

New Possibilities for the Determination of Volatile Organic Compounds by Their Molecular Ions in Air Using μ s-Pulsed GD TOFMS

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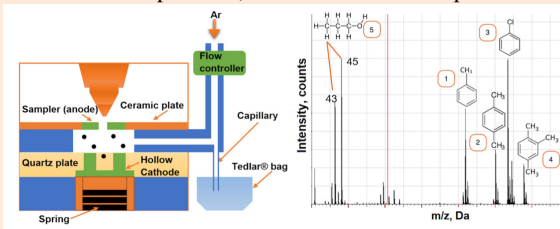
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ABSTRACT: A recent trend in glow discharge analysis, previously considered as a ‘purely inorganic’ technique, is related to the effective ionisation of volatile organic compounds (VOCs). This approach was demonstrated to be capable of analysing VOCs in both model gas mixtures and ambient air. In the current study, the possibility of the direct determination of VOCs of different classes of organic compounds (including toluene, *p*-xylene, chlorobenzene and 1,2,4-trimethylbenzene) in ambient air using microsecond pulsed glow discharge time-of-flight mass spectrometry (μ s-Pulsed GD TOFMS) with copper hollow cathode was demonstrated. The ionisation processes with the formation of molecular ions M^+ , which can be used for quantification, were discussed. The fragmentation of detected molecular ions of VOCs was found to be quite low, which benefits both qualitative and quantitative determination. The ease of identification and relative simplicity of the mass spectrum is promising for the analysis of VOC mixtures. One of the possible applications of the designed method is the direct determination of VOCs in human exhaled breath for the diagnosis of lung diseases, including lung cancer. However, revealing its potential applicability for this purpose requires further research.



INTRODUCTION

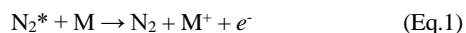
A recent trend in glow discharge analysis, previously considered a ‘purely inorganic’ technique, is related to the effective ionisation of the volatile organic compounds (VOCs). This approach was demonstrated to be capable of analysing VOCs in both model gas mixtures and ambient air.^{1,2}

Several studies addressed the application of glow discharge mass spectrometry (GDMS) in molecular analysis.¹⁻⁵ Fandino *et al.* investigated two variants of GDMS application: as a detector in gas chromatography and under a continuous flow of VOCs (benzene, toluene, ethylbenzene, and xylene) in an artificial air mixture.³ The afterglow of the discharge was used for the

ionisation, employing mainly the Penning process. The limits of detection (LODs) of the VOCs in artificial air were *ca.* 1 ppb. The authors pointed out the similarity of acquired GDMS spectra to electron impact spectra. However, these similarities were not sufficient for simple mass spectra library-based identification, especially for the multicomponent systems. Additionally, the determination of VOCs in real ambient air or human exhalation is a more challenging task than for the artificial air mixture, mainly due to the presence of moisture with high variability. Moisture affects all ionisation processes in the glow discharge.

Nunome *et al.* used a novel coaxial discharge cell consisting of a cylindrical anode with a meshy cylindrical cathode inside.² The

authors referred to their ionisation process as soft Penning ionisation (SPI). Such cell geometry considerably separates the zones of discharge *per se* and the zone of chemical ionisation of the VOCs, reducing the fragmentation of the analytes. Pulsed glow discharge (duty cycle 50%) was maintained in ambient air without the use of noble gases. The ions were detected by a quadrupole mass spectrometer. The authors demonstrated that under low pressure in the discharge cell (0.8-1.2 kPa) the primary ionisation process was the Penning mechanism (Eq. 1):

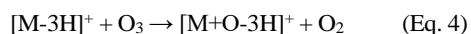
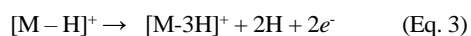


where M is the analyte under study, e^- the electron. The use of the SPI source ensured a high degree of fragmentation of the high molecular mass compounds in the sample of the smoke, which hampered reliable identification. Under higher pressure (1.5-2.5 kPa), the primary ionisation mechanism switched to NO^+ association (Eq. 2):



Consequently, the peaks corresponding to $[\text{M} + \text{NO}]^+$ became dominating under relatively low fragmentation. Additionally, the monitored ion shifted towards the higher mass range, reducing potential interferences and ion scattering. At the same time, the presence of the water-based cluster ions $[(\text{M} + \text{NO})(\text{H}_2\text{O})_n]^+$ was indicated, which hampers the identification. Finally, the use of saturated vapours of VOCs was reported in the study.³ It resulted in a concentration level 4-6 orders of magnitude higher than for human exhalation which potentially limits the use of $[\text{M} + \text{NO}]^+$ for the purpose of breath analysis.

