

APARATURA

BADAWCZA I DYDAKTYCZNA

Application of capillary electrophoresis for selected inorganic ions determination after explosive transformation of pyrotechnic materials

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ABSTRACT:

Capillary electrophoresis (CE) method was applied for qualitative and quantitative determination of ions: ClO_3^- , ClO_4^- , NO_3^- , NH_4^+ , K^+ in pyrotechnic materials after explosive transformation. After explosion of fire-cracker with black powder and military fire-cracker, soil samples from explosion area were collected, extracted and analyzed by CE method. Determined limits of quantifications were from 0.78 mg/L for K^+ to 3.12 for NO_3^- . The CE method allowed to distinguish pyrotechnic materials on the basis of selected ions determination in pyrotechnic materials residues.

Zastosowanie elektroforezy kapilarnej do oznaczania wybranych jonów nieorganicznych w pozostałościach po przemianie wybuchowej materiałów pirotechnicznych

Słowa kluczowe: materiały pirotechniczne, elektroforeza kapilarna, jony nieorganiczne

STRESZCZENIE:

Zastosowano metodę elektroforezy kapilarnej (CE) do oznaczenia jakościowego i ilościowego jonów: ClO_3^- , ClO_4^- , NO_3^- , NH_4^+ , K^+ w pozostałościach po przemianie wybuchowej materiałów pirotechnicznych. Po wybuchu petardy hukowej FP3 i petardy wojskowej pobrano próbki gleby z miejsca wybuchu i poddano je ekstrakcji, a następnie analizie metodą CE. Wyznaczone granice oznaczalności wynosiły od 0,78 mg/l dla K^+ do 3,12 dla NO_3^- . Metoda CE pozwoliła na rozróżnienie materiałów pirotechnicznych na podstawie oznaczenia wybranych jonów w pozostałościach po wybuchu.

1. INTRODUCTION

One of the many problems of the modern world becomes the intensity of the terrorist activity. Terrorists in their operations often use different kind pyrotechnic materials. The easier is the access to pyrotechnic material and the simpler method of its construction, more often it is used in terror attacks. Pyrotechnic materials are very often used by various criminal groups [1, 2]. Lately there is an intense growth of the offences number with the use of pyrotechnic mixtures in the different kind of bursters. Mixtures and pyrotechnic materials are usually binary mechanical mixtures of oxidants (oxygen carriers) and flammable substances in a form of organic compounds or other fuels such as the red phosphorus, powders of metals, carbon, sulphur. In burning and thermite pyrotechnic mixtures as flammable substances can be used: magnesium, aluminum, their alloys and mixtures, while in smoke – mainly organic compounds. Nitrates, chlorates and perchlorates compose main oxidants in pyrotechnic burning masses, oxides of metals – in smoke mixtures. To the composition of pyrotechnic mixtures different additives are introduced, such as: salts granting the colour to the flame (barium salts – green, strontium – red, sodium – yellow, copper – blue), organic dyes to coloured smokes, the binders (shellac, rosin, gum acacia, synthetic resins). The basic kind of pyrotechnic mixtures explosive transformation is the quick combustion (deflagration). Many mixtures also undergo detonation, at the suitable stimulation. The pyrotechnic effect, including the speed of the combustion, depends on the preparation technology – the fragmentation degree of the mass components, their purity, mixing accuracy and density of compression. The most masses, especially containing chlorates and perchlorates, have explosive properties. They are applied in military technology to elaboration of missiles, rockets, bombs, signal cartridges, means of simulation (crackers) and of instruction [3-6].

There are many analytical methods used for the determination of substances in pyrotechnic materials residues: ion chromatography (IC) [7], gas chromatography coupled to mass spectrometry (GC-MS) [8, 9], scanning electron microscopy-energy dispersion X-ray (SEM/EDX) [10], infrared spectrometry (IR) [9], capillary electrophoresis (CE) [11, 12].

