

# A Technical Comparison of SIFT-MS and GC-MS

Developed for GC-MS users, this document describes how selected ion flow tube mass spectrometry (SIFT-MS) differs from gas chromatography mass spectrometry (GC-MS) both in its technical features and its operational capabilities. Both techniques analyze volatile organic compounds (VOCs), but have different fundamental strengths, which means the techniques complement rather than replace each other.

SIFT-MS is a form of direct mass spectrometry that analyses whole air in real time with typical detection limits at parts-per-trillion level (by volume). Real-time analysis is achieved by using precisely controlled soft chemical ionization that does not require chromatography. These factors also allow long-term calibration stability, reduced maintenance, and easy configuration of SIFT-MS instruments. Consequently, SIFT-MS is an ideal tool for rapid screening and real-time monitoring applications, especially where users may have non-technical backgrounds.

Alternatively, GC-MS provides very good specificity, but relies on electron impact ionization and chromatographic separation. Therefore it is relatively slow, has high maintenance requirements, and must be operated by skilled personnel, when compared to SIFT-MS. As a result, GC-MS complements the fast screening capabilities of SIFT-MS with slow but very selective analysis.

## Contents

### 1. Introduction

### 2. An overview of SIFT-MS

### 3. Principles of SIFT-MS

- a. Chemical ionization in SIFT-MS
- b. Chemistry of the SIFT-MS reagent ions
- c. How does SIFT-MS control the chemistry so precisely?
- d. Quantitation in SIFT-MS
- e. Calibration of SIFT-MS instruments

### 4. Operational advantages of Syft SIFT-MS compared to GC-MS

- a. Ease of use
- b. Remote operation
- c. Reduced maintenance
- d. Technical support

### 5. Summary

## 1. Introduction

GC-MS is a well-recognized technique for analysis of VOCs, offering high specificity as well as reliable quantitation (when calibrated). However, GC-MS requires a highly-skilled operator, and is not well suited to rapid analysis, due to the rather slow chromatographic process.

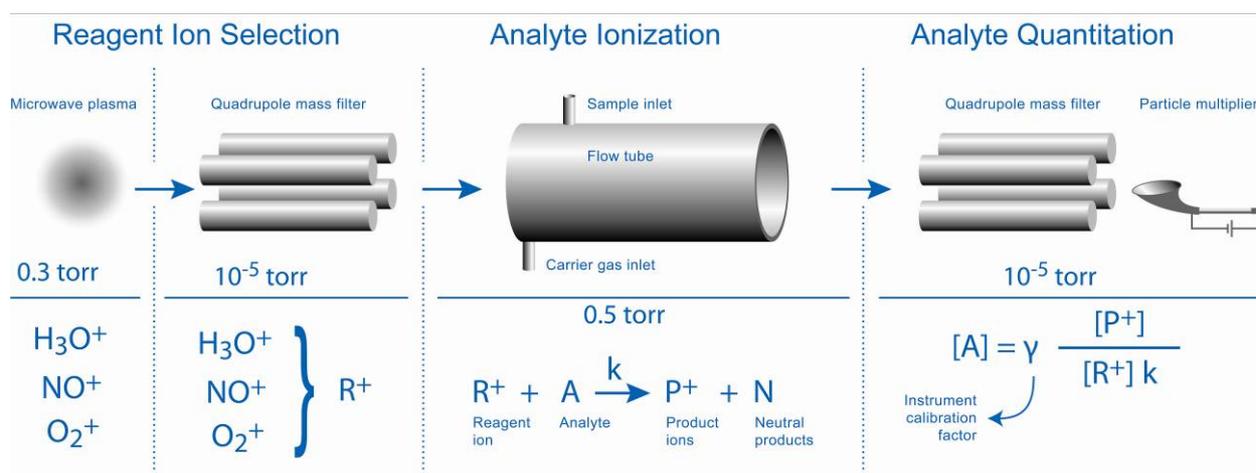
SIFT-MS complements GC-MS by providing real-time analysis of VOCs from whole air to part-per-trillion (by volume) concentrations. Real-time analysis combined with straightforward instrument operation procedures, make SIFT-MS an ideal option for screening applications where rapid analysis is advantageous, or where highly-trained personnel may not always be available to operate the instrumentation.

