FI SEVIER

#### Contents lists available at ScienceDirect

# Talanta

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



# Chemical analysis of post explosion samples obtained as a result of model field experiments



Rafal Borusiewicz\*, Grzegorz Zadora, Janina Zieba-Palus

Institute of Forensic Research, Westerplatte 9, 31-033 Krakow, Poland

#### ARTICLE INFO

Article history: Received 4 January 2013 Received in revised form 10 July 2013 Accepted 24 July 2013 Available online 30 July 2013

Reywords:
Forensic analysis
Explosives
Post-blast residues
HPLC

### ABSTRACT

Five different explosives were detonated in a series of field experiments. Each experiment (detonation of the charge of each specific explosive) was repeated three times. The experiments were conducted under controlled conditions, exceeding those of research published so far. Detonated charges were uniform in size and, as far as possible, in shape. The explosives used originated from the same batch. Additionally, the same kind of electric detonators were used. Witness plates (sheets of galvanised steel 100 cm × 90 cm × 0.5 mm) were used to collect post-blast residues in a reproducible way. They were placed relatively close to the charge to minimise the influence of the wind. Samples were collected by systematic swabbing of the surface of the plate by acetone moistened cotton swabs. Samples were packed tight, transferred to the laboratory, and extracted with methanol. Extracts were concentrated by solvent evaporation, cleaned by centrifugation, and analysed using HPLC-DAD. Each extract was analysed three times and the mean value of the amount of the given explosive within the extract was calculated. For each of the explosive materials used the results of the repetition of the experiments proved them to be irreproducible. After each detonation of a specific charge different amounts of given explosives were found in post-blast samples. Also, the intuitively expected relationship between the distance from the charge and amount of post-blast residues were not observed. These results are consistent with previously published results of field experiments. The lack of reproducibility may be explained by differences in efficiency of detonation. The efficiency of a detonation may be influenced even by small differences in the shape of the charge as well as by the position and properties of the detonator. The lack of dependency between the amount of the explosive in the post-blast samples and the distance from the charge may be explained by the fact that during detonation, particles of unreacted explosives are not uniformly dispersed in all directions.

© 2013 Elsevier B.V. All rights reserved.

# 1. Introduction

The detection of explosive materials at a crime scene enables investigators to distinguish between an explosion caused by an explosive as opposed to, for example, explosions caused by over pressurisation of hydraulic systems or accidental ignition of fuelair mixtures (flammable gases, vapors of flammable liquids, or dust mixed with air). Information about what kind of explosive was used also helps to establish its possible source and thus to identify the perpetrator. The procedures of sample preparation for different types of materials as well as the parameters of chromatographic analysis are published and available [1]. Nevertheless, there are still many problems to overcome. The most difficult problem concerns representative sampling and the consequent interpretation of analytical results. Detonation is a complex phenomenon that is

likely to be affected by the kind, size, and shape of the main explosive charge, along with the position and orientation of the detonator, and even the weather conditions at the time of detonation. To better understand those phenomena some authors conducted field experiments [2–11]. To collect the post explosive samples in a repetitive way and to eliminate contamination from previous detonations different approaches were utilised: detonation of the charges suspended above a layer of fresh snow or snow covered ice [4–7], using trays placed on the ground or a plastic tarp [5,7,8], or using witness plates placed vertically, and perpendicularly to the direction of the shock wave propagation [2,3,9–11].

Surprisingly, for all of the published research the results of experimental repetitions proved to be unrepeatable as different amounts of explosive residues were detected after each detonation in the same experimental setup [4–8]. The differences in the calculated amounts of given explosives remaining after detonation were very high and ranged over a few orders of magnitude, even if only high-order detonations were taken into account [4–6]. Furthermore an expected correlation between the amount of detected

<sup>\*</sup> Corresponding author. Tel.: +48 12 6185785; fax: +48 12 4223850. E-mail address: rborusiewicz@ies.krakow.pl (R. Borusiewicz).

explosives and distance from the detonated charge was not confirmed by experimental data [2–5,7].

Another expected correlation between the size of the charge (amount of explosive before detonation) and the amount of explosive within post explosion samples was also not confirmed by the results of field experiments [4,7].

The lack of reproducibility for detonation experiments is most often explained by the fact that the amount of unreacted explosive depends on the efficiency of the detonation. This can be affected even by small and random changes in the properties of an explosive, the shape of the charge, or the properties and position of detonator [2]. The same factor is most probably responsible for the lack of correlation between the size of the charge and the amount of explosive in the residues. Bigger charges can leave less residues compared to smaller ones if the detonation was more efficient.

