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DETECTION OF VOLATILE ORGANIC COMPOUNDS WITH A DIFFERENTIAL ION MOBILITY SPECTROMETRY

Key words

Spectrometry, VOCs, IMS, DMS.

Abstract

Recently growing importance of control of indoor air. The requirements for such detectors are very high: a sensitivity of several tens of ppb; the detection of a large number of substances or to indicate the total amount of volatile organic compounds (VOCs), work in high humidity ranges.

A very good solution for the determination of the VOCs is to use IMS (Ion Mobility Spectrometers) or DMS (ang. Differential Mobility Spectrometry) technology, which has a relatively low price while meeting the above requirements.

The most important difference between classical spectrometer IMS and the DMS is the electric field. For the IMS it is a constant magnetic field of low intensity – around several hundred volts per cm, meanwhile for the DMS it is at least several kilovolts per cm and is a field with a relatively high frequency from 1 up to several MHz.

Another area in which the detection of VOC is becoming increasingly important, is early diagnosis of serious diseases of civilization, eg. diabetes, lung or liver disease – the diagnosis can be made based on the analysis of exhaled air, preferably in conjunction with the study of emissions substances from the skin.

Issues related to the prevention and early detection of the above mentioned diseases are rapidly developed, eg. in the US or in the UK. Given the scale of the problem and the challenges of a potential diagnostic method, the proposed technology DMS/IMS begins to be considered as possible to apply.

Spectrometers of this type are also developed in Poland by WICHiR. Research results on the selected VOCs are showed in this presentation.

Introduction

Ion Mobility Spectrometry is a technique which has high sensitivity and a short analysis time (a few seconds), and the possibility of continuous monitoring.

Figure 1 shows the principle of a linear spectrometer (DT IMS).

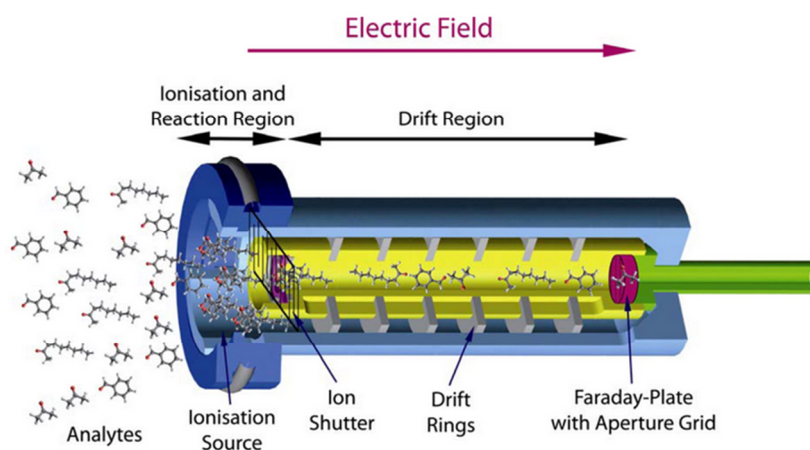


Fig. 1. Functional diagram of linear ion mobility spectrometer (DT IMS) [1]

In this case, we have a constant linear electric field in which ions are separated in the drift area. The time at which the ions cover the distance from the dispensing grid to the collecting electrode indicates the mobility of the ions, which is the basis for identification of analysed chemicals.

A variation of the ion mobility spectrometer is Differential Ion Mobility Spectrometry.

The principle of the operation of the Differential Ion Mobility Spectrometer is shown in Fig. 2.

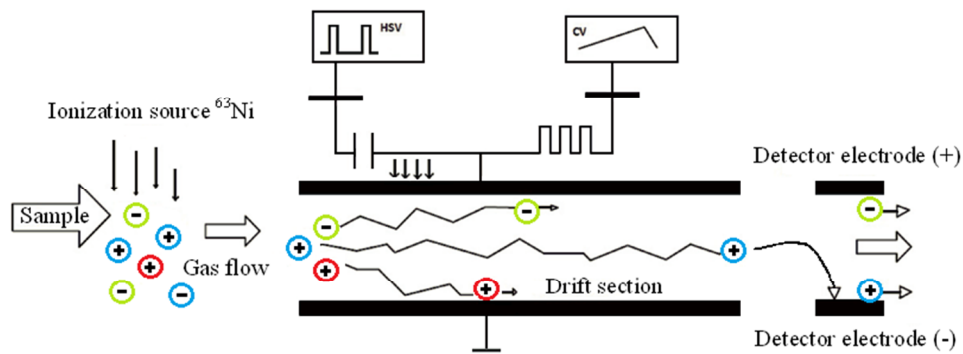


Fig. 2. Scheme of ions flowing through the DMS spectrometer [3]

The ion separation area consists of two electrodes between which flows ionized gas with a constant speed, and the ions oscillate between electrodes. An electric field of high intensity from 10 kV/cm up to 50 kV/cm is created between the electrodes as illustrated in Fig. 3.

