SIFT-MS for Volatile Organic Compounds Pollution Monitoring

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The pollution of air and water with volatile organic compounds (VOCs), both hazardous and odorous, is of significant concern due to impacts on human health and quality of life, as well as the environment. The selected ion flow tube mass spectrometry (SIFT-MS) technique has been increasingly adopted to monitor source emissions and their dispersion, enabling a more rapid response to pollution incidents. To this end, the flexibility of SIFT-MS instrumentation for both laboratory- and field-based analysis, including in mobile laboratories, has been valuable.

Keywords: selected ion flow tube mass spectrometry ; SIFT-MS ; VOCs ; air quality monitoring ; pollution monitoring

1. Introduction

Tropospheric ozone is generated by the photochemical oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x, comprising NO and NO_2) [1]. The Republic of Korea (South Korea), and especially the Seoul megacity, has a longstanding issue with elevated ozone levels [1][2][3][4]. Background ozone levels are approximately 80 parts per billion by volume (ppbV) [4][5]. The large collaborative Korea-United States Air Quality campaign (KORUS-AQ) [4][5] provides one example of a major multinational study that has sought to provide measurements that improve understanding of the cause of the elevated ozone levels. In addition to local ozone production, this study pointed to the wider regional problem of elevated ozone, an issue that more recent publications are continuing to investigate (see, for example, [1][6]).

The effective measurement of the VOCs that contribute both to ozone formation and secondary organic aerosols (SOAs) is important. The KORUS-AQ report [4] identified that, in addition to automobile emissions, fugitive solvent emissions are a significant contributor to elevated VOC levels. In South Korea, the conventional measurement of photochemical smog precursors follows the United States Environmental Protection Agency's Photochemical Assessment Monitoring Stations (PAMS) approach and typically uses thermal desorption-gas chromatography-flame ionization detection (TD-GC-FID) for the analysis of over 50 hydrocarbons and several oxygenates [7]. There are 18 PAMS stations collecting precursor data in South Korea [8], and it is made available publicly in monthly air quality reporting [9]. Kang et al. [10] have recently described a two-year TD-GC-FID study with hour-by-hour monitoring from a single PAMS site in central Seoul. However, although this approach is widely deployed, it is only suited to the determination of ambient (or fenceline) concentrations of ozone precursors at fixed locations.

Gaining a better understanding of fugitive emissions from industry, especially in industrial parks with many similar businesses in close proximity, requires mobile analytical tools that acquire data in real-time because events are frequently transient. TD-GC-FID is not suitable for mobile measurement due to the long analysis time (tens of minutes) which would average several locations into one measurement. As early as 2016, this need was identified by the Korean Ministry for the Environment, and in 2017 a detailed report on the evaluation was published [11]. In this study, selected ion flow tube mass spectrometry (SIFT-MS) was the primary technology evaluated for VOC measurement, and this more broadly than ozone precursors. Subsequently, SIFT-MS instrumentation has been increasingly utilized as a complementary tool to the existing regulatory measurements, because it provides mobile, real-time analysis. The move to more extensive monitoring has been driven by increased regulation [12]. Although SIFT-MS instruments do not conduct regulatory analysis, they enable more rapid detection of pollution incidents and identification of the responsible emission source, enabling sampling to be triggered for regulatory analysis. Hence, they support improved air quality management.

2. Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)

Conventional environmental VOC analysis primarily utilizes GC analysis [13] (with various options for sample introduction and detection, depending on the regulatory method). The most fundamental component of the technique is the chromatographic separation which is usually optimized to resolve all analytes as a function of time (**Figure 1**). A typical GC analysis will take tens of minutes to complete. Furthermore, to achieve low or sub-ppbV detection limits, significant volumes of air may need to be collected and concentrated prior to analysis, further delaying the reporting of analytical results. In the TD-GC-FID approach used for ozone precursor monitoring, pre-concentration is achieved using adsorption onto a suitable adsorbent material, followed by rapid heating to focus a concentrated sample into the GC injector during the sample injection (**Figure 1**) [14]. Both sample preconcentration and the gas chromatography column can discriminate

against certain chemical functionalities and hence the suitability of configuration is an important consideration in GC method development.

