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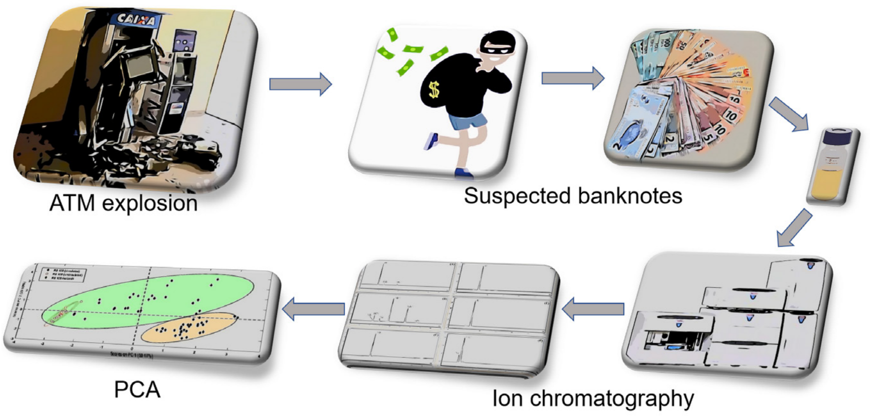
Technical Note

Assessment of Banknotes as a Matrix for Detecting Post-Explosion Residues of Fuel-Oxidizer Explosive Mixtures Using Ion Chromatography

Lúcio Paulo Lima Logrado[1,2], **Jez Willian Batista Braga**[2,3]*, **João Carlos Ambrósio Laboissiere**[1]

[1]*Instituto Nacional de Criminalística, Polícia Federal do Brasil, 70610-200, Brasília, DF, Brazil*
[2]*Instituto de Química, Universidade de Brasília, 70910-000, Brasília, DF, Brazil*
[3]*Instituto Nacional de Ciência e Tecnologia de Bioanalítica (INCTBio), 13083-970 Campinas, SP, Brazil*



Banknotes are commonly subjected to chemical analysis in forensic laboratories in the search for post-explosion residues. This matrix presents unique challenges due to the potential presence of target analytes resulting from everyday use, as well as the lack of control samples for comparison. In addition to their relevance in attacks against Automated Teller Machines (ATMs), banknotes are of significant interest when confiscated from suspicious individuals, vehicles, and locations, as they can provide valuable evidence in establishing a connection to this type of crime scene. In such cases, the absence of bulk particles, alternative materials, and control samples is common. This study employed ion chromatography to analyze uncirculated, circulated, and seized banknotes, aiming to determine their ionic profiles. This investigation provides insights into the background levels of target ions in banknotes and aids in the analysis of post-explosion residues. A simple, fast, and precise extraction method was proposed, yielding RSD values below 10% for most analytes in uncirculated banknotes. The study revealed the presence of various ions of interest, some in significant concentrations, even in uncirculated banknotes. PCA analysis demonstrated a clear separation of uncirculated notes based on their banknote value. However, this clustering behavior was not observed in circulated banknotes due to natural variations in analyte concentrations. Interestingly, when uncirculated, circulated, and seized R$ 100 banknotes were analyzed together, the seized samples from an ATM robbery showed a distinct separation from the other groups, indicating the potential for developing classification models.

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INTRODUCTION

The analysis of explosives and post-explosion residues is a critically important area in forensic chemistry, providing crucial insights into various incidents involving the use of explosives. This type of analysis plays a key role in addressing fundamental questions related to the crime, including: i) Was there an explosion? ii) What was the cause of the explosion? iii) Who was responsible for the explosion? iv) Are there any indications of a clandestine explosives production facility? v) Can any patterns or trends be identified?[1,2]

According to a previous study conducted by our research group, in Brazil, most cases involving the use of explosives are targeted against Automated Teller Machines (ATMs). This issue is also prevalent in several other countries worldwide.[2] The study further revealed that these crimes predominantly involve the use of Improvised Explosive Devices (IEDs) based on black powder, mixtures containing chlorate and/or perchlorate salts, and explosive emulsions.[2]

Figure 1 depicts the unpredictable nature of scenarios resulting from this type of crime, which can vary from the failure of the explosive device with minimal damage to the complete destruction of bank branches, causing significant structural damage. This unpredictability arises from various factors, including the type, quality, and containment of the explosive used, the expertise of the perpetrator, and the structural characteristics of the ATM location.[3]

Figure 1. Unsuccessful ATM explosion attempt (left),[4] effective ATM explosion with relative level of destruction (center)[5] and ATM explosion with high level of destruction of a bank branch with damage including its building structure (right).[6]

All these diverse variables introduce varying levels of complexity in both the investigation of explosion scenes and the subsequent laboratory analysis of post-explosion residues. When bulk material is available, a wider range of analytical techniques can be employed, resulting in more robust findings and mitigating potential issues related to matrix interference. Examples of analytical techniques commonly used in these cases include Raman microscopy,[2,7-9] FTIR,[2,10,11] GC-MS,[2] and DART-MS.[12]

Nevertheless, in some cases of explosions, only invisible residues may be left at the crime scene, necessitating solvent extractions for analysis and using a more limited set of techniques. Among these techniques, ionic chromatography with conductivity detection (IC-CD) is the most employed worldwide for the identification of inorganic components present in explosives.[13-15]

In the analysis of post-explosion residues using IC-CD, the objective is to identify the ions present in the original composition of the explosive mixture, as well as ions of substances formed during the explosive reaction. The interpretation of the ionic profile obtained from the analysis of cations and anions is evaluated to reach a conclusion regarding the identification of the explosive. Table I provides information on the original components and the main analytes of common fuel-oxidizer explosive mixtures frequently employed in ATM robberies in Brazil, including black powder, $KClO_3$-based mixtures, and explosive emulsion.[1,14-16]