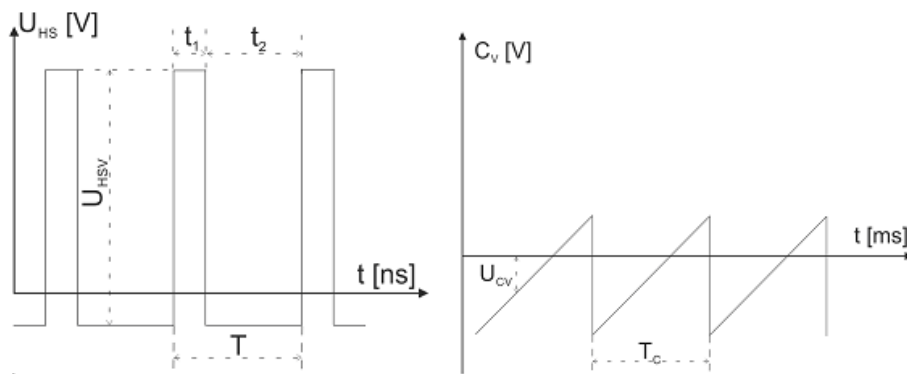


Fig. 3. Voltage diagram controlling DMS electrode

In the differential ion mobility spectrometer (DMS), the influence of an electric field is essential for the appearance of ions in the ion current detecting section. These changes are compensated using the compensation voltage (Fig. 3 on the right side). The measure of changing mobility is shown in the spectra by the compensation voltage. To approx. 12 kV/cm, the effect is negligible; above this value the process of changing mobility depending on the field strength begins as in Fig. 4. For some ions, an increase in mobility and for the others, generally for heavy ions, a reduction of the mobility can be observed.

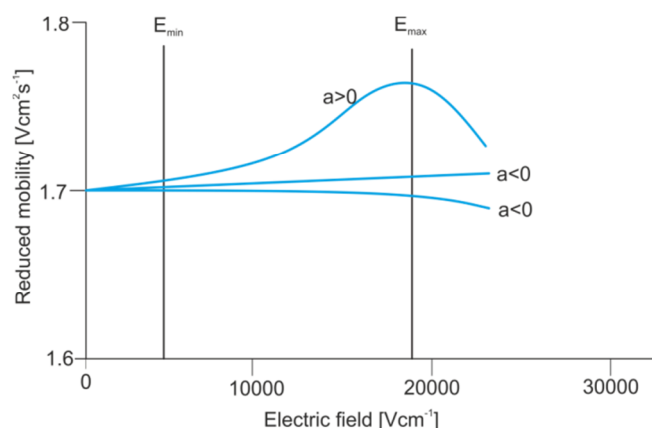


Fig. 4. An example of the dependence of changes in ion mobility due to field strength [5]

For an idealized system, an applied rectangular voltage of 30% is used to control the electrode as shown in Fig. 3, so the phase t_1 field strength E_1 is determined according to the equation [1], and for the cycle t_2 , field strength E_2 is described by the formula [2].

$$E_1 = \frac{U_{HSV} * \frac{t_2}{T} + U_{CV}}{d} \quad [1]$$

$$E_2 = \frac{U_{HSV} * \frac{t_1}{T} - U_{CV}}{d} \quad [2]$$

Only those ions whose difference in mobility for low and high electric fields that are compensated by an appropriate voltage CV can reach the collecting electrode.

When the generated voltage HSV has a constant value, and the voltage CV changes from minus CV_{max} to plus CV_{max} , then characteristic pattern of emerging peaks is formed – time of recording data for a specific HSV is marked as T_c (Fig. 3).

After changing the voltage HSV , we make a scanning in terms of CV voltage again. In general, the range of HSV voltage is from 100 V to 1200 V in steps of 5 V. The range of CV voltage is from -30 V to + 8 V.

