Recent Advances in Capillary Electrophoresis Instrumentation for the Analysis of Explosives

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Abstract

Due to its high versatility, capillary electrophoresis (CE) is a well-established analytical separation technique that has experimented novel instrumentation developments during the last years. New strategies have been proposed to achieve high-sensitive methods, portable CE or miniaturized devices. All these developments are of high interest for the analysis of explosives, which usually requires highly selective approaches. This review provides a recent perspective (from the beginning of 2008 to March 2015) on the use of CE for the analysis of explosives. First, a general description of explosives is made, emphasizing the role of separation techniques and specifically CE. Next, the most recent works focused on the analysis of explosives by conventional CE, portable CE and microchip CE are compared and critically discussed. Besides, other emerging techniques for the analysis of explosives are referred and compared to CE results. Finally, future perspectives for the analysis of explosives by CE are proposed.

Keywords: Capillary electrophoresis; explosive; inorganic; instrumentation; microchip; organic; portable CE; recent CE; review; sensor

List of abbreviations: *AD (amperometric detection), ANAL (ammonium nitrate aluminium powder), ANFO (ammonium nitrate fuel oil), APTS (8-aminopyrene-1,3,6-trisulfonic acid), BGE (background electrolyte), C4D (capacitively-coupled contactless conductivity detector), CE (capillary electrophoresis), CIMC (chemical ignition Molotov cocktail), DESI-MS (desorption electrospray ionisation-mass spectrometry), DNAN (2,4-dinitroanisole), EDGN (ethylene glycol dinitrate), HMTD (hexamethylene triperoxide diamine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), HPLC (high performance liquid chromatography), IC (ionic chromatography), id (internal diameter), IED (improvised explosive device), LIF (laser-induced fluorescence), LOD (limit of detection), microstructured-capillary electrophoresis (MCE), MSC (microstructured capillary), NB (nitrobenzene), NC (nitrocellulose), NG (nitroglycerin), NTO (1,2,4-triazon-5-one), NQ (1-nitroguanidine), PBS (phosphate buffered saline), PCA (principal component analysis), P-CE (portable-capillary electrophoresis), PDC (2,6-pyridinedicarboxylate), PETN (pentaerythritol tetranitrate), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), RSD (relative standard deviation), SDS (sodium dodecyl sulphate), SERS (surface enhanced Raman spectroscopy), SI-CE (sequential injection capillary electrophoresis), SIMCA (soft independent modelling by class analogy), TATP (triacetone triperoxide), TNT (trinitrotoluene).*

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Introduction

An explosive is a substance or device that subjected to heat, impact, friction, or detonation, releases a large amount of energy. This energy in the form of hot gases, originated during the explosion, expand rapidly creating a pressure wave, called "shock wave". Depending on their chemical structure, use, or nature, different classification of explosives may be done **[1, 2]**. For example, they can be divided into high-order explosives (whose expansion speed ranges between 50000-10000 m/s) or low-order explosives (with expansion speed between 300-3000 m/s). High-order explosives can be subcategorized in: primary explosives, such as nitroglycerin (NG), hexamethylene triperoxide diamine (HMTD) or triacetone triperoxide (TATP), which are the less stable, thus used in small quantities in primers or detonators; secondary explosives like pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), dynamite or trinitrotoluene (TNT), being more stable to mechanical shock, but also more energetic; and tertiary explosives, such as ammonium nitrate fuel oil (ANFO), or ammonium nitrate aluminium powder (ANAL), the most stable explosives, requiring an intermediate explosive booster of secondary explosive to initiate. On the other hand, low-order explosives or propellants are those explosives that can be detonated only under extreme conditions. Black powder (made of sulphur, charcoal, and potassium nitrate) and smokeless gunpowders (principally made of nitrocellulose, NC) can be categorized within this type of explosives. Black powders can be used in pyrotechnic composition of fireworks, whereas smokeless gunpowders are part of modern ammunitions **[3]**, although they can also be employed for the fabrication of improvised explosive devices (IEDs).

Note that, despite being explosive substances, these materials can also be classified depending on their final use, as their chemical properties lead to different applications. On the one hand, some explosives, such as PETN, RDX, HMX, C-4 or Semtex are usually employed by military forces, being their availability limited for other areas. On the other hand, other explosives like TNT, ANAL, ANFO, dynamite or nitroglycerin are more common substances, as they are used for civil and commercial purposes, such as building demolitions, firework displays, tunnel excavations, or airbag

fabrication. These applications make the analysis of explosives relevant for specific fields, like defence, environment or industry **[4]**.

Apart from the above-mentioned uses, explosives are unfortunately employed in terrorism acts. In fact, during recent years, too many terrorist attacks using a wide variety of explosives have occurred. For example, in the Bali resort bombings in 2002 TNT was used, in the Madrid train station bombings in 2004 dynamite was employed, in different attempts to blow up aircrafts in 2001 and 2009 PETN was used or in the Boston bombings in 2013 an IED based on black powder was employed **[2].** Thus, given the variety of explosives usable for terrorist acts, it is evident that the analysis of all them is of high relevance from a forensic standpoint.

Different approaches have been carried out to perform the analysis of explosive samples. For example, spectroscopy techniques have been successfully applied to a wide variety of samples and caseworks, and readers interested on this issue can consult a recent review **[2]**. Nevertheless, traditional separation techniques are still used for the analysis of explosives. Basically, the above mentioned techniques allow the identification and quantification of many types of species, at very low concentrations **[5, 6]**. Despite their destructive character, these advantages make them useful techniques for the analysis of explosives. For example, one of the most established separation technique, high performance liquid chromatography (HPLC), is the official and regulated-by-law method for some high-order explosive analyses in specific matrices in the US **[7],** or IC for the analysis of low-order explosives **[6]**. Nevertheless, note that working groups specialized in the analysis of explosives have established guidelines for the analysis of intact explosives and post-blast residues **[8, 9]**. These guidelines evidence that several analytical techniques are usually required for the analysis of these samples.

In this context, other separation techniques have provided promising results for the analysis of explosives. This is the case of capillary electrophoresis (CE). Despite not being as established as HPLC, this technique is less expensive, requires little amount of solvents and samples, and what is more important, presents huge versatility **[10]**. Some important developments during recent years have been the microchip technology, as well as portable CE (P-CE) instrumentation, advances that provide satisfactorily some of the requirements of explosive analysis, such as the need of

highly-selective and high sensitive assays with potential for *in situ* analysis on the field to avoid transporting the sample. Actually, different reviews devoted to the advances of CE in explosives can be consulted in the literature **[11-13].** However, during the last years, new approaches have been developed for the analysis of explosives, and also new instrumentation has been optimized and applied to these samples. Figures of merit of this recent research are of interest from a forensic standpoint, but also to note the recent CE instrumentation developed and its applicability.

Therefore, and starting from the last reviews published, this manuscript aims to critically review the recent works (from the beginning of 2008 to March 2015) on the analysis of explosives by CE to give continuity to those previous reviews reported **[11-13]**. Thus, the first section starts with the traditional CE analysis of explosives and shows the potential advantages of this technique in the field of forensics and homeland security, showing also its limitations. Subsequently, the following sections focus on the critical revision of the last works published regarding the analysis of explosives by the different CE formats: conventional CE, P-CE due to the recent development of portable equipment and microchip CE. For these sections, samples, their preparation, and details on the technique and CE conditions are summarized in a table for comparative purposes. The last section summarizes the achievements by CE in the analysis of explosives providing also a brief comparative between this separation technique and other emerging techniques. Finally, conclusions and perspectives on the use of CE for the analysis of explosives are made.

Basics in CE for the analysis of explosives and their residues

Prior to discuss the most recent literature devoted to the analysis of explosives by the different CE formats, it is relevant to describe some basics regarding the performance of this technique and its capabilities to detect explosives, as well as a comparison with the typical analytical techniques employed at forensic laboratories.

As stated above, CE is an established technique useful for the separation of (macro) molecules under the application of an electric field between the extremes of the capillary. This technique presents some advantages, such as its simple instrumental, versatility, and expensiveness compared to other separation techniques. These advantages have been exploited during the last years and nowadays new portable equipment, novel CE formats or even original CE conditions have been developed to enhance the CE performance. In this review, recent studies devoted to the analysis of explosives by novel CE approaches from a forensic and homeland security standpoints are collected.

