

# Ultra-Trace Real Time VOC Measurements by SIFT-MS for VIAQ

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## ABSTRACT

Vehicle interior air quality (VIAQ) measurements are currently conducted using the offline techniques GC/MS and HPLC. To improve throughput, speed of analysis, and enable online measurement, specialized instruments are being developed. These instruments promise to reduce testing cost and provide shortened analysis times at comparable accuracy to the current state of the art offline instruments and methods. This work compares GCMS/HPLC to the Voice200*ultra*, a specialized real-time instrument utilizing the technique selected ion flow tube mass spectrometry (SIFT-MS). The Voice200*ultra* is a real-time mass spectrometer that measures volatile organic compounds (VOCs) in air down to the parts-per-trillion level by volume (pptv). It provides instantaneous, quantifiable results with high selectivity and sensitivity using soft chemical ionization. The VOC measurement capabilities of the Voice200*ultra* is being compared to gas chromatography-mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC), which are the internationally accepted industry standard. In this study, we compare the analytical capabilities of SIFT-MS to the accepted standard measurement techniques by GCMS/HPLC by measuring the VOCs in new vehicle interiors. We quantify formaldehyde, acetaldehyde, benzene, toluene, ethylbenzene, xylene, styrene, and acrolein (the eight chemicals found in the GB list specified by the Chinese government) as well as many other compounds, including acetone and butanone. The comparability between SIFT-MS and GCMS/HPLC is excellent with an average  $R^2$  values of at least 0.89 for all compounds excluding formaldehyde and acrolein. This excellent correlation demonstrates that the Voice200*ultra* is able to accurately measure these target species with excellent selectivity in the complex sample matrix of a new car cabin interior. Levels of acrolein and formaldehyde as measured by HPLC were extremely low and the lack of correlation for these two compounds is attributed to the intrinsic issues with the HPLC technique for the measurement of these compounds.

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## INTRODUCTION

Measurement of Volatile Organic Chemicals (VOCs) and odorants has become a customer satisfaction and regulatory requirement in the Asia-Pacific region and elsewhere. Both target compounds of potential concern, residual solvents, and minor chemical constituents all are potential sources of odor to customers. The VOCs and odorants of interest cover a broad range of chemical types, which creates a significant measurement challenge. Offline analysis using GC/MS and HPLC/UV-vis are the industry standard approach, but to decrease the time between measurement and data review, alternative instrumental methods are under development.

One such method is based on selected ion flow tube mass spectrometry, or SIFT-MS [1]. This is a form of direct mass spectrometry that can analyze trace amounts of VOCs and gases. It can perform real-time, quantitative analysis at the parts-per-trillion

level by volume. It uses chemical ionization reactions coupled with mass spectrometric detection to rapidly quantify VOCs. The VOCs are identified and quantified in real time from whole-gas samples based on the known ion-molecule reaction rate coefficients for reaction of the chemically ionizing species (reagent ions) with the target analytes.

The most common reagent ions used are  $H_3O^+$ ,  $NO^+$  and  $O_2^+$ , which react with trace VOCs in well-characterized ways, but do not react with the major components of air. Generally, the soft chemical ionization used in SIFT-MS yields a smaller range of product ions, and predominantly molecular or pseudomolecular ions. This is in contrast to electron impact mass spectrometry (as used in GC/MS, for example). Hence the need to separate chemicals using chromatography is circumvented, speeding sample throughput and providing simultaneous quantification of many VOCs. Use of several

reagent ions to independently quantify target analytes also reduces interferences, increasing the specificity of SIFT-MS versus competing whole-gas analysis technologies.

In comparison, gas chromatography-mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) are currently the internationally accepted “gold standard,” used to analyze VOC levels from vehicle interior air. They are both offline batch-only techniques requiring preconcentration of the analytes. Neither is used to individually provide analysis for all the compounds of interest. Formaldehyde, acrolein, and molecules smaller than C6 and polars are not measured by the current VIAQ GC/MS method, so HPLC/UV-vis is used to quantify DNPH-CHOs.

