REAL-TIME ANALYSIS OF UNITED STATES EPA METHOD TO-14A COMPOUNDS USING SIFT-MS

Vaughan S. Langford, Daniel B. Milligan, Diandree Padayachee, Barry J. Prince, Murray J. McEwan
Syft Technologies Limited, Christchurch, New Zealand
Email: vaughan.langford@syft.com

Introduction

Selected ion flow tube mass spectrometry (SIFT-MS) is a real-time analytical technique that offers potential for rapid screening of volatile organic compounds (VOCs) to ultra-trace levels in air.[1] Quantitation limits in the low part-per-trillion range (by volume; pptv) are achieved without sample preparation or preconcentration and results compare well with those obtained at an accredited laboratory using the United States' Environmental Protection Agency (US EPA) TO-15 Compendium Method.[2]

This paper presents the results obtained during development of a rapid analytical method that targets compounds in the US EPA TO-14A Compendium Method. A Syft Technologies Voice200*ultra* SIFT-MS instrument was used in this study. The quantitation limits specified by the TO-14A method are achieved within a few seconds for each analyte. SIFT-MS also offers significantly enhanced dynamic and linearity ranges compared to the canister-GC/MS method.

Methods

SIFT-MS uses ultra-soft, precisely controlled chemical ionization coupled with mass spectrometric detection to rapidly quantify VOCs in gases to low part-per-trillion levels (by volume; pptv).

Three standard chemical ionization agents (reagent ions or precursor ions) are applied in SIFT-MS: H_3O^+, NO^+ and O_2^+. These reagent ions react with trace VOCs in well controlled ion-molecule reactions but do not react with the major components of air, enabling SIFT-MS to analyze air for trace VOCs to low pptv levels without preconcentration. The reagent ions are switched within 10 milliseconds, providing unsurpassed selectivity among direct MS techniques. Figure 1 provides a schematic representation of the SIFT-MS methodology.
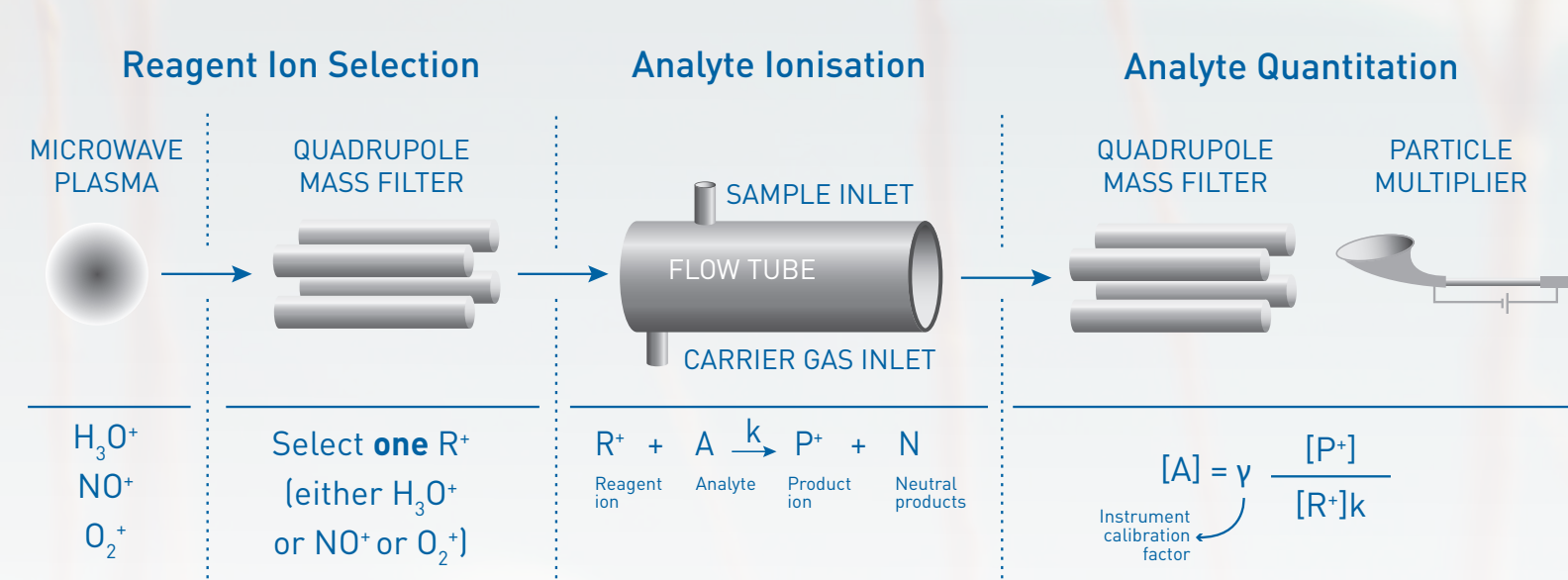

Figure 1. Schematic diagram of the SIFT-MS technique.

