



Research paper / Praca doświadczalna

Development of explosives detection method based on FAIMS (Field Asymmetric Ion Mobility Spectrometry) and thin layer chromatography (TLC)

Opracowanie metody wykrywania substancji wybuchowych w oparciu o spektrometrię ruchliwości jonów w zmiennym polu elektrycznym (FAIMS, Field Asymmetric Ion Mobility Spectrometry) oraz chromatografię cienkowarstwową (TLC)

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Abstract: A new method of hyphenation of thin layer chromatography (TLC) and field asymmetric ion mobility spectrometry (FAIMS), is presented. Coupling chromatography with spectrometry enables the simultaneous separation and identification of individual species. During chromatographic experiments the elution was carried out using normal- and reversed-phase systems. The detection was performed with MO-2M and PILOT-M handheld detectors. The chromatographic bands were located using ultraviolet detection and a spray reagent containing diphenylamine. The bands containing explosives were separated and placed in thermal desorbers of the detectors. They were applied as vapour intensifiers. During experiments, a more effective way of desorption from TLC sheets using a conventional dry block heater was demonstrated. The best results were obtained using the MO-2M detector an normal-phase separations. By applying such separation, it was possible to detect 10 µg of trinitrotoluene, hexogen, pentaerythritol tetranitrate and CL-20 on TLC plates.

Streszczenie: W pracy przedstawiono połączenie dwóch metod: chromatografii cienkowarstwowowej (TLC) oraz spektrometrii FAIMS. Połączenie (sprzężenie) metody chromatograficznej np. z metodą spektrometryczną pozwala na szybki rozdział mieszaniny i identyfikację jej składników. Do rozdzielonych chromatograficznych zastosowano normalny lub odwrócony układ faz, jako detektory użyto spektrometry MO-2M i PILOT-M. Pasma chromatograficzne lokalizowano w promieniowaniu ultrafioletowym lub po zastosowaniu odczynnika wywołującego z difenyloaminą. Po lokalizacji na rozwiniętych płytkach pasm chromatograficznych wycinano ich fragmenty, które desorbowano termicznie w fabrycznych desorberach urządzeń lub na zaprojektowanym stanowisku z podgrzewaczem laboratoryjnym. Desorpcję termiczną zastosowano w celu zwiększenia emisji par substancji wybuchowych z płytek krzemionkowych. Stosując detektor MO-2M oraz płytki krzemionkowe rozwijane w normalnym układzie faz zidentyfikowano w rozdzielonych pasmach chromatograficznych, zawierających po 10 µg, heksogenu, trotylu, pentrytu oraz CL-20.

Keywords: heksogen, trinitrotoluene, pentaerythritol tetranitrate, CL-20, chromatographic method, spectrometric method, coupling

Słowa kluczowe: heksogen, trotyl, pentryt, CL-20, metoda chromatograficzna, metoda spektrometryczna, sprzężenie

Symbols and abbreviations

CL-20	Hexanitrohexaazaisowurtzitane
IMS	Ion Mobility Spectrometry
FAIMS	Field Asymmetric Ion Mobility Spectrometry
PETN	Pentaerythritol tetranitrate
RDX	Hexogen
R_f	Retention factor
TLC	Thin-Layer Chromatography
TNT	Trinitrotoluene
UV	Ultraviolet

1. Foreword

In recent decades, ion mobility spectrometry (IMS) or its variant – field asymmetric ion mobility spectrometry (FAIMS), significantly expanded its applicability and currently, apart from a quick, preliminary detection of explosives, drugs or chemical weapons, is used in food testing, environmental protection and the pharmaceutical industry [1]. The interest in IMS is mainly due to the simple design of the detectors, easy operation, low investment and operating costs. Additionally, the speed of the IMS spectrometer measurements, their high sensitivity and operation under normal pressure, made the IMS more commonly used when coupled with other chromatographic methods and mass spectrometry. The examples of coupling methods were discussed in the latest publications on the analysis of explosives, e.g. HPLC-IMS in nitrocellulose propellants [2], GC-IMS in the trace amounts of blasting explosives [3] and MS-IMS in drugs and explosives [4].

