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Trace detection of inorganic oxidants using desorption electrospray ionization (DESI) mass spectrometry

Invited Paper

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Abstract: Desorption electrospray ionization (DESI), an established ambient ionization method in mass spectrometry (MS) for the analysis of organic compounds, is applied here to trace detection of inorganic salts, including inorganic oxidants. In-situ surface analysis of targeted compounds, including nitrogen-, halogen- and sulfur-salts, down to sub-nanogram levels, was performed using DESI-MS. Successful experiments were carried out in both the negative and the positive ion modes; simple anions and cations as well as small cluster ions were observed. Various surfaces are examined and surface porosity effects were briefly explored. Absolute detection limits on porous polytetrafluoroethylene (PTFE) of 120 pg (surface concentration 0.07 ng mm^{-2}) and 50 pg (surface concentration 0.03 ng mm^{-2}), were achieved for sodium chlorate and sodium perchlorate, respectively. The compounds of interest were examined in the presence of a hydrocarbon mixture to assess matrix effects: only a two- or three-fold decrease in the target ion intensity was observed. Commercial fireworks were analyzed to determine perchlorate salts in complex mixtures. This work demonstrates the potential applicability of ambient ionization mass spectrometry to forensic investigations involving improvised explosives.

Keywords: *Perchlorate and chlorate ions • DESI MS • Ambient ionization methods • Oxidants • Explosives*

1. Introduction

An important facet of forensic and counterterrorism investigations is the rapid collection of evidence to determine the type, quantity and composition of explosives [1]. There are over two hundred explosive materials officially listed [2], including nitrated organic compounds, inorganic salts, and compounds containing peroxide functional groups [3]. Highly effective explosives include the nitro compounds, nitrate esters and nitroamines commonly used for military applications [4]. Likewise, inorganic compounds such as nitrogen-oxygen or oxygen-halogen salts, are frequently employed in thermic compositions [2,5]. The availability of these compounds, which may be used as fuel oxidizers, raises safety concerns related to their safe handling and storage in addition to unlawful transportation or usage. Detection of targeted compounds is needed for control and regulation purposes as well as for forensic applications.

In situ surface detection of inorganic thermic compounds presents an analytical challenge [6], both in terms of sensitivity and feasibility. Ion chromatography either alone [7] or in combination with other techniques such as scanning electron microscopy-energy dispersion X-ray emission [8], X-ray diffraction [9], and infrared spectroscopy [10], has been utilized to determine the main components of inorganic improvised explosives devices (IED). Capillary electrophoresis with different detection systems has been successfully applied to the determination of inorganic ions [11-17]. Techniques for the determination of anions that do not involve separation include: electrospray (ESI) mass spectrometry (MS) [18-21], inductively coupled plasma (ICP) MS [22], spectrophotometry [23], ion-selective potentiometry and other electrochemical techniques [24,25], as well as wet chemical color tests [1,26].

In the search for a sensitive and selective method for the analysis of inorganic salts that is also feasible for *in situ* applications, desorption electrospray ionization (DESI) [27,28] was examined. The principal advantage of this approach is the lack of any requirement for sample preparation. DESI is rapidly becoming an established mass spectrometry ionization method for organic compounds [29-36]. The process involves spray solvent

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droplet impact on a sample surface, creation of a solvent-layer at the surface and its break-up upon droplet impact resulting in creation of numerous offspring droplets which include dissolved analytes [30]. In this study, inorganic salts, including inorganic oxidants (NH_4NO_3, $NaNO_3$, $NaClO_3$, $NaClO_4$, $(NH_4)_2SO_4$ and Na_2SO_4), were analyzed using DESI MS both as the pure materials and in complex matrices.

2. Experimental procedure

All experiments were conducted using a Thermo Electron Corporation (San Jose, CA, USA) LTQ ion trap mass spectrometer equipped with an Omni Spray® ion source from Prosolia Inc. (Indianapolis, IN, USA). Mass analysis was performed using the following instrumental settings: automatic gain control enabled (AGC ON), maximum injection time 100 ms, microscan count 2, capillary voltage 15 V, tube lens voltage 65 V and capillary temperature 150°C. DESI spray source was operated under 55 degrees angle of incidence to the horizontal. Nitrogen gas operated at 140 psi was used to assist nebulization processes and 4.5 kV voltage was applied to the spray emitter in order to increase charge density. A mixture of methanol and water (1:1, v/v) was used as the spray solvent (flow rate 3.0-3.5 μL min^{-1}).

