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Improvement of the NO2-CI-MS Ion Source for Real-Time Industrial VOC Monitoring: Implications for Sustainable Development

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Abstract

High concentrations of organic compounds (VOCs) emitted by industries are a major source of air pollution in cities and a global climate change risk, which hinders the achievement of sustainable development targets. Strict monitoring is essential to make sure that the regulatory frameworks, including the EU Industrial Emissions Directive (IED) and the general United Nations Sustainable Development Goals (SDGs), are adhered to. Even though mass spectrometry (MS) is the workhorse of emissions monitoring, the standard ionization sources, Single-Photon Ionization (SPI) and Proton Transfer Reaction (PTR), are inadequate: SPI does not ionize saturated hydrocarbons, and PTR generates too much fragmentation to be used in complex industrial matrices. This paper fills these gaps by comparing a new Nitrogen Dioxide Chemical Ionization (NO_2-CI-MS) source to the conventional SPI and PTR techniques. The proposed NO_2-CI-MS system, through experimental measurement and control of the electric field, has provided better selectivity and ionization efficiency on alkanes, olefins, and aromatic species with high sensitivity and low fragmentation, thus overcoming the key constraints of the current technologies to detect trace-level pollutants needed to implement stringent policies. Additional pressure optimization of the ion-source increases stability in the long-term operation. The results support SDGs 11 (Sustainable Cities and Communities) and 13 (Climate Action) by providing a dependable tool for monitoring industrial VOCs and environmental management. The technology can directly assist in compliance monitoring in the EU IED and offer a technical basis towards achieving SDGs 11 and 13.

1. Introduction

VOCs are the primary sources of tropospheric ozone and secondary organic aerosols, and therefore, they are the major threats to the sustainability of the global environment. The unregulated industrial emissions of VOCs spoil the quality of air in cities and increase the greenhouse effect, which directly hinders the realization of the UN SDGs (Tang et al. 2025). SDG 11 (to reduce the urban environmental footprint) and SDG 13 (to incorporate climate action into industrial policies) are prerequisites of efficient monitoring and mitigation of these pollutants. According to the recent source-apportionment studies, the definition of industrial emission profiles in megacities is the key to the creation of effective pollution-abatement policies (Carlisle et al., 2023), which means that the precise real-time detection technology is the key to the industrial green shift.

Although there is a pressing environmental need, the current data analytical platforms are frequently incapable of addressing the data needs of strict regulatory adherence and decarbonization (Kim et al. 2024). The best technique to examine VOCs is mass spectrometry (Hegen 2023), which relies on the ionization source. The traditional soft-ionization methods like SPI have low fragmentation but fail to ionize saturated hydrocarbons, which are key constituents of petrochemical emissions because they have high ionization energies (Wang et al. 2016). PTR-MS is sensitive but too fragmenting of higher-order alkanes, which makes it difficult to interpret the spectrum and limits the data's usefulness in the

enforcement of policies (Buszewski et al. 2013). Such constraints make it difficult to measure the footprint of emissions by enterprises, which makes it hard to manage industries sustainably.

To overcome these loopholes, the proposed paper examines Nitrogen Dioxide Chemical Ionization Mass Spectrometry (NO_2-CI-MS) as a better option for holistic monitoring of emissions. Recent developments indicate that NO_2^+ reagent ions allow ionization of low-volatility and saturated hydrocarbons to occur through stable ion-molecule complexes with little fragmentation (Epping and Koch 2023). Its capability to analyze aromatics, alkanes, and other analyses is in line with the industrial monitoring standards and high standards like the EU IED. The proposed NO_2-CI-MS technology is found to enhance the ionization of saturated hydrocarbons by approximately 20 percent compared to the industrial VOC monitoring approaches that have been reported in ESPR over the last several years (Schulte et al. 2023; Carrera et al. 2025), which is more suitable in complex industrial emission situations.

This paper compares and contrasts SPI, PTR, and NO_2-CI-MS technologies. NO_2-CI-MS is confirmed as an effective real-time monitoring tool by experimental research on ionization yields, selectivity, and electric-field modulation. The objective of the study is to fill the gap between the high-tech equipment and the environmental policy, and to give the technical foundation that the industries should align their operations with the global sustainability objectives.

2. Experimental Background and Motivation

To examine and compare the performance of new ionization techniques to detect volatile organic compounds (VOCs), a large-scale experimental campaign was conducted in January-April 2024 (Broholm et al. 2015). This was a collaborative effort involving two analytical laboratories: the Nanjing TOFWERK, which is a pioneer in the precision engineering of ion sources and time-of-flight mass spectrometry, and the Dalian Science and Technology Innovation Park, an affiliate of the Chinese Academy of Sciences specializing in applied atmospheric and analytical chemistry. The urgent need to have an effective approach to the real-time monitoring of different VOC species triggered the given research, and the latter need can be described by high concentrations of industrial plants, complicated emissions fingerprints, and regular control inspections. Due to the broadness of the chemical species that are likely to be found in these environments, including simple alkanes and reactive aromatics, it is clear that the platform used to conduct the analysis should cover a large chemical space with high sensitivity, low fragmentation, and a stable response (Palacio Lozano et al. 2022). In this connection, three ionisation schemes have been chosen to be comparatively evaluated:

- Single Photon Ionisation Mass Spectrometry (SPI-MS) using a krypton discharge lamp as a source of photons of an energy of 10.6eV (Breitenlechner et al. 2022).
- Proton Transfer Reaction Mass Spectrometry (PTR-MS) using a cluster of reagent ions such as H_2O^+, O_2^+, NO^+, and Ar^+.

- Nitrogen Dioxide Chemical Ionization Mass Spectrometry (NO_2-CI-MS) with 1% NO_2 in ultra-pure nitrogen as the reagent gas.