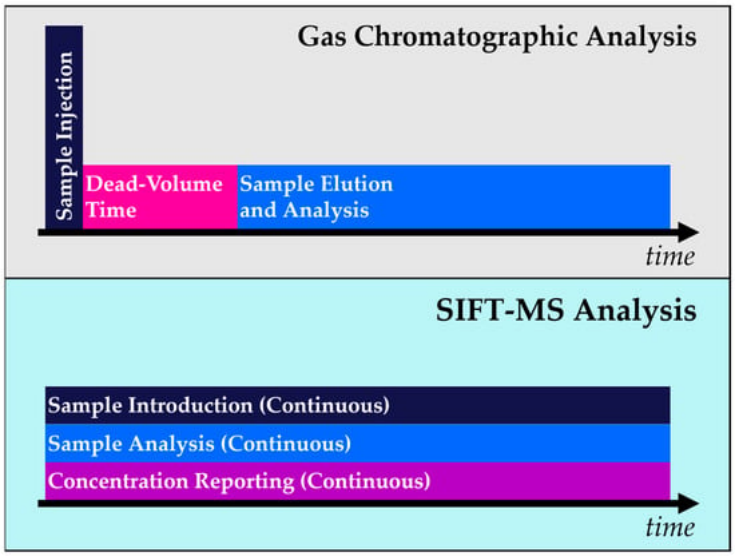

Figure 1. A schematic illustration of the fundamental difference in measurement approach between the GC and SIFT-MS techniques where compounds are resolved, respectively, in time and using direct chemical ionization coupled with mass spectrometry.

In contrast, SIFT-MS is a direct-injection mass spectrometry (DIMS) technique in which air is introduced, analyzed, and reported continuously (**Figure 1**). The reporting rate depends on the analytical method but is typically from 5 to 120 s for multiple analytes at sub-ppbV concentrations.

The SIFT-MS technique has been described in detail elsewhere [15][16]. Briefly, continuous sample ionization is achieved by using ultra-soft chemical ionization that efficiently ionizes a very broad range of VOCs but does not ionize the bulk constituents of air. A microwave discharge through air is used to generate the reagent ions, with up to eight available (H_3O^+, NO^+, $O_2^{+\bullet}$, $O^{-\bullet}$, OH^-, $O_2^{-\bullet}$, NO_2^-, and NO_3^-) on commercial SIFT-MS instruments [17]. Rapid switching of reagent ions provides high specificity because the multiple reaction mechanisms give independent measurements of each analyte, while the elimination of chromatographic separation means that it is straightforward to analyze VOCs of diverse chemical functionalities in a single procedure [18][19][20]. Instrument detection limits in the part-per-trillion by volume (pptV) range are typically achieved for 1-s ion dwell times for direct analysis of air with no preconcentration or drying required [21][22].

The literature reviewed below utilized the Voice200*ultra* model SIFT-MS instruments (Syft Technologies Limited, Christchurch, New Zealand) with positive reagent ion sources operating on nitrogen carrier gas [15][23][24]. Since the instruments are being used for quantitative analysis of pollutants with reference to regulatory limits, calibration has been utilized widely in contrast to library-based quantitation [18]. A similar approach has been used in the field-based environmental monitoring conducted by Shaw and co-workers [22][25][26][27]. Calibrations are routinely linear [28] in real-time monitoring applications, as observed previously [21].

