

1 **Applications of Direct Injection Soft Chemical Ionisation-Mass**
2 **Spectrometry for the Detection of Pre-blast Smokeless Powder Organic**
3 **Additives**

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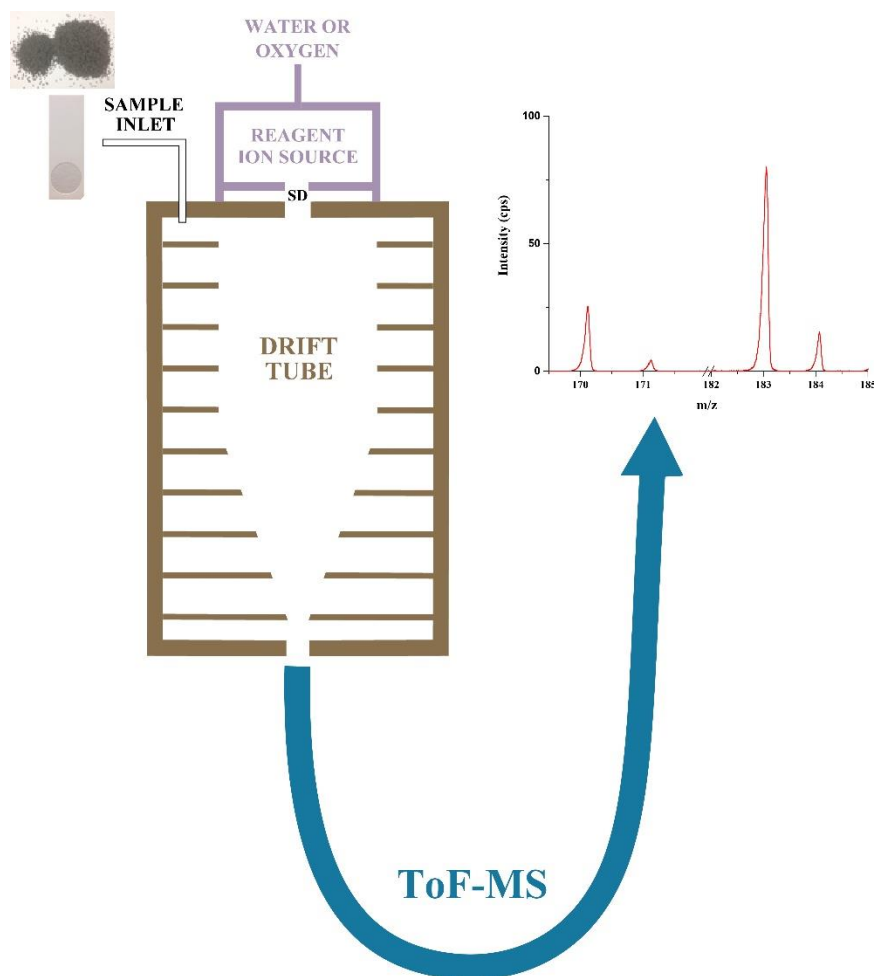
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17 Key words: Soft Chemical Ionisation-Mass Spectrometry; SCIMS; Proton Transfer Reaction
18 Mass Spectrometry; PTR-MS; Smokeless Powders; Smokeless Powder Additives

19
20 **Graphical Abstract**



24 **Research highlights**

25

26 - **Use of Direct Injection Soft Chemical Ionisation-Mass Spectrometry for smokeless**
27 **powder organic additives analysis**

28 - **Study of the underlying water and oxygen chemistry in positive ion mode**

29 - **Comparison of fragmentation patterns for H_3O^+ and O_2^+ reagent ions**

30 - **Performance evaluation for the method in terms of sensitivity, linear dynamic range**
31 **and precision**

32 - **Application to commercial pre-blast samples**

33 **Abstract**

34 Analysis of smokeless powders is of interest from forensics and security perspectives. This
35 article reports the detection of smokeless powder organic additives (in their pre-detonation
36 condition), namely the stabiliser diphenylamine and its derivatives 2-nitrodiphenylamine and
37 4-nitrodiphenylamine, and the additives (used both as stabilisers and plasticisers) methyl
38 centralite and ethyl centralite, by means of swab sampling followed by thermal desorption and
39 Direct Injection Soft Chemical Ionisation-Mass Spectrometry. Investigations on the product
40 ions resulting from the reactions of the reagent ions H_3O^+ and O_2^+ with additives as a function
41 of reduced electric field are reported. The method was comprehensively evaluated in terms of
42 linearity, sensitivity and precision. For H_3O^+ , the limits of detection (LoD) are in the range of
43 41-88 pg of additive, for which the accuracy varied between 1.5-3.2%, precision varied
44 between 3.7-7.3% and linearity showed $R^2 \geq 0.9991$. For O_2^+ , LoD are in the range of 72 pg to
45 1.4 ng, with an accuracy of between 2.8-4.9% and a precision between 4.5-8.6% and $R^2 \geq$
46 0.9914. The validated methodology was applied to the analysis of commercial pre-blast gun
47 powders from different manufacturers.

48 **1. Introduction**

49 Smokeless powders are a large and complex family of products used as propellants in
50 ammunition cartridges,¹ categorized as low explosives (they burn rapidly instead of
51 detonating).² They are commonly employed in forensic analyses as their residues can be used
52 as evidence for firearms discharge.^{3,4} They are also relevant from a Homeland Security
53 perspective, as they are readily available and can be employed in the manufacturing of
54 improvised explosive devices (IEDs).⁵ They exhibit a complex composition, consisting of an
55 explosive material (nitrocellulose, nitroglycerin, nitroguanidine or different mixtures of them),¹
56 heavy metals,^{1,6} and a large number of different classes of organic compounds.^{1,7,8} The latter
57 became of great interest after the introduction of heavy-metal free ammunition in the market.³
58 Within the organic additives category we can include plasticizers, stabilisers, opacifiers, flash
59 suppressants, coolants, surface lubricants and dyes.^{2, 9-13} The aim of these additives is to
60 increase the shelf-life and modify the burning characteristics of the powder.^{5,14} Different
61 concentrations and/or different additives are characteristic of a given manufacturer, producing
62 therefore a chemical fingerprint for each powder.¹⁵ It is thus also important to determine their
63 content throughout the manufacturing quality control process. Among all the possible additives
64 there are a number of key chemicals usually present and regarded as characteristic of smokeless
65 powders.^{1,12,16} The most common are the stabiliser diphenylamine (DPA) and its derivatives 2-
66 nitrodiphenylamine (2-NO₂-DPA) and 4-nitrodiphenylamine (4-NO₂-DPA), and the additives
67 (used both as stabilisers and plasticisers) methyl centralite (MC) and ethyl centralite (EC),
68 which are the subject of this current paper - for structural information see table 1.

69 Several analytical techniques have been used for the qualitative and/or quantitative
70 detection of smokeless powders, either in their pre and/or post-blast forms,^{9,10} including High-
71 Performance Liquid Chromatography (HPLC),¹⁷⁻¹⁹ Liquid Chromatography-Mass
72 Spectrometry (LC-MS),^{8,20-22} Fourier Transform Infrared Spectroscopy,²³ Gas
73 Chromatography (GC),^{12,14,24} Capillary Electrophoresis (CE),^{25,26} Ion Mobility Spectrometry
74 (IMS),²⁷ Solid Phase Microextraction-Ion Mobility Spectrometry (SPME)-IMS,^{12,28}
75 (Nano)Electrospray Ionization (nESI)-Tandem Mass Spectrometry,²⁹⁻³¹ Laser Electrospray-
76 Mass spectrometry (LEMS),^{15,32} Desorption Electrospray Ionization-Mass spectrometry
77 (DESI),^{33,34} Direct Analysis in Real Time- Mass Spectrometry (DART-MS),³⁵ Time-of-Flight
78 Secondary Ion-Mass Spectrometry (ToF-MS),³⁶ and Raman Spectroscopy.^{23,37} Most of the
79 above-mentioned techniques require time-consuming sample preparation step(s) - exception of
80 DESI and DART; or if not, they require complicated set-ups, such the use of lasers as the means
81 for sample vaporization (LEMS) or heated purified gases (DART). Here is where Direct

82 Injection (DI) Soft Chemical Ionisation-Mass Spectrometry (SCIMS) can compete (and/or be
83 complementary) with these techniques for rapid, selective and sensitive detection of chemical
84 compounds in complex environments. DI-SCIMS is an analytical technique for mass
85 spectrometric gas analysis based on the ionization of neutrals by ion/molecule reactions with a
86 reagent ion (such as H_3O^+ , O_2^+ or NO^+). This occurs within the controlled environment of a
87 drift tube (DT) under the effect of an electric field E . The resulting ionised analyte molecules
88 are then mass analysed by mass spectrometer. It is a direct injection technique as samples are
89 injected directly into the drift tube of the instrument.