Test compound selection was across 3 broad categories of industrial importance: alkanes (propane, octane, undecane), olefins (propylene, pentene), and aromatic hydrocarbons (benzene, toluene, p-xylene). The selection of these compounds was to represent a common chemical diversity of emissions associated with petrochemical processing and solvent utilization, and sources associated with combustion. All the experimental measurements were carried out at constant operating parameters to make them comparable. The pressure of the ion source was kept at 550 Pa, which is an optimized condition that allows the occurrence of both chemical ionization and photon-based ionization without turbulence or signal saturation. The concentrations of VOCs in the current study were progressively varied between 0 and 640 parts per billion (ppb) using a dynamic dilution system that incorporated high-resolution mass-flow controllers. The criteria used to evaluate them were the total ion current (TIC), peak signal intensity, relative abundance of quasi-molecular ions, linearity with concentration gradients, and fragmentation patterns. The S-P-MS system showed better results in the analysis of aromatic hydrocarbons, benzene, and toluene, whose ionisation potentials are lower than the energy of the incident photons, resulting in strong and clean molecular-ion peaks with minimal fragmentation. However, the system did not ionise alkanes like propane and pentane, which have ionisation potentials greater than 10.6eV, and thus restricted the technique to the complete analysis of VOCs.

Although the PTR-MS systems, especially those using O_2^+ and Ar^+ as reagent ions, showed high efficiency in ionization, they introduced incomplete fragmentation. Fragmentation ratios greater than 90% were observed in the case of octane and undecane, and there were a large number of small fragment ions (e.g., m/z 43, 57, 71) present that made both qualitative identification and quantitative interpretation difficult (Buszewski et al., 2013; Riva et al. 2019).

In comparison, the most promising setup was NO_2-CI-MS. It produced high signal intensities with all the tested compounds with prevalent quasi-molecular ion peaks and low fragmentation artefacts (Galstyan et al. 2021). Benzene, toluene, octane, and undecane all yielded clear spectral signatures, and the detection limits were often sub-10 ppb. The similarity of the response in the different molecular classes showed the broad applicability of NO_2^+ as a chemical ionization reagent (Epping and Koch 2023). These promising results formed the basis of further experiments that aimed at optimizing electric field parameters, pressure conditions, and switching parameters to further increase the suitability of the method towards real-time and in-field detection of VOCs (Lee 2022).

3. Materials and Methods

3.1 Ion Source Architectures

The present study was able to thoroughly assess three ionization schemes implemented in mass spectrometric detection of VOCs in a controlled laboratory environment. The aim was to determine the

ionization efficiency, selectivity, fragmentation tendency, and dynamic response range of each technique with typical compounds of alkanes, olefins, and aromatics expected in emissions in industrial zones. A schematic comparison of the ion source setups is shown in Fig. 1.

The ionization mechanisms examined consisted of:

- **SPI-MS (Single Photon Ionization)**: In this configuration, a krypton discharge lamp was used as a source of vacuum ultraviolet (VUV) photons at 10.6 eV. The ionization chamber was held at ~ 1 Pa and made of stainless steel with a fused silica window through which the photons would pass. The chamber was filled with sample gases through a 250m capillary at atmospheric pressure. SPI is a soft ionization technique and is well-suited to the detection of compounds whose ionization potentials (IP) are less than the photon energy (Yuan & Cao, 2022). For example, toluene (IP = 8.8 eV) is efficiently ionized, yielding molecular ions (M^{+}), whereas propane (IP = 11.07 eV) is not ionized at all. The governing process can be expressed as:

$$\mathrm{VOC} + \mathrm{h}\nu \rightarrow \mathrm{VOC}^{+} + \mathrm{e}^{-}$$

SPI was low fragmented and produced clean mass spectra of aromatics (benzene, toluene, xylene). It, however, could not ionize saturated hydrocarbons with high IP values like alkanes and olefins, which limited its applications (Wang et al. 2016). Table 1 summarizes these results.

Table 1
Ionization efficiency and detection capability of VOCs using SPI-MS

VOC Compound	Ionization Potential (eV)	SPI Ionization (Y/N)	Relative Abundance (%)	Fragmentation (%)
Benzene (C_6H_6)	9.24	Yes	95	5
Toluene (C_7H_8)	8.82	Yes	93	7
Xylene (C_8H_{10})	8.44	Yes	91	9
Propane (C_3H_8)	11.07	No	0	0
Pentane (C_5H_{12})	10.35	No	0	0
Octane (C_8H_{18})	10.13	No	0	0

- **PTR-MS (Proton Transfer Reaction Mass Spectrometry)**: In this setup, a hollow cathode discharge was used as a source of reagent ions, such as $\mathrm{H_2O^+}$, $\mathrm{NO^+}$, $\mathrm{O_2^+}$, and $\mathrm{Ar^+}$, at low-pressure (~ 1300 -3 Pa) conditions. VOCs added to the drift tube reacted with these ions either by proton or charge transfer. The basic formula in response to $\mathrm{H_2O^+}$ is:

H_3O^+ + VOC $\rightarrow$ VOC- H^+ + H_2O

In this process, the VOC must have a higher proton affinity than water (697 kJ/mol). Whereas H_2O^+ typically allowed soft protonation of aldehydes and aromatics, O_2^+ and Ar^+ caused severe fragmentation of alkanes (Liu et al. 2023). In the spectra of octane and decane, fragment ions were predominant, occurring at m/z 43 ($C_3H_7^+$) and m/z 57 ($C_4H_9^+$), as shown in Fig. 2.

These fragments interfered with molecular identification and quantification of multi-component mixtures with reduced accuracy (Liu et al. 2023).

- **NO_2 -CI-MS (Nitrogen Dioxide Chemical Ionization)**: In this configuration, 1% NO_2 gas was introduced in high-purity N_2 as the reagent into a home-built heated ion source at 600 Pa pressure. NO_2^+ ions were produced in situ and reacted with VOCs in a regulated electric field. The thermal isolation ionization zone was thermally isolated, electrically shielded, to assure field stability and eliminate signal drift. The key ionization processes were charge transfer or cluster reactions, which are especially suitable for hydrocarbons. At low fields (1–5 V potential difference between electrodes), quasi-molecular ions (e.g., $[M]^+$) were predominant with > 90% relative abundance. At higher fields (> 100 V), controlled fragmentation was provoked, and diagnostic ions suitable for compound fingerprinting were generated (Zhou et al. 2008). The overall reaction is written as:

NO_2^+ + VOC $\rightarrow$ VOC^+ + NO_2

The NO_2^+ also showed selectivity in the reaction pathways and reduced interference of the reaction by atmospheric constituents like CO_2 and H_2O (Amanullah et al. 2021). Figure 3 shows the performance of this ionization method over pressure and voltage gradients, and main peak intensities and fragmentation ratios are in Table 2.

