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Simultaneous determination of inorganic and organic gunshot residues by capillary electrophoresis

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Abstract

A capillary electrophoresis method was developed to analyze simultaneously 11 organic and 10 inorganic components of gunshot residues as a cheaper and possibly more specific method comparing to traditional techniques. Pre-capillary complexation and simultaneously a micellar phase were combined to determine not only the metal but also the organic residues from a firearm. In order to test the possibility to apply the developed method to real cases, residues from shot samples from different firearms were analyzed and their results were compared with those obtained with electrothermal atomic absorption spectroscopy, an established technique for gunshot residue analysis. Good agreement between both techniques for lead was found.
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1. Introduction

Gunshot residues are produced when a firearm is discharged; these residues can be deposited on the hands of the perpetrator. In targets and weapons, these residues correspond to unburned powder, particles from the primer and case of the cartridge and also, metals from the barrel of the gun [1–4].

The analysis of gunshot residues is one of the most important tests in forensic science. It has been used to estimate firing distances, to identify bullet holes and the most important task, to determine whether or not a person has discharged a firearm [1–4]. Nevertheless, the results from those tests have been controversial because of the lack of specificity in most of the traditional techniques used to do it. Since the work of Harrison and Gilroy, gunshot analysis has been based on the determination of heavy metals (usually lead, barium and antimony), which originate from the primer of the cartridge. Several techniques of elemental analysis have been used such as color reactions, neutron activation analysis (NAA), electrothermal atomic absorption spectroscopy (ET-AAS), and inductively coupled plasma mass spectroscopy (ICP-MS) [1–4]. The most accepted technique at the moment is scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), which combines a morphological (SEM) and elemental (EDX) identification of the metal residues [1]. Although it is considered specific, heavy metal analysis offers a moderate diagnostic sensitivity, requires expensive instrumentation and is highly demanding in terms of professional skills, manpower, maintenance and service. As a result of this, its application as a routine technique is difficult. Besides, it has been recently found that some particles can be misidentified with gunshot residues, decreasing the specificity of (SEM-EDX) analysis [5]. Additionally, an emerging problem is given by the modern trend to produce primers free of heavy metals; this would lead to obtain false negatives [6]. For the reasons described above, there is a need of a fast, cheap and specific technique that can be used routinely in laboratories with high load of work.

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Table 1
Characteristic organic and inorganic gunshot residue components

Compound	Abbreviation	Usage
Nitroglycerin	NG	Propellent
Resorcinol	Rs	Stabilizer
2,4-Dinitrotoluene	24-DNT	Flash inhibitor
2,6-Dinitrotoluene	26-DNT	Flash inhibitor
2,3-Dinitrotoluene	23-DNT	Flash inhibitor
Dimethyl phthalate	MF	Plasticizer
Diethyl phthalate	EF	Plasticizer
Dibutyl phthalate	BF	Plasticizer
Diphenylamine	DPA	Stabilizer
Methyl centralite	MC	Stabilizer
Ethyl centralite	EC	Stabilizer
Antimony	Sb	Fuel
Iron	Fe	Bullet material
Barium	Ba	Oxidizing agent
Calcium	Ca	Fuel
Magnesium	Mg	Fuel
Aluminum	Al	Fuel
Nickel	Ni	Bullet material
Zinc	Zn	Bullet material
Lead	Pb	Explosive (lead styphnate)
Copper	Cu	Bullet material

These compounds do not represent a comprehensive list of chemicals that may be found in gunshot residues.

Meng and Caddy [4] suggested that a way to enhanced the specificity of the bulk analysis is to look simultaneously for the inorganic and organic gunshot residues (Table 1). Attempts have been made in this sense analyzing separately the organic residues by liquid or gas chromatography and inorganic residues by the techniques mentioned before [7]. Capillary electrophoresis has been used to analyze explosive compounds and gunshot organic residues in forensic samples [8], soil [9], explosives [10], etc., by micellar electrokinetic chromatography (MEKC) and, cation analysis, usually using a complexing agent [11–13]. The purpose of this work is to develop a CE method to analyze simultaneously the organic and inorganic gunshot residues as a cheaper, faster, and more specific alternative than the common techniques used at the moment.

2. Experimental

A P/ACE MDQ Beckman capillary electrophoresis system (Beckman Coulter Fullerton, CA, USA) was used with polyimide bare fused silica capillaries (Polymicro Technologies, Arizona, USA) with a total length of 79.2 cm (69.2 cm to detector) × 75 μm i.d. Direct UV detection was carried out with a diode detector. A positive voltage of 30 kV, temperature of 25 °C and hydrodynamic injection of 5 s and 0.5 p.s.i. (1 p.s.i. = 6894.67 Pa) were usually used. For ET-AAS analysis a Perkin-Elmer SIMAA 6000 ET-AAS (Perkin-Elmer, Norwalk, CT, USA) was used.