All relevant working solutions were prepared in methanol/water (1:1, v/v). Inorganic salt solutions (1.4 μL) were deposited onto a substrate, air dried, and analyzed using typical DESI conditions [28]. To investigate matrix effects, 1.4 μL of a hydrocarbon matrix was added to a deposited inorganic salt. The following substrates were investigated: high porosity polytetrafluoroethylene (PTFE), nonporous PTFE, aluminum foil, cotton fabric, wood and paper. The nonporous PTFE and the wood substrates were rinsed with methanol; other surfaces were used as obtained. Analytes of interest were desorbed under ambient conditions then analyzed both in the positive and negative ion mode, directly from the substrates. Ten to thirty microscans were averaged for each mass spectrum presented here with an exception of sodium nitrate when analyzed in the positive ion mode (single scan, two microscans averaged). Each of the mass spectra presented is background subtracted, unless otherwise stated.

Direct surface detection of salts in the presence of a hydrocarbon mixture was investigated in order to evaluate matrix effects. This was done using paper and cotton substrates. Two sets of salt samples were examined: (i) the pure reference sample of $NaClO_3$ or $NaClO_4$ deposited on each of the surfaces; (ii) the corresponding salt samples with a hydrocarbon matrix added. The substrate was scanned across the samples at an average speed of 15 mm/min while recording the DESI mass spectrum. Ion chronograms based on the *m/z* values (± 0.5Th, 1 Th = 1 Da/charge) of the targeted compounds were recorded for each sample set, the ions examined were $[ClO_3]^-$ *m/z* 83 and 85 or $[ClO_4]^-$ *m/z* 99 and 101. The detected peaks in the selected chronograms showed appropriate isotopic patterns for chlorine ^{35}Cl : ^{37}Cl, 100% : 32% (±5%). The magnitude of the matrix effect was calculated from the relative peak areas corresponding to the detection of an analyte in the reference (no matrix) sample and in the sample with the hydrocarbon matrix.

All chemicals used in this work were high-purity commercial samples that were used as supplied. Ammonium nitrate was obtained from J.T. Baker Chemical Co., (Phillipsburg, NJ, USA), sodium nitrate, ammonium sulfate and sodium sulfate from Mallinckrodt Specialty Chemicals Co. (Paris, KY, USA), sodium chlorate and sodium perchlorate from Sigma-Aldrich (St. Louis, MO, USA). WD-40 lubricant containing petroleum distillates, used as a hydrocarbon matrix, was available from WD-40 Company (San Diego, CA, USA). Methanol, either chromatographic or analytical grade, was obtained from Mallinckrodt Inc. (Paris, KY, USA). Water was purified using a Millipore-Q water purification system (Millipore, Billerica, MA, USA) to achieve a resistivity of 18.2MΩ*cm at 25°C and a total organic carbon (TOC) value below 5 parts-per-billion (ppb). Samples of fireworks, "Color Butterfly" (flammable rocket T0510; UNO336, 1.4G), were commercially available from US Fireworks (Edwardsburg, MI, USA). The paper tube of the firework, filled with the combustible material, was disassembled and the combustion material was removed. Samples of paper were cut and subjected to DESI-MS analysis.

3. Results and discussion

Traces of inorganic salts, currently used in thermic compositions [2,5], were detected using DESI-MS from various surfaces, under ambient conditions. The absolute limits of detection (LOD) achieved for the pure compounds investigated are given in Table 1 in addition to the ions indentified at concentrations near the LOD.

3.1. Chlorates and perchlorates

Qualitative detection of these salts was performed based on the presence of chlorate ions $[ClO_3]^-$ *m/z* 83, 85 or perchlorate ions $[ClO_4]^-$ *m/z* 99, 101. The isotopic fingerprint of chlorine-containing ions was readily identified in the high picogram range for pure materials.

