

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

Jennifer H. Zhu
 Ford Motor Company

Christopher Nones, Yan Li, Daniel Milligan, and Barry Prince
 Syft Technologies

Mark Polster and Mark Dearth
 Ford Motor Company

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/m³)	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