90 There are several analytical techniques that belong to the DI-SCIMS category,^{38,39} with
91 Proton Transfer Reaction-Mass Spectrometry (PTR-MS) arguably the most widespread. PTR-
92 MS was purposely design for the monitoring of volatile organic compounds (VOCs),⁴⁰ but has
93 developed further to analyse liquid and solid compounds,³⁸ being successfully applied to the
94 detection of explosives and explosive-related compounds in positive ion mode.⁴¹⁻⁵⁰
95 Technically speaking, PTR-MS only refers to the use of hydronium as the reagent ion. Given
96 that in this study we investigated reactions involving O_2^+ and H_3O^+ the term SCIMS is a more
97 accurate description of the instrument for this work.

98 In this paper we report the first DI-SCIMS studies of the additives to smokeless
99 powders; namely DPA, 2- NO_2 -DPA, 4- NO_2 -DPA, MC and EC, using H_3O^+ and O_2^+ as the
100 reagent ions. We can expect efficient reactions with H_3O^+ because the proton affinities for
101 amine and amide-based compounds are higher than that of water. Certainly studies involving
102 ESI-MS,³¹ and IMS,⁵¹ show that these neutrals can be detected with a high sensitivity. Based
103 on the identified ions, analytical figures of merit (limits of detection, linear dynamic range,
104 repeatability and reproducibility) are established. This information should help in the
105 development of a highly selective analytical technique for smokeless powders organic additives
106 detection using DI-SCIMS.

107

108 **2. Experimental Details**

109 **2.1. Proton Transfer Reaction Mass Spectrometry (PTR-MS)**

110 A Kore Technology Ltd. Series I PTR-ToF-MS instrument was used. Details of using PTR-
111 MS is given in detail elsewhere,^{38,47} and therefore only pertinent issues will be briefly
112 mentioned here. Recently this instrument was equipped with a radio frequency ion funnel drift
113 tube and fast reaction region reduced electric field, E/N , switching capabilities.⁵⁰ However, for
114 these studies the RF operation was not used.

115 **2.1.1 Fast reduced electric field switching**

116 Details of the fast switching have been given elsewhere.⁵⁰ In brief, this new hardware
117 development feature allows the rapid switching of the reduced electric field with transition
118 times less than 140 ms (0.1-5 Hz) within the reaction region. This alters the reagent ion
119 composition and ion-molecule collisional energies, leading to differences in product ions
120 between the two operational E/N values. This new hardware development allows for the
121 manipulation of the ion-chemistry, modifying the product ion distribution to provide more
122 information to aid in assignment of the neutral responsible for the observed product ion(s).

123

124 **2.1.2 H₃O⁺ production**

125 Water vapour is introduced into a hollow cathode glow discharge where, after ionisation via
126 electron impact and subsequent ion-molecule processes, the terminal reagent ion is H₃O⁺.
127 These ions are transferred from the ion source into the drift tube by an applied voltage gradient
128 where they react with the analyte M by donating their protons at the collisional rate, providing
129 M has a proton affinity greater than that of water (PA(H₂O) = 691 kJ mol⁻¹). This process can
130 be either non-dissociative (resulting in the protonated molecule MH⁺) and/or dissociative.
131 Dissociative proton transfer results in product ions, which depending on their m/z values, may
132 be useful for the identification of a compound. Fragmentation may be spontaneous upon proton
133 transfer or may require additional energy which is supplied through collisions with the buffer
134 gas resulting during the migration of ions under the influence of the electric field, E . Ions are
135 separated using a time of flight mass analyser and detected by means of a multichannel plate.
136 O₂⁺ is also formed as an impurity due to air back flow from the reactor into the ion source
137 region,⁴³ however the instrument was operated in a manner that this was below 2% of the H₃O⁺
138 signal intensity.

139

140 **2.1.3 O₂⁺ production**

141 For the production of O₂⁺, water vapour in the discharge is replaced by pure oxygen (99.998%
142 purity, BOC Gases, Manchester, UK). This leads to the formation of mainly O₂⁺ reagent ions
143 (> 95%).⁵³ Once injected into the DT, O₂⁺ reacts with the analyte M via charge transfer,
144 provided that the ionisation potential of M is less than that of O₂.⁵⁴ Similarly to 2.1.2, this
145 reaction may be non-dissociative and/or dissociative, and fragmentation may be spontaneous
146 upon charge transfer or require additional energy. H₃O⁺ is also observed due to residual water
147 vapour in the system, with signal intensity below around 2.5% of the O₂⁺ signal for the
148 experimental conditions used throughout.

149 It is worth to highlight that when using O_2^+ as the reagent ion, it is possible to start
150 measurements at lower E/N values than when using H_3O^+ . This is a consequence of the lack of
151 water clustering for O_2^+ . This reagent ion signal had to be inferred from its corresponding
152 isotopologue $^{16}O^{18}O$ at m/z 33.99, owing to detection saturation at m/z 31.99.

153

154 **2.2. Operational parameters**

155 A thermal desorption unit (TDU) connected to the inlet of the drift tube through passivated
156 (Silconert[®]) stainless steel (10 cm length), was used to introduce the samples. Details of the
157 TDU have been given elsewhere.⁴¹ The TDU, connecting lines and drift tube were operated at
158 a temperature of 150°C (maximum possible temperature). PTFE swabs (ThermoFisher
159 Scientific, Cheshire, UK) onto which known quantities of additives were deposited were placed
160 into the TDU. For this study laboratory air was used as the carrier gas. Prior to making contact
161 with the swab, the carrier gas was passed through an oxygen/moisture trap (Agilent OT3-4) -
162 not used for O_2^+ mode- and hydrocarbon trap (Agilent HT200-4). Upon closure of the TDU a
163 seal is created, and the carrier gas is heated to the temperature of the TDU before it flows
164 through a series of apertures in the heated metal plate. This heated air then passes through the
165 swab and into the inlet system driving any desorbed material through to the drift tube creating
166 a temporal concentration “pulse” of typically between 10-20 seconds of an analyte in the drift
167 tube.⁴¹ For the product ion distribution and branching ratio studies each swab provided one
168 measurement, which was replicated three times and then the results were averaged and any
169 background signals were subtracted.

170 The drift tube was maintained at a pressure of 1.1 mbar and the glow discharge (for
171 both water vapour and oxygen) was set at 1.3 mbar (which is a combination of the reagent
172 neutral pressure and air back flowing from the drift tube).

173 For the fast switching experiments, the acquisition time per point was set to 40 ms and
174 ion signals were averaged for each individual cycle.

175 In the following only product ions with a product ion distributions (PID) greater than
176 1% are reported and the m/z of the lightest isotopologue will be given. However, when
177 calculating the product ion distributions all of the isotopologues are taken into account.