Table I. Common explosives mixtures used in Brazil and major target ions in post-explosion residues

Explosives	Composition	Major target ions in post-explosion residues
Black Powder	KNO_3, C, S	SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SCN^-, OCN^-, K^+
$KClO_3$/sulfur-mixture	$KClO_3$, sulfur	Cl^-, ClO_4^-, ClO_3^-, K^+, SO_4^{2-}
Explosive emulsion	NH_4NO_3, fuel oil	NH_4^+, Na^+, NO_3^-

As depicted in Table I, except for explosive emulsion, the presence of potassium cation (K^+) is detected, which is prevalent in the majority of our cases. Potassium salts are commonly used in pyrotechnic products due to their low hygroscopicity. However, salts of other cations, such as lithium (Li^+), sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), can also be utilized for this purpose and should be considered as possible analytes of interest, although less frequently encountered.[16]

As indicated in Table I, most analytes are common ions that can originate from sources other than explosives, including their natural occurrence in the environment,[1,14-16] materials commonly used in evidence collection and laboratory sample processing,[17] and even the materials that support post-explosion residues themselves. For this reason, when analyzing post-explosion residues, especially those involving fuel-oxidizer explosive mixtures, it is crucial to have knowledge about the various materials involved, such as matrices, sampling and laboratory materials. This understanding facilitates the interpretation of the obtained results. While some studies have investigated background levels of these target analytes in various locations/matrices,[18-21] and sampling materials commonly used in routine laboratory practices,[17,22] no specific study has been conducted to determine the background levels of these analytes in a crucial matrix for this type of analysis: banknotes. This is particularly relevant in regions where ATM explosions are frequent.

An ATM explosion often leaves various types of trace evidence, allowing for the collection of multiple materials at the post-explosion scene. These materials may include fragments of plastic, metal, and paper from Improvised Explosive Devices (IEDs) or objects/structures affected by the explosion. Additionally, it is possible to collect soil, clothing, banknotes, swabs, and cotton balls or disks impregnated with residues. The collection of multiple types of materials generally increases the chances of obtaining results that enable a simpler and more conclusive interpretation, as it allows for the selection of more suitable materials that are less prone to interference issues.

Nevertheless, there are instances when the banknotes seized for forensic analysis do not come directly from the explosion scene but are obtained from suspicious individuals, vehicles, properties, or found abandoned on the street. These banknotes can be submitted to the forensic laboratory with the aim of establishing a connection to criminal activities involving ATM robberies using explosives. Unlike in post-explosion scenes, in these cases, there is often not more than one type of material, but rather only the banknotes. In these situations, the lack of control samples (blanks), coupled with the inherent presence of target analytes even in banknotes unrelated to ATM robberies, poses a significant challenge in interpreting the results of the analysis. Figure 2 illustrates some real cases involving the collection of banknotes for post-explosion residue analysis.

Figure 2. Examples of banknotes seized in different situations and sent to the laboratory for post-explosion residue analysis: ATM post-explosion scene (left),[23] suspect vehicle (center),[24] suspect banknotes found on the street (right).[25]

Some studies have focused on identifying explosives in banknotes through direct analysis of bulk particles.[7,8,26] However, the analysis becomes considerably more challenging when bulk particles are absent, requiring prior extractions. In such cases, the background level of target analytes present in the banknote matrix becomes highly relevant. Based on our experience, this is the most common scenario, particularly when the banknotes are not directly obtained from post-explosion locations but from suspicious individuals, vehicles, or locations. As previously mentioned, the limited presence of residues and the impracticality of collecting control samples greatly hinder the interpretation of results through direct observation of ion chromatograms.

Chemometric models can be useful for data analysis of complex matrices containing interferences or variations from different sources.[27] The application of these models is quite popular in spectroscopy and have been applied to help explosive analysis in near infrared,[28] laser-induced thermal emission[29] and laser-induced breakdown spectroscopy data.[30] However, the application of chemometrics for the analysis of ion IC-CD data is scarce, probably because the chromatograms usually present very good resolution and a lower number of peaks in comparison with other chromatographic techniques, which leads to univariate analysis. To the best of our knowledge, no study has been reported applying multivariate analysis to explore the IC-CD data of banknotes involved in post-explosion cases.

In this context, this paper presents an exploratory study that examines the viability of using IC-CD analysis to identify banknotes containing post-explosion residues. Furthermore, a simple, fast, and precise water extraction method was proposed to enable the analysis of the target analytes usually present in post-explosion cases. The study clarifies the background level of target ions that can be detected through water extraction in uncirculated, circulated, and seized banknotes containing post-explosion residues. The exploratory and pattern recognition analysis of the data was performed using principal component analysis (PCA).

MATERIALS AND METHODS

Reagents and materials

A total of 166 real banknotes were included in the analysis. This comprised ten uncirculated banknotes and fifteen circulated banknotes for each denomination, including R$ 2, R$ 5, R$ 10, R$ 20, R$ 50, and R$ 100. Additionally, sixteen seized banknotes of R$ 100 were included in the study. The uncirculated banknotes were obtained from the Banco do Brasil branch of the Central Bank of Brazil, while the circulated banknotes were collected randomly from various tolls and commercial establishments in Brazil. The suspected banknotes were obtained through a seizure conducted by the Federal Police.