However, compared to other separation techniques, CE has its own limitations **[14]**. In the case of forensic applications related to the analysis of explosives, three main goals are pursued: i) increased selectivity to minimize matrix effects in the sample; ii) obtain robust equipment allowing enough precision in the results, thus providing unambiguous interpretation; and iii) enhanced sensitivity of the systems to be able to perform the detection of both bulk and trace analytes found in the sample. Sensitivity of CE is comparable to other separation techniques. LODs in the order of ng have been achieved in IC recently **[15, 16]**. However, robustness is a drawback that CE has evidenced if compared to other techniques such as IC **[8]** or HPLC **[17]**. For example, different inorganic and organic species were recently analysed by IC, obtaining precision values in terms of RSD below 2.1% considering peak heights and n= 10 for cations and n= 8 for anions **[15]**. More recently, IC was coupled to MS for the determination or organic and inorganic anions, providing RSD values under 0.43 in retention times and below 25% in peak areas **[18]**. Considering CE, robustness may be also impoverished if employing complex separation media with additives, which sometimes are required to achieve a proper separation among the analytes under detection. Due to these reasons, orthogonal techniques are usually employed to

confirm the results. As an example, if evidence comes from a crime where organic explosives have been used, then HPLC is an ideal technique **[17]** to complement CE analysis. On the other hand, if inorganic explosives or their residues (ions) are analysed, then CE is usually complemented with validated methods by IC, given the reported analytical performance of this technique **[8]**.

Throughout the next sections, works related to the analysis of explosives by CE using new methodologies, platforms and formats, are addressed in order to show the high potential that this technique possesses, for the detection of different and small amounts of explosives (even at trace levels depending on the CE configuration and performance). However, it is important to consider that from a forensic standpoint this technique needs to be complemented with other techniques with confirmatory capacity as spectrometric techniques, or to be used as hyphenated technique (e.g. CE coupled to mass spectrometry).

Conventional CE

During the last years, the use of conventional CE over other approaches is evidenced, as can be seen in **Table 1**. Nevertheless, and compared to previous studies **[11-13]**, new advances have been achieved and will be discussed according to the analytes of interest. As can be seen, most of the works have focused on the analysis of cations and anions, as some of them can be considered as marker ions (after an explosion) for the potential identification of inorganic salts contained in the explosives **[19-22, 24-27],** and only one study was devoted to the analysis of carbohydrates **[23].** Despite the analysis of high-order explosives has also been carried out **[28]**, studies have focused on environmental analysis rather in forensic purposes, and only few works on CE have been devoted to this issue **[29, 30]**. Finally, other research has been carried out for the determination of intact pre-blast nitrostarch and nitrocellulose, a secondary explosive that may be present in some explosives of interest such as dynamites or home-made explosives **[31-35].**

Regarding the analysis of cations and anions, CE is a promising candidate due to its potential to detect charged (macro)molecules at low concentrations, which is of great advantage when collecting post-blast residues at crime scene. However, some of the anions and cations can be also found in the environment, thus matrix effects and

contamination must be considered. Of special importance is one study made in 2008, where K. G. Lahoda et al. comprehensively evaluated the presence of explosive residues on 16 different matrices, collecting the samples in 28 different cities from the US, and resulting in 286 different samples. The large number of samples collected at different places allowed a good results interpretation. Organic explosives were detected by gas chromatography, whereas the inorganic residues were studied by electrokinetic chromatography with UV detection, at 208 nm (cations) and 235 (anions). Despite not showing the resulting electropherograms, global results shown that potential ions found in explosive residues, such as ammonium, nitrite, perchlorate, thiocyanate and cyanate, were hardly found, whereas others like nitrate, chloride or sulphate are more common at crime scene, thus they can interfere in the results and must be specially considered **[19]**.

Sarazin et al. developed a CE method for the analysis of cations and anions in post blast extracts from acid–aluminium burst residues, which had not been analysed before by EKC-UV, detecting the species at 214 nm. The method was optimized, especially the concentration of 2,6-pyridinedicarboxylate (PDC) in the background electrolyte (BGE) used to create the chelated form of aluminium, the cation of interest, avoiding the formation of other chelates from non-monovalent cations such as copper, iron, calcium, or zinc chelates. Results shown that no interference anions were found, and despite not being as sensitive as IC, the high concentrations found in real samples allowed CE to analyse successfully these samples, where the expected ions, chloride from the acid, and aluminium (III), were detected **[20]**.

Sarazin et al. also optimized three different CE-UV methods for the analysis of anions, cations, and carbohydrates, including species of interest for the analysis of post-blast residues from explosives and IEDs, and carrying out comprehensive studies on matrix interferences **[21-23]**. The method for anions sought the applicability to most of the explosive samples in order to be used by the French security forces, thus a general method was proposed. Compared to previous methods, this one allowed also the separation and identification of the ion azide, usually present in detonators. Relative standard deviations (RSDs) of normalized times for the 15 studied matrices was below 0.75 % in all the cases. Finally, pipe-bomb residues were analysed to quantify chloride and chlorate anions (16 and 30 $mg \cdot L^{-1}$, respectively), which authors

claimed as possible chlorate salts used in the fabrication of the explosives, and also elevated concentrations of carbonate (26 $mg \cdot L^{-1}$), that could come from explosive compositions but also from CO_2 contamination from the atmosphere **[21]**. Regarding the method for cations, indirect UV at 190 nm was employed. In order to detect the cations, authors proposed a bilayer inside the capillary (with hexadimethrine bromide as first layer and polyvinylsulfonic acid sodium as second layer). After optimizing the medium and adding 18-crown-6 ether to improve the separation efficiency between some cations, they were applied to the analysis of residues from explosions made on cash dispensers, detecting evident cations (potassium, calcium, sodium and magnesium) plus ammonium from the explosive ammonium nitrate. Residues from fireworks contained ammonium, potassium, calcium and barium, whereas firecracker residues comprised potassium, calcium, sodium and magnesium **[22]**. The third method was optimized to successfully separate and detect different carbohydrates (fructose, glucose, galactose and sucrose), which are detected after the detonation of a home-made explosive **[23]**. Finally, the three previous discussed methods were tested in a simulated bombing attack, where an IED made of ammonium nitrate and icing sugar was fabricated and detonated **[24]**. To show these efficient CE methodologies, **Fig. 1** shows the resulting electropherograms of the residues collected after the bombing simulation. Besides, note that these methodologies were also compared to previous methods developed by IC, and despite obtaining poorer limits of detection (LODs), CE was successfully applied in all the cases, providing separation with less BGE consumption and cost-effective conditions compared to IC.

C. Martín-Alberca et al. developed a qualitative method to detect potential anion markers from chemical ignition Molotov cocktails (CIMCs). After preparing 24 different CIMCs by mixing different combination of sulphuric acid, potassium chlorate and perchlorate, sugar, petrol, kerosene, fuel, ethanol and methanol at different proportions, only 10 worked properly. UV detection was performed at 250 nm, where various anions were detected (chlorate, perchlorate, sulphate and chloride). After observing the chlorate and perchlorate peak areas at specific times during a period of 50 hours, authors confirmed that chlorate degraded to perchlorate over time, on the basis of proposed reactions for CIMCs. Finally, the combination of perchlorate, chloride, chlorate and high levels of sulphate were proposed as reliable markers for

CIMCs **[25, 26]**. The authors also employed the same CE methodology to detect anions and cations in consumer fireworks: after a physical characterization of the 6 types of consumer fireworks studied, which authors claimed an essential help for results interpretation, they were analysed and chemically characterised **[27]**.

Other works have focused on the analysis of high-order explosives by CE due to the flexibility of this technique for these compounds. Nevertheless, the aim of this research is usually the detection of explosives and their residues for environmental purposes, where electromigration techniques play an important role. Readers interested in the use of these techniques for a wide variety of environmental samples can consult recent literature **[28]**. Some of these works deal with the analysis of samples such as soils or water. For instance, B. Giordano et al. performed the determination of different high-order explosives (HMX, RDX, TNB, DNB, DNT and NT) from seawater, analysed directly in a CE system with UV detection at 254 nm. In this case, the method was optimized in terms of separation medium (by modifying the surfactant relative amount in the BGE) and injection (long electrokinetic injections) achieving LODs between 0.07-0.8 $mg \cdot L^{-1}$ **[29]**. D. Nie et al. also attempted the determination of different high-order explosives (TNT, TNB, DNT and DNB) by CE using amperometric detection with (a carbon disk electrode modified with mesoporous carbon material). The method developed reached high selectivity, and concentrations between 0.003 and 0.005 $mg \cdot L^{-1}$ were detected due to the efficiency of the modified carbon disk that provided enhanced electrocatalytic activity. In addition, the precision of the method was also demonstrated (RSDs<5) by analysing real water samples from a river and a coking plant **[30].**