The South Korean environmental applications illustrate the tremendous flexibility of the SIFT-MS technique for volatile compound monitoring, both in terms of sample delivery and instrument deployment. **Table 1** summarizes the instrument configurations and installation types used across the applications as discussed below. The widespread field deployment of SIFT-MS instruments is noteworthy in the South Korean adoption of SIFT-MS: 11 are in air monitoring sheds, 39 are used primarily for monitoring VOCs while the mobile laboratory is in motion, and one is on board the ship *Isabu*. Together with field-based research conducted in China [25][29], the UK [22][27], and Vietnam [26][30], this demonstrates the robustness of the quadrupole mass filter (QMF)-based SIFT-MS instrumentation. Coupled with real-time data visualization and internet connectivity, field-based systems enable real-time decisions to be made [31][32].

Table 1. SIFT-MS instrument configurations used for environmental applications in South Korea.

Configuration	Installation Type	Typical Application(s)	Selected References [1]
Direct analysis with manual sample introduction	**Research laboratory**	**Emission source analysis; custom sampling configurations; general application scoping/evaluation**	**[11][33]**
Autosampler (usually syringe injection)	**Research and routine laboratory**	**High-throughput sample analysis (e.g., aqueous headspace, sample bags [2], thermal desorption tubes)**	**[11][34][35]**

Configuration	Installation Type	Typical Application(s)	Selected References [1]
Automated multiport sampling (sample, blank, and calibration lines)	Air monitoring shed	Emission source analysis; fenceline monitoring; ambient monitoring	[11][26][36]
	Mobile laboratory (fixed location operation only)	Emission source analysis; emissions inventory data acquisition; fenceline monitoring; ambient monitoring; pollution mapping	[27][37][38]
	Moving laboratory (fixed location operation also)	Pollution mapping; full incident response (with drone sampling to identify pollution source)	[22][39][40][41]

[1] Including selected non-Korean publications. [2] Supporting emission source analysis, acquisition of emissions inventory data, and drone-based sampling workflows.

Finally, a comment on the preferential adoption of SIFT-MS over the related proton transfer reaction mass spectrometry (PTR-MS) technique [42][43], as utilized in the KORUS-AQ study [4][5], is necessary. PTR-MS has been widely utilized in academic atmospheric research [44][45][46], especially its time-of-flight (TOF) variant [45], whereas SIFT-MS has been utilized to a limited extent [15][18]. In South Korea, the need, driven by increased regulation [12], has been for mobile measurements of VOCs. The availability of an existing SIFT-MS mobile laboratory solution was a key reason for its preferential adoption together with the ability of SIFT-MS to identify and target VOCs quantitatively immediately on site. Moreover, in SIFT-MS instruments, the use of QMFs for mass-selective detection, rather than the TOF systems utilized in most modern PTR-MS instruments [43], provides greater robustness for analysis on-the-move and operation that is less sensitive to temperature.