New capillaries were conditioned by rinsing them with ethanol for 2 min, 0.1 M hydrochloric acid for 2 min, NaOH 1 M at 40 °C for 5 min and NaOH 1 M for 5 min. Between

runs, the capillary was rinsed with deionised water for 1 min, NaOH for 1 min, and again with deionised water for 1 min and background electrolyte for 2 min.

Gunshot residues standards: nitroglycerine, (obtained from Nitradisc, a medication of Searle) resorcinol, 2,4-dinitrotoluene, 2,6-dinitroluene, 2,3-dinitrotoluene, methyl phthalate, ethyl phthalate, butyl phthalate (Sigma–Aldrich, St Louis, MO, USA), diphenylamine (J.T. Baker, Xalostoc, Mexico), ethyl centralite, methyl centralite (kindly provided by Ing. Nimrichtr from Explosia, Pardubice-Semtím, Czech Republic) and AAS standards of lead, barium, antimony, copper, zinc, nickel, iron, aluminium, calcium and magnesium (High Purity Standards, Charleston, SC, USA).

Organic standards were dissolved in ethyl alcohol (J.T. Baker) to provide 10 mM stock solutions. Standard solutions were prepared by direct mixing of 1000 ppm AAS standard concentrates with the organic stock solutions. To prepare metal complexes CDTA (diaminocyclohexane tetraacetic acid) (Sigma–Aldrich) was added from a 5 mM solution, to give a 2.5-fold molar excess from the total concentration of metals to ensure the total complexation of the metals [14]; sodium tetraborate (J.T. Baker) was added in a 100-fold less concentration than the used in the electrolyte, and sodium dodecyl sulfate (SDS) (Sigma–Aldrich) was also added in the same concentration that the solution used in the sampling procedure.

Sodium tetraborate and SDS were used for the preparation of the electrolyte; the necessity to add CDTA to the electrolyte was studied. The pH of the electrolyte was adjusted with diluted solutions of sodium hydroxide or hydrochloric acid when it was necessary. All the chemicals used were analytical-reagent grade and deionized water was used to prepare all solutions.

Field amplification experiments were done by injecting hydrodynamically a sample plug (low conductivity), which corresponds to 50% of the capillary volume. In a first step a negative voltage was applied and the sample plug was electroosmotically pumped out of the injection extremity of the capillary until the current reached the value from a normal run; this means that the main part of the low conductivity plug had been pushed out from the capillary and the stacking process was completed, then the voltage was switched to a positive value to start a run [15].

Samples from gunshots were obtained by swabbing technique. In this technique the maculation zone (Fig. 1) is scrubbed with a piece of cotton of 1 cm² embedded in a solvent. The gunshot residues were recuperated by sonication of the pieces of cotton into 2 mL of solvent. Several solvents for sampling were tested and the recuperation of organic and inorganic standards added to the hand was studied [16]. A sampling procedure with masking tape [1,3,4] was also studied in the same way to find the proper sampling methodology.

Liquid extraction of organic residues was carried out with 2 ml of ethyl acetate, 50 μl of ethylene glycol was added to prevent full evaporation; the solvent was evaporated under a
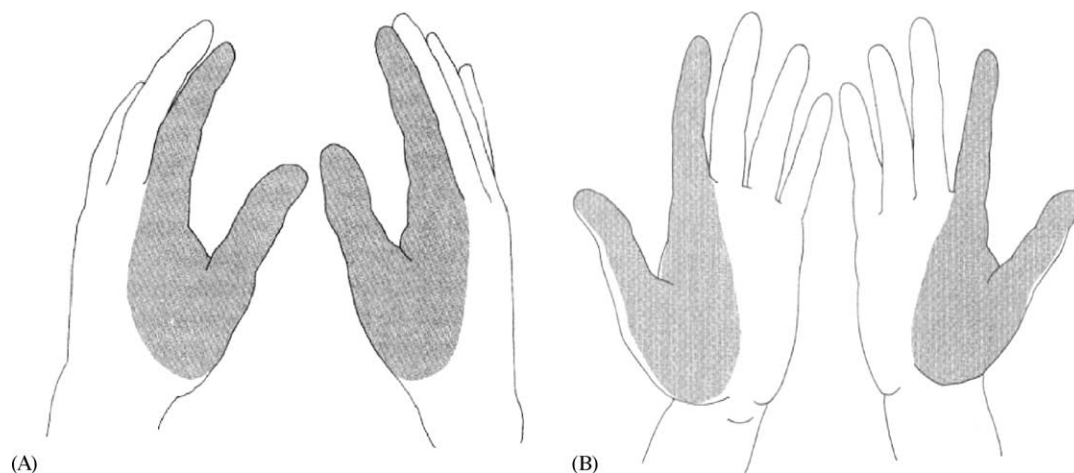
Fig. 1. Zones of sampling for gunshot residues: (A) web and (B) palm [2].