Standard ion solutions were prepared following the procedures of the Forensic Chemistry Laboratory of the National Institute of Criminalistics of the Federal Police, which is certified according to ISO 17025, including the analysis of post-explosion residues within its scope. Anion standard solutions were prepared from a 500 mg L^{-1} stock solution prepared from sodium salts (chloride (Vetec Ltd.), chlorite, perchlorate, nitrite (Sigma-Aldrich Ltd.), sulfate (Cinetica Ltd.), thiosulfate (Carlo Erba Ltd.), nitrate (QEEL Ltd.) and chlorate (Baker Ltd.)) and potassium salts (thiocyanate (Vetec), cyanate (Sigma-Aldrich Ltd.)). Cation standard solutions were prepared from a commercial stock solution (Dionex Six Cation-II Standard (lithium 50 mg L^{-1}, sodium 200 mg L^{-1}, ammonium 250 mg L^{-1}, potassium 500 mg L^{-1}, magnesium 250 mg L^{-1} and calcium 500 mg L^{-1})). All standards solutions and extracted samples were prepared using ultrapure water (18, 2 MΩ cm at 25 ^{o}C) obtained from a Millipore Direct-Q5 purification system.

Instrumentation

Ion chromatography was performed with a Thermo Scientific Dionex ICS-5000 Ion Chromatography System with self-regenerating electrolytic suppression and AS-AP Autosampler. The anion separations were performed in a Dionex IonPacTM AS19 column (2 x 250 mm) using a EGC eluent generator configurated with a potassium hydroxide (KOH) eluent cartridge, operating in multi-step gradient mode, starting from 10 mM (0 min) to 45 mM (40 min), whereas the suppressor current was set to 28 mA. For cation separations, a Dionex IonPacTM CS12A column (2 x 250 mm) was operated under an isocratic condition, 20 mM (30 min) methane sulfonic acid (MSA) generated in-situ from reagent water with EGC eluent generator using an MSA cartridge, and the suppressor current was set to 15 mA. The temperatures of the column and detector cell were held at 30 ^{o}C and 25 ^{o}C, respectively. A loop size of 10 mL and constant flow rate of 0.25 mL min^{-1} for both methods. After each run, approximately 2 mL of pure milli-Q water (18,2 MΩ cm at 25 ^{o}C) was pumped into the column to avoid cross contamination. Instrument control and data acquisition were performed using Chromeleon® software.

Two calibration curves were prepared for each analyte (except for sodium and cyanate), one for low concentrations and another for higher concentrations. Only linear determination coefficients (R^2) over 0.99 were used. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated through linear regression method, using the Equation 1:[31]

$$\mathrm{LOD\ or\ LOQ} = \frac{\mathrm{F\ x\ SD}}{\mathrm{b}} \qquad \text{Equation 1}$$

Where F are the factors 3.3 or 10 for LOD or LOQ, respectively; SD is the residual standard deviation of the linear regression; and b is the slope of the regression line, both for low concentrations curves. The resolutions were calculated by the Chromeleon software, according with Equation 2:

$$\mathrm{R} = 2\ \mathrm{x}\ \frac{\mathrm{t_{ref\ peak}} - \mathrm{t_r}}{\mathrm{BW_{ref\ peak}} + \mathrm{BW_r}} \qquad \text{Equation 2}$$

Where $t_{ref\ peak}$ is the retention time of the reference peak for the resolution; t_r is the retention time of the current peak; $BW_{ref\ peak}$ and BW_r are the widths of the two peaks.

The target analytes of this study were: chloride (Cl^-), chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), sulfate (SO_4^{2-}), nitrite (NO_2^-), nitrate (NO_3^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-), cyanate (OCN^-), potassium (K^+), ammonium (NH_4^+), sodium (Na^+), lithium (Li^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}).

Sample preparation

Initially, a study was conducted to establish a sample preparation methodology that would enable the use of a small volume of water and good reproducible results. Uncirculated banknotes were employed to evaluate various factors, including the type of plastic tube, the way the samples were placed in these tubes (folded or rolled), the water volume, and the sonication time (5, 15, and 30 minutes). The findings indicated that the optimal extraction condition was obtained using 2.500 mL of water in a 4.30 mL plastic tube with a rolled banknote. Interestingly, all tested time periods yielded comparable results, suggesting that the extraction of target analytes is rapid. The methodology used in sample preparation is described in detail below and depicted in Figure 3.

Each banknote was carefully rolled up and inserted into a 4.30 mL plastic tube. Subsequently, 2.500 mL of ultrapure water was added to the tube, which was then sealed with its respective lid. The tube was subjected to sonication for five minutes, followed by vortexing for one minute, and subjected to centrifugation at 4000 rpm for five minutes. The resulting solution was filtered through a 0.45 µm filter directly into an IC-CD vial. Additionally, a dilution step was performed by transferring a portion of the solution into another IC-CD vial at a dilution ratio of 1:20. Both vials, containing the original and diluted solutions, underwent IC-CD analyses in duplicate.

