

Ph.D. Eng. Mirosław Maziejuk

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APPENDIX 2B

Summary of scientific achievements in relation to habilitation procedure

Warsaw, December 2016 r.

1. First name, lastname

Miroslaw Maziejuk

2. Held diplomas and scientific degrees

- Diploma of doctor of technical sciences in the field of electronics, specialty in metrology, Faculty of Electronics, Military University of Technology, 1995
Dissertation title: Digital probe for measurement of nuclear explosion impact with a programmable imitator of light impulse.
supervisor: Ph.D. hab. Eng. Józef Pawelec
- Diploma of master engineer in chemistry with specialty in electrical equipment of chemical armies, Faculty of Chemistry and Engineering Physics, Military Academy of Technology, 1981

3. History of employment

od 2010 – at present	Military Institute of Chemistry and Radiometry- Deputy Head of Radiometry and Camouflage Department/adjunct
2004-2008	Military University of Technology, Institute of Optoelectronics – designer / specialist electronics
2001-2006	Military Institute of Chemistry and Radiometry- adjunct
1983-1996	Military Institute of Chemistry and Radiometry- assistant

4. The main scientific achievement related to the article 16 paragraph 2, from the act of 14 march 2003 on the academic degrees and academic title, as well as the art degrees and title**4.1. Title of the scientific achievement:**

Tests on the chemical substance identification processes with the use of differential ion-mobility spectrometry and application of ion-mobility spectrometry in detection of chemical contamination

4.2. List of selected publications related to the scientific achievement:

- [H1] M. Maziejuk, W. Harmata
The ionmobility spectrometer as a component of systems used to detect high-toxicity compounds

- Przemysł Chemiczny, 2006, 85, 11, 1495-1499
IF = 0,429
- [H2] M. Ceremuga, **M. Maziejuk**, M. Szyposzyńska, Sz. Szmidt
Determination of identification parameter of soman by differential ion mobility spectrometer
Przemysł Chemiczny, 2013, 92, 1, 55-59
IF = 0,367
- [H3] M. Ceremuga, **M. Maziejuk**, M. Szyposzyńska, T. Sikora
Determination of the effective temperature of soman by differential mobility spectrometer
Przemysł Chemiczny, 2013, 92, 1, 96-100
IF = 0,367
- [H4] **M. Maziejuk**, M. Ceremuga, M. Szyposzyńska, T. Sikora
Effect of temperature on separation of sarin (GB) ions in differential mobility spectrometry
Przemysł Chemiczny 2013, 92, 6, 946-949
IF = 0,367
- [H5] A. Zalewska, **M. Maziejuk**, M. Ceremuga, A. Buczkowska, T. Sikora
Use of semi-permeable membranes in gaseous analyzers with differential ion mobility spectrometric detection
Przemysł Chemiczny, 2014, 93, 4, 464-467
IF = 0,399
- [H6] **M. Maziejuk**, M. Ceremuga, M. Szyposzyńska, T. Sikora, A. Zalewska
Identification of organophosphate nerve agents by the DMS detector
Sensors and Actuators B, 2015, 213, 368-374
IF = 4,758
- [H7] **M. Maziejuk**, J. Puton, M. Szyposzyńska, Z. Witkiewicz
Fragmentation of molecular ions in differential mobility spectrometry as a method for identification of chemical warfare agents
Talanta, 2015, 144, 1201-1206
IF = 4,035
- [H8] **M. Maziejuk**, A. Szczurek, M. Maciejewska, T. Pietrucha, M. Szyposzyńska
Determination of benzene, toluene and xylene concentration in humid air using differential ion mobility spectrometry and partial least square regression
Talanta, 2016, 152, 137-146
IF = 4,035/2015
- [H9] Z. Witkiewicz, U. Perycz, **M. Maziejuk**, J. Puton
Coupling gas chromatography with ion mobility spectrometry
LCGC Europe, 2016, 29, 6, 294-303
IF = 0,481/2015
- [H10] A. Szczurek, **M. Maziejuk**, M. Maciejewska, T. Pietrucha, T. Sikora

BTX compounds recognition in humid air using differential ion mobility spectrometry combined with a classifier
Sensors and Actuators B, 2017, 240, 1237-1244

IF = 4,758/2015

Series of publication related to the main scientific achievements consists of 10 publications (total impact factor **19,996**)

4.3. Patents

- [1] Field Asymmetric Ion Mobility Spectrometry (FAIMS) type ion mobility spectrometer chamber used for detection of chemical contamination has edge contacts made of silver paste, provided on edge surfaces of top and bottom ceramic plates
Patent Number: WO2012158052-A1 PL394898-A1 FI201305985-A GB2504884-A DE112012002128-T5 CN103534589-A EP2710362-A1 PL218395-B1 US2016069836-A1
- [2] Ion mobility spectrometer chamber, has ion current amplifier integrated with ion collecting electrode, and ceramic plate placed in casing that is made of plastic, where casing is fixed with ceramic rings through grooved slats.
Patent Number: PL396616-A1 PL218460-B1
- [3] Spectrometer chamber i.e. ion-mobility spectrometry chamber, for gas analysis, has control electrodes and collecting electrodes that are arranged at differential mobility spectrometer zone
Patent Number: WO2013122485-A1 PL398138-A1 WO2013122485-A8
- [4] Air intake of mobile pollution indicator, has flow resistance detector connected to air inlet and outlet to and from valve, while detector, sensor and valve are connected to microprocessor control system
Patent Number: WO2014189394-A1 PL403995-A1
- [5] Device for recognizing or detecting e.g. toxic industrial substances in motor vehicle, has chamber supported on inlet and outlet supports having gas feeding hole and gas discharge hole to/from chamber in flat top surfaces of chamber
Patent Number: WO2014098630-A1 PL402111-A1
- [6] Dehumidifying and purifying system for air serving in contamination indicators, has chamber that is connected in parallel to inlet and outlet of gas, filter and orifice are located between outlet and inlet to chamber
Patent Number: WO2014200370-A1 PL404290-A1

[7] Instrument for determination of contamination, has exchanger with semi-permeable membrane which is arranged between two Differential Mobility Spectrometry (DMS) chambers

Patent Number: WO2015112033-A1 PL406896-A1

4.4. Presentation of the scientific aim of the aforementioned theses and achieved results with presentation of their potential application

Introduction

Contamination with dangerous chemical substance is a serious threat to the natural environment as well as human health and life. The chemical contamination signalling devices which detect chemical warfare agents (CWAs) [1] as well as industrial toxic industrial chemicals (TICs) are used to warn against potential threats [2]. Early warning against contamination is especially important in the modern world. In case of war or act of terror, quick detection of CWA and TIC with high sensitivity and reliability is very important. Recently, CWA was used in conflict in Syria and, earlier, in Iraq. An effective method which allows for continuous air monitoring is ion mobility spectrometry (IMS) [3]. It is actually a perfect method to be applied in contamination signalling devices due to the possibility to detect and identify the majority of organic substances deemed to be highly toxic.

The second aspect is monitoring air in terms of detection of volatile organic compounds (VOCs) [4,5]. More and more often, the need of continuous monitoring work conditions or air quality in important public facilities is emphasised. Testing internal air quality is a significant challenge due to high variability of organic compounds present in internal air. The differentiated level of contaminations at which these compounds occur also constitutes an obstacle in their marking. In this case, the application of signalling devices using the ion mobility spectrometry is highly useful due to:

- very short time of reaction to occurrence of a chemical substance - even within single seconds;
- high sensitivity to CWA, as well as many VOCs;
- relatively low price.

Introduction to IMS and DMS (differential ion mobility spectrometry) spectrometry technology

IMS uses the differences in mobility of ionised particles in carrier gas under the influence of electric field [6-8]. A classical IMS spectrometer is one which has weak linear electric field with value from 100 to 300 V/cm in which ions move in gas under atmospheric pressure. The scheme of structure of IMS detector is presented in Fig. 1.