stream of dry nitrogen. The residues were reconstituted with a solution 5 mM CDTA, and 0.4 mM borate

3. Results and discussion

3.1. Inorganic gunshot residues separation

In order to separate the inorganic residues, pre-capillary complexation was selected using CDTA as complexing agent since it forms stable anionic complexes with all the metals under study, and it was reported to give the best separation of all the aminopolicarboxilic acids for lanthanoid elements [17]. In pre-capillary complexation all the metal has to be complexed. Species diagram for all the metals with CDTA were elaborated and it was found that the range of pH, where all the metals forms stable complexes with CDTA, was 7.5–10. At lower pH values the least stable complexes (Ba–CDTA) were not formed, while at pH higher than 10 the complexes with trivalent metals disappear because the metal hydroxy complexes [$–(OH)_4$] become the predominant species, negatively affecting the UV detection. The CDTA complexes have negative charge, making necessary to use counter electro-osmotic conditions. In these conditions borate buffer was recognized to be the optimal electrolyte system [14]; therefore, it was used in the initial experiments to optimize the separation.

Several parameters were tested to find out the best separation conditions for metal residues. The pH of borate electrolyte in the range of 8–10 was studied. It was observed that pH has little effect on the separation selectivity (data not shown). This is due to the very stable metal–CDTA complexes that does not allow the formation of hydroxo complexes with divalent metals, thus the charge (selectivity) remains unchanged in the range of tested pH. Since pH 9.2 provided the optimal buffer capacity, it was selected for subsequent analysis.

The effect of electrolyte concentration was also studied. Borate concentration changed the selectivity of the separation

(Fig. 2), specifically for zinc and nickel complexes; this effect could be related to parasite reactions between the CDTA complexes and borate [18]. Separation of the most problematic metals (zinc, nickel, lead) was achieved using 40 mM borate buffer.

It was reported that, in pre-capillary complexation, it is necessary to add a low concentration of CDTA to the background electrolyte to prevent dissociation of complexes inside the capillary [14]. Nevertheless, since CDTA absorbs at the same wavelength as the complexes, it is advisable to add the least amount of CDTA to the electrolyte to obtain the best LOD's. It was observed that the complexes with the smallest complexation constant (Ba, Ca, Mg) dissociated inside the capillary when no CDTA was added to the electrolyte making necessary to add CDTA to the buffer to preserve them. A 0.5 mM CDTA concentration was found to be enough to preserve the metallic complexes (Fig. 3).

3.2. Organic gunshot residues separation

In order to achieve the separation of the organic gunshot residues, it was necessary to add a micellar phase to the background electrolyte because almost all of them lack any acid–base properties. As counter electroosmotic conditions were used to achieve the separation of the inorganic residues, SDS micelles were tested to analyze simultaneously both kinds of residues.

Since the most important parameter in MEKC is the amount of micellar phase in the electrolyte, SDS concentration was increased until the organic gunshot residues were separated. Baseline resolution was achieved at concentrations above 16 mM of SDS. Later on, it was found that the presence of SDS did not change the selectivity and separation of the metal–CDTA complexes (data not shown), allowing the simultaneous separation of organic and inorganic gunshot residues in a single run.

Nevertheless, it was found that the Fe–CDTA complex could interfere with some organic residues at determined SDS
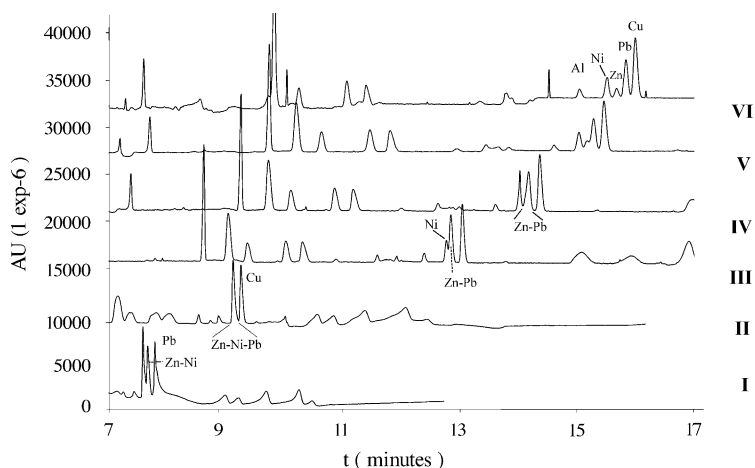
Fig. 2. Effect of borate concentration on the separation of inorganic residues: (I) 5 mM, (II) 15 mM, (III) 25 mM, (IV) 30 mM, (V) 35 mM, (VI) 40 mM. Electrolyte: borate buffer pH 9.2, 25 mM SDS, bare fused silica capillary 79.2 cm total length × 75 μm i.d. Hydrodynamic injection: 0.5 p.s.i. for 5 s at 25 C; 30 kV positive voltage, UV detection at 214 nm. Pb and Zn 10 mg/L, Cu, Ni and Al 20 mg/L.

concentrations. The separation of all the residues (organic and inorganic) was obtained at a concentration of 16 mM SDS or above 20 mM (Fig. 4). The SDS concentration of 16 mM was selected because it provided the smallest analysis time.