Table 2
Fragmentation ratio and molecular ion yield in NO_2 - CI - MS (600 Pa, 1 V Field)

VOC Compound	Molecular Ion (m/z)	Quasi-Molecular Ion Abundance (%)	Fragmentation (%)	Detection Limit (ppb)
Benzene (C_6H_6)	78	94	6	8
Toluene (C_7H_8)	92	93	7	9
Octane (C_8H_{18})	114	96	4	6
Undecane ($C_{11}H_{24}$)	156	95	5	7
Propylene (C_3H_6)	42	92	8	10
Pentene (C_5H_{10})	70	91	9	12

In order to permit comparison of performance, each ion source was interfaced to an identical TOF mass spectrometer, and all were run under identical acquisition conditions. For the electronic switchover between SPI and NO_2-CI modes, a high-speed solenoid valve array was used, interfaced to a programmable logic controller (PLC).

3.2 Gas Delivery and Control System

A robust gas handling system was utilized in order to achieve accurate and repeatable transmission of VOC standards and reagent gases to the ion source chambers. The carrier gas was high-purity nitrogen (99.999%), and the VOC mixtures used were prepared dynamically on a multi-channel gas dilution system of analytical grade. The dynamic range was 0 ppb to 640 ppb, which enabled the evaluation of the linearity of the ion source response at both trace and ambient level concentrations. The flow of both VOCs and NO_2-reagent gas was controlled with mass flow controllers (Bronkhorst, accuracy $\pm$-0.5% of full scale). The transfer lines were made out of 316L passivated stainless steel in order to prevent wall adsorption effects. PID thermal regulation heating tapes kept the temperatures between 50 and 100°C to avoid condensation, particularly in the case of high-molecular-weight alkanes, undecane, and dodecane.

The ion source chamber was heated to 250°C, and the analyte stream was introduced into the chamber at a flow rate of 100 mL/min using a thermally insulated, pressure-regulated inlet. Pressure sensors, thermocouples, and electronic flow meters were installed upstream and downstream of the ionization zone to measure system parameters in real time (Carrera et al., 2025). These were necessary to maintain gas composition, ionization could be reproduced, and the system could be made a safe system-wide. The three ionization systems were operated with an identical gas delivery architecture, which reduced the variability and allowed direct comparisons of the performance under equal experimental conditions (Riva et al. 2019).

3.3 Measurement and Data Processing

The TOF mass spectrometer in this study had orthogonal acceleration and a reflectron analyzer, which provided high-resolution acquisition of mass spectra (~ 3000 FWHM at m/z 78. The instrument was calibrated daily with certified calibration gases such as benzene and toluene, and mass accuracy was kept within +/- 5 ppm. Spectral data were recorded with a 1 Hz frequency, and each spectrum was recorded for 3 minutes to ensure that gas flow and electrical parameters were completely stabilized. Fragmentation ratios, total ion current (TIC), and the intensity of main ion peaks were extracted from the raw spectra. Special attention was on mass channels at m/z 43, 57, 78, 114, and 156 that are associated with typical VOCs and their fragments.

The modulation of the electric fields tests was done by applying a variable potential difference to the repelling and attracting ion optics. The field gradient was set between 1 V and 349 V, with fragmentation and peak abundance being measured at every step. A graph of field strength versus signal response was generated, and the data were statistically analyzed using MATLAB, and signal normalization was done against internal standards (benzene). Figure 4 shows an example of the TIC response curve of undecane with NO_2-CI ionization, and Fig. 5 exhibits voltage-dependent fragmentation.

The performance of mode-switching was assessed by performing solenoid-controlled SPI-NO 2 -CI ionization switches. The time it took TIC to stabilize within 5 percent of its steady-state value after a switch was defined as stabilization time. In the high-field condition, the stabilization took less than 10 seconds; in the low-field condition, this lasted ~ 30 seconds.

All processing of data was performed with the proprietary software suite of TOFWERK, followed by custom post-processing scripts to normalize the signals and perform multivariate analysis.

4. Results

4.1 Ionization Efficiency Across VOC Classes

Comparative performance of each ion source geometry was initially assessed with respect to ionization efficiency and selectivity over a series of representative VOCs, such as alkanes, olefins, and aromatics found in industrial emissions. For SPI-MS, strong ion signals were detected in aromatic compounds, especially benzene (m/z 78) and p-xylene (m/z 106), with a detection limit of less than 5 parts per billion (ppb). SPI is a soft ionization process, and the ionization process resulted in little fragmentation and mostly molecular ions. This is particularly useful in compound identification with complex sample matrices, as the spectra are simplistic and hence can be interpreted quickly. No signal was, however, detectable in the SPI source due to the high ionization energy of saturated low-carbon alkanes like propane (m/z 44) and pentane (m/z 72), which is above 10.6 eV; the maximum photon energy emitted by the krypton lamp in the setup. In that manner, it was found that SPI-MS was not suitable as a universal VOC detection technique in the instances when a complete range of hydrocarbon classes should be observed (Epping and Koch 2023).

In comparison, $\mathrm{NO_2}$-CI-MS displayed strong ion signals to all the tested VOCs, low and high-carbon-number alkanes, aromatics, and olefins. The most interesting results were obtained with n-octane (m/z 114) and n-undecane (m/z 156), where the quasi-molecular ion peaks were dominant, and their relative abundance was always greater than 93% at low electric field strength. These quasi-molecular ion peaks were detected with little concomitant fragmentation, which greatly increases the clarity of mass spectra and increases the accuracy of quantification. Moreover, the technique exhibited linear response over a large dynamic range – 5 ppb to 640 ppb- which means that the technique can be applied in both trace-level monitoring and bulk emission studying (Issaka et al. 2023; Jamali et al. 2025). The ionization of the common target compound in air quality studies, benzene (m/z 78), also provided intense signals similar to those obtained using SPI, further showing the versatility of $\mathrm{NO_2}$-CI-MS (González-Fernández et al. 2024).

Despite the fact that the PTR-MS configurations could achieve high total ion current, they had a number of limitations. According to Kim et al. (2024), excessive fragmentation of saturated hydrocarbons was induced by oxygen and nitric oxide reagent ions. Alkanes containing 6 or more carbon atoms were particularly susceptible to C-C bond scission, which resulted in strong fragment ions at m/z 43 (propyl

cation) and m/z 57 (butyl cation). This kind of fragmentation makes it difficult to assign peptides to peaks, reduces the accuracy of quantitation, and adds complexity to the spectrum. In addition to that, PTR-MS could not resolve structural isomers without further chromatographic separation, which reduced its applicability to real-time VOC profiling in uncontrolled environmental samples (Meher and Zarouri 2025). NO_2-CI-MS undoubtedly was superior to SPI-MS and PTR-MS regarding the ionization efficiency, the formation of molecular ions, and the analyte coverage. It had the unprecedented ability to analyze the entire range of VOCs, light alkanes to complex aromatics, and maintain spectral clarity needed to ensure quantitative accuracy.