Literature includes studies on coupling the IMS method with thin-layer chromatography, a method, which nowadays seems slightly forgotten. The authors of a 2015 article [5] reported for the first time the possibility of detecting drugs by coupling thin-layer chromatography and IMS. The study focused on the determination of the most effective way of coupling both methods. It discusses TLC-IMS coupling through direct and indirect electrospaying from a TLC plate and the substance analysis by thermal desorption from the plates placed in a specially designed thermal desorption unit connected directly to the IMS detector. In 2016, a second article by the same team was published [6], in which an innovative TLC-IMS coupling method using laser desorption was used. Using this method, drugs, amino acids and selected explosives were determined on the plates. The authors highlight a very short analysis time and an ability to identify substances in the overlapping chromatographic bands. The latter was made possible by adjusting the laser parameters.

From the point of view of quick identification of explosives, the combination of IMS and TLC is an interesting and practical solution. TLC is a simple method for separating mixtures and qualitative analysis which can also be carried out outside of the laboratory, e.g. at the explosion site. The information obtained from the analysis of TLC data, i.e. the R_f factor values and characteristic colour reactions of the explosives on the plates in the presence of specific reagents [7], combined with IMS detection, allow the identification of the explosives with a high degree of certainty. IMS analyses can also be carried out in the field using handheld or portable detectors. Considering these facts, the authors have evaluated the capability of detecting explosives directly on the chromatographic plates using IMS detectors, in particular, their FAIMS (Field Asymmetric IMS or DMS – Differential Mobility Spectrometer) variants. The study involved cutting the fragments of the TLC plates with selected substance spots and carrying out IMS

analysis of those fragments, either directly or using the default thermal desorption unit. In the studies referenced above, complex methods were used to increase the substance desorption from the TLC plates, i.e. electrospraying [5] or laser desorption [6]. Using these methods outside of the laboratory, i.e. in the field, seems unfeasible. Another novel aspect of the study will be the use of two types of chromatographic plates, in which the separation is carried out using normal or reversed phase separation methods.

2. Experimental section

2.1. Tested materials

2.1.1. Chemical compounds

1 mg/ml and 5 mg/ml solutions in acetonitrile of the following explosives were prepared for the tests:

- CL-20 (HNIW),
- tetra(hydroxymethyl)methane tetranitrate (pentrite, PETN),
- 1,3,5-trinitro-1,3,5-triazine (hexogen, RDX),
- 2,4,6-trinitrotoluene (TNT).

HPLC grade solvents were used: acetonitrile, chloroform, methanol and tetrahydrofuran produced by POCh (Poland).

2.1.2. Other materials

The following thin-layer chromatography plates with aluminium matrix and fluorescent indicator by Merck were used: Kieselgel 60 F₂₅₄ and Silica Gel 60 RP-18 F_{254s}. The chromatographic separation was carried out in 500 ml glass vessels with sealed polypropylene caps (Roth).

2.2. Test methods

2.2.1. Test equipment

Two Russian made portable IMS detectors for explosives were used: MO-2M (Siebel Ltd.) and PILOT-M (Lavanda-JU), both utilising FAIMS technology. The spectrometers were also fitted with the default thermal desorption unit for analysing samples at low air moisture with temperature control. Both devices can detect trace amounts of TNT, RDX, PETN, nitroglycerine and other related explosives. The main difference between the detectors is the sample ionisation method used. The source of radiation was an ⁶³Ni isotope in the MO-2M and a corona discharge in the PILOT-M detector. The MO-2M was also fitted with an autocalibration system which automatically adjusts its parameters to external conditions, as opposed to the other detector which requires external calibration. Additionally a Talboys laboratory heater was purchased from Troemner. Figures 1 and 2 show both detectors.



Figure 1. Detector MO-2M with desorber



Figure 2. Detector PILOT-M with desorber

2.2.2. TLC method

Analysis was carried out using 5×10 cm chromatographic plates. Before applying the test sample, the plates were rinsed with acetonitrile and thoroughly dried. The solutions of CL-20, PETN, RDX and TNT in acetonitrile were applied to the plates using a capillary. The spots contained 10 µg of the sample. The plates were placed in a chromatographic chamber containing 15 ml of the mobile phase. Mixtures of ethyl acetate (from 25 to 75% vol.) with hexane and chloroform were used as eluents in the normal phase chromatography and mixtures of methanol with water and tetrahydrofuran with water (from 50 to 70 vol.% of the organic component) were used in the reverse phase chromatography. After developing at a distance of 7 cm and drying, the plates were observed under 254 nm UV radiation to identify the CL-20, RDX and TNT bands as shadows on a green or blue background. The PETN band was visualised by spraying the plate surface with a 5 wt.% solution of diphenylamine (DPA) in methanol. The solution yielded grey-blue bands for CL-20, PETN and RDX. The visualisation provided preliminary information about the type of compound

analysed. The substances visible in the UV and after spraying with DPA solution are nitramines (CL-20 and RDX). The PETN stain invisible in the UV (nitric acid ester) was appeared similar to the nitramines, whereas the TNT stain (nitroaromatic compound), visible in the UV, did not change colour as a result of the reagent used. To obtain a fragment of the plate containing PETN and not sprayed with the DPA solution, PETN was eluted onto the plate as a wide band. After drying, half of the plate was covered with a glass plate and the other half sprayed with the DPA solution. The appearance of half of the band showed which fragment of the unsprayed surface needed to be cut for analysis. For the remaining substances, 1×1 cm fragments of plate were cut for further analysis.