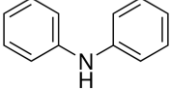
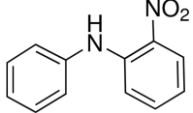
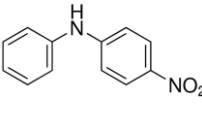
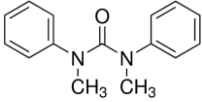
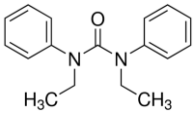
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179 **2.3. Chemical standards and smokeless powder samples**

180 Table 1 gives details of the molar mass and structure of the five compounds investigated in this
181 study.

182

183 Table 1. Molecular weight, linear formula and chemical structure for the components
 184 investigated

Additive	Molar weight, g mol ⁻¹	Linear formula	Chemical structure
Diphenylamine (DPA)	169.22	(C ₆ H ₅) ₂ NH	
2-nitrodiphenylamine (2-NO ₂ -DPA)	214.22	C ₆ H ₅ NHC ₆ H ₄ NO ₂	
4-nitrodiphenylamine (4-NO ₂ -DPA)	214.22	C ₆ H ₅ NHC ₆ H ₄ NO ₂	
Methyl centralite (MC)	240.30	[C ₆ H ₅ N(CH ₃) ₂] ₂ CO	
Ethylcentralite (EC)	268.35	[C ₆ H ₅ N(C ₂ H ₅) ₂] ₂ CO	

185
 186 These chemicals were individually purchased from AccuStandard Inc., (New Haven, CT, US)
 187 and used without additional treatment. DPA came dissolved in MeOH, MC and EC came
 188 prepared in a mixture of MeOH:AcN 1:1 (V/V), 2- and 4-NO₂-DPA in AcN. Concentrations
 189 in all cases were 100 μg·mL⁻¹. Further dilutions of this mother solutions in the appropriate
 190 solvent(s) (HPLC grade) were prepared when needed. Typically, 1 μL of a solution of the
 191 required concentration was spotted onto the swab and left to evaporate the solvents for 1 min
 192 prior to insertion into the TDU.

193 Smokeless powders (either used for guns or rifles) were acquired in a local ammunition
 194 wholesaler. Rifle powders are typically single based (the only energetic material is
 195 nitrocellulose) and gun powders are double based (nitrocellulose together with nitroglycerine).
 196 When needed, 1 g of powder was dissolved in 10 mL of dichloromethane (HPLC grade) for 10
 197 minutes at room temperature with the help of an ultrasonic bath. Once the solvent evaporated
 198 at room temperature, the residue was dissolved in 100 mL of a mixture of MeOH:Acetonitrile
 199 1:1 (V/V). Again, 1 μL was spotted onto the swab and left solvents to evaporate for 1 minute
 200 prior to insertion into the TDU.

201

202 3. Results and Discussion

203 **3.1. Analysis of standard additives. Fragmentation patterns and branching ratios studies**
204 **in H₃O⁺ and O₂⁺ modes.**

205 **3.1.1- Diphenylamine (DPA)**

206 In H₃O⁺ mode (data not shown), the protonated parent [DPA.H]⁺ at a *m/z* of 170.10 dominates
207 across the *E/N* range studied (80-200 Td). One other product ion is observed at high *E/N* values
208 (180 Td and above) at *m/z* 92.05. This is assigned to [C₆H₅NH]⁺, resulting from the loss of
209 benzene from the protonated parent, increasing its intensity from negligible at low *E/N* to a
210 maximum of 5% at 200 Td.

211 In O₂⁺ mode (data not shown), only DPA⁺ at *m/z* 169.09, resulting from non-dissociative
212 charge transfer, is observed for all the *E/N* values (60-200 Td).

213

214 **3.1.3- 2-nitrodiphenylamine (2-NO₂-DPA) and 4-nitrodiphenylamine (4-NO₂-DPA)**

215 Figure 1 shows the PID plots for (a) 2-NO₂-DPA and (b) 4-NO₂-DPA for their reaction with
216 H₃O⁺ as a function of *E/N* (for the range from 80 to 200 Td). For both chemicals, the
217 fragmentation pattern is very similar, and only differences ascribe to the *ortho* effect (**amine**
218 **and nitro groups in adjacent positions for 2-NO₂-DPA**) are observed. For both isomers the
219 protonated parent, *m/z* 215.08, is the dominant ion, with the exception of the 2-isomer at *E/N*
220 values above 190 Td, where a product ion at *m/z* 197.07 (loss of H₂O) takes over. For the 4-
221 isomer a loss of a hydroxyl group, giving a product ion at *m/z* 198.08, is also observed. This is
222 consistent with the *ortho* observed behaviour, where [M-OH₂]⁺ replaces the [M-OH]⁺
223 fragment ion.^{47,55} For the 2-isomer, a subsequent loss of an hydroxyl group (only observed at
224 *E/N* > 160 Td) leads to the product ion at *m/z* 180.06, the intensity of which increases as the
225 *E/N* increases. Finally, another product ion at *m/z* 169.07 corresponding to the nitro group loss
226 from the protonated parent, is observed in both isomers with different intensities (maximum
227 values of ca. 8.5% for 2-isomer and ca. 14% for the 4-isomer, at 200Td), and becoming relevant
228 only above 150 Td in both cases.

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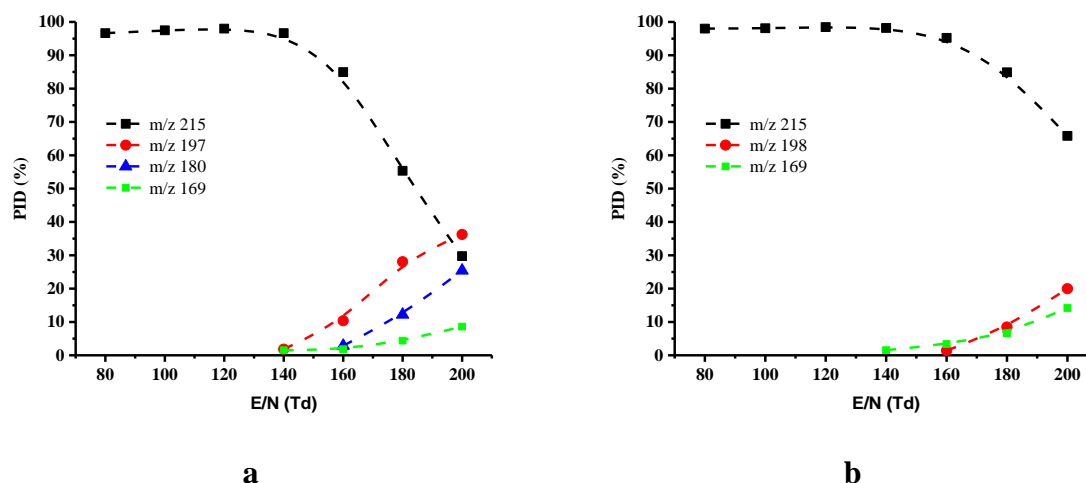


Figure 1. PID plots resulting from the reaction of H₃O⁺ with (a) 2-NO₂-DPA and (b) 4-NO₂-DPA as a function of reduced electric field (80 to 200 Td).

231

232 In O₂⁺ mode (PID plot not shown) and for both 2- and 4-NO₂-DPA, the parent ion at *m/z* 214.07,
 233 the result of non-dissociative reaction channel, dominates. Its intensity decreases as the reduced
 234 electric field increases, dropping down to 25% at 180 Td of the initial intensity at 80 Td. Other
 235 fragment ion, at *m/z* 163.22 (unassigned in this paper), is observed in both cases, the intensity
 236 of which slightly decreases as the reduced electric field increases (from ~2% at 60 Td to 3.5%
 237 at 200 Td for 2-NO₂-DPA, and from ~3.5% to 7% for 4-NO₂-DPA). This unidentified ion is
 238 consistent with the observations reported by Perez et al.³²

239

240 3.1.4- Methyl centralite (MC)

241 In H₃O⁺ mode the protonated parent at *m/z* 241.13, [MC.H]⁺, is observed as the dominant ion
 242 up to around 190 Td (figure 2(a)). Other observed product ions are *m/z* 134.06, assigned to
 243 [PhNCH₃CO]⁺ (resulting from the loss of *N*-methylaniline from the protonated parent), and *m/z*
 244 106.07 (a subsequent loss of a CO molecule leaving a [PhNCH₃]⁺ ion), which only yields a
 245 significant intensity above 140 Td and becomes dominant above 190 Td.