Table 1. Summary of DESI MS detection of inorganic salts from nonporous PTFE surface

Analyte	Ion mode[a]	LOD	Identified species
$NaClO_3$	N	350 pg	$[ClO_3]^-$ (< 1 ng); $[Na(ClO_3)_2]^-$ (≥ 5 ng); $[Na_n(ClO_3)_{n+1}]^-$ (≥ 50 ng); n=2,3
$NaClO_4$	N	200 pg	$[ClO_4]^-$ (<1ng); $[Na(ClO_4)_2]^-$ (≥ 5 ng); $[Na_n(ClO_4)_{n+1}]^-$ (≥ 50 ng) ; n=2-4
NH_4NO_3	N	15 ng	$[NO_3]^-$ (<1ng); $[H(NO_3)_2]^-$ (≥ 15 ng); $[NO_3+HNO_2+nH_2O]^-$ (≥ 50 ng); n=0-3
$NaNO_3$	N	1 ng	$[NO_3]^-$ (< 1 ng);$[Na(NO_3)_2]^-$ (≥ 1 ng); $[Na_n(NO_3)_{n+1}]^-$ (≥ 15 ng); n=2-6
	P	15 ng	$[Na(NaNO_3)]^+$ (≥ 15 ng); $[Na(NaNO_3)_n]^+$ (≥ 50 ng); n=2-7
$(NH_4)_2SO_4$	N	30 ng[b]	$[HSO_4]^-$ (≥ 15 ng); $[HSO_4(H_2SO_4)]^-$ (< 50 ng); $[NaSO_4(H_2SO_4)]^-$ (≥ 50 ng);
Na_2SO_4	N	30 ng[b]	$[HSO_4]^-$ (≥ 15 ng); $[NaSO_4(Na_2SO_4)]^-$ (< 50 ng); $[HSO_4(Na_2SO_4)_n]^-$ (> 50 ng); $[NaSO_4(Na_2SO_4)_{n+1}]^-$; n=1,2
	P	N/A	$[Na(Na_2SO_4)_n]^+$; $[Na_2(Na_2SO_4)_5]^{2+}$; n=2-4;

[a]*N = negative ionization mode; P = positive ionization mode*
[b]*LOD determined base on the signal-to-noise ratio (S/N=3) from three replicate measurements*

