



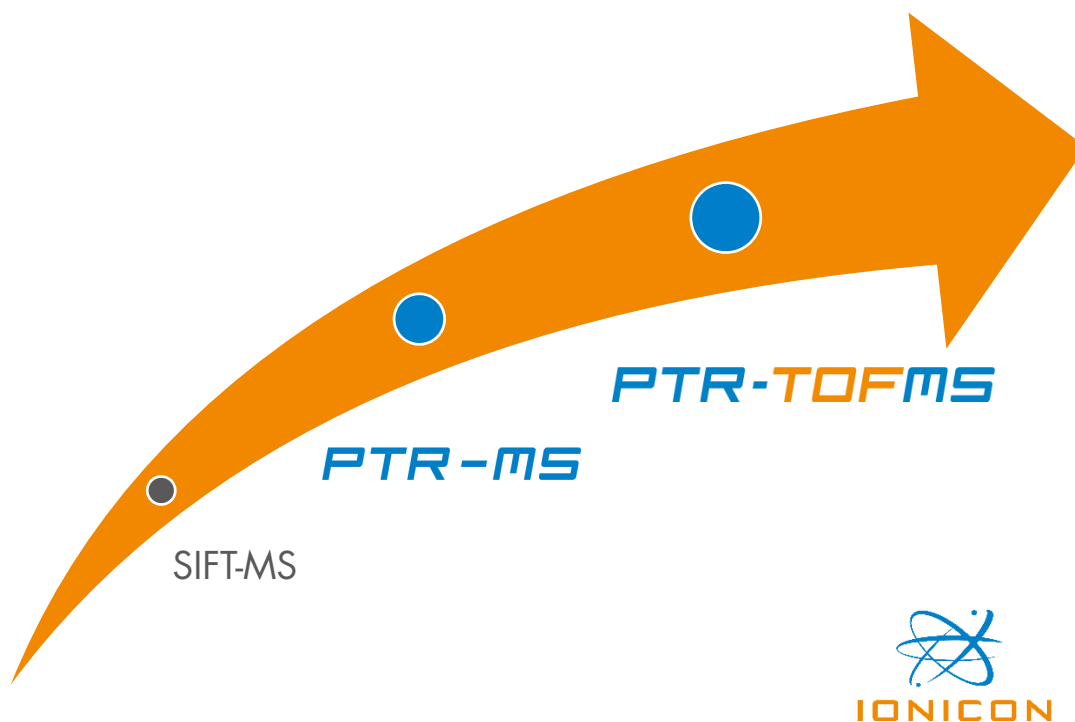
ULTRA-SENSITIVE SOLUTIONS FOR REAL-TIME TRACE GAS ANALYSIS

From SIFT to PTR-TOFMS:

AN EVOLUTION THAT RESULTED IN PERFECTION

The success story of PTR-TOFMS has its roots in the so-called "Flowing Afterglow Technique", introduced in the 1960s. From this starting point continuous research and innovation work by various experts, who wanted to eliminate instrumental drawbacks and shortcomings, have led to different technological milestones resulting in the development of PTR-MS and ultimately PTR-TOFMS.

A well-founded and concise overview of this history can e.g. be found in the book by Ellis and Mayhew [1].



Back to the basics: SIFT-MS

As a first evolutionary step Selective-Ion-Flow-Tube – Mass Spectrometry (SIFT-MS) solved some of the key limitations of the flowing afterglow technique. In SIFT-MS a mass filter is installed for selecting the reagent ions, which results in high reagent ion purity but also makes the construction of the instrument challenging and, most importantly, limits the number of available reagent ions because of the transmission efficiency of the mass filter, which can by rules of physics never reach 100%.

