



Adoption of SIFT-MS for VOC Pollution Monitoring in South Korea

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Abstract: 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. South Korea is a highly industrialized and densely populated nation and suffers from significant VOC and ozone pollution. In recent years, South Korea has implemented more stringent controls on industry to address air and water pollution, requiring more real-time and on-site analysis. 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. SIFT-MS has been applied to emission source characterization, fenceline monitoring, ambient monitoring, pollution mapping, and incident response (including the use of drone-based sampling) for hazardous air pollutants (HAPs), odor nuisance species, and compounds that have high ozone formation potential (OFP) and/or contribute to secondary aerosol (SOA) formation. This review summarizes the South Korean application of SIFT-MS to the monitoring of VOC pollutants.

Keywords: selected ion flow tube mass spectrometry; SIFT-MS; VOCs; air analysis; water analysis; air quality monitoring; pollution monitoring; mobile laboratory; drone sampling

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 NO₂) [1]. The Republic of Korea (South Korea), and especially the Seoul megacity, has a longstanding issue with elevated ozone levels [1–4]. 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



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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.

The adoption of SIFT-MS for real-time air monitoring in South Korea is the focus of this review. Most of this research has been presented at Korean conferences or published in Korean-language journals and reports from government agencies and has had poor visibility globally and went unreported in recent reviews [13,14]. It is structured as follows. First, the SIFT-MS technique is briefly summarized and contrasted with the operational principles of conventional gas chromatography (GC) methods, and its integration in practical field-based monitoring systems is outlined. Second, the air quality applications of SIFT-MS in South Korea are reviewed systematically, organized by type of application. Next, the emerging application for headspace analysis of VOCs in water is covered briefly. Finally, general conclusions are made together with brief comments on probable future directions.

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

Conventional environmental VOC analysis primarily utilizes GC analysis [15] (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) [16]. 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.

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 [14,17]. 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 [18]. 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 [13,19,20]. 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].



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.

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 [14,23,24]. 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 [13]. A similar approach has been used in the field-based environmental monitoring conducted by Shaw and co-workers [22,25–27]. 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
	Air monitoring shed	Emission source analysis; fenceline monitoring; ambient monitoring	[11,26,36]
Automated multiport sampling (sample, blank, and calibration lines)	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)	[22,39-41]

Table 1. Cont.

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 [44–46], especially its time-of-flight (TOF) variant [45], whereas SIFT-MS has been utilized to a limited extent [13,14]. 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.

3. Air Quality Analysis

The high level of industrialization in South Korea, especially in the northwest and southeast [47], and widespread use of motor vehicles (e.g., 10 million in the Seoul metropolitan area [48]) have led to high levels of VOCs and ozone, necessitating greater regulation and increased measurement. Since the quality of life in this densely populated peninsula (516 people/km² in 2023 [49]) is impacted by more than just ozone precursors, a broad range of analytes are targeted using SIFT-MS. These comprise hazardous air pollutants (HAPs; Table A1 [50]), volatiles with high ozone formation potential (OFPs), those that contribute to the formation of secondary organic aerosols (SOAs), and odor nuisances (Table A2 [51]). Often the compounds targeted using SIFT-MS comprise volatiles from multiple agency lists, so they are dealt with together here. This is a significant advantage of SIFT-MS compared to conventional chromatographic analysis. The direct (column-free), soft chemical ionization in SIFT-MS instruments enables effective, quantitative analysis of most VOCs in the same instrument configuration irrespective of the functional group [13]; no sample preparation (including derivatization), column change, or detector change is required. Hence the application of SIFT-MS simplifies VOC analysis compared to GC analysis, it does not just make it faster [52].

When breaches of air quality regulations occur, it can be difficult to identify the entity that is responsible due to industrial complexes often comprising large numbers of businesses, a significant number of which are from the same industry and hence can release similar volatile pollutants. This complexity, coupled with concern for protecting the population and the environment, has stimulated the evaluation of techniques that more rapidly alert to degraded air quality [11]. This section describes the vital contribution that SIFT-MS is making to improve air quality across the groups of pollutants listed above with published campaign results from national, local, and academic organizations across the more densely populated and industrial northwest-southeast transect (Figure 2). Applications of SIFT-MS are broad, as summarized in Table 2 and reviewed in the following subsections. Where a reference covers several applications, the discussion is located based on the article's focus.



Figure 2. Published air monitoring campaigns (colored according to application) using SIFT-MS have primarily occurred in the more populous and industrial northwest and southeast regions of South Korea. (Map of South Korea, on which annotations have been made, is from https://commons.wiki media.org/wiki/File:Map_of_Korea-blank.svg, by FriedC, CC3.0; accessed on 2 June 2023).