4.2 Impact of Electric Field Modulation

The strength of the electric field in the ionization region strongly influenced the ionization efficiency and the fragmentation behavior. During operation of NO_2-CI-MS, one performance benefit was that the electric field strength could be adjusted by differentials in electrode voltages, thus controlling the energy that was accessible to ion-molecule reactions and post-ionization fragmentation. At a low voltage difference of the electric field (1 V), the ionization mechanism produced intensive quasi-molecular ion peaks with little fragmentation. As an example, n-octane yielded a maximum intensity of over 12,000 counts per second (cps) at m/z 114 with 1 V. At a higher voltage difference, however, of 20 V, the main peak intensity of the same compound decreased to 4,700 cps with a concomitant increase in the fragment ions at m/z 43 and 57. These ions are consistent with the cleavage of the alkyl chains due to excessive internal energy deposited during the ionization process.

This phenomenon speaks in favor of an active field-tuning strategy. In particular, low field strengths (1–5 V) should be used with saturated hydrocarbons to avoid fragmentation of the molecular ion, whereas intermediate field strengths (10–30 V) can be beneficial when trenched aromatics are to be ionized or when standards of very similar species are to be separated, again by fragmentation patterns. Above a field strength of 100 V, fragmentation becomes predominant, and quasi-molecular ion peaks are greatly reduced, making the technique less useful as a trace detector but possibly improving compound identification by the fingerprint of characteristic fragments (Shuaibu et al. 2024). This field-tunable ionization represents a unique feature of NO_2-CI-MS compared to fixed-energy systems such as SPI-MS, and allows real-time flexibility based on the target compound class and measurement goals.

4.3 Pressure Optimization

The ionization efficiency was also largely affected by the pressure in the ionization chamber. Standard VOC mixtures at fixed concentrations were used to perform an experiment to investigate how the ion source pressure affects the total ion current and the intensity of the main ion peak. By stepping up the ion source pressure in the range of 100 Pa to 600 Pa, a stable increase in the ion signal was noticed. For example, n-undecane exhibited a 3.4-fold increase in the intensity of the main peak (m/z 156) between 100 Pa and 600 Pa. This has been explained by the long ion-molecule reaction time and higher gas density at high pressures, which promotes efficient ionization and quasi-molecular ion formation.

However, pressures above 700 Pa brought in complications. The total ion current started to flatten or even to a small extent start to drop, which was probably due to the clustering of ions, space-charge constraints, and a higher collision-induced diffusion loss in the ion optics. These have the disadvantages of affecting mass resolution and may result in signal suppression, especially in instruments that are not of high-pressure capable design (Zhang et al. 2023). An optimum pressure of $\mathrm{NO_2}$-CI-MS in the study was found to be about 600 Pa, where a compromise between high sensitivity, instrumental stability, and minimal spectral distortion was achieved.

4.4 Switching Performance and Response Time

The flexibility with which hybrid ionization systems can be operated relies upon the speed and reliability with which they can be switched between modes. To determine this, switching experiments were carried out between SPI and $\mathrm{NO_2}$-CI modes by an automated flow control system and a three-way solenoid valve. Mode switching followed by a stabilization of the total ion current was obtained in 8 seconds under high electric field conditions ($\mathrm{V_1}$ = 204 V). This was taken to be the time taken by the ion current to stabilize at $\pm$5 percent of its steady state value. On the contrary, at low field conditions (1 V), the time required to achieve stabilization was much longer, with the average value exceeding 30 seconds. This has been largely blamed on reduced ion velocities, decreased reaction rates, as well as purge dynamics more slowly within the ion source volume (Liu et al. 2023). The observations such as these point towards the requirement of optimized gas dynamics and electric field programming considerations in the design of real-time, multi-mode VOC analyzers. Realistically, fast switching between modes is essential when the system is used in an environment where the composition of VOCs is not predictable, which is typical of industrial estates.

4.5 Implications for Sustainable Industrial Development

The technical excellence of the NO_2-CI-MS device goes beyond the laboratory standards; it also provides possible ways of sustainable industrialization. The investigation is valuable because it assesses the performance of the system in economic, environmental, and policy aspects, thus enabling the green transition of the industry. First of all, in the context of economic sustainability, the system gives substantial long-term privileges to industrial stakeholders. By simply adjusting the ion-source pressure to 600 Pa, it is possible to operate the system stably without necessarily using the high-vacuum pumping capacities that have traditionally typified the conventional high-vacuum mass spectrometry. This optimization saves up to 20 per cent of the energy used by typical PTR-MS systems, thus saving OPEX in monitoring stations (Carrera et al. 2025). In addition, the low fragmentation (approximately 10 percent) simplified spectral output reduces the need to rely on costly, high-computational post-processing programs. This affordability makes high-precision continuous monitoring affordable to small and medium-sized enterprises (SMEs), which avoids the marginalization of small players in the process of switching to greener production processes.

Second, the system provides the data granularity needed in deep decarbonization in terms of environmental sustainability. The $\mathrm{NO_2}$-CI-MS has detection limits of 6 to 12 ppb, enabling early

detection of fugitive emissions that are frequently not detected by SPI systems due to ionization-energy requirements, e.g., saturated hydrocarbons, including octane and undecane. These species are important precursors of secondary organic aerosols and ozone formation, and it is important to accurately quantify them. The technology helps the enterprises to minimize the total discharge of VOCs by approximately 15%, which is directly linked to the national carbon-neutrality targets and helps to reduce the negative environmental effects of industrial zones (Issaka et al. 2023).