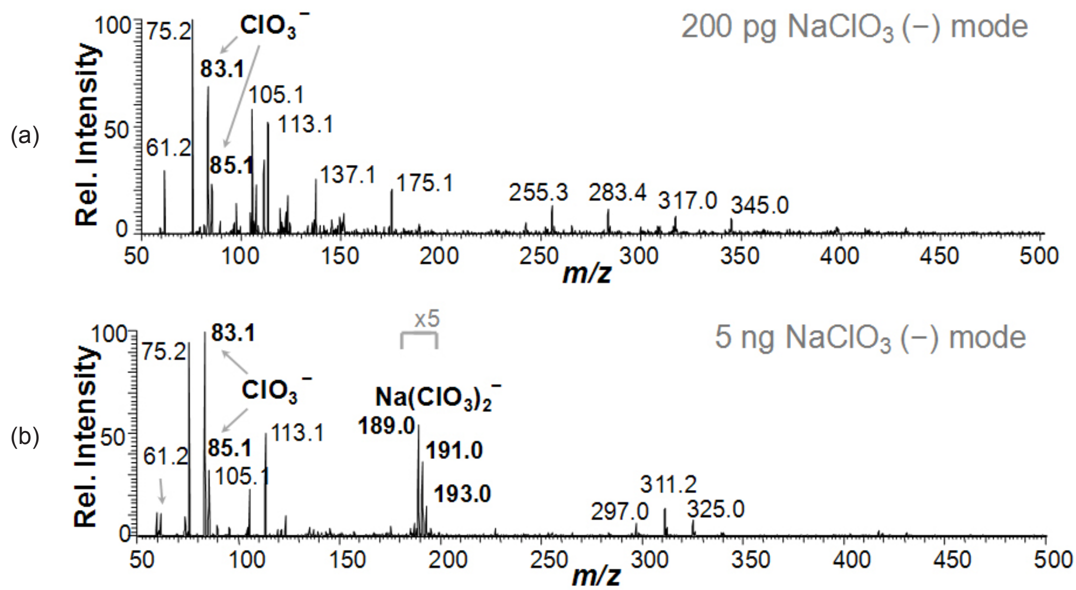


Figure 1. DESI mass spectra of (a) 200 pg sodium chlorate deposited on porous PTFE surface; (b) 5 ng sodium chlorate deposited on nonporous PTFE surface. Ions of *m/z* 59.2, 61.2 and 75.2 (±0.1) are interpreted here as originating from trace solvent impurities. They are commonly observed during negative ion mode DESI-MS analysis of salts deposited on various surfaces. Ions of *m/z* 105, 113, 137, 175, 255, 283, 317, 345 are interpreted as due to the trace impurities either originally present on the substrate or brought to the surface during sample deposition.

Samples of sodium perchlorate were detected with an absolute limit of detection (LOD) of 200 pg from nonporous PTFE (surface concentration 0.06 ng mm^{-2}) and with a 50 pg LOD from high porosity PTFE (surface concentration 0.03 ng mm^{-2}). Samples of sodium chlorate were detected with an absolute limit of detection (LOD) of 350 pg from nonporous PTFE (surface concentration 0.09 ng mm^{-2}) and with a 120 pg LOD from high porosity PTFE (surface concentration 0.07 ng mm^{-2}). Detection of salts from other surfaces was also investigated and the results are presented below. The size (*i.e.*, diameter) of the sample deposited on the surface makes a significant contribution to this difference. It determines analyte concentration per unit area, as well as the amount of material available to be sampled by the impacting DESI solvent plume [37]. For instance 1.4 μL of an aqueous salt solution deposited onto a nonporous PTFE surface yielded an ~2 mm diameter sample spot yet the same solution gave a ~7 mm diameter spot on, for example, a cotton substrate. Consequently the analyte surface concentration on the cotton fabric is expected to decrease by the factor of ca. 50.

Chlorate and perchlorate cluster ions ($[Na(ClO_3)_2]^-$ and $[Na(ClO_4)_2]^-$), which indicate the identity of the original salt, were observed when the sample amount was increased to the low nanogram range (LOD ~5 ng) in negative-ion mode MS. Results are shown in Figs. 1 and 2. Fig. 2a illustrates how the analyte signal approaches chemical noise levels as the detection limit (tens of pg) is approached.

3.2. Nitrates

DESI-MS analysis of sodium nitrate and ammonium nitrate was performed in both the negative and positive ion modes (Fig. 3). The qualitative identification of nitrate ions was based on the presence of two species: the nitrate ion $[NO_3]^-$ *m/z* 62 and either the nitrate cluster ion $[H(NO_3)_2]^-$ *m/z* 125 or $[Na(NO_3)_2]^-$ *m/z* 147. Nitrate ions were readily detected at sub-nanogram levels in the negative ion mode. However, the presence of nitrate cluster ions was restricted to samples deposited in nanogram amounts; the threshold for these signals was 1 ng (surface concentration 0.3 ng mm^{-2}) for sodium nitrate and 15 ng (surface concentration 4.8 ng mm^{-2}) for ammonium nitrate, respectively, for nonporous PTFE surfaces. The difference in detection limits obtained for nitrate ions originating from the ammonium or sodium salts are interpreted as a result of the dissimilarity in ionic radii of cluster ions formed during DESI processes. The LOD reported here are based on the presence of nitrate ion as well as nitrate clusters. In the case of small clusters (where the number n < 10), the ionic radii can influence the abundances of salt clusters by affecting their solvation energy [38]. Nitrate cluster ions in the positive ion mode were observed in the nanogram range when sodium nitrate was deposited (~10 ng). In the case of ammonium nitrate no characteristic positively-charged cluster ions were detected from the salt deposited on PTFE surfaces in amounts below 500 ng per sample.