Vehicle interior air quality (VIAQ) is of concern because there are many volatile organic compounds that are released into the interior vehicle cabin air. These VOCs are generated and released from interior organic polymer materials such as adhesives, fabric, plastic, and polyurethane foam as they age. The VOCs diffuse from their source to the surface of the component, at which point they diffuse into the cabin air. VOC levels in the interior air of new cars are targeted by regulations.

## MATERIALS AND METHODS

The VOC levels in four vehicles were monitored by GCMS/HPLC and SIFT-MS. These vehicles were conditioned with doors closed and windows rolled up and tested in a temperature and humidity controlled environment at Allen Park Test Lab. The vehicles were prepared for testing by removing shipping covers from interior parts and by installing the floor mats. A length of ¼ inch high density polyethylene (HDPE) tube was placed in the vehicle. The inlet of the sampling line is located near the position of the driver’s nose and the outlet of the tube is external to the vehicle, passing through a door compression seal.

The standard procedure for collecting interior air samples from the vehicle is as follows: Open all vehicle doors for four hours to allow the vehicle to equilibrate with its surroundings. Next, the doors are closed for a sixteen-hour equilibration period. After the equilibration period, a pump automatically turns on to pull vehicle cabin air for thirty minutes through the HDPE tube into the sampling cart, where it is split into two streams. One stream enters the SIFT-MS for analysis, and the other stream enters the sampling system where discrete volumes are collected onto two thermal desorption (TD) tubes and two DNPH cartridges. The flow rate is 0.83 L/min through the DNPH cartridges and 0.2 L/min through the TD tubes. The tubes and cartridges are evaluated according to internal Ford methods (similar to ISO 16000-3 for HPLC and ISO 16000-6 for GC/MS) by a Ford internal laboratory within a week of collection. They are stored at 2 - 4° C prior to analysis. Samples were periodically collected from the four vehicles over four weeks.

### SIFT-MS

The SIFT-MS evaluated was a Voice200ultra from Syft Technologies. The SIFT-MS is calibrated by controlling gas pressures produced in the reaction chamber, therefore controlling ion transmission

efficiency into the downstream quadrupole. Ion signals from a gas standard are controlled to uniform and consistent day-to-day values during validation. The SIFT-MS converts the ion signal into concentration units. Note that it reports a single value for the sum of ethylbenzene and xylene isomers due to their similar molecular weight.

The Voice200 is validated daily using an independently certified gas standard mixture which validates the mass calibration and quantifies the transmission efficiency through the downstream quadrupole. In SIFT-MS, the ion-molecule reactions inside the flow tube are well understood and occur at known reaction rates. Using these reaction rates, SIFT-MS is able to quantify compounds to an accuracy of ±25% without individual compound calibration. However, SIFT-MS is able to achieve a better accuracy (±5% *rsd*) by performing compound specific calibration using individual, certified gas standards.

The Syft Calibrant Standard (or “Syft Standard”) is a certified gas standard prepared for Syft Technologies. The compounds have been chosen by Syft based on three main factors. The compounds must have:

1. Product masses that are distributed evenly throughout the mass range of the standard quadrupole system for Voice-series instruments.
2. Sufficient volatility and stability for use in a certified gas mixture.
3. Simple SIFT-MS ion chemistry for at least one reagent ion, which ensures the best day-to-day repeatability for benchmarking quantitation.

Table 1 lists components of the Syft Calibrant Standard, in alphabetical order. The balance is nitrogen gas.

Table 1. Components gases in the Syft Calibrant Standard at 25°C, 1 atm.

