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Functional Sample of the Portable Device for Fast Analysis of Explosives

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***Abstract*—**The construction of original functional sample of the portable device for fast analysis of energetic materials has been described in the paper. The portable device consisting of two parts – an original miniaturized microcolumn liquid chromatograph and a unique chemiluminescence detector – has been proposed and realized. In a very short time, this portable device is capable of identifying selectively most of military nitramine- and nitroester-based explosives as well as inorganic nitrates occurring in trace concentrations in water or in soil. The total time required for the identification of extracts is shorter than 8 minutes.

***Keywords*—**Chemiluminescence, microcolumn liquid chromatograph, nitramines, nitroesters, portable device.

I. Introduction

CURRENTLY, there is great interest in finding new methods to detect and identify nitramine- and nitroester-based explosives. One of the reasons for this interest is contamination of the environment by these substances, especially military training areas, and the adverse effects of energetic materials on the health of people. Security risks represented by energetic materials are another reason for this interest, especially in connection with terrorism [1]-[2]. The submitted publication is a continuation of the paper presented at WSEAS conference, Sicily, in the last year [3].

Not only the explosives themselves, but also their biodegradation products represent the risks for the environment and the health of people [4].

Problems occur in taking of samples in the real environment, which is difficult with regard to qualified sampling techniques, pre-concentration of samples and their transport to a laboratory and after-treatment in a controlled environment so that the best results can be achieved [5]. The reason is low concentrations of explosives in real samples (10 ppb for TNT) [6] which enable only a narrow selection of a suitable method for detection and determination.

Contemporary portable devices for analyzing energetic materials can use only a limited number of detection principles e.g. measurement of ion mobility spectra [7], evaluation of changes in properties of surface acoustic wave [8], principle of fluorescence quenching [9], monitoring of intensity of luminescence [10] and Raman scattering [11].

In addition to gas chromatography, microcolumn high-performance liquid chromatography (μLC) coupled to suitable detection system could meet requirements of selectivity, contamination resistance, automation, and eligibility for trace analysis of energetic materials in the environment as well.

Construction of present liquid chromatographs is really complicated for simple miniaturization and there is no suitable detector for detection of traces of energetic materials that could work with the miniaturized high performance liquid chromatograph at present time.

The next text describes the novel portable device for fast analysis of energetic materials in the environment which is assembled from an automated microcolumn liquid chromatograph of simple construction and miniaturized chemiluminescence detector.

II. Experimental

A block diagram of the whole device is shown in Figure 1. The device consists of miniaturized microcolumn liquid chromatograph and chemiluminescence detector. The designed device is controlled by a microprocessor control unit and data are gathered by a computer.

A. Miniaturized Microcolumn Liquid Chromatograph

A block diagram of separation part of the device is shown in Figure 1A. A linear actuator (Transmotec, Sweden) is connected to piston of a glass syringe (1) (SGE Analytical science, Australia). The needle of the syringe is connected to central port of selector valve (2) (Vici Valco, USA) via PEEK fingertight union (Upchurch Scientific, USA) and fused-silica capillary. This part of capillary forms also the sample loop. Mobile phase reservoir (3) is connected via fused-silica capillary to the first port, sample vial (4) is connected to the second port, and capillary column (5) (Agilent Technologies, USA) is connected to the third port of the selector valve. All fused-silica capillaries (Microquartz, Germany) have an i.d. of 220 μm while capillaries of 75 μm i.d. are used at column input and output.

Desired volume of the mobile phase was sucked into the syringe at the first step of analysis. Then the selector valve was switched to the next port and 10 μl of sample was sucked into the sample loop. After that the valve was switched to the third port and sample and mobile phase were pushed through

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the column.