Focusing on the determination of macromolecules contained in explosives smokeless gunpowders, M.A. Fernández de la Ossa et al. used CE with laser induced fluorescence (LIF) detection at 488 nm to determine the nitrocellulose (NC) in smokeless gunpowders, previous a derivatization process. For this reason, sample preparation was in this case more difficult than works focused on anions and cations separations. A derivatization agent was used to provide charge and fluorescence properties at the wavelength of the LIF detector. Pulverized gunpowders were derivatized with different agents, and finally 8-aminopyrene-1,3,6-trisulfonic acid (APTS), was the most effective reagent to derivatize the sample. The method was

optimized in terms of sample preparation and CE conditions, providing a very selective method, as only the NC derivatized was detected under the detection wavelength of the LIF detector. Finally, a visual differentiation was evidenced from samples with NC with low nitrogen content (<12%) such as collodions (non-explosive samples) and samples with NC with high nitrogen content (>12%) like gunpowders (explosives), method whose limits of detection were increased with stacking strategies **[31]**. To demonstrate the real applicability of the method, the authors analysed over 60 samples containing NC of high and low nitrogen content, as well as cellulose, in order to differentiate explosives from potential interferences at crime scene, such as cigarettes, varnishes, nail polishes, or paper. After obtaining the raw electropherograms and perform different corrections (alignment and correction of the baseline) the entire electropherograms were treated (practice called fingerprinting) to carry out different statistical analysis. Principal component analysis (PCA) allowed the differentiation between samples with high and low nitrogen content. Whereas soft independent modelling by class analogy (SIMCA) was required to finally differentiate 12 of the 14 types of samples studied **[32]**. **Fig. 2a** shows the electropherograms with the polymeric profiles of three different samples analysed in this study (double-base gunpowder, paper and nail polish) were differences in their profiles were visually clear and statistically confirmed. More recently, E. Alinat et al. have modified this method, by performing an acid depolymerisation prior to the derivatization process. Under this methodology, authors claimed a more efficient method to derivatize large polymeric chains from NC, and they were able to quantify the nitrogen content by using an offline spectrometric technique (matrix assisted laser desorption ionization-time of flight- mass spectrometry) **[33]**.

Finally, M. Calcerrada et al. employed the derivatization process previously described in conventional CE-LIF **[31, 32]**, but employing microstructured capillary electrophoresis (MCE) where the conventional separation capillary is replaced by a microstructured capillary (MSC). In the first work, two different MSCs were used in the CE equipment to carry out comparative studies with conventional capillaries of 25 and 50 µm internal diameter (id). The larger charge capacity and improved sensitivity of a 6-hole MSC allowed the first determination of nitrostarch by CE-LIF **[34]**. Then, a 6-hole MSC was deeper studied, and a methodology was optimized for the first determination

of NC in dynamite samples. The method was optimized in terms of sample preparation and CE conditions, capillary length, voltage and temperature. The MSC provided similar precision to conventional capillaries, and traces of NC were detected in real samples **[35]**. **Fig. 2b** shows the resulting electropherogram from a diluted dynamite sample, where the NC profile is shown. These works demonstrated the possibility of using microstructures as pioneering separation platform in commercial CE for complex samples, since previous works had been employed multichannels, but in microchips or in-house CE instruments instead of commercial equipment **[36]**.

Portable CE

During the last years, a clear development of portable CE equipment has been achieved, as can be seen in **Table 1**, where the most relevant works are summarized **[37-40]**. Contrary to the reviews previously reported **[11-13]**, we introduced P-CE separately from conventional CE, due to the high relevance that this technology has acquired during the last years for the analysis of explosives. These developments have been achieved due to the relativity simplicity of CE to portable format, compared to other separation techniques which require more complex instrumental.

It is important to note that, contrary to conventional CE systems, where different analytes have been determined and detection modes have been evaluated, P-CE has only be employed for the detection of anions and cations using capacitively-coupled contactless conductivity detectors (C^4D). Besides, none of these equipment has temperature control, which causes poorer precision of the results. For this reason, internal standards are recommended when using this instrumentation. On the contrary, other clear advantages over conventional equipment have been demonstrated.

In 2008, J. P. Hutchinson et al. identified inorganic ions in post-blast residues using a commercially available P-CE in-house modified. This pioneering approach through P-CE allowed the determination of both cations and anions from residues. Firstly, interferences were tested in order to know the species found in the environment or added during the sample preparation. Despite contamination was detected, it did not interfere in the result interpretation. With the developed methodology, the authors prepared four home-made explosives and their respective residues after detonation were analysed. Marker ions expected from the formulations of the explosives agreed with the results. Besides, a comparison with an IC method was performed, and despite obtaining higher LODs for the P-CE, results were in excellent agreement. Finally, a fast analysis (<45 s) was proposed for the method for anions, by eliminating some of the ions (not usually markers of the explosives), and diminishing the capillary length. In spite of obtaining very fast separations, authors suggested that a baseline resolution would be needed in order to avoid false positive or false negative results **[37]**.

More recently, G. A. Blanco et al. proposed the identification of anions from IEDs using sequential injection CE (SI-CE). In SI-CE, sample and background electrolyte (BGE) are alternatively flowed through the interface under computer-controlled conditions of flow and voltage, allowing fine control on the injection conditions. **Fig. 3a** depicts a scheme of the equipment employed. The SI-CE instrument consisted of a double syringe pump used to deliver sample and BGE through the system. A two-position injector valve was employed to alternately deliver sample or BGE to the interface. After selecting the ions of interest, authors optimized the method to achieve a good separation. The selectivity of inorganic anions in CE was modified by the introduction of an ion-exchange component to the electrophoretic separation, which is known as ion-exchange electrokinetic chromatography. Poly(ethylenimine) was added to the BGE in order to separate the ions, although poor reproducibility (RSD of 5% for n=6) was obtained in migration times, being not acceptable for identification purposes. Nevertheless, a IS was employed to perform electropherogram treatments and make the method reproducible enough. After selecting the BGE, the hardware was optimized, by selecting a capillary and an injection to obtain excellent LODs and a proper separation efficiency in terms of peak resolution. Besides, the method allowed highly reproducible analysis as can be seen in **Table 1**. When analysing the residues from the explosion of the in-house made explosive, various anions were successfully detected, as can be seen in **Fig. 3b [38]**.

J. Sáiz et al. fabricated a dual P-CE for the concurrent determination of anions and cations, and applied it to the detection of these species in consumer fireworks. Contrary to previous P-CE equipment, this one was comprised of two different capillaries, with different lengths to perform the separation of anions and cations separately. Different voltages were also needed for each capillary. However, the system required the same BGE for the two parallel separations. **Fig. 4a** depicts a scheme of this P-CE. The BGE was first selected to be able to separate both anions and cations. As nor temperature control neither IS was used, the identification of ions was performed by spiking the samples with the ions of interest. After the method development, figures of merit shown, for example, the possibility of increasing the voltage during the separation to detect low-mobility ions, or increasing the injection time to detect ions at very low concentrations. Finally, authors analysed real fireworks

(fuses and charges) and apart from ions expected in the electropherogram (due to knowledge in the sample composition) other ions were also identified, due to interferences from the matrix, or irregularities in the manufacturing process. **Fig. 4b** shows the electropherograms of one of the samples **[39]**. Thanks to the dual detection, fireworks were for the first time analysed for the detection of cations and anions, providing a more complete information than previous works, where only anions were determined **[27]**.

Finally, E. G. Kobrin et al. used a custom-made P-CE equipment to detect residues from different explosives. Contrary to the previous works, sample introduction strategy was in this case performed by the dual opposite end injection (first the anions and then the cations). Two IS were employed to obtain more precise results. By studying different matrices, different anions from the explosives were detected. In less than 4 minutes, 10 cations and anions were detected. In addition, the entire electropherograms from the samples (profiling) was taken to carry out PCA analysis, and the identification of specific explosives was achieved **[40]**.

Microchip CE and CE sensors

Finally, this heading deals with the CE principle in its smallest format, the microchip CE. Surprisingly, despite being a promising technology, scarce research has been published during the period from 2008 to March 2005, compared to that reported during previous years **[11-13, 41]**.

In **Table 1** only a study on explosives used this type of technology. E. Piccin et al. used a microchip for a sensitive and rapid microchip protocol to measure nitrate ester explosives. Despite obtaining low sensitivity for PETN, the microchip shown potential, detecting the analytes at pg level, during an assay that only required 160 s. **Fig. 5a** shows the results from the mixture of explosives studies. Reproducibility of the method was also obtained, as can be seen in **Fig. 5b** during a series of analysis of the standards mixture **[42]**. As drawbacks, this microchip was not tested in real post-blast or pre-blast samples, which could be relevant for the implementation of this technology in an extended way, which is advantageous in terms of speed, sensitivity, efficiency, portability, cost and sample size compared to conventional CE. Such important are the ideas and advantages regarding microchip CE, that new patents have proposed the use of portable and simple devices, which could be considered as chemical sensors, to overcome fast analysis of explosives. For example, an embodiment of a mobile app electrophoresis analysis system for providing chemical information **[43]**. Other example is the invention of a device for detecting the presence of a hazardous target molecule in a sample, such as biological agents, toxic chemicals, poisonous gases, narcotics or traces of explosive material or residues, and where an electrophoretic or dielectrophoretic field gradient between the sample and the substrate is required **[44]**.