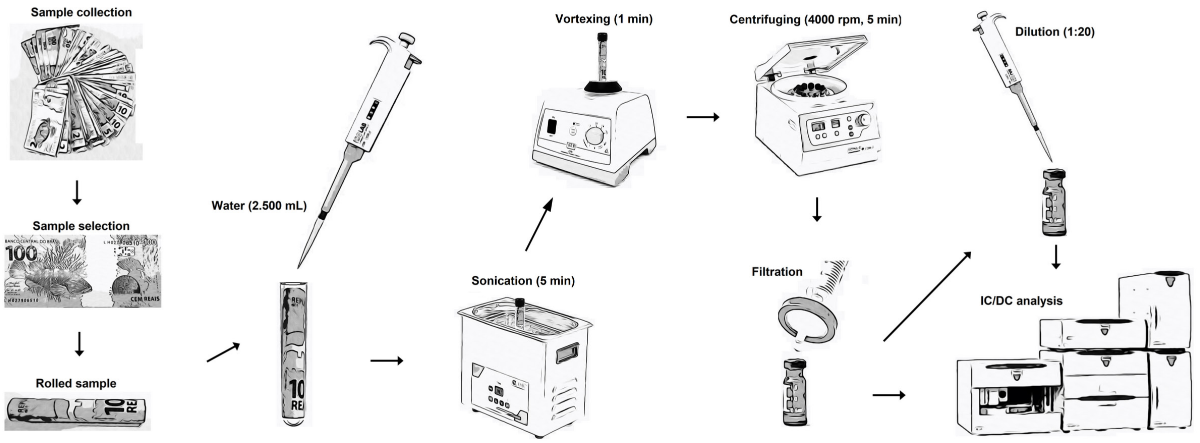

Figure 3. Schematic diagram of the sample preparation for the IC-CD analysis.

Statistical analysis

All chromatograms were processed in the Chromeleon software to obtain the peak areas for all analytes, data were autoscaled before analysis. Principal Component Analysis (PCA) were performed using PLS-Toolbox version 8.8.1 (2022) for MATLAB R2022a. The data matrix was composed by the peak areas of the sixteen target analytes previously described and the PCA was performed using Singular Value Decomposition (SVD) and 95% confidence level for Q residuals and Hotelling T^2 limits for outlier detection.

RESULTS AND DISCUSSION

Table II presents the figures of merit obtained for the method used to quantify the ten anions and six cations in the samples. All analytes demonstrated very good resolution, and the detection and quantification limits were deemed suitable for determining explosive residues in banknotes and other common forensic samples.

Table II. Figures of merit from anion and cation of interest standard samples

Analyte	t_R (min)	Range (mg L^{-1})		Resolution	LOD (mg L^{-1})	LOQ (mg L^{-1})
		Curve 1	Curve 2			
Cl^-	9.037	0.20-1.00	0.80-300.00	4.95	0.009	0.031
ClO_2^-	7.574	0.20-1.00	0.80-300.00	2.78	0.022	0.073
ClO_3^-	12.160	0.20-1.00	0.80-300.00	1.97	0.010	0.033
ClO_4^-	36.680	0.20-1.00	0.80-300.00	3.14	0.019	0.062
SO_4^{2-}	19.070	0.20-1.00	0.80-200.00	3.83	0.036	0.117
NO_2^-	10.847	0.20-1.00	0.80-150.00	1.34	0.009	0.031

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Table II. Figures of merit from anion and cation of interest standard samples (continuation)

Analyte	t_R (min)	Range (mg L^{-1})		Resolution	LOD (mg L^{-1})	LOQ (mg L^{-1})
		Curve 1	Curve 2			
NO_3^-	14.374	0.20-1.00	0.80-300.00	2.27	0.037	0.120
$S_2O_3^{2-}$	27.464	0.20-1.00	0.80-150.00	2.07	0.053	0.175
SCN^-	32.977	0.20-1.00	0.80-100.00	3.51	0.004	0.013
OCN^-	11.394	0.20-1.00	------	1.79	0.011	0.036
K^+	6.400	0.063-2.500	2.50-250.00	7.93	0.044	0.144
NH_4^+	5.193	0.031-1.250	1.25-125.00	4.37	0.015	0.050
Na^+	4.587	------	0.80-150.00	2.43	0.279	0.921
Ca^{2+}	12.970	0.063-2.500	2.50-250.00	3.13	0.023	0.076
Mg^{2+}	10.427	0.031-1.250	1.25-250.00	3.25	0.022	0.074
Li^+	3.900	0.006-0.250	0.25-25.00	3.09	0.005	0.015

The results in Table III show that the presence of several ions of interest was observed in all banknotes, including the uncirculated ones. These detected ions include chloride (Cl^-), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), calcium (Ca^{2+}), ammonium (NH_4^+), magnesium (Mg^{2+}), and nitrate (NO_3^-). However, most of the uncirculated banknotes presented considerably lower concentrations than the circulated banknotes and, as expected, the former showed a more homogeneous concentration (lower RSD) profile of the ions studied. This result highlights the relevance of knowing the ionic profile of materials commonly submitted to analysis, especially in the absence of a control/blank, in order to avoid false positive or inconclusive results. Furthermore, it emphasizes the importance of prioritizing the search for the minority ions, such as perchlorate (ClO_4^-), chlorate (ClO_3^-), chlorite (ClO_2^-), nitrite (NO_2^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-) and cyanate (OCN^-). Depending on the composition of the explosive (Table I), these minority ions may represent valuable information to determine the presence of an explosive residue. However, in the samples used in this study, these minority target ions were not identified, further increasing the degree of difficulty in interpretation of the results.