The same experimental setup was employed for the determination of *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane, monitoring the $[\text{M} + \text{O} - 3\text{H}]^+$ ions.⁴ These ions are formed as follows:



The sensitivity obtained exceeded that of the previous study,³ providing the LODs of *ca.* 1 ppm (determined by background ions). However, the LODs are still to be improved for the real implementation of the scheme. Additionally, the sophisticated composition of exhaled air containing a wide range of compounds,^{6,7} some of which are potentially prone to fragment in the discharge, may interfere with the $[\text{M} + \text{O} - 3\text{H}]^+$ ions. Certain fragments can be isomeric and identical to those formed by other compounds and may make it futile to use high-resolution mass spectrometry. Finally, the acquisition of $[\text{M} + \text{O} - 3\text{H}]^+$ ions shifts the monitored m/z only by 13 Da, which barely affects the background for the low mass range.

The aim of the current study is to develop a μs -Pulsed GD TOFMS method for the direct, fast, and highly sensitive determination of VOCs in the air using molecular ions under the minimised level of fragmentation of the analytes.

MATERIALS AND METHODS

Instrumentation. A time-of-flight mass spectrometer Lumas-30 (Lumex, St. Petersburg, Russia) with direct current pulsed glow discharge was used for the measurements. The instrument provides ion determination in the mass range up to 350 Da with a mass resolution of $m/\Delta m \approx 800$. The instrument and its analytical features were described previously.⁸⁻¹¹ The discharge cell included a copper hollow cathode and a sampler cone (anode). In the current study, the cathode of 6 mm inner diameter and 3.5 mm depth produced from high purity copper (99.999%) was used. The distance between the cathode bottom and the sampler orifice (stainless steel, 1.5 mm orifice diameter) was 6 mm. The discharge gas was high purity (99.9999%) argon (Linde Gas Rus, St. Petersburg, Russia). The working parameters are presented in Table 1. The spectra were recorded with a delay τ_i after the discharge pulse, for details see Ganeev *et al.*¹¹ The discharge was carried out at a frequency F with a pulse duration of τ_d . The intensity of isotope components was obtained by integrating the mass spectrum using an integration window of ± 0.15 Da from a peak centre. The schematic of the discharge cell is demonstrated in Fig. 1.

Sample introduction. The detection of VOCs was investigated by introducing air, containing the VOC vapours, into the argon flow. The argon flow was directed to the discharge cell of the time-of-flight mass spectrometer. For ionisation, glow discharge with a pulse duration of 1-5 μs and a voltage of 1400 V was used. To produce air-VOC mixtures of known composition, corresponding compounds were introduced into Tedlar® bags of 3 L volume

Table 1. Mass Spectrum Acquisition Parameters

Parameter	Value
Hollow cathode material	Cu
Pulse repetition period T_i , μs	200-400
Discharge pulse voltage, V	900-1600
Pressure, Pa	24-34
Discharge frequency, kHz	3.2
Pulse duration τ_d , μs	1-5
Repelling pulse delay τ_r , μs	1-300

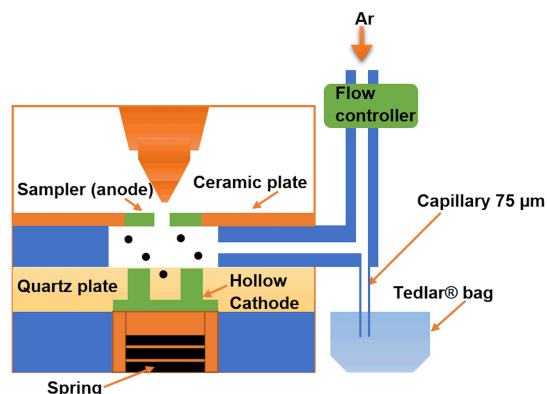


Fig. 1 A schematic of the discharge cell for the ionisation of VOCs in pulsed discharge TOFMS.

(Sigma-Aldrich, Merck, Darmstadt, Germany). After the introduction of VOCs, the Tedlar® bag was heated with a fan for 2-3 minutes to ensure full evaporation. Since the concentrations of the VOCs in the bag were below the saturated vapour concentration for the analytes, total evaporation of the VOC matter enabled its quantification in the bag. The capillary was introduced through a septum into the Tedlar® bags and the laboratory air, or air containing the VOCs, entered the discharge cell at a constant rate through the capillary due to the drop in pressure between the discharge cell and the ambient atmosphere. The switch between the Tedlar® bags was undertaken through repositioning the capillary's edge. There were no valves in the sample introduction system. Before the analysis of every VOC containing sample, the background spectra of the bag filled with ambient air were acquired.