The data is stored in an array of all of the collected HSV voltages. The result is a three-dimensional plot as in Fig. 5.

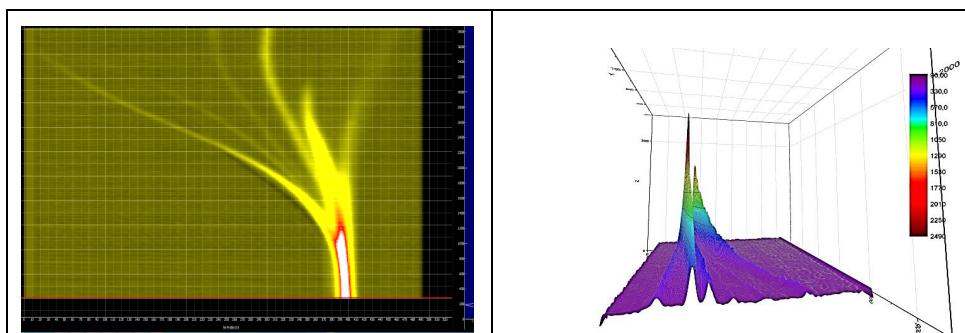


Fig. 5. Example spectrogram for detected substance in two forms of graphic presentation

For very high HSV voltage, a very high electric field strength is generated in the spectrometer, which in turn causes that the ions gained high kinetic energy, which is high enough to fragment many of them. Figure 5 shows the example of fragmentation. A significant decrease in the amplitude of one of the peaks is observed for the subsequent HSV voltage.

1. Equipment – Experimental Methods

Measurements were carried out using a DMS with a ceramic chamber as illustrated in Figure 6. The spectrometer has been made by gluing together ceramic plates. Ceramic plates of the DMS chamber consisted up to 96% Al_2O_3 . The electrodes in the drift region are two plates with a size of 5 x 25 mm spaced apart by 0.25 mm, while the collecting electrodes have a dimension of 5 x 5 mm. The nickel electrode placed below the flowing gas was covered with radioactive nickel ^{63}Ni , which allows for the ionization of the sample.

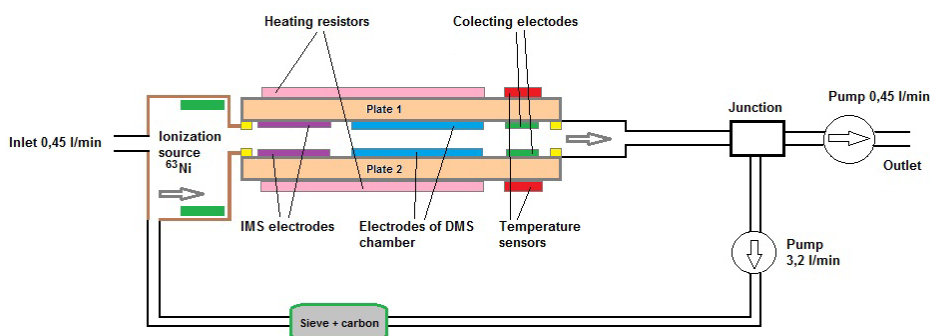


Fig. 6. Schematic of the DMS spectrometer

This kind of spectrometer was used in the PRS-1W device, which is a signalling device for chemical and radioactive contamination. In case of

coupling it with a PC computer with n-PRS software, it can be used as a gas analyser.

Figure 7 illustrates the PRS-1W signalling device, which was used in the tests presented below.



Fig. 7. Signalling device PRS-1W [6]

The parameters of the steering system for the DMS spectrometer are as follows:

- HSV generator frequency – 3 MHz
- Voltage amplitude range (peak to peak) 100–1200 V
- Maximum obtained field strength 35 kV/cm
- Maximum normalized field intensity 160 Td
- Gas flow rate 3 l/min

A special vapour generator for low concentrations of tested gas was built in the Military Institute of Chemistry and Radiometry.