Mentioned in Tables 1 and 2, in section 3, TLC separation conditions were:

- NP-1: Kieselgel 60 plate, eluent: ethyl acetate/hexane (25/75 vol.%),
- NP-2: Kieselgel 60 plate, eluent: chloroform,
- RP-1: Silica Gel 60 RP-18 plate, eluent: methanol/water (70/30 vol.%),
- RP-2: Silica Gel 60 RP-18 plate, eluent: tetrahydrofuran/water (70/30 vol.%).

2.2.3. FAIMS method

The analyses using spectrometry began by switching the devices on, and in case of the PILOT-M detector, setting the device using the supplied calibrator. Using an automatic pipette, 10 µl of acetonitrile was applied to the 1×1 cm fragments of rinsed TLC plate and placed in the thermal desorption units. Following a negative result, a subsequent part of the study was conducted. Since the thermal desorption units allow the sample to be heated of 50 to 60 °C (data provided by the manufacturer), the detection capabilities of the devices were evaluated after heating the TLC plate fragments to higher temperatures, which would cause an increase in the vapour pressure of the adsorbed substances. The Talboys laboratory heater with aluminium insert, inside which the fragment of TLC plate was placed, was used in the analysis. A photograph (Figure 3) shows the equipment ready for analysis to start.

After setting the required temperature and switching the heater on, the device was left for approx. 15 mins, until the set temperature was reached. The actual temperature at the plate surface was checked using a contact-free thermometer. Before the actual run, the reaction of the detector to the heated insert and the heated 'clean' fragments of the chromatographic plates were evaluated to avoid any potential false signals. The plates with applied test samples were placed on the aluminium insert and left for approx. 2 min until heated and, using the spectrometers, measurements were carried out for the presence of explosive vapours. The experiment was carried out at a heater temperature of 70 to 100 °C.



Figure 3. The experimental set-up applied for studying of the influence of temperature on explosives detection (in the lower part Talboys heater, in the upper detector PILOT-M)

3. Results and discussion

The composition of the binary mobile phase, including an initial eluent and an organic modifier, was determined starting with a 1:1 mix ratio. Based on the obtained TLC separations, the content of the organic modifier was either increased or decreased. In further tests, ethyl acetate/hexane (25/75 vol.%) and chloroform were selected as eluents for normal phase chromatography, whereas, methanol/water (70/30 vol.%) and tetrahydrofuran/water (70/30 vol.%) were selected as eluents for reversed phase chromatography. Figures 4 and 5 show the sample chromatograms.

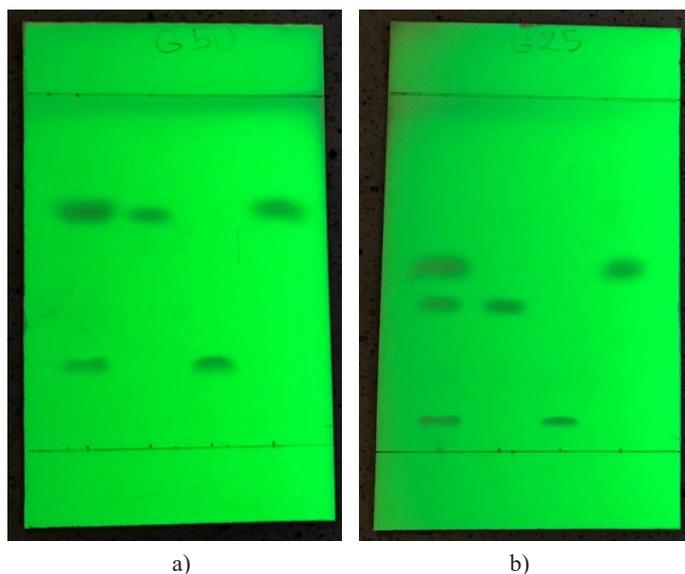


Figure 4. Chromatograms obtained for normal phase system using eluents containing mixture of ethyl acetate/hexane: 50/50 vol.% (a) and 25/75 vol.% (b); as a reminder, from the left the spotted samples are: the mixture of substances, CL-20, RDX, and TNT

