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Research paper

The Effect of Humidity and Dopants on the Detection of TNT Vapor by Differential Ion Mobility Spectrometry (DMS)

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Abstract: The aim of this study was to investigate the effect of an external factor, i.e. humidity, on the detectability of TNT vapor by Differential Ion Mobility Spectrometry (DMS). The values of TNT signal amplitude and asymmetric voltage were measured as a function of relative air humidity. The influence of the use of a semi-permeable membrane and the additive agent - dopant (nicotine and dichloromethane) on the detection under varying air humidity conditions was also investigated. The analysis of the obtained results confirms that the introduction of dopant to the analyzed stream contributes to the change of TNT detection parameters. The DMS detector allows you to observe the signal in two polarizations (positive and negative), which is an advantage compared to the competitive FAIMS method.

It was observed that water vapor content above 30% causes the formation of two analytical signals for TNT. This, in turn, may improve the identification process. The addition of nicotine and dichloromethane reduces the amplitude of the air signal, which has a beneficial effect on TNT detection.

Keywords: differential ion mobility spectrometry, DMS, explosives, trinitrotoluene, effect of humidity, dopants, nicotine, dichloromethane

Supplementary Information (SI)

SI contains a datasheet with the results for HSV asymmetric voltage and average TNT signal amplitude for a given relative air humidity.

1 Introduction

The detection of trace amounts of explosives is essential, as these substances, in addition to conventional military application, have been increasingly used by terrorists. For security as well as environmental protection reasons, novel and improved technologies and methods have been developed to facilitate the detection of even minimal quantities of explosives. The most popular methods used for the detection of explosives rely on spectrometric techniques, such as Ion Mobility Spectrometry (IMS) [1-8] and its alternative form, *i.e.* Differential Ion Mobility Spectrometry (DMS) [9-13]. The DMS method has proven effective in the detection and identification of volatile organic compounds (VOCs) [14]. These compounds often come from human industrial activities, contributing to air pollution. They are also present in paints, washing-up liquids, aerosols, glues, and even burning candles [15, 16]. Unfortunately, they are not neutral to human health.

Ion mobility spectrometry based instrumentation has been widely used as portable equipment for explosive vapor detection due to a number of advantages (including the option of real-time detection, detection in the atmosphere, detection with no additional carrier gas, low weight and size of the instrument and the miniaturization option) [17]

The authors of this study yet again carried out experiments to examine the effect of air humidity on the detection of trace amounts of explosives [8]. The research was conducted using the Field Asymmetric IMS (FAIMS) method. In this paper, the authors investigated the effect of humidity on the detection rate of TNT vapors using the DMS method. Presently, this method is used in Poland to test for chemical warfare agents. The authors have undertaken the effort to examine how DMS can be applied to the analysis of explosive vapor amounts several orders of magnitude lower than in the case of contamination detection. To improve the sensitivity of the DMS device, the effect of using a semi-permeable membrane and dopant on the detection process under conditions of varying humidity was also investigated. The analysis was focused on TNT, as the most common bulk

explosive, characterized by fine and higher vapor volatility compared to other explosives. The DMS detector allows you to observe the signal for positive ions and negative ions, which is an advantage compared to the competitive FAIMS method. Previously, we conducted research related to air humidity, in which we used the FAIMS method [8].

2 Experiments

2.1 Methods

2.1.1 DMS method

DMS is an analytical method which utilizes a high alternating electric field. It is also referred to as FAIMS spectrometry. The method can be used to detect a variety of substances such as explosives, drugs, CW agents and a number of other organic and inorganic compounds [18]. It operates on the principle of nonlinear dependence of ion mobility on the strength of an electric field [19-21].

The ion mobility value depends on the properties of a specific ion (mass, shape), the particle type, drift gas (mass, volume, electrical properties) and the electric field strength which plays a particularly important role. The ion mobility ratio (K) depends on the value of the electric field strength to a larger extent when attributing high values.

The DMS spectrometer consists of a reaction region, where ions are formed as a result of ionization, and a drift region, where ions become separated. The separated ion-particle products of the reaction travel to the collecting electrode, where they become neutralized and induce a measurable analytical signal. In the DMS method, the formed ions are transferred from the ionization region to a channel formed by two parallel electrodes, separated by 0.25 mm. The drift of ions is enabled by the flow of a carrier gas (air). The electric field, perpendicular to the ion drift, is generated by a periodic high asymmetric voltage (HSV), *i.e.* a separation field with a maximum amplitude of 50 kV/cm (granting a maximum voltage of up to 1,250 V for the DMS detector) and a frequency of up to 3 MHz, which results in oscillatory motion of the molecules perpendicular to the direction of the flow of the carrier gas. Additionally, a low compensation voltage (CV) with an amplitude of -30 to +8 V and a frequency of 10 Hz is used, thus changing the drift trajectory of ions and allowing them to travel to the measuring electrode [10, 14]. It is specific to each ion and depends on such parameters as the temperature, humidity and separation field strength. The

application of appropriate compensating voltage is required for the capture of ions by the collecting device.

Perpendicular direction of gas flow in DMS distinguishes this technique from IMS, in which gas flow is parallel to the electric field. Ions in DMS are separated based on differences in their mobility in an electric field of low and high intensity at atmospheric pressure. In the case of low electric field strength, the mobility of ions does not depend on the size of the electric field. In DMS, ion mobility is affected by low and high electric field strengths. The reduced field strength allows the comparison of DMSs from different companies. The relationship between ion mobility and electric field strength is expressed by the following equation [11]:

$$K\left(\frac{E}{N}\right) = K_0 \left[1 + \alpha\left(\frac{E}{N}\right)\right]$$

where K_0 is reduced ion mobility [$\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$], E/N is the electric field in Townsend units ($1 \text{ Td} = 10^{-17} \text{ V} \cdot \text{cm}^2$), which is known as the normalized molecular density, and $\alpha(E/N)$ is the normalized function describing electric field mobility dependence.

The DMS measurements are presented in the form of spectra called ionograms (spectrograms) showing the relationship between the specific ion current voltage (HSV) and CV. DMS analysis can be performed in positive (cation capture) and negative (anion capture) polarization modes simultaneously. A detailed description of the DMS method is reported in the literature [12, 22, 23].