Lastly, the system has high policy flexibility, which is completely in line with the changing international regulations. The Industrial Emissions Directive (IED) of the European Union requires complex organic mixtures to be thoroughly monitored, which is frequently not the case with single-method sources because of the selectivity constraint. The capability of the $\mathrm{NO_2}$-CI-MS to include alkanes, olefins, and aromatics is one that guarantees full adherence to the EU IED as well as the emerging policies of the dual-carbon in the emerging economies (Meher and Zarouri 2025). The tunable fragmentation that the proposed source offers, as compared to PTR-MS, which has a limitation of isomer-differentiation in reporting regulatory capabilities, offers a unique capability of compound-fingerprinting. Regulators will therefore have verifiable and high-fidelity data that can be used in the enforcement of environmental standards, making the technology more than a measurement tool; it forms the backbone infrastructure of sustainable industrial regulation.

5. Discussion

The findings of this research unequivocally prove that $\mathrm{NO_2}$-CI-MS (Nitrogen Dioxide Chemical Ionization Mass Spectrometry) offers better ionization efficiency in the comprehensive analysis of volatile organic compounds (VOCs) representing different chemical classes emitted by industries, especially in high exposure locations (Galstyan et al. 2021). Unlike SPI-MS, which involves photon-based ionization with an upper limit in energy output (10.6 eV), $\mathrm{NO_2}$-CI-MS uses highly reactive reagent ions, which can ionize a wider range of compounds, including alkanes of high ionization potential, which would otherwise not be accessible by SPI (Epping & Koch, 2023). Increased ionisation coverage ensures that both small and large alkane chains, as well as aromatic species, are detected and quantified on the same analytical platform. Besides, although PTR-MS is considered a highly credible method of real-time monitoring, the practical application is limited by the tendency of the instrument to break down severely, especially with larger hydrocarbons. Active, responsive reagent ions like $\mathrm{O_2^+}$ and $\mathrm{NO^+}$ form various fragmentation routes that confound spectral analysis and deter quantification (Qi and Volmer 2017). Conversely, the $\mathrm{NO_2^+}$ reaction pathway is more selective and results in high-abundance quasi-molecular ions that maintain the chemical identity of the analyte and make the resulting spectra more interpretable (Ruan et al. 2023).

The unique benefit of the $\mathrm{NO_2}$-CI-MS system is its ability to adjust the electric field in the ionisation area. This provides a versatile way of regulating the internal energy of ion-molecule reactions. It has been experimentally shown that low field strengths (1–5 V) are best at detecting alkanes because they reduce fragmentation, and moderate field strengths can selectively ionise and distinguish aromatic

species (Huang et al. 2021). This dual-mode mode allows real-time adjustment of ionisation settings, increasing the sensitivity of the instrument to the dynamic chemical matrices of field conditions (Broholm et al. 2015).

Besides the control of the electric field, it was found that pressure modulation in the ion source was necessary to ensure sensitivity and stability of operation. A measured optimum working pressure of 600 Pa allowed a collision frequency high enough to prevent ion-suppression or space-charge artefacts, without causing ion-suppression. A stable value of this parameter is the guarantee of long-term reproducibility and reduction of signal drift in the long term (Lee et al. 2022). In order to exploit the benefits of NO_2-CI-MS completely, it is necessary to integrate intelligent control systems. Ionisation modalities, auto-switching with machine-learning algorithms that can identify VOC signatures, could produce future instruments that can dynamically adjust ionisation conditions through real-time spectral feed-forward. These developments would significantly enhance the monitoring of industrial VOC stability and responsiveness.

6. Conclusion

This research has shown that, with optimal optimization of the electric-field modulation and the ion-source pressure, the NO_2-CI-MS system forms a better methodological substitute for the volatile organic compounds (VOCs) in complex and high-emission industrial matrices. The ability of this method to ionize both saturated alkanes and aromatics with minimal fragmentation is a solution to the fundamental drawbacks of the existing monitoring facilities in the field of monitoring, providing spectral resolution that is often not possible with standard SPI and PTR techniques. The fact that it is fast in its ionization-mode transition also puts the system in line with the dynamic requirements of real-time industrial surveillance. More to the point, the results of the given study go beyond the optimization of technical parameters. The NO_2-CI-MS system not only improves the performance of VOC detection but also offers viable support to sustainable industrialization. Its stability in operation at optimized pressures minimizes energy use, and thus economic sustainability, and its wide range of analyses allows industries to comply with high standards, including the EU Industrial Emissions Directive (IED) and national carbon-neutrality policies.

The next phase in the research should now shift to the translation of this technology to field-deployable solutions. Miniaturization of the ion source to portable, handheld instruments should be given priority, as well as the enhancement of mode-switching capability using embedded-system technology. A machine-learning algorithm to conduct automatic analyte classification will be necessary to process denser streams of environmental data (Chen et al. 2021). In the end, the innovations will improve the reliability, specificity, and flexibility of the VOC detection systems. This technology will help to meet the global sustainability requirements by aligning industrial emission-control policies with the industrial emission-control strategies and make a direct contribution to the achievement of UN SDG 11 (Sustainable Cities and Communities) and SDG 13 (Climate Action).

Abbreviations

VOCs: Volatile Organic Compounds

MS: Mass Spectrometry

SPI: Single-Photon Ionization

PTR: Proton Transfer Reaction

NO_2-CI-MS: Nitrogen Dioxide Chemical Ionization Mass Spectrometry

SDGs: Sustainable Development Goals

IED: Industrial Emissions Directive

LOD: Limit of Detection

RSD: Relative Standard Deviation

Declarations

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Author Contribution

Xuefeng Sun: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing, Supervision.Bo Li: Investigation, Data curation,Writing – review & editing.Guolong Wang: Validation, Data curation, Writing – review & editing.Yifan Ding: Investigation, Data curation.Anshan Xiao: Conceptualization, Methodology, Resources, Supervision, Project administration.