The lack of correlation between the distance from the charge and the amount of explosive results, most probably, from the problems with representative sampling—particles of unreacted explosive which are dispersed by detonation are not homogenous in size and shape. Some bigger pieces being heavier can travel longer distances and if by chance they are sampled they can have influence on the results [2,4,5,8]. Another important factor which can influence the direction of the expansion of post explosion residues (and thus affect the results) is wind. The influence of wind was clearly confirmed by the results of detonations on snow. The soot darkened area was never circular but always skewed by the wind [4–6].

As it can be seen, there are many possible factors which can influence the amount and distribution of post explosive residues. The results of previously published research indicate that an explosion is a highly unreproducible process both for amount, and distribution of explosives residues. Nevertheless these conclusions cast doubts because they were drawn from limited data. Such limitations include: reliance of data from single experiments, or the experimental setup was not uniform for consequent experiments—charges of different sizes, shape, variations in the position of the detonator or differences in the booster charge utilised. Additionally, only one type of explosive material was used.

The aim of the presented research was to clarify the aforementioned doubts by conducting more extensive field experiments and in a more stringent and controlled way than previously published research. Uniform charges of explosives were detonated three times in the same experimental setup. Witness plates were situated close to the charges to eliminate the influence of wind.

The experiments (three detonations in the same experimental setup) were conducted for five of the most common explosives: TNT, RDX, PETN, dynamite, and Composition B.

# 2. Materials and methods

# 2.1. Materials and apparatus

Analysis was conducted using a liquid chromatograph with a diode array detector (LaChrom Elite, VWR-Hitachi, Radnor, Pennsylvania, USA) equipped with a CN column (LiChroCART 250-4; LiChrospher  $^{(g)}$  100 CN 5  $\mu m$ , Merck, Darmstadt, Germany). The capacity of the sample loop was 20  $\mu l$ . Gradient elution was conducted with a mixture of water, methanol, and acetonitrile (all solvents of gradient grade for liquid chromatography by Merck). The mobile phase was pumped at 1 mL/min. Each run lasted for 30 min. The equilibration time was 5 min. The analytical wavelength used for the calibration and analysis was 205 nm. The analytical signals (*y*), as peaks areas in arbitrary units, were measured using EZChrom Elite 3.1.7, Scientific Software Inc. The program of elution is

Table 1

The program of gradient elution for HPLC-DAD analysis. The mobile phase was pumped at 1 ml/min. The last two rows (30-35 min) describe the equilibration step.

Time [min]	Methanol [%]	Water [%]	Acetonitrile [%]
0	5	85	10
5	5	75	20
25	65	15	20
26	80	0	20
30	80	0	20
30.1	5	85	10
35	5	85	10

 Table 2

 Concentration of analytes in standard mixtures which were used for calibration.

Standard number	EGDN [mg/ml]	NG [mg/ml]	RDX [mg/ml]	TNT [mg/ml]	PETN [mg/ml]
1	0.0465	0.0465	0.0461	0.0471	0.0466
2	0.0326	0.0326	0.0323	0.0330	0.0326
3	0.0233	0.0233	0.0231	0.0236	0.0233
4	0.0140	0.0140	0.0138	0.0141	0.0140
5	0.0046	0.0046	0.0046	0.0047	0.0047

presented in Table 1. An exemplary chromatogram obtained for a standard mixture of analysed compounds (standard no. 1, see Table 2) is presented in Fig. 1.

#### 2.2. Calibration, LOD and LOQ

Standard mixtures for the five most common organic explosives (EGDN, NG, PETN, TNT, and RDX) were used for calibration. Solutions of PETN, TNT, and RDX were obtained by dissolving pure substances in methanol (explosives produced by NITROERG, Bierun, Poland). For NG and EGDN, ready standard solutions were utilised: 0.1 mg of NG in ethanol and 0.1 EGDN in acetonitrile (both standards by AccuStandard inc, New Haven, CT, USA). Ready standard mixtures were stored in a fridge, in the temperature 0 °C. The concentration of analytes in standard mixtures are presented in Table 2. Four analyses were conducted for each of the five calibration levels. For each of the analytes the equation of the calibration curve was calculated using linear the regression method. Parameters of the calibration curves described by equation y=ax+b are given in Table 3.