Compound	Mol. Weight (g/mol)	Conc. (µg/m <sup>3</sup> )	Conc. (ppmv)
Benzene	78	6376	2
Ethylene	28	2289	2
Hexafluorobenzene	186	15205	2
Isobutane	58	4741	2
Octafluorotoluene	236	19293	2
1,2,4,5-Tetrafluorobenzene	150	12262	2
Toluene	92	7521	2

### GCMS/HPLC

To compare and contrast with the SIFT-MS data, aromatic hydrocarbons (benzene, ethylbenzene, xylene, styrene, toluene) were collected onto Gerstel, Inc Carbotrap 300 TD tubes and are measured by GC/MS. These tubes adsorb C2 and larger compounds in air. The carbonyls (acrolein, formaldehyde, acetaldehyde, acetone, butanone) were collected by reaction with DNPH stabilized on silica, subsequently eluted with acetonitrile, and analyzed by HPLC. The equipment used for these analyses is listed below in Table 2. Results from GC/MS are converted from mass values (ng) to the reported concentration values (ug/m<sup>3</sup>) and results from HPLC are converted from ug/ml to ug/m<sup>3</sup>. The duplicate TD and DNPH results are averaged.

Table 2. Equipment used to analyze TD/DNPH samples.

Thermal Desorption System	Gerstel, TDS/TDSA2 with CIS 6
Tube Conditioner	Gerstel TubeConditioner TC
TD Tube	Gerstel Carbotrap 300
GC/MS System	Agilent GC 6890N Agilent MS 5975B VL MSD
DNPH Cartridge	Waters Sep-Pak DNPH-Silica Cartridges Plus-Short Body (360 mg)
HPLC System	Agilent 1100 Deltabond AK Column

### RESULTS AND DISCUSSION

Overall, the SIFT-MS shows excellent correlation between the Voice200ultra SIFT-MS and the conventional GCMS/HPLC analyses for all but two of the compounds studied, notably acrolein and formaldehyde. Figure 1 below shows the correlation between SIFT-MS and GCMS/HPLC for the benzene, ethylbenzene + xylene, acetaldehyde, acetone, butanone, styrene, and toluene.

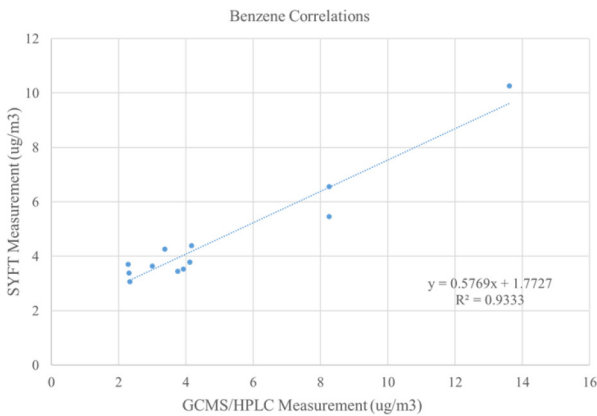


Figure 1a. Correlation between SIFT-MS and GCMS/HPLC for benzene measurements.

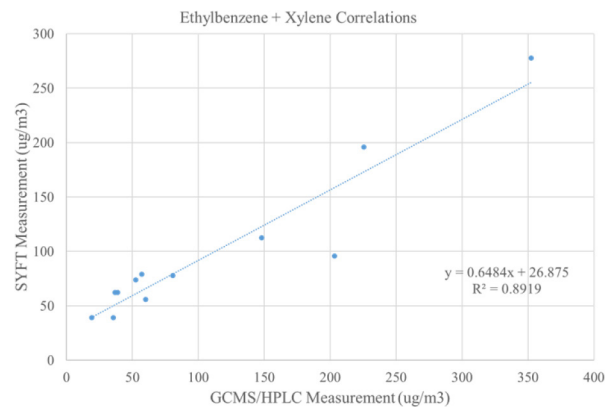


Figure 1b. Correlation between SIFT-MS and GCMS/HPLC for ethylbenzene + xylene measurements.

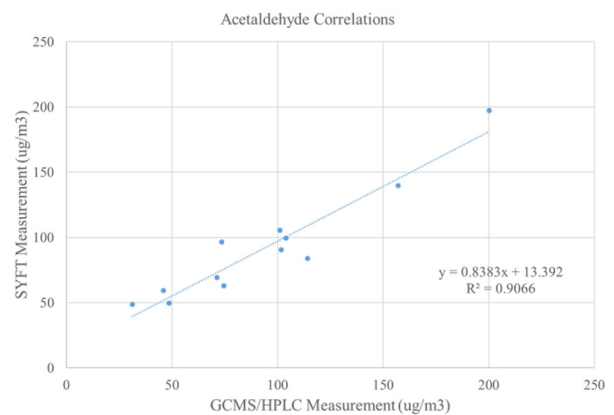


Figure 1c. Correlation between SIFT-MS and GCMS/HPLC for acetaldehyde measurements.