Method development

A SIFT-MS method was initially developed with the LabSyft Method Editor software using records in the Syft compound library. This method was refined and calibrated by analysis of a certified TO-14A standard mixture (from six litre passivated stainless steel SUMMA canisters).

On-site monitoring

A Syft Technologies Voice200*ultra* instrument was deployed in air monitoring sheds at three locations in or near Auckland, New Zealand. Air was sampled into the instrument using a flow-past system (Figure 2). A GAST sampling pump was used to draw several litres per minute of ambient air through Teflon tubing past the instrument's sample inlet.
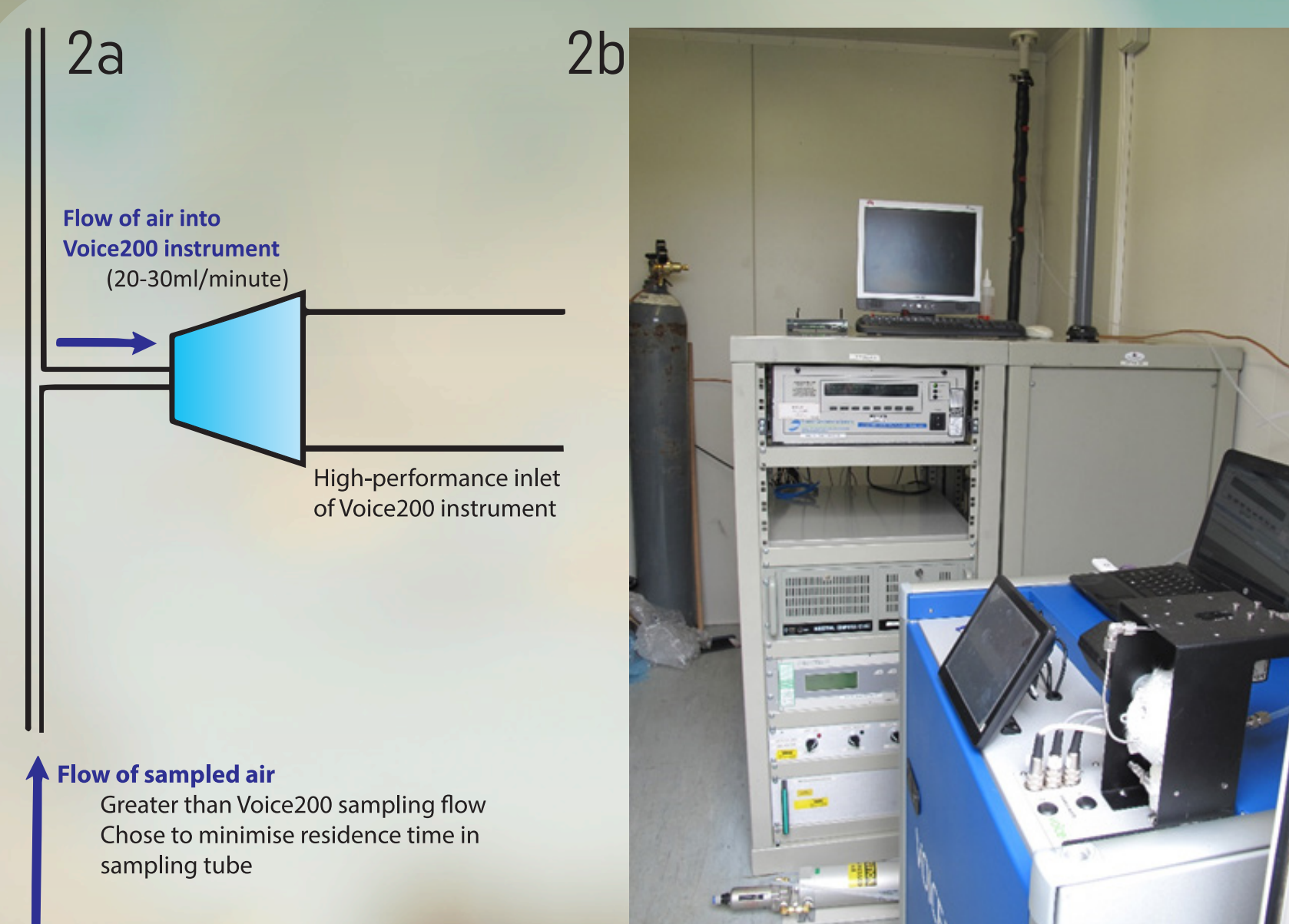

Figure 2a. Example flow-past set-up used to minimise residence time in the sampling tube due to small sampling flow rate of the SIFT-MS instrument.
Figure 2b. The installation at the Auckland Council air monitoring site at Glen Eden.