## 2. An overview of SIFT-MS

SIFT-MS uses soft chemical ionization reactions coupled with mass spectrometric detection to rapidly quantify VOCs in real time from whole-gas samples. Three standard chemical ionization agents (or reagent ions) are used in SIFT-MS:  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$ . These reagent ions are mass selected (Figure 1) and react with trace VOCs in very well controlled ion-molecule reactions but do not react with the major components of air, allowing SIFT-MS to analyze whole air for trace VOCs to pptv levels.

Soft chemical ionization yields a smaller number of product ions per compound than electron impact mass spectrometry (as used in standard GC-MS, for example), so gas chromatographic separation is unnecessary. This speeds sample throughput and provides instantaneous quantification of VOCs. Use of multiple reagent ions also greatly reduces interferences, markedly increasing the specificity of SIFT-MS compared with most other direct mass spectrometry technologies.

**Figure 1.** Schematic representation of the SIFT-MS technique.



## 3. Principles of SIFT-MS

This section describes the principles of the SIFT-MS technique that are essential to understanding how it complements GC-MS. In particular, it focuses on how soft chemical ionization is applied very precisely in SIFT-MS, allowing it to provide unparalleled selectivity among direct mass spectrometry techniques, and creating an ideal companion technique for GC-MS.

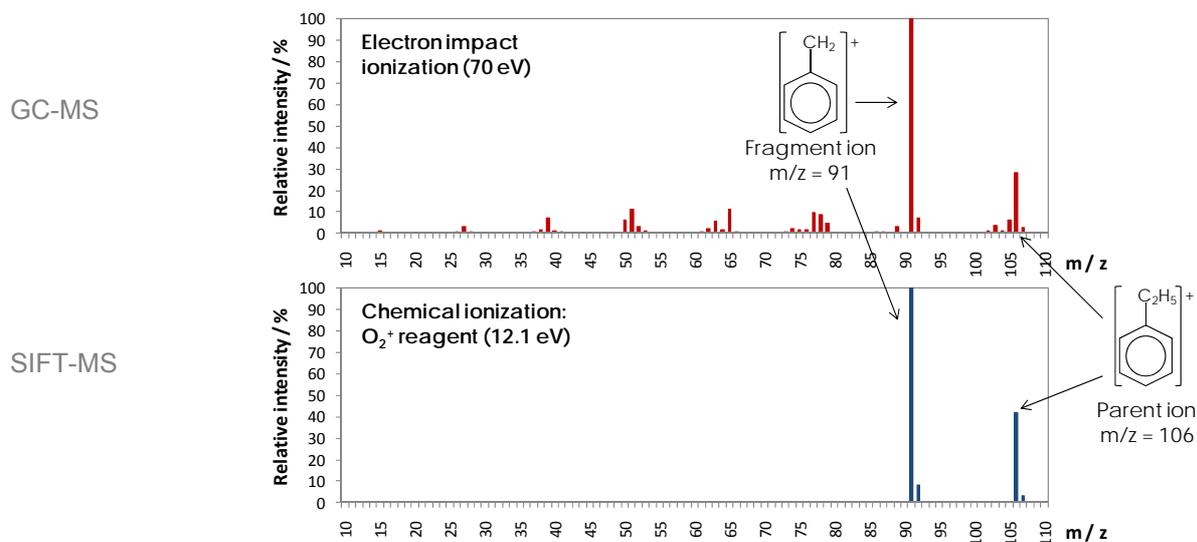
### a. Chemical ionization in SIFT-MS

Chemical ionization (CI) uses a molecular ion to transfer charge on to the target compound (analyte). CI is “softer” than many other types of ionization, so it transfers less energy to the analyte, resulting in less fragmentation. SIFT-MS is a unique CI-MS technique because it precisely controls ion energies to allow repeatable, real-time quantitative analysis. Another benefit is long-term calibration stability.

SIFT-MS uses softer chemical ionization (CI) agents than GC-MS and terms them “reagent ions” (or “precursor ions”). The standard reagent ions used in SIFT-MS are  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$ . By applying these ions in a soft ionization process, SIFT-MS encounters significantly reduced fragmentation compared to harsher CI and electron impact (EI) ionization.