However, similar to flowing afterglow also SIFT-MS was not invented as an analytical technique but rather for measuring kinetics in a lab environment. That is, when using SIFT-MS for trace gas analysis, in addition to its limited sensitivity, there are several other drawbacks:

- ✘ The constant need of a carrier gas (typically helium) for the flow tube in SIFT-MS results in limited mobility of the instrument, and additional running costs.
- ✘ The flow created by the carrier gas considerably dilutes the sample and therefore lowers the sensitivity even further.
- ✘ The sequence "reagent ion source – mass filter – flow tube – mass filter" results in a huge demand on the vacuum system, as the needed pressures in the respective parts differ by orders of magnitude and thus a bulky pumping system is required.
- ✘ Because the reaction region in a SIFT instrument does not involve any electric drift field the chemical ionization process cannot be controlled via the reduced electric field strength (E/N). This is a major drawback as far as selectivity is concerned.

The latter problem has been addressed in Selected-Ion-Flow-Drift-Tube (SIFDT) – MS, where a static but variable electric field is applied along the axis of the flow tube reactor of a SIFT instrument. Although already invented in the 1980s the huge advantage of having an adjustable E/N in SIFDT-MS has only been (re-)discovered in 2015 [2] in a prototype setup. However, the remaining drawbacks are inherent and cannot be solved by instrumental amendments.

A giant leap in evolution: PTR-MS

All of the above-mentioned shortcomings have been overcome with the introduction of PTR-MS in the 1990s [3]:

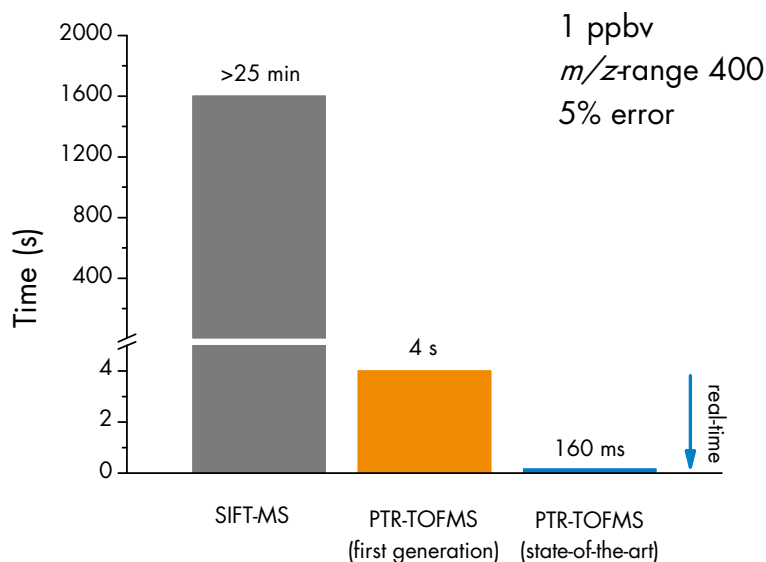
- ✘ Because of the sophisticated design of the reagent ion source no mass filter is necessary to guarantee high purity levels of reagent ions. That is, the reagent ions are directly injected into the reaction region, which enables extremely high sensitivities.
- ✘ The air containing the trace compounds to be analyzed acts as a buffer gas, thus no additional carrier gas is necessary, which prevents any dilution effects.
- ✘ As the reagent ion source and the reaction region are at comparable pressure levels (10^0 hPa) the vacuum system can be kept relatively simple.
- ✘ These two advantages further result in a compact and maintenance-friendly pumping system.
- ✘ The reduced electric field strength E/N is well-defined and can be tuned from virtually fragmentation-free to forced fragmentation for improved selectivity.

In summary, after decades of research, real-time trace gas analysis culminated in the development of the extremely sensitive, robust and easy-to-use PTR-MS technology. There was, however, one more step to perfection: The coupling of PTR with Time-Of-Flight (TOF) mass spectrometers.

