VOC measurements in ambient air using Selected Ion Flow Tube Mass Spectrometry—automation and calibration considerations

Environmental Chemistry group, water Science Forum and the Separation Science Group
Friday 3rd of March

Marvin Shaw*1, Freya Squires*1, Lucy Carpenter*1, Alastair Lewis*1, Jim Hopkins*1, Mark Perkins*2
*1 Wolfson Atmospheric Chemistry Laboratories, University of York, UK
*2 Anatune Ltd, Cambridge, UK
Dr Marvin Shaw
National Centre for Atmospheric Science Research Associate.
Wolfson Atmospheric Chemistry Laboratories (University of York).

Research Area
Urban Air Quality. Emission and Atmospheric Processing of Volatile Organic compounds (VOCs).

- Application of low cost electrochemical sensors for urban air quality monitoring.
- Determination of VOC mixing ratios and eddy covariance fluxes, using chemical ionisation mass spectrometry, from both ground based and airborne platforms.

Dr Mark Perkins
Product Specialist-SIFT MS (Anatune, Canbridge)

UK and Ireland distributor for Syft Technologies’ SIFT-MS

Channel Partner of Agilent

UK and Ireland distributor for GERSTEL
Overview

1. Overview of the SIFT-MS technique
2. Sensitivity and Limit of Detection Optimization
3. Development of Autonomous Air Monitoring System
4. Early Results of Field Deployment for Autonomous Operation (Beijing, China).
1. Overview of SIFT-MS technique - Instrument schematic
In SIFT-MS, all three reagent ions are generated from the same gas mixture: humidified air. **No** external gas lines, mechanical valves, or gas supplies are required!
SIFT-MS provides the softest, most controlled ionization of any MS technique – including other CI-MS techniques.

Traditionally it provides reliable quantitation based on library reaction rate data without need for specific compound calibration.

For the accurate quantitative determination of Volatile Organic Compound (VOC) mixing ratios in ambient air independent calibration to National Physics Laboratory (NPL) traceable gas standards is advised.
2. Sensitivity and limit of detection optimization

- At the Wolfson Atmospheric Chemistry laboratories we have a dedicated calibration facility for the routine calibration of field and laboratory equipment.

- Gas blending units are recertified and calibrated yearly.

- Primary stock Hydrocarbon standards are traceable to the NIST or NPL scale.

- To optimise SIFT-MS sensitivity and limit of detection a dry gas of fixed multi component VOC concentration was generated (1 ppb) using a multi gas calibrator (Monitor Europe S6100).

- Optimization steps included:
  - Ion source optimisation
  - Ion lens optimisation
  - Flow tube pressure optimisation
  - Detector voltage optimisation
2. Sensitivity and limit of detection optimization

- 1 ppb dry multicomponent VOC generated
- 250 ms ion dwell time

- Standard flow conditions. (25 sccm sample, 100 sccm N₂)
2. Sensitivity and limit of detection optimization

- Ion capping/count limit is an arbitrary value in the Labsyft software (10,000 – 1,000000).
- Controls the time spent monitoring both the reagent and product ions generated.
- Lower values (10,000-100,000) traditionally used to extend detector lifetime.
- Measurements shown represent triplicate measurements performed on “zero air”
  - Sample flow 100 sccm
  - Carrier flow 25 sccm
  - Normalised flow 4.0
  - 1min averaged

Limit of detection = $2 \times \text{stdev of blank}$
2. Sensitivity and limit of detection optimization

- 1 ppb dry multicomponent VOC generated
- 250 ms ion dwell time
- 1 min averaged

**Ionicon PTR-QMS 500 (2014)**
- Drift tube pressure: 2 mbar
- Drift tube temperature: 40°C
- Drift tube Voltage: 480 V
- E/N ratio: 110 Td

**Syft Technologies Voice 200 Ultra (2016)**
- Flow tube pressure: 410 mTorr
- Flow tube temperature: 140°C
- Flow tube voltage: 50V
- Sample flow 100 sccm
- Carrier flow (N₂) 25 sccm

![Graph showing sensitivity and limit of detection optimization for various VOCs.](image-url)
2. Sensitivity and limit of detection optimization

- 1 ppbV dry multicomponent VOC generated
- 250 ms ion dwell time
- 1 min averaged

**Ionicon PTR-QMS 500 (2014)**
- Drift tube pressure: 2 mbar
- Drift tube temperature: 40°C
- Drift tube Voltage: 480 V
- E/N ratio: 110 Td

**Syft Technologies Voice 200 Ultra (2016)**
- Flow tube pressure: 410 mTorr
- Flow tube temperature: 140°C
- Flow tube voltage: 50V
- Sample flow: 100 sccm
- Carrier flow (N₂) 25 sccm

![Graph](image)
2. Sensitivity and limit of detection optimization

- 1 ppbV dry multicomponent VOC generated
- 250ms ion dwell time
- 1 min averaged

**Ionicon PTR-QMS 500 (2014)**
- Drift tube pressure: 2 mbar
- Drift tube temperature: 40°C
- Drift tube Voltage: 480 V
- E/N ratio: 110 Td

**Syft Technologies Voice 200 Ultra (2016)**
- Flow tube pressure: 410 mTorr
- Flow tube temperature: 140°C
- Flow tube voltage: 50V
- Sample flow 100 sccm
- Carrier flow (N\textsubscript{2}) 25 sccm
3. Development of autonomous air quality monitoring system

Zero Air Generator

KNF PTFE Membrane pump

Sample Manifold

Sample gas 100 sccm ambient air

1/16” SS needle valve

Carrier gas 25 sccm N6 Research grade N₂

0.5L min⁻¹

Overflow

1/16” SS tubing

3way 2 position Solenoid valves

Sample Air Zero Air Cal Gas
3. Development of autonomous air quality monitoring system
3. Development of autonomous air quality monitoring system