The DMS detectors on which the measurements were made were constructed at the Military Institute of Chemistry and Radiation (Warsaw, Poland). The purified air flow through an evaporator; its flow rate was regulated using the Bronkhorst mass controller (regulation range: 0-10 L/min). The parameters of the control unit for the DMS spectrometer were as follows:

- high-speed, high-voltage (SV) generator frequency: 3 MHz,
- selective voltage (peak-to-peak): 13-154 Td,
- compensation voltage: -5.2 to 1.4 Td; 10 Hz,
- maximum electric field intensity: 50 kV/cm,
- length of DMS electrodes: 25 mm,
- length of DMS chamber: 50 mm,
- distance between DMS electrodes: 0.25 mm,
- gas flow rate through detector: 3 L/min,
- detector temperature: 45 °C,
- ionization: Ni-63.

2.1.2 Sample ionization

The first step in the DMS method involves the ionization of the sample, which takes place at atmospheric pressure. The analyte can be converted to an ionic form in various ways. The most commonly used ionization methods include corona discharge, use of a radioactive isotope (*e.g.* ^{63}Ni , tritium), photoionization, laser ionization, thermal ionization [23]. Explosive chemicals exhibit high electronegativity resulting from their structure, and as a result of ionization they form mostly anions. Hence the analysis of explosives is possible mainly in negative polarization. The detection efficiency (shape of calibration curve and detection limit) is determined by an appropriate ionization capacity of the analyte and the ion formation processes. These processes can be adjusted to obtain the highest possible sensitivity and adequate selectivity of measurements by modifying certain parameters such as temperature and gas composition. The substances added to the carrier gas are called dopants.

2.1.3 Measurement system

In order to study the effect of humidity on the detection of TNT vapor, a system was designed, as shown in the diagram in Figure 1. The analyte (33.7 mg of TNT) was placed in a glass flask (150 mL) and heated in a water bath. The analyte was then transferred to a reactor supplied with air with varying levels of humidity (carrier gas). Subsequently, the analyte was analyzed with the chemical detector operating on the basis of differential ion spectrometry (DMS). In front of the detector a membrane and a flask containing dopant used for specific measurements were placed (Figure 1(b)). The dopant flow was controlled. Nicotine and dichloromethane in amounts of 50.5 mg and 400 μL , respectively were used as dopants. Measurements with dopants were carried out in a similar way to measurements with TNT.

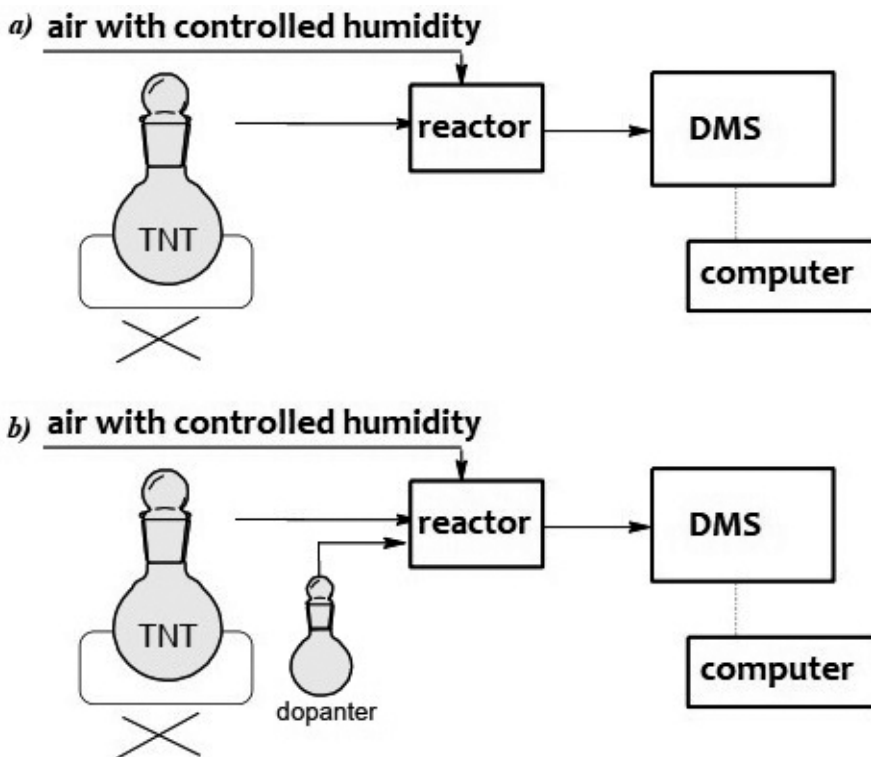


Figure 1. Scheme of measurement system (a) and with application of dopant (b)

2.1.4 Dopants

When pure carrier gas is introduced into the spectrometer reaction region gas-specific reaction ions are formed. These can serve as a source of electric charges to be used in the ionization of the analyte molecules. When the carrier gas is doped, the reaction ions include ionized dopant molecules or its fragments, called alternative reaction ions. They differ significantly from the ions formed from pure carrier gas. The addition of dopants entails the modification of the value of the alpha function and the increase in the compensation voltage, which may contribute to the improved detection limit, sensitivity as well as increased selectivity [24, 25]. The ions interact with the analyte and interferences differently than in the case of reaction ions formed solely by ionization of a pure carrier gas.

The dopants improve analytical response, due to the following factors:

- reactant ions interact with an analyte and do not react with the detection disturbing molecules, which do not form ions, consequently contributing to the reduction of noise. The change in the mobility of ions may take place,

compared to the corresponding ions formed with no dopants in the carrier gas. This effect can be used to spread the peaks in the spectrum and to prevent overlap between the peaks from reactant ions and the ions of the sample. In the case of DMS, we observe differences in mobility for low and high electric fields therefore, the change in the α coefficient describing the change in mobility when a high field intensity is applied – HSV should be taken into account.

- the products formed with alternative reactant ions may show greater stability. They do not undergo decomposition during the flow through the drift region and, as a result, the spectra contain more analytically useful data.