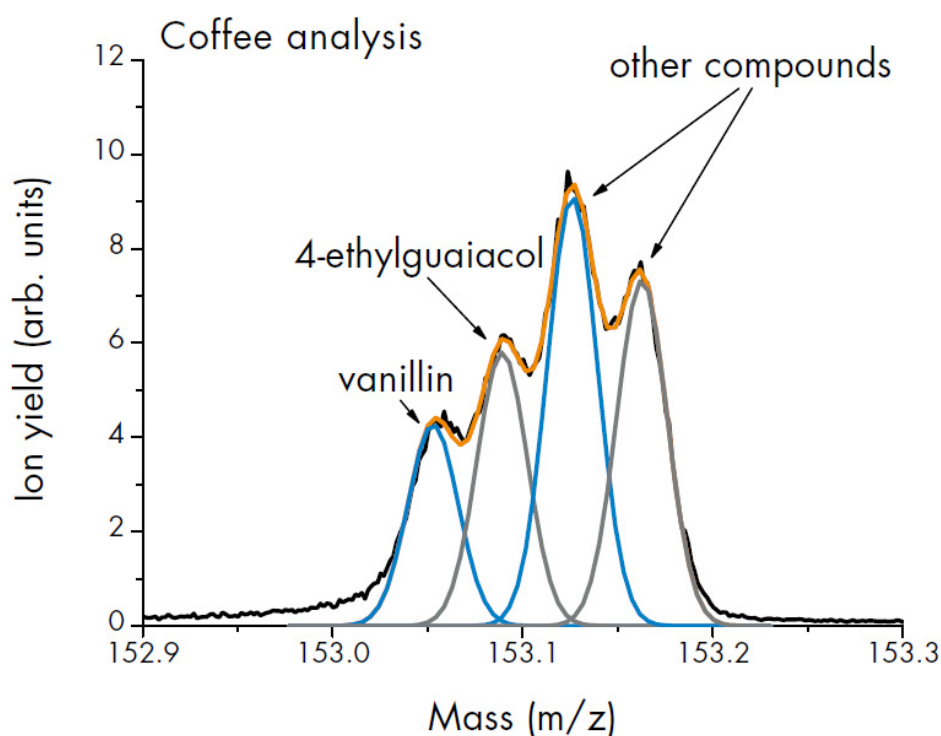
The final step to perfection: PTR-TOFMS

So far, commercially available SIFT-MS instruments employ quadrupole mass filters for product ion analysis. In PTR-MS, on the other hand, TOF mass analyzers have been introduced in commercial instrumentation already in 2009 [4]. Although these first generation instruments had a lower sensitivity than the quadrupole based PTR-QMS devices at that time, the introduction of TOF mass analyzers in PTR-MS presented several convincing advantages:

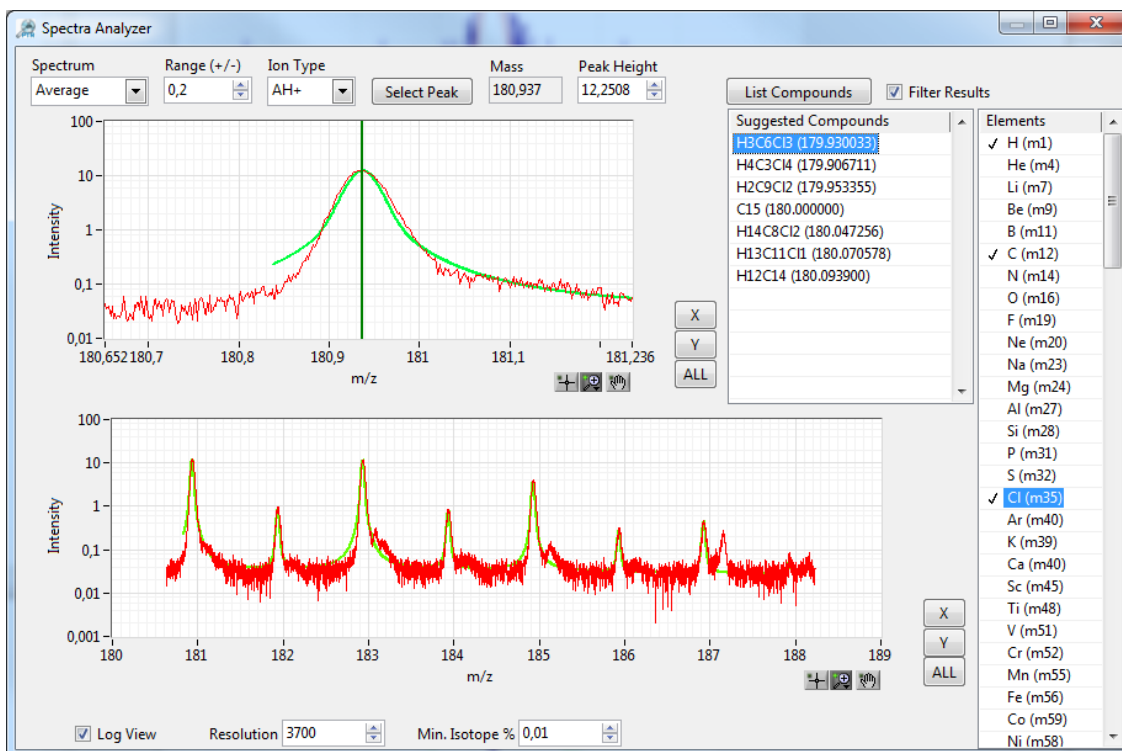
- ✘ In contrast to the nominal mass resolution of quadrupole mass filters TOF analyzers can resolve isobaric compounds, which is an essential requirement for the analysis of complex samples.
- ✘ In the same time quadrupole based analyzers acquire a single m/z , a PTR-TOFMS instrument acquires a full mass spectrum - in high resolution.
- ✘ All m/z are recorded in a spectrum, i.e. the information on all product ions, their isotopes and fragments is available for analysis and discovery, whereas in quadrupole based systems only selected m/z are recorded.
- ✘ The speed of acquisition in PTR-TOFMS is not dependent on the number of compounds monitored.



This graph clearly demonstrates the superiority of TOF mass analyzers over quadrupole mass filters and consequently of PTR-TOFMS over SIFT-MS in terms of measurement speed. This example assumes that an m/z range of 400 is to be measured. A further assumption is that the maximum allowable error for a concentration of 1 ppbv must be below 5% (error is the square-root of the count-rate according to the laws of statistics) to ensure high data quality. It can be seen that a PTR-TOFMS instrument of the first generation, i.e. with about 100 cps/ppbv sensitivity, needs an integration time of about 4 s to get the full mass spectrum. A state-of-the-art PTR-TOFMS instrument with about 2500 cps/ppbv sensitivity can measure 1 ppbv over an m/z range of 400 within less than 200 ms, i.e. in true real-time. SIFT-MS with a quadrupole mass filter on the other hand has to measure 400 nominal m/z separately, which leads to a total measurement time of over 25 min (with 100 cps/ppbv sensitivity). That is, SIFT-MS is definitely far away from real-time and close to a timescale needed by offline techniques such as GC-MS. Importantly, even if the sensitivity of a SIFT-MS instrument would be considerably increased by an order of magnitude, the integration time for a full mass spectrum would be in the range of several minutes and thus still far away from real-time. Furthermore, the SIFT-MS mass spectrum has a nominal resolution and carries significantly less information than a high-resolution TOF spectrum such as this one, recorded at the analysis of complex coffee headspace matrix with an IONICON PTR-TOF 6000 X2 instrument:



The four different isobaric ions, which can be clearly separated and quantified independently with high resolution PTR-TOFMS, would appear as a single signal at nominal m/z 153 in a SIFT-MS instrument. This means that, for example, hazardous substances cannot be separated from harmless compounds and protonated molecules cannot be distinguished from fragments in SIFT-MS if they are isobars.



Substance identification is particularly easy with high resolution PTR-TOFMS, because the exact m/z of a peak in the mass spectrum already gives a good indication of the chemical composition of the respective ion. Moreover, isotope ratios can be used for additional confirmation. With SIFT-MS only nominal m/z are acquired, which makes substance identification very ambiguous. Furthermore, the monitoring of every additional isotope adds up to the measurement time. For example, even if the sensitivities would be comparable, a SIFT-MS instrument needs 6 s to acquire data of a protonated molecule including five of its isotopes while a PTR-TOFMS instrument gets this data plus the full mass spectrum in high resolution already within 1 s.