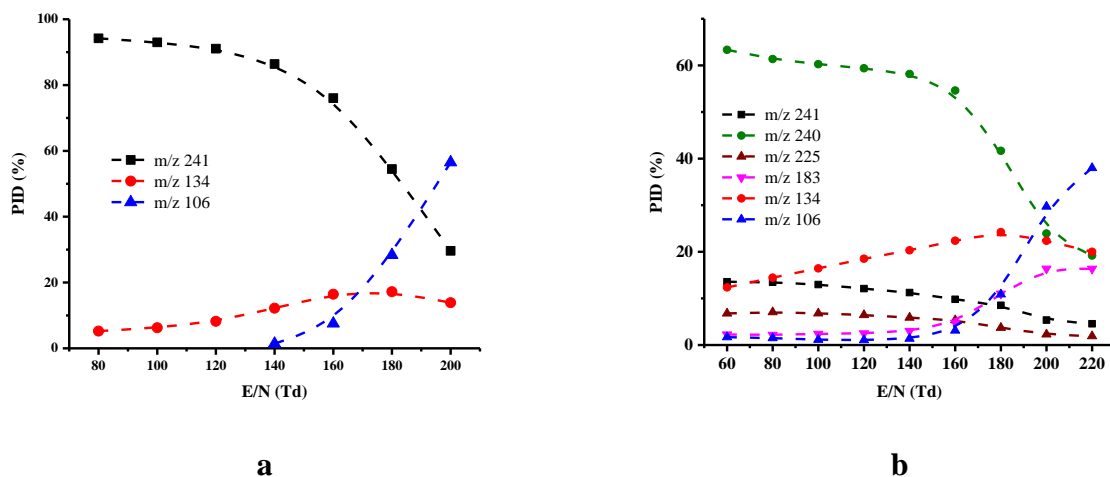


Figure 2. PID plots resulting from the reaction of MC with (a) H₃O⁺ reagent ion (80 to 200 Td) and (b) O₂⁺ reagent ion (60 to 220 Td) as a function of reduced electric field.

246

247 In O₂⁺ mode (PID shown in figure 2(b)), non-dissociative charge transfer results in an ion at
 248 *m/z* 240.12, [MC]⁺, that dominates. Only at very high E/N values, > ca. 200 Td, the ion at *m/z*
 249 106.10 becomes dominant. Additional observed product ions are *m/z* 225.10 (loss of a CH₃
 250 group) and *m/z* 183.01 (not assigned in this paper and being relevant only after 170 Td).

251

252 3.1.5- Ethyl centralite (EC)

253 EC has a very similar structure to that of MC, so a similar fragmentation pattern is to be
 254 expected. For water chemistry the protonated parent, [EC.H]⁺, at *m/z* 269.17, is dominant
 255 across all the *E/N* range (figure 3(a)). Observed fragment product ions are *m/z* 148.08 (via loss
 256 of *N*-ethylaniline from the protonated parent), and at *m/z* 120.08 (loss of CO), which only
 257 becomes relevant above 120 Td. Two more product ions are observed at *m/z* 93.06, assigned to
 258 be charged aniline [PhNH₂]⁺, after the additional loss of a CH₂CH molecule, and *m/z* 92.05,
 259 [PhNH]⁺, only becoming relevant at *E/N* > 140 Td. That these two ions are only and
 260 simultaneously observed for EC is consistent with results shown by Gilbert-López et al. in a
 261 LC/ESI-ToF-MS.⁵⁶

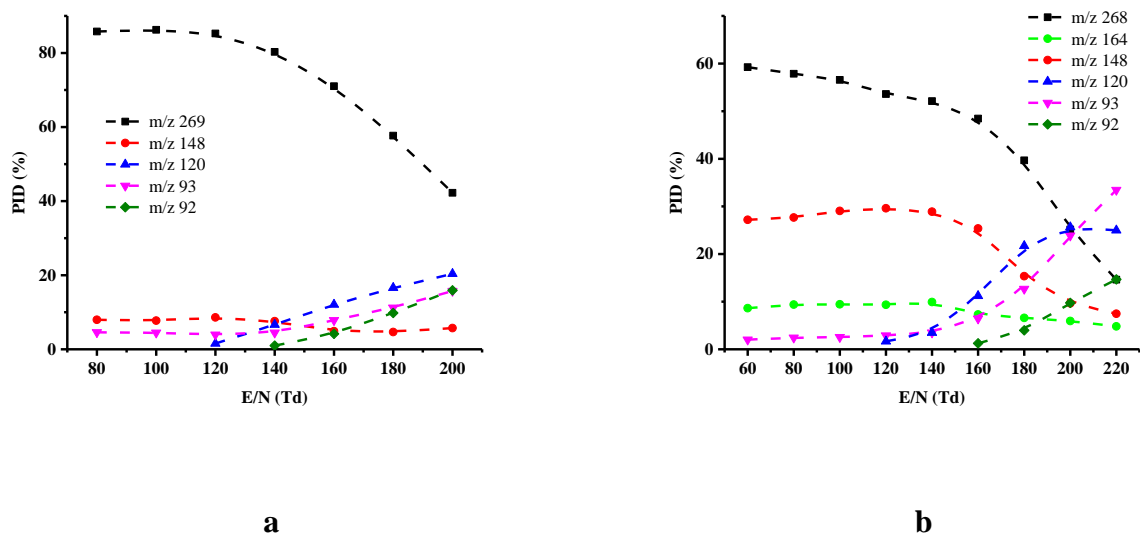


Figure 3. PID plots resulting from the reaction of EC with (a) H_3O^+ reagent ion (80 to 200 Td) and (b) O_2^+ reagent ion (60 to 220 Td) as a function of reduced electric field.

262

263 For oxygen chemistry, PID shown in figure 3(b), the ion resulting from charge transfer at m/z
 264 268.16, dominates, and only at reduced electric field values above 200 Td loses its dominance.
 265 Identified product ions are to the same as those for water chemistry, namely m/z 148.08, 120.08,
 266 93.06 and 92.05, but in addition another product ion at m/z 164.00 is also observed, the intensity
 267 of which remains almost constant for the range 60 to 140 Td, after which its intensity decreases
 268 to ca. 5% at 220 Td.

269

270 3.2. Method validation. Analytical figures of merit

271 Following the establishment of the product ions, the performance of the method was evaluated
 272 in terms of limits of detection (LoD), linear dynamic range and precision for both H_3O^+ and
 273 O_2^+ reagent ions (see table 2). Serial calibration solutions of different concentrations for each
 274 standard additive were prepared. Calibration curves, using peak areas normalised to 10^6 reagent
 275 ions, as function of concentration using least-square linear regression analysis were plotted.
 276 Instrumental LoDs were evaluated based on the minimum analyte concentration yielding to a
 277 signal to noise ratio equal to three. Noise was defined as the average of 10 blank samples for a
 278 given mass. Although the conjunction of protonated parent and fragment ions is useful for
 279 selectivity purposes, to determine the sensitivity of the method only the dominant ion resulting
 280 in the best LoD was used, i.e. the most intense ion signal (in terms of ncps) at a given E/N value
 281 was used to determine the LoD. Precision of the method was determined in terms of
 282 repeatability (measurements of 5 replicates within short intervals of time (typically 1-5 min)

283 by the same operator under the same experimental conditions) and reproducibility (five
284 replicates over five different days by the same operator under the same experimental
285 conditions), with each replicate being the mean of three measurements. Linearity was studied
286 covering a concentration range from 0.1 to 1500 ng of each compound at ten concentration
287 values with three replicates at each concentration. No carryover effects were observed and
288 under the experimental conditions after ca. 10 seconds the base line was recovered for all the
289 compounds of interest. 30 s integration time was used throughout in order to record a stable
290 background prior and after a desorption event.

291 In H_3O^+ mode, the coefficient of determination R^2 was higher than 0.9991 for all
292 compounds. Instrumental limits of detection varied from 41 to 88 pg. Precision, expressed in
293 terms of relative standard deviation (RSD), was found in all cases to be below around 3% for
294 intra-day (repeatability) and below 7% for inter-day (reproducibility) studies.

295 In O_2^+ mode, the coefficient of determination R^2 was higher than 0.9914 for all
296 compounds. Instrumental limits of detection varied from 72 pg to 1.4 ng. Special mention
297 should be noted to the cases of DPA, where the existence of an endogenous high background
298 signal at the m/z of interest led to a LoD much higher than that of the rest of compounds, but
299 still in the low ng region. Precision was found in all cases to be below around 5% for intra-day
300 (repeatability) and below 8.6% for inter-day (reproducibility) studies.