Table III. Mean concentrations (mg L^{-1}) and RSD%, shown in parentheses, of identified target ions (mg L^{-1}) present in each set of uncirculated (u), circulated (c) and seized (s) banknotes extracts

Bank Notes/ Ions	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	NO_3^-
R$ 2 (u)	71.6 (3)	124.5 (3)	33.9 (5)	21.5 (3)	24.1 (4)	57.5 (6)	2.6 (8)	2.8 (34)
R$ 2 (c)	1631.7 (49)	205.2 (52)	1060.8 (51)	571.3 (55)	31.4 (42)	243.0 (110)	37.8 (73)	17.6 (56)
R$ 5 (u)	199.8 (4)	150.4 (5)	82.8 (4)	28.5 (4)	7.7 (4)	89.2 (4)	2.0 (166)	5.2 (178)
R$ 5 (c)	2083.1 (54)	234.6 (37)	1159.0 (50)	627.5 (51)	21.8 (45)	193.7 (66)	35.8 (86)	23.0 (55)
R$ 10 (u)	252.7 (4)	297.3 (5)	82.2 (5)	34.5 (3)	6.7 (4)	137.9 (4)	19.0 (148)	1.8 (96)

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Table III. Mean concentrations (mg L^{-1}) and RSD%, shown in parentheses, of identified target ions (mg L^{-1}) present in each set of uncirculated (u), circulated (c) and seized (s) banknotes extracts (continuation)

Bank Notes/ Ions	**Cl^-**	**SO_4^{2-}**	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**NH_4^+**	**NO_3^-**
R$ 10 (c)	2500.1 (39)	309.9 (47)	1438.4 (36)	794.8 (38)	30.9 (35)	249.6 (63)	48.7 (77)	26.5 (42)
R$ 20 (u)	198.3 (3)	171.5 (2)	85.9 (4)	40.3 (4)	7.7 (3)	134.0 (5)	1.1 (151)	2.9 (273)
R$ 20 (c)	2675.5 (24)	239.5 (40)	1559.8 (24)	863.4 (29)	32.6 (25)	274.9 (52)	70.6 (71)	28.6 (46)
R$ 50 (u)	224.5 (6)	168.1 (7)	74.3 (7)	39.7 (3)	8.1 (5)	115.9 (6)	9.4 (13)	3.2 (70)
R$ 50 (c)	2162.5 (38)	247.3 (28)	1395.8 (40)	779.1 (36)	31.6 (36)	414.5 (59)	59.6 (93)	16.1 (79)
R$ 100 (u)	293.8 (4)	303.9 (4)	81.1 (4)	50.1 (4)	10.3 (17)	159.9 (21)	37.2 (136)	1.2 (240)
R$ 100 (c)	1363.4 (59)	418.9 (28)	686.8 (62)	414.5 (65)	20.3 (46)	297.8 (79)	138.5 (51)	1.8 (192)
R$ 100 (s)	2269.1 (17)	238.4 (25)	1018.0 (16)	522.0 (17)	20.0 (17)	142.5 (28)	29.4 (110)	0.7 (397)

The results presented in Table III also draw special attention to the typical expected results for $KClO_3$/sulfur-based mixtures, as the most prevalent anions detected in all banknotes (Cl^- and SO_4^{2-}) align with the major anions found in the post-explosion residues of these mixtures. Consequently, they exhibit a closely matching anionic IC-CD profile. Additionally, in terms of cation analysis, the presence of potassium ions is also a complicating factor, as potassium is a very common counter-ion in explosive mixtures, as mentioned earlier.

It is important to clarify that, unlike the typical chromatogram example for a $KClO_3$-based mixture depicted in Figure 4, where the concentrations of the analytes enabled the identification of significant minor ions, such as ClO_3^-, there are instances where only the major ions are detected, further complicating the interpretation of results. This situation can arise due to various factors, including a more thorough explosive reaction, a minimal amount of residue, the utilization of a technique with a high detection limit, or an improper collection/sampling or extraction process.

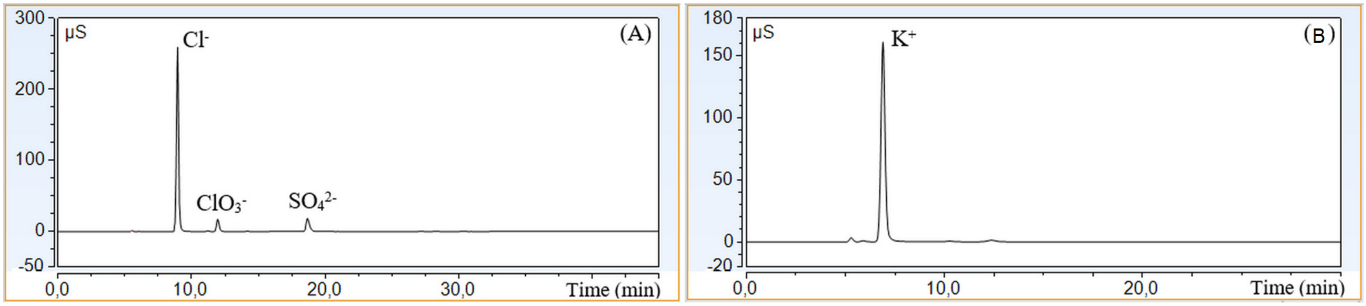

Figure 4. Typical anion (A) and cation (B) exchange ion chromatograms of post-explosion residues of an explosive mixture based on potassium chlorate and sulfur.

In order to illustrate the aforementioned challenge in result interpretation, Figure 5 demonstrates the striking similarity in IC-CD anionic profiles obtained from (1) a forensic case involving the analysis of post-explosion residue on a cotton ball collected at an ATM explosion scene (Figure 5A), (2) one of the circulated banknotes examined in this study (Figure 5B), and (3) residues from a controlled burning of a $KClO_3$/sulfur mixture, where the minor ions (such as chlorate and/or perchlorate) were not detectable due to their insufficient concentrations (Figure 5C). Regarding the results for cations, the analysis of the controlled burning residue reveals the presence of K^+ as the sole cation in the profile (Figure 5F), which generally facilitates the interpretation of the results. However, in real cases, the cationic profile is often not as clean as in controlled burning, with the detection of various other naturally occurring ions (Figure 5D). When this occurs, the resulting cationic profile for the banknotes (Figure 5E) and a real case can be quite similar as well.