3.3. Sulfates

DESI data for ammonium sulfate deposited directly on nonporous PTFE surface in the negative ion mode showed the following ions: $[HSO_4]^-$ *m/z* 97, $[HSO_4(H_2SO_4)]^-$ *m/z* 195 with 30 ng LOD (S/N=3) (surface concentration 9.6 ng mm^{-2}). At higher concentrations (≥ 50 ng), the sodium substituted cluster, $[NaSO_4(H_2SO_4)]^-$ *m/z* 217, was observed. Sodium sulfate was detected with 30 ng LOD (S/N=3) in the negative ion mode; in this case qualitative identification was based on the presence of the hydrogen sulfate ion, $[HSO_4]^-$ *m/z* 97, and the sodium sulfate cluster ion, $[NaSO_4(Na_2SO_4)]^-$ *m/z* 239. At higher concentrations (≥ 50 ng), sodium sulfate cluster ions, $[NaSO_4(Na_2SO_4)_{n+1}]^-$ where n = 1,2, as well as the hydrogen sulfate/sodium sulfate clusters, $[HSO_4(Na_2SO_4)_n]^-$, were observed. Positive ion mode DESI MS analysis of sodium sulfate yield ions of the general formula $[Na(Na_2SO_4)_n]^+$, where n=2-4, as well as $[Na_2(Na_2SO_4)_5]^{2+}$.

3.4. Surface effects

Sampling of chlorate and perchlorate sodium salts from various flat surfaces was performed using DESI-MS in the negative ion mode. The results are listed in Table 2. PTFE surfaces were found to be most suitable for DESI analysis of inorganic salts due to the improved sensitivity and signal stability compared to the other substrates investigated in this study namely glass, wood, aluminum foil, cotton fabric and filter paper. This is consistent with previous studies performed on small organic molecules [28,30] for which insulating surfaces with low affinity toward analytes give the best results. LODs in the sub-nanogram range were achieved for nonporous surfaces such as glass or metal. Detection limits for the salts analyzed from either cotton, wood or filter paper surfaces were in the tens of nanograms.

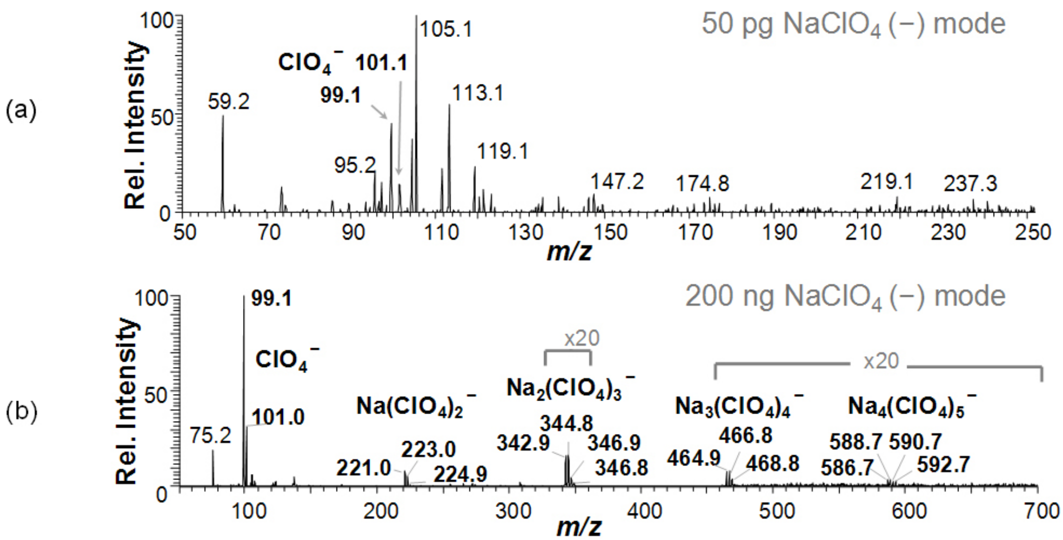


Figure 2. DESI mass spectra of (a) 50 pg sodium perchlorate deposited on porous PTFE surface, (b) 200 ng sodium perchlorate deposited on nonporous PTFE surface.