The calculations with application of t-Student test were made in the aim to confirm the linearity range, which was determined by minimum and maximum concentrations of the analytes in standard mixtures which were used for calibration. (see Table 2). The following two null hypothesis ( $H_0$ ) were considered:

- a) the calculated slope (a) is equal to zero ( $H_0$ : a=0),
- b) the calculated intercept (b) is equal to zero ( $H_0$ : b=0).

In the case of linear dependency y=axe+b the expected result is to reject the null hypothesis for slope and accept the null hypothesis for the intercept.

The limit of detection (LOD) and limit of quantification (LOQ) were also determined for each of organic explosives. Fluctuations of the baselines in the proximity of analytes peaks, caused by unknown co-extracted impurities were measured in the form of peak areas. Ten values of peaks areas were obtained for each of the analytes and they were used to calculate the concentrations, using

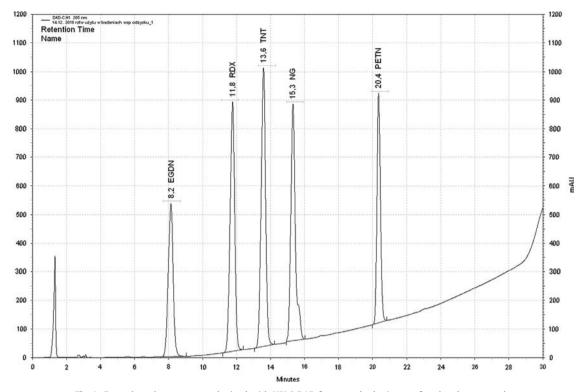


Fig. 1. Exemplary chromatogram obtained with HPLC-DAD for a standard mixture of analysed compounds.

**Table 3** Parameters of the calibration curves described by equation y=ax+b.

Analyte	а	b	r <sup>a</sup>	LOD [mg/ml]	LOQ [mg/ml]
EGDN	$1.95 \times 10^{8}$ $\pm 3.04 \times 10^{5}$ $0.23^{b}$	$-1.07 \times 10^{5}$ $\pm 8.58 \times 10^{4}$ $< 0.0001^{b}$	0.998	0.0007	0.0020
RDX	$2.62 \times 10^{8}$ $\pm 3.95 \times 10^{5}$ 0.47	$-8.17 \times 10^{4}$ $\pm 1.10 \times 10^{5}$ $< 0.0001$	0.998	0.0011	0.0033
TNT	$\begin{array}{l} 2.74 \times 10^8 \\ \pm 5.62 \times 10^5 \\ 0.47 \end{array}$	$\begin{array}{l} -1.17\times 10^5 \\ \pm 1.61\times 10^5 \\ < 0.0001 \end{array}$	0.996	0.0016	0.0046
NG	$\begin{array}{l} 1.79 \times 10^8 \\ \pm 2.91 \times 10^5 \\ 0.53 \end{array}$	$\begin{array}{l} -5.26 \times 10^4 \\ \pm 8.20 \times 10^4 \\ < 0.0001 \end{array}$	0.998	0.0014	0.0043
PETN	$\begin{array}{c} 1.71 \times 10^8 \\ \pm 2.89 \times 10^5 \\ 0.52 \end{array}$	$\begin{array}{l} -5.33 \times 10^4 \\ \pm  8.16 \times 10^4 \\ < 0.0001 \end{array}$	0.997	0.0014	0.0041

<sup>&</sup>lt;sup>a</sup> r-Pearson correlation coefficient,

appropriate calibration curves. After that, mean of concentration  $(\bar{x})$  as well as standard deviation (s) were calculated for each of organic explosives and these values were used for LOD calculation:

$$LOD = \overline{x} + 3s \tag{1}$$

The LOQ was calculated from equation:

$$LOO = 3LOD. (2)$$

# 2.3. Monitoring of the instrument stability

To monitor the HPLC-DAD stability in time with each batch of samples, a standard mixture was analysed. For this purpose standard no. 1 (see Table 2) was used. Shewhart's charts were drawn for the analysed explosives. A control chart is a diagram

which includes the values of any variables (e.g. concentration) for a standard in relation to time (i.e. day of measurement). The diagram consists of a centre line, drawn at the mean which is calculated from all measurements along with upper and lower warning limits. These are drawn as separate lines,  $\pm$  1 SD,  $\pm$  1.96 SD, and  $\pm 3.09$  SD above and below the centre line (where SD is the standard deviation of the concentration for all measurement values). The control chart allows the analyst to check whether measurement errors occurred on a specified day, which might influence the results. When the measurement point for the standard crosses the so-called "alarm lines" (  $\pm$  1.96 SD lines), this indicates that a new calibration is required. If the measurement point for the new standard sample and new calibration crosses the alarm line again, the user should check the measurement system. If the measurement point for the standard crosses the so-called "action lines" ( $\pm$ 3.09 SD lines), the user should start a control procedure, which is consistent with a laboratory quality system.