CE compared to other emerging techniques

Throughout the previous sections it has been evidenced the potential of CE and its diverse formats to analyse explosives and their residues. Also, note that the classical analysis of explosives by CE includes the use of IC as ideal orthogonal separation technique to complement and/or confirm the results obtained by CE **[6]**. Nevertheless, it is important to briefly mention the results obtained during recent years by using other emerging techniques for the analysis of explosives. Some of the most employed in this field are Raman spectroscopy and mass spectrometry including its coupling with other separation and spectroscopic techniques. As the aim of this review is focused on the CE achievements, only specific examples of other techniques are included to compare the strengths and weaknesses of these techniques over CE.

Regarding Raman spectroscopy, a recent review focused on its use for the analysis of explosives has been reported **[2]**. This technique possesses some advantages which make it ideal for explosive analysis. On the one hand, samples can be analysed directly in the equipment, thus sample preparation is usually easier compared to separation techniques. For example, M. López-López et al. analysed for the first time dynamite using Raman spectroscopy and some of its major components (ammonium nitrate, ethylene glycol dinitrate and sawdust) were successfully detected without no sample treatment. To perform this analysis, Raman mapping was carried out to create chemical images which allowed the differentiation among these components in the heterogeneous sample through their Raman spectra **[45]**. However, for the detection of nitrocellulose, a minor compound in dynamites, a sample treatment based on the flocculation of this substance was previously required. The determination of nitrocellulose in dynamite was also achieved by CE, where a sample derivatization was required for the detection at pg levels of nitrocellulose contained in this sample **[35]**. If using surface enhanced Raman spectroscopy (SERS) to enhance the spectrum signal, sample preparation becomes more tedious, not only because of the addition of metal nanoparticles, which adds a step in the procedure, but also due to the irreproducibility problems that SERS present compared to other techniques. However, some results are promising for further investigation. For example, S. Botti et al. applied SERS with commercial substrates such as klarite®, to detect PETN, EDGN,

RDX and TNT at tens of pg concentration levels **[46]**. Other advantage of Raman spectroscopy is its potential to identify compounds in a sample (fingerprinting), as Raman spectra are unique for each compound **[45, 46]**. Nevertheless, when samples are composed of homogeneous mixtures, a separation technique is usually more useful, as this analysis allows a separation of the components previous its detection and confirmation with other techniques or validated methods **[24]**. Besides, quantification of analytes is a difficult task when employing Raman spectroscopy, thus this technique is not usually applied for environmental applications where quantification can be required, being its use more focused on the detection of potential compounds for security purposes or in forensic casework. To summarise, the advantage of Raman spectroscopy relies on its faster analysis times and easier sample preparation than separation or other spectrometric techniques, apart from its possible miniaturization which makes it useful for *in situ* analysis **[46]**.

MS has been established as a powerful analytical technique in many analytical fields and more specifically in forensic chemistry, due to its potential to unequivocally detect the compounds present in a sample and also their quantification capability at trace levels and with high precision. For example, desorption electrospray ionisation mass spectrometry (DESI-MS) has been deeply employed in the analysis of high-order explosives such as TNT and HMX, reaching their detection at pg and fg levels, being ideal for trace analysis **[47]**. MS has also the possibility of being coupled to other techniques to improve the analysis performance. For example, HPLC-MS can be used to separate and subsequently unequivocally detect analytes present in the samples. A. L. Russell et al. applied this technique to determine the composition of intensive munitions explosives (IMX). Two of them, which contained 2,4-dinitroanisole (DNAN), 1,2,4-triazon-5-one (NTO), 1-nitroguanidine (NQ) and RDX were subjected to analysis, reaching detection limits ranging from 0.007 to 0.009 $mg \cdot L^{-1}$ **[48]**. Finally, note that CE can also be coupled to MS techniques, providing additional selectivity compared to CE with DAD detection and allowing the confirmation of the detected molecules. This hyphenated technique has been used in the forensic analysis of some samples such as drugs (amphetamine, methadone, morphine) **[49]**, being also very common its use in metabolomics **[50]**. Nevertheless, it has a limited use in the analysis of explosives and their residues **[49]** and no papers were published during the revised period.

Other emerging technique which is resulting useful for the analysis of explosives and other forensic evidence is ion mobility spectrometry (IMS). This technique, coupled to MS, has recently proven to be very efficient for the analysis of high-order explosives. J. lee et al. used a corona discharge ionization combined with IMS-MS to analyse RDX, TNT, PETN, HMX and DNT. The results obtained regarding the LODs which ranged between 0.1 ng for RDX and 10 ng for DNT, evidenced its potential for trace analysis **[51]**. Consecuenlty, the use of MS or its coupling to separation techniques provides an improved sensitivity and confirmation of the molecules detected, at the expense of more expensive and complex equipment and limitations regarding the portable formats compared to CE.

Finally, it is important to highlight the relevance that non-electrophoretic miniaturised devices are acquiring during the last years **[52]**. For example, A. Choodum et al. proposed the use of an iPhone as novel platform for the development of a rapid and on site semi-quantitative analysis of TNT in soil samples, after a colorimetric test. Taking advantage of the camera, pictures were taken after the colorimetric test, and calibration curves between the RGB values and the concentration of the colorimetric product were obtained, with acceptable relative errors (RSDs between 0.4-6.3%) and good precision (RSDs between 2.09 and 7.43%) **[53]**. Also, fluorescent sensors seem promising devices for the detection of nitroaromatic explosives. Y. Gong et al. created a thriphenylene-2,6,10-tricarboxylate and Tb^{3+} bulding block to perform the selective sensing of TNT, TNP, 2,4-DNT, 2,6-DNT and nitrobenzene (NB). Apart from obtaining reproducible analysis for at least 5 times before regenerating the block, the device was able to detect solutions of those explosives at 5 $mg \cdot L^{-1}$. In other approach, S. Zhang et al. developed other metal-organic framework called NENU-503 (composed of $[Cd_2Cl(H_2O)(L)] \cdot 4.5$N,N-dimethylacetamide) to selectively detect nitroaromatic groups, and differentiate NB, 1,3-DNB and TNP with different nitro groups by the shift of the peak spectra **[54]**. From the above-mentioned results, it is clear that sensing devices are nowadays emerging as promising candidates for fast and portable equipment, which present a real interest for *in situ* analysis for security homeland. However, these sensors are not as established as conventional analytical techniques, being CE, among others, more robust techniques.

Summarizing, these new approaches regarding Raman spectroscopy, MS and sensing devices present real advantages which make them ideal for the analysis of explosives. Considering some recommendations for the analysis of explosives **[8, 9]**, it is evidenced that results obtained from these techniques are needed as complementary or confirmatory analysis obtained from CE and IC, with the aim of obtaining reliable results, precision, and capability for trace analysis of explosives.

Conclusions and perspectives

In general terms, recent research has demonstrated the potential of CE for the separation, identification and often quantification of specific species of interest for the analysis of explosives. In fact, regarding the samples, a wide variety of commercial and military explosives has been studied through this technique, obtaining promising results (in terms of separation efficiency, cost, analysis time and LODs).

It is clear that conventional CE still plays an important role in the analysis of explosives, as it is the most established and robust instrumentation. In addition, new methodological approaches and instrumentation developments have supplied some requirements of explosive analysis. Also, statistical treatments are being used to facilitate the results interpretation. All the above mentioned indicates that conventional CE is still an interesting field for the developments in the analysis of explosives.

Regarding P-CE, this instrumentation is a candidate for the *in situ* analysis of explosives at crime scene or in environmental monitoring areas, since more than acceptable results, compared to conventional CE, have been achieved through this emerging instrumentation. In addition, P-CE is easier to develop than other separation techniques and even more versatile than conventional CE, thus this field needs to be further explored. For example, the problems of reproducibility may be addressed in order to obtain more precise results. Besides, other detection modes have not been optimized, and the studies of explosives in this equipment is still limited to some explosives.

Finally, during the time period revised (from the beginning 2008 to March 2015), poor research has been devoted for the analysis of explosives through microchip technology, despite a considerable background is evidenced from previous reviews. However, recent inventions reveals that the ideas and goals of these technologies are as attractive as previous years.

Future investigations should be focused on the development of improved CE instrumentation which provides higher selectivity, more robust equipment and also higher sensitivities. This, together with the miniaturisation developments already achieved, will increase the potential of CE in the analysis of explosives.

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Figure Captions

Figure 1. CE-UV results of an aqueous extract, containing collected residues from a simulated bombing attack in a bus (home-made explosive made of ammonium nitrate and icing sugar). In a) analysis of anions (1, nitrite; 3, thiosulfate; 8, carbonate; IS, formate; 9, phosphate); b) analysis of cations (1, ammonium; 4, calcium; 5, sodium; IS, litium; c) analysis of carbohydrates (IS, naphtalensulfonate; 1, fructose; 2, glucose, 3, sucrose. Figures modified from **[24]** with permissions of Elsevier. CE conditions described in **Table 1**. (In colour on the web only).