References

1. Colombi, N.K.; Jacob, D.J.; Yang, L.H.; Zhai, S.; Shah, C.; Grange, G.K.; Yantosca, R.M.; Kim, S.; Liao, H. Why is ozone in South Korea and the Seoul metropolitan area so high and increasing? Atmos. Chem. Phys. 2023, 23, 4031–4044.
2. Zastrow, M. South Korea cracks down on dirty air. Nature News, 17 October 2017.
3. Kim, Y.P.; Lee, G. Trend of air quality in Seoul: Policy and science. Aerosol Air Qual. Res. 2018, 18, 2141–2156.
4. Crawford, J.; Kim, Y.; Fried, A.; Lefer, B.; Jordan, C.; Lee, G.; Simpson, I.; Al-Saadi, J.; Kim, J.; Woo, J.; et al. KORUS-AQ Final Science Synthesis Report. Available online: https://espo.nasa.gov/sites/default/files/documents/5858211.pdf (accessed on 1 November 2023).
5. Crawford, J.H.; Ahn, J.-Y.; Al-Saadi, J.; Chang, L.; Emmons, L.K.; Kim, J.; Lee, G.; Park, J.-H.; Park, R.J.; Woo, J.H.; et al. The Korea–United States Air Quality (KORUS-AQ) field study. Elem. Sci. Anth. 2021, 9, 00163.
6. Kim, J.; Park, J.; Hu, H.; Crippa, M.; Guizzardi, D.; Chatani, S.; Kurokawa, J.; Morikawa, T.; Yeo, S.; Jin, H.; et al. Long-term historical trends in air pollutant emissions in South Korea (2000–2018). Asian J. Atmos. Environ. 2023, 17, 12.
7. United States Environmental Protection Agency. Photochemical Assessment Monitoring Stations (PAMS). Available online: https://www.epa.gov/amtic/photochemical-assessment-monitoring-stations-pams (accessed on 2 November 2023).
8. Park, J.H.; Kang, S.; Song, I.-H.; Lee, D.-W.; Cho, S. Characteristics of long-term behavior of VOC species in Korea—PAMS data analysis. J. Korean Soc. Atmos. Environ. 2018, 34, 56–75.
9. Korea Ministry of Environment. Statistics White Paper. Available online: https://library.me.go.kr/#/search/org-statistical/si?all=0&rq=PUBLISHER%3D(*%ED%99%98%EA%B2%BD%EB%B6%80*%20OR%20*%ED%99%98%EA%B2%BD%EC%B2%98*%20OR (accessed on 3 November 2023).
10. Kang, S.; Kim, J.-A.; Lee, M.; Park, J.; Jeon, E.; Shim, M.; Shin, Y. An analysis of the temporal variability in volatile organic compounds (VOCs) within megacity Seoul and an identification of their sources. Atmos. Pollut. Res. 2022, 13, 101338.
11. Korea Ministry of Environment. Technologies for Responding to Atmospheric Environment Policies: Development of Monitoring Technologies for Priority Hazardous Air Pollutants in Urban Areas. December 2017. Available online: https://www.nl.go.kr/NL/contents/search.do?srchTarget=total&pageNum=1&pageSize=10&insiteschStr=&schQuery=&mainSrchField=1&kwd=%EB%8F%84%EC%8B%9C%EC%A7%8 (accessed on 27 July 2023).
12. Korea Ministry of Environment. Fine Dust Management Comprehensive Plan 2020–2024, pp. 41–42. Available online: http://www.me.go.kr/home/file/readDownloadFile.do?fileId=182580&fileSeq=1 (accessed on 1 August 2023).
13. Dettmer-Wilde, K.; Engewald, W. Practical Gas Chromatography; Springer: Berlin/Heidelberg, Germany, 2014; 902p.
14. United States Environmental Protection Agency. Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program—Revision 2—April 2019. Available online:

https://www.epa.gov/sites/default/files/2019-11/documents/pams_technical_assistance_document_revision_2_april_2019.pdf (accessed on 3 November 2023).

