



Calhoun: The NPS Institutional Archive
DSpace Repository

NPS Scholarship

Publications

2008-02-01

**Gas Analytical Technologies for Physical
Protection of Oil and Gas Objects by Vladimir
Gruznov and M. Baldin; Strategic Insights, v. 7
issue 1 (February 2008)**

Gruznov, Vladimir

Monterey, CA; Naval Postgraduate School

Strategic Insights, v.7 issue 1 (February 2008)
<https://hdl.handle.net/10945/11189>

This publication is a work of the U.S. Government as defined in Title 17, United States Code, Section 101. Copyright protection is not available for this work in the United States.

Downloaded from NPS Archive: Calhoun



Calhoun is the Naval Postgraduate School's public access digital repository for research materials and institutional publications created by the NPS community. Calhoun is named for Professor of Mathematics Guy K. Calhoun, NPS's first appointed -- and published -- scholarly author.

Dudley Knox Library / Naval Postgraduate School
411 Dyer Road / 1 University Circle
Monterey, California USA 93943

<http://www.nps.edu/library>

Gas Analytical Technologies for Physical Protection of Oil and Gas Objects

Strategic Insights, Volume VII, Issue 1 (February 2008)

by [Vladimir Gruznov](#) and [M. Baldin](#)

Strategic Insights is a bi-monthly electronic journal produced by the Center for Contemporary Conflict at the Naval Postgraduate School in Monterey, California. The views expressed here are those of the author(s) and do not necessarily represent the views of NPS, the Department of Defense, or the U.S. Government.

Introduction

A difficult problem of explosives detection is not solved by a single method alone. For effective detection, complementary methods are used, among which methods of detection by odor are considered to be potentially useful.

Drugs can put the personnel of oil and gas sectors off their guard and create conditions for accidents and terrorist acts. Thus it makes sense to include drug detectors in the security system of objects.

The problems of gas analysis for detection of explosives and drugs are common:

- Low saturated vapor pressure of these substances, the packaging can considerably reduce the amount of vapor at the surface of the analyzed objects containing explosives and drugs;
- Low detection limit (no more than 10^{-14} g/cm³ at present) and a high selectivity of detectors are required to avoid the effect of interference compounds;
- Short detection time: 1÷5 s or 5÷30 s depending on the control conditions; and
- Development of small-sized detectors with a low power consumption.

The saturated vapor concentration of different explosives in air under normal environmental conditions is presented in [Table 1](#).

It is evident from the table that a very high linear range of the detector sensitivity is required for the detection of all indicated substances – 10^7 for detection of EGND and RDX.

The intensity of evaporation of plastic explosives is approximately 100 times lower as compared with hexogene.

Table 1: Saturated vapor concentration of different explosives in air.

Explosives	Concentration (Parts of explosives per 10^{12} air parts)[1]	Concentration (g/cm^3)
EGND (ethyleneglycoldinitrate)	100 000 000	$2,3 \cdot 10^{-7}$
NG (nitroglycerine)	580 000	
DNT (dinitrotoluol)	55 700	$1,4 \cdot 10^{-9}$
TNT (trinitrotoluene)	9 400	$3,7 \cdot 10^{-11}$
PETN	18	$9,2 \cdot 10^{-14}$
(pentaerythritol)		
RDX (hexogene or cyclonite)	6	$1,7 \cdot 10^{-14}$

In reality it is difficult to get rid of the explosive traces and vapors. [Figure 1](#) shows a cloud of vapors surrounding a person under normal conditions. The cloud rises with a speed of 0,2-0,5 m/s. Sampling of explosive traces from the object surface with a napkin followed by the sample analysis in a gas analyzer performs well.

Figure 1: Vapor cloud surrounding a person



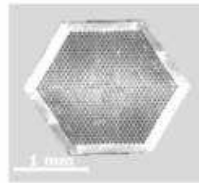
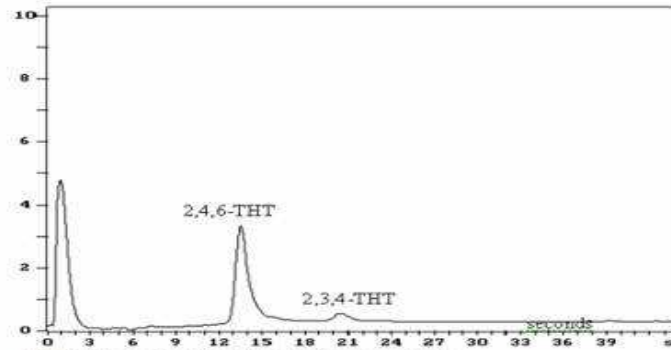
The results of a high-speed gas chromatography, ion mobility increment spectrometry and chromato-mass-spectrometry for the high-speed detection and identification of analyzed substances are presented in the report.