Figure 2 compares ionization of ethylbenzene using 70-eV EI (as used in GC-MS) and 12.1-eV  $\text{O}_2^+$  CI (as used in SIFT-MS). Reduced fragmentation means chromatography is unnecessary, which allows SIFT-MS to be applied as a real-time technique.

**Figure 2.** Electron impact and chemical ionization of ethylbenzene illustrates the much simpler fragmentation observed for SIFT-MS than standard GC-MS.



Fragmentation and chromatography mean GC-MS can have higher selectivity than the somewhat cleaner mass spectra produced by SIFT-MS. Therefore, in certain applications involving *complex* mixtures, SIFT-MS is ideal as a rapid screening tool, while GC-MS is ideal for methodical identification and quantitation of every compound. The strength of SIFT-MS is its fast, broad analysis and hence it is complementary to rather than competitive with GC-MS.

### **b. Chemistry of the SIFT-MS reagent ions**

This section provides a short overview of the gas-phase reaction mechanisms for the three standard SIFT-MS reagent ions:  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$ .

#### **I. The SIFT-MS $\text{H}_3\text{O}^+$ reagent ion**

The  $\text{H}_3\text{O}^+$  reagent ion almost always reacts with analyte “A” via the proton transfer mechanism:



The product is generally detected at one mass unit higher than the neutral mass. For compound “A” to react, it must have a proton affinity (PA) greater than that of water ( $\text{PA} = 691 \text{ kJ mol}^{-1}$ ). If this condition is fulfilled, then a reaction occurs on every ion-molecule collision (100% efficiency).

#### **II. The SIFT-MS $\text{O}_2^+$ reagent ion**

Oxygen has an ionization potential of 12.1 eV and is the strongest SIFT-MS reagent ion.  $\text{O}_2^+$  transfers charge to analytes with lower ionization potentials by removing an electron:



$\text{O}_2^+$  also often ionizes molecules with sufficient excess energy to produce fragment ions (for example, the 91 m/z product of ethylbenzene in Figure 2).



The efficiency of the charge transfer process is often less than 100% (*i.e.* not all collisions between the  $\text{O}_2^+$  reagent ion and a molecule lead to a reaction).

### III. The SIFT-MS NO<sup>+</sup> reagent ion

The ionization potential of NO is 9.1 eV, so it ionizes fewer compounds via the charge transfer mechanism than does O<sub>2</sub><sup>+</sup>.



As for O<sub>2</sub><sup>+</sup>, charge transfer efficiency is often less than 100%. Although dissociative charge transfer is less common for NO<sup>+</sup> than O<sub>2</sub><sup>+</sup> due to the lower ionization energy, it still occurs for certain compounds.

NO<sup>+</sup> often reacts by two other very useful mechanisms:



### IV. Real-time resolution of isomeric and isobaric compounds

The triple reagent ion system of SIFT-MS is able to resolve certain isobaric and isomeric compounds. A simple example is provided in Table 1 for the acetone and propanal isomers of C<sub>3</sub>H<sub>6</sub>O. The NO<sup>+</sup> reagent ion provides the most effective differentiation because it reacts via a different mechanism for the two compounds and yields a single product ion for each.