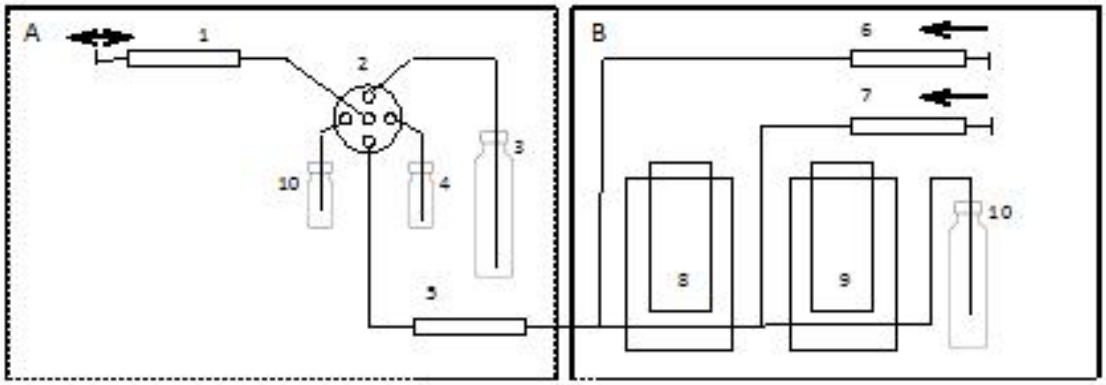

Fig. 1 Block diagram of µLC-Cl device
1 – syringe with mobile phase, 2 – selector valve, 3 – mobile phase reservoir, 4 – sample, 5 – capillary column, 6 – syringe with supporting solution, 7 – syringe with luminol solution, 8 – flash Xenon lamp, 9 – photomultiplier tube, 10 – waste

B. Chemiluminescence Detector

A block diagram of detection part of the device is shown in Figure 1B. The second linear actuator (Transmotec, Sweden) is connected to syringe with supporting solution (6) and syringe with luminol solution (7). The mobile phase flowing out of separation capillary column is mixed with a special supporting solution improving detection sensitivity in fingertight PEEK tee. Resultant solution flows through the fused-silica capillary of 100 µm i.d. and is irradiated using 15W flash Xenon lamp (8) (Hamamatsu, Japan). End of the capillary is inserted into the wide bore silica capillary of i.d. 530 µm through Teflon tee, where the luminol solution is added. Intensity of light emitted as a result of chemiluminescence reaction is measured by photomultiplier tube (9).

Electrical parts are extra-low voltage. Linear actuators are powered by 12 V, selection valve and flash Xenon lamp are powered by 24 V. As a source of energy, two small lead accumulators, both of capacity of 1.2 Ah are used.

C. Reagents

All solvents and chemicals used in this work were purchased from Sigma-Aldrich. Deionized water was obtained from a Millipore water purifier (Molsheim, France).

D. Verifying function

To verify the proper function of the device, a mixture of hexogen (RDX, at the concentration of 1×10^{-7} M), octogene (HMX, 1×10^{-7} M), and pentrit (PETN, 1×10^{-6} M) was used. A sample volume of 10 µl was injected to the column. A mobile phase consisted of 55 % v/v methanol in water at the flow rate of 6.5 µl/min was used. Separation was performed using the column Zorbax SB-C18, 0.5×35 mm filled by 3.5 µm particles at room temperature. Analyses were repeated continuously during 5 hours to demonstrate repeatibility of the results.

Response of the system to other nitramines, nitroesters and explosives marker was also tested. Standard solutions of 2,4,6-trinitrophenylmethylnitramine (tetryl, 3.5×10^{-7} M), nitroglycerine (NG, 1×10^{-6} M), ethyleneglycoldinitrate (EGDN, 1×10^{-6} M), and 2,3-dimethyl-2,3-dinitrobutane (DMDNB, 5×10^{-6} M) were prepared and analyzed under the conditions mentioned above.

Suitability of the system to analyze real samples was verified using a sample of soil containing no energetic materials which was spiked by solution of HMX, RDX (both at 1×10^{-7} M), and PETN (1×10^{-6} M). A small amount of spiked soil (ca 1 cm^3) was extracted with 10 ml of 10% v/v methanol in water (hand shaking for 2 minutes in 20 ml vial), filtered and analysed. The samples of real soils obtained from the place where explosives in soil are expected were prepared in the same way.