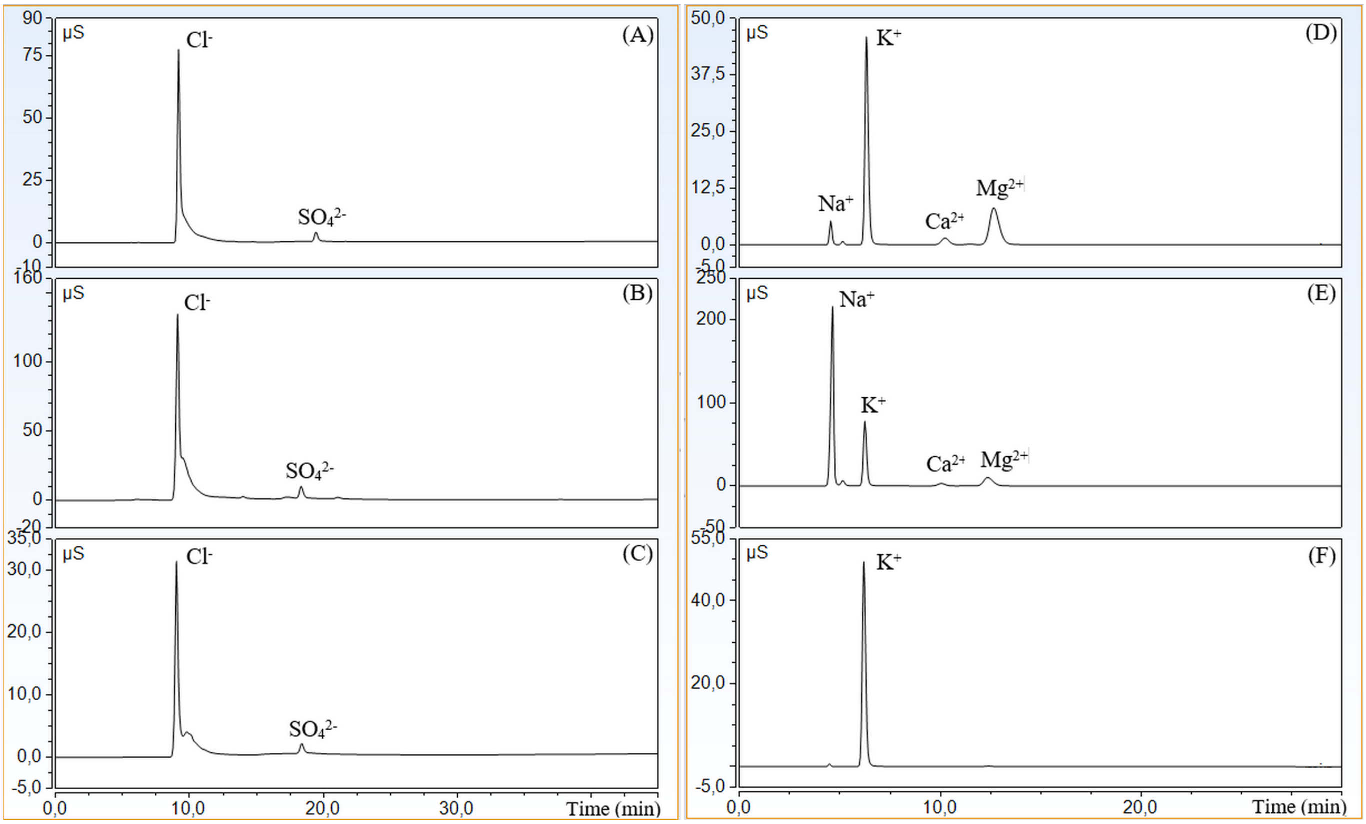

Figure 5. Anion (left) and cation (right) exchange ion chromatograms of post-explosion residue from a real post-explosion residue collected with a cotton ball (A, D), one of the circulated R$ 20 bank notes used in this study (B, E) and a controlled burning of a $KClO_3$/sulfur mixture (C, F).

Due to this difficulty of interpretation, that especially occurs in cases involving banknotes, unsupervised exploratory analyses based on PCA were carried out to verify the existence of patterns in this forensic problem. The results were obtained using the concentrations of six ions of interest (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}) for three sets of data, as follows: i) uncirculated banknotes, ii) circulated banknotes and iii) uncirculated, circulated and seized R$ 100 banknotes. These analytes were selected because they were common ions observed in all three groups of data (uncirculated, circulated and seized banknotes).

The first two principal components explained 91% of the variance present in the ionic profile formed by the six ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}) detected in the uncirculated banknotes. The score plot presented in Figure 6 show that the uncirculated banknotes form well defined clusters according to each of the denominations studied (banknote value). This interesting pattern might be related to the ink and other materials used for the manufacture of each note value. Based on the loadings plot, it can be seen that: i) all ions are important for both principal components (PC), except for Cl^- in relation to PC2; ii) magnesium has the opposite sign to the other ions, appearing to explain a significant part of the different behavior of the R$ 2 notes; iii) K^+ and Ca^{2+} ions present a high correlation.

Although the presence of distinct clusters in non-circulating banknotes (Figure 6A) may not appear to be of forensic interest, it is still an interesting finding that also highlights the accuracy and precision of the proposed method. Additionally, it reveals that banknotes have two categories of interferents: intrinsic ones related to their manufacturing process and extrinsic ones related to their circulation. The latter can be better observed in the following results presented for circulating banknotes.