Table 2. Summary	of South Korean	literature for	SIFT-MS-based	air qualit	y monitoring
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Year	Primary Application(s) ¹	Analyte Class(es) ² {Number of Analytes}	Location(s)	Reference
2017	Ambient	HAPs {44}	Seoul	Korea Min. Env. [11]
2017	Ambient	HAPs {36}	Seoul, Shiwa, Daesan	Lee et al. [53]
2018	Ambient	HAPs + SOAs {60}	Geoje	Son et al. [36]
2018	Pollution mapping	HAPs {29}	(Multiple; not stated)	Lee et al. [39]
2019	Fenceline	HAPs + Odor {17}	Daegu	Yu et al. [37]
2019	Incident response	OFPs + SOAs {14}	Gyeonggi	Ryu et al. [54]
2020	Ambient	OFPs {53}	Busan	Hwang et al. [55]
2020	Emission source	Odor {43}	Incheon	Kil et al. [56]
2020	Incident response	HAPs + Odor {11}	Ansan	Shin et al. [57]
2020	Pollution mapping	HAPs + Odor {9}	Sihwa	Shin et al. [40]
2020	Pollution mapping	HAPs + Odor {10}	Sihwa	Shin et al. [58]
2020	Pollution mapping	HAPs {25}	Ulsan	Youn et al. [41]
2021	Ambient	HAPs {3}	Daegu	Kim [59]

Year	Primary Application(s) ¹	Analyte Class(es) ² {Number of Analytes}	Location(s)	Reference
2021	Ambient	HAPs (84)	Hyeon	Lee et al. [60]
2021	Ambient	OFPs {31}	Pohang, Sangju	Kim et al. [61]
2021	Ambient	HAPs {105}	Ulsan	Yu et al. [62]
2021	Emission source	Odor {4}	(Laboratory)	Woo et al. [63]
2021	Emission source	Not stated	(Land transport tunnel)	Song et al. [64]
2021	Emission source	SOAs {not stated}	(Ship based)	Hwang et al. [65]
2021	Emission source	Odor {44}	Gyeonggi	Park et al. [66]
2021	Emission source; Ambient	SOAs {70}	Busan	Jang et al. [67]
2021	Incident response	HAPs {8}	Sihwa	Shin et al. [28]
2021	Pollution mapping	HAPs {64} + Odor {20}	Busan	Choi et al. [68]
2021	Pollution mapping	HAPs {18}	Daegu	Youn [69]
2022	Ambient	HAPs {16}	Ulsan	Yu et al. [70]
2022	Emission source	HAPs + Odor {8}	Busan	Kim et al. [71]
2022	Fenceline	HAPs {53}	Daesan	Yu et al. [38]
2022	Incident response	HAPs {64} + Odor {20}	Busan	Choi et al. [72]
2022	Incident response	HAPs {9,12,12}	Sihwa, Ansan, Hwaseong	Shin [73]
2023	Ambient	HAPs {105}	Ulsan	Choi et al. [74]
2023	Fenceline	HAPs + Odor {18}	Daegu	Kim [75]

Table 2. Cont.

¹ Bold text indicates the first reported South Korean application using SIFT-MS. ² HAPs = hazardous air pollutants; SOAs = secondary organic aerosols; OFPs = VOCs with ozone formation potential.

3.1. *Emission Sources*

The application of SIFT-MS to emission sources began with those causing odor nuisance which is unsurprising as SIFT-MS provides broad-spectrum odorant analysis in one run [13,19,20,76]. Kil et al. described the profiling of odor sources, with the intention of using the profiles for future complaint tracking [56]. Following many odor complaints during 2018 in Songdo International City, Incheon, these researchers utilized a mobile SIFT-MS instrument to profile various odor sources, including a sewage treatment facility, a daily waste collection facility, a gas facility, and a waste recycling facility (in decreasing order of overall odorant intensity). Various odorants were identified for the facilities, supporting the original goal of the study; the fast resolution of complaints, and the identification of compounds that should be targeted for future reduction.

Park et al. [66] applied SIFT-MS to the characterization of odor sources at a waste treatment facility. They targeted 44 odorants, including sulfur compounds, ammonia, amines, alcohols, aldehydes, and ketones across eight waste treatment steps, including combustion, neutralization, solidification, storage, and drying. Different raw materials were evaluated: industrial waste, oil/solvents/paint, dust and cinder, organic sludge, and food waste. The main odor-causing substances observed were ammonia, amines, sulfur-containing species, and aldehydes. The highest concentration VOCs (methanol, ethanol, and acetone) did not have a significant odor impact.

In support of odor analysis from swine production facilities, Woo et al. [63] used SIFT-MS to investigate the recovery behaviors of C_2 - C_5 straight-chain volatile fatty acids (VFAs) from polyester aluminum (PEA) gas sampling bags. The most significant losses were observed over the first 12 h after sampling, which is unsurprising given the volatility of the VFAs. Modeling the recovery behavior proved challenging, with only acetic acid exhibiting satisfactory performance for odor samples collected at a swine production facility.