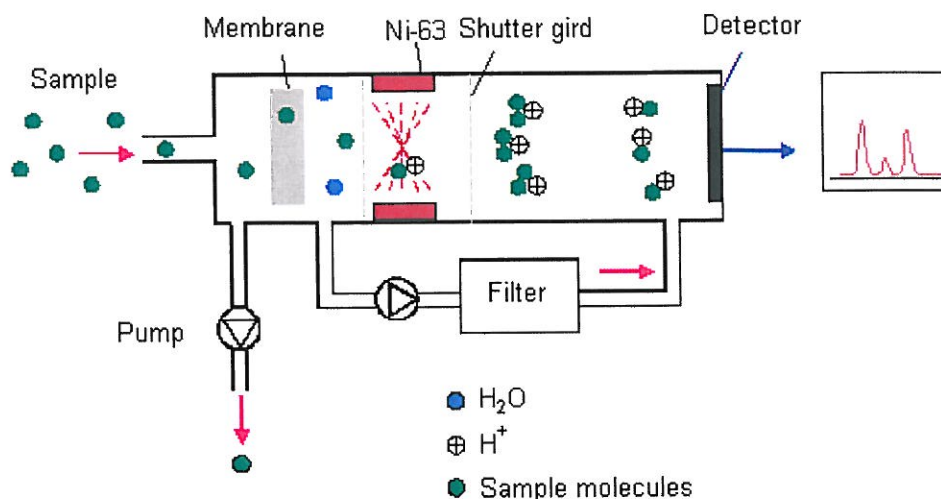


Fig. 1. The operating principle for IMS.

The IMS spectrometer chamber is divided into two areas: ionisation area which stretches from the screen grid (at a constant high potential) - to the dosing grid as well as the area of ion separation called a drift area, from the dosing grid to the collecting electrode [9] (at a 0V potential).

The dosing grid functions as a regulator of ion inflow to the drift part. Ions are let in during the period from 30 to 300 μ s and, then, ions are separated according to their variable mobility in the drift area. They reach the collecting electrode in different times, these are generally single milliseconds up to a few dozen of milliseconds (for ions with very low mobility and/or for low electric field).

Metal rings are located in the drift area which, thus, shape the field, decreasing in a linear way towards the collecting electrode. A grid, neutralising the influence of ion occurrence on the signal of the collecting electrode, is located in front of the collecting electrode.

The field is shaped in such a manner so that ions move through linear tracks from the area of dosing grid to the collecting electrode.

The principle of differential operation of the ion mobility spectrometer

In case of weak electric fields, ion mobility is practically independent of the electric field intensity. Increase in the electric field leads to significant change in ion mobility and, therefore, mobility changes in the electric field function. The nature of these changes depends on the type of ions, their mass, shape, temperature of carrier gas as well as ion energy. An example method of mobility variations is presented in Fig. 2

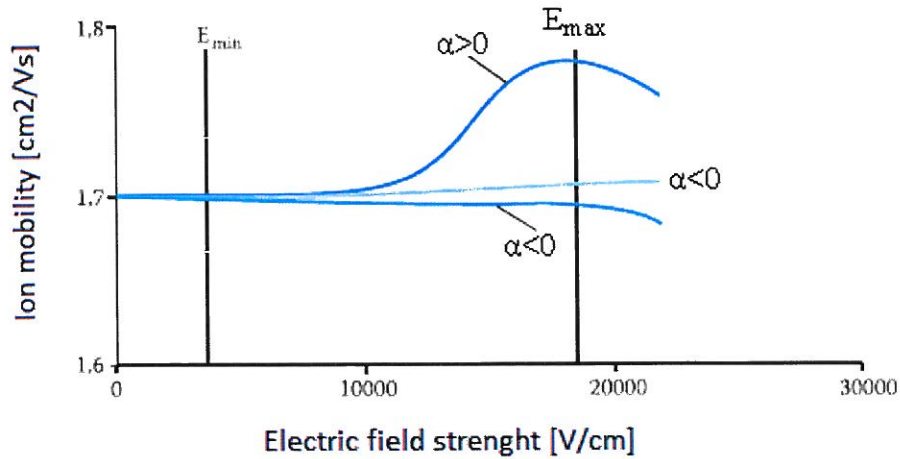


Fig. 2. Mobility dependence on electric field for three different ion species [10].

The dependence of ion mobility on the electric field has the form of:

$$K = K_0[1 + \alpha(E/N)] \tag{1}$$

Where: K_0 - reduced ion mobility for a weak electric field, $\alpha(E/N)$ - dependence of change in reduced mobility in the function of electric field intensity and molecular density, K - ion mobility.

DMS detector is made from parallel plates with electrodes layered on each plate, to which high voltage is applied, generating electric field with high intensity and high frequency [11]. Ion segregation takes place in the collecting electrode under the influence of the electric field generated in the detector volume.

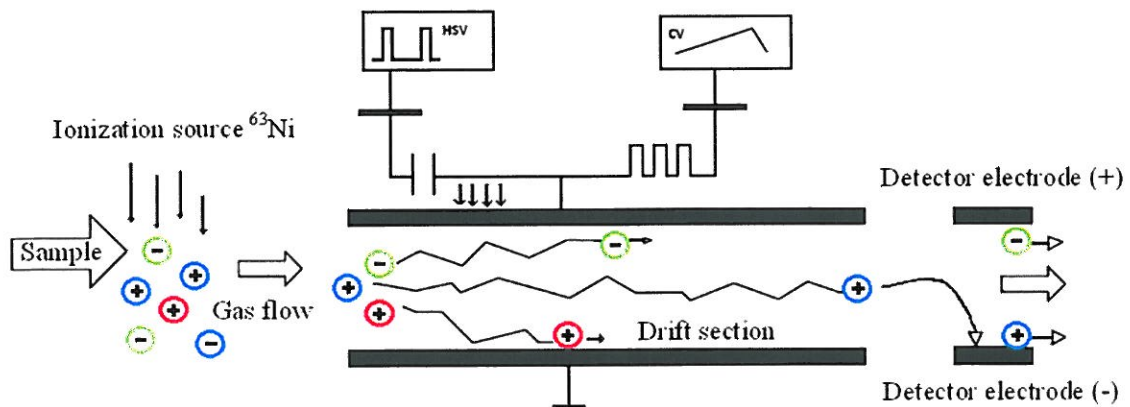


Fig. 3. Ion flow through differential mobility spectrometer [H8].

The observed separation of ions present in flowing gas is caused by different mobility in fields with lower and higher intensity. Fig. 3 presents an example ion flow through detector chamber volume. The capture of ions the mobility of which does not meet the condition of stable flow through the detector chamber takes place under the influence of alternate electric field applied to the electrodes. Therefore, this is a specific type of an ion filter. Therefore, depending on the changes in compensatory voltage, the spectrogram as in the figure above is received.

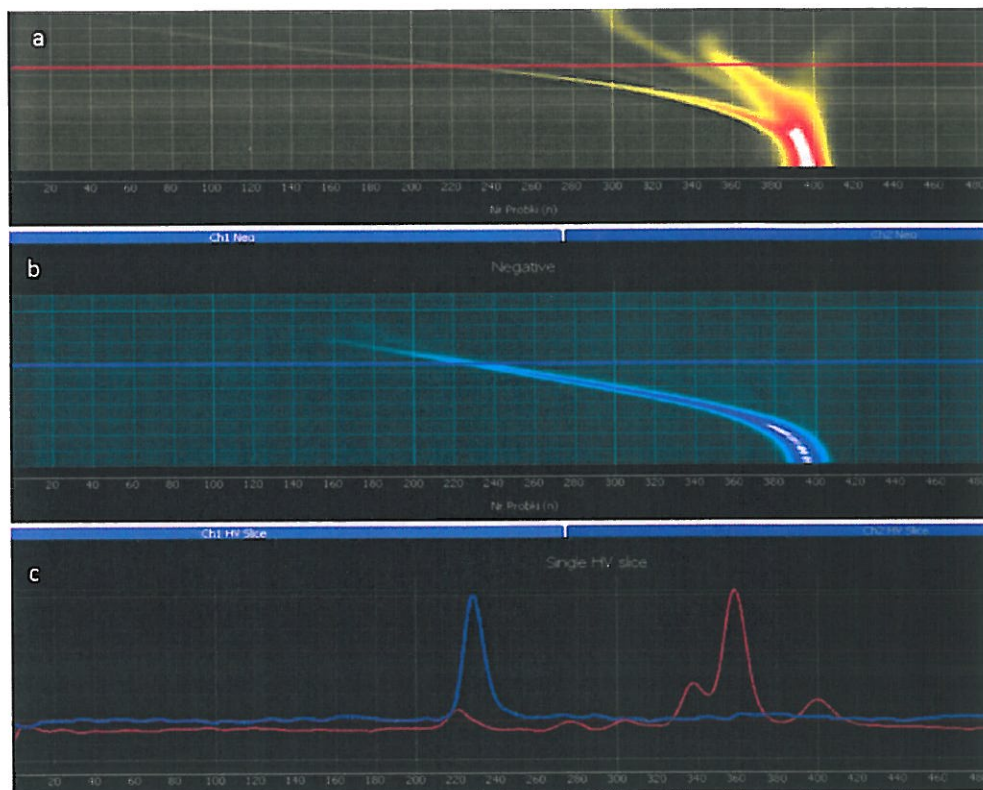


Fig. 4. Dispersion plots recorded for (a) positive ions of 2,3-dimethylo-2-butanol, (b) negative ions of 2,3-dimethylo-2-butanol and (c) for the particular HSV voltage

Scientific aim

The aim of my works was the development of technology of ion mobility spectrometry, particularly, differential ion mobility spectrometry as well as development of new methods of identification of chemical contamination for this technology.