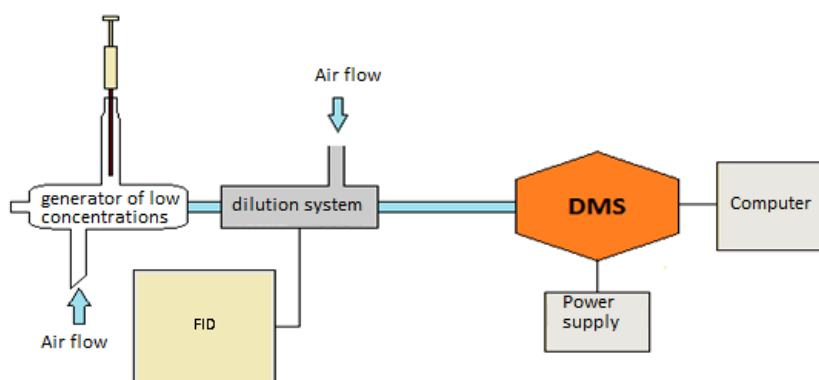


Fig. 8. Measuring station for VOCs

VOCs concentrations are controlled by the FID, and other gases are controlled by the GC analyser.

2. Detection possibilities for Differential Ion Mobility Spectrometer for selected VOC

2.1. Components of gasoline

The following components of gasoline were analysed:

- Pentane
- Hexane
- Heptane
- Decane
- Cyclohexane

Spectra from pentane to decane are individual, but we can identify these substances by comparing two curves. Please notice the curves depicting the fragmentation elements and second curve, the last red line on the right spectra, of decane.

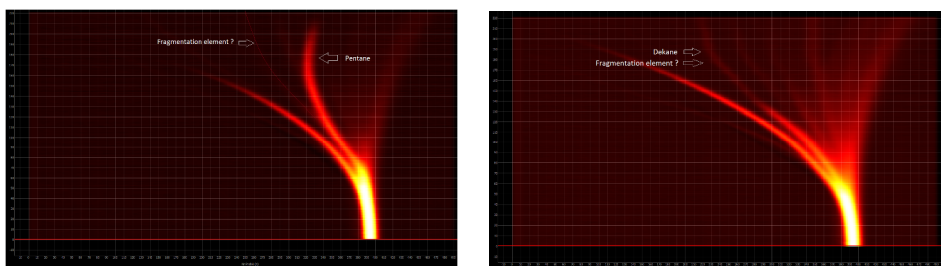


Fig. 9. Spectrograms of pentane and decane

As the size of the molecular chain grows, its decomposition energy decreases [7], thus the electric field at the observed fragmentation is lower. It is a very characteristic parameter. The data are recorded in Table 1 together with sensitivities.

Table 1. Characteristic point of detection gasoline components by DMS spectrometer

Substance	LOD [ppm]	Fragmentation point
n-Pentane	20	HSV 192 Td, CV 0.85 Td
n-Hexane	29	HSV 179 Td, CV 0.54Td
n-Heptane	29	HSV 138Td, CV 0.41Td
n-Decane	25	The disintegration at very low HSV voltage – less than 100 Td (it is below DMS resolution)

LOD is the limit of detection. In this case, the peak LOD observed by the DMS spectrometer is below 8 mV, which looks like very low orange line.

Therefore, the sensitivity of the Differential Ion Mobility Spectrometry for the detection of petrol vapour is quite high, so this method can be used for the detection of impurities.

2.2. BTX – benzene, toluene, xylene

BTXs are substances are markers in tests of indoor air.

They have carcinogenic effects; therefore, measurements are focused on their identification.

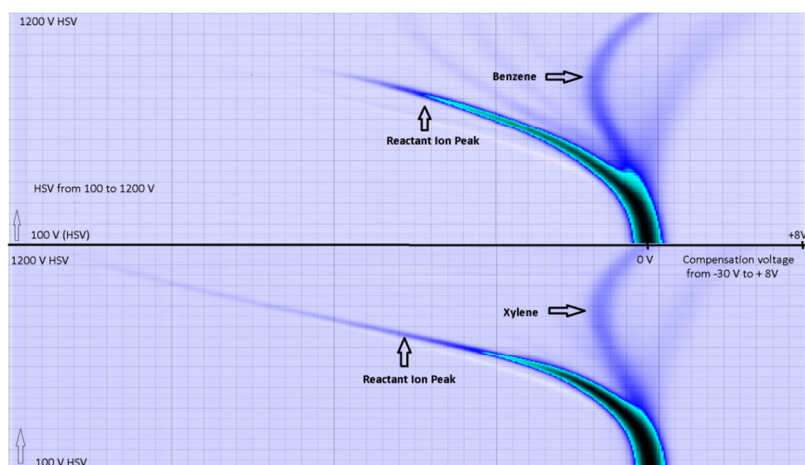


Fig. 10. Benzene and xylene spectrograms

From a comparison of these two spectra, it can be seen that the responds of the PRS-1W is very similar, since the position of peaks in the graph are almost in the same area. Small differences may be seen only for 780 V of HSV (in the middle of HSV spectrogram).