To select other reagent ions (O_2^+ , NO^+), both in PTR-MS and SIFT-MS, allows to acquire additional information. In some cases this can be used to resolve some overlapping compounds. In PTR-TOFMS this need is greatly reduced, since the separation of isobars is intrinsically solved in a high resolution TOF spectrum. However, different reagent ions in combination with full TOF mass-spectra yield an unprecedented level of information which cannot be matched with a quadrupole based analyzer such as SIFT-MS.

A clear advantage of IONICON PTR-TOFMS instruments is the included creation of NH_4^+ reagent ions, which can simply and efficiently be produced from water and nitrogen. SIFT-MS needs hazardous, corrosive and toxic ammonia for NH_4^+ generation [3] which makes the use of this important reagent ion prohibitive in many environments.

On top of using different reagent ions, PTR-MS allows nearly unlimited further ionization modes by altering the collisional energy level, E/N . By that fragmentation can be reduced or enhanced. This yields direct information on the structure of the molecule and is particularly well suited to separate structural isomers.



Acquiring spectra using different ionization modes (a selection of different reagent ions and E/N levels) is heavily exploited in IONICON's AME software that performs the interpretation of the combined data by sophisticated pattern matching algorithms and is a well-proven technology for automated VOC monitoring solutions IONICON offers.

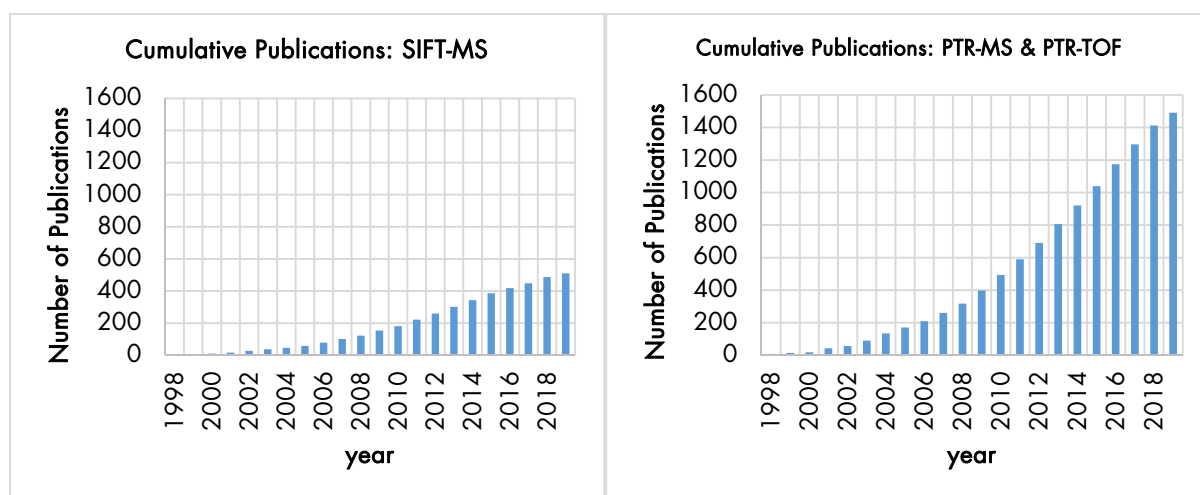
To summarize, this is how SIFT-MS compares to the advanced IONICON PTR-TOFMS technology:

	SIFT-MS	IONICON PTR-TOFMS
Measurement time for mass spectrum up to m/z 400 at low concentrations	tens of minutes	well below one second
Measurement of mass spectra	one nominal m/z after the other	instantaneous
Separation of isobars via exact mass	no	yes
Compound identification via exact mass	no	yes
Quantification of compounds not defined prior to the start of the experiment	no	yes
Generation of NH_4^+ reagent ions without the need of hazardous ammonia	no	yes
Adjustment of the E/N in the reaction region	no	yes