Figure 2. Determination of derivatized nitrocellulose for different purposes by CE-LIF. In a) electropherograms of non-explosive/explosive samples containing nitrocellulose prior discrimination through principal component analysis (modified from **[29]** with permissions of Elsevier); b) dynamite sample where traces of nitrocellulose are detected (taken from **[32]** with permissions). CE conditions described in **Table 1**. (In colour on the web only).

Figure 3. Determination of different cations and anions using sequential injection in P-CE-C^4D. In a) prototype with sequential injection for the identification of two IEDs; in b) resulting electropherograms of two IEDs. CE conditions described in **Table 1** (taken from **[35]** with permissions of ACS). (In colour on the web only).

Figure 4. Determination of different cations and anions using dual P-CE-C^4D. In a) prototype with dual injection; in b) resulting electropherograms for the analysis of the charge and fuse of a consumer firecracker. CE conditions described in **Table 1**. (Modified from **[36]** with permissions of Elsevier). (In colour on the web only).

Figure 5. Microchip CE-ED for the analysis of nitrate ester explosives. In a) the resulting electropherogram of a standard mixture (a, ethylene glycol dinitrate, b, propylene glycol dinitrate; c, nitroglycerin; d, pentaerythritol tetranitrate); in b) a reproducibility study of the CE micrhochip (a,b and c as in **Fig. 5a**). Figure taken from **[39]** with permissions of RSC. CE conditions in **Table 1**. (In colour on the web only).

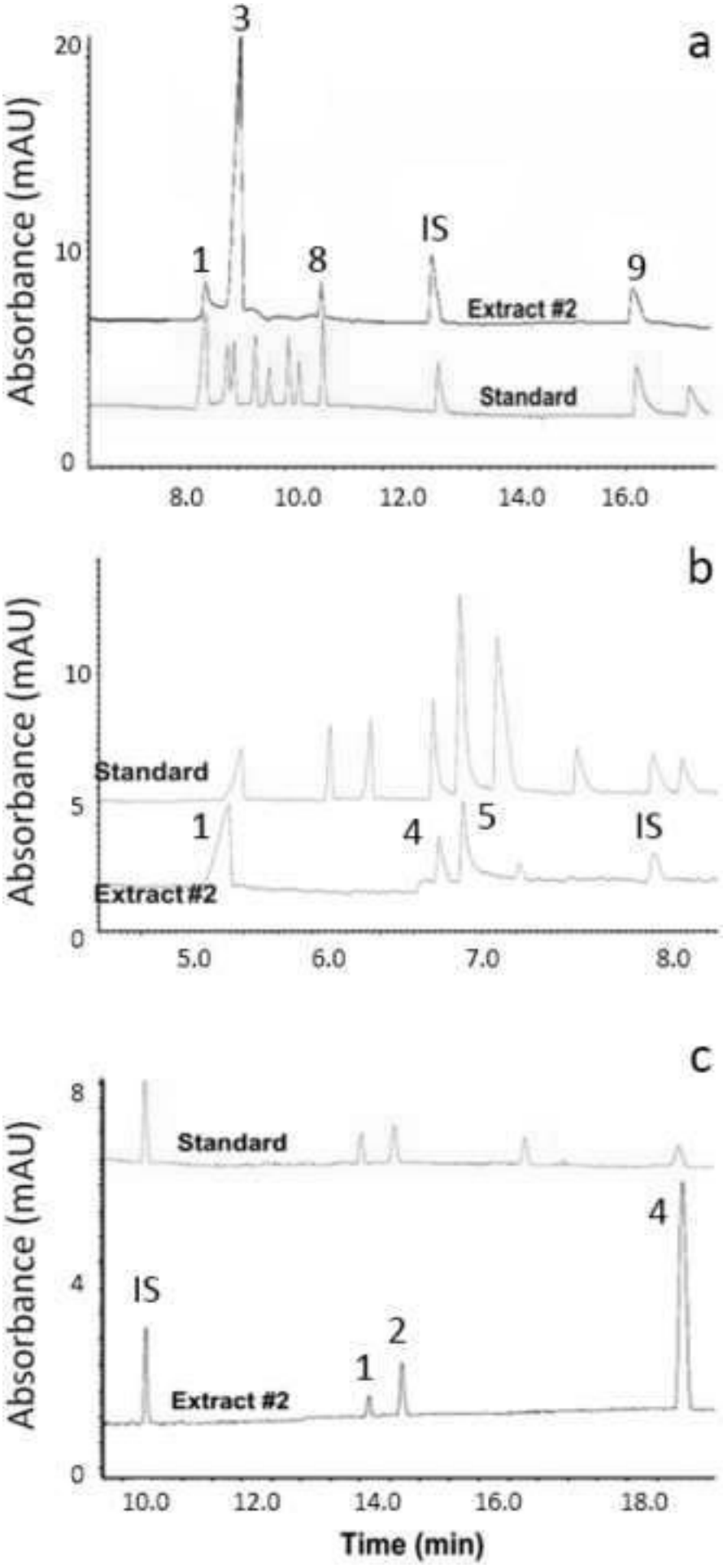
Table 1. Recent publications focused on the analysis of explosives and related compounds by CE.[1]