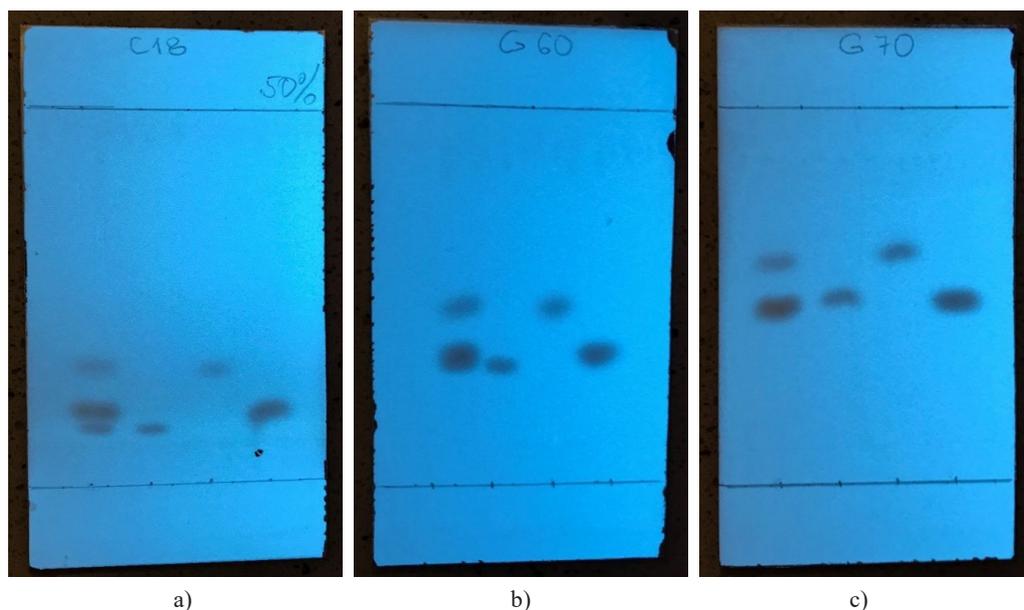


Figure 5. Chromatograms obtained for reversed phase system using eluents containing mixture of methanol/water: 50/50 vol.% (a), 60/40 vol.% (b), and 70/30 vol.% (c); as a reminder, from the left the spotted samples are: the mixture of substances, CL-20, RDX, and TNT

Table 1 shows the obtained average R_f factors for the analysed substances and the results of blank tests for plates without the analytes, developed in the above-mentioned eluents. The data are from 5 experiments. The blank test results show that the MO-2M detector can be used with the Talboys heater within the entire

temperature range (70-100 °C), and that the PILOT-M detector reacted and signalled the presence of explosives, mostly nitroglycerine, on the plates within the temperature range specified above. Since a positive reaction of the MO-2M detector at the heater temperatures over 100 °C was observed sporadically, 90 °C was used in all tests.

Table 1. Results of TLC analysis – the values of calculated R_f factors and blank tests for the detectors when using ‘clean’ chromatographic plates. The blank tests were carried out for plates without analytes developed in the eluents specified above. Plus ‘+’ sign indicates a false positive signal. 10 µg of analysed substance was applied on each plate

TLC separation conditions	R_f values				Blank determination for the detector			
					MO-2M		PILOT-M	
	Explosive substance				Set 1*	Set 2**	Set 1	Set 2
CL-20	PETN	RDX	TNT					
NP-1	0.38	0.43	0.01	0.48	–	–	–	+
NP-2	0.19	0.57	0.11	0.63				
RP-1	0.43	0.30	0.65	0.42				
RP-2	0.30	0.23	0.36	0.27				

Notes: * Set 1 – detector with a thermal desorption unit, ** Set 2 – detector with a thermal desorption unit, additional sample heater; measurements at 90 °C.