Kim et al. [71] reported field-based testing that supported the implementation of odor emission standards for painting facilities. They correlated total hydrocarbons (THC) measured at the emission source using a portable flame ionization detector (FID) with the quantitative SIFT-MS analysis of eight VOCs (six of which are regulated for odor) from gas sample bags collected at the outlet. The study was conducted across 21 painting facilities of various types in Busan during routine operation. The dominant VOCs by concentration were, in decreasing order, the xylenes (including ethylbenzene), toluene, and butyl acetate. Butyl acetate, however, was the dominant odorant based on odor activity, followed by the xylenes (and ethylbenzene), and toluene. With stack emissions commonly in the partper-million-by-volume (ppmV) range, they recommended that painting facilities move to low-odor alternatives for paints and diluents to reduce odor impact.

SIFT-MS has also been utilized for the analysis of VOC emissions from transportation. Hwang et al. [65] analyzed ship VOC emissions as part of a wider determination of emission factors aimed at reducing data losses on research vessels due to contamination from incomplete combustion in the engine. The average emission factor was determined to be 30.6 ± 12.5 g/kg of fuel, with NO_x being dominant (63%).

An investigation of the impact of recently imposed strict limits on sulfur content in shipping fuels (reduced from 3.5 to 0.1%) [77] utilized SIFT-MS to investigate the organic component [67] of ultrafine particulate emissions (less than 2.5 μ m; PM_{2.5}) from ships. Speciation of PM_{2.5} was a challenging task since there were contributions from local sources and SOAs. Jang et al. utilized a SIFT-MS-equipped mobile laboratory at two sites near the north port of Busan, the largest port city in Korea, to monitor 70 VOCs with 30-s time resolution over a five-day period each quarter. Ship emissions were the largest contributor to SOA formation (37.8%). In the summer, a reduction in SOA of 28% was observed before and after the implementation of the new fuel regulation (from 2020 to 2021). At the inland measurement site, an 11.5% reduction in organic carbon was observed, possibly also due to the fuel quality improvement.

Road vehicle emission sources in South Korea have received little dedicated investigation using SIFT-MS. In a preliminary study, Song et al. [64] reported the utilization of SIFT-MS to analyze VOCs and their migration in a road tunnel. Roadside emission measurements were, however, discussed substantially in the initial evaluation of SIFT-MS by the Korea Institute of Science and Technology (KIOST) [11]. A recent study conducted in the United Kingdom by Cliff et al. [27] illustrates the utility of SIFT-MS for the determination of emission factors from transport sources.

3.2. Fenceline Monitoring

The fenceline monitoring of HAPs and odor nuisance compounds is located at a distance from the emission source and is subject to dispersion effects based on the instantaneous meteorological conditions. Hence the application of high-sensitivity, real-time instrumentation, such as SIFT-MS, is very beneficial.

Yu et al. [37] of the National Institute of Environmental Research (NIER) utilized a SIFT-MS mobile laboratory for the characterization of 17 air pollutants and odorants emitted from textile dying facilities at an industrial complex in Daegu. In agreement with the Korean chemical inventory (Table A1 [50]), they observed significant concentrations of toluene (up to nearly 1 ppmV), as well as methyl ethyl ketone (MEK) and dichloromethane (up to 130 ppbV). The most frequently detected pollutants at higher concentrations were, in descending order, toluene, methanol, acrolein, dichloromethane, and acetone. These results were similar to the chemical emissions described for the industrial area by the Pollutant Release and Transfer Register (PRTR) data [78] since companies are obliged to report chemical use in the PRTR under the Korean Chemical Substances Control Act [79]. The hydrogen sulfide concentration was about 10-fold higher than the instrument the quantitation limit at one measurement site and was judged to be the main cause of odor there. These authors suggested improvements to the early real-time mobile measurement system that would enable it to become an even more valuable tool, including automatic integration of wind direction and speed, and PRTR and SEMS (Stack Emission Management System) data. Subsequent studies (Table 2) utilized improved systems.

More recently, Yu et al. [38] have published results from an extended air monitoring campaign at a petrochemical plant in Daesan in the northwest region. Target VOCs (53 in total) were drawn from air environment conservation, odor prevention, and HAP lists, and monitored at five sites using a SIFT-MS instrument in a mobile laboratory. TD-gas chromatography-mass spectrometry (GC/MS) analysis was conducted at two fixed monitoring stations (one at the complex and one some distance to the south). They concluded that measurements made using the mobile SIFT-MS instrument enabled a wider scope for the pollutant dispersion study and facilitated the association of formaldehyde emissions with traffic rather than industry.