301

302 **Table 2.** Figures of merit for the compounds investigated in this study using H₃O⁺ and O₂⁺ chemistry. Normalised counts per second for one
 303 million reagent ions have been used throughout. Only the dominant ion was used and LoDs were calculated at the *E/N* value that gave us the best
 304 sensitivity. The linear dynamic range in nanograms (ng) is given for each explosive and the corresponding *R*² provided. The precision of the
 305 method was evaluated by the determination of the repeatability and reproducibility in terms of percentage of relative standard deviation (% RSD)
 306 of peak areas.

COMPOUND	Reagent ion	Monitored ion, <i>m/z</i>	<i>E/N</i> (Td)	Linear dynamic range (ng)	<i>R</i> ²	LoD (pg)	Precision (RSD, %)	
							Repeatability (n=5)	Reproducibility (n=5)
							300 pg	300pg
DPA	H ₃ O ⁺	[DPA.H] ⁺ , 170.10	140	0.15-1500	0.9991	72±6	2.9	5.1
	O ₂ ⁺	[DPA] ⁺ , 169.09	110		0.9914	1.4±0.1*	4.9	8.6
2-NO2-DPA	H ₃ O ⁺	[2-NO ₂ -DPA H] ⁺ , 215.08	140	0.1-1500	0.9998	41± 2	2.4	5.2
	O ₂ ⁺	[2-NO ₂ -DPA] ⁺ , 214.07	80		0.9954	72±5	3.1	6.1
4-NO2-DPA	H ₃ O ⁺	[4-NO ₂ -DPA H] ⁺ , 215.08	140	0.1-1500	0.9996	51±5	1.5	4.0
	O ₂ ⁺	[2-NO ₂ -DPA] ⁺ , 214.07	80		0.9941	83±2	2.8	4.5
MC	H ₃ O ⁺	[MC.H] ⁺ , 241.13	130	0.2-1500	0.9997	88± 4	2.1	3.7
	O ₂ ⁺	MC ⁺ , 240.12	60		0.9965	310±9	3.2	5.1
EC	H ₃ O ⁺	[EC.H] ⁺ , 269.17	140	0.15-1500	0.9995	60± 7	2.2	4.1
	O ₂ ⁺	EC ⁺ , 268.16	80		0.9955	287±6	3.8	6.3

307

308 *expressed in ng. As a result of an endogenous background signal at the mass of interest sensitivity was compromised.

309 3.3. Application to commercial samples

310 Six commercial smokeless powders samples from three different manufacturers were analysed.
311 The concentration of additives was calculated using the standard calibration curves obtained
312 for section 3.2. Results, see table 3, show the identified additives and its content in the
313 smokeless gun powder (expressed as percentage) for the different samples for H_3O^+ and O_2^+
314 reagent ions at 140 Td (a compromise E/N value between high signal intensity and low
315 fragmentation). These results are in good agreement with those found in the smokeless powders
316 database.⁵⁷ Figure 4 shows two mass spectra exemplifying two of the samples for water
317 chemistry - similar plots (not shown) were found for the rest of the samples and for oxygen
318 chemistry.

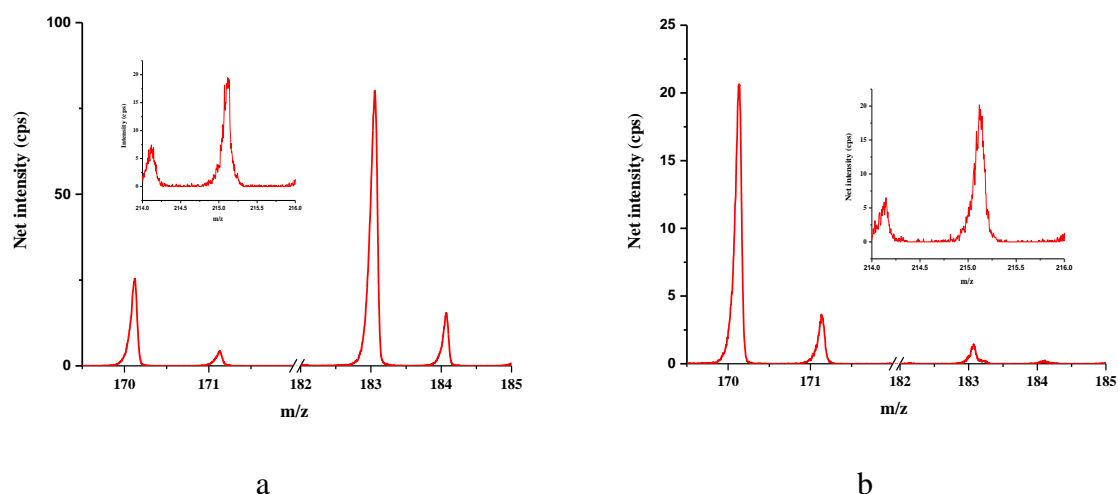


Figure 4. Mass spectra using water chemistry and reduced electric field of 140 Td for (a) IMR4198 and (b) Hodgdon BL-C(2) showing regions around m/z 170 and 215 and the different composition for both powders. (The insertion represents an expansion of the mass range around m/z 215 (x 20).)

319
320 Based on our previous water chemistry work,^{41,47,50} and besides the detection of the
321 additives studied for this work, dinitrotoluene was also clearly observed showing two intense
322 product ions peaks at m/z 183.04 and 201.05, assigned to the protonated parent, DNT.H^+ , and
323 its first water cluster, $\text{DNTH}^+.\text{H}_2\text{O}$. This was observed for 3 of the samples. It is possible to
324 assign dinitrotoluene to be the 2,4-isomer. As reported recently by González-Méndez *et al.*^{47,50}
325 monitoring product ions at m/z 183.04 and 201.05 allows assignment to 2,4-DNT, but that the
326 presence of m/z 136.04 (elimination of HONO from the protonated parent) and m/z 91.06
327 (elimination of two nitro groups) observed at the high E/N setting (200 Td and above) indicates
328 the presence of 2,6-DNT. These two latter peaks were not observed. No detailed product ion

329 distribution studies for DNT and O_2^+ exist (to the best of our knowledge), but in O_2^+ mode, the
330 charge transfer reaction channel leading to a peak at m/z 182.03 (assigned to $[DNT]^+$) was
331 observed.

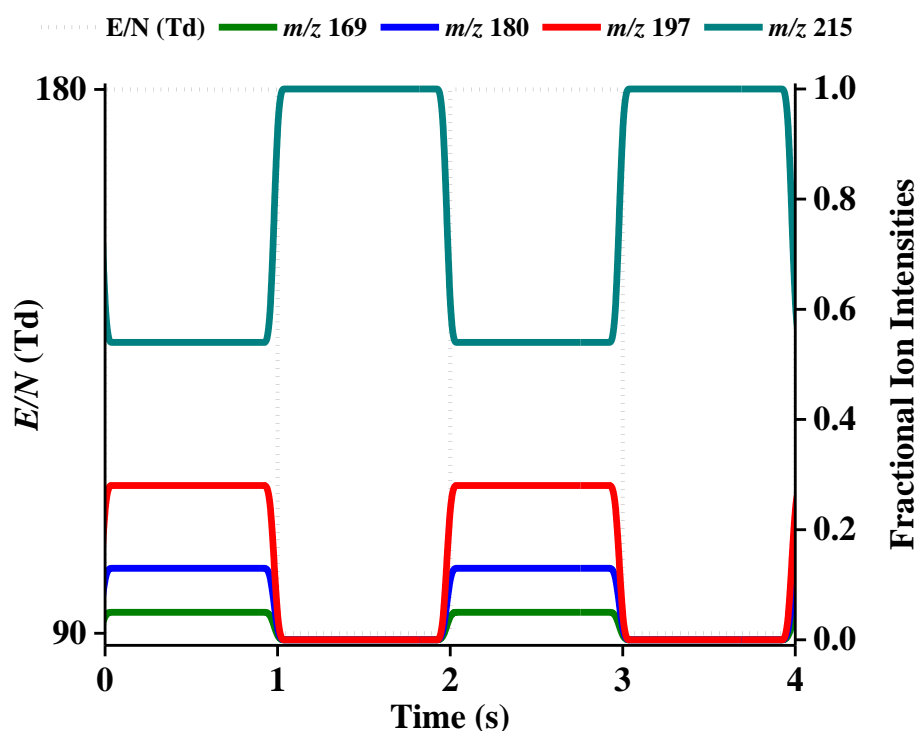
332 The other 3 samples showed an intense peak at m/z 228.03. Fast switching experiments
333 and previous studies dealing with 2,4,6-trinitrotoluene (TNT) and nitroglycerine (NG)
334 confirmed this to be NG.^{41,49,50} NG produces a characteristic signal at m/z 46.01 (NO_2^+) at high
335 E/N values, whilst TNT does not, thus a quick change in the E/N from low (80 Td) to high (180
336 Td) allows to assign this peak to NG.