Constant air monitoring at detection of toxic substances with a very low level of concentration is usually performed with IMS or DMS spectrometers. This technology can very often detect substances dangerous for human, even below the threshold of their harmful influence. The detection threshold for many substances is constituted by singular ppb or even tenths of ppb.

Such low concentrations require skilful preparation of all components of the analyser, starting from the spectrometer, through the gas system, carrier gas preparation system.

The second aspect of this analysis method of spectrometer signal as well as tests on behaviour of occurring peaks for different influences, e.g. pressure, temperature, moisture or high concentrations of interfering substance.

Articles and patents presented in a monothematic publication cycle: **“Tests on the chemical substance identification processes with the use of differential ion-mobility spectrometry and application of ion-mobility spectrometry in detection of chemical contamination”** included the following concepts:

1. Application of a classical ion mobility spectrometer for detection of dangerous substances - articles [H1], [H9], patent [2]
2. Tests on differential ion mobility spectrometer in terms of detection abilities - articles [H2], [H3], [H4], [H5], [H6], [H7], patents [1], [3], [4], [5], [6], [7]
3. New concepts of gas substance identification for DMS spectrometry - articles [H8], [H10]

Application of a classical ion mobility spectrometer for detection of dangerous substances

The technology of ion mobility spectrometry was developed in years 1890-1910, but the practical solutions were introduced to analytical methods not sooner than in the 60's of the 20th century. Detectors which use the method of ion mobility spectrometry [H1] are most often used to detect highly toxic chemical substances. The structure of IMS chamber allows for its application in signalling devices of chemical contamination. ALERT a chemical contamination signalling device with IMS chamber as a detector was developed and performed in the Military Institute of Chemistry and Radiometry (the author is the main constructor) (Fig. 5).



Fig. 5. Chemical warfare detector ALERT-1M [H1].

Figures 6 and 7 show examples of spectrograms registered with ALERT signalling device on the moment of contamination and for a test substance of organophosphorus type. Identification of a detected substance is performed by spectre comparison. In case of lack of the analysed substance in the spectrogram, only reactant ion peak (RIP) is visible (Fig. 6). Upon introduction of the analysed substance into the system, the second test substance peak appeared in the spectre (Fig. 7).

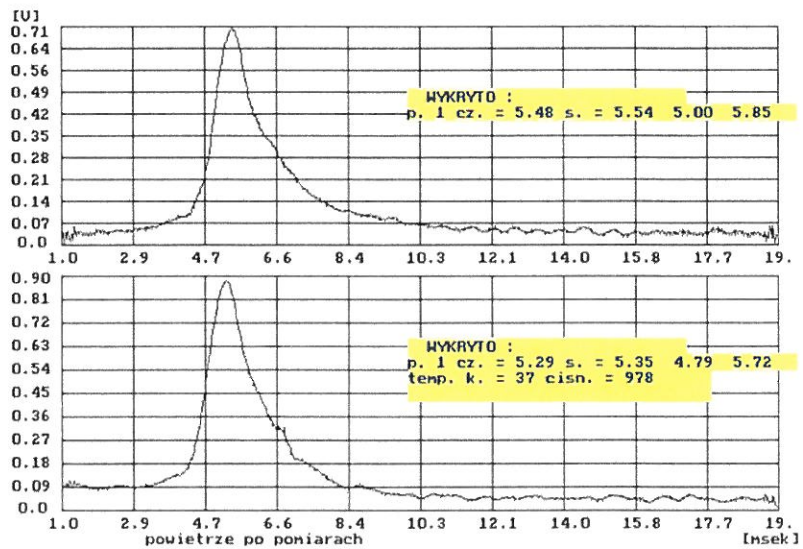


Fig. 6. An illustrative spectrogram recorded by an ALERT chemical warfare detector at the moment of no contamination (RIP signal only) [H1].

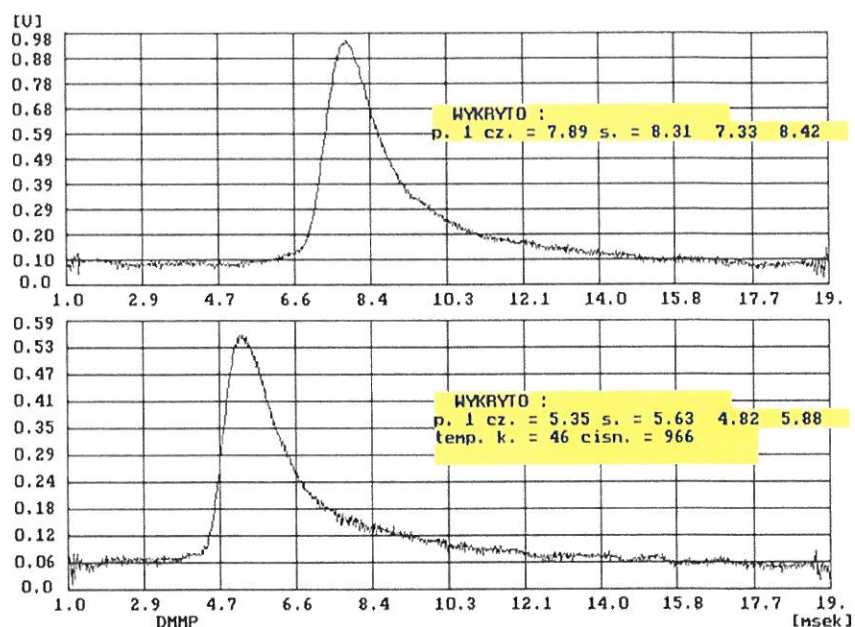


Fig. 7. An illustrative spectrogram recorded by an ALERT chemical warfare detector at the moment of feeding an organophosphorus test contaminant to the signaler [H1].

Many global companies develop the technology of ion spectrometry with very good results. Works aim to develop spectrometers with very high resolution as well as mobile devices in hand-pocket casings in the size of pocket calculators. Fig. 8 shows IMS spectrometers illustrating advances in their miniaturisation.

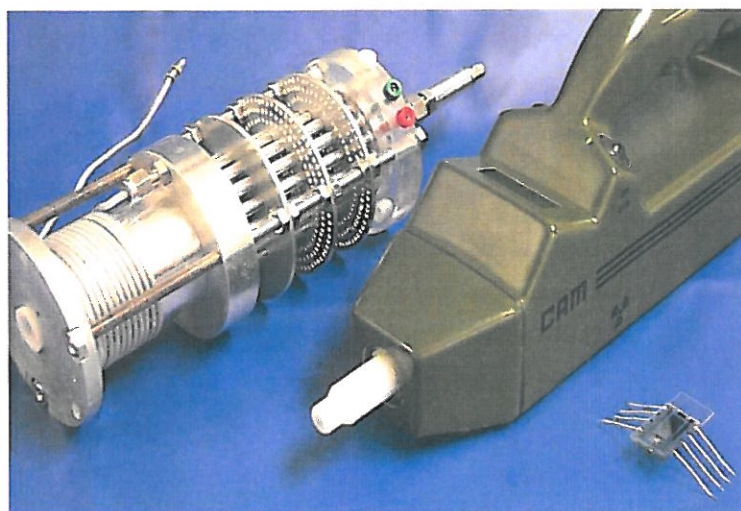


Fig. 8. Three generations of spectrometers of IMS [12] [H1].

The first device on the left is an example of first spectrometer structures. In the middle there is a commercial version of CAM gas signalling device for detection of highly toxic chemical substances. On the right, there is the newest generation of spectrometers type RF-IMS

(radio frequency ion mobility spectrometry) the rule of operation of which is similar to an ion trap.

Developmental tendencies show that the change of methods of highly toxic chemical substance detection is to be expected in the near future. Ion mobility spectrometers will still play a dominant role. Developmental works will aim to increase selectivity, decrease the number of false alarms and construct a new generation of devices the rule of operation will be similar to an ion trap.