# 2.4. Comparison of organic solvents for extraction of the explosives from the cotton swabs

Within the literature there is a variation in the type of solvent utilised for the extraction of explosives from solid samples [2,3,6,8,12–18]. Therefore, before starting the field experiments research was conducted to ascertain which of the three organic solvents (methanol, acetone, or acetonitrile) is the most suitable to conduct the extraction of explosives from cotton–wool swabs. Sterile cotton–wool meant for medical use (Paso-Trading, Pabianice, Poland) was used. A given volume (5 ml) of a standard mixture of explosives (standard no 1 – see Table 2) was spiked, using automatic pipette, on each of three pieces of cotton–wool placed in the beakers and they were left to dry. Each piece of cotton–wool was then extracted with two portions of each of the solvents in a following way: a piece of cotton–wool was placed into a beaker and the solvent was added in such a volume to cover it. The beaker was placed in a ultrasonic bath (Sonic-2 by Polsonic,

 $<sup>^{\</sup>rm b}$  Significance probability (p-value) obtained during suitable hypothesis testing with application of t-Student test.

Warsaw, Poland) for 10 min. The extract was then separated and placed into another beaker and the second portion of the solvent was added to the sample, which was sonicated again for 10 min. Extracts were combined and concentrated by solvent evaporation using water a bath (MLL 147 by AJL Electronic, Krakow, Poland) to a volume smaller than 5 ml. The concentrated extract was transferred into a measuring cylinder and the solvent was added to a total volume of 5 ml. The extract was mixed and 1.5 ml of it was transferred into a micro tube (Eppendorf, Hamburg, Germany). Solid particles were separated by centrifugation (Centrifuge 5415D by Eppendorf) and the obtained clean extract was analysed three times by HPLC-DAD. Additionally, the standard mixture no. 1. which was spiked to the cotton-wool, was analysed three times. Mean values of the signals in combination with the standard deviations, and standard errors of the mean (SEM) were calculated. As the volumes of the extracts were the same as the volume of the standard mixture spiked on pieces of cotton-wool (5 ml), the effectiveness of the extraction was calculated as a ratio of mean values of the signals for the extract and standard according to the following equation:

$$E = \frac{\overline{X}_{ex}}{\overline{X}_{st}} 100\% \tag{3}$$

Where, E-effectiveness of extraction;  $\bar{x}_{ex}$ -mean signal for the extract; and  $\bar{x}_{st}$ -mean signal for the standard.

The uncertainty ( $\delta E$ ) was calculated according to the following equation [19]:

$$\delta E = \sqrt{\left(\frac{\text{SEM}_{ex}}{\overline{x}_{ex}}\right)^2 + \left(\frac{\text{SEM}_{st}}{\overline{x}_{st}}\right)^2} 100\%$$
 (4)

Where,  $SEM_{ex}$ —standard error of the mean for the extract and  $SEM_{sr}$ —standard error of the mean for the standard.

Values of SEM for the extracts and the standard were calculated according to the following equation:

$$SEM = \frac{SD}{\sqrt{n}}$$
 (5)

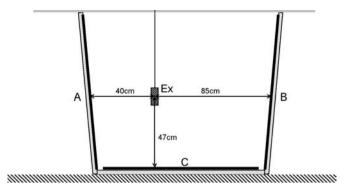
Where, SD-standard deviation and n-number of analyses.

# 2.5. Extraction procedure

The samples (cotton swabs) from the field experiments were extracted with two portions of methanol using the same method as described for the experiments to select the most effective solvent for extraction (point 2.4). The extract obtained for each of the samples was analysed three times by HPLC-DAD.