337 Both Alliant powders show evidence of 2,4-DNT and also peaks at m/z 170.10,
338 215.08, and 269.17, assigned to $[DPA.H]^+$, $[2-,4-NO_2-DPA.H]^+$ and $[EC.H]^+$, respectively.
339 Fast E/N switching experiments confirm the identity of these species based on the presence or
340 absence of fragment ions at different reduced electric fields. Fast switching experiments
341 based on figures 1(a) and 1(b), for both Alliant Red Dot and Unique powder, as shown in
342 Figure 5, confirmed the identity of m/z 215.08 to be the 2-nitrodiphenylamine isomer. The
343 presence or absence of m/z 197.07 and 198.08 would rule out one or another. Also, the
344 presence of m/z 180.06 would confirm the existence of 2- NO_2 -DPA.

345 For the Hodgdon samples only H322 did show evidences of 2,4-DNT, but BL-C(2)
346 showed a signal at m/z 228.03, assigned again to NG based on fast switching experiments. Both
347 Hodgdon samples showed clear signals at m/z 170.10 and 215.08. Fast switching experiments
348 confirmed m/z 215.08 to be 2-nitrodiphenylamine for Hodgdon-BL-C(2). However, in O_2^+
349 mode no evidence for 2-nitrodiphenylamine was observed.

350 Both IMR samples showed a clear and intense peak for 2,4-DNT, and peaks at m/z
351 170.10, 215.08, 241.13 and 269.17 were also observed. Fast switching experiments confirmed
352 the nitrodiphenylamine to be a mixture of the 2- and 4-isomers.

353
354



355
 356 **Figure 5.** Changes in the fractional ion intensities averaged over each cycle using fast E/N
 357 switching experiments at 1 Hz between 90 Td and 180 Td for Alliant Red Dot. The product
 358 ions showed are distinctive of 2-NO₂-DPA. The dotted line represents the E/N during each
 359 phase.

360
 361 As stated in the introduction, owing to the complex composition of smokeless powders
 362 the presence of unidentified peaks was expected, the majority coming from the plasticizers
 363 used in the manufacturing process. This was confirmed by additional unidentified peaks for all
 364 the powders at m/z 149.02 (reported by Scherperel *et al.* as a dibutyl phthalate fragment),²⁹
 365 205.09 and 279.16 (the latter is assigned to be protonated dibutyl phthalate [DBP.H]⁺ by Reese
 366 *et al.*,⁸ and Perez *et al.*¹⁵). It is evident that a more detailed study dealing with these is needed
 367 if a complete chemical analysis is required.

368 Table 3. Smokeless powders analysis in H₃O⁺ and O₂⁺ modes at 140 Td, showing the detected (or undetected) additives for six different samples
 369 from three different manufacturers. Numbers indicate the content of additive in the powder (in %, mean of n=5) and its error (expressed as RSD).

	Reagent ion	DPA	2-NO ₂ -DPA	4-NO ₂ -DPA	MC	EC	2,4-DNT	NG	
Smokeless powder manufacturer and model	Alliant Unique	H ₃ O ⁺	2.0 ± 0.25	1.1 ± 0.2	ND	ND	1.2 ± 0.1	ND ^a	✓ ^b
		O ₂ ⁺	1.6 ± 0.4	0.9 ± 0.3	ND	ND	1.0 ± 0.3	-- ^c	--
	Alliant Red dot	H ₃ O ⁺	2.3 ± 0.2	1.4 ± 0.3	ND	ND	1.1 ± 0.2	ND	✓
		O ₂ ⁺	2.1 ± 0.3	1.0 ± 0.2	ND	ND	0.9 ± 0.2	--	--
	Hodgdon BL-C(2)	H ₃ O ⁺	1.1 ± 0.1	0.6 ± 0.1	ND	ND	3.0 ±	ND	✓
		O ₂ ⁺	0.9 ± 0.1	ND	ND	ND	2.7 ±	--	--
	Hodgdon H322	H ₃ O ⁺	1.6 ± 0.6	0.4 ± 0.2	ND	2.0 ± 0.2	ND	✓	ND
		O ₂ ⁺	1.3 ± 0.4	ND	ND	1.6 ± 0.3	ND	--	--
	IMR 4350	H ₃ O ⁺	4.1 ± 0.3	0.4 ± 0.1	0.6 ± 0.2	2.1 ± 0.3	1.2 ± 0.1	✓	ND ^a
		O ₂ ⁺	4.0 ± 0.5	0.4 ± 0.2	0.4 ± 0.1	1.9 ± 0.2	1.0 ± 0.3	--	--
	IMR 4198	H ₃ O ⁺	5.0 ± 0.1	ND	ND	ND	ND	✓	ND
		O ₂ ⁺	4.7 ± 0.3	ND	ND	ND	ND	--	--

370

371 ^aN.D. indicates not detected; ^b✓ indicates observed and identified but not quantified and ^c-- indicates not experimentally tested for.

372 **4. Conclusions**

373 We have shown that direct injection soft chemical ionisation-mass spectrometry, using both
374 water and oxygen reagent gases, can analyse smokeless powder organic additives. This has
375 been applied to their identification for commercial powders in their pre-detonation condition.

376 This method makes use of commercially available swabs and thermal desorption,
377 allowing complete analysis of samples within ~ 10 s. For a series of the most common organic
378 additives for smokeless powders, fragmentation patterns have been established and analytical
379 figures of merit have been reported. Achieving the best LoDs for oxygen chemistry requires
380 using lower reduced electric fields values than those used for water chemistry. Oxygen
381 chemistry has been tested to be less sensitive than water chemistry for the compounds of
382 interest. Fragmentation has been shown to be very similar in terms of the observed ions and
383 their identity for both reagent ions. For H_3O^+ and O_2^+ the most intense ions are usually coming
384 from the non-dissociative channels.

385 Fast switching experiments aided in the identification and distinguish between isomers,
386 based on the presence or absence of fragment ions at different reduced electric fields.

387 When applied to commercial samples, results have shown that the content of the organic
388 additives investigated in this study changed between the samples, helping to differentiate
389 among samples and manufacturers.

390 Future work will include extending the number of additives and plasticisers and
391 commercial samples. Moreover, and also importantly, analysis of post-blast samples to ensure
392 organic gunshot residues can be detected in a rapid, sensitive and selective way using this DI-
393 SCIMS technology. Similarly to recent studies,⁴⁷ the potential use of a radio frequency ion-
394 funnel drift tube to check for improvements in both sensitivity and selectivity is worthwhile to
395 mention.

396

397 **5. Acknowledgements**

398 RGM is an Early Stage Researcher who acknowledges the support of the PIMMS Initial
399 Training Network which in turn is supported by the European Commission's 7th Framework
400 Programme under Grant Agreement Number 287382.

401

402 **6. References**

403 1. Heramb, R. M.; McCord, B. R., The manufacture of smokeless powders and their
404 forensic analysis: a brief review. *Forensic Sci. Commun* **2002**, 4 (2).