Sample (n)	Analyte	Sample preparation	CONVENTIONAL CE mode-detection		CE conditions	Analytical performance	Ref.
286 Samples from 16 matrices (28 cities)	Cl^-, NO_2^-, NO_3^-, ClO_4^-, ClO_3^-, SCN^-, SO_4^{2-}, OCN^-, K^+, $NH4^+$, Na^+, Ca^{2+}, Mg^{2+}	Extraction (1 mL H_2O) Centrifugation (8 min, 1000 rpm)	EKC	UV 208, 235nm	BGE:15 mM HIBA, 6 mM imidazole, 4 mM 18-c-6, 3 mM NTS, and AcN 5% (v/v), at pH 6.5 Capillary: 40.2 cm, 50µm id Injection: 7/5s Separation: 10kV, 25 °C	LOD: 1-15 $mg{\cdot}L^{-1}$ SD_{tmig}<0.013 (cations), 0.035 (anions)	[19]
Post-blast samples from acid-aluminium mixtures	Cl^-, NO^{3-}, Al^{3+}	Solution (H_2O)/ sonication (H_2O, hot) 10 min	CZE	UV 254nm	BGE: 10 mM PDC, at pH 4.5 Capillary: 60 cm, 50 µm id Injection: 0.4 psi, 15 s Separation: 30 kV, 25 °C	Linear range: 1-30 $mg{\cdot}L^{-1}$ LOD: 0.3-1.2 $mg{\cdot}L^{-1}$ LOQ: 1-4 $mg{\cdot}L^{-1}$ RSD_{tmig}<2.5 (n=9) RSD_{Area}<3.9 (n=9)	[20]
Post blast samples (pipe-bomb) from 15 matrices.	CH_3COO^-, $C_7H_5O_2^-$, CO_3^{2-}, ClO_2^-, F^-, $S_2O_3^{2}$, PO_4^{3-}, Cl^-, NO_2^-, NO_3^-, ClO_4^-, ClO_3^-, SCN^-, SO_4^{2-}, OCN^-, I^-, N_3^-, $C_2O_4^{2-}$	Extraction (H_2O, hot), sonication (10min)	CZE	UV 214nm	BGE:100 mM tris, 25 mM CrO_3, 25 mM Na_2CO_4 and EtOH 6% (v/v), at pH 8.2 Capillary: 96/87 cm, 50µm id Injection: -2 kV, 50s/-2 kV, 40s Separation: 30kV, 15 °C	Linear range: 2-20 $mg{\cdot}L^{-1}$ LOD: 0.29-0.64 $mg{\cdot}L^{-1}$ LOQ: 2 $mg{\cdot}L^{-1}$ RSD_{tmig}<1.09 RSD_{Area}<2.85	[21]
Post-blast samples (in cash machines, fireworks, firecrackers) 5 matrices.	NH_4^+, K^+, CH_3NH_3+, Ca^{2+}, Na^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cs^+, Fe^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Li^+	Extraction (H_2O, hot), sonication (10min)	EKC	UV 190nm	BGE: 15 mM Guan:Ac, 3 mM 18-C-6, at pH 4.0 Capillary: 80 cm, 75µm id Injection: 0.7 psi, 4 s Separation: 30 kV, 20 °C	Linear range: 3-30 $mg{\cdot}L^{-1}$ LOD: 0.6-1.1 $mg{\cdot}L^{-1}$ LOQ: 3 $mg{\cdot}L^{-1}$ RSD_{tmig}<2.39 RSD_{Area}<3.45	[22]
Post-explosion extract (1) and smoke device extract (1)	Frc, Glc, Lac, Suc	Extraction (H_2O, hot), sonication (10min)	CZE	UV 270nm	BGE: 98 mM NaOH, 120 mM NaCl, at pH 12.99 Capillary: 60 cm, 50µm id Injection: 0.7 psi, 5 s Separation: -14 kV, 26.5 °C	Linear range: 3-30 $mg{\cdot}L^{-1}$ LOD: 5-10 µM LOQ: 3 $mg{\cdot}L^{-1}$ RSD_{tmig}<2.39 RSD_{Area}<3.45	[23]
Samples from a simulated bombing attack (ammonium nitrate and icing sugar)	Cl^-, NO_2^-, NO_3^-, ClO_4^-, ClO_3^-, SCN^-, SO_4^{2-}, $CHOO^-$, $C_2O_4^{2-}$, PO_4^{3-}, $S_2O_3^{2-}$, $CH_3NH_3^+$, Sr^{2+}, Ba^{2+}, Li^+, K^+, NH_4^+, Na^+, Ca^{2+}, Mg^{2+}, Frc, Glc, Lac, Suc	Extraction (H_2O, hot), sonication (10min)	CZE EKC	UV	Electrophoretic and detection conditions employed in **[18, 19, 20]** for the anions, cations and carbohydrates, respectively (optimized methods)	Studied in **[18, 19, 20]**	[24]
Residues from 23 CIMCs.	SO_4^{2-}, ClO_4^-, ClO_3^-, Cl^-	Solution (H_2O) and sonication (30 min, ambient temperature)	CZE	UV 250nm	BGE: 2,25 mM PMA, 6,5 mM NaOH, 0,75 mM and TEA mM, at pH 7.7 Capillary: 58 cm, 50 µm id Injection: 0.5 psi, 5 s Separation: -30 kV, 20 °C	Not performed	[25,26]
20 Samples (fireworks)	NO_3^-, ClO_4^-, ClO_3^- Cl^-, SO_4^{2-}, Br^-, $S_2O_3^{2-}$, NO_2, SCN^-, OCN^-	Solution (H_2O) for preblast, extraction (H_2O) for postblast	CZE	UV 250nm	Same as **[22,23]** (30 °C)	RSD_{tmig}<2,06%; RSD_{area}<20.22%	[27]
Seawater	HMX, RDX, TNB, DNB, NB, TNT, 4-Am-DNT, 2-Am-DNT, 2,4-DNT, 2,6-DNT, 2-NT, 3-NT, 4-NT	No treatment	CZE	UV 254 nm	BGE: 10 mM sodium tetraborate, 200 mM sodium cholate, 10% (v/v) EtOH Capillary: 31.2 cm, 50 µm id Injection: 10 kV, 100s/ 1psi Separation: 10 kV, 25 °C	LOD: 0.0012-0.0082 $mg{\cdot}L^{-1}$	[29]
3 water samples (cooking plants, tap water, river)	TNT, TNB, DNT, DNB	Filtration (0.22µm) Degasification	EKC	AD	BGE: 10 mM PBS, 10 mM SDS, at pH 6.5 Working potential: -0.7 V Capillary: 55 cm, 25 µm id Injection: 17 kV, 10 s Separation: -17 kV, no T control	Linear range: 3-30 $mg{\cdot}L^{-1}$ LOD: 0.003-0.0047 $mg{\cdot}L^{-1}$ RSD_{Conc}<5% (n=5)	[30]
7 Smokeless gunpowders	NC	Derivatization: 2 µL of $1 \cdot 10^{-4}$ mg/mL APTS in 15% (v/v) AcOH and 2 µL of 1.0 M SCBH in THF to 0.30 mg of gunpowder 65 ◦C 4 h.	CZE	LIF 488nm	BGE: 1 M formate, at pH 2.0 Capillary: 50.2 cm, 50 µm/ 75.2 cm, 75 µm Injection: 0.5 psi, 5 s/15 s Separation: -20 kV, 25 °C	LOD: 12-22 $mg{\cdot}L^{-1}$	[31]
64 Non-explosive and explosive nitrocellulose based samples	NC	Same as **[28]**. Except for paper samples (scratching)	CZE	LIF 488nm	BGE: 1 M formate, at pH 2.0 Capillary: 50.2 cm, 50 µm id Injection: 0.5 psi, 5 s	$RSD_{electroph}$ = 6% for five replicates and 3 % for n=5 (PCA and	[32]

						Separation: -20 kV, 25 °C	SIMCA)	
Cellodextrins and 2 NC samples	NC	Depolimerization (HCl) Derivatization: 5.84 µL of 0.02M APTS in 15% (v/v) AcOH and 1.95 µL of 1.0 M SCBH in THF to 20 µL hydrosylates of gunpowder 70 ◦C for 2 h.	Microstructured	CZE	LIF 488nm	BGE: 60 mM 6-aminocaproic acid, and 0.02% HPMC at pH 4.5 Capillary: 65 cm, 50 µm id Injection: 0.7 psi, 10 s Separation: -30 kV, 20 °C	$RSDt_{mig}$<1.1 (n=6) RSD_{Area}<3.5 (n=6)	[33]
Starch (1 sample) Nitrostarch (1 sample)	NC	Same as **[28]**		CZE	LIF 488nm	BGE: 1 M formate, at pH 2.0 Capillary: 30 cm, 50 µm id Injection: 0.5 psi, 5 s Separation: -20 kV, 25 °C	Not performed	[34]
Dynamite (4 samples)	NC	Same as **[28]**		CZE	LIF 488nm	BGE: 1 M formate, at pH 2.0 Capillary: 31 cm, 24.5±0.9 µm Injection: 4 psi, 5 s Separation: -10 kV, 20 °C	$RSD_{electroph}$=4-19 RSD_{tmig}<0.5 LOD: 10 $mg{\cdot}L^{-1}$	[35]
Residues in soil from 4 homemade devices (IEDs with inorganic salts and gunpowder)	Anions: Cl^-, $S_2O_3^{2-}$, NO_2^-, NO^{3-}, SO_4^{2-}, ClO_4^-, SCN^-, ClO_3^-, OCN^-, F^-, Cl^-, PO_4^{3-}, CO_3^{2-}, $CH_3CO_2^-$, $C_7H_5O_2^-$ Cations: NH_4^+, K^+, $CH_3NH_3^+$, $C_2H_5NH_3^+$,Ca^{2+}, Na^+, Sr^{2+}, Mg^{2+}, Mn^{2+},Zn^{2+}, Ba^{2+}	Swabing Solution (H_2O) Sonication (5min)	PORTABLE	EKC	C^4D	**Anions.** BGE: 70 mM tris, 70 mM CHES, at pH 8.6 Capillary: 90 cm, 75 µm id Injection: 1 psi, 5 s Separation: -25 kV, no T control **Cations**. BGE: 10 mM His, 50 mM acetic acid, 1 mM HIBA, 0.7 mM 18-c-6, pH 4.2 Capillary: 73 cm, 75 µm Injection: 0.1 psi, 5 s Separation: -25 kV, no T control	Linear range: 0-10 $mg{\cdot}L^{-1}$ LOD: 0.026-0.24 $mg{\cdot}L^{-1}$ $RSDt_{mig}$<1.14 (n=10) RSD_{area}<13.40 (n=10)	[37]
Post-blast samples (IEDs) on soils	Cl^-, NO_3^-, ClO_3^-, N_3^-, F^-, ClO_4^-, SCN^-, SO_4^{2-}, PO_4^{3-}	Extraction and solution (H_2O) sonication (5min)		CE	C^4D	BGE: 50 mM tris, 50 mM CHES, 0.05 % (w/v) PEI, pH 8.6 Capillary: 35 cm, 25 µm id Injection: -1 kV, 1 s Separation: -25 kV, no T control	Linear range: 0.025-3 $mg{\cdot}L^{-1}$ LOD: 0.018-0.079 $mg{\cdot}L^{-1}$ $RSDt_{mig}$<2.07 (n=48) $RSD_{c\cdot area}$<12.5 (n=48)	[38]
4 Consumer fireworks	NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, NO^{3-}, ClO^{4-}, ClO_3^-, SO_4^{2-}	Solution (H_2O), stirring (2 min)		EKC	C^4D	BGE: 60 mM MES, 2 mM 18-c-6, at pH 6.0 Capillary (x2): 60 cm (cations), 67 cm (anions), 25 µm id Injection: 1 min Separation: -10 kV (cations), 20 kV (anions), no T control	Linear range: 1-5600 µM LOD: 1-5 µM $RSDt_{mig}$<0.4 (n=9) RSD_{area}<7.1 (n=9)	[39]
Post blast samples from 8 explosives (Dynamite, PETN, TNT, RDX, PENO, ANFO, V40, C4)	NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, Cl^-, NO^{3-}, NO^{2-}, SO_4^{2-}, N^{3-}	Solution for sand (H_2O) or sawing for metal and concrete (H_2O), shaking (1 min)		EKC	C^4D	BGE: 20 mM MES, 20 mM his, 30 µM CTAB, 2 mM 18-c-6, at pH 6.0 Capillary: 50 cm, 50 µm id Injection: hand pressure, 3 s. Separation: -16 kV, no T control	Linear range: 1-500 µM LOD: 3.7-35.7 µM RSD_{area}<9.9 (n=3)	[40]
Standard solutions	EGDN, PGDN, NG, PETN	Solution in the BGE	MICROCHIP	ECK	ED	BGE: 15 mM sodium tetraborate, 20 mM SDS, at pH 9.2 Chip: 88x17 mm plexiglass, 82 mm length Injection: 1.5 kV, 2 s Separation: 1.5 kV, no T control	Linear range: 10-60 $mg{\cdot}L^{-1}$ LOD: 0.3-0.5 $mg{\cdot}L^{-1}$ $RSD_{intensities}$<2.3 (n=6)	[42]