Dopants can influence the ionization process by controlling the proton transfer reaction, complexing or charge exchange. They are selected in such a way as to exhibit a lower proton or electron affinity as compared to the analyte, however a higher affinity as compared to the interferences. A favored charge exchange with the analyte results in a clear separation and an increased ionic potential. Dopants are used to improve the detection in the negative mode, which is particularly important for detection of explosive particles. In this case, as carrier gas dopants, halogen derivatives of hydrocarbons are typically used [26]. The detection of explosives is based on the halogenated ion adduct, formed by electron fragmentation (electron capture dissociation, ECD) of a hydrocarbon [27].

2.2 Materials

The study included one of the most widely used high explosives, trinitrotoluene (TNT). TNT is relatively easy to detect with the use of explosive vapor detectors because of high volatility (the average vapor concentration is 9.5 ppb at 25 °C) [28]. The vapor pressure of an explosive depends on the ambient temperature (increases with increasing temperature), and for TNT an increase of each 5 °C doubles its value [29, 30].

The TNT ionization mostly contributes to the formation of $[\text{TNT-H}]^-$ and $[\text{TNT}]^-$ ions, which are usually detected by the IMS method [31]. In the humid environment, the hydrated ions such as $\text{H}_2\text{O}\cdot[\text{TNT-H}]^-$ and $\text{H}_2\text{O}\cdot[\text{TNT}+2\text{O-H}]^-$ are observed.

In the present study, nicotine was used as a dopant. Nicotine is a pyridine alkaloid found in many plants, for example in the root and leaves of cultivated tobacco (*Nicotiana tabacum*). The other dopant of choice in this study is dichloromethane. This halogen derivative of methane is mainly used as solvent in a variety of industries.

3 Results and Discussion

3.1 Air spectrogram

The obtained results were analyzed using pyPrs software (dedicated to DMS detector, held by the Military Institute of Chemistry and Radiometry), which were used to visualize, compare and identify measured data. The study started with a qualitative analysis of dry air with relative humidity of 2%. A spectrogram consisting of three parts was obtained with use of the software (Figure 2).

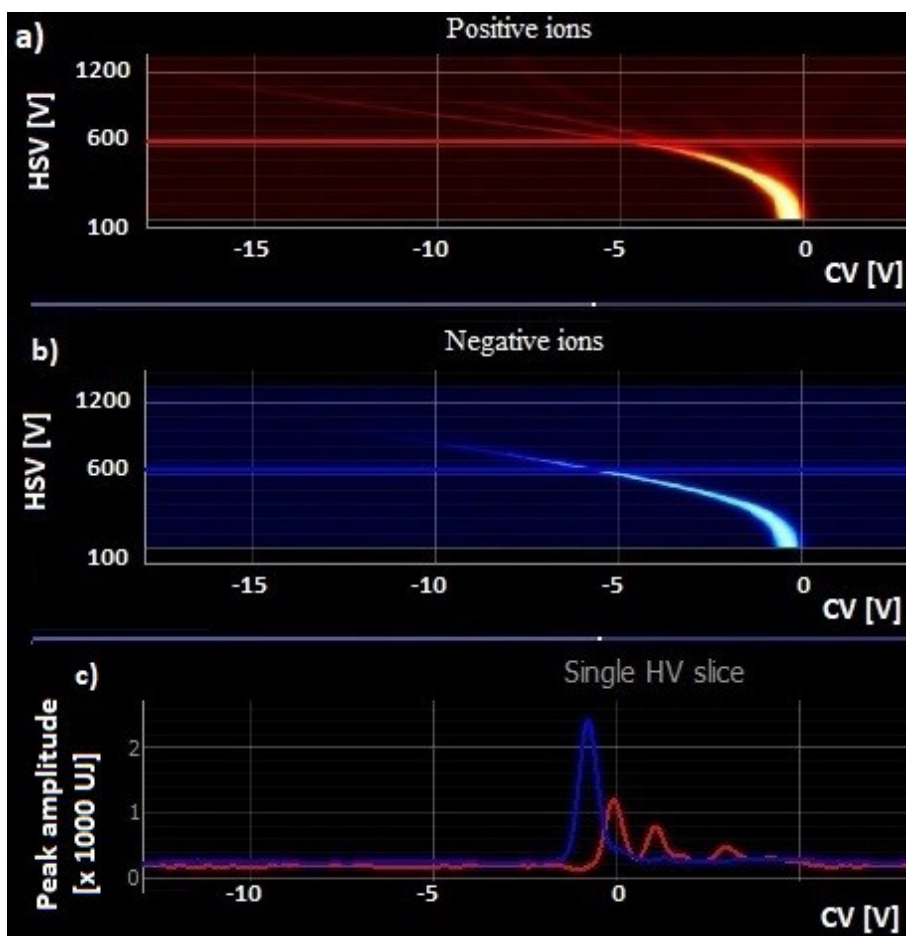


Figure 2. Spectrograms for dry air in positive polarization (a), in negative polarization (b) and peaks in positive and negative polarization (c) at an asymmetric voltage (HSV) of 600 V

The first two parts present the spectra of positive (a) and negative (b) ions across the entire range of asymmetric voltage, HSV. The third region shows both peaks in positive and negative polarization for a specific HSV voltage value, as generated by the software. The vertical axis shows peak amplitude, whereas the horizontal axis shows the value of the CV. Across the whole range of possible voltages of the HSV generator from 100 to 1200 V scans, with a step change in voltage of 5 V were performed. The CV changes from -20 to $+5$ V. The ionograms show characteristic peaks for the analyzed air (RIP - Reactant Ion Peak), which indicate the water vapor content in the investigated gas flow. The peak inclination towards a vertical axis changes depending on the level of humidity.

3.2 TNT spectrogram

A series of measurements were performed at a temperature ranging between 25 and 95 °C and at the air flow rates of 2 and 5 L/min in order to select the optimal conditions for the production of TNT vapor. The choice of parameters was determined by the capability to reach a required concentration, which allowed for the interpretation of peaks from the DMS spectrometer, *i.e.* temperature of 95 °C and a flow rate of 5 L/min. A characteristic signal in negative polarization originating from the ions of a sample was observed (Figure 3). Measurements were performed three times. As the result the mean value was reported. The standard deviations were so small that they did not need to be interpreted.