Gas Chromatography

A high-speed separation of a wide range of organic substances in a matter of 10-60 s is achieved by multicapillary columns (MCC) [2] with following characteristics: length, 22 cm; efficiency,

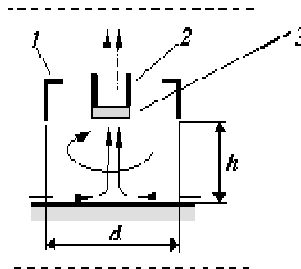
2000÷3000 theoretical plates (t.p.) for trinitrotoluene; the number of capillaries, 1000 +100; capillary diameter, 20÷40 μ m, the type of a stationary liquid phase: SE-30, OV-17, and SE-54, Carbowax-20M, OV-61, OV-7, OV-210, OV-215; film thickness, 0,15-0,2 μ m.

Figure 2: A MCC cross-section and a chromatogram of the trinitrotoluene isomer mixture showing a high-speed analysis in a matter of 30s



For remote sampling of explosive vapors from the analyzed object surface we developed a technique of a remote vortex sampling ([Figure 3](#)) The technique consists in blowing an object with a whirled air stream. This results in an air flow from the object to the vortex device. This air flow traps explosive vapors from the object and transfers them to a concentrator—as you can see on [Figure 3](#), or directly to the gas analyzer.

Figure 3: Circuit diagram of a vortex sampler: 1—whirl chamber, 2—path for pumping air through a concentrator, 3—concentrator



To determine the dependence of a pressure drop at the object surface versus distance h , it was assumed that a total rising air flow consisted of a flow from an object and a side flow. From this assumption an equation that allows one to determine relative pressure drop at the object surface was obtained:

$$\Delta P = 1 / [1 + K_p * h/5d]^2, (1)$$

where K_p is a constant value, d is a diameter of a whirl chamber.

Upon direct suction pressure drop at the object surface is determined by equation:

$$\Delta P = 1 / (1 + K_d * h)^4, (2)$$

where K_d is a constant value.

Analysis (1) and (2) demonstrate that upon vortex sampling with the increase of h pressure drop at the object surface is 100 times slower than upon direct suction. That is proved experimentally and theoretically [3]. It is determined that for the efficient sampling the ratio between the whirled and suction flows should be in the range between 0,5–1.

For efficient check of the objects (person, luggage, carry-on luggage) for the presence of explosives remote handheld vortex samplers with a power consumption of 5 W are developed. Sampling distance is from 0 to 20 cm from the analyzed surface. The use of the sampler is given on [Figure 5](#). (pos 2.).

Special concentrators and optimal modes of their operation are developed for high-speed vapor trapping in 2÷5 s.

An express mode of concentration with incomplete vapor trapping was considered.

A concentrator in the form of a bundle of n parallel capillaries with diameter d and length l was used.

The concentrator efficiency was characterized by breakthrough, β .

With the theory of vibrational relaxation of molecules that sorb at the surface (or desorb from the surface) an equation for β was obtained:

$$\beta = \exp(-Q_d/Q),$$

where Q is an air flow rate through the concentrator, is $Q_d = 6\pi D n l / S$, D is a coefficient of explosive vapor diffusion, S is a probability of explosive molecules adhesion to the concentrator surface. Signal A^Y of the chromatograph is:

$$A^Y = Q/Q_d [1 - \exp(-Q_d/Q)] (3)$$

From (3) follows that Q should be chosen almost equal to Q_d .

Based on the analysis of the high-speed thermal desorption efficiency, ε_i , of the concentrator, sample injection is determined:

$$\varepsilon_i = [1 - \exp(-t_d/a)] \times [1 - \exp(-t_i/b)],$$

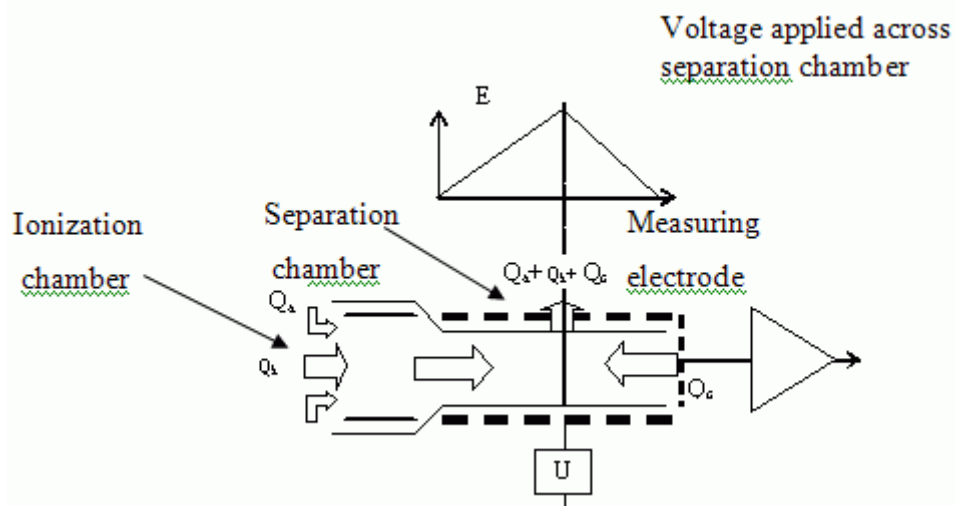
where α and b are constant values, t_d - time of desorption from the concentrator, t_i - time of sample injection.

As is evident it is possible[4] to achieve a short time of injection of 0,5 s. We used concentrators from a metal grid with a diameter of 0,08 mm.

The concentrator is placed into the sampler. After sampling the concentrator is removed with a gripping unit to the injection device of a gas-chromatograph, where upon the thermal desorption explosive vapors are injected into the separation column.

The development of a gas chromatography with air as a carrier-gas for explosive detection is an actual problem. Circuit diagram of such a detector is given on [Figure 4](#).

Figure 4: Circuit diagram of ion detector with a varying selectivity (IDVS)



The above mentioned technologies were used to develop a portable gas chromatographic detector EKHO –B with air as a carrier gas.

The device is characterized by the microprocessor control of analysis, PC for data processing and data display. Besides a concentrator injector the device contains a syringe injector for injecting liquid and gaseous samples, and an automatic sample loop that allows sampling every minute.

The main characteristics of EKHO–B:

- detection limit for 2, 4, 6 TNT – 10^{-14} g/cm³;
- time of vapor analysis 2, 4, 6 TNT – 15 sec; time of concentrator sampling – 5 to 10 sec.

The EKHO–B can be used both for detection and identification of explosives. The identification of the explosives is performed by a database of responses to these explosives. The database is embedded in the device and can be updated.

On [Figure 5](#) the device EKHO–B and its characteristics are shown, where 1 – EKHO–B; 2 – a car inspection; 3 – chromatogram of explosive mixture.

Figure 5: EKHO-B, the chromatogram is obtained with a GC with IDVS and air as a carrier gas

Express analysis of explosives and CW-agents in gaseous and liquid samples:

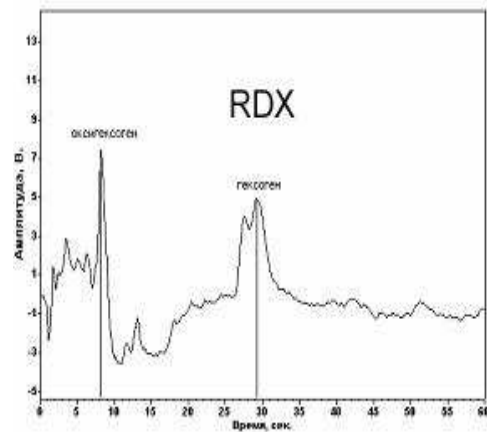


- Power consumption, W – no more than 70
- Weight without accumulator, kg – 6
 - Weight with accumulator, kg – 9
 - Sampler weight, kg – 1
- Detector – ion detector with a varying selectivity
- Gas chromatographic column – multicapillary column 20 cm

1.



2.



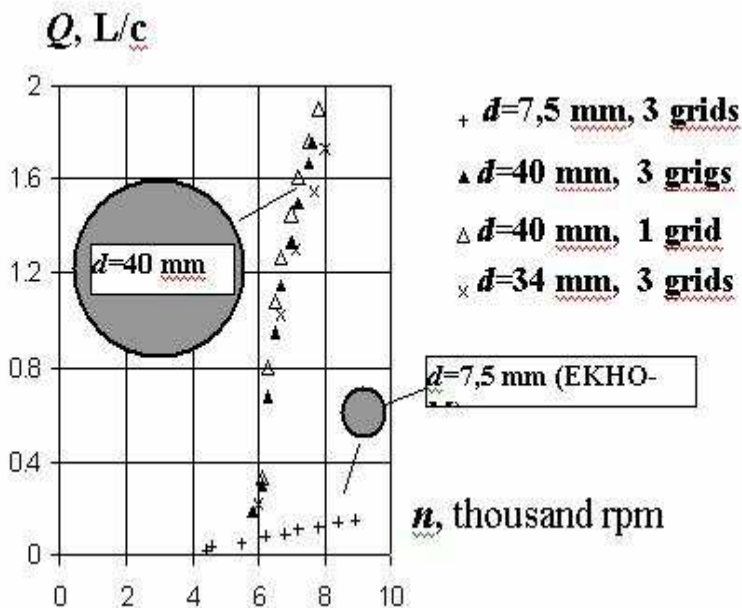
3.