In case of inorganic ion determination by capillary electrophoresis method, indirect UV detection is applied, because many ions don't absorb light in UV and Vis range. In indirect detection method the UV-absorbing solute of the same charge is added to the background electrolyte and serves as the visualizing reagent. When solute ions migrate through the detector window, they are measured as negative peaks relative to the absorbing solute. By reversing the signal and reference wavelengths of the detector, a positive signal is obtained. The area of the peak generated is related to the determined ion concentration. The migration speed of the UV-absorbing ion must closely match that of the ion being detected otherwise the analyte peak shape is severely distorted resulting in poor sensitivity [13].

Due to the fact that some oxidants used in pyrotechnic mixtures, such as ammonium nitrate, are applied as chemical fertilizer, during the analysis of the postexplosive residues it is very important to collect and examine the control sample. This can exclude the presence of the plant chemical fertilizers from soil in pyrotechnic mixture [3, 4]. The aim of this work was application of capillary electrophoresis for qualitative and quantitative determination of ions: ClO_3^- , ClO_4^- , NO_3^- , NH_4^+ , K^+ in pyrotechnic material residues after explosive transformation.

2. EXPERIMENTAL

2.1 Apparatus and materials

In order to prepare standard solutions of selected inorganic ions, salts of: KClO_4 , KClO_3 , NH_4NO_3 and KNO_3 (pure for analysis, Chempur, Poland) were dissolve in deionized water. Capillary electrophoresis system with UV-Vis detector, P/ACE MDQ from Beckman Coulter (USA) was used for analyzes. For selected anions and cations determination, Cation and Anion Analysis Kit (No. A53540 and A53537) from Beckman Coulter were used. These sets contained chemical reagents for conditioning and rinsing the capillary and for separation and determination of selected anions and cations: deionized water, borate buffer, 0.1M NaOH, 0.1M HCl and others not described in details by the producer. Selected inorganic ions were determined in residues of explosive materials: fire-cracker FP3 with black powder (Fig. 1) and military fire-cracker with fuse detonator (Fig. 2).

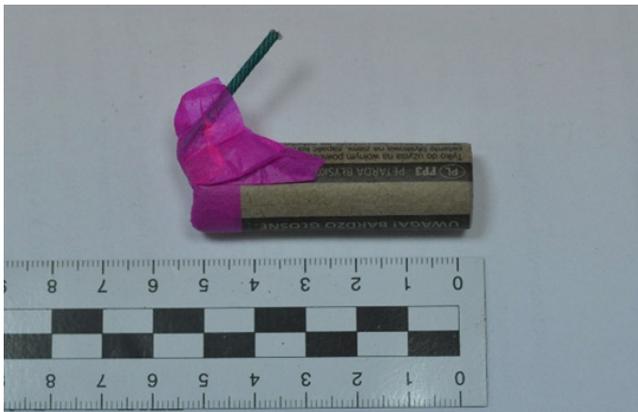


Figure 1 Fire-cracker FP3 prepared for detonation (authors photo)



Figure 2 Original military fire-cracker with fuse detonator (authors photo)

2.2 Capillary electrophoresis

For qualitative and quantitative determination of selected ions capillary electrophoresis method with UV-Vis detection was applied. The scheme of the apparatus is shown in Figure 3. Fused silica capillary of 60.2 cm length and internal diameter 75 μ m. The capillary was sequentially rinsed and conditioned by deionized water, 0.1M NaOH solution and borate buffer. The determination of anions and cations was carried out in the same capillary but during the separate analyzes. During the analyzes of anions and cations the voltage of 30 kV was applied for 5 minutes. Electropherograms of anions were register at wavelength of 254 nm and cations at 200 nm, in both cases using indirect detection mode.

