Motor Vehicle Emissions Testing Using SIFT-MS

Introduction

Motor vehicles are well known contributors to urban pollution. They emit various pollutants, including unburned or partially burned fuel, oxides of nitrogen, sulfur dioxide, carbon monoxide and particulates. While particulates are often visible to the naked eye as smoke, most exhaust pollutants are invisible to the eye and pass unnoticed into the environment.

Many of the pollutants are of real health and environmental concern. Consider, for example, the four "priority organic contaminants" listed by the New Zealand Ministry for the Environment (2002): benzene, 1,3-butadiene, formaldehyde and acetaldehyde. These compounds are also included in the United States Environmental Protection Agency's (US EPA) list of mobile source air toxics (MSATs) [US EPA (2000)]. They – and many other organic pollutants – are produced from the exhausts of vehicles due to partial combustion of fuel. Benzene and 1,3-butadiene are linked to human leukaemia, while formaldehyde and acetaldehyde are also classified as probable human carcinogens by the US EPA.

To date, there has not been a technology that can rapidly, specifically and economically measure a broad range of volatile organic pollutants from motor vehicle exhausts. Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) fills this gap, offering the dual benefit of real-time analysis of exhaust pollutants in ambient air and at the exhaust of the vehicle.

Relevant Characteristics of SIFT-MS

SIFT-MS is a powerful analytical technique that utilises chemical ionisation reactions coupled with mass spectrometric detection to rapidly quantify targeted volatile organic compounds (VOCs) [Spanel and Smith (1996); Freeman and McEwan (2002)]. VOCs are identified and quantified in real time from whole-gas samples based on the known reaction rate coefficients for reaction of the chemically ionising species (so-called precursor ions) with the target analytes.

The precursor ions used are H_3O^+, NO^+ and O_2^+, which react with trace VOCs in well characterised ways but do not react with the major components of air (nitrogen, oxygen, and argon). Analysis can be made in the presence of high water concentrations, carbon monoxide and carbon dioxide.

The soft chemical ionisation used in SIFT-MS yields a smaller range of product ions than is common in electron impact mass spectrometry (as used by gas chromatography – mass spectrometry (GC-MS)). Hence the need for gas chromatographic separation of the sample is circumvented, speeding sample throughput and providing instantaneous quantification of VOCs. Use of several precursors to independently quantify target analytes also greatly reduces interferences, markedly increasing the specificity of SIFT-MS versus competing whole-gas analysis technologies.

While SIFT-MS detection limits are compound specific, the Voice100 in its standard configuration has typical limits of single-digit part-per-billion by volume (ppb). The linear range extends into the tens of parts-per-million by volume (ppm). Samples are readily analysed at higher concentrations by decreasing the flow of sample into the instrument, thereby compromising the detection limit slightly.

Table 1 lists some compounds in motor vehicle exhaust emissions that are ideally suited to analysis by standard versions of the Voice100 SIFT-MS instrument.

Table 1: Compounds analysed in motor vehicle emissions, using SIFT-MS.

Acetaldehyde	Acetone
Benzene	1,3-Butadiene
Cyclohexane	Ethylbenzene
Formaldehyde	Hexane
Nitrogen oxides (NO, NO_2)	Toluene
Total volatile organic compounds	Xylenes

The Voice100 is also capable of analysing compounds such as carbon monoxide, carbon dioxide, oxygen and sulfur dioxide, depending on instrument model and options.

Experimental

Samples were taken from the exhaust of four cars that had been operating for some time at operational temperature (i.e., they were fully "warmed up"). Mylar balloons were used to collect the samples and these were analysed immediately using a Syft Technologies Voice100 instrument in selected ion mode (SIM). In this mode the compounds are targeted and quantified in real time. Routine emission tests like these can be undertaken in under one minute, whereas more detailed characterisation of a vehicle's emissions (such as for research purposes) take a little longer.