Discharge parameter optimization and calibration. The following parameters were optimised: discharge pulse duration, discharge cell pressure, discharge pulse frequency and repelling pulse delay relative to the discharge pulse. Constant air pressure of 61.3 Pa was maintained in the cell, which was determined by the air introduction capillary geometry (inner diameter of 75 µm and length 8 cm). The argon partial pressure in the discharge cell was regulated using a piezoelectric device (measured under switched off air-flow). A five-component VOC mixture was used for the optimisation (Table 2, C4). Three four-component VOC mixtures were used for calibration (Table 2, C1-C3).

Statistics. All measurements, including the determination of the LODs and the precision of the method (as relative standard deviation – RSD), were undertaken in 6 replicates ($n = 6$). All results are expressed as the mean \pm confidence interval ($n = 6$, $P = 0.95$).

The LODs were estimated using the following equation (Eq. 5) based on refs.^{12,13}:

$$\text{LOD} = 3 \cdot C \cdot \Delta I_{bg} / (I - I_{bg}) \quad (\text{Eq. 5})$$

where I = integral intensity of the compound under study, I_{bg} = background intensity in the range ± 0.15 Da from the peak centre, ΔI_{bg} = standard deviation of background intensity, C = concentration of the compound in the sample.

RESULTS AND DISCUSSION

Contrary to a previous study,³ we introduced a supplementary argon flow into the discharge cell since the discharge could not be properly initiated without it. The increase of air pressure reduced the sensitivities of the VOCs and increased the intensity of the copper associates, as observed in our previous study.⁵ The optimised pressure provided signal maximisation of the analytes and led to minimisation of the background intensities. VOC ionisation was undertaken *via* short discharge pulses (2.0-3.5 µs).

Table 2. Concentrations of VOCs in Mixtures used. Mixtures C1-C3 Were Used for Calibration; Mixture C4 Was Used for Optimisation

VOC	C1	C2	C3	C4
Propanol-1, ppm	0	0	0	87
Toluene, ppm	12	35	94	94
Chlorobenzene, ppm	15	45	120	120
<i>p</i> -Xylene, ppm	12	35	93	93
1,2,4-Trimethylbenzene, ppm	12	36	95	95

Table 3. Ionisation Energies (IE) of VOCs and Inorganic Gases¹⁴

Compound	Molecular weight	IE, eV	Compound	Molecular weight	IE, eV
CO	28	14.0	Benzene	78	9.2
N ₂	28	15.6 (11.1*)	Toluene	92	8.8
NO	30	9.3	<i>n</i> -Heptane	100	9.9
O ₂	32	12.1 15.8	<i>o</i> -Xylene	106	8.6
Ar	40	11.6* 11.7*)	<i>p</i> -Xylene	106	8.4
CO ₂	44	14.3	<i>m</i> -Xylene	106	8.6
SO ₂	64	12.3	<i>n</i> -Octane	114	9.8
Acetonitrile	41	12.2	Chlorobenzene	113	9.1
Propanol-1	60	10.2	1,2,4-Trimethylbenzene	120	8.3

*Excitation energy of metastable level is shown in parentheses.

Such short pulses effectively excited the metastable level of the molecular nitrogen (N₂*). The excited N₂* molecules induced the ionisation of VOCs *via* the Penning process (Eq. 1).

At the same time, short pulses ensured a low degree of compound dissociation and low background intensities. This indicates high selectivity and improves the LOD values. The efficiency of the Penning process in the ambient air atmosphere (Eq. 1) is related to the fact that the excitation energy of the metastable N₂* (11.1 eV) exceeds that of most of the VOCs. The ionisation energy of some VOCs and inorganic gases presents in the atmosphere and/or the exhalation are indicated in Table 3. As shown in Table 3, only acetonitrile has a higher ionisation energy than that for metastable N₂* and metastable argon (Ar*).¹⁴ The ionisation energies of other VOCs suffice to exploit metastable levels of N₂* and Ar* for an effective Penning process.