Table 2 shows the results of runs for TLC plate fragments with explosives, using the MO-2M and PILOT-M detectors. A situation where the identification signal of the substance was obtained in at least 3 out of 5 measurements was considered a positive reaction of the detectors. This is consistent with the IMS detector testing program presented in 2013 by one of the co-authors of the study [8]. Table 2 shows the results based on an evaluation of the experimental data. A ‘TNT’ signal was obtained for CL-20, since the detector was not calibrated to detect CL-20, and the ions formed by its molecules behave similarly to those formed by TNT. The analysis of other substances, i.e. PETN, RDX and TNT yielded unique detector signals. The results show that in the analysis using the default thermal desorption units, better results were obtained using the PILOT-M spectrometer. Three substances – PETN, RDX and TNT were detected by the device on the TLC plates developed in normal or reversed phase, whereas the MO-2M detector detected only RDX and TNT. In the conditions set for the experiment, CL-20 was not detected by either of the detectors. The specifications provided by the manufacturers of both detectors include sensitivity data for TNT only, which is identical in both cases at no less than 10^{-13} g/cm³ [9, 10]. The reports show that the total ion current in the IMS detector with ionisation by a corona discharge (in this case, PILOT-M) is higher by an order of magnitude than in the detector using a source of β ionisation (in this case, MO-2M) [11]. This results in better sensitivity and a higher signal to noise ratio, however, it is not consistent with the specifications provided by the manufacturers. Considering the fact that PETN vapour pressure is over a thousand times lower than TNT [12], a higher theoretical sensitivity of PILOT-M [11] can be verified by the described experiments using the thermal desorption units (Set 1).

Table 2. Results of analysis for the TLC plate fragments using MO-2M and PILOT-M detectors (each band/stain contained 10 µg of analysed substance)

TLC separation conditions	Detector Reaction			
	Explosive substance			
	CL-20	PETN	RDX	TNT
MO-2M Set 1*				
NP-1	–	–	+	+
NP-2				
RP-1				
RP-2				
MO-2M Set 2**				
NP-1	+**	+	+	+
NP-2				
RP-1	–			
RP-2				
PILOT-M Set 1***				
NP-1	–	+	+	+
NP-2				
RP-1				
RP-2				

Notes: * Set 1 – detector with a thermal desorption unit, ** Set 2 – detector with a thermal desorption unit, additional sample heater; measurements at 90 °C; *** a ‘TNT’ signal was obtained.

In the second part of the experiment, the default thermal desorption units were replaced with the Talboys laboratory heater used for heating the cut fragments of the plates. As described in section 2, the PILOT-M detector cannot be used with the heater due to false positive signals for the ‘clean’ TLC plates within the selected temperature range (60 to 100 °C). In the experiment, the MO-2M detector worked well with the heater within the selected temperature range, however, the heater temperature was set at 90 °C to almost completely eliminate the possibility of false signals. The „MO-2M Set 2” data (Table 2) show that for non-modified silica plates developed in the normal phase, all analysed explosives were detected, including CL-20 which was not detected using the default thermal desorption unit. For plates with the RP C-18 phase developed in the aqueous organic eluents using the Talboys heater, CL-20 was still not detected, probably due to the strong adsorption of CL-20 on the plates modified with octadecyl phase (C-18) resulting from non-polarity of the molecules, characterised by a low dipole moment – 0.58 D [13]. Another factor limiting the detection of CL-20 vapours by the IMS detectors is its particularly low vapour pressure, which at 10⁻¹⁸ bar [14] is approx. 10⁶ lower than for RDX and PETN, and one of the lowest among the known explosives [12].

4. Summary

- ◆ The study showed the capability of a simple combination of thin-layer chromatography (TLC) and spectrophotometric detection using IMS, particular FAIMS, detectors. The best results were obtained using an MO-2M detector for detecting explosives pre-separated at the silica gel plates in a normal phase system. After identifying the chromatographic bands on the developed plates, the fragments were cut and placed in the thermal desorption unit. The inlet nozzles of the spectrometers were located at a distance of 1 to 2 cm from the surface of the plate. To summarise, the analyses can provide a large amount of analytical data: TLC analysis – R_f values in two chromatographic systems; colour reaction with DPA and visual inspection in the UV band – determination of a specific group of explosives (nitramines, nitroaromatics or nitric acid esters); and FAIMS analysis – determination of a specific explosive.
- ◆ In accordance with the international requirements of different groups and standardisation committees, e.g. SWDRUG [15], analytical methods of different categories of significance can be used in the analysis of drugs and other unknown substances [16]. These are methods providing:
 - category A: structural information,
 - category B: information on specific physical and chemical properties, and
 - category C: other methods.

Using a specific type and number of methods may allow a high probability of positive substance identification to be achieved. The analyses presented in the study use IMS and TLC methods and colour reactions. According to the recommendations [16], these are two category B methods and one C category method yielding the overall result which is sufficient for the unambiguous identification of the unknown explosive.

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