Results and Discussion

Figure 1 illustrates the effectiveness of Voice100 exhaust gas analysis for a selection of the compounds listed in Table 1. The four vehicles tested here were petrol-powered. Two vehicles had catalytic converters (yellow and green) installed and two did not (blue and red). These results demonstrate that catalytic converters have a marked effect on the emissions of toxic compounds from motor vehicle exhaust.

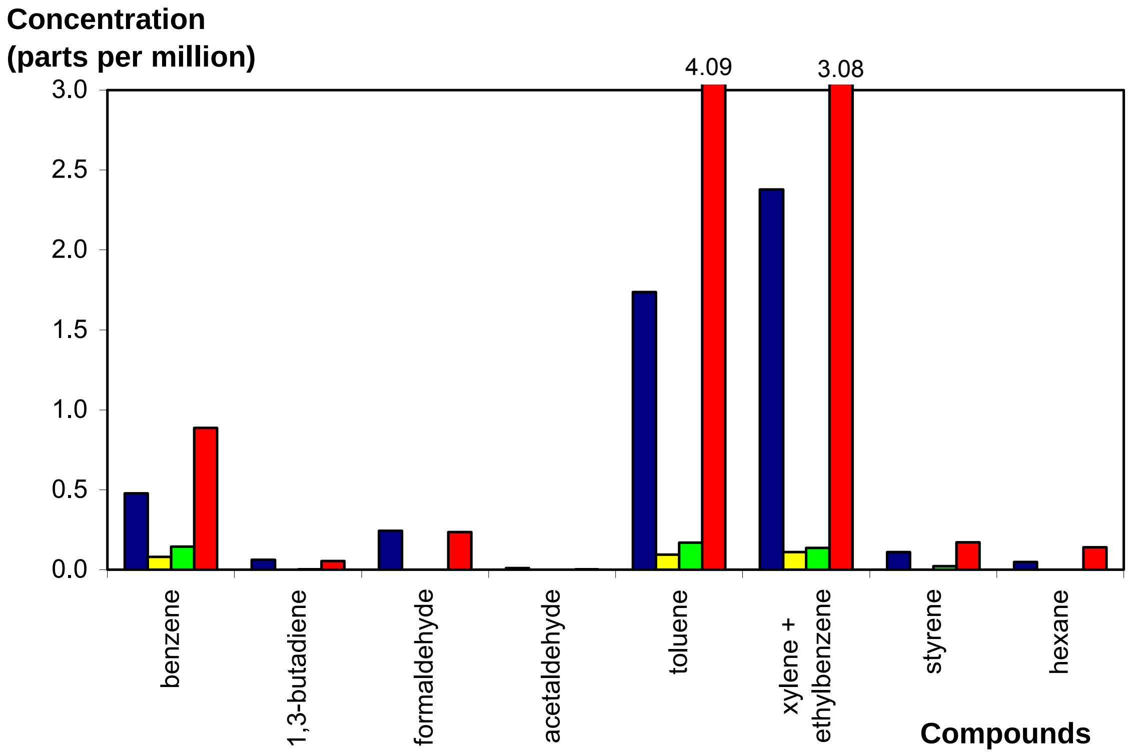

Figure 1: *The results of Voice100 analysis of the exhaust gases of four petrol-powered vehicles. The cars indicated by the yellow and green bars have catalytic converters, whereas the cars corresponding to the blue and red bars do not.*

Conclusion

SIFT-MS allows real-time analysis of motor vehicle exhaust emissions for volatile organic compounds (VOCs). The Voice100's ability to analyse with high sensitivity in the presence of high moisture while a vehicle is running, offers unprecedented opportunities to quantify VOC emissions. Applications include:

- Continuous emissions analysis throughout the normal running cycle;
- Monitoring emissions as catalytic converters and other engine components age;
- Characterising emissions as fuel formulations change;
- Analysis of engine efficiency.

References

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