The increase of discharge pulse frequency, in principle, increases the sensitivity of VOC determination (cps/ppm). Thus, the use of the highest frequency possible seems to be reasonable to employ. At the same time, a frequency increase, corresponding to the decrease of the pulse period T_i , causes some change in the integral intensities for the mass spectra acquired. Fig. 2 shows the corresponding dependence for 5 VOCs and ⁶³Cu⁺ on the pulse period in the range of 200 to 400 µs. The use of a discharge pulse period shorter than 200 µs was not possible, due to the specific requirements of the detecting system; for $T_i > 400$ µs, discharge instability or failed ignition was observed. The data in Fig. 2 indicate that the longer T_i increases the signal intensities for the VOCs, especially for 1,2,4-trimethylbenzene and *p*-xylene. The

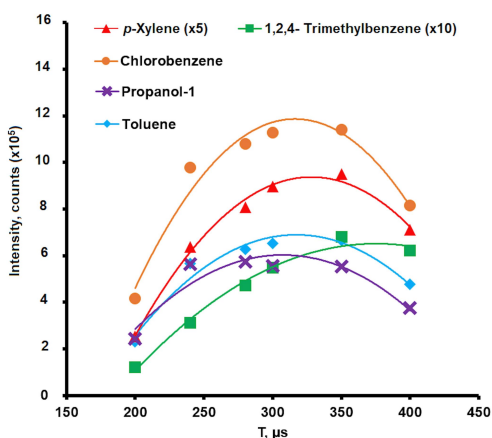


Fig. 2 The dependencies of mass spectrum signal intensities for 5 VOCs on the discharge pulse period. Air partial pressure 61.3 Pa, argon pressure 25.0 Pa, pulse duration 2.5 μs , repelling pulse delay 110 μs . C4 VOC mixture was used for the optimisation (Table 2).

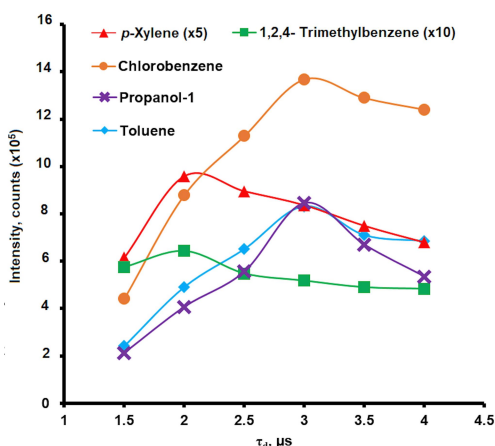


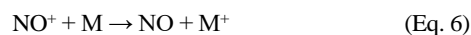
Fig. 3 The dependencies of mass spectrum signal intensities for 5 VOCs on the discharge pulse duration. Air partial pressure 61.3 Pa, argon pressure 25.0 Pa, discharge pulse period 250 μs , repelling pulse delay 110 μs . C4 VOC mixture was used for the optimisation (Table 2).

optimal T_i -value was found to be in the range of 250-350 μs . Finally, the period of 250 μs was selected since this value also provided increased sensitivities in cps/ppm.

Figure 3 shows the dependence of signal intensities for 5 VOCs on the discharge pulse duration. The increase of pulse duration caused some increase of VOC molecular ion intensities, possibly related to the improved excitation efficiency of the discharge gas and, thus, higher concentration of N_2^* . The optimal discharge pulse duration was found to be in the range of 2.5-3.5 μs . Longer pulses accelerate the sputtering of the cathode material, increasing the concentration of the copper atoms in the plasma, reducing the concentration of N_2^* and the output of the Penning process (Eq. 1), due to the non-elastic collisions of the electrons with the copper atoms.

The increase of discharge cell pressure considerably reduced the mass spectral intensities of the molecular ions (argon pressure

above 28.7 Pa) and increased the intensities of the background components (Fig. 4). This effect is probably related to the accelerated sputtering of the Cu cathode and, consequently, the elevated electron temperature and the reduced concentration of the metastable N_2^* . The increase of the pressure from 24.0 to 28.7 Pa led to a considerable increase in the mass spectrum signal intensities of chlorobenzene and toluene. The increase was also observed for the NO^+ , Cu^+ and m/z 43 component ($[\text{M-OH}]^+$) for propanol-1. At the same time, the intensities of p -xylene and 1,2,4-trimethylbenzene were slightly affected. The intensity maxima for chlorobenzene, toluene, and component m/z 43 for propanol-1 are shifted towards higher pressure, compared to p -xylene and 1,2,4-trimethylbenzene. A possible explanation may be related to the asymmetric charge transfer with NO^+ (see Eq. 6). The intensity of this reaction increases up to 30 times with the increase of pressure from 24.0 to 28.7 Pa.