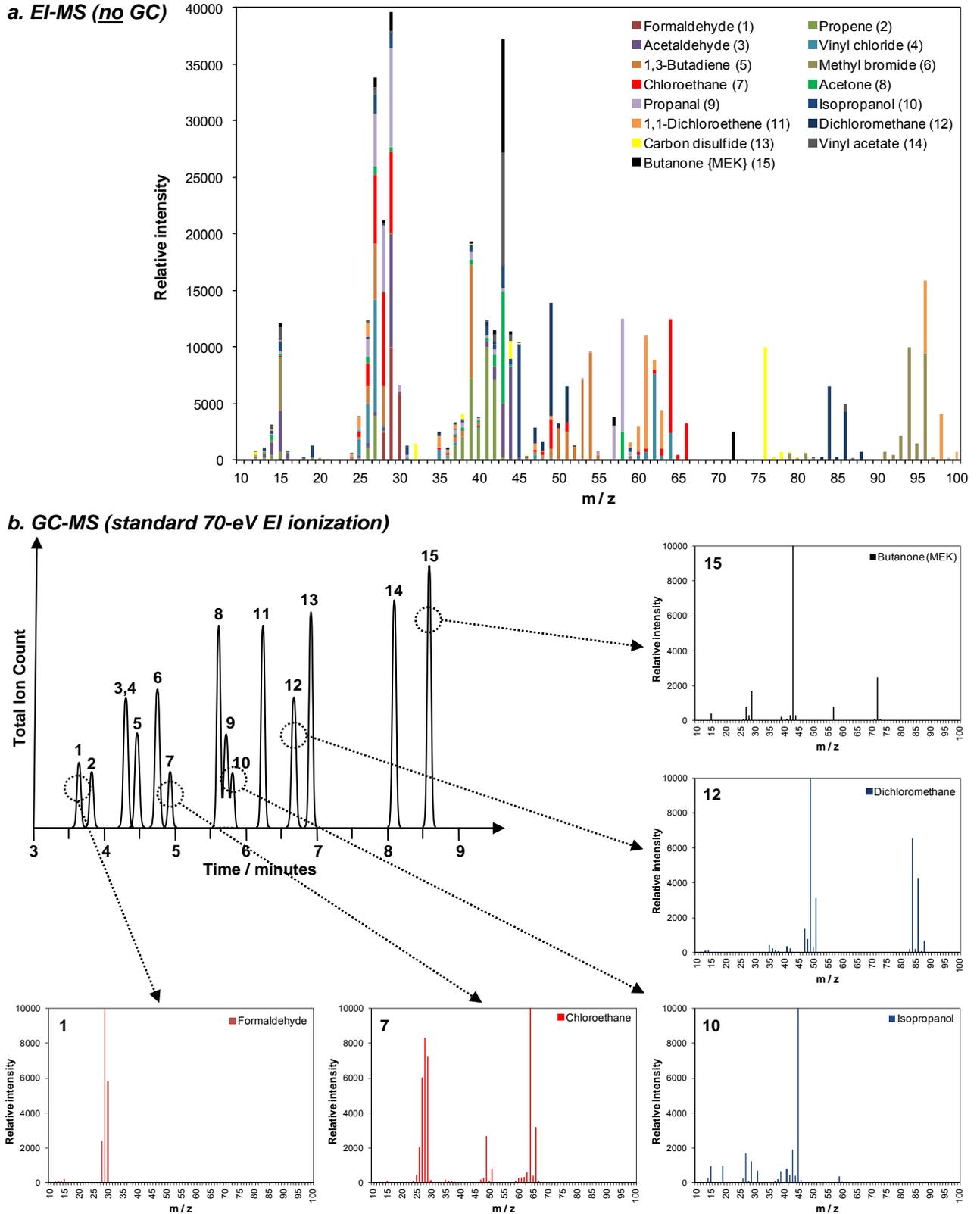
**Table 1.** Product ions formed from reaction of the SIFT-MS H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> reagent ions with isomeric compounds acetone and propanal.

Reagent ion	Acetone product ion (m/z)	Propanal product ion (m/z)
H <sub>3</sub> O <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> CO.H <sup>+</sup> (59)	CH <sub>3</sub> CH <sub>2</sub> CHO.H <sup>+</sup> (59)
NO <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> CO.NO <sup>+</sup> (88)	CH <sub>3</sub> CH <sub>2</sub> CO <sup>+</sup> (57)
O <sub>2</sub> <sup>+</sup>	(CH <sub>3</sub> )CO <sup>+</sup> (58); CH <sub>3</sub> CO <sup>+</sup> (43)	CH <sub>3</sub> CH <sub>2</sub> CHO <sup>+</sup> (58); CH <sub>3</sub> CH <sub>2</sub> CO <sup>+</sup> (57)