Results and Discussion

Method development

Method validation data are summarised in Table 1. Low- to mid-pptv detection limits are typical and linearity is very good. However, selective analysis is not currently achieved for some of the target compounds, due to limited reagent ion reactions with some of small the halogenated species (just O_2^+) and formation of common CCl_2^+ and CCl_2F^+ product ions.

Table 1: SIFT-MS limit of detection (LOD) data for target compounds and concentration data for the nominally 1.5, 2.5 and 5 ppbv samples.

n.d. = not detected (not present in mixture).

Compound(s)	Compounds reported	LOD[2] / ppbv	Nominally 5ppb Sample / ppbv	Nominally 2.5ppb Sample / ppbv	Nominally 1.25ppb Sample / ppbv	Correlation coefficient
benzene	1	0.068	4.82	2.59	1.54	1.000
toluene	1	0.037	5.80	3.30	2.08	1.000
ethylbenzene and xylenes (o- + m + p-)	4	0.040	4.59	2.70	1.75	1.000
trimethylbenzene (1,3,5- + 1,2,4-)	2	0.050	4.63	2.69	1.82	0.999
styrene	1	0.043	4.62	2.69	1.79	1.000
chlorobenzene	1	0.082	4.70	2.65	1.66	1.000
benzyl chloride	1	0.006	n.d.	n.d.	n.d.	N/A
dichlorobenzenes (1,2- + 1,3- + 1,4-)	3	0.034	4.68	2.66	1.71	1.000
1,2,4-trichlorobenzene	1	0.153	5.21	2.40	1.34	0.996
methyl chloride	1	0.037	n.d.	n.d.	n.d.	N/A
chloroform + dichloromethane + tetrachloroethane	3	0.169	4.65	2.67	1.72	1.000
carbon tetrachloride	1	0.088	4.49	2.75	1.86	1.000
ethyl chloride; 1,1-dichloroethane	2	0.272	4.70	2.65	1.70	1.000
trichloroethane (1,1,1- + 1,1,2-)	2	0.198	4.38	2.81	1.90	0.998
vinyl chloride + 1,2-dichloroethane	2	0.085	4.75	2.63	1.80	0.997
dichloroethylene (1,1- + 1,2-)	2	0.208	4.53	2.73	1.64	0.997
trichloroethylene	1	0.080	4.62	2.69	1.66	1.000
tetrachloroethylene	1	0.181	4.63	2.69	1.79	1.000
1,2-dichloropropane	1	0.160	4.60	2.70	1.87	0.999
dichloropropene	1	0.044	4.79	2.61	1.71	0.998
hexachlorobutadiene	1	0.301	5.14	2.43	1.45	0.994
methyl bromide	1	0.112	n.d.	n.d.	n.d.	N/A
1,2-dibromoethane	1	0.032	4.46	2.77	2.03	0.999
Freon 11	1	0.179	4.46	2.77	1.96	1.000
Freon 114 + Freon 113	2	0.120	Note 3	Note 3	Note 3	N/A
Freon 12 + Freon 114	2	0.183	4.83	2.58	1.87	0.990

Notes to the table:
1. The number of compounds reported together multiplied by the nominal concentration gives the expected concentration. For example, ethylbenzene and the three xylenes are reported together. For the nominally 5-ppbv standard, a 20-ppbv result is expected.
2. Calculated from three standard deviations of the mean of blank measurements for a 2-second measurement.
3. The sum of Freon 113 and Freon 114 could not be determined; this can be resolved through calibration.

On-site monitoring

Recently a Voice200*ultra* instrument was deployed for continuous air monitoring in conjunction with Auckland Council, New Zealand. The focus was primarily on biogenic compounds and pollutants from motor vehicles (which includes the aromatics from the TO-14A method).