At the start of the 70's of the 20th century, the concept of application of ion mobility spectrometer as a detector for a gas chromatograph (GC) was developed. The collecting electrode was added to the electrometer and the result was registered on a paper band. I presented theoretical considerations on the topic of GC-IMS in the article [H9]. For the first time, the combination of a gas chromatograph and ion mobility spectrometer was described by Karasek and Keller [13]. Capillary columns (CCs) and multicapillary columns (MCCs) are used in In GC-IMS systems. The capillary columns are similar in size to columns used in GC (length of ca. a few dozen metres), unlike in case of short multicapillary columns (length of ca. a few dozen centimetres). Figure 9 presents a gas chromatograph and IMS detector connection diagram. GC-IMS systems are commercially available. A miniaturization of this system is also possible [14,15].

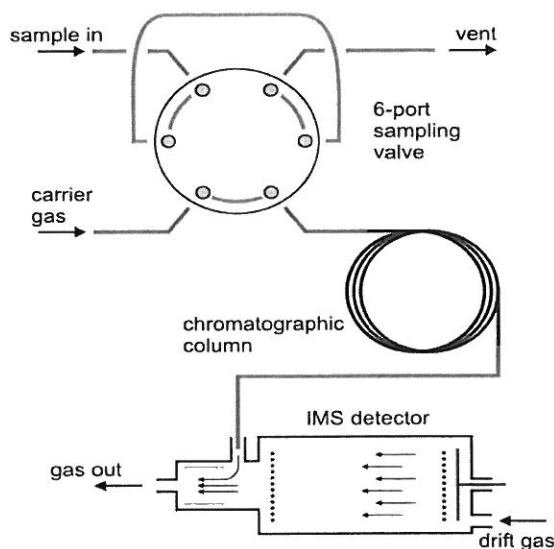


Fig. 9. Connection of IMS to GC columns [H9].

According to the definition, ion mobility spectrometers are devices which perform a very fast analysis. Therefore, an advantage of combination of GC-IMS is "fast" gas chromatography [16,17,18]. The analysis performed with a GS-IMS method is usually complete in 3-5 minutes. As a result of GC-IMS analysis, we obtain a three-dimension spectre which is a dependence of signal intensity on retention time and drift time. An example of such a spectrum is presented in Figure 10.

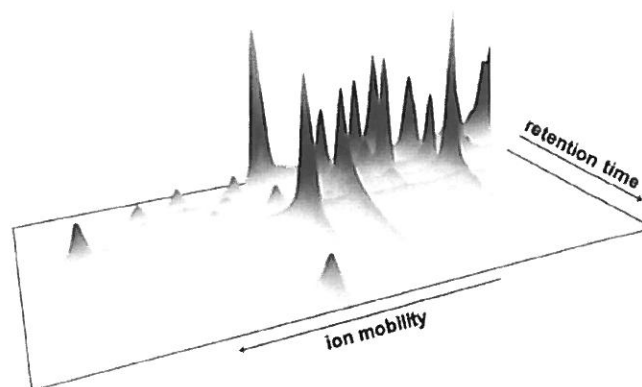


Fig. 10. An example of three-dimensional measurement results obtained with GC-IMS system 19], [H9].

GC-IMS system, due to multiple advantages, is applied to, e.g. detect explosives [20], chemical warfare agents [21], volatile organic compounds [22] as well as in direct analysis of exhaled air.

The next articles concern the second variant of method of ion mobility spectrometry, that is differential ion mobility spectrometry.

Tests on differential ion mobility spectrometer in terms of detection abilities

The application of modified ion mobility spectrometry methods in analysers and signalling devices requires their testing, verification of their correct operation, detective possibilities as well as susceptibility to false alarms.

Tests were divided into the following divisions:

- testing the influence of temperature and moisture on peak position;
- testing ion fragmentation as a method of chemical substance identification

Testing the influence of temperature and moisture on peak position

Substance identification is performed on the basis of reduced mobility (mobility referred to standard conditions, temperature, pressure, electric field).

A standard data calculation formula is relationship (2). It is a relationship which reliably reflects the real measures in case when moisture in IMS chamber is constant.

$$K_o = K \cdot \left(\frac{273}{T} \right) \cdot \left(\frac{P}{760} \right) \quad (2)$$

The influence of moisture is generally eliminated by introduction of a membrane [H5]. When moisture increases, ion mobility decreases as a result of increase in the number of added water particles $M^+(H_2O)_n$ (value n increases).

In case of differential ion mobility spectrometry, ion behaviour is similar, i.e. the number of water particles increases along with moisture increase. Similarly to temperature - increase in temperature causes decrease in the number of neutral particles (e.g. water) as well as increase in the length of free path of an ion. Increase in pressure reduces the free path of an ion.

Therefore, in case of expression of the electric field as E/N , where N is a number of gas particles, i.e. so-called reduced field, the influence of pressure on the peak position is neutralised, no deviations are observed.

The influence of temperature is not compensated due to the measurement method in the differential spectrometry. The deviation of ion mobility for the high field in relation to the low field is measured, therefore, the change in mobility depends on the ion temperature and gas drift temperature. The number of neutral particles associated to the ion in a high and low field phase is different. When we reach very high field values, the number of associated particles equals 0. It results in "bending" mobility characteristics. The mobility ceases to grow and starts to decrease due to the increase in effective ion temperature and, according to the theoretical relationship published in most textbook for ion mobility spectrometry, mobility decreases.

$$K = \frac{3q}{16N} \cdot \left(\frac{2\pi}{\mu k T_{ef}} \right)^{1/2} \frac{1 + \alpha}{\Omega} \quad (3)$$

CW identification with the use of DMS on an example of soman is presented in my article [H2]. Soman (GD) identification was performed on the basis of approximation with the use of polynomials of third degree. Table 1 includes the functions of particular soman peaks.

Table 1. Functions of particular characteristic soman peaks at different soman concentration in the air [H2].

FUNCTION	15 µg/m ³
RIP	$f(x) = -0,1382x^3 - 4,5984 x^2 - 77,2276 x + 314,3172$
MONOMER	$f(x) = 178,1590 x^3 - 74,3799 x^2 - 519,7658 x + 570,8439$
DIMER	$f(x) = 50,5508 x^3 - 369,5784 x^2 + 1078,1415 x - 326,5221$
42 µg/m ³	
RIP	$f(x) = -0,1284x^3 - 4,3469 x^2 - 75,4096 x + 317,1723$
MONOMER	$f(x) = 213,8037x^3 - 46,7172 x^2 - 522,9494 x + 570,9054$
DIMER	$f(x) = 29,9050x^3 - 2934,2123 x^2 + 1062,1092 x - 462,3172$
179 µg/m ³	
RIP	$f(x) = -0,1260x^3 - 4,3251 x^2 - 75,3104 x + 316,9378$
MONOMER	$f(x) = 261,2156 x^3 - 52,1516 x^2 - 560,5966 x - 568,6945$
DIMER	$f(x) = 42,0663 x^3 - 353,8349 x^2 + 1155,6702 x - 522,0765$
316 µg/m ³	
DIMER	$f(x) = 112,9428 x^3 - 821,8646 x^2 + 2148,7777 x - 1198,2012$

If peaks coming from a monomer or dimer are connected to all HSV voltages, then, we receive a curve which is a reflection of a tested substance (Fig. 11). The analytical curves are recorded in the memory in the scaling process. Identification of detected substances means determination of a newly created curve with a curve recorded in the memory. This verification is performed with the use of mean square deviation.

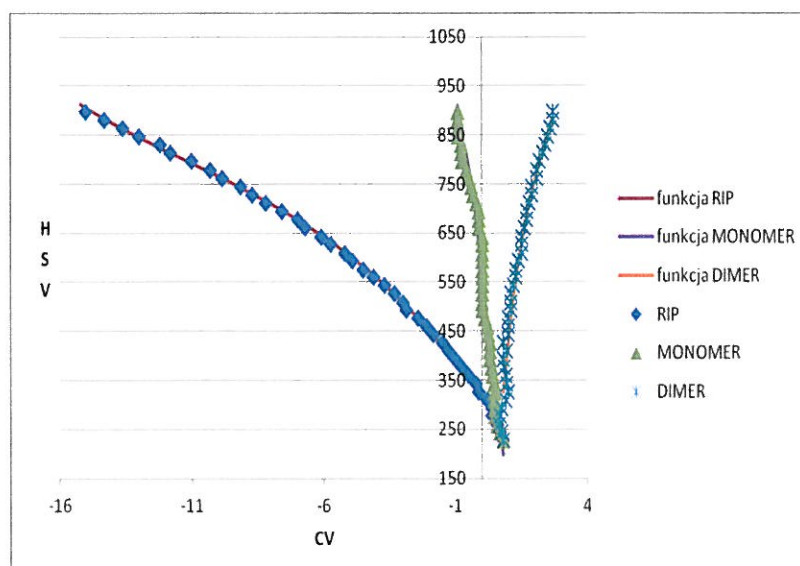


Fig. 11. Graph of the functions of soman 15 µg/m³ with experimental points [H2].