[Diagram of air quality monitoring system]

- Zero Air Generator
- KNF PTFE Membrane pump
- Carrier gas 25 sccm N6 Research grade N₂
- Sample gas 100 sccm ambient air
- 1/16” SS needle valve
- 3way 2 position Solenoid valves
- 1/16” SS tubing
- 0.5L min⁻¹

Sample Air Zero Air Cal Gas
3. Development of autonomous air quality monitoring system

Zero Air Generator

KNF PTFE Membrane pump

1/16" SS needle valve

Sample Manifold

Sample gas 100 sccm ambient air

1/16" SS needle valve

Overflow

0.5L min⁻¹

Calibrant flow 0.5L min⁻¹

Sample Air Zero Air Cal Gas

3way 2 position Solenoid valves

Overflow

Carrier gas 25 sccm N6 Research grade N₂

Sample

Manifold

Sample gas

0.5L min⁻¹

-1

-1
3. Development of autonomous air quality monitoring system

- Labsyft batch scanner was used to sequentially step through multiple analysis methods over each 72 hour period.

- Any combination of a total of 13 48VDC outputs on-board the Hex controller can be triggered in each analysis method.

- These were used to autonomously switch solenoid valve positions allowing analysis of ambient air, zero air and calibrant gas.

- An “in house built” calibration device was autonomously triggered every 72 hours which sequentially delivered 0, 1, 2, 4 and 8ppb of VOCs by blending a 5ppm NPL standard with “zero air”.
4. Early results of field deployment (Beijing, China)

- SIFT-MS deployed as part of the Air Pollution and Human Health in a Chinese Megacity programme. Funded by Natural Environment Research Council (NERC), Medical Research Council (MRC) and the Natural Science Foundation of China (NSFC).

- Collaborative project between UK and Chinese scientists with an aim to identify the concentrations and sources of urban air pollution in Beijing, how people are exposed to it, how it effects their health and what can be done about it.

- Project consists of separate 6 week winter (Oct-Dec 2016) and summer (May – July) field campaigns.

- “Iron Tower site” Institute of Atmospheric Physics (IAP), Beijing, China.

Main objectives (SIFT-MS)

1) Establish whether the SIFT-MS, automated calibration and zeroing system is robust and reproducible enough for routine field deployment.

2) Evaluate the accuracy and precision of the SIFT-MS for determining real time trace level VOC mixing ratios. (GC/MS, GC/FID, PTR-TOF).

3) Evaluate the performance of the SIFT-MS for eddy covariance flux derivation (PTR-TOF). Sample inlet fixed at 102 m (agl).
4. Early results of field deployment (Beijing, China)

- Automated calibration carried out on the 26th of November 2016.
- Shows comparison of actual concentration from automated blender against .
- SIFT-MS had a tendency to underestimated concentration for the duration of the 6 week campaign.
4. Early results of field deployment (Beijing, China)

- Instrument initially tuned on the 21/11/16, and then not tuned for remainder of campaign.
- ~30-40% reduction in raw instrument sensitivity over a 3 week period.
- Subsequent data corrected for sensitivity drift.
4. Early results of field deployment (Beijing, China)

- Comparison of SIFT-MS mixing ratio data (1 min averaged) at 102m (agl) against GC-FID data (20 minute averaged) between the 22nd November and 11th of December.

- Good correlation between NO+ and O₂+ reagent ion products.

- H₃O+ reagent ion products overestimate benzene.

- Observed 4 main pollution periods.
4. Early results of field deployment (Beijing, China)

- Comparison of SIFT-MS mixing ratio data (1 min averaged) at 102m (agl) against GC- FID data (20 minute averaged) between the 22nd November and 11th of December.

- Good correlation between H$_2$O$^+$, NO$^+$ and O$_2^+$ reagent ion products.

- Observed 4 main pollution periods.
4. Early Results of Field Deployment (Beijing, China)

- Comparison of SIFT-MS mixing ratio data (1 min averaged) at 102m (agl) against GC-FID data (20 minute averaged) between the 22nd November and 11th of December.

- C₂ benzenes are the sum of isomers of Xylene and Ethylbenzene concentrations.

- Poor correlation between 26 of November and 30th of November is due to painting of exterior walls of a local building with solvent based paints.

- Good correlation between H₃O⁺, NO⁺ and O₂⁺ reagent ion products after the 30th of November.

- Observed 4 main pollution periods.
4. Early Results of Field Deployment (Beijing, China)

- Comparison of SIFT-MS mixing ratio data (1 min averaged) at 102m (agl) against GC-FID data (20 minute averaged) between the 22nd November and 11th of December.

- Good correlation between NO+ reagent ion products.

- H$_3$O+ overestimation is likely due to Isobaric interference at m/z 59.

Observed 4 main pollution periods.
4. Early Results of Field Deployment (Beijing, China)

- Comparison of SIFT-MS mixing ratio data (1 min averaged) at 102m (agl) against GC-FID data (20 minute averaged) between the 13th November and 11th of December.

- Good correlation between NO+ and O₂+ reagent ion products.

Observed 5 main pollution periods.
4. Early results of field deployment (Beijing, China)

- 3 day back trajectory dispersion plots (HYSPLIT) show that high pollution periods correlate with low wind speeds and southerly air masses transecting Central Beijing.

- Relatively lower pollution periods correlate with north westerly air masses transecting suburban/rural Beijing.

Created using HYSPLIT dispersion model
http://www.ready.noaa.gov
Thank you for your attention

Dr Marvin Shaw
Wolfson Atmospheric Chemistry laboratories
Work no: (01904 3224753)
marvin.shaw@york.ac.uk