Sensors and Actuators B 247 (2017) 343–348

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

The air humidity effect on the detection of TNT, PETN and NG by the FAIMS technique

Wojciech Pawłowski[a], Anna Zalewska[b], Łukasz Matyjasek[c], Monika Karpińska[d,*]

[a] Department of High-Energetic Materials, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-66 Warsaw, Poland
[b] Department of High-Energetic Materials, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[c] Chemistry Department, Central Forensic Laboratory of the Police, Al. Ujazdowskie 7, 00-583 Warsaw, Poland
[d] Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-66 Warsaw, Poland

ARTICLE INFO

Article history:
Received 28 November 2016
Received in revised form 10 February 2017
Accepted 6 March 2017
Available online 14 March 2017

Keywords:
Explosives
FAIMS
Humidity
Ionization
Forensic science

ABSTRACT

The effect of air humidity on the effectiveness of the detection of trace amounts of explosives was studied using the detectors based on the FAIMS technique. Two detectors employed: PILOT-M and MO-2M differed by the way the air containing NG, TNT, or PETN vapors was ionized. The air humidity level was found to affect sensitivity of the detectors used in a different manner. In detecting TNT vapors a rise in the air humidity level results in a drop of the signal level, whereas for PETN the signal rises for either detector. This is of major significance when working with the detectors for the explosives vapors detection based on the FAIMS technique.

1. Introduction

The threats associated with the use of explosives by criminals and terrorists continues unabated over the years. Detection of various components of explosives is extremely important in the protection of human life, infrastructure and property. Detection of explosives is primarily based on the scanning of individuals and objects or on searching of a given area to discover a concealed bomb. Detecting explosives can be subdivided into two major categories, notably bulk detection and trace detection, the latter involving the detection of particles or vapors [1]. Explosive traces can be gathered by making contact with objects or bodies that contain micro particles of explosives with another surface (contact traces) or else as a result of a transfer of particles of explosives from the surrounding air (contactless traces).

Studies on a quantitative determination of traces of a "fingerprint" size [2–7] and for the methods of their detection [8–10] are known. The traces represent the evidence that is material in the investigation that connects a person with the event. A typical "fingerprint" trace contains a multitude of particles of an overall mass ranging around 100 mg [1]. A single "fingerprint" trace (the multilayer trace produced upon a contact with plastic explosive) was shown to be able to contain 300–500 ng pentaerythritol tetranitrate (PETN), or cyclotrimethylenetrinitramine (RDX). Hence, in considering sensitivity of the detection systems (over a range of 20–200 pg) it may be realized that even if in a single trace there would be 5% of explosives, this quantity would be greater than the one required for a positive detection.

In the case of detection of vapors of explosives (particles in a gas phase) the way they are sampled by the detecting device is of significance. The effective technique of the screening of the expected carriers of traces of explosives should be based on a proper way of sampling and should use the devices that are capable of sampling vapors from above the surface under examination. Currently for the detection of traces of explosives invisible with a naked eye a wide range of techniques are employed that involve a number of chemical or physical phenomena (e.g. ion mobility spectrometry, mass spectrometry, Raman spectroscopy, or chemiluminescence) [1,11–13]. There are also works under way on the application of arrays of electrochemical sensors for the identification of vapors of explosives, even though these systems have a lower sensitivity [14]. It is important to use methods that allow performing fast and accurate real-time analysis with minimal amounts of explosives

* Corresponding author at: Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.
E-mail addresses: wojtek@ch.pw.edu.pl (W. Pawłowski), azalewska@ch.pw.edu.pl (A. Zalewska), lukasz.matyjasek@policja.gov.pl (Ł. Matyjasek), mkarpinska@ch.pw.edu.pl (M. Karpińska).

http://dx.doi.org/10.1016/j.snb.2017.03.022
0925-4005/

and without complex stages of sample preparation, that are also safe for the operator.

Among the most widely used explosives are: nitroglycerin (NG), trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), tetryl, nitrocellulose (NC) and ammonium nitrate (AN). For the studies carried out within this project NG, TNT and PETN were chosen - compounds that differ substantially from each other in vapor pressures. RDX was not examined because its volatility is close to the volatility of PETN. Detection of the above-mentioned explosives can be made by sampling the substance being either in a condensed or vapor form. The concentration of vapors of explosives, in ng l^{-1} is, respectively: PETN-0.09, TNT-70, NG-4000 ng l^{-1}, while their vapor pressure exponentially depends on temperature [15]. This exponential relationship is the reason for a tremendous effect of temperature on the concentration of vapors of explosive materials. By way of example, for the solid TNT the vapor pressure value is doubled with every successive 5 °C temperature rise [6]. For the compounds of a lower vapor pressure (PETN) the temperature effect on the vapor pressure detection is still greater [4]. Since the portable explosives vapor detection equipment is used both inside closed spaces and outdoors, the knowledge on the effect of environmental factors such as temperature or humidity is of great significance. It is a matter of common knowledge that with rising temperature the vapor pressure grows, hence also detectability increases. On the other hand, little or no information has thus far been available on whether, and how, the detection is affected by humidity. This aspect has especially aroused attention of the authors of this communication, because in their practice of working with complex mixtures of explosives sometimes they noticed different reactions of the detector on the same material depending on the changes of the air humidity.