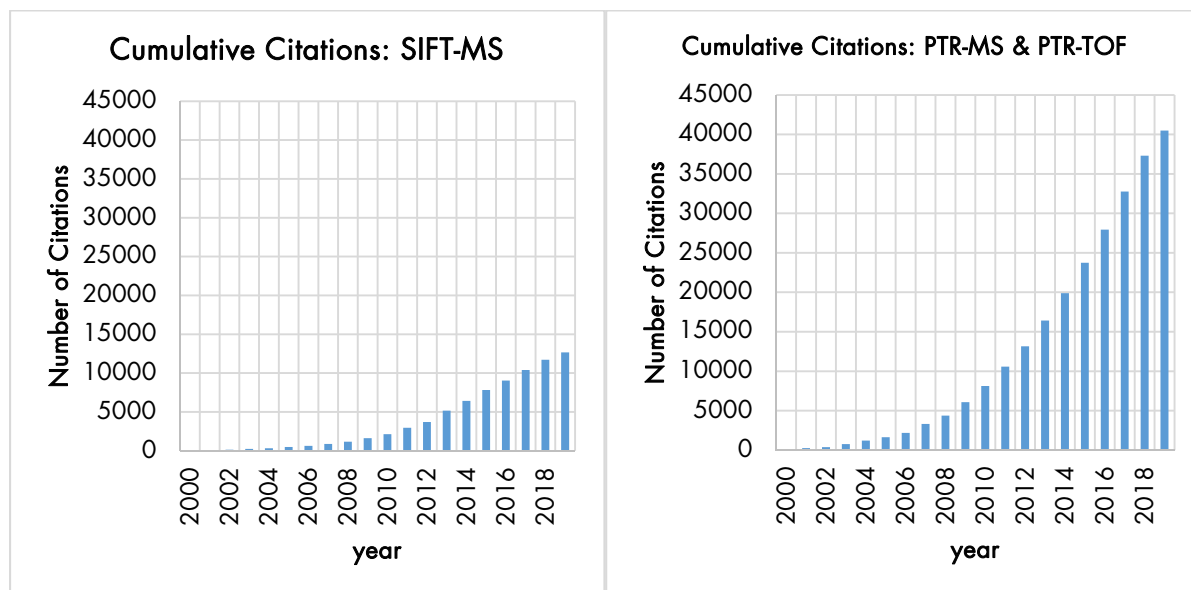
PTR-MS is trusted - all over the world

Ever since the PTR-MS technology was commercialized by IONICON in 1998, the interest in the emerging “gold standard” for real-time organic trace gas analysis has been growing quickly. In the last two decades more than 400 instruments were sold by IONICON. Analytical scientists and process engineers from all over the world have quickly adopted these new instruments which are continuously becoming more popular, performant and versatile as the company’s R&D activities go on.



PTR-MS compared to the less advanced SIFT-MS technology also has much more impact in the literature which a recent Web of Science query^a reveals. In terms of published peer-reviewed academic journal articles PTR-MS scores 3x the amount of papers than those dealing with SIFT-MS, roughly 1,500 compared to 500, respectively. Moreover citations of these articles confirm the trend. PTR-MS related publications have been cited an astonishing 40,000+ times whereas SIFT-MS has less than 13,000 citations in the same timeframe.

^a Queries to Web of Science on 20. 8. 2019: TOPICS: cumulative [ptr-ms] and [ptr-tof] vs. [sift-ms], Timespan=All years. Indexes=SCI-EXPANDED, SSCI, A&HCI, CPCI-S, CPCI-SSH, ESCI.



This confirms that while SIFT-MS being one of the many evolutionary steps in the development of real-time trace gas analyzers and especially for the more mature PTR-MS technology in particular, SIFT-MS never played such an important role and also has not been able to attract the same level of attention as PTR-MS in the last two decades.

References

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