Polynomial functions allow for approximation of experimental curves (obtained from real measurements) which makes it possible to unequivocally determine the position of characteristic peaks depending on the voltage of an electric field generator in the spectrometer. It was also noticed that approximating functions are in lesser (DIMER) or bigger (RIP) extent convergent with twin functions obtained in the same measurement conditions, but for different concentration of a substance. This fact can be used to develop so-called CWA "finger prints".

Such identification is highly precise, but, unfortunately, requires a very large number of measurements for different HSV voltages.

Many substances, e.g. sulphur mustard (HD), lewisite or methyl salicylate (MS) are detectable when carrier gas moisture along with a tested sample does not exceed 5%. In article [H5], I presented how to select barrier material for a PRS-1W signalling device and the influence of moisture on possibilities to detect steams and gases. Three types of polymer films with different concentration, which are an active membrane layer, were tested: polydimethylsiloxane (PDMS), polyetherimide (PEBAX) and ethylene polyglycol (PEOX). Table 2 and 3 presents the results of tests conducted for soman and sulphur mustard. The best analyte permeability was presented by membranes with PDMS and PEBAX polymer film of 5% concentration.

Table 2. Mustard The results of sulphur mustard detection in the system with a semipermeable membrane [H5].

Polymer film (membrane)	Sulphur mustard concentration, $\mu\text{g}/\text{m}^3$	Sulphur mustard peak amplitude
—	250	600
	800	1200
PDMS 1%	237	364
	792	846
PDMS 5%	285	284
	800	650
PEOX 10% (5 mm/min)	250	111
	880	295
PEOX 10% (2.5 mm/min)	247	229
	815	570
PEBAX 3%	221	174
	811	380

Table 3. The results of soman detection in the system with a semipermeable membrane [H5].

Polymer film (membrane)	Soman concentration, $\mu\text{g}/\text{m}^3$	Soman peak amplitude
—	22	498
	60	1063
	155	1520
PDMS 0.1%	19	154
	53	385
	130	616
PDMS 0.5%	10	119
	32	196
	89	477
PDMS 1%	28	154
	66	267
	140	434
PDMS 5%	29	147
	51	276
	215	798
PDMS 7%	20	Below the limit of detection
	56	128
	137	235
PEOX 10% (5 mm/min)	44	Below the limit of detection
	78	Below the limit of detection
	140	50
PEOX 10% (2.5 mm/min)	37	161
	70	207
	100	309
PEBAX 5%	20	Below the limit of detection
	45	219
	250	669

The next article concerned the behaviour of GB ions in different temperatures of carrier gas [H4]. As a result of the conducted tests, it was concluded that the peak position and disintegration point depend on the temperature of carrier gas.

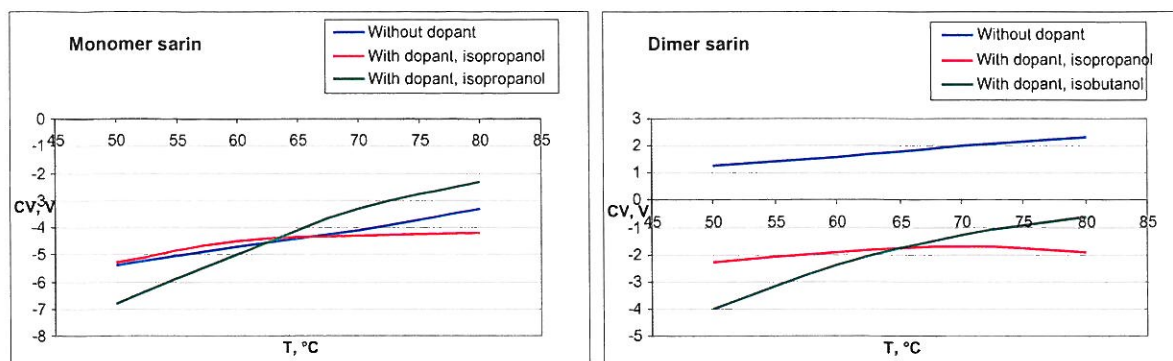


Fig. 12. Compensation voltage as a function of gas temperature [H4].

With the increase in temperature, there was a movement of peaks coming from a sarin dimer and monomer towards higher values of compensation voltage (CV). The dependence of CV on sarin monomer and dimer temperature is presented in Fig. 12. The largest influence was observed in the case when carrier gas included isobutanol. The course of the curve for soman dimer is interesting. In case of absence of admixtures in carrier gas, dimer peak occurs at positive values of CV. Upon introduction of admixtures to carrier gas, peak movements towards negative values of CV were observed.

Testing ion fragmentation as a method of chemical substance identification.

Very high electric field results in the fact that effective ion temperature is significantly higher than the carrier gas temperature. Therefore, ion can disintegrate under the influence of ion impacts with neutral carrier gas particles.

The total ion energy is a sum of thermal energy (equal to thermal energy of surrounding gas) and energy obtained from the electric field:

$$\frac{3}{2}kT_{eff} = \frac{3}{2}kT + \frac{1}{2}Mv_d^2 \quad (4)$$

where: k - is a Boltzmann constant, T_{eff} - ion effective temperature, M - drift gas particle mass, a v_d - ion speed arising from drift in the electric field. In case of low values of electric field, ion effective temperature equals thermodynamic temperature T .

When field is high, above 10 kV/cm, ion energy dispersion delivered by the field between impacts is not full which results in the fact that increase in the field leads to ion energy increase. This power can be calculated to temperature [H3]. Increase of T_{eff} causes exceeding the particle disintegration energy the consequence of which is monomer disintegration. Peaks coming from monomer disintegration, characteristic for the analysed compound, appear for strictly specified energies. The determination of particle disintegration temperature is highly important due to its specificity as each ion has its own, unique value.

Therefore, not only peak position in the spectrogram, but also ion effective temperature can be used to identify the substance type. Knowledge of the value of effective temperature can constitute a very precise identification parameter of any air contamination. Assessment of this parameter can significantly influence the increase of selectivity of an analysis which uses the ion mobility spectrometer with strong asymmetrical electric field.

Similarly to article [H7], I indicated that, regardless of the type of DMS spectrometer (DMS #1 - distance between electrodes 0.25 mm or DMS #2 - distance between electrodes 0.5 mm) and carrier gas temperature, the fragmentation points depend on ion energy which can be calculated. It was performed for sarin (GB), sulphur mustard and methyl salicylate. Exemplary results of tests of impact of the analyser temperature on the shape of dispersion charts are presented in Fig. 13. Tests were performed for GB with the use of DMS #1 detector.

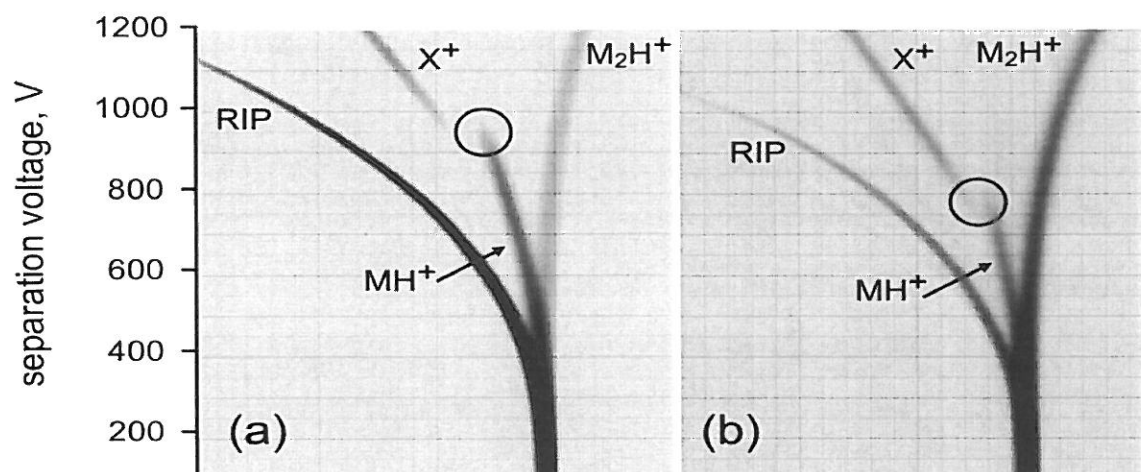


Fig. 13. Dispersion plots for GB in positive mode at (a) 0°C and (b) 40°C obtained by DMS #1 [H7].