- 405 2. Bender, E. C., Analysis of low explosives. In *Forensic Investigation of Explosions*,
406 Taylor & Francis Ltd., Bristol, PA: 1998.
- 407 3. Schwoeble, A.; Exline, D. L., *Current methods in forensic gunshot residue analysis*.
408 CRC Press: 2000.
- 409 4. Chang, K. H.; Jayaprakash, P. T.; Yew, C. H.; Abdullah, A. F. L., Gunshot residue
410 analysis and its evidential values: a review. *Australian journal of forensic sciences* **2013**, *45*
411 (1), 3-23.
- 412 5. MacCrehan, W. A.; Smith, K. D.; Rowe, W. F., Sampling protocols for the detection
413 of smokeless powder residues using capillary electrophoresis. *Journal of Forensic Science*
414 **1998**, *43* (1), 119-124.
- 415 6. Abrego, Z.; Ugarte, A.; Unceta, N.; Fernández-Isla, A.; Goicolea, M. A.; Barrio, R. J.,
416 Unambiguous Characterization of Gunshot Residue Particles Using Scanning Laser Ablation
417 and Inductively Coupled Plasma-Mass Spectrometry. *Analytical Chemistry* **2012**, *84* (5),
418 2402-2409.
- 419 7. Dennis, D.-M. K.; Williams, M. R.; Sigman, M. E., Assessing the evidentiary value of
420 smokeless powder comparisons. *Forensic science international* **2016**, *259*, 179-187.
- 421 8. Reese, K. L.; Jones, A. D.; Smith, R. W., Characterization of smokeless powders using
422 multiplexed collision-induced dissociation mass spectrometry and chemometric procedures.
423 *Forensic Science International* **2017**, *272*, 16-27.
- 424 9. Goudsmits, E.; Sharples, G. P.; Birkett, J. W., Recent trends in organic gunshot residue
425 analysis. *TrAC Trends in Analytical Chemistry* **2015**, *74*, 46-57.
- 426 10. Taudte, R. V.; Beavis, A.; Blanes, L.; Cole, N.; Doble, P.; Roux, C., Detection of
427 Gunshot Residues Using Mass Spectrometry. *BioMed Research International* **2014**, *2014*, 16.
- 428 11. Dalby, O.; Butler, D.; Birkett, J. W., Analysis of gunshot residue and associated
429 materials—a review. *Journal of forensic sciences* **2010**, *55* (4), 924-943.
- 430 12. Joshi, M.; Rigsby, K.; Almirall, J. R., Analysis of the headspace composition of
431 smokeless powders using GC-MS, GC- μ ECD and ion mobility spectrometry. *Forensic*
432 *Science International* **2011**, *208* (1-3), 29-36.
- 433 13. Meng, H.; Caddy, B., Gunshot residue analysis—a review. *Journal of Forensic Science*
434 **1997**, *42* (4), 553-570.
- 435 14. Mach, M.; Pallos, A.; Jones, P., Feasibility of gunshot residue detection via its organic
436 constituents. Part I: Analysis of smokeless powders by combined gas chromatography-
437 chemical ionization mass spectrometry. *Journal of Forensic Science* **1978**, *23* (3), 433-445.

- 438 15. Perez, J. J.; Watson, D. A.; Levis, R. J., Classification of Gunshot Residue Using Laser
439 Electrospray Mass Spectrometry and Offline Multivariate Statistical Analysis. *Analytical*
440 *Chemistry* **2016**, *88* (23), 11390-11398.
- 441 16. MacCrehan, W. A.; Bedner, M., Development of a smokeless powder reference
442 material for propellant and explosives analysis. *Forensic Science International* **2006**, *163* (1–
443 2), 119-124.
- 444 17. Cascio, O.; Trettene, M.; Bortolotti, F.; Milana, G.; Tagliaro, F., Analysis of organic
445 components of smokeless gunpowders: High-performance liquid chromatography vs. micellar
446 electrokinetic capillary chromatography. *ELECTROPHORESIS* **2004**, *25* (10-11), 1543-
447 1547.
- 448 18. Meng, H.-h.; Caddy, B., Detection of N,N'-diphenyl-N,N'-diethylurea (ethyl centralite)
449 in gunshot residues using high-performance liquid chromatography with fluorescence
450 detection. *Analyst* **1995**, *120* (6), 1759-1762.
- 451 19. López-López, M.; Bravo, J. C.; García-Ruiz, C.; Torre, M., Diphenylamine and
452 derivatives as predictors of gunpowder age by means of HPLC and statistical models. *Talanta*
453 **2013**, *103*, 214-220.
- 454 20. Laza, D.; Nys, B.; Kinder, J. D.; Kirsch-De Mesmaeker, A.; Moucheron, C.,
455 Development of a Quantitative LC-MS/MS Method for the Analysis of Common Propellant
456 Powder Stabilizers in Gunshot Residue*. *Journal of Forensic Sciences* **2007**, *52* (4), 842-850.
- 457 21. Wu, Z.; Tong, Y.; Yu, J.; Zhang, X.; Yang, C.; Pan, C.; Deng, X.; Wen, Y.; Xu, Y.,
458 The Utilization of MS-MS Method in Detection of GSRs. **2001**.
- 459 22. Thomas, J. L.; Lincoln, D.; McCord, B. R., Separation and detection of smokeless
460 powder additives by ultra performance liquid chromatography with tandem mass
461 spectrometry (UPLC/MS/MS). *J Forensic Sci* **2013**, *58* (3), 609-15.
- 462 23. López-López, M.; Ferrando, J. L.; García-Ruiz, C., Comparative analysis of smokeless
463 gunpowders by Fourier transform infrared and Raman spectroscopy. *Analytica Chimica Acta*
464 **2012**, *717*, 92-99.
- 465 24. Zeichner, A.; Eldar, B.; Glatstein, B.; Koffman, A.; Tamiri, T.; Muller, D., Vacuum
466 collection of gunpowder residues from clothing worn by shooting suspects, and their analysis
467 by GC/TEA, IMS, and GC/MS. *Journal of forensic sciences* **2003**, *48* (5), 961-972.
- 468 25. Cruces-Blanco, C.; Gámiz-Gracia, L.; García-Campaña, A. M., Applications of
469 capillary electrophoresis in forensic analytical chemistry. *TrAC Trends in Analytical*
470 *Chemistry* **2007**, *26* (3), 215-226.

- 471 26. Bernal Morales, E.; Revilla Vázquez, A. L., Simultaneous determination of inorganic
472 and organic gunshot residues by capillary electrophoresis. *Journal of Chromatography A*
473 **2004**, *1061* (2), 225-233.
- 474 27. West, C.; Baron, G.; Minet, J. J., Detection of gunpowder stabilizers with ion mobility
475 spectrometry. *Forensic Science International* **2007**, *166* (2–3), 91-101.
- 476 28. Joshi, M.; Delgado, Y.; Guerra, P.; Lai, H.; Almirall, J. R., Detection of odor signatures
477 of smokeless powders using solid phase microextraction coupled to an ion mobility
478 spectrometer. *Forensic Science International* **2009**, *188* (1–3), 112-118.
- 479 29. Scherperel, G.; Reid, G. E.; Waddell Smith, R., Characterization of smokeless powders
480 using nanoelectrospray ionization mass spectrometry (nESI-MS). *Analytical and*
481 *Bioanalytical Chemistry* **2009**, *394* (8), 2019-2028.
- 482 30. Wu, Z.; Tong, Y.; Yu, J.; Zhang, X.; Pan, C.; Deng, X.; Xu, Y.; Wen, Y., Detection of
483 N,N[prime or minute]-diphenyl-N,N[prime or minute]-dimethylurea (methyl centralite) in
484 gunshot residues using MS-MS method. *Analyst* **1999**, *124* (11), 1563-1567.
- 485 31. Tong, Y.; Wu, Z.; Yang, C.; Yu, J.; Zhang, X.; Yang, S.; Deng, X.; Xu, Y.; Wen, Y.,
486 Determination of diphenylamine stabilizer and its nitrated derivatives in smokeless
487 gunpowder using a tandem MS method. *Analyst* **2001**, *126* (4), 480-484.
- 488 32. Perez, J. J.; Flanigan, P. M.; Brady, J. J.; Levis, R. J., Classification of Smokeless
489 Powders Using Laser Electrospray Mass Spectrometry and Offline Multivariate Statistical
490 Analysis. *Analytical Chemistry* **2013**, *85* (1), 296-302.
- 491 33. Zhao, M.; Zhang, S.; Yang, C.; Xu, Y.; Wen, Y.; Sun, L.; Zhang, X., Desorption
492 Electrospray Tandem MS (DESI-MSMS) Analysis of Methyl Centralite and Ethyl Centralite
493 as Gunshot Residues on Skin and Other Surfaces. *Journal of Forensic Sciences* **2008**, *53* (4),
494 807-811.
- 495 34. Morelato, M.; Beavis, A.; Ogle, A.; Doble, P.; Kirkbride, P.; Roux, C., Screening of
496 gunshot residues using desorption electrospray ionisation–mass spectrometry (DESI–MS).
497 *Forensic Science International* **2012**, *217* (1–3), 101-106.
- 498 35. Li, F.; Tice, J.; Musselman, B. D.; Hall, A. B., A method for rapid sampling and
499 characterization of smokeless powder using sorbent-coated wire mesh and direct analysis in
500 real time - mass spectrometry (DART-MS). *Science & Justice* **2016**, *56* (5), 321-328.
- 501 36. Mahoney, C. M.; Gillen, G.; Fahey, A. J., Characterization of gunpowder samples using
502 time-of-flight secondary ion mass spectrometry (TOF-SIMS). *Forensic science international*
503 **2006**, *158* (1), 39-51.