Kim [75] also utilized a van-mounted instrument for monitoring VOC pollutants in four industrial complexes in Daegu from January to June 2022. The study monitored 18 gaseous pollutants using the moving measurement platform, including benzene, formaldehyde, acetaldehyde, and hydrogen sulfide. No seasonal variation was observed in this study, which is unsurprising given the industrial focus of the monitoring. The benefits of monitoring using a moving platform were again emphasized because it enables the intermittent use of chemicals to be traced due to the high time resolution of measurements.

3.3. Ambient Monitoring

Moving further from industrial emission sources, the real-time analysis of HAPs in ambient air is advantageous compared to time-averaged approaches, such as TD-GC/MS, because deeper insights into pollution sources (including variations with time of day) and the impact of meteorological conditions can be gained. Utilization of SIFT-MS for ambient VOC monitoring has been reported in New Zealand [21,80], China [25,29], and Vietnam [26,30], but it has been used most extensively in South Korea.

Results from the first Korean environmental monitoring campaign that used SIFT-MS were presented in conference proceedings of the Korean Society of Atmospheric Environment in 2017 [53]. The instrument was located at several fixed monitoring sites in greater Seoul and monitored 36 VOCs from the Korean HAP list (HAPs; Table A1 [50]). This study was foundational to the subsequent widespread use of SIFT-MS for real-time monitoring of VOCs. In 2017, a substantial report was published [11], which thoroughly evaluated SIFT-MS as part of a tool for "(near) real-time monitoring of HAPs".

Improved responsiveness to air pollution events and reduced time to obtain analytical results compared with conventional grab sampling, such as Tedlar bags, sorbent tubes, and canisters, was demonstrated by KIOST in a 60-compound analytical method with a cycle time of 3.2 min [36]. Good linearity was achieved over the calibration range (0.174–100 ppbV), with repeatability (measured using relative standard deviation, %RSD) less than 10%, and sub-ppbV limits of detection (LODs), across broad chemical functionalities (including amines, hydrocarbons, organosulfur compounds, and volatile fatty acids).

Hwang et al. [55] utilized a SIFT-MS instrument in a mobile laboratory to investigate the diurnal variation of VOCs (together with carbon dioxide and ozone) at representative urban and harbor sites in Busan, Korea, from January and April 2019. The mobile SIFT-MS laboratory enabled measurements to be made near emission sources for 53 VOCs (including alkanes, alkenes, aromatics, alcohols, carboxylic acids, esters, aldehydes, ketones, and halogenated compounds). Carbonyl compounds accounted for 60% and 70% respectively, of the OFP at urban and harbor sites. Formaldehyde showed the highest ozone production per concentration index (OPCI). This study suggests a potential SIFT-MS application for monitoring VOCs implicated in ozone formation.

A mobile SIFT-MS instrument was used by Kim et al. [61] to monitor 31 VOCs with high OFP in two locations that suffer from chronic ozone issues (Pohang on the east cost and Sangju in central South Korea, respectively). However, there appears to be an issue with the reported concentration units in this article, because the total VOC (TVOC) was in the 136 to 543 ppmV range, and several VOCs in tens of ppmV were unrealistically high. It is likely that this is due to the inadvertent substitution of ppmV for ppbV.

Kim [59] focused on benzene, toluene, and ethylbenzene, plus the xylenes (BTEX) monitoring in Daegu City. Daegu has seven central-city industrial complexes that emit harmful air pollutants, with BTEX primarily emitted from the dominant textile and metal industries. Emissions from four urban industrial complexes and one residential area were monitored from March to June 2021 to identify the distribution characteristics of BTEX in industrial complexes and residential areas. Benzene concentrations were in the 0.36 to 0.56 ppbV range at all monitoring sides, including the residential area, in compliance with the Korean standard (1.5 ppbV) (Table A3 [81]). Average toluene concentrations for the industrial complexes ranged from 5.5 to 25.3 ppbV (versus 2.9 ppbV in the residential area), while xylene + ethylbenzene was in the range of 5.0 to 8.2 ppbV for the industrial complexes.

Lee et al. [60] investigated VOC pollution arising from small-scale ship repair yards in Hyeon, southeast Korea. They targeted 84 VOCs using a SIFT-MS instrument in a mobile laboratory. Temporal variations in VOC concentrations were considerable due to diverse activities being undertaken at the repair yards and hence demonstrated the high value of real-time monitoring compared to the time-averaged TD-GC approach.