The ionisation energies of toluene and chlorobenzene (Table 3) are comparable to that of NO (corresponding ionisation energy differences are 0.37 and 0.20 eV, respectively). However, for p -xylene and 1,2,4-trimethylbenzene, the ionisation energies differ more considerably (0.83 and 1.0 eV, respectively). Notably, the

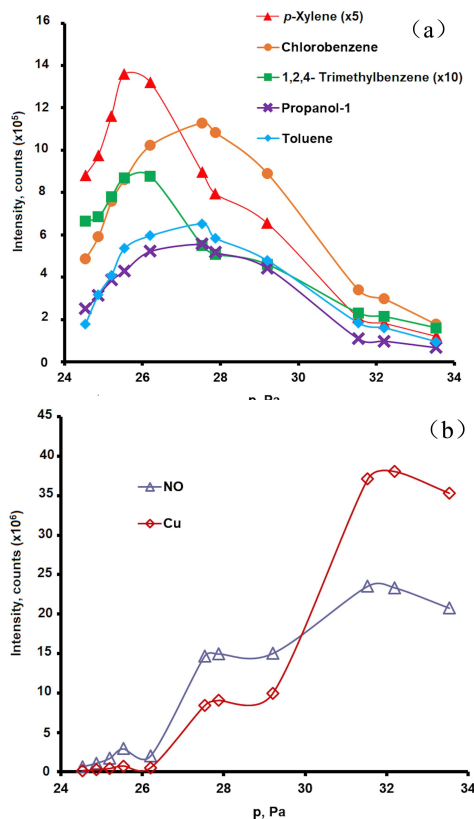


Fig. 4 Dependencies of mass spectrum signal intensities: a – 5 VOCs; b – NO^+ and Cu^+ on argon pressure in the discharge cell. Discharge pulse duration 2.5 μs , discharge pulse period 250 μs , repelling pulse delay 110 μs . C4 VOC mixture was used for the optimisation (Table 2).

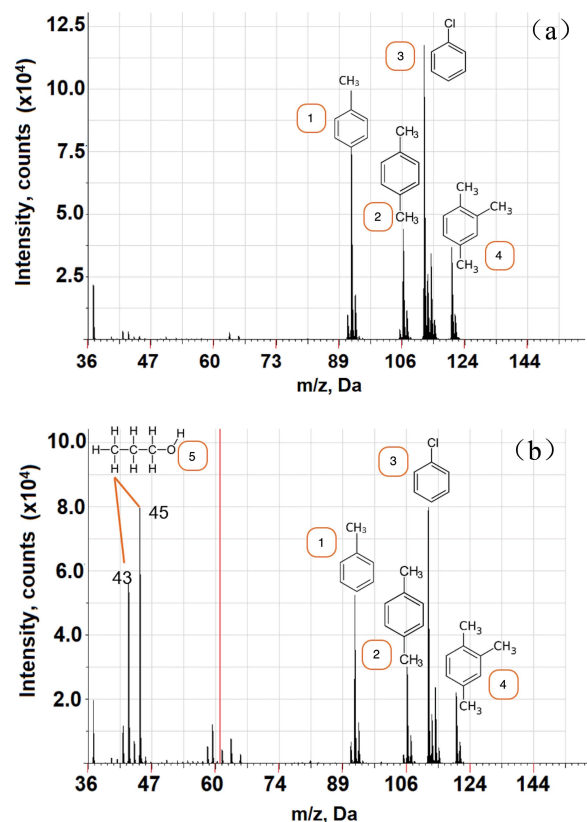
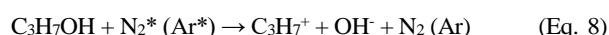


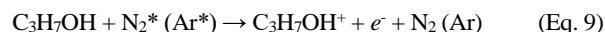
Fig. 5 a) A mass spectrum of 4 VOC mixture (without propanol-1) – Sample C3 (Table 2); b) A mass spectrum of 5 VOC mixture (with propanol-1 present) – Sample C4 (Table 2). Air pressure 61.3 Pa, argon pressure 25.0 Pa, discharge pulse duration 2.5 μ s, discharge pulse period 250 μ s, repelling pulse delay 110 μ s. 1 – toluene, 2 – *p*-xylene, 3 – chlorobenzene, 4 – 1,2,4-trimethylbenzene, 5 – propanol-1.

use of reaction (Eq. 6) to increase the intensities of some VOCs is accompanied by a considerable elevation of the background components. Thus, the high NO^+ concentration mode was not used in further studies.