[1] Abbreviations appearing in the Table, alphabetically ordered: 18-c-6 (18-crown-6 ether), Ac (acetate), AcN (acetonitrile), AcOH (acetic acid), AD (amperometric detection), ANFO (ammonium nitrate fuel oil), APTS (8-aminopyrene-1,3,6-trisulfonic acid), C4 (composition C explosive), C4D (capacitively-coupled contactless conductivity detector), CHES (N-cyclohexyl-2-aminoethanesulfonic acid), CIMC (chemical ignition Molotov cocktail), CTAB (hexadecyltrimethylammonium bromide), CZE (capillary zone electrophoresis), DNT (2,4-dinitrotoluene), DNB (1,3-dinitrobenzene), ED (electrochemical detection), EKC (electrokinetic chromatography), EtOH (ethanol), Frc (fructose), Glc (galactose), Guan (guanidine), HIBA (2-hydroxyisobutyric acid), His (histidine), HPMC [(Hydroxypropyl)methyl cellulose], id (internal diameter), IED (incendiary explosive device), Lac (lactose), LIF (laser-induced fluorescence), LOD (limit of detection), LOQ (limit of quantification), MECK (micellar electrokinetic cromatography), MES (4-morpholineethanesulfonic acid), NC (nitrocellulose), EDGN (ethylene glycol dinitrate),NG (nitroguanidine), NTS (1,3,6-naphtalensodiumsulfate), PBS (phosphate buffered saline), PCA (principal component analysis), PDC (pyridinium dichromate), PGDN (propylene glycol dinitrate), PEI (polyethylenimine), PENO (finland plasti explosive), PETN (pentaerythritol tetranitrate), PMA (pyromellitic acid), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), SCBH (sodium cyanoborohydride), SD (standard deviation), SDS (sodium dodecylsulfate), SIMCA (soft independent modelling of class analogies), Suc (sucrose), TEA (triethanol amine), THF (tetrahydrofuran), TNT (2,4,6-trinitrotoluene), TNB (1,3,5-trinitrobenzene), tris (tris(hydroxymethyl)aminomethane), UV (ultraviolet), V40 (name of a hand granade explosive).

Figure-1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IS
9
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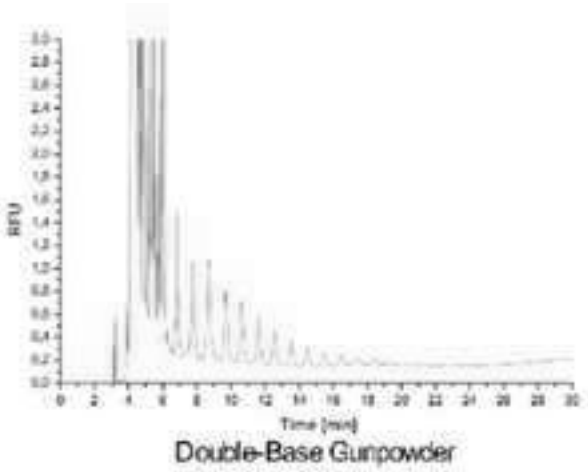
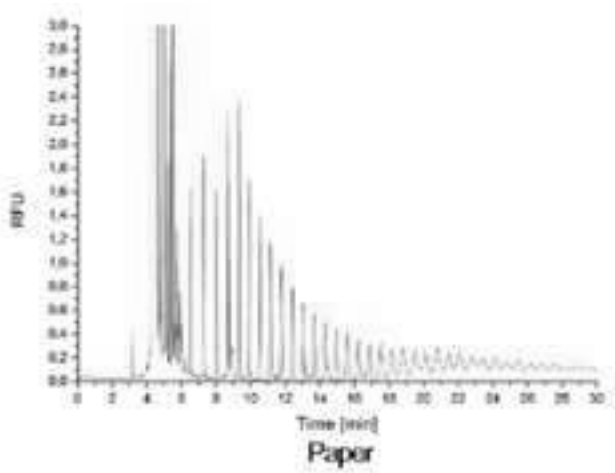
14.0
16.0
b
10
5
0
Absorbance (mAU)
Standard
1
4
5
IS
Extract #2
5.0
6.0
7.0
8.0
c
8
4
0
Absorbance (mAU)
Standard
4
IS
2
1
Extract #2
10.0
12.0
14.0
16.0
18.0
Time (min)

Figure-2



Double-Base Gunpowder



Paper

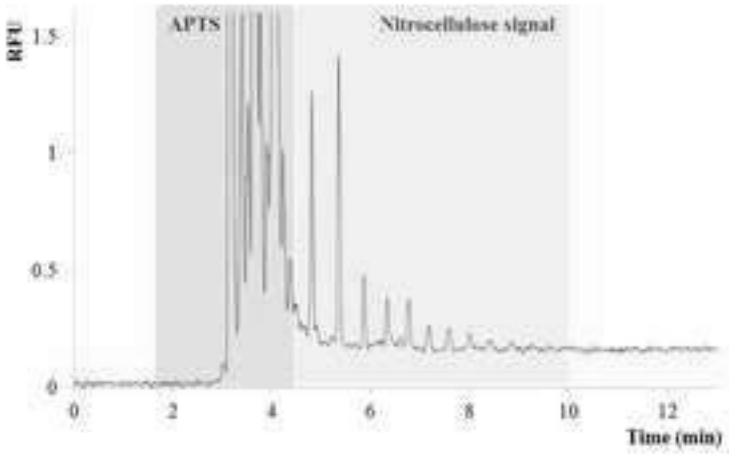
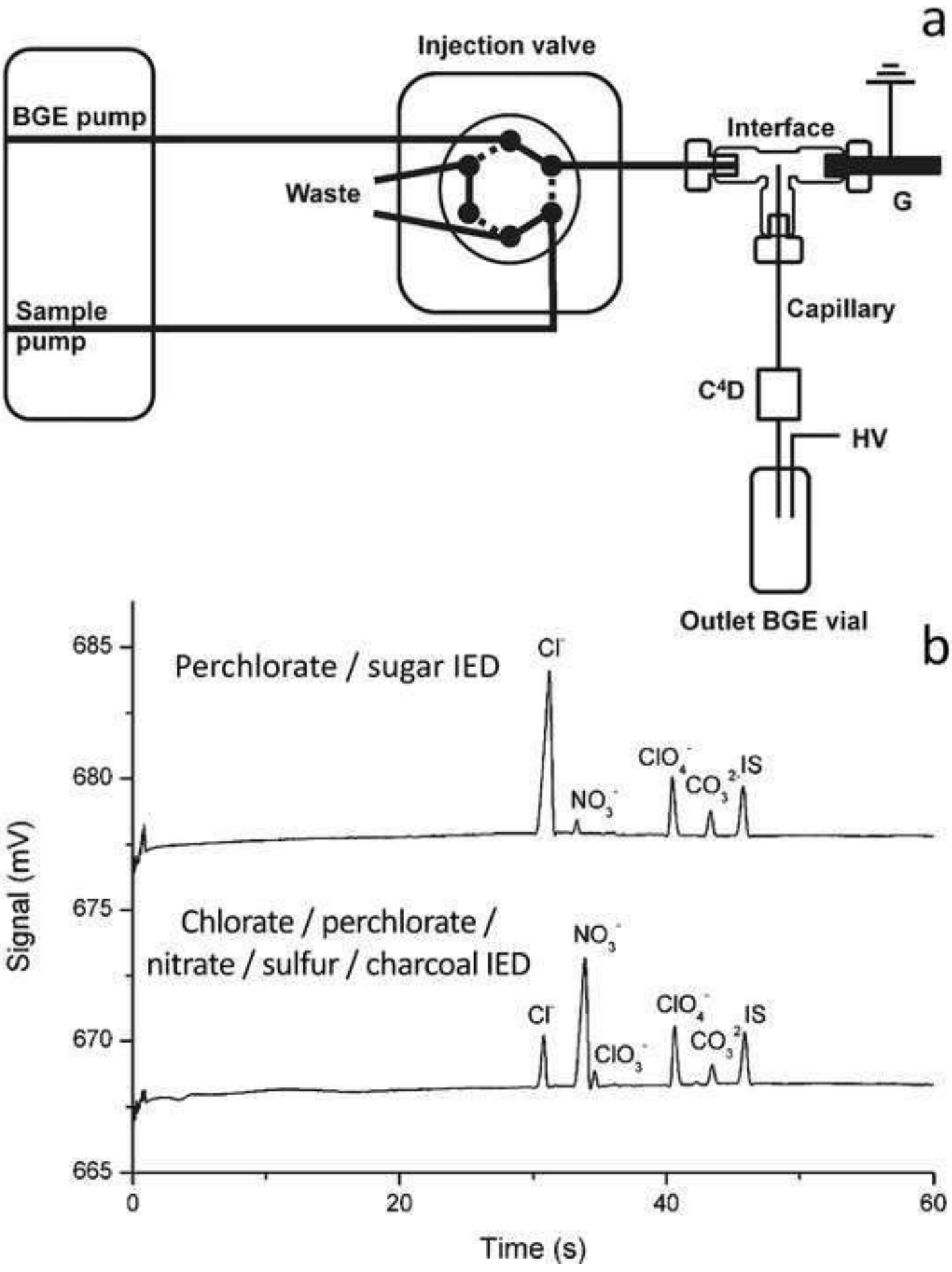