15. Smith, D.; Španěl, P.; Demarais, N.; Langford, V.S.; McEwan, M.J. Recent developments and applications of selected ion flow tube mass spectrometry (SIFT-MS). Mass Spectrom. Rev. 2023, e21835.
16. Smith, D.; Španěl, P. Selected ion flow tube mass spectrometry (SIFT-MS) for on-line trace gas analysis. Mass Spectrom. Rev. 2005, 24, 661–700.
17. Hera, D.; Langford, V.S.; McEwan, M.J.; McKellar, T.I.; Milligan, D.B. Negative reagent ions for real time detection using SIFT-MS. Environments 2017, 4, 16.
18. Langford, V.S. SIFT-MS: Quantifying the volatiles you smell…and the toxics you don't. Chemosensors 2023, 11, 111.
19. Langford, V.S.; Billiau, C.; McEwan, M.J. Evaluation of the efficacy of SIFT-MS for speciation of wastewater treatment plant odors in parallel with human sensory analysis. Environments 2020, 7, 90.
20. Langford, V.S.; Du Bruyn, C.; Padayachee, D. An evaluation of selected ion flow tube mass spectrometry for rapid instrumental determination of paper type, origin and sensory attributes. Packag. Technol. Sci. 2021, 34, 245–260.
21. Prince, B.J.; Milligan, D.B.; McEwan, M.J. Application of selected ion flow tube mass spectrometry to real-time atmospheric monitoring. Rapid Commun. Mass Spectrom. 2010, 24, 1763–1769.
22. Wagner, R.L.; Farren, N.J.; Davison, J.; Young, S.; Hopkins, J.R.; Lewis, A.C.; Carslaw, D.C.; Shaw, M.D. Application of a mobile laboratory using a selected-ion flow-tube mass spectrometer (SIFT-MS) for characterisation of volatile organic compounds and atmospheric trace gases. Atmos. Meas. Tech. 2021, 14, 6083–6100.
23. Langford, V.S.; Gray, J.D.C.; Maclagan, R.G.A.R.; Milligan, D.B.; McEwan, M.J. Real-time measurements of nitrosamines in air. Int. J. Mass Spectrom. 2015, 377, 490–495.
24. Smith, D.; McEwan, M.J.; Španěl, P. Understanding gas phase ion chemistry is the key to reliable selected ion flow tube-mass spectrometry analyses. Anal. Chem. 2020, 92, 12750–12762.
25. Shaw, M.; Acton, J.; Squires, F.; Carpenter, L.; Lewis, A.; Hopkins, J. Evaluation of Direct Mass spectrometry for VOC concentration and emission determination in Beijing. In Proceedings of the Atmospheric Science Conference (UK), York, UK, 3–4 July 2018.
26. Hien, T.T.; Huy, D.H.; Dominutti, P.A.; Chi, N.D.T.; Hopkins, J.R.; Shaw, M.; Forster, G.; Mills, G.; Le, H.A.; Oram, D. Comprehensive volatile organic compound measurements and their implications for ground-level ozone formation in the two main urban areas of Vietnam. Atmos. Environ. 2022, 269, 118872.
27. Cliff, S.J.; Lewis, A.C.; Shaw, M.D.; Lee, J.D.; Flynn, M.; Andrews, S.J.; Hopkins, J.R.; Purvis, R.M.; Yeoman, A.M. Unreported VOC emissions from road transport including from electric vehicles. Environ. Sci. Technol. 2023, 57, 8026–8034.
28. Shin, H.J.; Seo, H.J.; Joo, K.H.; Park, S.J. A study on reliability improvement of management for air pollution emission sources using selected ion flow tube mass spectrometers. J. Korean Soc. Urban Environ. 2021, 21, 97–104.
29. Crilley, L.R.; Kramer, L.J.; Ouyang, B.; Duan, J.; Zhang, W.; Tong, S.; Ge, M.; Tang, K.; Qin, M.; Xie, P.; et al. Intercomparison of nitrous acid (HONO) measurement techniques in a megacity (Beijing). Atmos. Meas. Tech. 2019, 12, 6449–6463.
30. Dominutti, P.A.; Hopkins, J.R.; Shaw, M.; Mills, G.; Le, H.A.; Huy, D.H.; Forster, G.L.; Keita, S.; Hien, T.T.; Oram, D.E. Evaluating major anthropogenic VOC emission sources in densely populated Vietnamese cities. Environ. Pollut. 2023, 318, 120927.
31. Anonymous. Analysis of Fine Dust Using Drone in Hwabuk Industrial Complex. Available online: https://www.youtube.com/watch?v=718NDVldbT4 (accessed on 1 August 2023).
32. Anonymous. Production of Pollution Map by Conducting Non-Face-to-Face Forecasting Activities Using a SIFT-MS Instrument Mounted in a Moving Laboratory and Drones. Available online: https://www.youtube.com/watch?v=Qcvv68C5k08 (accessed on 1 August 2023).
33. Park, J.-E. Analysis of Volatile Organosulfur Compounds of Marine Origin Using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS). M.Sc. Dissertation, Korea University, Seoul, Korea, August 2021. Available online: https://dcollection.korea.ac.kr/srch/srchDetail/000000252171 (accessed on 27 July 2023).
34. Kim, K.-B.; Kim, M.-H.; Chung, S.-Y.; Shin, E.-J.; Lee, S.-H.; Choi, J.-W.; Kang, Y.-S. Compatibility evaluation of online headspace with direct mass spectrometry for real-time water quality monitoring in chemical accidents. J. Environ. Anal. Health Toxicol. 2020, 23, 27–36.
35. Lee, S.-H.; Shin, E.-J.; Zoh, K.-D.; Kang, Y.-S.; Choi, J.-W. Direct mass spectrometry with online headspace sample pretreatment for continuous water quality monitoring. Water 2020, 12, 1843.
36. Son, H.-D.; An, J.G.; Ha, S.Y.; Kim, G.B.; Yim, U.H. Development of real-time and simultaneous quantification of volatile organic compounds in ambient with SIFT-MS (selected ion flow tube-mass spectrometry). J. Korean Soc. Atmos. Environ. 2018, 34, 393–405.
37. Yu, J.; Ryu, S.; Kim, J.; Kim, J.; Park, J.; Gong, B. Characteristics of emissions for air pollutants and odorous substances in a domestic dying industrial complex by using a real-time mobile monitoring system. J. Odor Indoor Environ. 2019, 18, 362–370.