Seasonal (winter-summer) behaviors and the annual average distribution of 105 HAPs in Ulsan (southeast Korea) were investigated at three locations (industrial, urban, and 'non-urban') using a SIFT-MS instrument in a mobile laboratory [62]. Concentrations of the dominant VOCs were highest in the industrial area. The measured formaldehyde concentrations were consistent with other Korean cities, while average benzene levels just met the Korean standard of 1.5 ppbV (Table A3 [81]). Little summer-winter variation in VOC emissions was observed at the coastal industrial location, whereas in the urban and inland 'non-urban' areas the emissions were higher in the summer. There was little diurnal change in VOC levels in the non-industrial areas for the dominant VOCs, whereas they nearly doubled at night in the industrial area. In a follow-up study, Yu et al. [70] monitored 16 HAPs at the same sites. The annual average concentrations of major VOCs were highest in the Yeocheon-dong industrial area. In this coastal area, summer weather patterns (with south or southeast winds) played a significant role in the variation of concentration. As for the previous study [62], higher concentrations of VOCs were measured at night than during the day at the industrial site. It was concluded that better management of emissions in industrial areas is needed, as is long-term monitoring of VOCs.

Most recently, Choi et al. [74] utilized a mobile SIFT-MS instrument in a residential area of Ulsan to investigate the extent of drift from nearby industry. Of the 105 HAPs and odorous species targeted, ammonia occurred at the highest concentration, while aliphatic hydrocarbon concentrations were also significant due to the nearby petrochemical complex. Contributions from vehicle emissions were observed during periods of traffic congestion. The results were consistent with other studies made in residential areas near petrochemical plants.

3.4. Pollution Mapping

The standard TD-GC method for HAP analysis in Korea does not provide an adequate understanding of the dispersion of pollutants due to the cost, complicated analysis, and time-averaged results [75]. Additional data from more measurement locations are required and this can be delivered by deploying robust SIFT-MS instruments in mobile laboratories, enabling real-time collection at both fixed locations and while moving.

Lee et al. [39] first addressed this need in 2018, conducting VOC analysis "on the move" using SIFT-MS mounted in a mobile laboratory. Using this mobile system, they also conducted 24 h monitoring at three fixed sites for the same suite of 29 HAPs. They demonstrated a proof-of-concept application of on-the-move SIFT-MS analysis for the creation of pollution maps and identification of hotspots. Through the integration of concentration data with location and meteorological conditions, they concluded that the

concentrations of HAPs in industrial complexes can be effectively investigated by using a mobile measurement vehicle equipped with SIFT-MS.

Subsequently, Shin et al. [40,58] have described the development of a mobile laboratory and used it to map pollution at the Sihwa Industrial Complex in northeast Korea, a complex with various types of industrial emission sources. Like Lee et al. [39], Shin et al. [40,58] combined analysis on the move and at multiple fixed sites in their monitoring campaigns. The first measurement campaign [40] targeted nine HAPs and odorous compounds, with toluene and MEK dominant at up to approx. 180 and 170 ppb, respectively, in locations with chemical or ink manufacturing, and coating of metals. Other VOCs were measured at lower concentrations. The second campaign [68] focused on the so-called chemical block at the western end of the same complex, where 10 HAPs and odor compounds were monitored at 10 fixed locations. Similar measurement results were observed both day and night for all analytes except MEK (with higher daytime concentrations). At several locations, higher hydrogen sulfide concentrations were measured at night. These studies confirmed the utility of monitoring VOCs while moving to efficiently manage air emission sources.

Youn et al. of the Korea Environment Corporation (KECO) [41,69] also described the development of a mobile SIFT-MS measurement system with integrated weather measurement and global positioning system (GPS) instrumentation. The characteristic dominant compounds for each facility were identified through continuous measurement for 24 h at fixed locations. Spatial distribution characteristics were studied through real-time measurement while driving on the industrial facility's roads. The system was evaluated in several measurement campaigns, including for monitoring 25 HAPs at a petroleum manufacturing industrial complex in Ulsan (coastal southeast Korea) [41]. Sources emitting high levels of pollutants could be approximately located by correlating real-time monitoring results with the wind direction and speed. Methanol was observed at the highest concentration both at the fixed sites and during on-the-move monitoring. The mobile measurements were used to create pollution maps which show the spatial distribution of pollutants. Such data can enable pollution sources to be identified but also illustrates the difficulty involved in selecting fixed monitoring points in industrial facilities with many potential emission sources. A mobile SIFT-MS laboratory enables both approaches to be used. Youn concluded that "this measurement system using SIFT-MS is a useful tool for evaluating the temporal and spatial concentrations of HAPs in the ambient air of the vicinity of industrial complexes instead of conventional analysis techniques such as gas chromatography" [69] (p. 123).

Choi et al. [68] have utilized a moving SIFT-MS laboratory to map HAP emissions from two industrial complexes in coastal Busan, southeast Korea. They monitored 84 VOCs (including 20 designated as odor nuisances) to identify pollutants with major impact at these complexes. Figure 3 shows pollution maps for 12 HAPs measured in the Sasang industrial area. These results demonstrated the real-time, broad-spectrum analysis provided by the SIFT-MS technique [13,14], including chromatographically challenging species such as ammonia, hydrogen sulfide, and formaldehyde.