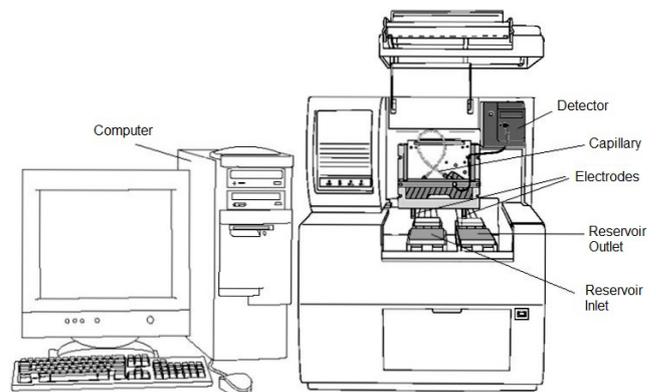


Figure 3 The scheme of capillary electrophoresis system [14]

2.3 Standard solution preparation and calibration curves determination

Standard solution was prepared by dissolution of salts containing determined ions (ClO_3^- , ClO_4^- , NO_3^- , NH_4^+ , K^+) in deionized water in order to prepare five solutions with different concentrations of each ion, in ranges shown in Table 1. Each solution was analyzed three times by CE method. Calibration functions and linearity ranges were determined for each of determined ions, also linear regression coefficients R^2 were calculated (Tab. 1). Limit of detection LOD (signal level three times higher than average amplitude of noise) and limit of quantification LOQ ($\text{LOQ} = 3 \times \text{LOD}$).

2.4 Real samples of explosive materials preparation

In order to determination of selected ions in pyrotechnic material residues, their controlled explosions were carried out. Next samples after the explosion were collected and solid – liquid extraction was performed. Military fire-cracker with fuse detonator was ignite using match striker. Fire-cracker FP3 with “wisco” type fuse was ignite by matches. Both fire-crackers, after ignition, were left on the ground about 10 meters

Table 1 Calibration parameters of CE method

determined ion	linearity range [mg/l]	R^2	function equation	LOD [mg/l]	LOQ [mg/l]
NO_3^-	3.12 – 50.0	0.995	$y = 0.015x - 1.396$	1.04	3.12
ClO_4^-	1.56 – 25.0	0.999	$y = 0.012x - 2.275$	0.52	1.56
ClO_3^-	1.56 – 25.0	0.996	$y = 0.009x - 1.072$	0.52	1.56
NH_4^+	2.50 – 20.0	0.998	$y = 0.002x - 0.747$	0.83	2.50
K^+	0.78 – 25.0	0.999	$y = 0.001x - 0.259$	0.26	0.78

from the person carrying the experiment. Next, from the explosion area, 150 g of soil with pieces of each firecracker samples were collected into 900 ml jars, "twist off" type, and 200 ml of distilled water was added into each jar. The jars were closed and shaken for 20 minutes, then left for decantation. The next step was filtration of aqueous solution after decantation through paper filter and received samples were analyzed by CE method. Obtained aqueous samples will be named further as real samples. Also control sample of the soil, before the explosion was collected, in order to check the possibility of determined ions presence in the area before the explosion. This sample was prepared in the same way as samples after the explosion.

3. RESULTS AND DISCUSSION

Primary CE analyzes of real samples (after firecracker explosion) shown, that concentrations of determined ions are much higher than concentration range of calibration determined. Real samples were 20 times diluted by deionized water. Also the analysis of the sample collected before the explosion was carried out in order to determine the level of background. In soil sample before explosion the following ions were found: NO_3^- (56.90 mg/L), NH_4^+ (22.10 mg/l) and K^+ (14.92 mg/l). CE analyzes of FP3 and military fire-cracker aqueous solutions samples after the explosion were carry out. Comparing the migration times of ions in standard solution and sample, ions qualitative determination in real samples was performed. Electropherograms of determined anions and cations in standard solutions and real samples are shown in Figures 4 and 5.