# 2.6. Experimental blasts, sampling, and analysis

The field experiments consisted of detonating charges of different explosives placed at a specific distance from three witness plates. These rectangular plates (100 cm  $\times$  90 cm  $\times$  0.5 mm) were composed of galvanised steel sheets. The experimental setup is shown in Fig. 2. Each of the charges consisted of the explosive material wrapped in aluminium foil with the electric detonator placed vertically. Each charge was wrapped in a piece of clean, white cotton towel  $(30 \times 60 \text{ cm}^2)$  and hung between two witness plates (Fig. 2, plates A and B), located at a distance of 40 cm and 85 cm, and above the third one (Fig. 2, plate C), 47 cm from the charge. For each experiment fresh (unused) plates were used. After detonation, remains of the cotton towel were collected (representing the material which was in direct contact with the charge before detonation) and witness plates were sampled by systematic, manual swabbing with cotton-wool moistened with acetone. Acetone was chosen for sample collection as it is a universal solvent thus enabling the efficient recovery of traces of organic



**Fig. 2.** Experimental setup for the detonation of charges of investigated explosive materials. A, B, and C—witness plates and Ex—charge of explosive material.

explosives from impermeable surfaces most efficiently. This method has been successfully used by other researchers [2,3,8]. After sampling, the swabs were placed in Erlenmeyer flasks, and tightly closed with ground glass stoppers secured with parafilm (Pechiney Plastic Packaging, Manasha WI, USA). The samples were then transported to the laboratory, extracted, and analysed.

Three series of field experiments were conducted. In each of the series, five charges of different explosives were detonated: 50 g of TNT (pressed charge), 50 g of dynamite (containing EGDN and TNT), 10 g of PETN (as eight pieces of 12 g/100 cm detonating cord), 10 g of RDX (pure, crystalline), and 10 g of Composition B (59.5% RDX, 39.5% TNT, 1% wax). The explosives used in the experiments were produced by NITROERG, Bierun, Poland. The explosive traces on the remains of the cotton towels and cotton swabs were extracted with methanol as described in Section 2.5 (Extraction procedure). Each extract was analysed three times using HPLC-DAD as described in Section 2.1 (Materials and apparatus) and the concentration [mg/mL] was calculated using an external calibration. The calibration process was described in Section 2.2 (Calibration) and the parameters of calibration curves are given in Table 3. If the result of the first analysis indicated that the concentration of a given explosive in the extract exceeded the calibration range, the extracts were properly diluted and analysed three times. On the basis of the concentration values for each of the extracts, the total content of the given analyte was calculated [mg] considering dilution where applicable. For each extract a mean value of the analyte content  $(\bar{x})$ , standard error of the mean (SEM), and relative standard error of the mean (RSEM) were

RSEM was calculated according to the following equation:

$$RSEM = \frac{SEM}{\overline{x}} 100\% \tag{6}$$

Where,  $\bar{x}$ —mean value of the analyte content in the extract.

# 3. Results and discussion

#### 3.1. Calibration, LOD, and LOQ

The parameters of the calibration curves (y=ax+b) are given in Table 3. The value of Pearson correlation coefficient (r) was higher than 0.995 for each of five analysed compounds, indicating that within the calibration range the dependence between the concentration and the signal is linear.

The calculated significance probabilities (p-values; Table 3) were above assumed significance probability ( $\alpha$ =0.05) when H<sub>0</sub>: b=0 was tested and below when H<sub>0</sub>: a=0. Therefore, it could be concluded that within the range determined by minimum and maximum concentrations of the analytes in standard mixtures

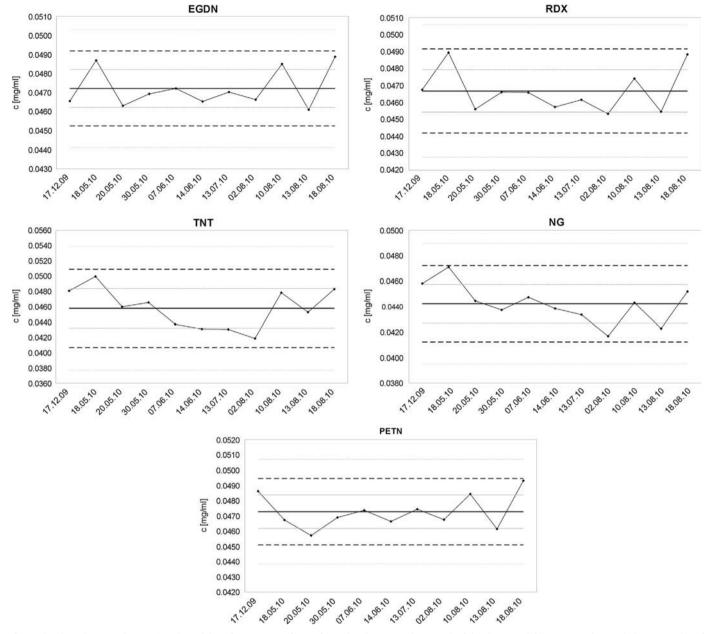


Fig. 3. Shewhart charts used to monitor the stability of the response factors for analysed compounds. On each of the charts a solid line was used to mark the mean value of the concentration, a dotted line was used to mark the mean  $\pm$  standard deviation, a dashed line was used to mark mean  $\pm$  1.96 standard deviation, and a dash-dot line was used to mark the mean  $\pm$  3.09 standard deviation.