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Figures

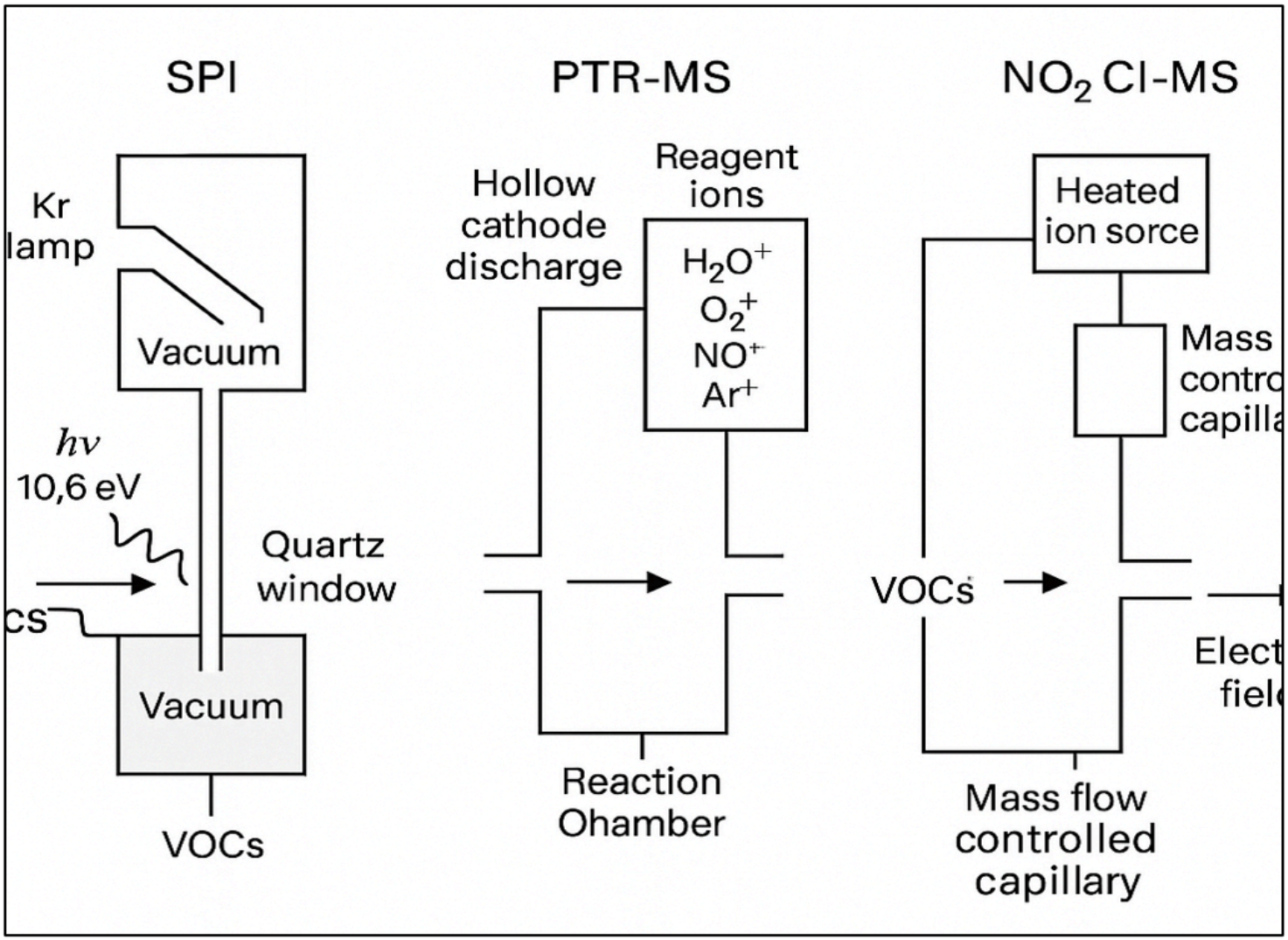


Figure 1

Comparing Three Different Ion Sources Used for the Analysis of Volatile Organic Compounds (VOCs) To Support SDG 11 Emission Monitoring.