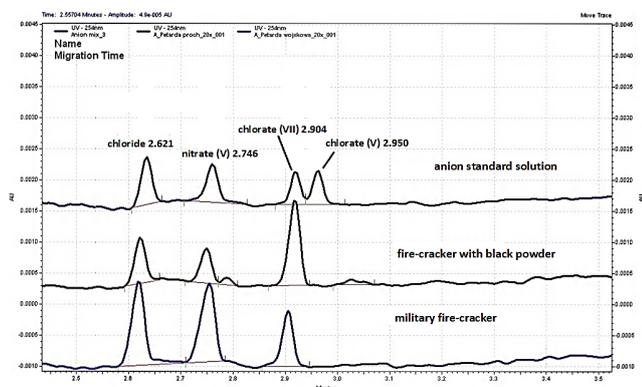


Figure 4 Electropherogram of anions in standard solution and real samples

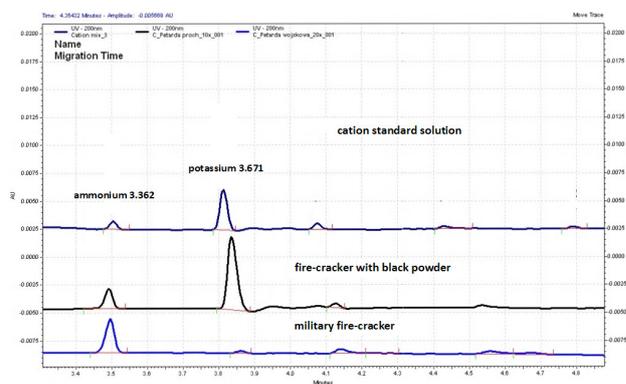


Figure 5 Electropherogram of cations in standard solution and real samples

In presented electropherograms (Fig. 4 and 5) it can be noticed, that the migration times of determined anions are less than 3 minutes and cations less than 4 minutes. On the basis of determine calibration functions, selected ions were determined quantitatively in real samples, subtracting the amount of ions present in the soil before the explosion. The concentration of ions were calculated for 1 kg of soil and presented in the diagram (Fig. 6).

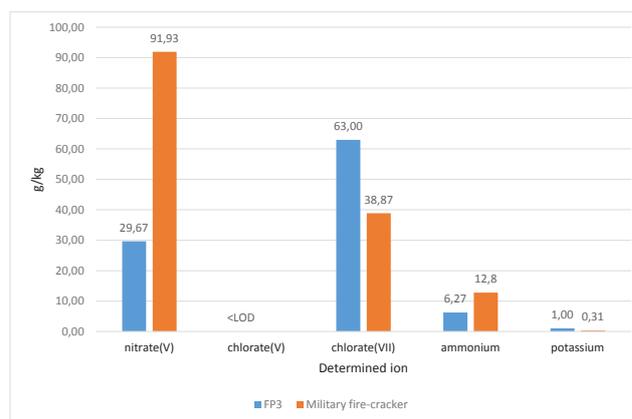


Figure 6 The diagram of determined ions concentration calculated in grams per 1 kilogram of soil sample

Considering obtained results it can be noticed that NO_3^- anions concentration in military fire-cracker sample is 3 times higher than in fire cracker with black powder sample. The concentration of ClO_4^- in military fire-cracker sample is almost 2 times lower than in fire-cracker FP3 sample. The concentration of ClO_3^- anions in both cases is lower than LOD. The amount of NH_4^+ fire-cracker FP3 sample is 2 times lower than in military fire-cracker sample, while the amount of K^+ is 3 times higher in fire-cracker FP3 sample than in military fire-cracker sample. Generally military fire-cracker contains higher amount of NO_3^- and NH_4^+ ions than fire-cracker FP3.

4. CONCLUSION

Capillary electrophoresis method is suitable for inorganic ions determination in residues after fire-cracker explosion. The ions migration time is very short, below 3 minutes for anions and 4 minutes for cations. Determined LOD and LOQ values allow to determine quite small amounts of selected ions in pyrotechnic material samples after the explosive transformation, at ppm level. On the basis of obtained results, identification and distinction of two similar pyrotechnic materials (fire-crackers) is possible. It should be mentioned that even if determination of simple inorganic

cations and anions by capillary electrophoresis is known from 90's of XX century, it is not applied in criminalistic investigations performed by police laboratories in Poland. Reminding and somehow adaptation of CE method for criminalistic investigation of pyrotechnic materials containing inorganic components would make a contribution to discover this method again by polish criminology. CE method is an alternative for ion chromatography and other techniques applied for ion determination in aqueous matrixes and can be used for determination of different ions than these presented in the work.

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