(see Table 2), function y=f(x) could be treated like a linear one (y=ax+b) for each of the five explosive materials.

Values of LOD and LOQ are presented in Table 3.

# 3.2. Instrument stability

On Shewhart's charts which were drawn for analysed explosives, the values of the concentration for standard samples analysed with each batch of field samples lay within the range mean  $\pm$  1.96 SD, indicating that calibration curves (external calibration) could be used to calculate the concentrations of the analytes (Fig. 3).

# 3.3. Comparison of extraction solvents

The effectiveness of extraction (*E*) of organic explosives from cotton swabs calculated for methanol, acetonitrile, and acetone are

given in Table 4. The results are consistent with those obtained by other authors [3]. Methanol proved to be the most effective solvent and was used to extract the post explosion samples.

# 3.4. Results of field experiments

The results of the field experiments are given in Table 5. Although every effort was made to reproduce the experimental setup for each repetition (the same batch of explosive material, the same kind and location of detonator, the same shape of charge, and distance from the witness plates) different results were obtained (e.g. for detonations of dynamite and the witness plate situated at a distance of 40 cm, the amount of EGDN found in extracts were 19.6 mg, 4.5 mg, and 1.5 mg). This result confirms those obtained by other researchers [4–8] and the statement that even small and random changes in the shape of the charge or position and properties of the detonator can influence the

**Table 4**Effectiveness of the extraction of explosive compounds from cotton swabs for methanol, acetonitrile, and acetone.

Effectiveness Analyte	of extraction (E) [%] Methanol	Acetonitrile	Acetone
EGDN	$55\pm0.6^{\text{a}}$	$50 \pm 0.9$	$49 \pm 0.5$
RDX	$67 \pm 0.6$	$54 \pm 0.7$	$64 \pm 0.6$
TNT	$66 \pm 0.6$	$54 \pm 0.6$	$62 \pm 0.5$
NG	$67 \pm 0.6$	$57 \pm 0.5$	$62 \pm 0.4$
PETN	$72 \pm 0.6$	$62 \pm 0.5$	$68 \pm 0.6$

<sup>&</sup>lt;sup>a</sup>  $E \pm \delta E$ , see Eqs. (1) and (2).