3.3. Optimization of system capillary electrophoresis parameters

3.3.1. Internal diameter and capillary length

Other parameters, like the length (60 and 79.2 cm) and internal diameter (50, 75 and 100 μm) of the capillary were studied. A 79.2 cm capillary length provided the best possible resolution; smaller capillaries did not separate completely all the residues. A 50 μm capillary provided more efficiency than others capillaries (100 or 75 μm) but higher limits of detection (LODs). The use of 100 μm was not recommendable because of the high current produced (217 μA). Since gunshot residues are found in small quantities, the LOD is considered a very important parameter, thus a capillary of

75 μm was selected. This capillary allows a baseline separation of all the residues under study with efficiencies (theoretical plates) around 300 000 for metal complexes and 100 000 for organic substances (Fig. 5).

3.3.2. Detection wavelength

The diode array UV–VIS detector was used to find the proper monitoring wavelength. A 200 nm wavelength was selected because of the best sensitivity observed (Table 2).

3.3.3. Sample size

Another approach to improve the LODs was injecting the largest possible volume of the sample [13,19]. The behavior of the chelates was different from the organic substances. It was possible to inject hydrodynamically 20 s at 0.5 p.s.i. of the metal complexes without significant lost of efficiency
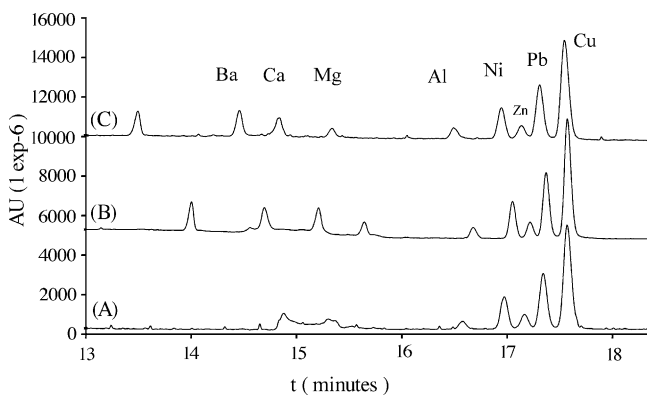

Fig. 3. Effect of CDTA concentration on the stability of metal complexes. Electrolyte: 40 mM borate buffer, 16 mM SDS, pH 9.2. (A) No CDTA, (B) 0.5 mM CDTA, (C) 1 mM CDTA. Metal concentration (mg/L): Ba 30; Mg, Ca, Al, Ni and Cu 20, Zn and Pb 10. Other conditions as in Fig. 2
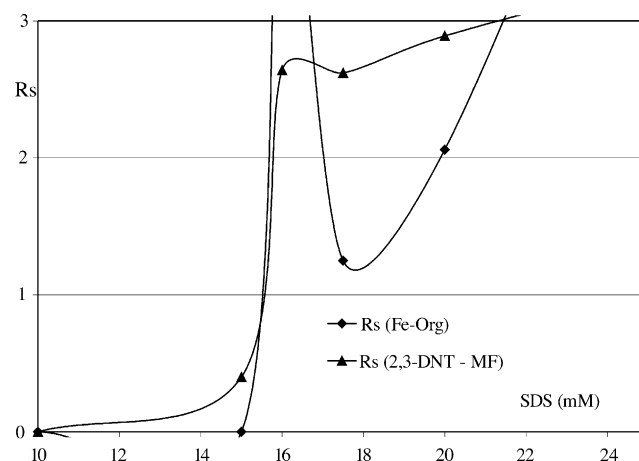