The importance of the sample spot size in DESI analysis was discussed above. An increase in sample size on a highly porous substrate like paper or cotton, when compared to nonporous PTFE, is expected to lower the analyte surface concentration in proportion to the change in surface area, which can easily be a factor of 50. The experimental data for chlorate and perchlorate salts show several orders of magnitude increase of the detection limits for paper and cotton compared with PTFE surfaces (Table 2). The loss of sensitivity with porous substrates is interpreted as due to two major factors: (i) decrease of the analyte surface concentration caused by three-dimensional transfer of the solution phase sample; (ii) decrease in analyte recovery caused by the physical properties of cellulosic material (*e.g.* adsorption, adhesion). Detailed information on the geometrical characteristics and bulk properties of cellulosic materials (*e.g.* bulk density, porosity, surface tension) related to the physical properties (*e.g.* wettability, permeability, adhesion properties) are described in the literature [39-41].

Table 2. Comparison of investigated surfaces

Analyte	Surface	LOD (absolute) [ng]	Surface concentration [ng mm^{-2}]
$NaClO_4$	High porosity PTFE	0.05	0.03
	Nonporous PTFE	0.20	0.06
	Glass	5	0.3
	Aluminum foil	0.50	0.2
	Filter paper	20	0.7
	Cotton fabric	38	1.3
	Wood	20	0.5
$NaClO_3$	High porosity PTFE	0.12	0.07
	Nonporous PTFE	0.35	0.09
	Glass	14	0.8
	Aluminum foil	0.70	0.2
	Cotton fabric	50	1.3
	Filter paper	30	1.0
	Wood	33	0.8

The most interesting substrate is PTFE and two specific types were examined, one a smooth nonporous PTFE and the other a high porosity PTFE. Interestingly, the high porosity surface showed the higher contact angle and small spot sizes and this effect overcomes the porosity and results in better detection limits.

3.5. Matrix effects

The implementation of DESI MS for specific detection purposes, such as the detection of inorganic improvised explosives, requires not only sensitive detection of fuel oxidizers from various surfaces but also detection of specific salts in the presence of relevant matrices. The effects of a hydrocarbon matrix (WD40) on the DESI-MS signal was investigated using chlorate and perchlorate salts deposited onto cotton fabric (Fig. 4) and filter

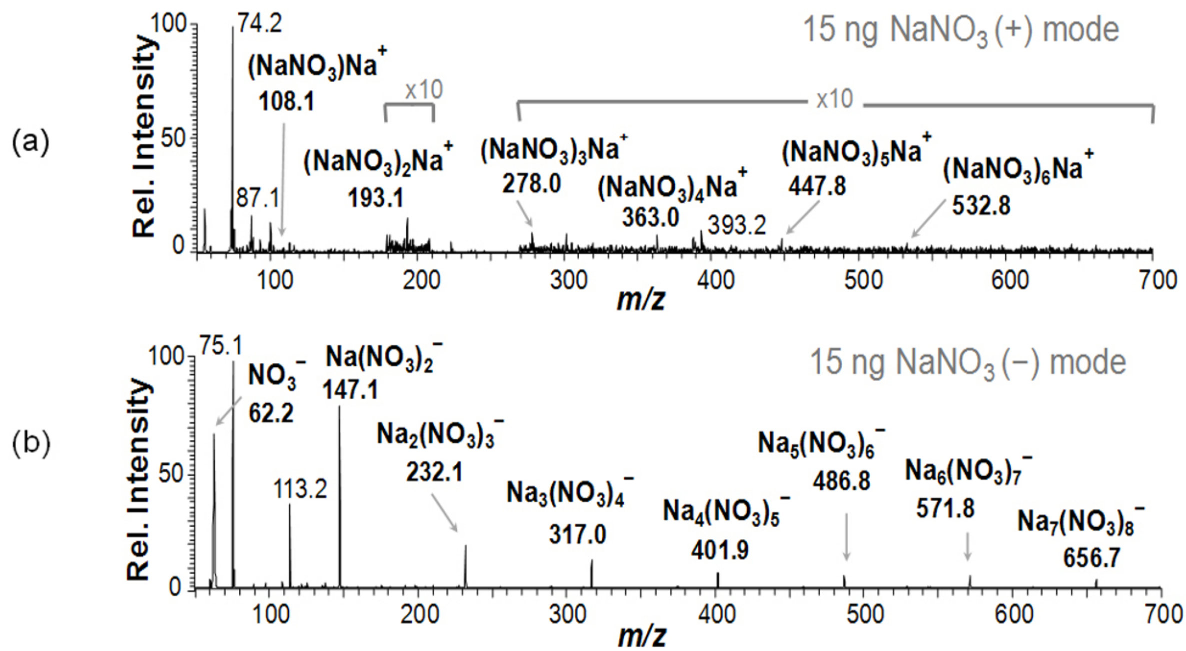
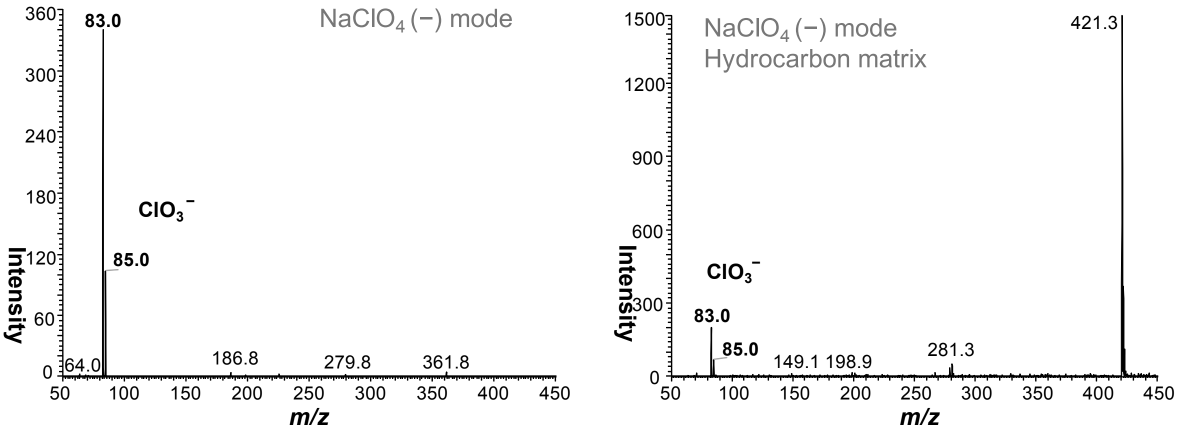