**Table 5**Mean values of the content of explosives in the analysed extracts.

Distance [cm]	Experiment 1	Experiment 2	Experiment 3			
ECDN from dynamite (mean content + SEM <sup>a</sup> [mg])						
0	$14.1 + 0.8(6)^{b}$	0.74 + 0.03(3)	$1.50 \pm 0.02(1)$			
40	$19.62 \pm 0.08(0.4)$	$4.52 \pm 0.07(1.4)$	$1.535 \pm 0.02(1)$			
47	$5.69 \pm 0.05(0.8)$	$5.91 \pm 0.09(1.6)$	$1.72 \pm 0.02(1)$			
85	$4.95 \pm 0.02 (0.4)$	$3.16 \pm 0.02(0.7)$	$0.579 \pm 0.003(0.5)$			
NG from dynam	$oldsymbol{nite}$ (mean content $\pm$ SE	EM [mg])				
0	$130 \pm 7(5)$	$8.9 \pm 0.1(1)$	$7.77 \pm 0.02(0.2)$			
40	$175 \pm 1(0.6)$	$11.3 \pm 0.2(2)$	$5.18 \pm 0.08(1.5)$			
47	$147 \pm 1.5(1)$	$16.1 \pm 0.3(2)$	$7.2 \pm 0.1 (1.6)$			
85	$122 \pm 1(1)$	$13.66 \pm 0.06 (0.4)$	$2.56 \pm 0.02 (0.8)$			
,	$ntent \pm SEM [mg])$					
0	$0.60 \pm 0.01(2)$	$0.219 \pm 0.010(4)$	n.d.			
40	$0.436 \pm 0.008(2)$	n.d. <sup>c</sup>	$0.103 \pm 0.002(1.6)$			
47	$0.1389 \pm 0.0005(0.4)$	n.d.	$0.197 \pm 0.002(1.0)$			
85	$0.227 \pm 0.002(0.8)$	n.d.	$0.137 \pm 0.001 (0.7)$			
•	$tent \pm SEM [mg]$ )					
0	$0.728 \pm 0.002(0.3)$	$0.72 \pm 0.02(2.6)$	$1.47 \pm 0.02(1)$			
40	$0.5864 \pm 0.0004(0.1)$	$1.47 \pm 0.05(3)$	$1.78 \pm 0.04(2.4)$			
47	$2.03 \pm 0.02(1)$	$2.37 \pm 0.03(1.5)$	$1.09 \pm 0.02(1.5)$			
85	$0.94 \pm 0.01 (1.3)$	$0.76 \pm 0.01 (1.8)$	$0.192 \pm 0.002(1)$			
TNT (mean cont	$tent \pm SEM [mg]$					
0	$17.8 \pm 0.2(0.9)$	$188 \pm 4(2.2)$	$35.6 \pm 0.5 (1.3)$			
40	n.d.	$9.0 \pm 0.2 (1.7)$	$22.1 \pm 0.1(0.5)$			
47	n.d.	$2.3 \pm 0.1(2.5)$	$7.68 \pm 0.04(0.5)$			
85	$0.058 \pm 0.001 (0.9)$	$0.141 \pm 0.001 (0.9)$	$7.2 \pm 0.1 (1.5)$			
RDX from Com	<b>RDX from Composition B</b> (mean content $\pm$ SEM [mg])					
0	$9.33 \pm 0.08(0.9)$	n.d.	$0.0615 \pm 0.0006(1)$			
40	$8.75 \pm 0.04(0.4)$	n.d.	$0.1007 \pm 0.0008(0.8)$			
47	$10.1 \pm 0.2(2)$	n.d.	$0.060 \pm 0.001(2)$			
85	$7.381 \pm 0.005 (0.07)$	$0.0562 \pm 0.0004 (0.6)$	$0.328 \pm 0.003 (1)$			
<b>TNT from Composition B</b> (mean content $\pm$ SEM [mg])						
0	$15.8 \pm 0.2 (1.2)$	n.d.	$0.106 \pm 0.002(2)$			
40	$17.25 \pm 0.08(0.4)$	n.d.	$0.0151 \pm 0.0001(0.7)$			
47	$5.49 \pm 0.10(2)$	n.d.	n.d.			
85	$1.469 \pm 0.003 (0.2)$	n.d.	n.d.			

<sup>&</sup>lt;sup>a</sup> SEM (Standard Error of the Mean).

efficiency of a detonation and the amount of unreacted explosive in post-blasts samples.

Analysis of variance (ANOVA) [20] was conducted to determine if there was a dependence between the distance from the charge and the amount of detected explosives for each of the experiments. The ANOVA analysis proved that for each experiment the results obtained for a given explosive and distance were similar and at the same time statistically different from results obtained for other distances. Nevertheless, the dependency which might be expected (the higher the distance from the charge the lower the amount of detected explosive) was not confirmed by statistical analysis. This result corresponds with results obtained

by other researchers [2–5,7]. This may be a result of two phenomena, either independently or combined: relatively big particles of unreacted explosive material from the surface of the charge are randomly dispersed by explosion and they could be thrown toward the more distant witness plate influencing the result of analysis, or that the detonator is never placed exactly in the centre of the charge and the charge itself is not spherical. Because the position of the detonator influences the direction of the expansion of the explosion gases [2], dispersion of particles of the unreacted explosive is not uniform and a higher amount can be directed toward the more distant witness plate.

# 4. Conclusion

The conducted experiments were more extensive, stringent, and uniform than previously published research. Three charges from each of five different explosive materials were detonated in the same experimental setup and samples were collected and analysed in the same way. Obtained results confirmed that an explosion is a highly unreproducible process both for the total amount and distribution of explosive residues in post-blast samples.

Although each of the experiments were conducted in a repeatable and uniform fashion (as much as possible in field conditions), the results proved to be unrepeatable for each of the five explosives tested. Different amounts of the explosives were found in the post-blast samples after each detonation of a specific charge. This lack of reproducibility may be explained by differences in the efficiency of a detonation which can, apparently, occur even for seemingly identical charges. Also, the intuitively expected relationship between distance from the charge and the amount of post-blast residues was not observed. This may be explained by the fact that during detonation particles of unreacted explosives are not uniformly dispersed in all directions.