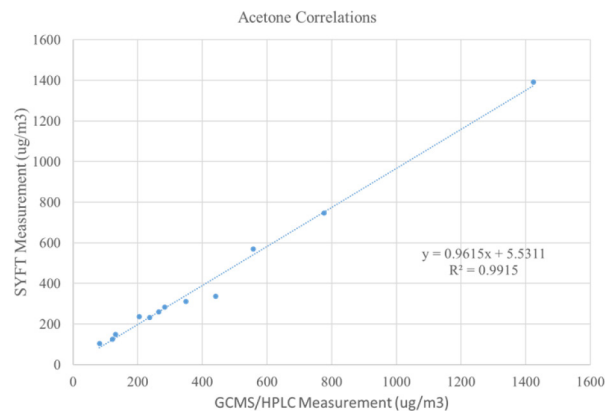


Figure 1d. Correlation between SIFT-MS and GCMS/HPLC for acetone measurements.

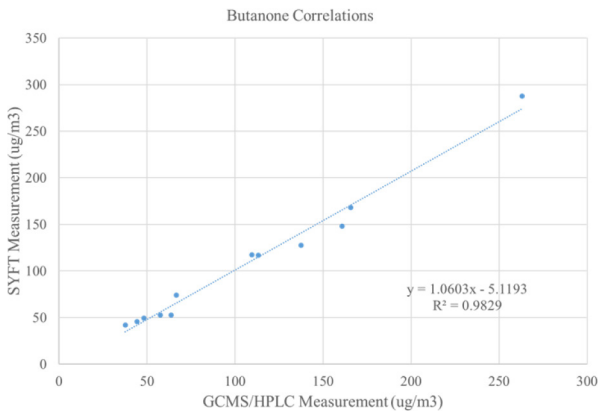


Figure 1e. Correlation between SIFT-MS and GCMS/HPLC for butanone measurements.

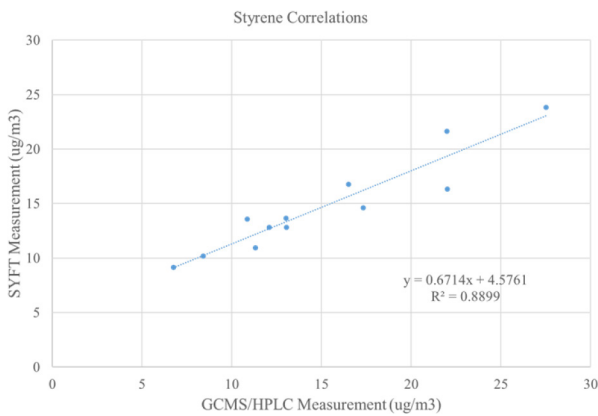


Figure 1f. Correlation between SIFT-MS and GCMS/HPLC for styrene measurements.

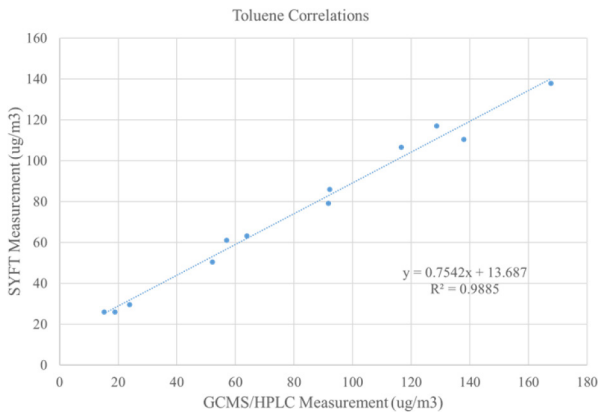


Figure 1g. Correlation between SIFT-MS and GCMS/HPLC for toluene measurements.