Figure 3. DESI mass spectra of 15 ng sodium nitrate deposited on nonporous PTFE: (a) recorded in positive ion mode, (b) recorded in negative ion mode. Ions of *m/z* 75.1, 74.2 and 113.2 (±0.1) are interpreted as originating from trace solvent impurities. They are commonly observed during positive ion mode DESI MS analysis of salts deposited on various surfaces.



(a) (b)

Figure 4. Negative ion mode DESI mass spectra of 210 ng sodium chlorate deposited on a cotton fabric (a) without hydrocarbon matrix (b) with 1.4 μL of WD40 deposited on the sample containing surface. Ions at m/z 281 and 421 originate from the hydrocarbon matrix.

Table 3. Summary of matrix effects

Analyte	Surface	Amount of analyte deposited on the surface [ng]	Matrix effect
$NaClO_3$ $NaClO_4$	paper	20 (LOD)	S/N < 3
		200	Signal decrease by the factor of 2
		500	Signal decrease by the factor of 2
	fabric	50 (LOD)	S/N < 3
		200	Signal decrease by the factor of 2-3
		500	Signal decrease by the factor of 2

paper surfaces. The hydrocarbon matrix and salts could undergo selective absorption unlike nonporous PTFE which repels most analytes. The results of this study are summarized in Table 3. The addition of 1.4 μL of the hydrocarbon matrix (WD40) onto the salt deposited on these surfaces resulted in a 2-3 fold decrease in the target ion signal intensity. The signal decrease was found to be dependent on the type of surface. Stable DESI signals were observed from both the paper and cotton fabric surfaces in the presence or absence of the hydrocarbon matrix. Larger matrix effects were observed for the cotton sample than the paper. However, the addition of WD40 onto the salt deposited on the paper surface resulted in a local increase in analyte signal at the edges of the sample. This is explained as an artifact caused by the salt migration with the solvent front after the matrix was added to the sample [42].