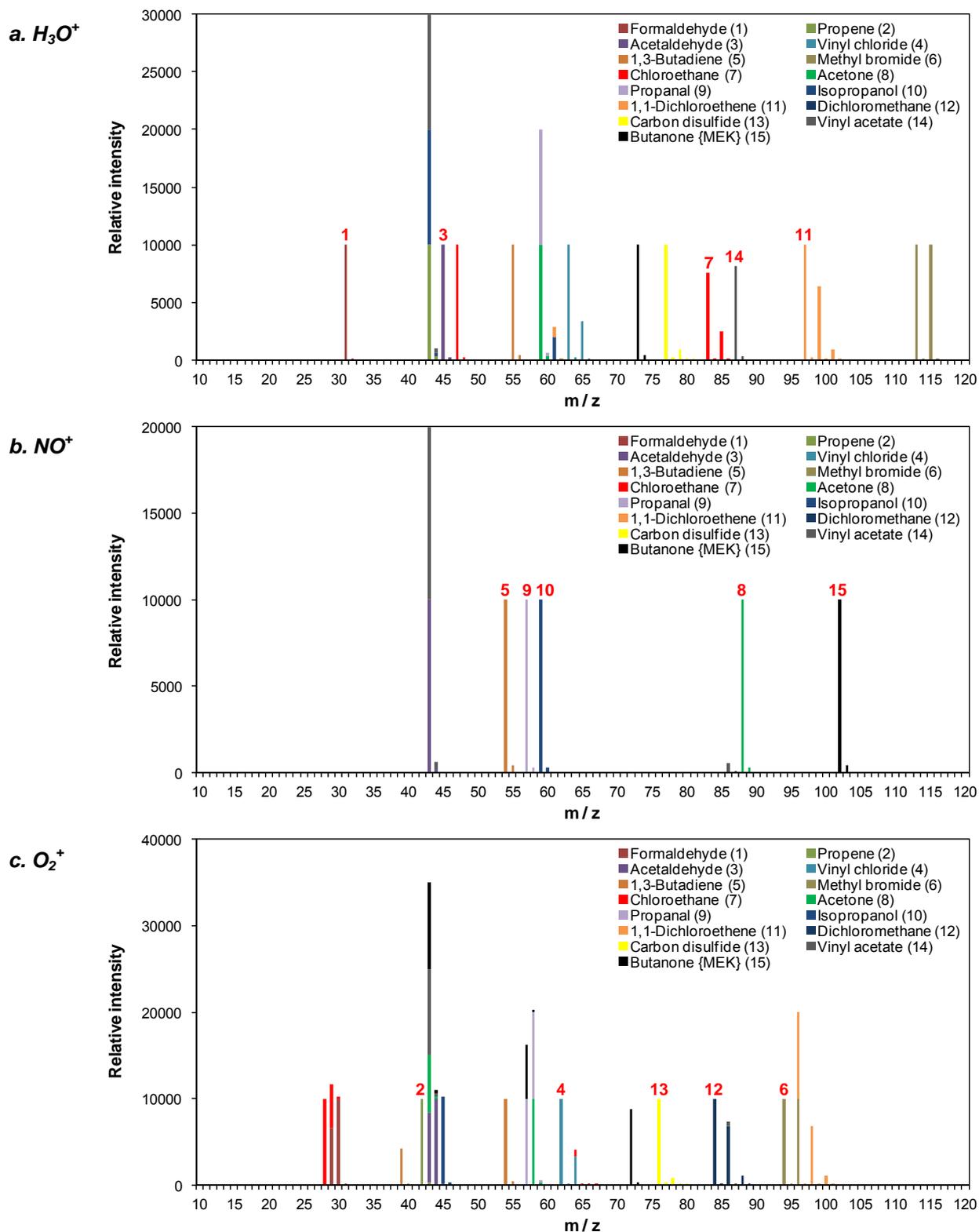
Figures 3 and 4 illustrate how a hypothetical multi-component sample is analyzed using electron impact mass spectrometry (using, GC, GC-MS and SIFT-MS), respectively. In Figure 3, the high degree of fragmentation arising from EI ionization is shown. Without GC, EI-MS is complicated and allows few compounds to be targeted uniquely. However, the same mode of ionization applied in GC-MS allows compounds to be separated in time through the GC column, while the relatively unique mass spectral “fingerprints” of each compound can be used to identify and quantify the compound.

In Figure 4, the same mixture is analyzed using the three standard SIFT-MS reagent ions. All fifteen compounds can be resolved in real-time without using chromatography.

**Figure 3.** 70-eV electron impact mass spectrometry (a) without and (b) with gas chromatography. The hypothetical 15-component sample is derived from the US EPA Compendium Method TO-15 and generated from mass spectra in the NIST library (<http://webbook.nist.gov/chemistry/>).



**Figure 4.** Three standard **SIFT-MS** reagent ions (a)  $H_3O^+$ , (b)  $NO^+$  and (c)  $O_2^+$  for real-time resolution of the 15-component sample shown in Figure 3. SIFT-MS data were taken from the Syft compound library. Red numbers identify some unique ions useful for quantitation.