- 504 37. Bueno, J.; Sikirzhytski, V.; Lednev, I. K., Raman spectroscopic analysis of gunshot
505 residue offering great potential for caliber differentiation. *Analytical chemistry* **2012**, *84* (10),
506 4334-4339.
- 507 38. Andrew M. Ellis, C. A. Mayhew, *Proton Transfer Reaction Mass Spectrometry:*
508 *Principles and Applications*. 1st ed.; Wiley: 2014.
- 509 39. Biasioli, F.; Yeretziyan, C.; Märk, T. D.; Dewulf, J.; Van Langenhove, H., Direct-
510 injection mass spectrometry adds the time dimension to (B)VOC analysis. *TrAC Trends in*
511 *Analytical Chemistry* **2011**, *30* (7), 1003-1017.
- 512 40. Lindinger, W.; Hirber, J.; Paretzke, H., An ion/molecule-reaction mass spectrometer
513 used for on-line trace gas analysis. *International Journal of Mass Spectrometry and Ion*
514 *Processes* **1993**, *129*, 79-88.
- 515 41. González-Méndez, R.; Reich, D. F.; Mullock, S. J.; Corlett, C. A.; Mayhew, C. A.,
516 Development and use of a thermal desorption unit and proton transfer reaction mass
517 spectrometry for trace explosive detection: Determination of the instrumental limits of
518 detection and an investigation of memory effects. *International Journal of Mass Spectrometry*
519 **2015**, *385*, 13-18.
- 520 42. Shen, C.; Li, J.; Han, H.; Wang, H.; Jiang, H.; Chu, Y., Triacetone triperoxide detection
521 using low reduced-field proton transfer reaction mass spectrometer. *International Journal of*
522 *Mass Spectrometry* **2009**, *285* (1–2), 100-103.
- 523 43. Mayhew, C. A.; Sulzer, P.; Petersson, F.; Haidacher, S.; Jordan, A.; Märk, L.; Watts,
524 P.; Märk, T. D., Applications of proton transfer reaction time-of-flight mass spectrometry for
525 the sensitive and rapid real-time detection of solid high explosives. *International Journal of*
526 *Mass Spectrometry* **2010**, *289* (1), 58-63.
- 527 44. Jürschik, S.; Sulzer, P.; Petersson, F.; Mayhew, C. A.; Jordan, A.; Agarwal, B.;
528 Haidacher, S.; Seehauser, H.; Becker, K.; Märk, T. D., Proton transfer reaction mass
529 spectrometry for the sensitive and rapid real-time detection of solid high explosives in air and
530 water. *Analytical and Bioanalytical Chemistry* **2010**, *398* (7-8), 2813-2820.
- 531 45. Sulzer, P.; Agarwal, B.; Jürschik, S.; Lanza, M.; Jordan, A.; Hartungen, E.; Hanel, G.;
532 Märk, L.; Märk, T. D.; González-Méndez, R.; Watts, P.; Mayhew, C. A., Applications of
533 switching reagent ions in proton transfer reaction mass spectrometric instruments for the
534 improved selectivity of explosive compounds. *International Journal of Mass Spectrometry*
535 **2013**, *354–355* (0), 123-128.
- 536 46. Agarwal, B.; González-Méndez, R.; Lanza, M.; Sulzer, P.; Märk, T. D.; Thomas, N.;
537 Mayhew, C. A., Sensitivity and Selectivity of Switchable Reagent Ion Soft Chemical

538 Ionization Mass Spectrometry for the Detection of Picric Acid. *The Journal of Physical*
539 *Chemistry A* **2014**, *118* (37), 8229-8236.

540 47. González-Méndez, R.; Watts, P.; Olivenza-León, D.; Reich, D. F.; Mullock, S. J.;
541 Corlett, C. A.; Cairns, S.; Hickey, P.; Brookes, M.; Mayhew, C. A., Enhancement of
542 Compound Selectivity Using a Radio Frequency Ion-Funnel Proton Transfer Reaction Mass
543 Spectrometer: Improved Specificity for Explosive Compounds. *Analytical Chemistry* **2016**,
544 *88* (21), 10624-10630.

545 48. González-Méndez, R. Development and applications of Proton Transfer Reaction-Mass
546 Spectrometry for Homeland Security: trace detection of explosives. PhD, University of
547 Birmingham, 2017.

548 49. Sulzer, P.; Petersson, F.; Agarwal, B.; Becker, K. H.; Jürschik, S.; Märk, T. D.; Perry,
549 D.; Watts, P.; Mayhew, C. A., Proton Transfer Reaction Mass Spectrometry and the
550 Unambiguous Real-Time Detection of 2,4,6 Trinitrotoluene. *Analytical Chemistry* **2012**, *84*
551 (9), 4161-4166.

552 50. González-Méndez, R.; Watts, P.; Reich, D. F.; Mullock, S. J.; Cairns, S.; Hickey, P.;
553 Brookes, M.; Mayhew, C. A., Use of Rapid Reduced Electric Field Switching to Enhance
554 Compound Specificity for Proton Transfer Reaction-Mass Spectrometry. *Analytical*
555 *Chemistry* **2018**.

556 51. Eiceman, G. A.; Karpas, Z.; Hill Jr, H. H., *Ion mobility spectrometry*. CRC press: 2013.

557 52. Blake, R. S.; Monks, P. S.; Ellis, A. M., Proton-Transfer Reaction Mass Spectrometry.
558 *Chemical Reviews* **2009**, *109* (3), 861-896.

559 53. Jordan, A.; Haidacher, S.; Hanel, G.; Hartungen, E.; Herbig, J.; Märk, L.;
560 Schottkowsky, R.; Seehauser, H.; Sulzer, P.; Märk, T. D., An online ultra-high sensitivity
561 Proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability
562 (PTR + SRI – MS). *International Journal of Mass Spectrometry* **2009**, *286* (1), 32-38.

563 54. Harrison, A. G., *Chemical Ionization Mass Spectrometry*. CRC Press: 1982.

564 55. Gross, J. H., *Mass Spectrometry. A textbook*. 2nd ed.; Springer: 2011.

565 56. Gilbert-López, B.; García-Reyes, J. F.; Ortega-Barrales, P.; Molina-Díaz, A.;
566 Fernández-Alba, A. R., Analyses of pesticide residues in fruit-based baby food by liquid
567 chromatography/electrospray ionization time-of-flight mass spectrometry. *Rapid*
568 *communications in mass spectrometry* **2007**, *21* (13), 2059-2071.

569 57. The Smokeless Powders Database <http://www.ilrc.ucf.edu/powders/index.php>
570 (accessed 08-03-2018).