Precise determination of the value of separation voltage (SV) at which the disintegration of monomer ion occurs is difficult to be performed. In order to unify the manner of result analysis, it was assumed, similarly like in article [26], that the value of voltage responsible for ion fragmentation is assessed on the basis of fading peak intensity of disintegrating ions. Table 4 includes full results of tests of influence of detector temperature on the value of SV at which the disintegration of GB occurs.

Table 4. The values of SV corresponding to the fragmentation of monomer ions of GB [H7].

Ambient temperature, °C	Detector temperature, °C	SV amplitude for fragmentation, V	E/N, Td)*
-10	0	955	107
0	10	930	105
10	20	875	102
20	30	830	100
40	40	760	94
40	50	710	91
40	60	685	91
40	70	665	91
40	80	630	88

)* The E/N values were calculated on the basis of maximal value of SV taking into account duty cycle and the change of gas density with temperature.

In the scope of works conducted on the differential ion mobility spectrometry, I developed a PRS-1W chemical warfare detector (Fig. 14), described in the publication [H6] as well as NCR (Nuclear Chemical Radiological) signalling device applied in the robot for detecting chemical and radioactive contamination [M2], [M3]. The constructive solutions applied in this detector were patented (patents 1, 3, 4, 5, 6, 7). The manner of identification of chemical substances with the use of PRS-1W detector was described in the publication [H6].



Fig. 14. Chemical warfare detector PRS-1W[H6].

A full spectre (3D), as in Fig. 4a, is collected for ca. 1 minute for a differential ion mobility spectrometry, whereas for a single spectre of one of selected HSV voltages only for 0.4 sec. Therefore, the quantity of data for analysis was significantly lowered by selection of the most important single spectres. The following voltages were selected: HSV 600, 700, 800, 900, 1000, 1100 and 1200 V, next, peak position was marked and corrected for up-to-date measurement conditions, i.e. temperature, pressure and moisture according to reference

conditions (gas temperature 45°C, pressure 1023 mbars, moisture 50 ppm). Substance types are indicated on the basis of the corrected peak position. The positions of peaks for CWA in standard conditions are presented in Fig. 15.

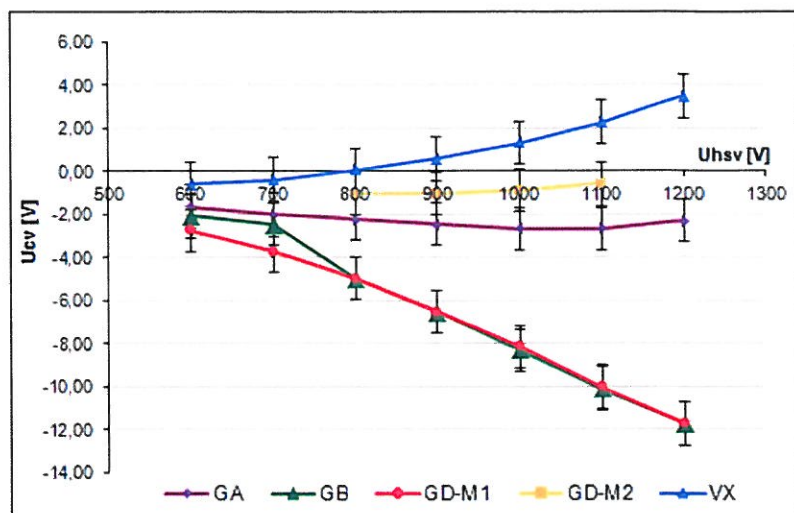


Fig. 15. Compensation voltage as a function of high-voltage separation of monomers of organophosphate nerve agents [H6].

New concepts of identification and determination of gaseous substance concentration for DMS spectrometry

The differential ion mobility spectrometry enabled to collect 3D spectres which provide a large quantity of information. Full scanning lasts ca. 40 seconds. When the change in chemical substance concentration is slowly-variable (above one minute), it is possible to use algorithms with long time of data collection and apply data analysis methods which were not used in ion mobility spectrometry before.

I described the first method in paper [H2] which concerns soman identification on the basis of approximation with the use of third degree polynomials.

If a single piece of a spectre (defined HSV and CV voltage) is treated as a response from a chemical sensor, then, a full spectre can be treated as a matrix of virtual sensors connected with data from a DMS spectrometer [H8] and [H10].

One of them is an algorithm of k-nearest neighbours (k-nn), publication [H10]. In this case, the classification consists in assignment of measurement to one of three testes compounds (benzene, toluene, xylene) in the presence of water vapour. With the use of traditional ion mobility spectrometry, benzene and xylene are practically not distinguishable and toluene is poorly distinguishable from benzene and xylene.

In case of DMS with the use of classic peak analysis method, there are also difficulties during classification of these methods. The application of k-nearest neighbour algorithm showed that these compounds can be differentiated at a very high level. Fig. 16 presents the

misidentification coefficient for the said compounds versus separation voltage HSV, without analysis of the nearest neighbours.

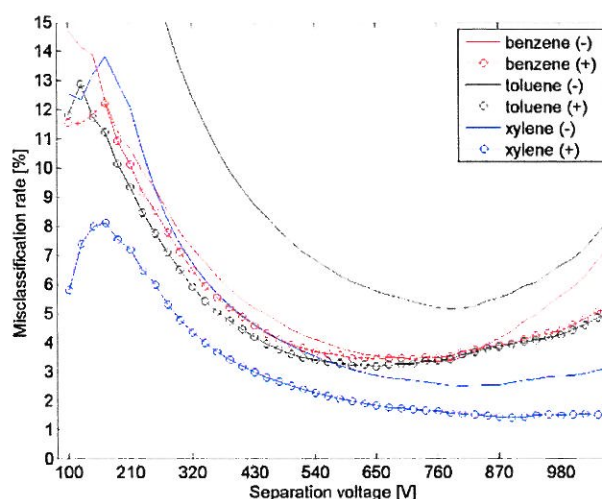


Fig. 16. Results of benzene, toluene and xylene recognition as a function of DMS separation voltage. The classification variables are raw DMS responses recorded at single separation voltage [H10].

Upon application k-nearest neighbour algorithm for all CV and HSV voltages, the results presented in table 5 were obtained (results were presented separately for positive and negative ions).

Table. 5. Results of benzene, toluene and xylene recognition. The classification was based on DMS responses recorded at all combinations (CV, SV) [H10].

Jon	Misclassification rate [%]		
	benzen	toluen	Ksilen
ujemny	0	0	0
dodatni	0.72	0.73	0

The presented data indicate that with the use of new methods of chemical substance classification for a DMS spectrometer, it is possible to obtain excellent effects of identification of various chemical substances.

Upon identification of a compound type (e.g. as presented above), it is necessary to determine the concentration of toxic substances and, in this case, it is possible to apply advanced mathematical methods, e.g. one-dimensional regression [H8]. A dependent variable in a regression model is the concentration of a tested compound. An input variable was the voltage amplitude on the collecting electrode for positive and negative ions of a DMS spectrometer, depending on the separating voltage and compensatory voltage. Two functions: linear (5) and quadratic equation (6) were treated as a model of relation between dependent and independent variables.

$$y = ax + b + \varepsilon \quad (5)$$

$$y = ax^2 + bx + c + \varepsilon \quad (6)$$

The combinations of separating voltage and compensatory voltage were treated as sources of chemical information. Points the value of which exceeded the background (electric noise) were used for the purpose of calculation. A regression model for each chemical compound for which the concentration was marked was built individually.

The calculation results indicate that the PLS (partial least squares) regression method very well describes the concentration of benzene, xylene, toluene and concentration of water vapour in air for a DMS spectrometer. Therefore, it can be used as one of new analytic methods in this type of spectrometers.