Figure 5 shows a mass spectrum range of 4 VOCs (a) and 5 VOCs (b) under optimised discharge parameters. Notably, primarily the molecular ions of the VOCs can be observed in the mass spectrum, followed by protonated and deprotonated ions with considerably lower intensity. However, for propanol-1, the molecular ion is virtually absent (Fig. 5b). Instead, two components of m/z of 43 ($[\text{M}-\text{OH}]^+$) and 45 ($[\text{M}-\text{CH}_3]^+$) were present. We suppose that such behaviour of propanol-1 may be related to its resonance dissociation in the discharge. The excitation energies of molecular nitrogen and argon (Table 3) are quite close to the bond energy for the methyl group in the $\text{C}_3\text{H}_7\text{OH}$ molecule (11.1 eV) and the bond energy of the OH group in the molecule (11.6 eV).⁴ Thus, highly effective resonance dissociation of $\text{C}_3\text{H}_7\text{OH}$ may take place:



The probability of the dissociation processes (Eq. 7 and Eq. 8) appears to be considerably higher than that of the Penning ionisation of propanol:



which may explain our observations for the propanol-1 mass spectrum.

Additionally, the intensity of C_3H_7^+ is considerably lower than that of $\text{C}_2\text{H}_4\text{OH}^+$, which corresponds to the higher difference between the OH-group bond energy and the metastable N_2^* level energy (0.5 eV) compared to that of the CH_3 -group (0-0.25 eV).

An analogous process was observed for *n*-octane, for which the difference between the bond energy of the methyl and excitation energy of N_2^* is also low (-0.2 eV). Fig. 6a demonstrates the μ -pulsed GD TOFMS mass spectrum of *n*-octane. The appearance energy values for *n*-octane fragmentation are shown in Table 4. The intensity of the fragment components of $[\text{M}-2\text{CH}_3]^+$ and $[\text{M}-3\text{CH}_3]^+$ is considerably higher than that for M^+ . On the other hand, for *p*-xylene, the methyl bond energy is higher than the excitation energy for N_2^* and Ar^* resulting in a relatively low degree of fragmentation (Fig. 6b, Table 5).

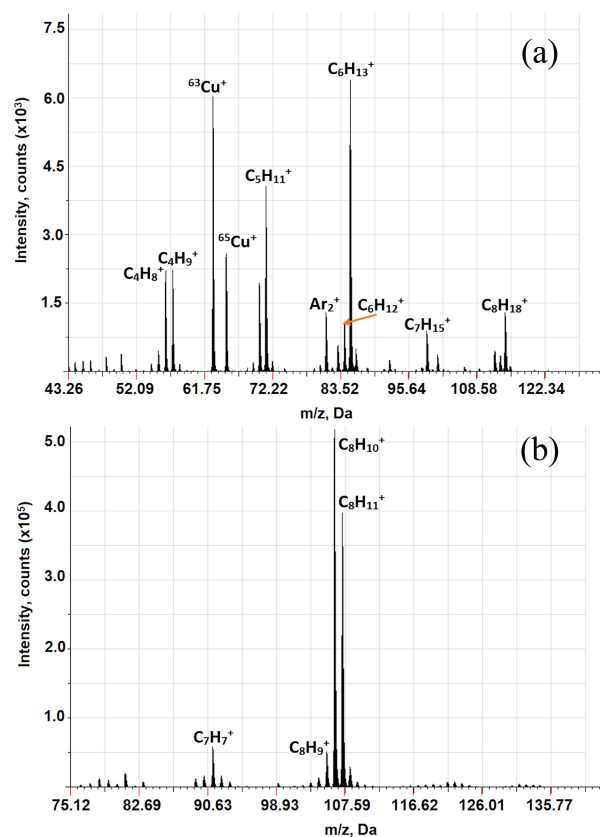


Fig. 6 a) A mass spectrum of *n*-octane (concentration 500 ppm); b) A mass spectrum of *p*-xylene (concentration 500 ppm). Air pressure 61.3 Pa, argon pressure 25.0 Pa, discharge pulse duration 2.5 μ s, discharge pulse period 250 μ s, repelling pulse delay 110 μ s.