Figure-3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Injection valve
BGE pump
Waste
Interface
G
Sample pump
Capillary
C4D
HV
Outlet BGE vial
b
Perchlorate / sugar IED
Cl-
NO3-
ClO4-
CO3 2-
IS
Chlorate / perchlorate / nitrate / sulfur / charcoal IED
ClO3-
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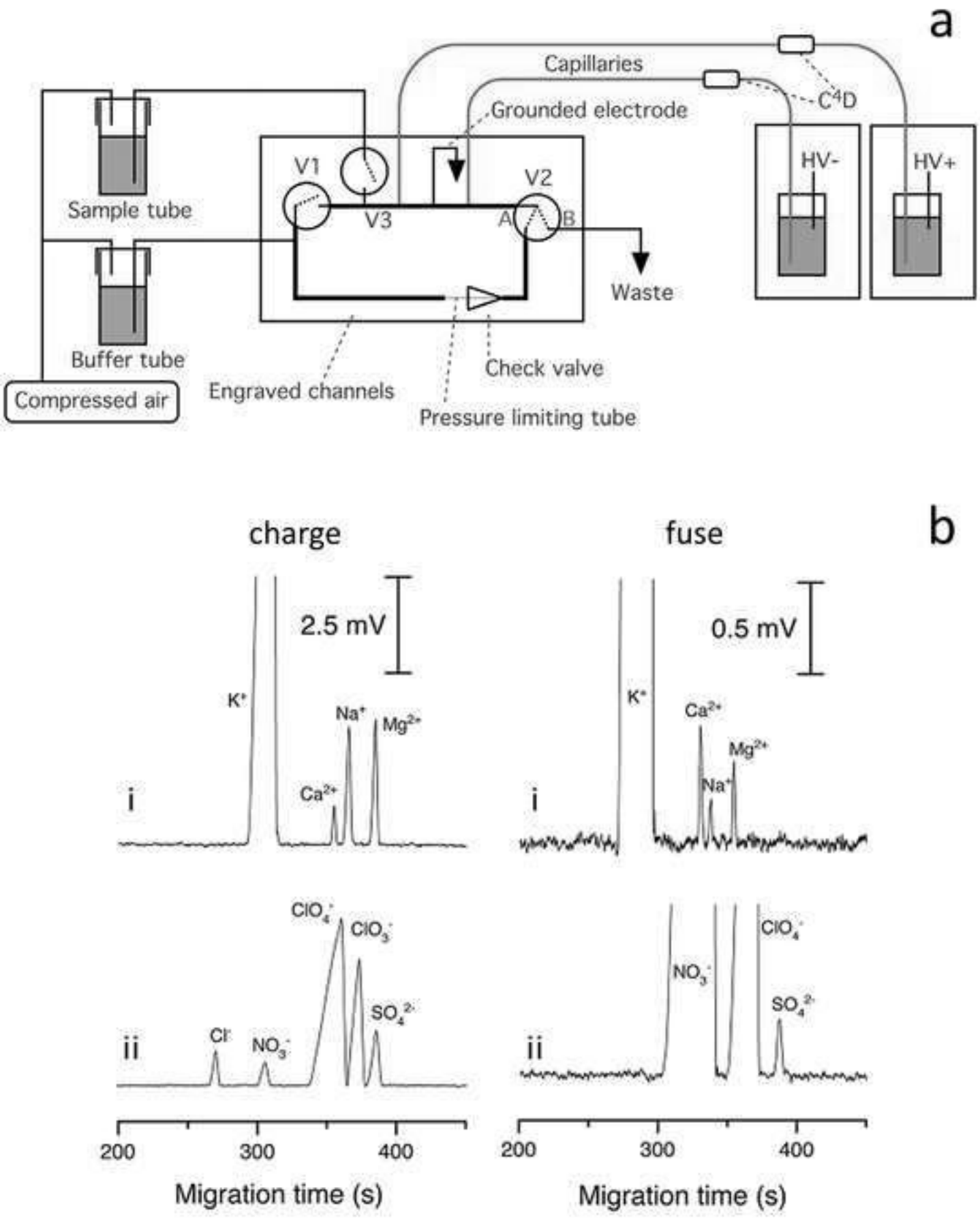
675
670
665
0
20
40
60
Time (s)

Figure-4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V3
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Buffer tube
Waste
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Engraved channels
Check valve
Pressure limiting tube
b
charge
fuse
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0.5 mV
K+
Na+
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Migration time (s)
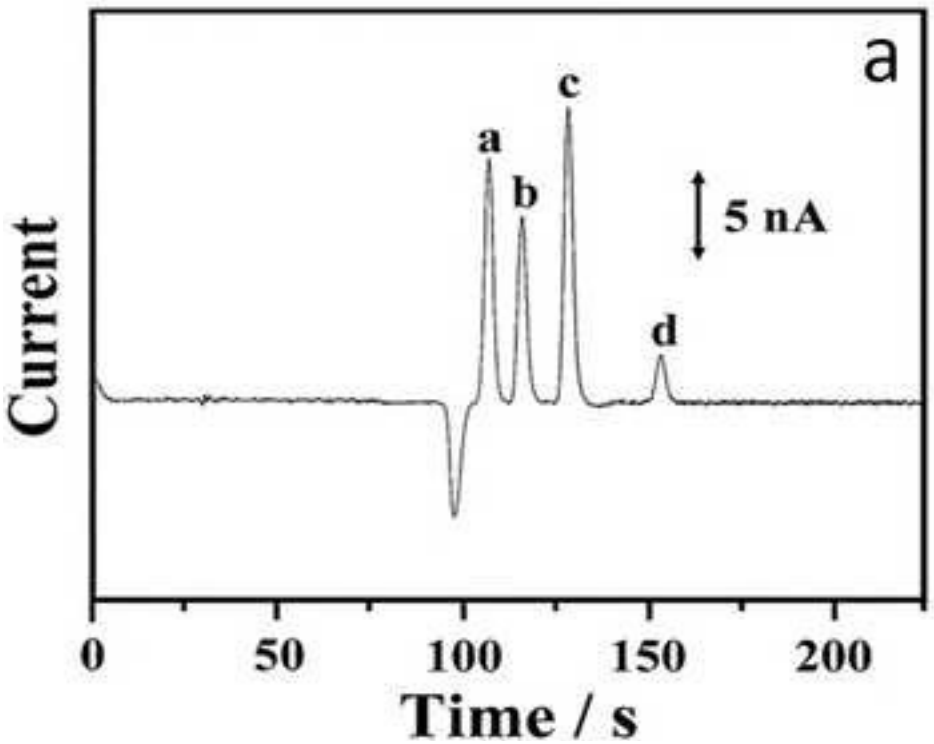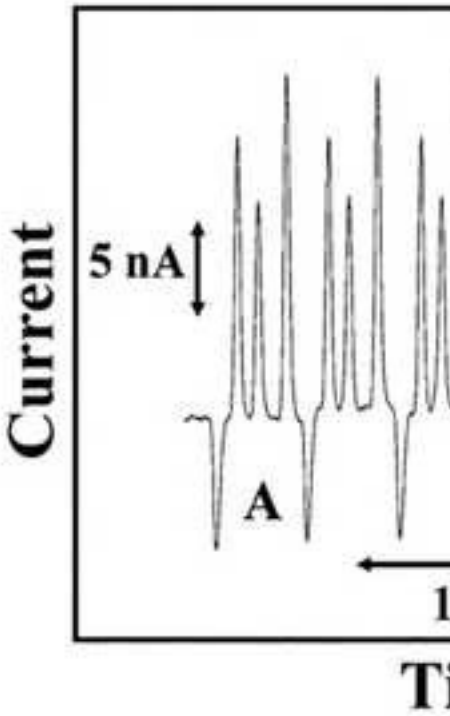
Figure-5