Fig. 4. Effect of SDS concentration on the separation of 2,3-DNT and MF and selected organic gunshot residues and Fe–CDTA. Electrolyte: 40 mM Borate, pH 9.2. Iron concentration: 10 mg/L, organic residue concentration: 0.0001 M. Other conditions as in Fig. 2
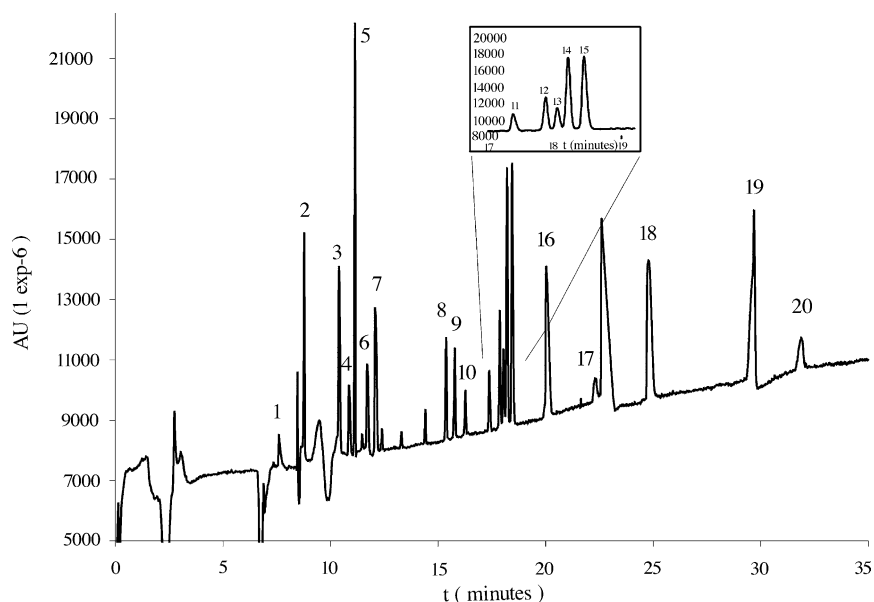
Fig. 5. Simultaneous separation of organic and inorganic gunshot conditions under optimal conditions. Electrolyte: 40 mM borate buffer, 16 mM SDS, 0.5 mM CDTA, capillary: 79.2 cm (69.2 cm detection length) × 75 μm i.d. Hydrodynamic injection: 0.5 p.s.i. for 5 s at 25 C, UV detection at 200 nm. (1) Sb (30), (2) resorcinol (11.1), (3) 24-DNT (10.93), (4) 26-DNT (14.57), (5) Fe (10), (6) 23-DNT (18.2), (7) MF (6.0), (8) Ba (30), (9) Ca (20), (10) Mg (20), (11) Al (20), (12) Ni (20), (13) Zn (10), (14) Pb (10), (15) Cu (20), (16) EF (17.8), (17) DPA (16.9), (18) MC (14.4), (19) EC (22.6), (20) BF (10). Standard concentrations in parentheses in mg/l.

or resolution, increasing the LOD by a factor of 3. On the other hand, the efficiency of organic gunshot residues peaks deteriorated faster with lost of resolution, band broadening and peak splitting. An injection of 5 s at 0.5 p.s.i. was used in the following experiments to avoid the effects observed for the organic residues when longer injection times were used.

Electrokinetic injection was also applied in an attempt to improve LODs; when a negative voltage was used, any organic or chelate compounds were introduced in the capillary. A positive voltage introduced the analytes into the capillary. Increments in the injection time and in the applied voltages lead to better detection limits, but the hydrodynamic injection behavior, characterized by lost in efficiency and resolution of organic compounds was also found.

Field amplification [15,20] was also tested but as expected, positive results were observed only for the metal complexes (a 80-fold increment was obtained for most of the metal complexes). Hydrodynamic injection was used for the quantification studies since it has less matrix effects, making quantification more reproducible and accurate [21]. The selected injection (5 s at 0.5 p.s.i.) is equivalent to injecting 0.5% of the capillary length or 19 nl of sample.

3.4. Calibration and detection limits

Peak purity measurements were above 0.95 for all components, thus the selectivity of the method was ensured. The method precision was evaluated through repeating six times the analysis of the standard solution in the same day. Migration time R.S.D. below 1% for all the analytes were obtained, and peak area R.S.D. were commonly less than 5% for most of the analytes. R.S.D. larger than 5% were obtained due to either the analyte concentration used in the standard solution was near to its LOD or a drift in the baseline in the zone of the peak (Table 3).

Calibration curves for every residue in the expected range of concentrations in the real gunshot samples were constructed using four to six levels of calibration. Each point was analyzed in triplicate. The most important parameters from the calibration graphs are given in Table 4. Linearity of peak area response described as $r^2 > 0.99$ over three orders of magnitude were obtained for most of the residues. The detection limits for all the substances were calculated in pure solutions from the calibration graphs as the blank signal plus three times their standard deviation (Table 4).

Table 2
Relative sensitivities at different wavelengths determined by comparison of peak areas

Wavelength (nm)	Sb	Rs	26-DNT	Fe	MF	Ba	Al	Pb	Cu	DPA	EC
200	6.8	1.8	1.5	1	3.8	2.6	3.2	2.8	1	2.1	1.9
205	3.7	1.4	1.3	1	2.2	2.1	2.1	2.2	1	1.5	1.5
214[a]	1	1	1	1	1	1	1	1	1	1	1
254	0	0.2	0.6	1	0.2	0	0	0.6	1.1	0.3	0.5

[a] Sensitivities related to 214 nm peak height. CE conditions and standard concentrations as in Fig. 5.