38. Yu, J.; Song, H.; Nam, S.; Yu, U.; Shin, I. A investigation of air quality characteristics around northwest petrochemical industrial complex. Rep. Chungnam Prov. Inst. Health Environ. 2022, 32, 107–124. Available online: http://www.chungnam.go.kr/orga/board.do?mnu_url=/mult/view.do&mult_seq=28375&searchCnd=0&mnu_cd=HERMENU00229&pageNo=1&pageGNo=0&showSplitNo=10 (accessed on 27 July 2023).
39. Lee, M.-S.; Jung, J.-Y.; Kim, H.-S.; Youn, S.-J.; Jin, B.-B. Air Monitoring of Hazardous Air Pollutants in Industrial Complex Using SIFT-MS. Available online: http://www.dbpia.co.kr/journal/articleDetail?nodeId=NODE07552290 (accessed on 27 July 2023).
40. Shin, H.-J.; Kim, J.-S.; Kong, H.-C. Measurement of VOCs in industrial complex using real-time air quality measurement equipment. J. Korean Soc. Urban Environ. 2020, 20, 35–42.
41. Youn, S.-J.; Jo, K.-H.; Kim, H.-S.; Song, G.-B.; Lee, S.-B.; Jeong, J.-Y. Measurement of hazardous air pollutants in industrial complex using mobile measurement system with SIFT-MS. J. Korean Soc. Atmos. Environ. 2020, 36, 507–521.
42. McEwan, M.J. Direct analysis mass spectrometry. In Ion Molecule Attachment Reactions: Mass Spectrometry; Fujii, T., Ed.; Springer: New York, NY, USA, 2015; pp. 263–317.
43. Taylor, A.J.; Beauchamp, J.D.; Langford, V.S. Non-destructive and high-throughput–APCI-MS, PTR-MS and SIFT-MS as methods of choice for exploring flavor release. In Dynamic Flavor: Capturing Aroma Release Using Real-Time Mass Spectrometry; Beauchamp, J.D., Ed.; American Chemical Society: Washington, DC, USA, 2021; pp. 1–16.
44. Blake, R.S.; Monks, P.S.; Ellis, A.M. Proton-transfer reaction mass spectrometry. Chem. Rev. 2009, 109, 861–896.
45. Yuan, B.; Koss, A.R.; Warneke, C.; Coggon, M.; Sekimoto, K.; de Gouw, J.A. Proton-transfer-reaction mass spectrometry: Applications in atmospheric sciences. Chem. Rev. 2017, 117, 13187–13229.
46. Forbes, P. Atmospheric chemistry analysis: A review. Anal. Chem. 2020, 92, 455–472.