In the case of direct detection of BTX based on peak analysis, this method is not very useful, but after searching of the full matrix and the characteristics points of spectra, they can be precisely detected and their concentrations can be determined.

Sensitivity to BTX is approximately 2 ppm.

2.3. Ethyl alcohol, acetone, ethyl acetate

These are substances that may be exhaled by a human and should be detected at very low concentrations.

Table 2 presents the research results – the fragmentation points and the limit of detection (LOD).

Table 2. Characteristic point of detection some VOCs components by DMS spectrometer

Substance	LOD [ppb]	Fragmentation points
Ethyl alcohol	20 ppb	HSV 192 Td, CV 0.85 Td
Acetone	10 ppb	
Ethyl acetate	10 ppb (Monomer) 100 ppb (Dimer)	HSV 166 Td, CV 1.02Td HSV 159 Td, CV 0.13Td

Research was carried out using the PRS-1W device, which has an internal analyte dilution system; therefore, it was not tested for sensitivity of the method. Tests demonstrated only that a Differential Ion Mobility Spectrometry technique could be very helpful.

3. Conclusions

- Organic substances may be fragmented at low electric field strengths.
- The resolution of the DMS spectrometer with channel 0.25 is too low, especially at low electric field intensity.
- Fragmentation points and fragments formed after the disintegration of the ions are very helpful in identifying organic substances.
- Identification with high reliability, over 90% is only possible using advanced computational techniques, for example, PLS or k-Nearest Neighbors (*k*-nn) algorithms.
- The sensitivity of the method, the possibility of continuous operation, and low price of the detector pointed to the need to develop this method and use it for monitoring indoor atmospheres or even to breathe analysing for screening tests for diseases.

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Wykrywanie lotnych związków organicznych za pomocą różnicowej spektrometrii ruchliwości jonów

Słowa kluczowe

Spektrometria, LZO, IMS, DMS.

Streszczenie

Coraz większego znaczenia nabiera kontrola powietrza wewnątrz pomieszczeń. Wymagania na takie detektory są bardzo wysokie: czułość na poziomie kilkudziesięciu ppb; wykrywanie dużej liczby substancji lub wskazywanie sumarycznej ilości lotnych związków organicznych (LZO), praca w wysokich zakresach wilgotności.

Bardzo dobrym rozwiązaniem do oznaczania LZO jest zastosowanie technologii IMS (ang. Ion Mobility Spektrometry) i DMS (ang. Differential Mobility Spectrometry), które charakteryzują się relatywnie niską ceną spełniając jednocześnie powyższe wymagania.

Najistotniejszą różnicą pomiędzy klasycznym spektrometrem IMS-em, a DMS-em jest pole elektryczne. Dla IMS-a jest to pole stałe o niewielkim natężeniu – kilkaset volt na cm, natomiast dla DMS-a jest to co najmniej kilkanaście kilowoltów na cm, przy czym jest to pole o dość wysokiej częstotliwości od 1 do kilku MHz.

Kolejna dziedzina, w której wykrywanie LZO nabiera coraz większego znaczenia to wczesna diagnoza groźnych chorób cywilizacyjnych, np. cukrzyca, choroby płuc czy wątroby – diagnoza ta może być dokonana na podstawie analizy wydychanego powietrza najlepiej w połączeniu z badaniem emisji ze skóry.

Zagadnienia związane z zapobieganiem i wczesnym wykrywaniem ww. chorób są bardzo raptownie rozwijane np. w USA i Wielkiej Brytanii. Biorąc pod uwagę skalę problemu oraz wyzwania stawiane potencjalnej metodzie diagnostycznej, proponowana technologia DMS/IMS zaczyna być rozważana jako możliwa do zastosowania.

Spektrometry tego typu są opracowane również w Polsce w WIChiR. Wyniki badań dla przykładowych LZO zostały przedstawione w niniejszej prezentacji.