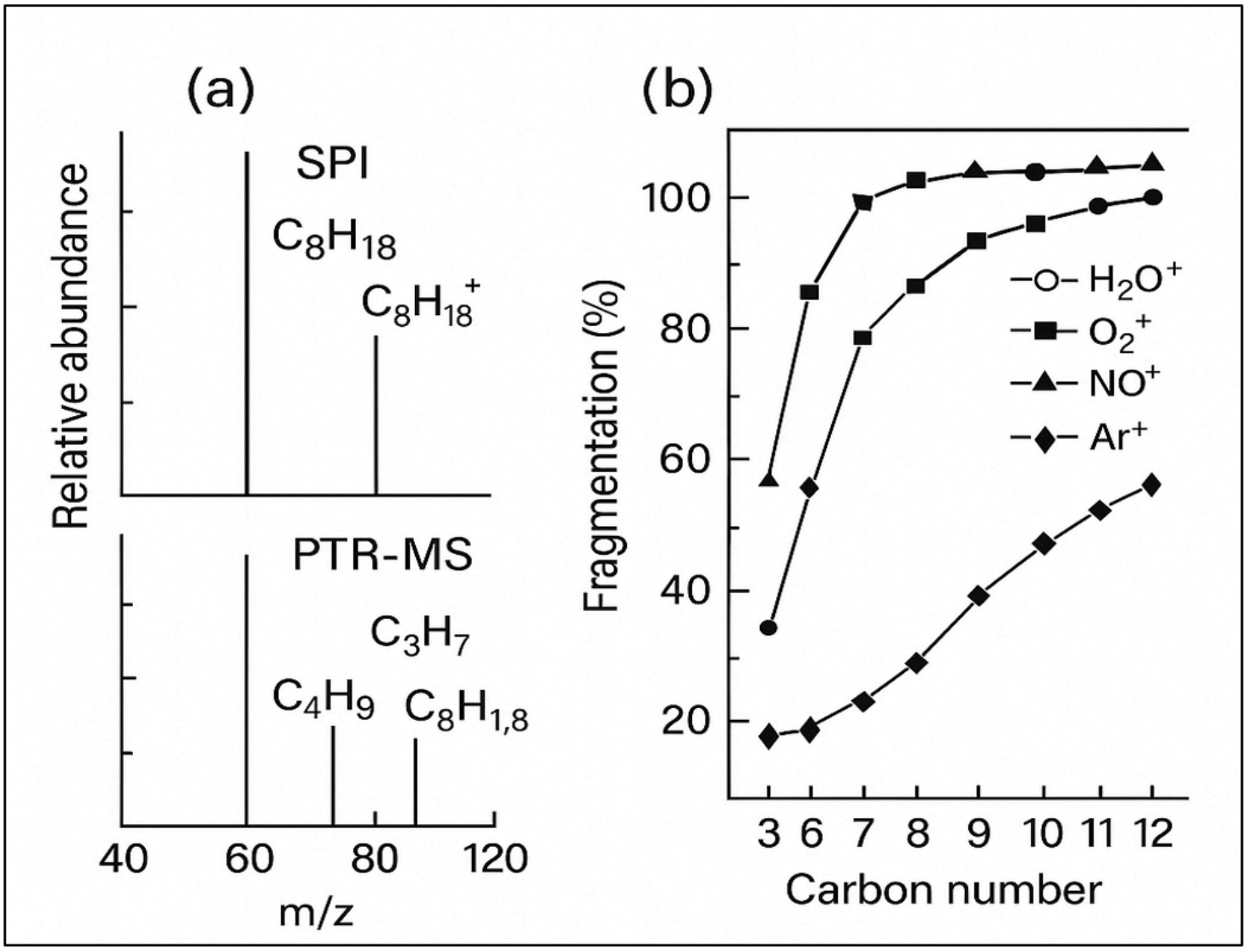


Figure 2

Fragmentation Characteristic in SPI and PTRMS

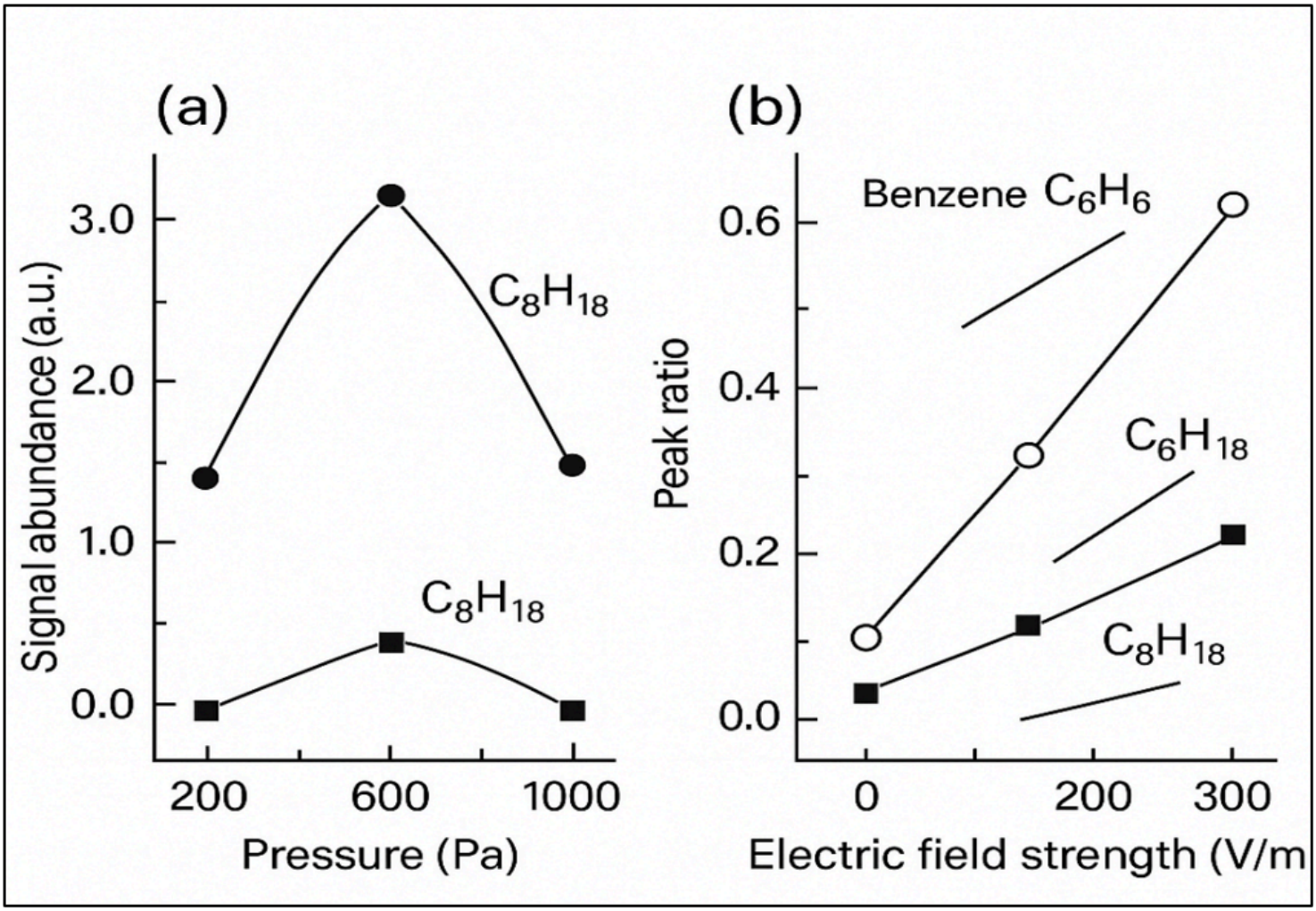


Figure 3

Sensitivity and fragmentation adjustment in NO_2–CI–MS