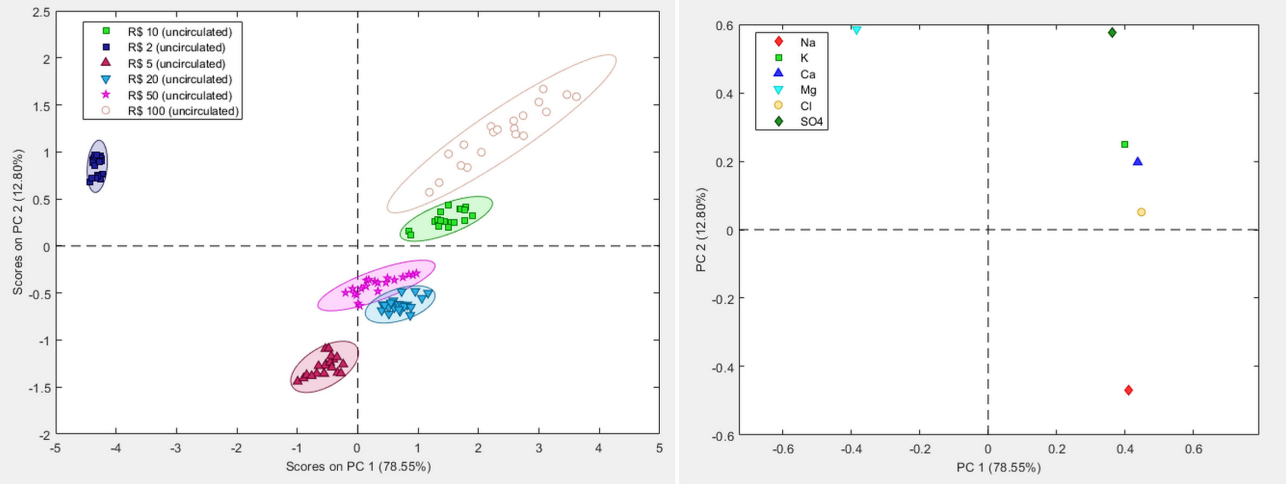

Figure 6. Scores plot (left) and loadings plot (right) for the first two principal components for uncirculated banknotes.

The two-dimensional PCA model for the circulating banknotes using the same ions explained only 78% of the variance, which may suggest the presence of a more complex variance structure in the data. As shown in Figure 7, the clear presence of clusters is no longer observed in the score plot. Furthermore, the loadings distribution is also significantly different from the one observed in the uncirculated banknotes. This result shows that, due to their circulation, the concentration of the analytes in each note value is changed and ionic profile becomes indistinguishable, obfuscating the intrinsic differences observed in uncirculated banknotes. Even with the use of the third and fourth PCs no clear pattern of class separation is observed.

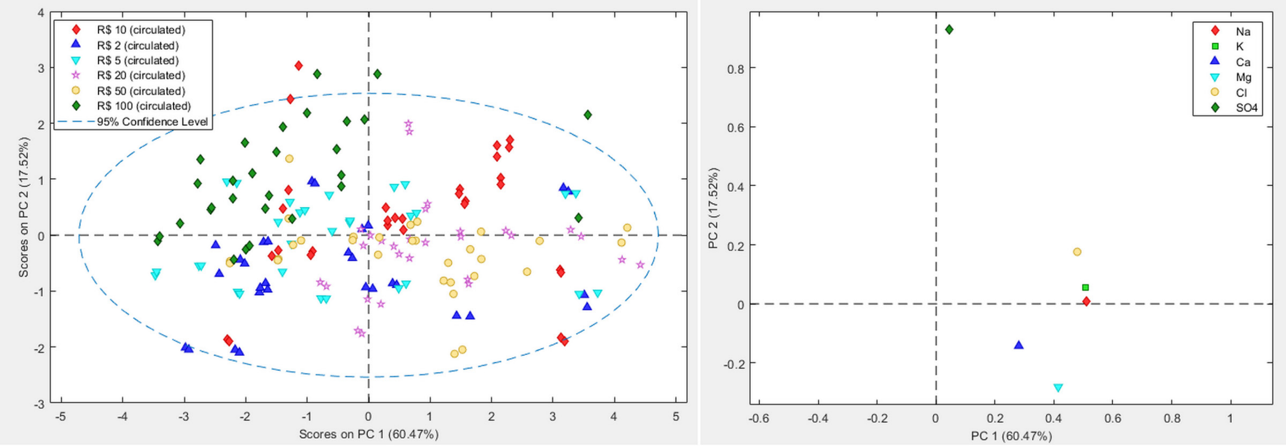

Figure 7. Scores plot (left) and loadings plot (right) for the first two principal components for circulated banknotes.

In the third dataset the first two PCs explained 90% of the variance and the score plot presented in Figure 8A shows that uncirculated/circulated and seized R$ 100 banknotes tend to form distinct groups, in which PC2 seems to be the most important component for the separation between the groups of seized and circulated banknotes. The uncirculated samples presented the most negative values in PC1, but were very close to the circulated samples. This proximity or overlap between uncirculated and circulated notes is, in a way, expected, since among the circulated banknotes there may be the presence of banknotes with just a little circulation, therefore, making them close to the uncirculated ones. Similarly, among the seized banknotes, there may be the occurrence of banknotes that suffered negligible contact with post-explosion residues, thus approaching to the non-suspicious circulated banknotes. After removing the 4 outliers (highlighted by red circles in Figure 8A), two referring to seized banknotes and two referring to circulated banknotes, the scores plot presented in Figure 8C is obtained, where a considerable separation between seized banknotes and the others two groups is observed, considering the 95% confidence ellipses.