The linear regression equations are listed in Table 3 below:

Table 3. Linear regression of correlation between SIFT-MS and GCMS/HPLC.

Benzene	$y = 0.57x + 1.77$	$R^2 = 0.93$
Ethylbenzene + Xylene	$y = 0.65x + 26.88$	$R^2 = 0.89$
Acetaldehyde	$y = 0.84x + 13.39$	$R^2 = 0.91$
Acetone	$y = 0.96x + 5.53$	$R^2 = 0.99$
Butanone	$y = 1.06x - 5.12$	$R^2 = 0.98$
Styrene	$y = 0.67x + 4.58$	$R^2 = 0.89$
Toluene	$y = 0.75x + 13.69$	$R^2 = 0.99$
Acrolein	$y = 1.98x + 66.31$	$R^2 = 0.017$
Formaldehyde	$y = 2.62x + 12.34$	$R^2 = 0.60$

All compounds other than acrolein and formaldehyde have R2 values greater than 0.89. Acetaldehyde, acetone, and toluene measurements correlate especially well with an R2 value of at least 0.95.

While these correlation results are key performance criteria when evaluating these disparate measurement technologies, the slope of the correlation line measures the comparison of the recoveries of the various chemicals. The SIFT-MS is consistently under-reporting the mass (concentration) of the aromatics observed in the sample gases. Given that the R2 of all species is above 0.89, one can deduce that for some reason the calibration of the aromatics is offset by some systematic error or difference. By observing the offset, one can simply and linearly correct the SIFT-MS data to reflect the GC/MS results using a response factor for each compound.

The most important characteristic that direct analysis techniques such as SIFT-MS need to demonstrate when compared with chromatographic techniques such as GC/MS and HPLC is that they can deliver the needed selectivity in the real sample matrix.

Demonstrating measurement correlations on synthetic samples and gas standards is a relatively simple undertaking for any technique, but only when these correlations are tested in the real sample matrix can a more meaningful evaluation of the technique's performance be carried out. The correlation data presented in this work demonstrates this critical point: that the Voice200ultra delivers similar selectivity as GC/MS and HPLC for the measurement of these target compounds in real matrix of a car cabin.

It can further be noted from the data that the sensitivity of the Voice200ultra is sufficient to provide accurate measurements to the levels observed for the targeted compounds in this study. The mass detection limit (MDL) of the SIFT-MS is defined as the mass fraction at which a signal can be distinguished from noise imparted by the entire analytical testing [2]. The MDL for the SIFT-MS measurements carried out in this work corresponds to three standard deviations of the signal from a sample blank [1]. These values were determined to be much lower than the laboratory air.

The disparity between the two methods for acrolein and formaldehyde is related directly to the offline HPLC technique and not a result of the SIFT-MS technique. It is well established that acrolein, especially, is difficult to quantify by HPLC due to the complex derivatization of acrolein because of tautomerization of its hydrazone in the acidic DNPH solution [3]. This leads to low recovery for acrolein. A similar problem exists for other unsaturated carbonyls. In addition, the background concentration in the blank cartridge itself leads to cartridge-to-cartridge variation. This variability will affect the accuracy of the HPLC measurements when VOC levels are near the limit of quantitation: the limit of detection for HPLC measurements is 0.007 ug/ml, or 1.41 ug/m<sup>3</sup>.

## CONCLUSION

SIFT-MS is a very promising technique for measuring VOC levels for VIAQ assessments. The Voice200ultra shows excellent correlation with the existing industry standard techniques of GCMS/HPLC, demonstrating that it delivers accurate, sensitive and selective measurements of car-cabin VOCs. It has the added benefit of being an in-line real-time measurement technique. The Voice200ultra can lead to improved throughput and speed of analysis. This will reduce test costs and provide shortened analysis times at a comparable (if not improved) accuracy compared to the current state-of-the-art offline instruments and methods. The results for acrolein and formaldehyde highlight problems with the current methods that can be avoided by the application of SIFT-MS.

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