second
Chromatogram of Hexogen vapors
adsorbed on a concentrator from air.
The chromatogram is obtained with a GC
with IDVS and air as a carrier gas.

A possibility to reduce detection limit was studied with a concentrator 40 mm in diameter with a sample reconcentration upon injection. The use of such a concentrator yields a 10 times increase of air flow rate, power consumption of the sampler is not increased therewith.

It is shown in [Figure 6](#). The increase of air flow rate with the same sampling time reduces the detection limit.

Figure 6: Air Flow Rate through the Concentrator of Different Diameters Versus Rotation Velocity of Centrifugal Pump Impeller



The concentrators are provided with a set of mesh grids with a mesh size of 0,08 mm. Engine power consumption is less than 5 W.

A concentrator of a diameter increased to 40 mm with a system of sample reconcentration assures the detection limit for explosives up to 10^{-15} g/cm. This system can be used for injecting samples from napkins with which upon special check the surface of suspicious objects is wiped.

Chromato-Mass-Spectrometry

To enhance analysis selectivity combined with a high-speed identification of detected compounds in the presence of interference substances a mobile-chromato-mass-spectrometer (MCMS) is developed[5].

The device includes: a mass-analyzer, magnetic, static with dual focusing; a high-speed concentrator-thermodesorber unit; a multi-channel chromatographic system with short multicapillary columns; a compact vacuum system based on two turbo-molecular pumps and a backing pump. The vacuum system is placed in an analytical unit and allows the device operation with a carrier-gas flow rate of $8 \text{ cm}^3/\text{min}$.

A high-speed injection device increases analytical performance capabilities of the device, as evidenced by the following parameters: a narrow sample pulse injected directly into the column without additional step of "thermal desorption-focusing," the rate of analysis in automatic mode of 50 samples/h; injection of gaseous and liquid samples; device operation at atmospheric pressure at the column inlet; enrichment factor of 10^4 upon analysis of impurities in air.

A "transfer line" method for connecting columns is realized in the multi-channel chromatographic system. The method consists in the use short capillary columns (3-10m), which outlet portion is in vacuum and is connected directly with ion source and the inlet one is kept at pressure near

atmospheric. Pressure drop between the inlet and outlet equal to 1 atm ensures carrier-gas flow through the column.

A multi-channel separation system[5] includes a number of chromatographic columns connected in parallel; each of the columns is placed in a separate thermostat with a temperature control. On one side the columns are connected to the ion source, and on the other side they can be connected to one injection device or to different ones. A mode of operation is isothermal. The operation parameters of the columns (type of a stationary liquid phase, geometric dimensions, temperature) differ and are determined according to a list of detected compounds. Such a system concept provides conditions for a high-speed separation of compounds differing in boiling temperature without temperature programming, which is an important factor for field devices and devices of automatic control.

A NIST/EPA database including about 120 thousand compounds is used to interpret mass-spectra. For setting the device parameters, processing the results a PC is used.

The MCMS has sensitivity and analysis time as EKHO gas chromatographs have.

Figure 7 gives the MCMS, the main parameters of the device and response to a drug of marihuana type.

Figure 7: Mobile Chromato-Mass-Spectrometer



Detection limit in air:

- without enrichment – 10^{-5} mg/l
- enrichment mode – 10^{-7} mg/l

Detection limit in extracts – 10^{-5} mg/ml

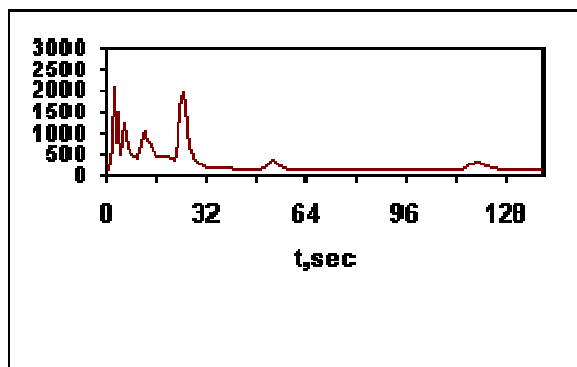
Rate of analysis – 10-100 analysis /h

Dimensions – 710x435x320 mm

Weight – 90 kg

Power consumption – 250 W

Mass range – 12-600 AMU.