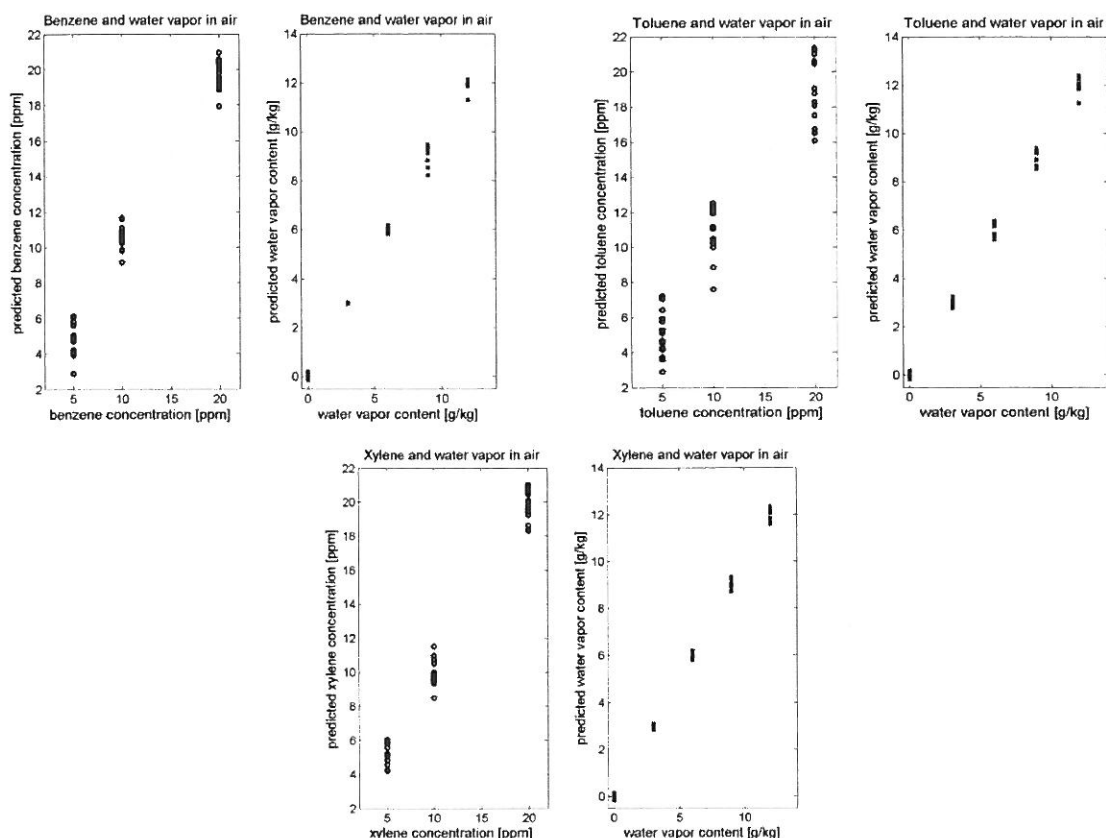


Fig. 17. Results of determination of (a) benzene concentration and water vapor (b) using DMS spectrometer (negative ions) and PLS regression.

The presented publications indicate that on the basis of the data obtained from the spectrometer and upon application of new analysis methods (even though known from chemometrics), but, so far, not used in analysis of data from such a IMS/DMS spectrometer, it is possible to improve the quality of the final result, i.e. significantly reduce the possibility

of incorrect identification as well as significantly improve the accuracy at determination of concentration of detected substances.

Summary

The ion mobility spectrometry is a method which due to its sensitivity and high specificity can be used to protect human against dangerous substances. It is still perspective in many fields of technology.

The presented publications indicate the continuous IMS development and, consequently, better and better identification of detected chemical substances. The works provide a practical result which consists in the application of IMS in chemical contamination signalling devices. The last publications indicate the possibility to use this method to evaluate inner air or even to test human breath in order to quickly diagnose their health condition. These concepts will be the next field of application of the aforementioned works.

REFERENCES:

- [1] S. Yamaguchi, R. Asada, S. Kishi, R. Sekioka, N. Kitagawa, K. Tokita, S. Yamamoto, Y. Seto, Detection performance of a portable ion mobility spectrometer with ^{63}Ni radioactive ionization for chemical warfare agents, *Forensic Toxicol.*, 28 (2010) 84–95.
- [2] R. Sferopoulos, A Review of Chemical Warfare Agent (CWA) Detector Technologies and Commercial-Off-The-Shelf Items, Human Protection and Performance Division DSTO Defence Science and Technology Organisation, Victoria 3207, Australia (2009).
- [3] G.A. Eiceman, Z. Karpas, H.H. Hill Jr., *Ion Mobility Spectrometry*, 3rd ed., CRC/Taylor & Francis, Boca Raton, 2013.
- [4] W. Vautz, J.I. Baumbach, E. Uhde, Detection of emissions from surfaces using ionmobility spectrometry, *Anal Bioanal Chem.*, 384 (2006) 980–986.
- [5] G. A. Eiceman, E. G. Nazarov, B. Tadjikov, R. A. Miller, Monitoring volatile organic compounds in ambient air inside and outside buildings with the use of a radio-frequency-based ion-mobility analyzer with a micromachined drift tube, *field analytical chemistry and technology* 4 (2000) 297–308.
- [6] H. Borsdorf, G.A. Eiceman, *Ion mobility spectrometry: principles and applications*, *Applied Spectroscopy Reviews* 41 (2006) 323–375.
- [7] J. Stach, J.I. Baumbach, *Ion mobility spectrometry - basic elements and applications* *IJIMS* 5 (2002) 1–21.
- [8] G.A. Eiceman, *Ion-mobility spectrometry as a fast monitor of chemical composition* *Trends Anal. Chem.* 21 (2002) 259–275.
- [9] M. Maziejuk, *Różnicowa spektrometria ruchliwości jonów*, Wydawnictwo WAT, Warszawa 2012.
- [10] R.A. Miller, E.G. Nazarov, G.A. Eiceman, A.T. King, A MEMS radio-frequency ion mobility spectrometer for chemical vapor detection, *Sensors and Actuators A* 91 (2001) 307–318.

- [11] M. Jakubowska, M. Maziejuk, M. Ceremuga, J. Siczek, W. Gallewicz, Ceramic DMS – type detector, *Int. J. Ion Mobil. Spec.* 15 (2012) 99–108.
- [12] <http://www.army-technology.com/contractors/nbc/graseby/>.
- [13] F.W. Karasek, R.A. Keller, *J. Chromatogr. Sci.* 10 (1972) 626–628.
- [14] A.B. Kanu, and H.H. Hill Jr., Ion mobility spectrometry detection for gas chromatography *J. Chromatogr. A* 1177 (2008) 12–27.
- [15] M. Camara, N. Gharbi, A. Lenouvel, M. Behr, C. Guignard, P. Orlewski, D. Evers, Detection and Quantification of Natural Contaminants of Wine by Gas Chromatography–Differential Ion Mobility Spectrometry (GC-DMS), *J. Agric. Food Chem.* 61 (2013) 1036–1043.
- [16] E. Aguilera-Herrador, S. Cárdenas, V. Ruzsanyi, S. Sielemann, M. Valcárcel, Evaluation of a new miniaturized ion mobility spectrometer and its coupling to fast gas chromatography multicapillary columns, *J. Chromatogr. A* 1214 (2008) 143–150.
- [17] J. Luong, R. Gras, H.J. Cortes, R.A. Shellie, *Int. J. Ion Mobil. Spec.* 15 (2012) 179–187.
- [18] S.A. Ghorashi, A.H. Alinoori, S. Hajjaligol, *Microelectr. J.* 45 (2014) 1634–1640.
- [19] W. Vautz, R. Slodzynski, C. Hariharan, L. Seifert, J. Nolte, R. Fobbe, S. Sielemann, B.C. Lao, R. Huo, C.L. Thomas, and L. Hildebrand, *Anal. Chem.* 85 (2013) 2135–2142.
- [20] G.A. Eiceman, E.V. Krylov, N.S. Krylova, Separation of ions from explosives in differential mobility spectrometry by vapor-modified drift gas, *Anal. Chem.* 76 (2004) 4937–4944.
- [21] C. Kwan, A.P. Snyder, R.P. Erickson, P.A. Smith, W.M. Maswadeh, B. Ayhan, J.L. Jensen, J.O. Jensen, A. Tripathi, Chemical Agent Detection Using GC-IMS: A Comparative Study, *IEEE Sensors Journal*, 10 (2010) 451–460.
- [22] M. Jünger, B. Bödeker, J.I. Baumbach, Detection of volatile organic compounds (VOCs) in exhaled breath of patients with chronic obstructive pulmonary disease (COPD) by ion mobility spectrometry, *Anal. Bioanal. Chem.* 396 (2010) 471–482.
- [23] J.I. Baumbach, Ion mobility spectrometry coupled with multi-capillary columns for metabolic profiling of human breath, *J. Breath Res.* 3 (2009) 1–16.
- [24] H. Sohn, J. Steinhanses, Use of ion mobility spectrometry for the preliminary evaluation of hazardous military waste sites -opportunities and limitations, *Int. J. Ion Mobil. Spec.* 1 (1998) 1–14.
- [25] G. Kaur-Atwal, G. O'Connor, A.A. Aksenov, V. Bocos-Bintintan, C.L.P. Thomas, C.S. Creaser, Chemical standards for ion mobility spectrometry: a review, *Int. J. Ion Mobil. Spec.* 12 (2009) 1–14.
- [26] X. An, G.A. Eiceman, J.A. Stone, A determination of the effective temperatures for the dissociation of the proton bound dimer of dimethyl methylphosphonate in a planar differential mobility spectrometer, *Int. J. Ion Mobil. Spectrom.* 13 (2010) 25–36.