# Acknowledgements

The authors wish to thank Dr. Ryszard Morawa (Department of Opencast Mining, AGH University of Science and Technology, Krakow, Poland) for professional help with performing the detonation experiments, Prof. Andrzej Parczewski (Faculty of Chemistry, Jagiellonian University, Krakow, Poland and The Institute of Forensic Research, Krakow, Poland) for his helpful comments, and Dr. Christopher Rogers (Natural History Museum, London, UK) for his helpful comments and language support.

This research was financially supported by the Ministry of Science and Higher Education, Poland, with the project no. N204-O/0020/32, and by The Institute of Forensic Research, Krakow, Poland, within the project no. V/K/2007–10.

# References

- [1] R. Borusiewicz, Prob. Forensic Sci. 69 (2007) 5–29.
- [2] P. Kolla, A. Sprunkel, J. Forensic Sci. 40 (1995) 406-411.
- [3] R.Q. Thompson, D.D. Fetterolf, M.L. Miller, R.F. Mothershead II, J. Forensic Sci. 44 (1999) 795–804.
- [4] T.F. Jenkins, M.E. Walsh, P.H. Miyares, A.D. Hewitt, N.H. Collins, T.A. Ranney, Thermochim. Acta 384 (2002) 173–185.
- [5] S. Taylor, A. Hewitt, J. Lever, C. Hayes, L. Perovich, P. Thorne, C. Daghlian, Chemosphere 55 (2004) 357–367.
- [6] A.D. Hewitt, T.F. Jenkins, M.E. Walsh, M.R. Walsh, S. Taylor, Chemosphere 61 (2005) 888–894.
- [7] J.C. Pennington, S. Brochu, M.R. Walsh, A.D. Hewitt, Residues Resulting from Blow-in-Place of Specific Munitions, Chapter 5 in Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report. U.S. Army Engineer Research and Development Center, Vicksburg, 2006, pp. 103–119. <a href="http://el.erdc.usace.army.mil/elpubs/pdf/tr06-13.pdf">http://el.erdc.usace.army.mil/elpubs/pdf/tr06-13.pdf</a> (accessed 10.07.2013).

<sup>&</sup>lt;sup>b</sup> In brackets— values of relative SEM [%].

c n.d.-not detected.

- [8] S. Taylor, E. Campbell, L. Perovich, J. Lever, J. Pennington, Chemosphere 65 (2006) 1405–1413.
- [9] J.P. Hutchinson, C.J. Evenhuis, C. Johns, A.A. Kazarian, M.C. Breadmore, M. Macka, E.F. Hilder, R.M. Guijt, G.W. Dicinoski, P.R. Haddad, Anal. Chem. 79 (2007) 7005–7013.
- [10] J.P. Hutchinson, C. Johns, M.C. Breadmore, E.F. Hilder, R.M. Guijt, C. Lennard, G. Dicinoski, P.R. Haddad, Electrophoresis 29 (2008) 4593–4602.
- [11] C. Johns, R.A. Shellie, O.G. Potter, J.W. O'Reilly, J.P. Hutchinson, R.M. Guijt, M.C. Breadmore, E.F. Hilder, J. Chromatogr. A 1182 (2008) 205–214.
- [12] A. Hilmi, J.H.T. Luong, S. Nguyen, J. Chromatogr. A 844 (1998) 97-110.
- [13] C.R. Bowerbank, P.A. Smith, D.D. Fetterolf, M.L. Lee, J. Chromatogr. A 902 (2000) 413–419.
- [14] C.W. Wiliford, R.M. Bricka, J. Hazard. Mater. 66 (1999) 1-13.

- [15] S. Calderara, D. Gardbas, F. Martinez, Forensic Sci. Int. 137 (2003) 6–12.
- [16] C.A. Groom, S. Beaudet, A. Halasz, L. Paquet, J. Hawari, J. Chromatogr. A 909 (2001) 53–60.
- [17] R. Boopathy, J. Manning, C.F. Kulpa, Int. Biodeterior. Biodegrad. 41 (1998) 67–74.
- [18] Halasz, C. Groom, E. Zhou, L. Paquet, C. Beaulieu, S. Deshamps, A. Corriveau, S. Thiboutot, G. Ampleman, C. Dubois, J. Hawari, J. Chromatogr. A 963 (2002) 411–418.
- [19] J.R. Taylor, An Introduction to Error Analysis, The Study of Uncertainties in Physical Measurements, second ed., University Science Books, Sausalito, California, 1997.
- [20] R.R. Sokal, F.J. Rohlf, Biometry: the Principles and Practice of Statistics in Biological Research, third ed., W. H. Freeman and Company, New York, 2000.