Table 3
Selectivity and reproducibility parameters of the method ($n = 6$)

Analyte	Migration time (min)	$-\mu_{eff}$ ($\times 10^{-5}$ cm^2 s^{-1} V^{-1})	Time R.S.D. (%)	Area R.S.D. (%)	Peak purity
Sb	7.56	4.328	0.31	12.20	0.9999
Nitroglycerine	8.49	9.379	0.65	2.46	0.9984
Resorcinol	8.84	10.201	0.34	3.85	0.9959
2,4-DNT	10.51	15.743	0.27	5.37	0.9623
2,6-DNT	10.99	17.005	0.30	2.66	0.9980
Fe	11.22	17.576	0.25	2.28	0.9945
2,3-DNT	11.85	19.037	0.32	2.04	0.9897
Methyl phthalate	12.22	19.824	0.33	1.66	0.9952
Ba	15.50	25.142	0.29	2.27	0.9995
Ca	15.92	25.657	0.29	1.78	0.9991
Mg	16.41	26.239	0.29	3.66	0.9998
Al	17.54	27.441	0.35	5.43	0.9999
Ni	18.03	27.916	0.33	1.62	0.9982
Zn	18.21	28.085	0.33	1.42	0.9994
Pb	18.38	28.241	0.34	1.34	0.9867
Cu	18.62	28.455	0.34	1.74	0.9768
Ethyl phthalate	20.34	29.852	0.52	1.95	0.9965
Diphenyl amine	22.66	31.395	0.52	17.95	0.9927
Methyl centralite	25.18	32.751	0.65	5.08	0.9955
Ethyl centralite	30.13	34.754	0.73	8.62	0.9969
Butyl phthalate	32.45	35.483	0.72	13.22	0.9997

CE conditions and standard concentrations as in Fig. 5.

3.5. Analysis of real samples

Before applying the method to real samples it was necessary to find the best sampling conditions. Swabbing and masking tape sampling were used, since they are the most used sampling methods [2,4]. Several solvents were tested in order to find the best sampling solvents for both methods (Table 5). A system with 5 mM CDTA, 12 mM SDS and 0.4 mM borate for scrubbing and leach out provided the best results for swabbing sampling, while leach out with methanol for masking tape sampling, give good recuperations for inorganic and organic residues. Both systems were used to perform the sampling.

Real samples from a 22 mm pistol, a 32 mm revolver and 38 mm revolver were taken with swabbing sampling under controlled conditions and analyzed by capillary electrophoresis (Fig. 6) and AAS for lead and barium. The results were analyzed by a variance analysis and by a multiple range test. A

Table 4
Calibration parameters ($N = 6$, $\alpha = 95$)

Analyte	m	b	r^2	Range (mg/l)	LOD (mg/l)
Sb	921 ± 127	−11771 ± 5704	0.9902	12.5–100	10.942
Nitroglycerine[a]	3312 ± 299	4118 ± 2041	0.9975	1.25–20	1.299
Resorcinol	2518 ± 68	89 ± 375	0.9997	0.28–11.1	0.109
2,4-DNT[a]	2969 ± 391	−966 ± 3033	0.9981	1.09–36.4	0.702
2,6-DNT	1262 ± 67	−143 ± 1044	0.9985	0.55–36.4	1.770
Fe	4032 ± 48.5	445 ± 301	0.9999	0.25–10	0.110
2,3-DNT[a]	1887 ± 191	−1933 ± 3309	0.9970	1.09–36.4	2.782
Methyl phthalate	3654 ± 124	−45 ± 632	0.9994	0.29–11.6	0.361
Ba	577 ± 18	−4 ± 323	0.9995	0.75–30	0.845
Ca	720 ± 50	1844 ± 663	0.9975	0.5–20	1.264
Mg	370 ± 20	353 ± 264	0.9985	0.5–20	0.980
Al	737 ± 17	369 ± 233	0.9997	0.5–20	0.434
Ni	1087 ± 34	58 ± 447	0.9994	0.5–20	0.565
Zn	1600 ± 65	−23 ± 407	0.9991	0.25–10	0.370
Pb	5090 ± 103	39 ± 606	0.9998	0.25–10	0.186
Cu	2241 ± 71	438 ± 928	0.9995	0.5–20	0.576
Ethyl phthalate	4798 ± 179	79 ± 1804	0.9992	0.33–13.3	0.455
Diphenyl amine[a]	7308 ± 678	1293 ± 8277	0.9975	1.06–33.8	2.387
Methyl centralite	5852 ± 246	266 ± 1223	0.9990	0.36–14.4	0.553
Ethyl centralite	5363 ± 204	−488 ± 2502	0.9992	0.4–16.1	0.561
Butyl phthalate[a]	2797 ± 2515.6	−4567 ± 15011	0.940	0.25–20	4.083

Capillary conditions as in Fig. 5.

[a] $N = 5$.