3.5. Incident Response: Combining Mobile SIFT-MS Analysis with Drone Sampling

Hazardous and odorous VOC emissions from industry can disperse far beyond the fenceline, but the maximum landing concentration distance is dependent on the height of the emission source, ambient temperature and pressure, and wind direction. Hence understanding environmental pollution as a function of altitude is important. Traditional approaches used manned aircraft and radiosondes, but cost and manipulation challenges hinder wider utilization. Drones are an attractive alternative because it is much easier to obtain pollution data both as a function of altitude and from sources that are difficult to access directly.



Figure 3. Pollution maps for 12 selected HAPs were generated from concentration data collected by a SIFT-MS instrument mounted in a moving laboratory traversing roads in the Sasang industrial area (Busan, South Korea) [68]. Concentration ranges shown depend on the analyte. Reproduced with permission from Dr S. Choi, *J. Korean Soc. Urban Environ.*; published by Korean Society of Environmental Engineers, 2021, under Creative Commons Attribution 4.0.

In 2019, NIER [54] first described the benefits of the complementary use of a SIFT-MS real-time VOC measurement system (targeting 14 HAPs and odor compounds) incorporating drone sampling. Figure 4 shows their proposed workflow for effectively tracing incidents to the emission source. The case study investigated suspected pollutant emission

sites in an urban industrial complex located in Gyeonggi-do (inland northwest Korea) during an incident in 2018. The area with high pollutant concentrations was identified using the combination of drone sampling and real-time mobile monitoring. The concentration of toluene exceeded 2.5 ppmV, while dichloromethane and methanol were up to 170 ppbV and 90 ppbV, respectively. Note that the SIFT-MS results are not used to determine compliance, they identify the source from which sample(s) for regulatory compliance will be taken and tested in a regulatory laboratory.



Figure 4. Schematic overview of the NIER pollution incident workflow using a real-time monitoring system (SIFT-MS) and drone sampling. Updated and redrawn from [54] with permission of Dr B.-J. Gong, NIER.

Shin [73] and coworkers [28,57] have utilized the complementary drone sampling and SIFT-MS analysis approach for several monitoring campaigns. First, at the Banwol National Industrial Complex in Ansan, northwest Korea [57], a mobile SIFT-MS system was used to measure VOCs at the fenceline of suspected pollution sources (nine locations). Next, samples were collected directly from suspected sources using drones. At three of the fenceline measurement locations, the concentrations of toluene, xylene, hydrogen sulfide, and MEK were much higher than in the background. The VOC concentrations determined from samples collected by drone correlated with the fenceline measurements. The authors reported that the use of drones and real-time air quality monitoring equipment enables rapid identification of pollution sources. This is especially significant for identifying smaller businesses that are responsible for pollution events, which are not so closely monitored by the authorities [73].

A follow-up study by Shin et al. [28] compared the regulatory GC/MS technique and the mobile SIFT-MS instrumentation currently used to efficiently manage air pollution emission sources (though not an official measurement method by air pollution test standards). SIFT-MS calibration data had higher correlation coefficients for linearity across the eight VOCs tested ($R^2 \ge 0.99$). Simultaneous measurements of five VOCs at five monitoring locations using SIFT-MS and GC/MS (on two dates three months apart) showed very good agreement (typically within 1 ppbV). The mean difference between techniques across all data (-0.034 ppbV) demonstrates that overall bias is negligible. Shin and co-workers concluded that measurements using SIFT-MS were reliable and that they could be used to efficiently manage sources of suspected high concentrations by measuring air pollutants in real-time.

Choi et al. [72] have investigated VOC and fine-dust air pollution as a function of altitude using drone sampling at four sites in Busan: at Noksan and Shinpyeong-Jangrim industrial complexes, the international airport's passenger terminal (a commercial area), and at Silla University (a green zone). The drone filled Tedlar[®] gas sampling bags were used at various altitudes (ground, 10 m, 20 m, 40 m, 60 m, 80 m, and 100 m) for analysis of

84 VOCs from a variety of Korean regulations using a SIFT-MS instrument in a mobile lab. VOC concentrations in industrial complexes were approximately twice as high as in green areas and 1.4-fold higher than in commercial areas, and the industrial complexes differed in relative pollutant levels. Both, however, had hydrogen sulfide levels above the Korean odor threshold. As the altitude increased, the concentration of air pollutants decreased, although under temperature inversion conditions the concentration increased. This result agrees with Kim et al. [61], who observed that lower-altitude drone sampling yielded higher VOC concentrations. These researchers estimated that air pollution measurement using drone sampling with ground-based analysis introduced about \pm 5% more measurement uncertainty than direct measurement methods.