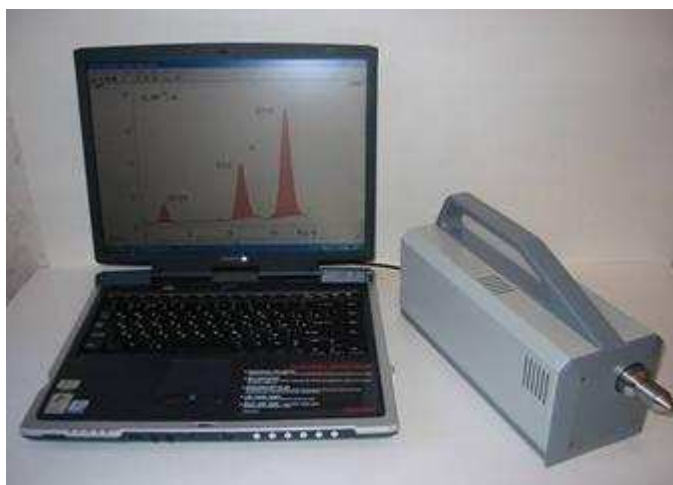
Ion Mobility Increment Spectrometry (IMIS)

To enhance speed of response upon detection of explosives and drugs, a method of ion mobility increment spectrometry is being developed. The method is based on taking gaseous samples, compound molecule ionization, spatial ion separation by the increment of a mobility coefficient in a strong electric field.

A possibility to detect TNT traces at a level of $2 \cdot 10^{-14} \text{g/cm}^3$ without preliminary concentration in a matter of seconds is shown [6, 7]. We have developed a method scheme that reduces the effect of environmental conditions on spectrometer response.

An IMIS prototype model with PC control is given on [Figure 8](#). The device can detect explosives (DNT, NTN, RDX, NG), drugs (cocaine, heroine, codeine, amphetamine). Time of one compound detection is less than 1 s. Time of detection of a list of compounds is 3-5 s, power consumption is 20 W.

Figure 8: Prototype Model of Ion Mobility Increment Spectrometer



Conclusion

In summary, it may be said that the above described methods and devices can be used under field and stationary conditions both for detection and identification of explosives, drugs, a number of toxic compounds and a list of other hazardous compounds. Different complexes for anti-terrorist protection of oil and gas objects can be developed based on these devices.

For more insights into contemporary international security issues, see our *Strategic Insights* home page. To have new issues of *Strategic Insights* delivered to your Inbox, please email ccc@nps.edu with subject line "Subscribe." There is no charge, and your address will be used for no other purpose.

References

1. B.C. Lionne, D.P. Roundbehler, E.K. Achter, J.R. Hobbs and D.H. Fine, *Journal of Energetic Materials*, 4 (1986): 447.

2. V.M. Gruznov, A.T. Shishmarev, V.G. Filonenko, M.N. Baldin, I.I. Naumenko, "Express analysis of environmental objects by means of portable gas chromatographs and multicapillary columns," *Journal of Analytical Chemistry* 54, no. 11 (1999): 1134-1139.
3. V.M. Gruznov, V.G. Filonenko, A.T. Shishmarev, "Sampling and sample injection upon high-speed detection of organic vapors," *Journal of Analytical Chemistry* 54, no. 11 (1999): 1134-1139.
4. V.M. Gruznov, M.N. Baldin, V.G. Filonenko, "High-Speed Gas Analysis for Explosives Detection," *NATO Science Series, II: Mathematics, Physics and Chemistry* 167 (2004): 87-99.
5. Alexei L. Makas, Mikhail L. Troshkov, "Field Gas Chromatography-Mass Spectrometry for Fast Analysis," *Journal of Chromatography B*, 800 (2004): 55-51.
6. I.A. Buryakov, "Express Analysis of Explosives, Chemical Warfare Agents and Drugs with Multicapillary Column Gas Chromatography and Ion Mobility Increment Spectrometry," *Journal of Chromatography B*, 800 (2004): 1-2, 75-82.
7. I.A. Buryakov, "The Analytical Characteristics of Ion Mobility Increment Spectrometer During the Detection of Explosive Vapours and Products of Their Degradation," *NATO Science Series, II: Mathematics, Physics and Chemistry* 167 (2004), 113-121.