Table 4. Appearance Energy for *n*-octane

Fragment ion	Appearance energy, eV
C ₄ H ₈ ⁺	11.2
C ₄ H ₉ ⁺	11.1
C ₄ H ₉ ⁺	11.4
C ₅ H ₁₀ ⁺	11.1
C ₅ H ₁₁ ⁺	11.0
C ₅ H ₁₁ ⁺	11.2
C ₆ H ₁₂ ⁺	10.3
C ₆ H ₁₂ ⁺	10.8
C ₆ H ₁₃ ⁺	10.9
C ₇ H ₁₅ ⁺	10.9

Table 5. Bond Energies for Some VOCs

Compound	Ion	Appearance energy, eV
Acetonitrile	C ₂ H ₂ N ⁺	13.9
	C ₂ H ₂ N ⁺	14.4
	C ₂ H ₂ N ⁺	14.0
Benzene	C ₅ H ₅ ⁺	15.7
Chlorobenzene	C ₆ H ₅ ⁺	11.8
Propanol-1	C ₃ H ₇ ⁺	11.6
Toluene	C ₆ H ₅ ⁺	13.7
<i>o</i> -Xylene	C ₇ H ₇ ⁺	11.8
<i>p</i> -Xylene	C ₇ H ₇ ⁺	11.9
<i>m</i> -Xylene	C ₇ H ₇ ⁺	11.8
<i>n</i> -Octane	C ₇ H ₁₅ ⁺	10.9

Table 6. LODs for VOCs in Air Mixture Assessed for 10 Min Mass Spectrum Acquisition Using 3 σ Criterion

VOC	LOD, ppb
Toluene	2
Chlorobenzene	3
<i>p</i> -Xylene	0.5
1,2,4-Trimethylbenzene	5

Notably, since the ionisation takes place in pulsed discharge afterglow under low atomic temperature (average discharge power of 3 W), the processes (6) and (7) may be accomplished only under the comparable energies of metastable N₂* and Ar* and the bond energy of the dissociating group. Indeed, the bond energy for CH₃ in *p*-xylene and toluene, as well as the Cl atom in chlorobenzene, are 11.9, 13.7 and 11.8 eV, respectively.¹⁴ Although the difference with excitation energy of molecular nitrogen appears to be not too large (0.8, 2.6 and 0.7 eV, respectively), the [M-CH₃]⁺ components are virtually absent in the mass spectrum. The intensities of protonated and deprotonated toluene ([M+H]⁺ and [M-H]⁺) are also relatively low.

Another notable fact, as can be seen in Fig. 5, under selected discharge conditions, the intensities of the copper components (⁶³Cu⁺ and ⁶⁵Cu⁺) are low. This indicates that all copper-based cluster components (such as CuOH⁺, CuAr⁺, CuO⁺, Cu₂⁺, etc.) are extremely low, not affecting the determination of the VOCs. The optimised discharge parameters providing the maximised VOC intensities under minimised intensities of the background components are as follows: air pressure 61.3 Pa, argon pressure 25.0 Pa, discharge pulse duration 2.5 μ s, discharge pulse frequency 4 kHz, repelling pulse delay 110 μ s. Lower values of pressure or shorter pulse duration resulted in unstable discharge.

Under the optimised discharge conditions, calibrations were established for 4 VOCs (Fig. 7). The relative uncertainty of the calibration points was within 10%. The LODs, evaluated using the 3 σ criterion for the registration time of 10 min, are presented in Table 6. The LOD values in the range of 0.5-5 ppb were achieved, which is perspective for the real application of the new approach for a wide range of analytical tasks, including the determination of VOCs in human exhalation.^{15,16}

When comparing our results with previous studies,^{1,3,5} the following aspects may be identified. The combination of several factors related to the nature of the pulsed glow discharge resulted in the combination of two beneficial outcomes for the online detection mode, which are often hard to achieve together. These are high ionisation efficiency and low degree of fragmentation of the VOCs. The reason for the low degree of fragmentation is related to the primary ionisation mechanism of the VOCs in the current study – the Penning process with metastable molecular nitrogen. Bouza *et al.* also used the Penning mechanism for VOC ionisation.¹ However, since Ar* rather than N₂* was used for the ionisation, which has a higher excitation energy (the difference of 0.66 eV), it resulted in a significantly higher fragmentation level for the VOCs.¹ Besides, we used a relatively low discharge power of 3 W, additionally reducing the degree of fragmentation. In our previous study,⁵ we used copper-associates CuM⁺ for the detection of VOCs and observed a low degree of fragmentation under the discharge parameters favouring their formation; however, it resulted in more than one order of magnitude reduced sensitivity compared to the use of molecular ions as in the current study.