5. Presentation of other scientific-research accomplishments

A) Monographs and publications in international and national journals

Monographs and chapter in monographs

- [M1] Monografia Maziejuk M., „Różnicowa spektrometria ruchliwości jonów”, Wydawnictwo WAT, Warszawa 2012 r.
- [M2] Sikora T., Maziejuk M., Ceremuga M., Buczkowska A, Mobilne laboratorium do poboru próbek środowiskowych i identyfikacji zagrożeń biologicznych, rozdz. 4. Technologie mobilne w polowej identyfikacji zagrożeń biologicznych str. 73-87, monografia, Wydawnictwo Politechniki Krakowskiej, 2014 r., ISBN 978-83-72742-806-6.
- [M3] Maziejuk M., Lisowski W., Ceremuga M., Szyposzyńska M., Mobilne laboratorium do poboru próbek środowiskowych i identyfikacji zagrożeń biologicznych, rozdz. 5. „Innowacyjny czujnik NRC do detekcji skażeń chemicznych wykorzystujący hybrydowy układ IMS-DMS”, str. 87-107, monografia, Wydawnictwo Politechniki Krakowskiej, 2014 r., ISBN 978-83-72742-806-6.
- [M4] Sikora T., Maziejuk M., Ceremuga M., Buczkowska A., Opracowanie koncepcji detektora do wykrywania skażeń biologicznych metodą fluorescencji wzbudzonej, II Międzynarodowa Konferencja Naukowa EpiMilitaris 2013 – Bioterroryzm, Warszawa 2013, str. 183-196.
- [M5] Maziejuk M. , Ceremuga M. „Ochrona przed skutkami nadzwyczajnych zagrożeń”, T.2 Redakcja naukowa: Z. Mierczyk R. Ostrowski, Rozdział: „Nowoczesne metody detekcji skażeń chemicznych”, str. 179-191, ISBN: 978-83-62954-09-4, Wydawnictwo WAT 2011.
- [M6] Maziejuk M., Ceremuga M., XXIV Międzynarodowa Konferencja Naukowo – Techniczna „Ochrona ludności przed skutkami nadzwyczajnych zagrożeń Ekomilitaris 2010, praca zbiorowa pod redakcją Z. Mierczyka, J. Wasilczuka, Zakopane 7-10 września, Nowoczesne metody detekcji skażeń, str. 253-264.

Publications

- [P1] Maziejuk M., Lisowski W., Szyposzyńska M., Sikora T., Zalewska A., Differential ion mobility spectrometry in application to the analysis of gases and vapors, Solid State Phenomena Vol. 223, (2015), 283-290.
- [P2] Maziejuk M., Lisowski W., Ceremuga M., Szyposzyńska M., Differential ion mobility spectrometry-application and development prospects, Analityka, 4, (2014), 8-15.
- [P3] Harmata W., Maziejuk M., Ceremuga M., Detektory do wykrywania skażeń chemicznych dla bezzałogowej platformy lądowej (STRAŻAK), Bezpieczeństwo i technika pożarnicza, 33, (2014), 93-105.
- [P4] Jakubowska M., Maziejuk M., Ceremuga M., Siczek J., Gallewicz W., Ceramic DMS – type detector, International Journal for Ion Mobility Spectrometry, (2012), 15, 99-108.

[P5] Maziejuk M., Mierczyk J., Spektrometry ruchliwosci jonow w zastosowaniu do wykrywania bojowych substancji toksycznych, Biuletyn WAT, 1, (2007), 159-177.

B) Conducting international and national research projects and participation in such projects

- Individual project: Tests on features of ionised CWA particles in an alternate electric field with high intensity and high frequency, No. PB 0033/TOO/2003/24, project manager.
- The application of FAIMS-IMS system for detection of chemical contamination, development project No. O R00 0008 12, 2010-2012, main performer.
- Mobile laboratory for taking environmental samples and identification of biological threats, No. O ROB 0031/01/D 31/1, 2011-2014 performer
- The mobile contamination signalling device, development project No. O ROB/0058/03/001, 2012-2014, main performer.
- Technologies for reducing danger caused by uncontrolled release of dangerous substances, No. O R00 0048 12, 2010, research-developmental project, Leader Scientific-Research Centre for Fire Safety, performer.
- Project within the scope of the program "Patent Plus - support for patenting inventions", "Structure and technology of ion mobility spectrometer construction", project manager.
- The mobile laboratory for testing contamination signalisation systems, O ROB 0059 001, 2012-2014, main performer.
- The elaboration of instrumental measurement methods, construction and tests of optoelectronic prototypes of devices for fast marking unintended transfer of chemical agents used to spray cultivated plants, development project: No. R14 020 03, 2007 r., main contractor.
- Miniature signalling device of biological threats for contamination detection signalling devices, Target project: No. 361/BO/B, 2007, project manager.
- The laboratory for identification of contamination at the level of tactic compound, No. O R00 0048 12 2010, project manager.

C) International and national awards for scientific achievement

- 2014 - II degree Prize in II Competition for the best scientific and research paper in the field of defensive capability awarded by the Competition Committee for the research paper titled: "Application of FAIMS-IMS system for detection of chemical contamination".
- 2014 - Distinction for the best patent or industrial pattern, protected with industrial property right in II Competition for the best scientific and research paper in the field of defensive capability awarded by the Competition Committee for the research

paper titled: "Application of FAIMS-IMS system for detection of chemical contamination".

- 2014 - Gold medal awarded by the International Jury of XVII International Salon of Inventions and Innovative Technologies "ARCHIMEDES 2014" in Moscow for the invention protected with 9 patents and concerning construction solutions applied in PRS-1 W Contamination Detection Device.
- 2012 - Prize of the President of the Republic of Poland for PRS-1 contamination detection device of new generation at XX Anniversary MSPO International Salon of Defensive Industry in Kielce in 2012
- 2011 - the first prize for the paper at XX International Conference of Association of Ion Mobility Spectrometry (ISIMS), Edinburg, Great Britain.
- 2011 - Gold medal at the International Exhibition in Brussels - Eureka 2011.
- 2011 - Gold medal at the International Warsaw Exhibition of Innovation - "IWIS 2011".
- 2010 - Gold medal at the International Exhibition of Innovativeness in Brussels, Brussels INNOVA 2010.
- 2009 - Silver medal at the Global Exhibition of Innovation - Seoul.
- 2005 - Gold medal with distinction at the 54th Global Exhibition of Innovation.
- 2004 - Distinction with an Honour Price of the Rector of Military Academy of Technology.
- 2004 - Gold medal at the 53rd Global Exhibition of Innovation.
- 2003 - Silver medal at the 52nd Global Exhibition of Innovation.

D) Presentation of papers at international and national thematic conferences

- 24th International Conference on Ion Mobility Spectrometry - ISIMS Cordoba 2015 "Detection of volatile organic compounds with differential ion mobility spectrometry".
- 23rd International Conference on Ion Mobility Spectrometry - ISIMS-Asheville 2014 r., "Fast identification method of chemical warfare agents (CWA) with high concentration of interfering compounds by DMS spectrometer".
- The International Scientific-Technological Conference titled: "Protection of human and natural environment from contamination", 2014 "Identification of chemical welfare with the use of IMS-DMS technologies".
- 1st scientific conference titled "Operation of the national system for detection of contamination and alarming in the light of present contamination threats" WAT Warsaw, 2014 "Application of differential ion mobility method in detecting toxic substances".
- Future Engineering, Scientific-Business Conference, Intelligent technological and organisational solutions for industry, Radom 2014, "Differential ion mobility spectrometry in application for the analysis of vapours and gases".

- XXI International Conference on Ion Mobility Spectrometry -ISIMS, Orlando, USA, 2012 „New IMS/DMS based instrument”.
- XX International Conference on Ion Mobility Spectrometry -ISIMS, Edinburgh, Great Britain 2011 „Ceramic DMS—type detector”.
- International Scientific-Technological Conference “Protection of human and natural environment from contamination”, 2010 “Modern methods of chemical combinations”.
- II International Scientific Conference EpiMilitaris 2013 - Bioterrorism.
- XXI International Scientific-Technological Conference, EKOMILITARIS 2007
- XIII International Conference on Ion Mobility Spectrometry Gatlinburg 2004
- XVI National Scientific-Technological Conference, “EKOMILITARIS-2002”, Zakopane, 2002

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