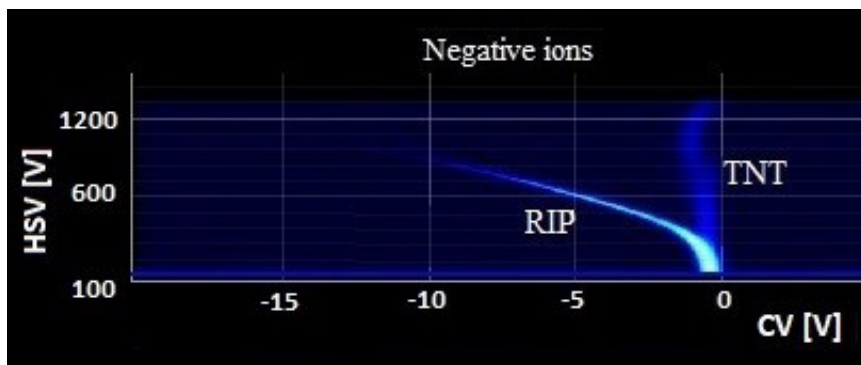


Figure 3. TNT spectrogram in negative polarization for HSV to 200 V

In the spectrogram shown in Figure 3, the TNT signal for HSV voltages up to 600 V appeared to be almost vertical, with a characteristic bending to the right and a separation into two signals above 600 V.

3.3 Effect of humidity on the detectability of TNT vapors

The effect of humidity on the detectability of TNT vapor was measured for air with a water vapor content ranging between 15% and 80%. It was found that the asymmetric voltage HSV depends on the amplitude of the TNT signal expressed in units of apparatus (UJ). Three measurements series were carried out and the average value of the TNT signal amplitude in negative polarization was calculated. The analysis of the results demonstrated the implicit correlation between TNT peak amplitude and the relative humidity of the air stream. Comparing the amplitude values for a given asymmetric voltage, it was observed that the increase in the amplitude of the TNT peak is proportional to the increase in moisture content (Figure 4). It was noted that the increase rate was higher for lower asymmetric voltages. The value of the signal amplitude within a specific water vapor content is higher for lower asymmetric voltages (e.g. for 50% humidity the average signal amplitude for a voltage of 305 V is 2022 UJ, while for a voltage of 450 V this value drops to 1534 UJ). The increase in the average signal amplitude for negative polarization in proportion to the increase in humidity or voltage may be due to the formation of the corresponding adducts.

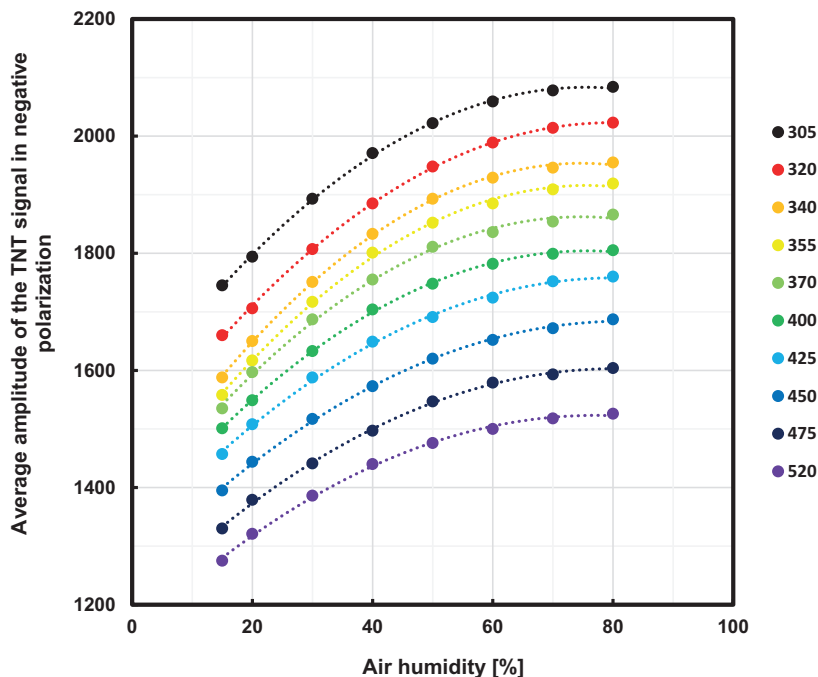


Figure 4. Average signal amplitude TNT in negative polarization vs. the humidity for different values of asymmetric voltage

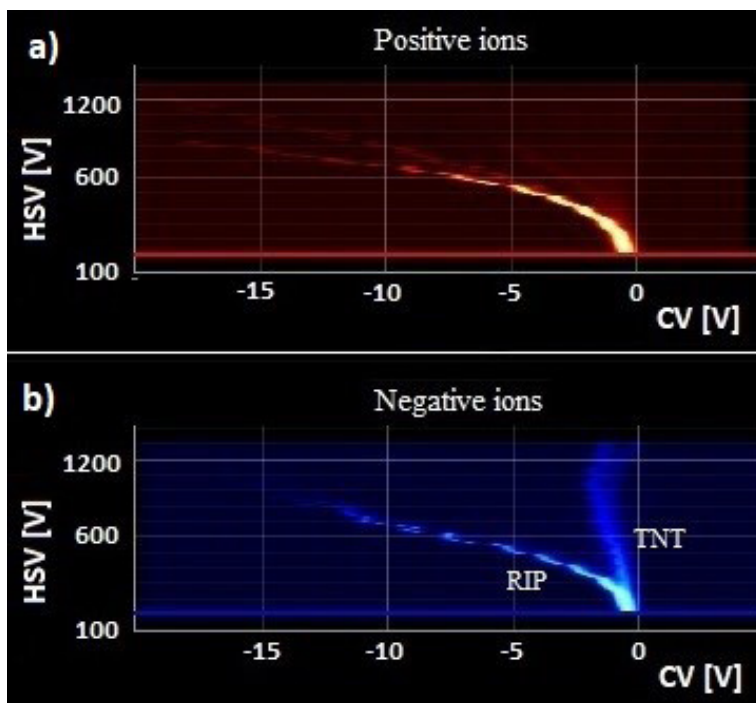


Figure 5. TNT spectrogram at 30% humidity in positive polarization (a) and in negative polarization (b)