Based on the loadings and scores plots (Figure 8B-C), apparently there is a correlation between the seized banknotes and higher concentrations of the ions Cl, K^+ and Na^+ that seems to be important for the distinction of the seized banknotes. Thus, considering that potassium chloride (KCl) is the main product in the explosive reaction of explosives based on chlorate and/or potassium perchlorate and that this type of explosive is widely used in criminal actions in Brazil,[2] this result indicates that the seized banknotes may have come into contact with residues of this type of material. Regarding the importance observed for the Na^+ ion, it may be related to the fact that these types of explosives are often not composed of pure potassium salts, but often with the presence of sodium salts.

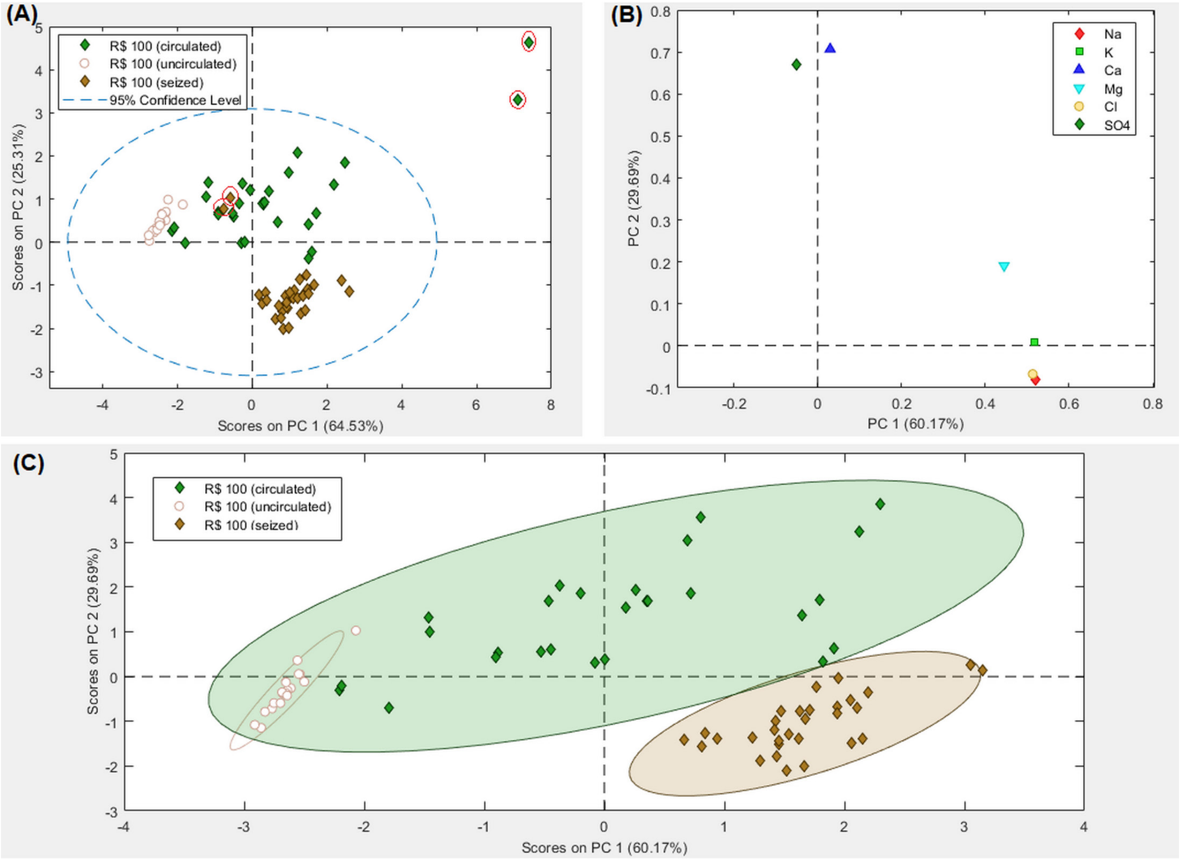

Figure 8. Score plot before removing the outliers (highlighted by red circles) (A), loadings and score plots (B and C, respectively) after removing the outliers for the first two principal components for uncirculated, circulated and seized R$ 100 banknotes. (ellipses) 95% confidence regions of each class.

CONCLUSIONS

The assessment of background levels for the main analytes usually detected in post-explosion residues was demonstrated, wherein their presence in both non-circulated and circulated banknotes was observed, with higher concentrations and greater variability in the latter. This finding highlights the importance of prioritizing alternative materials with lower susceptibility to interferences, whenever feasible, for such purposes.

On the other hand, the study also revealed the absence of highly relevant target ions, such as chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-), cyanate (OCN^-). Therefore, the absence of these ions in the analyzed banknotes is an important finding, as their potential presence in real cases within this context can be indicative of contact with post-explosion residues.

The chemometric analysis performed by PCA showed promising results for the identification of explosives on banknotes in the absence of bulk particles. In spite of the utilization of a limited dataset in this study, consistent results were attained in this case study, indicating that discrimination between unsuspected and suspected banknotes can be achieved through a straightforward water extraction process followed by IC-CD and PCA. Furthermore, a formal and robust classification model can be developed by investigating a larger sample of unsuspected circulating banknotes and validating this model with real-world cases and/or conducting controlled explosions using banknotes as matrices. This second study is currently underway in our laboratory and will be presented subsequently.

Although this study specifically focuses on Brazilian banknotes, it introduces, for the first time, the analysis of banknotes for the identification of post-explosion residue. This not only highlights the relevance within the context of Brazil but also draws attention to other countries facing similar challenges. It serves as an encouragement for them to conduct similar studies on their own banknotes.

Conflicts of interest

The authors declare no conflicts of interest.

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