III. Problem Solution

Chromatographic separation of the mixture of HMX, RDX, and PETN is shown in Figure 2. Good resolution and narrow peaks indicate correct chromatography process with no significant extra-column dispersion. Overlay of three chromatograms obtained during 5 hours operation displayed in Figure 3 indicates high repeatability of results and proper function of the entire system. Figure 4 and Figure 5 show the respond of analytical system to other nitramines, nitroesters, and explosives marker. Limits of detection (LOD) (Table 1) of all compounds of interest are in the range of concentrations from 1×10^{-7} M to 5×10^{-9} M.

Figure 6 shows a chromatogram of energetic materials free soil extract. Despite the fact that the soil extract usually presents very complex sample, only nitrates in the sample are detected during this analysis and it proves an excellent selectivity of the detector. Analyses of spiked sample of soil (Figure 7) and analyses of real samples (Figure 8, 9) demonstrate that nitramines and nitroesters can be easily detected, determined, and quantified in such complex samples

as the soil extracts without any problems and additional time consuming sample pre-treatment procedures.

TABLE I
CALCULATED LIMITS OF DETECTION OF THE SYSTEM (S/N =3)

Sample	LOD [mol.dm^{-3}]	Sample	LOD [mol.dm^{-3}]
$-NO_3^-$	7.5×10^{-7}	DMDNB	9.4×10^{-7}
HMX	5.0×10^{-9}	EGDN	1.5×10^{-7}
RDX	1.5×10^{-8}	NG	1.5×10^{-7}
Tetryl	2.0×10^{-8}	PETN	3.8×10^{-7}

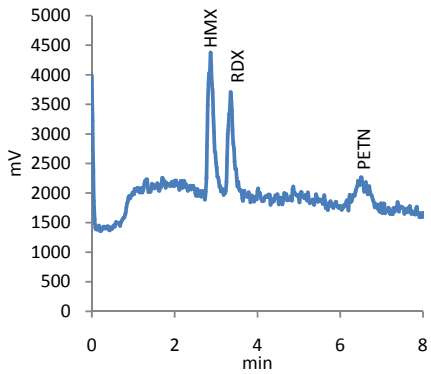

Fig. 2 Separation of test mixture of HMX, RDX 1×10^{-7} M and PETN 1×10^{-6} M

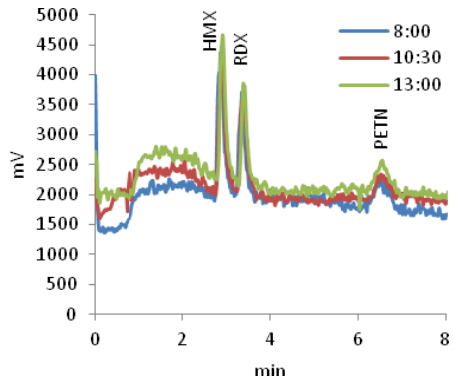

Fig. 3 Repeatability of measurement during the five hours operation

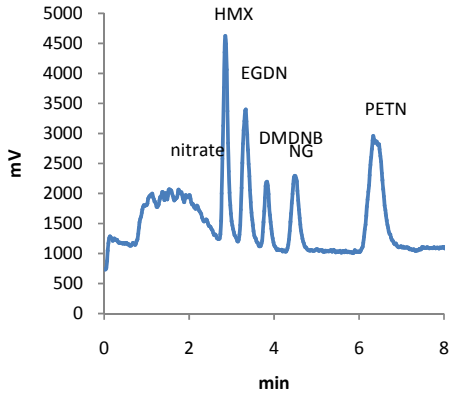

Fig. 4 Separation of test mixture containing nitrate 5×10^{-6} M, EGDN and NG 1×10^{-6} M and DMDNB 5×10^{-6} M