The first peak (RIP) in negative polarization shifts to the left as the air humidity increases. This shift indicates an increasing difference in ion mobility, which is related to the formation of a greater number of adducts. Presumably, with the increased concentration of water vapor in air, the total mass of the newly formed molecules increases. Thus, a decreasing asymmetric voltage is observed at which the TNT and air peaks become separated. The increase in signal amplitude and the spectral shift in negative polarization with the increasing humidity may be connected with the increased size of molecules. Apparently, this increase is proportional to the number of molecules, however the strength of the connection of successive water molecules is weakened. The separation of water molecules from larger adducts requires less energy, *i.e.* the application of a lower asymmetric voltage. By comparing the ionograms for two different levels of air humidity, a better peak separation was observed in the case of higher air humidity (Figure 6).

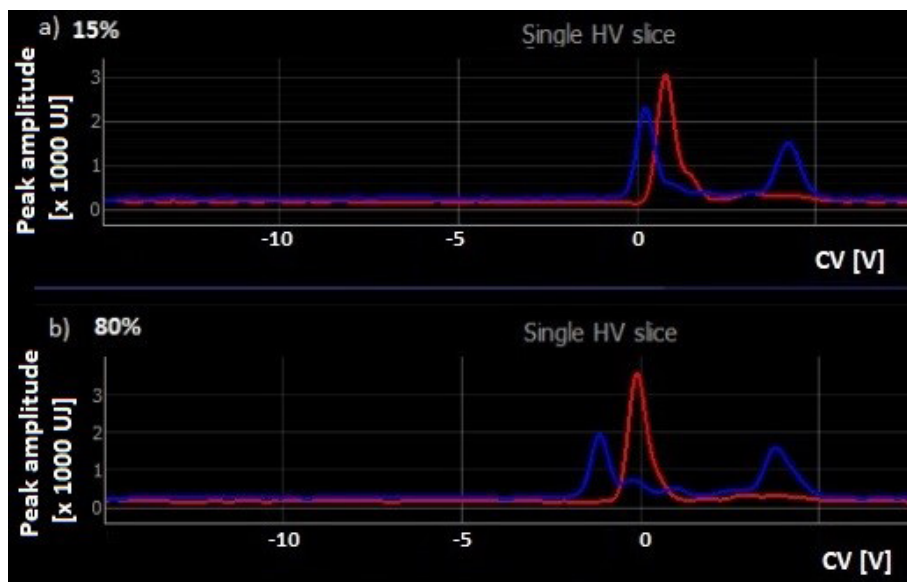


Figure 6. TNT ionogram for HSV = 515 V and humidity of 15% (a) and 80% (b)

The resulting ionograms served to determine the lowest asymmetric voltage (HSV) where the separation between TNT and air peaks could be observed (Table 1). The separation of TNT and air peaks is taking place at a lower value of asymmetric voltage and the air flow of higher humidity. For dry air (2% relative humidity) the minimum asymmetric voltage amounts to 345 V, whereas for humidity above 70% of the relative humidity the voltage becomes stable and is 270 V.

Table 1. The lowest values of asymmetric voltage for selected air humidity without a membrane and with a semi-permeable membrane for TNT

Air humidity [%]	Asymmetric tension [V]	
	without membrane	with membrane
2	345	390
15	305	–
20	300	370
30	280	360
40	275	360
50	275	360
60	275	350
70	270	350
80	270	350

3.4 The use of a semi-permeable membrane

Additionally, the study with the use of a semi-permeable membrane was performed in order to eliminate the water vapor from the air flow. For this purpose, a membrane which blocks water vapor and allows the free flow of explosive ions, was selected [31]. The trek foil (PET), covered with a separation layer, *i.e.* a thin polymer film (polydimethylsiloxane), was used as a carrier. The membrane module was placed at the DMS inlet. The measurements were carried out analogously to the TNT measurements and the analysis was carried out for the range of humidity between 2% and 80%. The resulting relationships between the asymmetric voltage, the average amplitude of TNT signals and the amount of water vapor are shown in Figure 7. When comparing the results obtained for the measurements taken in the absence of a membrane (Figure 4) and with the use of a membrane (Figure 7), a more significant decrease in average peak amplitude was observed for the measurements taken with the use of a membrane. A greater difference in the increase rate of the peak amplitude and increasing humidity was also observed for the measurements taken with the use of a membrane. For example, for an HSV value of 400 V and 50% humidity, the peak amplitude amounts to 1708 UJ with no membrane used, whereas this value is 1058 UJ when a membrane is present.

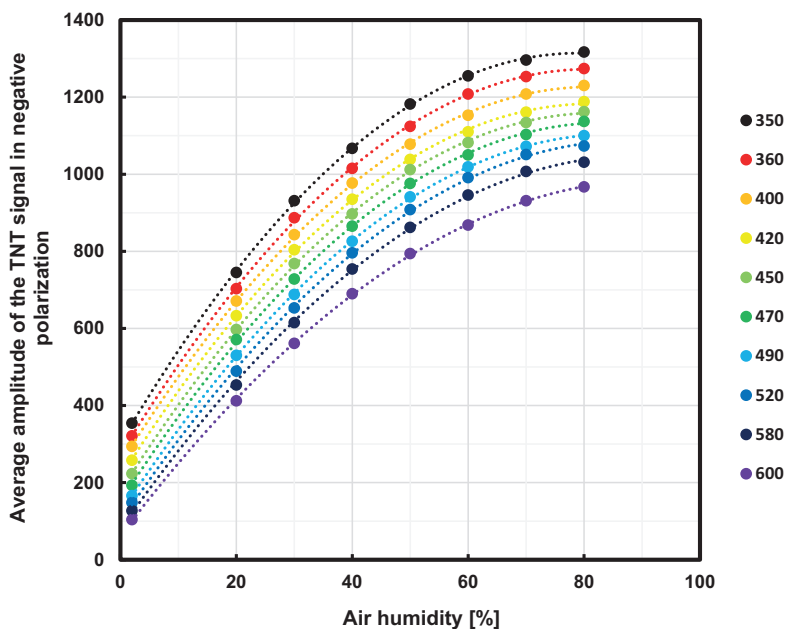


Figure 7. Average signal amplitude TNT with a membrane in negative polarization as a function of air humidity for different values of asymmetric voltage

The resulting ionograms were used to determine the lowest asymmetric voltage HSV, where a clear separation between TNT and air is taking place (Table 1). Comparing these values with the corresponding values obtained for the measurements with use of a membrane (Table 1), it was observed that the use of a membrane caused an increase in asymmetric voltage resulting in a clear separation between the air and TNT peaks.