### **c. How does SIFT-MS control the chemistry so precisely?**

Consistency of reagent ion energy is one of the most critical factors in controlling analyte ionization, which in turn provides very consistent product formation and reliable, stable quantitation. In SIFT-MS the use of a carrier gas enables the chemical ionization process to be controlled very effectively compared to EI ionization and other forms of CI mass spectrometry. The carrier gas used in SIFT-MS plays two very important roles in controlling ionization:

- It thermalizes the reagent ions prior to introduction of sample, which means that the energies of the reagent ions are as low and consistent as possible, providing predictable, precise, and soft chemical ionization.
- It transports the product ions and unreacted reagent ions down the flow tube to the detection region without addition of excess energy, such as use of an electric field to accelerate ions toward a detection region. Adding additional energy complicates mass spectra, reducing specificity and ability to uniquely quantify compounds.

### **d. Quantitation in SIFT-MS**

SIFT-MS SIM scans are analogous to GC-MS SIM scans and involve targeting VOCs in a well-characterized sample matrix. In this mode, specific reagent and product ions are selected and their count rates measured repeatedly. Combining this experimental information with the known rate coefficient ( $k$ ) for reaction of the reagent ion and analyte, and the dilution of the sample gas into the carrier gas, the absolute concentration of an analyte can be calculated and displayed in real time. Simply put, more VOCs in the sample will result in a greater proportion of the reagent ion reacting and hence more of the product ions for that VOC will be observed.

Movement of inert helium or hydrogen carrier gas through the flow tube entrains the reagent ions and analytes and provides a region of known conditions. It is in this region that reaction between the sample VOCs and ions occurs. This means the reaction time (the amount of time they have to react with each other) is a coefficient in any given SIFT-MS instrument.

At a known reaction time (determined by the flow conditions) the amount of reagent ion reacted will be proportional to the concentration of the analyte in the flow tube. Using a little math and the ratio of reagent and product ions along with the rate coefficient, it is possible to deduce the concentration of a VOC in the flow tube from the ratio of the product ion to the reagent ion count. From this point it is possible to relate the VOC concentration in the flow tube to the VOC concentration in the original sample, as the flow ratios of the sample and carrier gases into the flow tube gives the dilution ratio.

As long as the flow of the sample gas is small compared to the carrier gas flow and the total level of volatiles in the sample does not attenuate the reagent ion signal by more than about 10%, the number of VOC product ions is an absolute measure of the VOC in the sample. This gives a typical linear range of approximately from mid-ppt to about 50 ppm. Higher concentration samples can be analyzed either by attenuating the sample flow or by diluting the sample.

### **e. Calibration of SIFT-MS instruments**

SIFT-MS enables absolute quantitation of target compounds at high precision based on the compound data contained in the Syft library (namely, the reaction rate coefficient and the product masses together with their branching ratios). However, if high accuracy analysis is required, formal calibration is recommended, rather than simply relying upon the compound library. Once calibrated for a particular compound, the SIFT-MS calibration is usually valid as long as the instrument passes validation using the Syft automated daily validation standard.

SIFT-MS is a dedicated whole gas analyzer and cannot analyze liquid samples. Therefore suitable certified gas standards are used for calibration of SIFT-MS instruments. The two main options for suitable standards are compressed gases and permeation tubes.

## 4. Operational advantages of Syft SIFT-MS

The inherent technical features of SIFT-MS (such as the absence of chromatographic columns) has allowed Syft Technologies to develop instruments with significant usability advantages.

### **a. Ease of use**

Syft provides software solutions for its SIFT-MS instruments that make them easy to use and easy to integrate with existing information technology systems.

Although Syft Voice-series SIFT-MS instruments are sophisticated analytical devices, Syft has developed software that enables the powerful technology to deliver results even for minimally trained users. Features designed for such users include:

- Simplified workflows for very easy operation
- Intuitive touchscreen, menu-driven analysis
- Completely customizable target compound lists
- Instantaneous reporting of results as scans complete
- Alarms raised when a specific compound is above a user-defined threshold or if a pattern or trend indicates that a process is outside specification (for example, using multivariate statistics).