4. Water Analysis

As a gas-phase analysis technique, SIFT-MS cannot analyze VOCs through direct injection of environmental water samples. Instead, SIFT-MS does so indirectly via headspace analysis [82–85], and potentially via permeation through a membrane interface as was demonstrated using PTR-MS [86]. In South Korea, headspace-SIFT-MS analysis of water samples has been utilized in research and for in-line analysis of industrial wastewater. Note that in this section, the solution concentrations discussed are quoted. These take the form of mass-to-volume units (1 ppb is 1 μ g/L) in contrast with the volume: volume units used by convention in SIFT-MS gas-phase analysis [82].

4.1. Research Application

Research to date has focused on headspace analysis of reduced sulfur compounds (RSCs; especially dimethyl sulfide (DMS)) in seawater due to the contribution that this source makes to atmospheric sulfur load. RSCs are ultimately converted to sulfates (residing in aerosols) through oxidation reactions, affecting the acidity of precipitation and potentially affecting climate [87]. Since approximately 84.5% of naturally generated RSCs are released from the ocean and contribute significantly to aerosol generation in the marine atmosphere, the development of in situ real-time measurement methods is essential [88].

Park [33] evaluated headspace-SIFT-MS analysis for quantitative analysis of DMS in seawater because it provides a potential alternative to the popular, but low throughput, gas chromatography analysis. SIFT-MS results were accurate (approx. 99% across the range: 0.2–100 ppbV) and real-time quantification was possible with uncertainty better than 5%. Further method development for headspace SIFT-MS analysis of RSCs in seawater was described by Choi et al. [89]. Excellent linearity was obtained ($R^2 = 0.99-1.00$), but LODs in the range of 0.06–0.71 ppb (in solution) suggested that currently, the headspace-SIFT-MS approach was applicable to coastal areas where RSCs were more abundant. As of writing, it is uncertain whether headspace-SIFT-MS will have an application for routine DMS analysis in seawater.

4.2. Industrial Application

Korea Water and its collaboration partners have reported results from several headspace-SIFT-MS studies focused on measuring pollutants in industrial wastewater. The research is in the context of South Korean regulations [90,91] but with the view that the enhanced speed of SIFT-MS analysis, compared to the standard GC/MS method, can provide higher time resolution and therefore alert to pollution incidents more rapidly.

Yoon et al. [92] described coupling a syringe-injection autosampler with a SIFT-MS instrument for potential online application and evaluated performance for 12 hazardous VOCs. Although LOQs for the 12 analytes were relatively high (in the mg L^{-1} range), the study demonstrated the feasibility of near-continuous monitoring of hazardous pollutants in water. The approach was improved by Kim et al. [34], who compared online headspace-SIFT-MS performance with headspace-GC/MS for 20 hazardous VOCs. Performance evaluation was determined by comparing the linearity of the calibration curve, method detection limits, quantitation limits, accuracy, and precision. The online headspace-SIFT-MS

system performed similarly to the headspace-GC/MS system at higher concentrations, but accuracy and precision suffered at lower concentrations. Nevertheless, online headspace-SIFT-MS was deemed to have sufficient accuracy for application in chemical accidents while providing faster run times.

Further improvement was achieved by Lee et al. [35]. The latest iteration of the prototype system demonstrated suitability for deployment at the site, with simple maintenance requirements. The LODs for 22 out of 28 compounds evaluated met or exceeded the requirements set by the Korean Ministry of Environment.

5. Conclusions and Future Directions

The rapid adoption of SIFT-MS for air monitoring following the first published evaluations undertaken in 2016 and 2017 [11,53] is largely due to its value as an orthogonal technique to regulatory GC methods facilitating investigation of local, transient VOC emissions. The SIFT-MS mobile laboratories are rapidly deployable to the site, can identify emitted VOCs, quantitatively analyze these VOCs immediately in real-time, and stream measurement data directly to decision makers. Application has primarily been in air quality monitoring, covering a wide range of VOCs comprising hazardous air pollutants (HAPs), compounds with ozone formation potential (OFPs), volatiles that contribute to secondary organic aerosol (SOA) formation, and species that are odor nuisances. Some studies have focused on just one of these compound suites (or a subset thereof), whereas others targeted volatiles from two or more. Water analysis, via headspace, has also been utilized. This illustrates the flexibility of the SIFT-MS technique as a multi-parameter analytical tool.

SIFT-MS instrumentation has proved to be very adaptable and robust. Initial instrument installations analyzed discrete environmental samples in laboratories and continuously in air monitoring sheds. Users from academia, industry, and government agencies in South Korea identified the potential of incorporating instruments in mobile laboratories, monitoring first at fixed points, and then shortly after acquiring data on the move. Coupled with drone sampling, this has enabled SIFT-MS to find widespread applications of air pollutant monitoring, from characterization of emission sources to fenceline and ambient monitoring, to simplified pollution mapping, and incident response. Although SIFT-MS is not currently a regulatory method upon the results of which a prosecution can be based, when mounted in a mobile laboratory and coupled with drone sampling it enables sources of pollution to be identified far more effectively than conventional approaches. Sampling for regulatory analysis can then be conducted and the results utilized by the authorities.