Comparing the spectrograms for 30% and 80% relative humidity for measurements made without and with the membrane, a change in the characteristics and angle of the air peak with respect to the vertical axis was observed (Figure 8). When the membrane was used, the inclination angle of the peak became smaller. It should be noted that only a single TNT signal is visible when a membrane is used, while the separation is observed in the absence of membrane, which can be helpful in the identification. The use of a membrane may also have an effect on quantitative analysis, with a possible deterioration of the TNT detection limit.

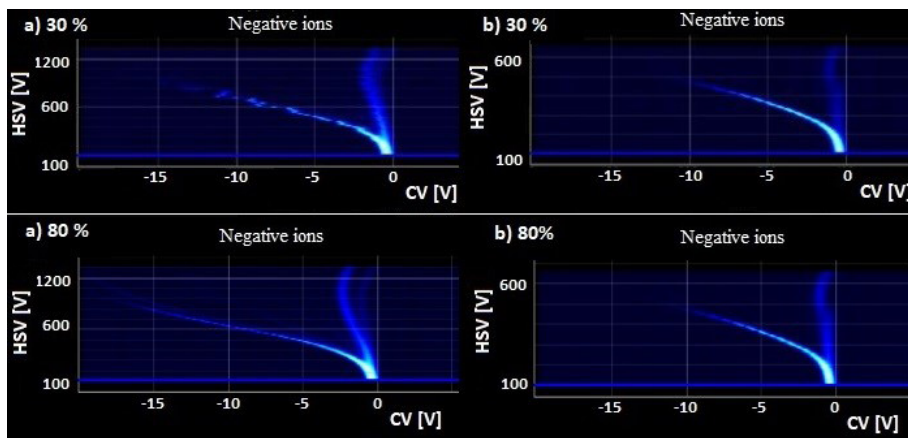


Figure 8. TNT signal in negative polarization for air humidity of 30% and 80%: without (a) and with (b) the membrane

By comparing the TNT spectra for negative and positive polarization for 50% humidity with the use of membrane for different values of asymmetric voltages (Figure 9), it was observed that in case of using the membrane, a higher asymmetric voltage is required for a signal separation. At the same time, the value of average amplitude for a specific asymmetric voltage is higher when using the membrane, but only for the values of asymmetric voltages below 900 V.

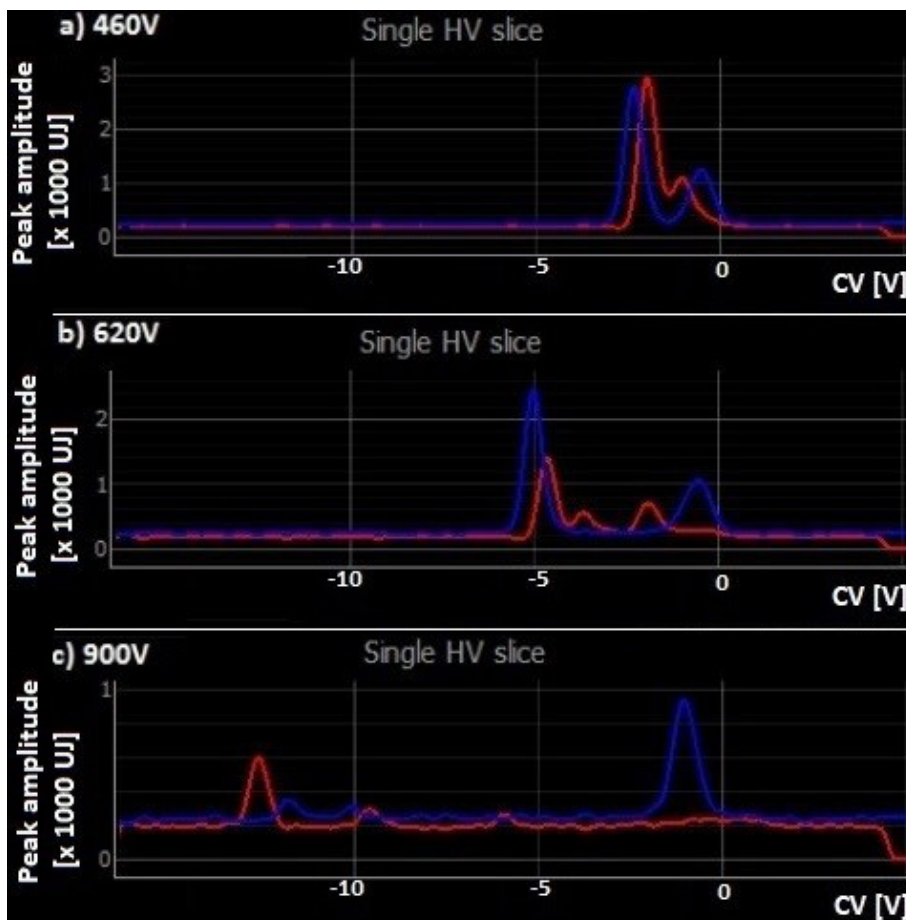


Figure 9. Spectrogram for the presence of membrane for 50% humidity and different values of asymmetric voltage

3.5 The use of dopants

The final part of the experiment included the introduction of an additive agent, *i.e.* dopant, into the air flow. The study began with a qualitative analysis of dry air containing nicotine (Figure 10). The signal from nicotine for HSV values from 100 to nearly 620 V is almost vertical, and a characteristic bending to the left can be observed above this value. In the TNT signal in the air of higher humidity, a characteristic separation into two signals could be seen.