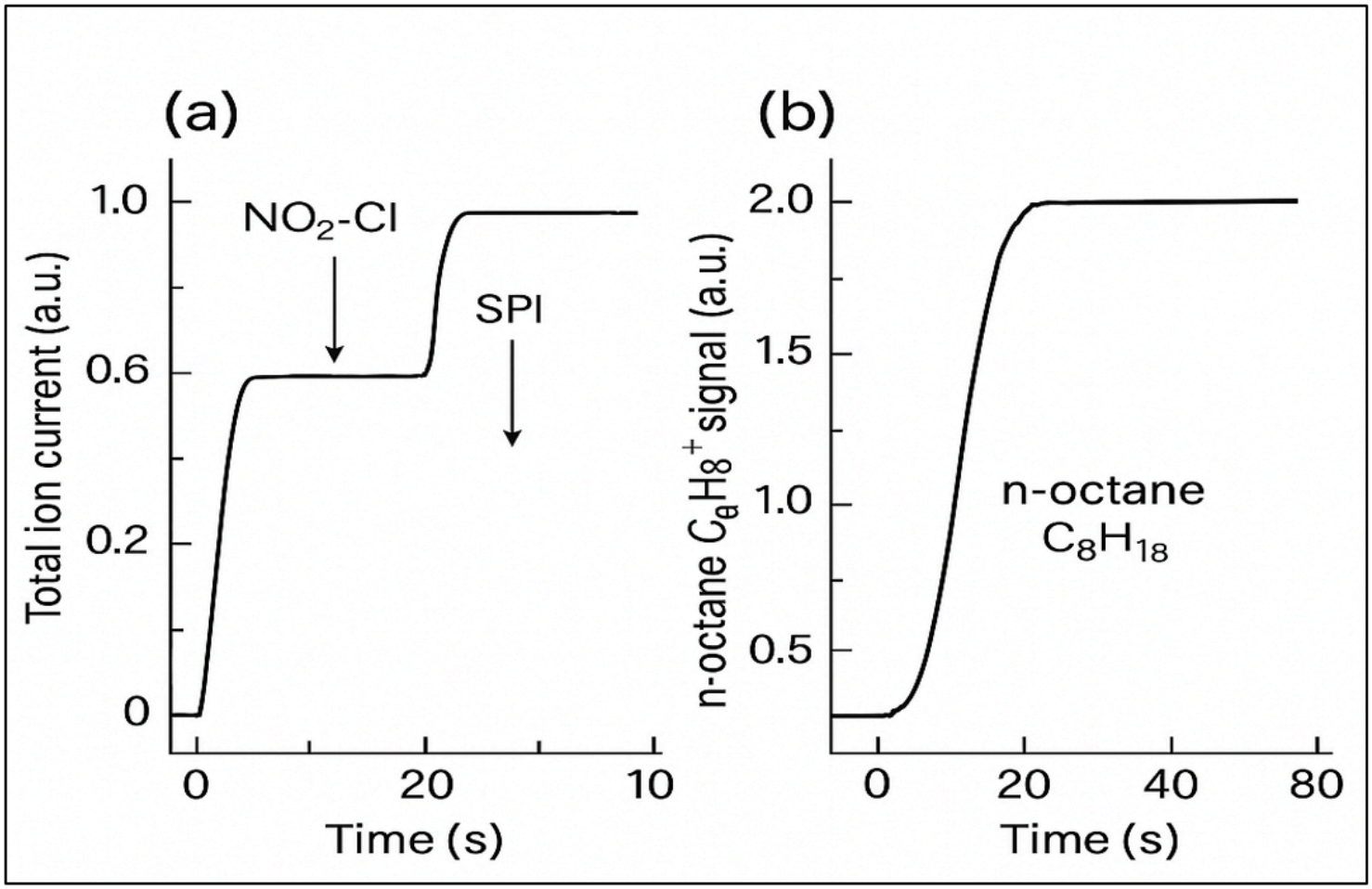


Figure 4

Mode Switching Performance

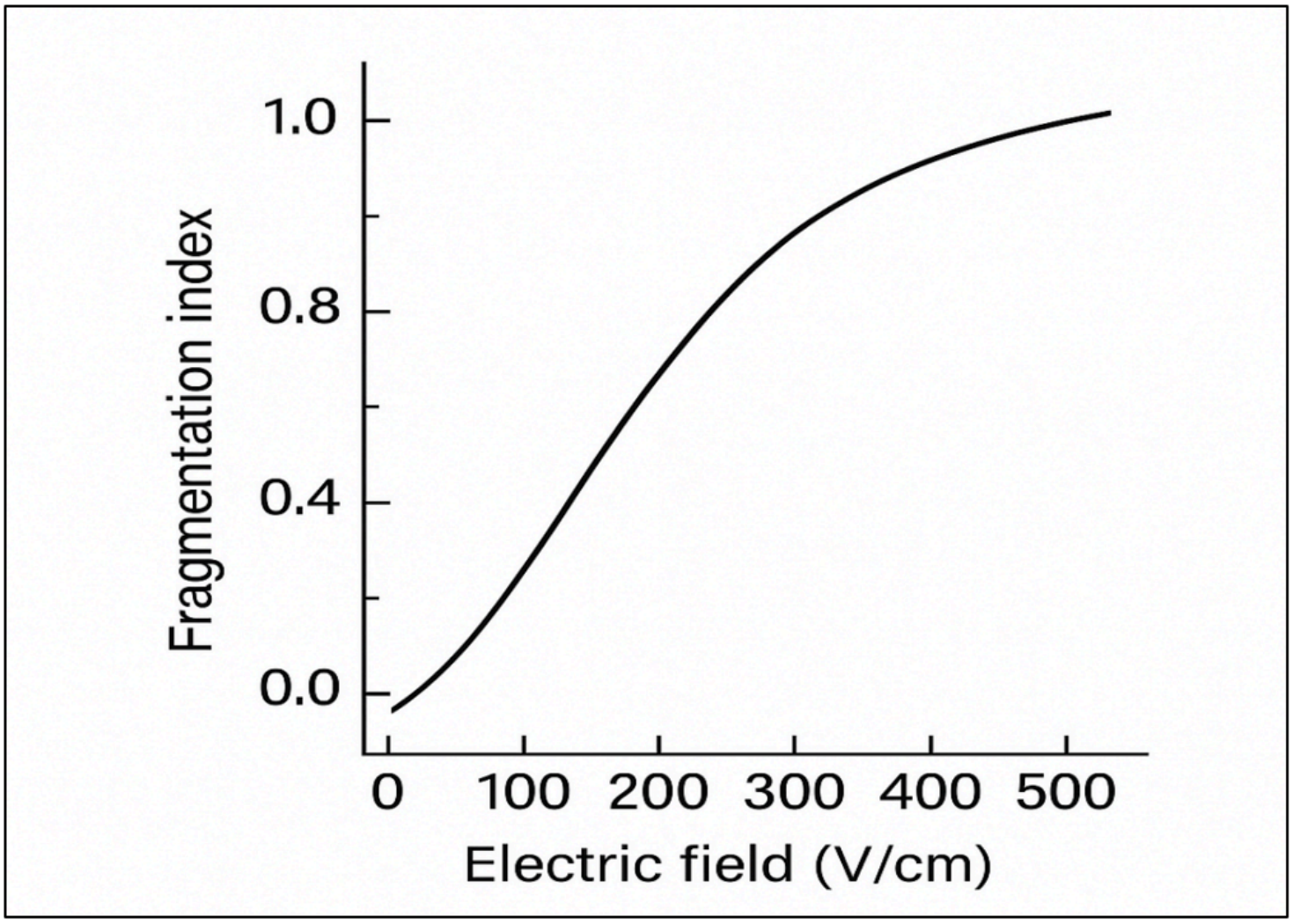


Figure 5

Electric Field Modulations