3.6. Real sample analysis

Samples of commercial fireworks were analyzed using DESI. Consumer fireworks commonly include inorganic oxidizing agents such as chlorate, nitrate or perchlorate salts [43]. Here, DESI MS was used to identify chlorate and perchlorate ions directly from the paper surface of the flammable rocket “Color Butterfly”. Typical results are shown in Fig. 5. Qualitative detection was performed based on the presence of perchlorate ions $[ClO_4]^-$ *m/z* 99, 101 and/or chlorate ions $[ClO_3]^-$ *m/z* 83, 85. The isotopic fingerprint of the chloride atom containing ions, ^{35}Cl : ^{37}Cl, 100% : 32%, was verified.

4. Conclusions

Unique applications of DESI in the analysis of inorganic salts directly from various surfaces without sample pretreatment have been demonstrated. Inorganic anions such as nitrates, chlorates and perchlorates were detected in the picogram range for the pure salts, whereas inorganic clusters containing both the anions and cations of interest and serving to identify the salt were observed in the nanogram range. Satisfactory detection limits were achieved for the chemical analysis of the salts directly from surfaces both in the presence and in the absence of a hydrocarbon matrix. Finally, traces of perchlorate salts were detected on paper originating from samples of commercial fireworks.

DESI-MS allows unambiguous determination of inorganic oxidizers directly from surfaces virtually instantaneously, providing real-time information – a critical requirement for screening or high-throughput analysis. Detection limits achieved would appear to satisfy such

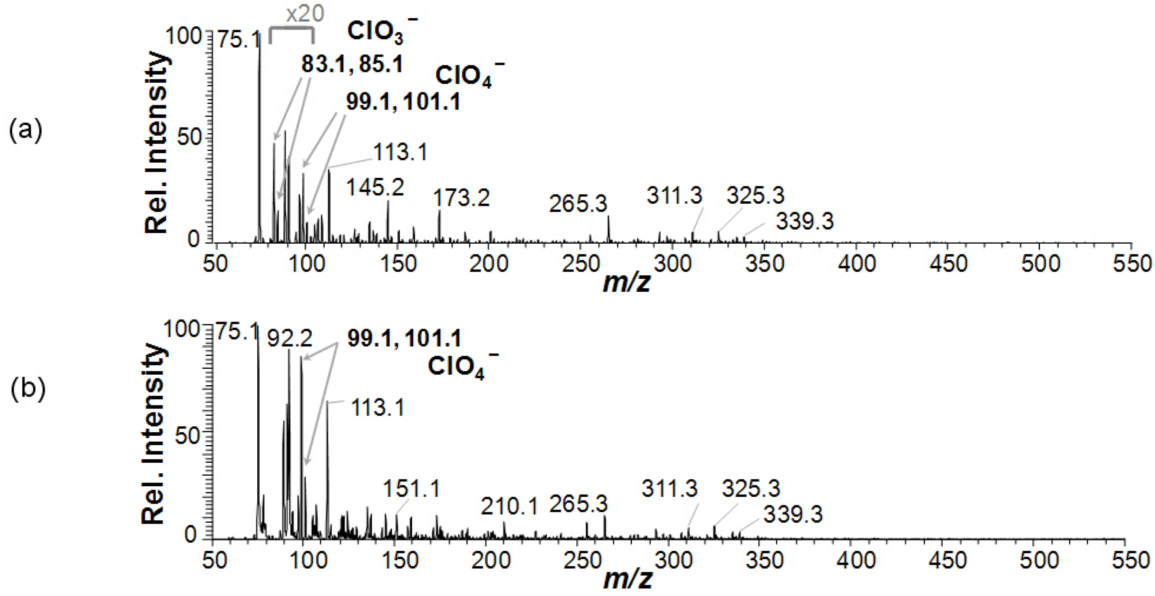


Figure 5. Negative ion DESI mass spectra of paper samples from commercial fireworks (a) spectrum obtained from analysis of paper tube containing combustive material (b) spectrum obtained from analysis of cover paper tube of firework (no background subtraction).

needs as the identification of inorganic salts in post-blast debris and small object screening. Small amounts of analyte may also be identifiable on the personal effects, working surfaces, and correspondence of those involved with these explosive materials. Furthermore, direct analysis of the post-explosion residues as well as mapping of unexploded particles found in the debris area can facilitate forensic investigations and provide evidence about the nature of the explosion for which the DESI capabilities such as 2D chemical imaging under ambient conditions [44,45] are well suited.

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