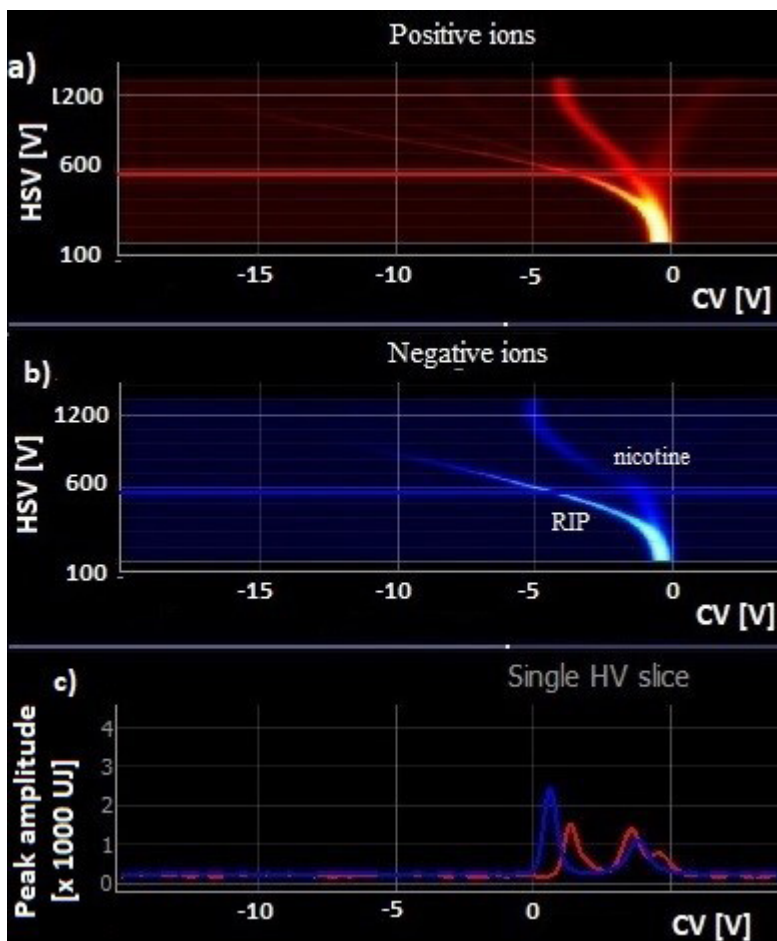


Figure 10. Spectrogram of nicotine in positive polarization (a), in negative polarization (b) and peaks in positive and negative polarization (c) for asymmetric voltage of 600 V (HSV)

By comparing TNT iongrams with and without nicotine, a positive effect of using nicotine as a dopant can be noted (Figure 11). The addition of nicotine contributed to the enhancement of TNT signal intensity and the decrease in the amplitude of the air signal at the same time. Nicotine is characterized by a high affinity for both the analyte and air. Formation of adducts with TNT ions contributed to the increased intensity of the TNT signal. The shift oscillations are higher for the measurements taken while dopants were used. The use of nicotine as a dopant with increased air humidity also has a positive impact on detection

(it contributes to increased intensity of the TNT signal and improved separation). In the case where there was no dopant, the separation of TNT into two signals could only be observed in the air with a relative humidity exceeding 30% only.

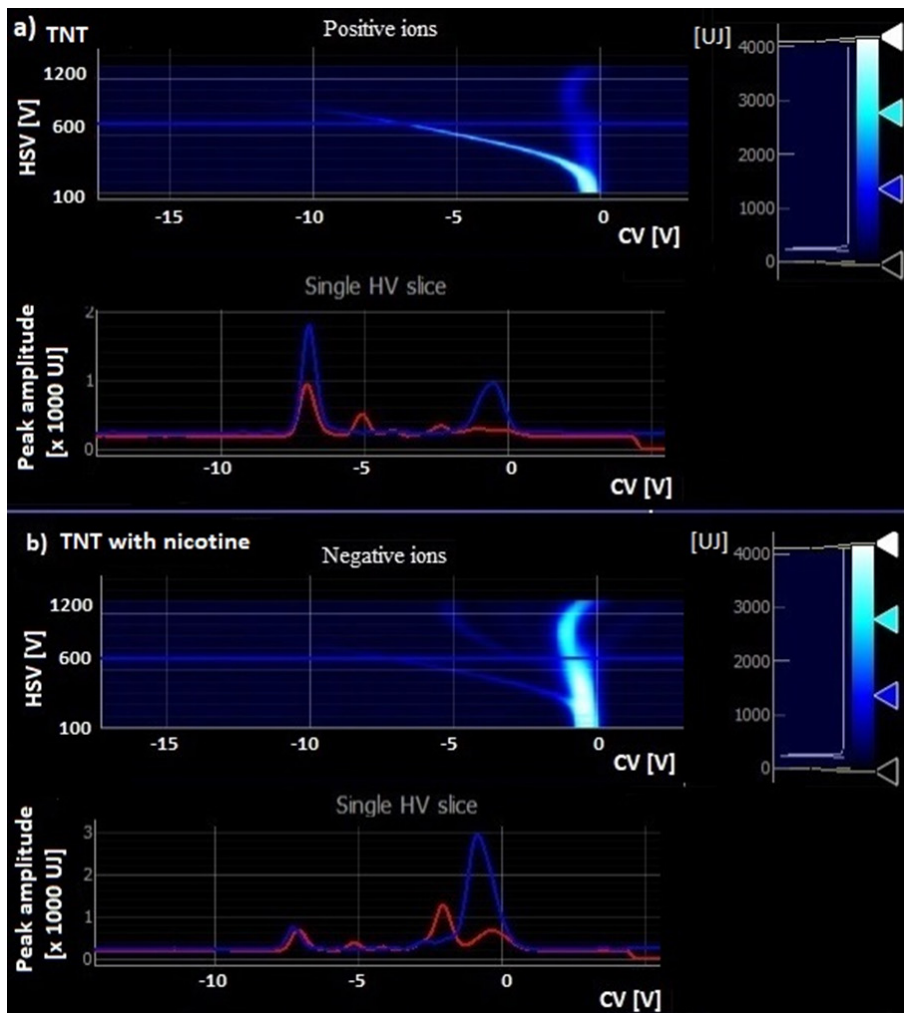


Figure 11. Spectrogram for asymmetric voltage of 700V in dry air: TNT (a) and TNT with nicotine (b)

Analogue measurements were performed for the other dopant, i.e. dichloromethane (Figure 12). When dichloromethane was added, the increase of the TNT signal intensity was not observed, however the air signal had changed.