Two weeks of monitoring data for each site is shown in Figure 3. Concentration trends are yet to be compared with meteorological data and that of other parameters, such as NO_x and ozone, when those data have been validated.
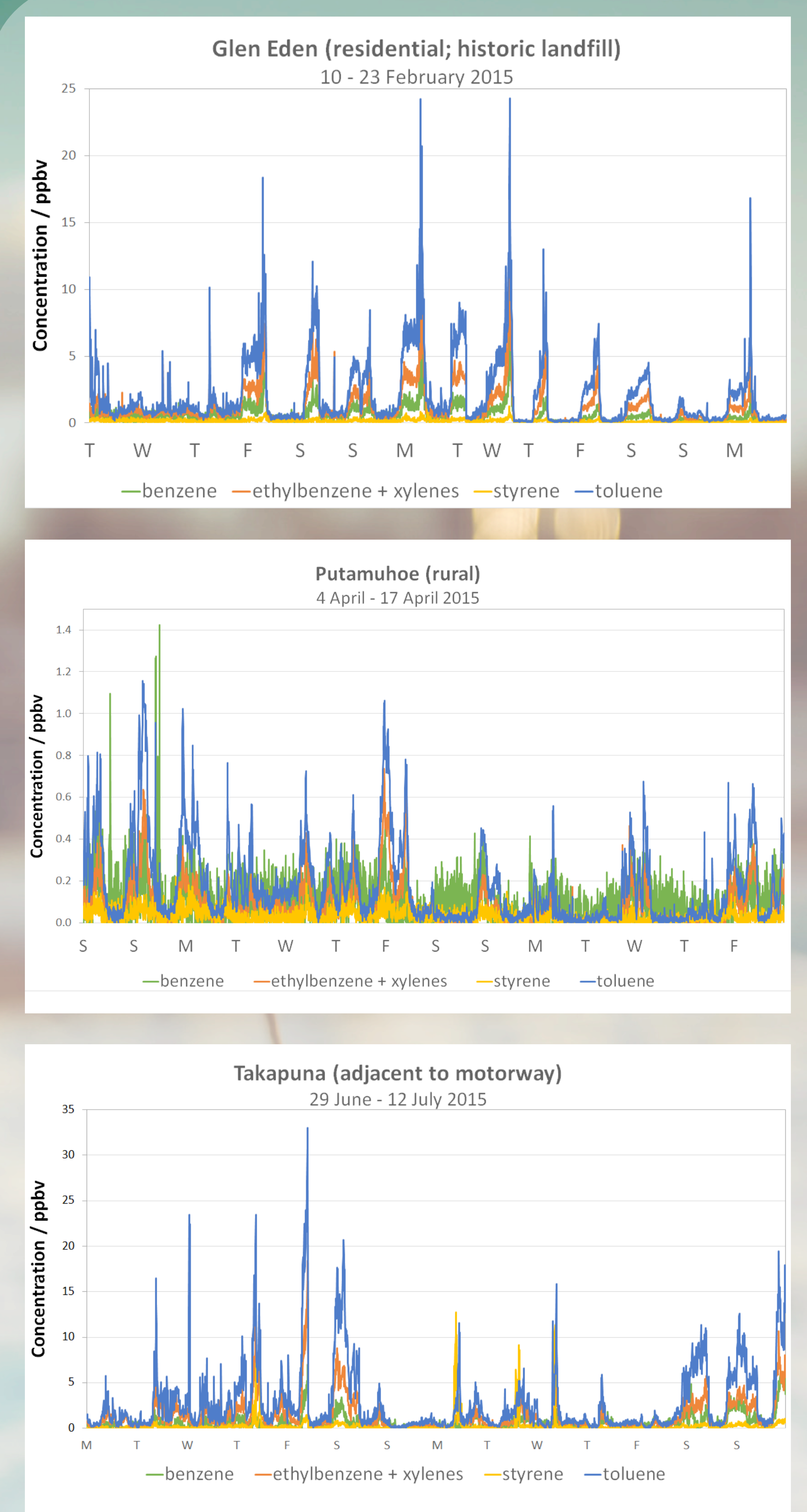

Figure 3. Real-time air monitoring at three sites in and near Auckland, New Zealand.

Conclusions

Direct mass spectrometry techniques, such as SIFT-MS, cannot resolve all isomers as required by the TO-14A method. However, this study has demonstrated that SIFT-MS (i) can be applied by laboratories as a rapid screening method prior to expensive regulatory analysis (e.g. of SUMMA canisters), and (ii) is well suited for deployment as a real-time analyser for TO-14A method compounds, such as in ambient or fence-line monitoring scenarios.

Future work will evaluate the newly developed negatively charged reagent ion option for SIFT-MS. This should provide greater selectivity for the TO-14A compounds that cannot currently be resolved.

References
1. Prince, B.J., Milligan, D.B., & McEwan, M.J. (2010). *Rapid Commun. Mass Spectrom.*, 24, 1763-1769.
2. Langford, V.S., Graves, I., & McEwan, M.J. (2014). *Rapid Commun. Mass Spectrom.*, 28, 10-18.