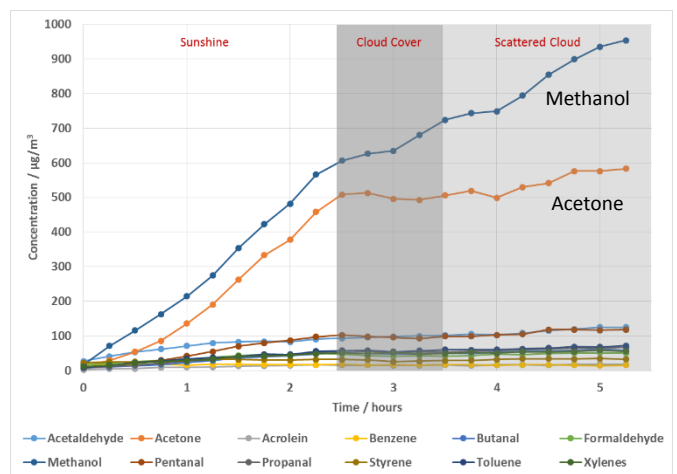


Figure 6a – Analyte concentrations over 5 hours of measurement – note the effect that the prevailing weather conditions had on the release of VOCs.

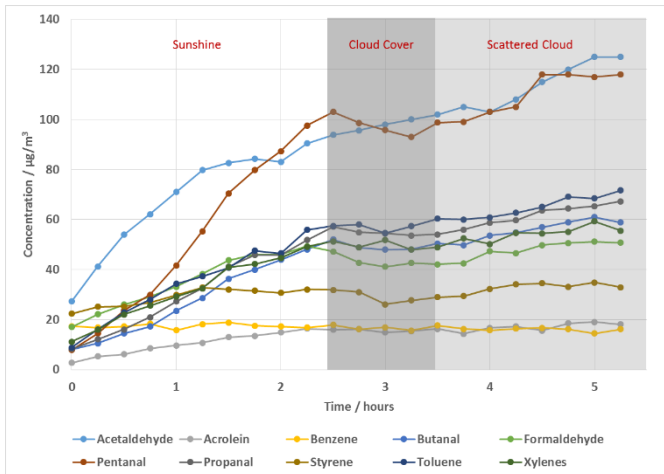


Figure 6b – Expanded plot of figure 6a, showing the lower concentration VOCs.

It can be seen from figures 6a and 6b and Table 2 that over the course of 5 hours all VOCs increase in concentration apart from benzene, with methanol and acetone being significantly higher. It is worth noting that both these compounds do not appear in the VIAQ lists in Table 1. Also, there is a direct correlation between increasing concentration and weather conditions. As expected, the greatest rise occurs in direct sun and that the release of VOCs stops in cloudy conditions.

Following the 5 hour heating cycle, a 15 minute vent cycle was performed. Figure 7 shows the continuous concentration profile for this, with the analyte concentrations at the start and end of the vent cycle, the maximum concentration seen, and percentage difference, and a 15 minute time-weighted average (TWA) concentration for each analyte tabulated in Table 3. A graphical representation of this is shown in figure 8.

It can be seen from figure 7 that there was an initial fast drop in concentration for all analytes, which would be expected as all the windows were open in the car. What was not expected was the subsequent rise in concentration for a number of the analytes that occurred between 4 and 8 minutes in the vent cycle. Of particular note is the large, temporary increase in acetaldehyde concentration, significantly above the permissible limits shown in Table 1.

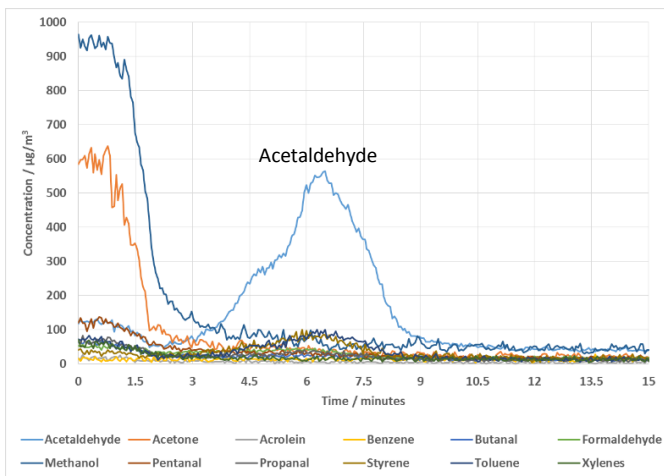


Figure 7 – Continuous measurement of VOC concentrations over a 15 minute vent cycle of the car cabin.

Compound (µg/m³)	Start	Max.	% diff.	Final	TWA 15 min
Formaldehyde	54	58	7	15	29
Acetaldehyde	118	564	378	37	150
Acrolein	17	28	65	0.1	7
Benzene	16	29	81	3	14
Ethylbenzene + xylenes	61	71	16	3	20
Toluene	73	101	38	6	35
Styrene	40	101	153	6	34
Acetone	585	637	9	11	92
Methanol	963	963	0	30	168
Propanal	66	83	26	7	24
Butanal	63	66	5	8	23
Pentanal	121	138	14	10	36

Table 3 – Start, maximum, % difference, final and 15 min time-weighted average concentration (µg/m³) for a 15 minute vent cycle.

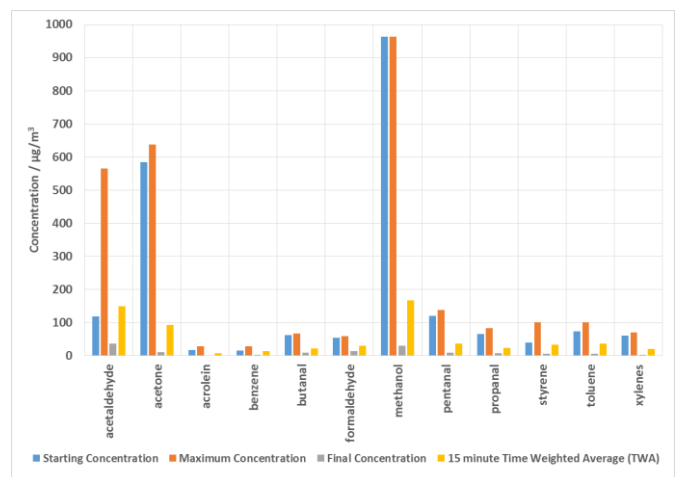


Figure 8 – Graphical representation of Table 3.

From Table 3, it is clear that all analytes, except for methanol show a higher maximum concentration than starting concentration. This is particularly significant for acetaldehyde, styrene and toluene. An interesting observation is the benzene concentration, which did not appear to rise at all during the heating cycle, but shows a clear increase during the vent cycle. The difference between starting and maximum concentration for all analytes is clearly observable in figure 8, with the blue bar representing the start and the orange bar showing the maximum concentration seen.

Discussion

It can be seen from the above data that SIFT-MS is a highly effective way to monitor car cabin VOC concentrations for VIAQ applications, even for difficult analytes, such as small oxygenated species like formaldehyde and acrolein. Of particular interest is the ability of SIFT-MS to follow dynamic concentration changes in real-time, giving rise to the unexpected observations seen in the above 15 minute vent cycle. One possible explanation for the peak in concentrations seen, is that the vehicle ventilation system acts as a sink for these VOCs, which are then released when the air-conditioning is activated. It is worth noting that the usual sorbent tube and single point time-weighted average approach would not be an accurate representation of the behaviour seen here, potentially demonstrating the limitations of the current Thermal Desorption GC-MS approach to VIAQ measurements.