The differences are visible in the characteristics and angle of inclination, which has a positive impact on TNT analytical result. The Cl^- ion is likely to occur as the product of halogen dopant ionization, which undergoes hydration. As a result, the air peak has shifted to the left side of the spectrogram due to a changed mobility. A clear separation between the air and TNT signals can be observed as well. A decrease in the amplitude of the air signal can be observed. Dichloromethane forms adducts with ionized air molecules, which does not entail any differences in the in amplitude of the TNT signal, although it does contribute to the improved detection sensitivity.

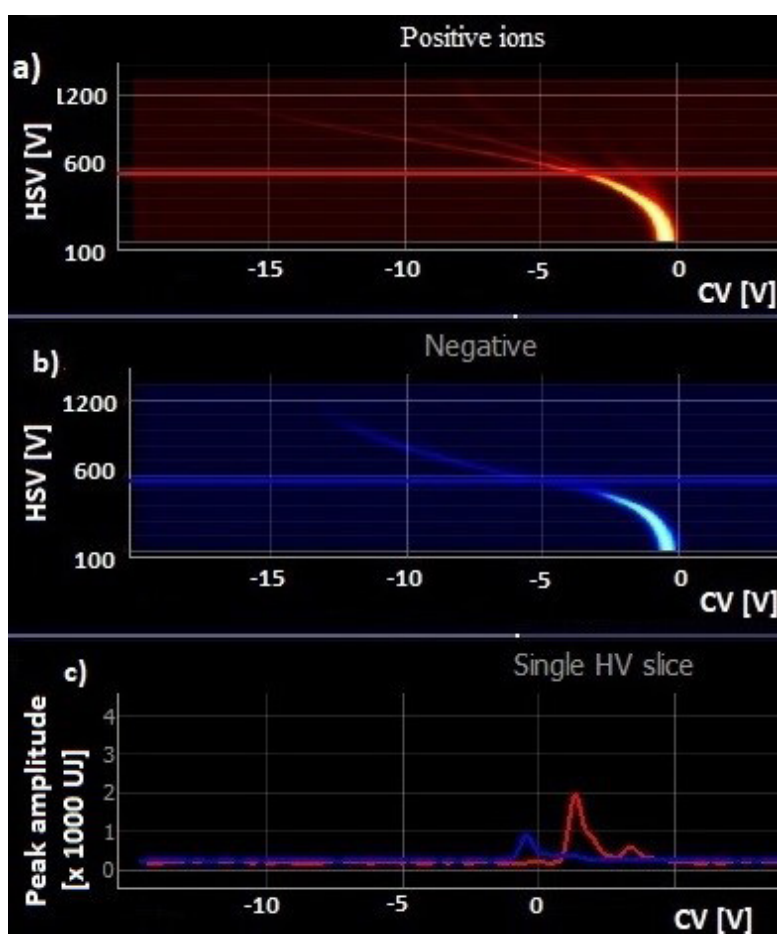


Figure 12. Spectrogram of dichloromethane in positive polarization (a), in negative polarization (b) and peaks in positive and negative polarization (c) for asymmetric voltage of 600 V (HSV)

4 Conclusions

- ◆ The conducted experiments made it possible to evaluate the effect of air humidity on the detection of TNT vapors by differential ion mobility spectrometry. The results clearly demonstrate that the air with high humidity content favors the detection of TNT vapors. The average amplitude of the TNT signal is higher in the investigated air flow characterized by a relative humidity of 80% than it was in the case of air humidity of 20%. Furthermore, the TNT signal becomes separated into two parts in the air of higher vapor content (above 30%). Under the influence of higher humidity, several different adducts with water (polyhydrate) are formed, and this causes the signal to separate. When the air humidity exceeds 30%, more water molecules attach, creating stable TNT ions (adducts). Two ions of TNT with different mobility are recorded. This phenomenon is also observed when using dopants. We add nicotine and dichloromethane to diversify the spectrum to register branches.
- ◆ Also, as humidity increases, the value of asymmetric voltage at which the TNT and air signals become separated decreases. The observed changes may be caused by the prolific formation of new adducts. The ions with changed mobility are formed and recorded in the air of high humidity.
- ◆ The possibility of using a semi-permeable membrane and dopant (nicotine and dichloromethane) was also investigated in this study. The use of a membrane can have a positive effect on the analysis in the air of low humidity by contributing to clear and readable ionograms. On the other hand, as the membrane provides an additional barrier in the ion pathway to the detector, only a single TNT signal is visible across the entire humidity range and its amplitude for a specific asymmetric voltage is smaller than in the case when a membrane is absent.
- ◆ The introduction of dichloromethane and nicotine as dopants into the air flow contributed to the change in TNT detection parameters. Dichloromethane, as a typical organic halogenated compound yielded Cl^- ions that could be hydrated. Thus, it had a positive effect on the analytical result by reducing the amplitude of the air signal. Nicotine reacted with the air and TNT and contributed to the increased amplitude of the TNT signal and decreased air amplitude at the same time. Hence, it had a favorable effect on the detection of TNT.
- ◆ In summary, it can be concluded that moisture in the air flow have the effect on the TNT detection by the DMS method. This effect may be unfavorable due to the changes in the position of the analyzed signal (signal ‘floating’),

however it should also be added that a water vapor content above 30% entails the formation of two analytical signals for TNT, thus possibly improving the identification. Appropriate semi-permeable membranes or dopants can be used to reduce the negative effect of humidity, although the possibility of impaired detection limits must also be taken into account.

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Contribution

- Monika Karpińska: conception, performing the experimental part, performing statistical analysis, other contribution to the publication
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