When analysing the VOC mass spectra, we noticed the presence of rather an intensive component of O₂⁺, related to the ionisation of inorganic gases present in the air. O₂ has a relatively low difference between its ionisation energy and excitation energy of the metastable level of argon (0.36 eV, Table 3). The ionisation of other inorganic gases, such as N₂, SO₂, CO, CO₂, etc., by the Penning process is not possible since their ionisation energies

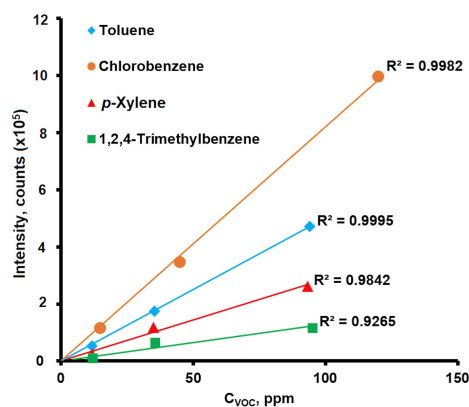


Fig. 7 Calibrations of VOCs obtained for 4 compound mixtures. Air pressure 61.3 Pa, argon pressure 25.0 Pa, discharge pulse duration 2.5 μ s, discharge pulse period 250 μ s, repelling pulse delay 110 μ s.

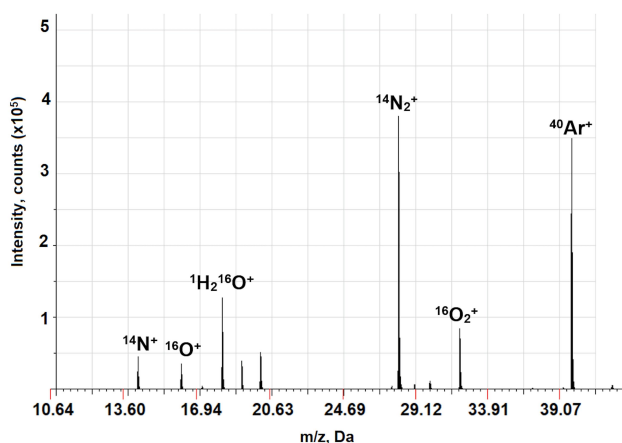


Fig. 8 A mass spectrum of an air sample indicating the system's applicability for the determination of inorganic components. Air pressure 61.3 Pa, argon pressure 25.0 Pa, discharge pulse duration 2.5 μ s, discharge pulse period 250 μ s, repelling pulse delay 8 μ s.

considerably exceed the excitation energy of the metastable Ar* and N₂*. However, since the analytical system used is capable of effective ionisation of the components with high-energy electron impact, we explored the prospect of determining inorganic gases in the air. Fig. 8 represents a mass spectrum of the air sample obtained under a short repelling pulse delay of 8 μ s. Under such repelling pulse delay, the ions formed by the high-energy electron packet are detected.^{11,17,18} The flow of the high-energy electron packet is formed at the front of the discharge pulse and is capable to ionise the components with the highest ionisation energies.^{9,11} The obtained mass spectrum (Fig. 8) indicates that the proposed analytical system may combine the determination of organic (VOCs) and inorganic components in the gaseous phase. This is an additional potential benefit of the designed analytical system, which requires further research.

CONCLUSIONS

The possibility of direct determination of VOCs of different classes of organic compounds (*i.e.* toluene, *p*-xylene, chlorobenzene, and 1,2,4-trimethylbenzene) in ambient air using TOF-MS with a μ s-DC pulsed glow discharge with copper HC was considered. Ionisation processes with the formation of the molecular ions M⁺, which can be used for quantification, were discussed. Effective Penning ionisation of different VOCs was demonstrated. At the same time, another ionisation process (electron ionisation) was shown to be feasible by variation of the repelling pulse delay. This process can be used for the determination of inorganic compounds (N₂, O₂, CO₂, H₂O, *etc.*)

The fragmentation of detected molecular ions of VOCs was found to be rather low, which benefits both the qualitative and the quantitative determination. The ease of identification and the relative simplicity of the mass spectrum is promising for the

analysis of VOC mixtures, which was also demonstrated. One of the possible applications of the designed method is the direct determination of VOCs in human exhaled breath for the diagnosis of lung diseases, including lung cancer. However, revealing its potential applicability for this purpose requires further research.

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Notes

The authors declare no competing financial interest.

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