2. High field asymmetric waveform ion mobility spectrometry (FAIMS)

The imminent terrorism awareness worldwide has stimulated the quest for increasingly more sensitive techniques for the detection of explosive materials. That is why in the explosives detection systems quite often use is made of the methods based on the ion mobility effect (IMS, ITMS, IIMS, FAIMS, DMS) [16–20]. These techniques are based on the existence of the difference in mobility of ions in generated electric fields of high and low strength. In the detectors ions originating from the explosives are formed by the action of radiation. Radioactive isotopes [21], UV radiation [22], corona discharge [23,24], electrospray [25] or plasma ionization [26] may be used as the source of ions. The IMS-based techniques allow to detect explosives at level as low as ca. 200 pg [27]. Thus they feature a high sensitivity (they are, next to the range of dogs' noses, the most sensitive explosive-detecting devices). Moreover, they are valued for the mobility of these detectors, for their being easy to operate, for their relatively low cost and a short time of analysis.

In the FAIMS method ions undergo separation in the gas phase under the influence of high and low electric fields (E) of asymmetric waveform due to differences in their mobilities (K) [28,29]. Ion mobility in this case is dependent on E and the number of gas molecules (N). It is assumed that factors such as electrostatic interactions resulting from dipole moments and charge distribution, hydraulic resistance resulting from the structure of molecules, molecular weight and shape of the particles will have an impact on the separation of ions in an electric field. Depending on the distribution of positive or negative charges ions are repelled or attracted by the electric field of given polarity, which results in a slowing or accelerating its drift towards the measuring electrode–change in the drift path. FAIMS technique enables detection of a substance vapor at concentration levels of 10^{-13} g cm^{-3}. The principle of operation of such devices is well known [30–32].

Under the experimental project two devices, notably: MO-2M and PILOT-M were used which employ for the measurements the FAIMS technique. In this technique ions undergo separation as a result of their mobility in the gas. The peaks recorded on the ionogram that correspond to individual chemical compounds are generated with reference to a standard substance which is TNT (MO-2M and PILOT-M devices). The compensating voltage employed that adjusts the ion drift trajectory sets the TNT peak at a standard position and subsequently the remaining explosive materials are being recorded with respect to the reference peak on the ionogram scale. The essential difference between the MO-2M and PILOT-M devices comes down to the ionization technique. The measurement with the MO-2M detector consists in the spectrometry in a variable electrostatic field. The particles sucked from the air undergo ionization by the action of a beta radioactivity radiation source (tritium ^{3}H) and subsequently they are lead into the drift tube through which they flow towards the detector. In the PILOT-M device, on the other hand, ionization occurs in the electrode zone, as a result of corona discharges. The negative ions produced in the negative corona zone carry away the electric charge to the lower-potential zone that surrounds the collecting electrode or they recombine to recover neutral atoms.

From the study on the detection of trace amounts of explosives by the FAIMS technique Authors of this report have noted a dependence of the detection sensitivity on the kind of explosive and on the parameters of their surrounding air. For that reason in determining the limits of detection (LOD) of the selected explosives (TNT, RDX, PETN, NG) with the use of the detectors that employ the FAIMS technique (SABRE 4000 and MO-2M) the Authors ensured constant temperature and humidity values [19]. Thus far the atmospheric conditions during the measurements were found to affect operation of the detectors that are based on the IMS [33] and FAIMS [34] techniques. The effect of temperature on results of the analysis is generally recognized. For that reason Authors had decided to pay attention to another parameter of significance which is air humidity and its effect on the detecting performance for TNT, NG and PETN as representatives of the explosives that differ radically by their vapor pressure. It should be emphasized that the detectors selected are portable and designed for applications both in closed premises and open areas (under windless conditions). The manufacturer of these pieces of equipment do not provide specifications for limits of detections for individual chemical compounds nor under which atmospheric conditions but only provide approximate sensitivity data, which are not very precise.

3. Experimental

Two FAIMS spectrometers, viz MO-2M (Siebel Ltd., Russia) and PILOT-M (LAVANDA-JU, Russia), were used in the measurements. The spectrometers were accommodated in a chamber provided with a humidity generator and a thermostat. A series of measurements was carried out at a constant temperature of 20 °C and at atmospheric pressures ranging from 1005 to 1015 hPa. The air humidity was varied over the range of 10 to 80%. Humidity level was controlled in a continuous way with a thermohygrobarometer model C 4130 from Test-Therm within a measuring accuracy of 2.5% and a resolving power of 0.1%. The acetone solutions prepared for TNT, and PETN and ethanol solutions for NG, of a suitable concentration, were applied onto swabs or filter paper which, after 30 s were subsequently brought close to the detector sampling tube five times at a distance of 2 cm. A blank test was run each time with