Table 5
Residue recuperation (%) using different solvents for sampling

Sampling		Ethyl phthalate	2,3-DNT	Ethyl centralite	Fe	Pb	Ba
Scrubbing	Leach out						
Water	Water	19	13	–	–	7	–
Water	CDTA	15.0	14.5	2	16	17	15
Nitric acid	CDTA	20	17.6	–	18	32	10
Nitric acid	Nitric acid	–	–	–	12	14	8
CDTA	CDTA	22	18.6	2	12.6	25	10
CDTA-SDS	CDTA	17.5	9.5	1	17	36	7
CDTA-SDS	CDTA-SDS	60	–	105	47	29	92
CDTA	CDTA-SDS	47	–	110	34	33	99
HNO_3	CDTA-SDS	77	–	144	22	17	5
Acetone	Acetone	8.8	1.7	3.5	2.2	–	–
Masking tape	Acetonitrile	0	0	0	0	0	0
Masking tape	Methanol	23	10.8	19	6.3	13.4	11.6
Masking tape	Chloroform	2	5.2	0	12.5	19.6	21

CE conditions as in Fig. 5 The recuperation were studied in the swabbing sampling from 100 µg of each residue under study previously put in the hand as indicated in [16]. In the masking tape technique 10 µg were used.
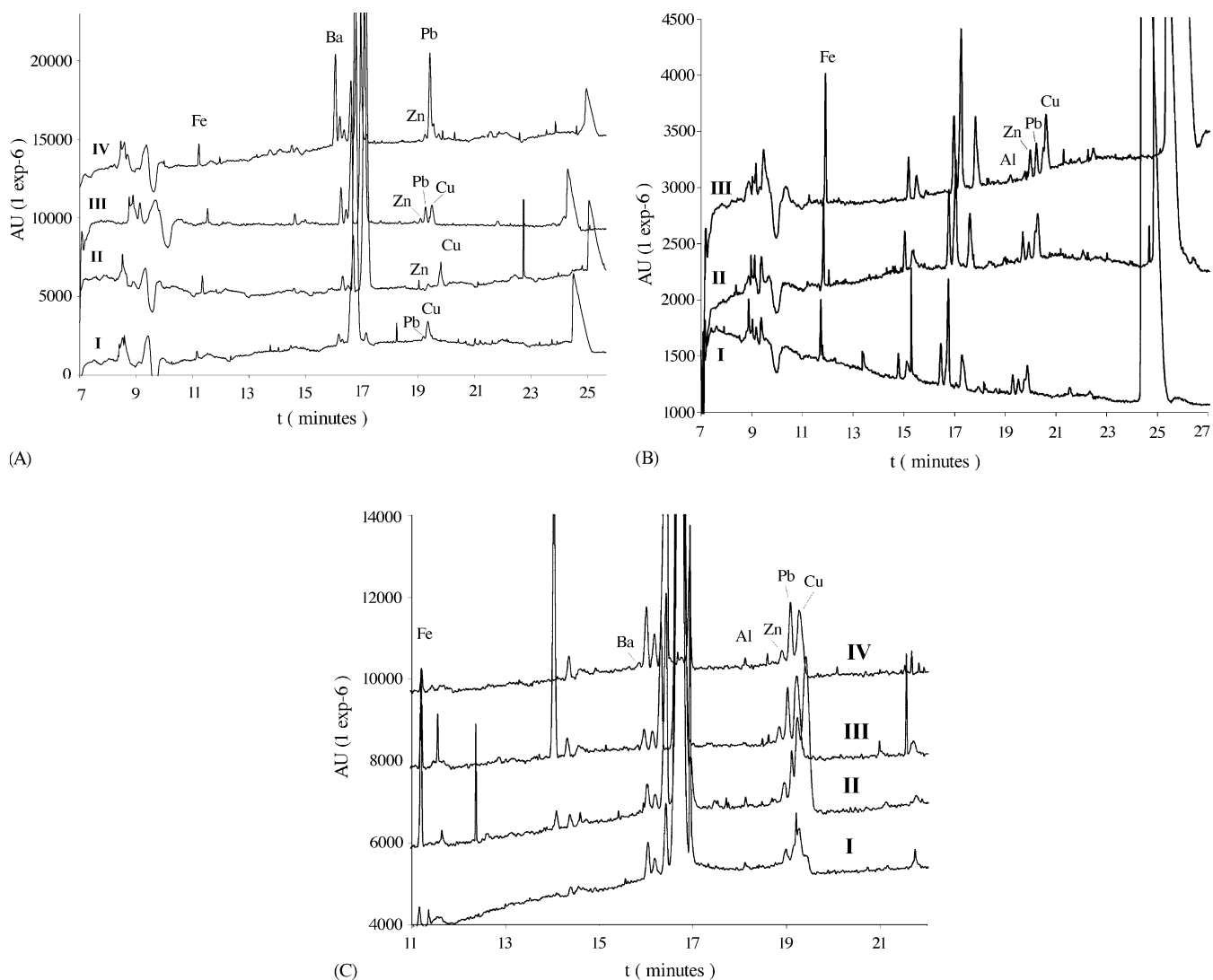