Future applications in air analysis will likely build on the work reviewed in this article, providing enhanced integration with location and meteorological measurement technologies for real-time data reporting. For water analysis, it is anticipated that the online monitoring of industrial wastewater will be adopted, requiring integration with automated sample delivery systems and reporting software. For both media, the SIFT-MS technique complements the incumbent regulatory methods by being able to address pollution events more rapidly. Hence in a highly industrialized and densely populated nation such as South Korea, the high-sensitivity, real-time VOC analysis provided by SIFT-MS instruments appears to be a necessity for improved public and environmental health.

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Glossary

BTEX	benzene, toluene, ethylbenzene, and xylenes
DIMS	direct-injection mass spectrometry
DMS	dimethyl sulfide
FID	flame ionization detector
GC	gas chromatography
GC/MS	gas chromatography mass spectrometry
GPS	global positioning system
HAP	hazardous air pollutant
KECO	Korea Environment Corporation
KIOST	Korean Institute for Oceanic Science and Technology
KORUS-AQ	Korea-United States Air Quality
LC	liquid chromatography
LOD	limit of detection
LOQ	limit of quantitation
MEK	methyl ethyl ketone
NIER	National Institute of Environmental Research (Korea)
OFP	ozone formation potential
OPCI	ozone production per concentration index
PAMS	photochemical assessment monitoring station(s)
PEA	polyester aluminum (sample bag material)
ppmV, ppbV, pptV	parts-per-million (billion; trillion) by volume
PRTR	Pollution Release and Transfer Register (Korea)
PTR-MS	proton transfer reaction mass spectrometry
QMF	quadrupole mass filter
RSD	relative standard deviation
SEMS	stack emission management system
SIFT-MS	selected ion flow tube mass spectrometry
TD	thermal desorption
TD-GC-FID	thermal desorption-gas chromatography-flame ionization detection
TD-GC/MS	thermal desorption-GC/MS
THC	total hydrocarbon
TVOC	total volatile organic compound
VFA	volatile fatty acid
VOC	volatile organic compound

Appendix A

Table A1. Korean hazardous air pollutants (HAPs) as defined in Table 2 of [50]. Note that only volatile compounds are detectable using SIFT-MS.

Acetaldehyde	Acrylonitrile
Aniline	Arsenic and compounds
Asbestos	Benzene
Benzidine	Beryllium and compounds

1,3-Butadiene	Cadmium and compounds
Carbon tetrachloride	Chlorine and hydrogen chloride
Chloroform	Chromium and compounds
1,2-Dichloroethane	Dichloromethane
Dioxin	Ethylbenzene
Ethylene Oxide	Fluoride
Formaldehyde	Hydrazine
Hydrogen cyanide	Lead and compounds
Mercury and compounds	Methyl disulfide
Nickel and compounds	Phenol and compounds
Polychlorinated biphenyls	Polycyclic Aromatic Hydrocarbons (PAHs)
Propylene oxide	Styrene
Tetrachloroethylene	Trichloroethylene
Vinyl chloride	

Table A2. Odor compounds listed in Table 1 of [51].

Acetaldehyde	Ammonia	Butyl acetate
i-Butyl alcohol	Butyraldehyde	n-Butyric acid
Dimethyl disulfide	Dimethyl sulfide (DMS)	Hydrogen sulfide
Methyl ethyl ketone (MEK)	Methyl isobutyl ketone (MIBK)	Methyl mercaptan
Propionaldehyde	Propionic acid	Styrene
Toluene	Trimethylamine	i-Valeraldehyde
n-Valeraldehyde	i-Valeric acid	n-Valeric acid
Xylene		

Table A3. Environmental standards for compounds of the Enforcement Decree of the Framework Act on Environmental Policy [81]. Only benzene is measured using SIFT-MS.

Compounds	Standard
SO ₂	Annual average: Below 0.02 ppm 24-h average: Below 0.05 ppm 1-h average: Below 0.15 ppm
СО	8-h average: Below 9 ppm 1-h average: Below 25 ppm
NO ₂	Annual average: Below 0.03 ppm 24-h average: Below 0.06 ppm 1-h average: Below 0.10 ppm
PM ₁₀	Annual average: Below 50 μg/m ³ 24-h average: Below 100 μg/m ³
PM _{2.5}	Annual average: Below 15 μg/m ³ 24-h average: Below 35 μg/m ³
O ₃	8-h average: Below 0.06 ppm 1-h average: Below 0.1 ppm
Pb	Annual average: Below 0.5 μ g/m ³
Benzene	Annual average: Below 5 μ g/m ³

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