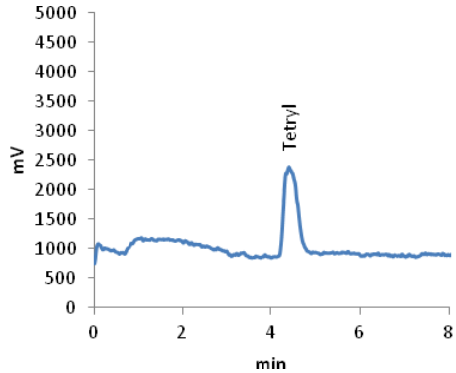

Fig. 5 Chromatogram of standard solution of Tetryl 3.5×10^{-7} M

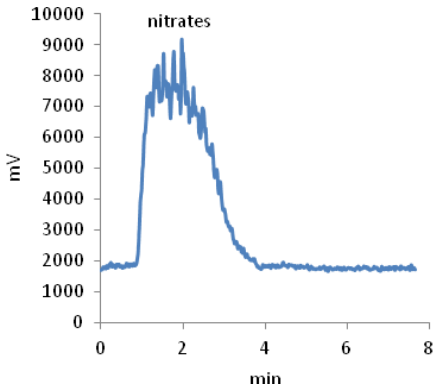

Fig. 6 Chromatogram of extract of energetic materials free soil; Nitrates detected

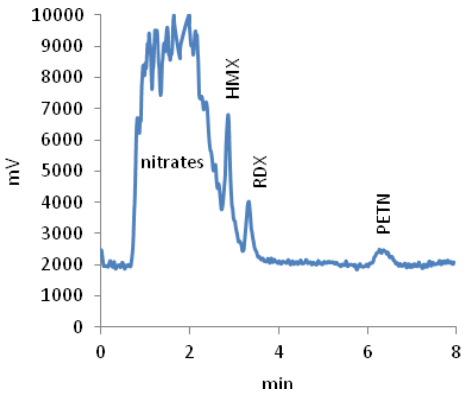

Fig. 7 Chromatogram of extract of spiked sample: soil spiked by HMX, RDX and PETN

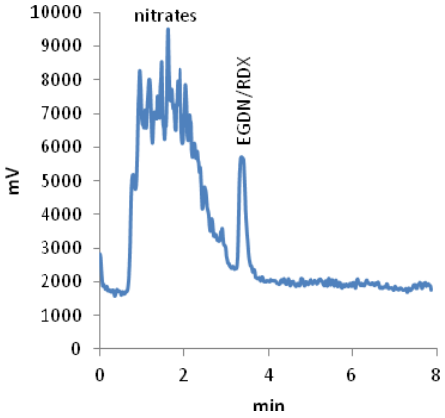

Fig. 8 Chromatogram of real soil extract; Nitrates and EGDN or RDX detected

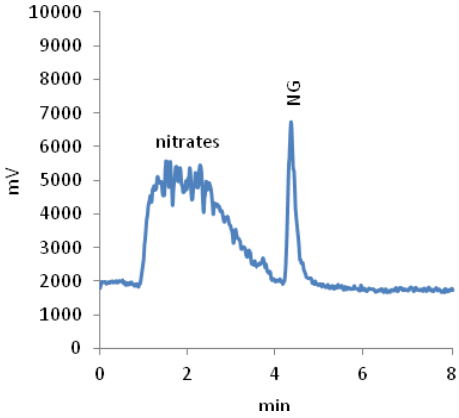

Fig. 9 Chromatogram of real soil extract; Nitrates and NG detected

IV. Conclusion

The novel portable device for analysis of energetic materials has been developed. The device consists of the miniaturized microcolumn liquid chromatograph and the chemiluminescence detector. Proper function of the device was demonstrated by analyses of standards, spiked sample of soil, and finally real samples of soil from ammunition disposal place. During the five hours operation high repeatability of results was achieved. Developed device is suitable to provide fast and very selective determination of inorganic nitrates and organic nitramines and nitroesters at trace concentrations without the need of complicated sample pre-treatment. Resistance to contamination and to long term decommissioning is another benefit of the designed novel system.

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