Fig. 6. Electropherograms obtained from (A) 32 mm shot; Orea Hnos. revolver, Smith and Wesson ammunition (B) 38 mm shot; Smith and Wesson revolver, El Aguila ammunition (C) 22 mm pistol shot; El Aguila ammunition. (I) Blank, (II) palm, (III) maculation zone one shot, (IV) maculation zone three shots. The samples were taken under optimized conditions using the swabbing technique. CE conditions as in Fig. 5
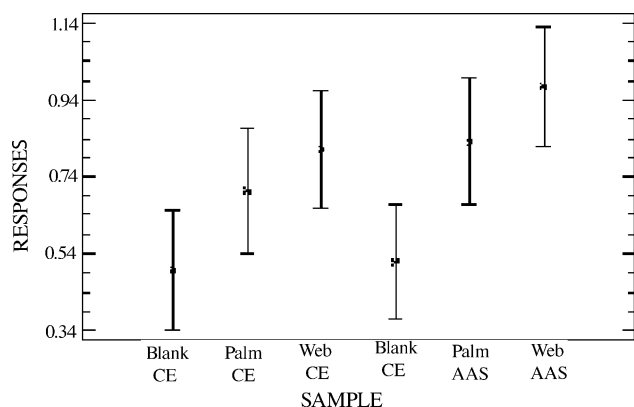
Fig. 7. Comparison of capillary electrophoresis and ET-AAS for the determination of lead deposited after gunshots ($n = 9$) from a 38 mm Smith and Wesson revolver. CE conditions as in Fig. 5

statistical difference between the lead determination by capillary electrophoresis and ET-AAS was not found (Fig. 7).

As gunshot residue test interpretation is sustained in the differences in the amount of residue found in the firing hand compared to the non-firing hand as well as the web area from the palm of the firing hand, the comparison of these three areas were done using the tests previously described. In this study more metal residues (lead, zinc, iron, calcium, copper) were observed in the firing hand than in the non-firing hand, but the residue amount found in the different zones of the tested firing hand were not statically different (Fig. 7); these could have an impact on the sampling procedure applied.

Since the organic residues were not detected in real samples using the swabbing and masking tape sampling, a liquid extraction was applied to 32 mm revolver samples, in order to concentrate these residues, as described in the experimental section. With this procedure, the detection of 2,3-

dinitrotoluene was enhanced and its presence was clearly demonstrated (Fig. 8).

4. Conclusions

A capillary electrophoresis method to determine simultaneously organic and inorganic gunshot residues was developed, issues as sampling methodology, selectivity, reproducibility and quantification were studied. Nevertheless, the LODs of some considered important residues, as barium, antimony and the organic gunshot residues were not good enough to detect them. However, after applying a preconcentration step, the presence of organic gunshot residues becomes evident.

Since on-line preconcentration techniques only produces positive results for metal chelates, a better option might be a pre-concentration technique like evaporation, extraction methodologies or changing the sampling procedure to obtain a more concentrated sample [22].

Because, inorganic residues lose no resolution when more sample is injected, another possibility is to analyze them by capillary electrophoresis separately, the inorganic substances injecting more sample and analyze the organic substances in another run or using another technique as gas chromatography.

Since it was proved that capillary electrophoresis detects other gunshot residues that the traditionally searched (Pb, Ba, Sb), this technique offers more tools to interpret a gunshot residue test to forensic scientists enhancing the specificity of the test. As the combined incidence of the organic and inorganic residues in the environment is rare, the developed method reduces the probability to confuse the data with some contamination, or even the need to use threshold levels.
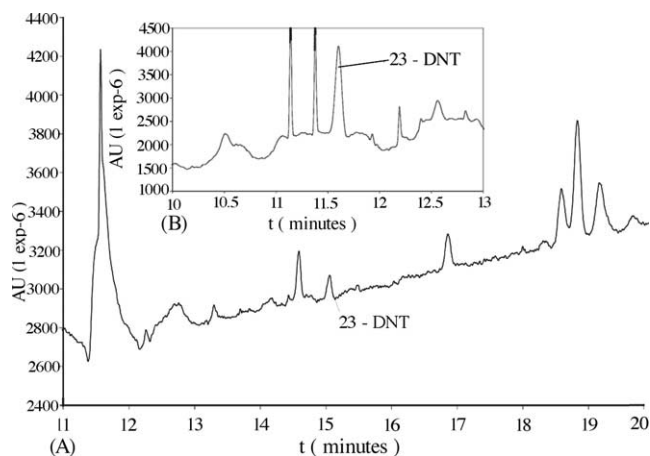
Fig. 8. Determination of 2,3-dinitrotoluene from the maculation zone after three shots with a 32 mm Orea Hnos. revolver. (A) Before liquid extraction capillary electrophoresis as in Fig. 5. (B) After liquid extraction and concentration of organic gunshot residues. CE electrolyte 16 mM SDS, 20 mM borate pH 9.2. Other conditions as in Fig. 5

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