Figure 5 illustrates how a laboratory-grade analysis has been configured for simple operation for non-technical users.

For technical users, Syft also offers the LabSyft software package, which allows advanced users to do many of the things they are familiar with when operating GC-MS or similar analytical equipment. This includes:

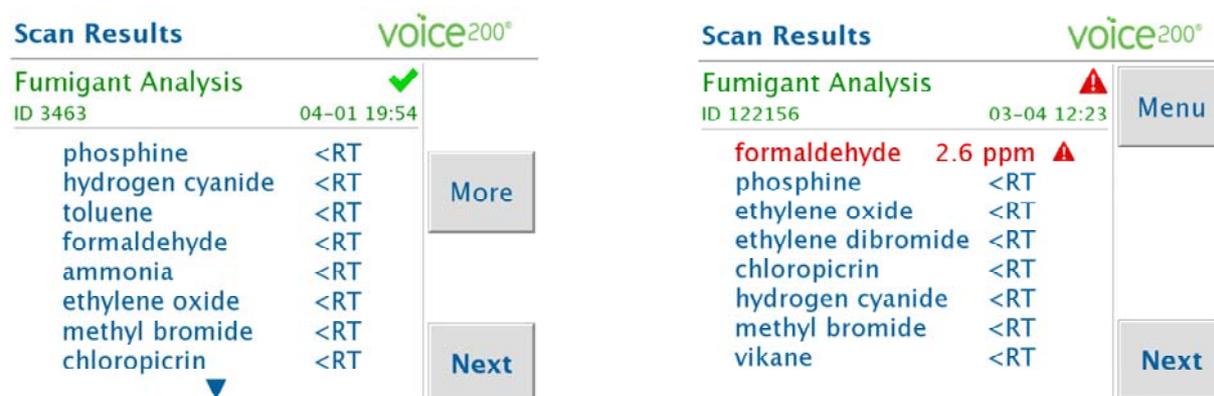
- Viewing data as it is generated
- Viewing manipulating and exporting data after a scan has finished
- Viewing, searching and expanding the compound library
- Creating and editing analytical methods
- Creation and execution of batch scanning schedules.

LabSyft runs under both Windows and Macintosh operating systems on a computer that is connected to the instrument, either directly or across a network. This means method files can be created, edited and stored on a remote computer, before being transferred to an instrument. Conversely data files can be transferred from the instrument to a remote computer for further analysis.

### **b. Remote operation**

Syft Voice-series SIFT-MS instruments are fully networkable, meaning instrument operation, data handling, and troubleshooting can be performed remotely, from anywhere in the world. This allows scanning to be fully automated, and top-level support and fault diagnostics can be quickly delivered to any location and time zone.

**Figure 5.** The Voice-Series software is readily configured for use and interpretation by non-technical operators. These screenshots from the Voice200<sup>®</sup> instrument's touchscreen show two results screens from a worker safety application. RT is a reporting threshold that the employer has chosen, below which the results are hidden from the operator to avoid causing unnecessary alarm. One screen shows a pass result with acceptable levels of target compounds, while the other shows unacceptable formaldehyde levels.



### c. Reduced maintenance

Elimination of chromatographic columns, very clean ion source and detection systems, and gas-only analysis mean that routine maintenance tasks are significantly reduced for SIFT-MS compared to GC-MS. In fact, significant causes of MS instability are mitigated and even eliminated in SIFT-MS, including factors such as:

- Electron source fluctuations, since the ion source and detection optics are physically separated
- “Dirty” lenses, which alter the fields seen by ions, since the bulk of gas present is inert helium
- Ion burns on quads, which affect transmission, because only low ion currents pass through the detection region end (picoampere range)
- Detection efficiency changes (e.g., multiplier changes), since the concentration is determined using a ratio of product and reagent ions.

A key benefit of eliminating columns and using clean, stable chemical ionization is that SIFT-MS has long-term calibration stability. Most users choose to confirm this daily by use of the automated instrument validation routine, which includes analysis of a multiple component certified gas standard (the so-called Syft Calibrant Standard), which confirms that the instrument's response through the entire mass range is stable.

#### **d. Technical support**

Syft and its distributors offer extensive maintenance and support services for Voice-series instruments, accessories and their applications. In particular, the remote access feature of the Voice-series instruments allows instruments to be monitored and supported anywhere that internet access is available.

Other examples of technical services include:

- **Scheduled Preventative Maintenance:** A regular, six-monthly maintenance visit, by a Syft-approved technician ensures that the Voice-series instrument is properly cared for. All instrument components that require regular maintenance are serviced to their individual manufacturer's recommendations. The recommended schedule for the periodic replacement or overhaul of components is implemented to ensure that all warranty requirements are met. Instrument performance is monitored and verified.
- **Syft-Sure On-Line System Support:** On-line system support ensures that users get helpful and timely responses from Syft technical support staff if they experience any difficulties with their equipment.

Users who need assistance can log support cases via the 'Support Portal' on Syft's website. The case is automatically forwarded to Syft's Support Network and the user is contacted by a Syft technician within contracted timeframes. Syft's technicians can make a remote data connection to the instrument to diagnose and rectify issues. If on-site intervention or replacement parts are required to resolve an issue, Syft-Sure Contract holders receive high-priority treatment.

### **5. Summary**

SIFT-MS offers high sensitivity, real-time and non-discriminatory analysis of VOCs in whole air in a very easy to use package. The absence of chromatography columns and very clean, precise chemical ionization reduce maintenance requirements and increase stability, compared to GC-MS. These factors make SIFT-MS a very powerful, complementary technique for GC-MS, which is a good compound identification tool, but cannot analyze rapidly and requires highly trained operators.

The following table summarizes key characteristics common to SIFT-MS and GC-MS.

S I F T - M S	Characteristic	G C - M S
VOCs and certain inorganic gases	<b>Compounds analyzed</b>	VOCs and semivolatile VOCs (SVOCs), inorganic gases
Gas (including headspace)	<b>Suitable matrices</b>	Gas (including headspace), liquid
A fraction of a second to minutes, depending on requirements	<b>Speed of analysis</b>	Typically 10 to 45 minutes (determined by elution time for analytes)
Real-time analysis at sub-ppbv concentrations / sub-ng L <sup>-1</sup>	<b>Detection limits</b>	Routinely sub-nanogram (ng) level, but dependent on system inertness, sample matrix and ionization method
Generally preparation free due to analysis of whole air	<b>Sample preparation</b>	Usually requires preparation and/or preconcentration (for example, solvent extraction, purge and trap, thermal desorption, SPME)
Real time analysis because there is no chromatographic separation of analyte, which also eliminates discrimination. Compounds resolved due to the relatively simple chemical ionization 'fingerprints'	<b>Analyte separation</b>	Separation of analytes using appropriate column and temperature program. May require several runs through the GC to separate analytes of differing polarity (discriminatory)
Three standard soft chemical ionization agents (H <sub>3</sub> O <sup>+</sup> , NO <sup>+</sup> , O <sub>2</sub> <sup>+</sup> )	<b>Ionization mechanism(s)</b>	Typically 70 eV electron impact ionization; sometimes chemical ionization
Quadrupole mass selection and particle multiplier detection (ion counting)	<b>Ion selection and detection</b>	Typically use quadrupole-based mass selection and measure ion current
Full Scan Mode and Selected Ion Monitoring (SIM) – the latter allows real-time quantitative analysis	<b>Data collection modes</b>	Full Scan Mode and Selected Ion Monitoring (SIM)
High – multiple reagent ions, but no chromatography	<b>Compound identification</b>	Very high due to chromatography
Real-time quantitation from reagent and product ion intensities, reaction rate coefficients and sample flow rate	<b>Quantitation</b>	From full calibration of system for particular analytical method
Calibration is required infrequently; for some applications it is not required at all	<b>Calibration</b>	Calibrated regularly using a set of dilutions of known concentrations
Routine validation using automated on-line analysis of certified gas standard	<b>Validation</b>	Validation involves use of spiked samples and blanks in the analytical sequence
Technical and non-technical operation	<b>Ease-of-Use</b>	Technical operators only
Low – primarily vacuum pumps	<b>Maintenance requirements</b>	High – frequent fouling of column and ion source

1. Typical performance data for the Syft Voice200<sup>®</sup> SIFT-MS instrument are given in the recent publication by B. Prince, D. Milligan and M. McEwan: *Rapid Communications in Mass Spectrometry*, 2010, 24, 1763–1769.



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