Supporting Information

Rapid trace detection of triacetone triperoxide (TATP) by complexation reactions during desorption electrospray ionization

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Abstract: Additional information is presented on the performance of the DESI method in the detection of triacetone triperoxide (TATP) in complex matrices (diesel, vinegar, Windex, and WD-40). Additional information/discussion is also presented regarding the collision-induced dissociation (CID) data for several experiments, including Na^+, K^+, Li^+, and NH_4^+ complexes with mixtures of labeled triacetone triperoxide (TATP-d) and labeled tetracetone tetraperoxide (TrATrP-d) and for experiments dealing with the detection of TATP by forming stable complexes with multiple dopants (Na^+, K^+, Li^+, and NH_4^+).

The performance of DESI in the detection of TATP in complex matrices (diesel, vinegar, Windex, and WD-40) and on paper and brick surfaces was evaluated. NaCl (10 mM) was added to the solvent spray (70:30, methanol/water) in order to form the $(TATP + Na)^+$ complex at m/z 245, increasing the method response for this peroxide-based explosive. Figure S-1 shows the positive ion reactive-DESI mass spectrum of TATP at the LOD of 10 ng in a diesel matrix and deposited on paper using NaCl (10 mM molar) in the solvent spray (methanol/water, 70:30). Note that the product ion spectrum of the complex $(TATP + Na)^+$ ion at m/z 245 (inset of figure S-1) is the same as the one shown in Figure 1 (see inset, right side, in Communication) which is for TATP on paper without any matrix. This shows the ability of the sodium to selectively pick up the TATP from the complex diesel matrix and at the same time confirms the TATP identity by using tandem mass spectrometry to screen out other interferents.

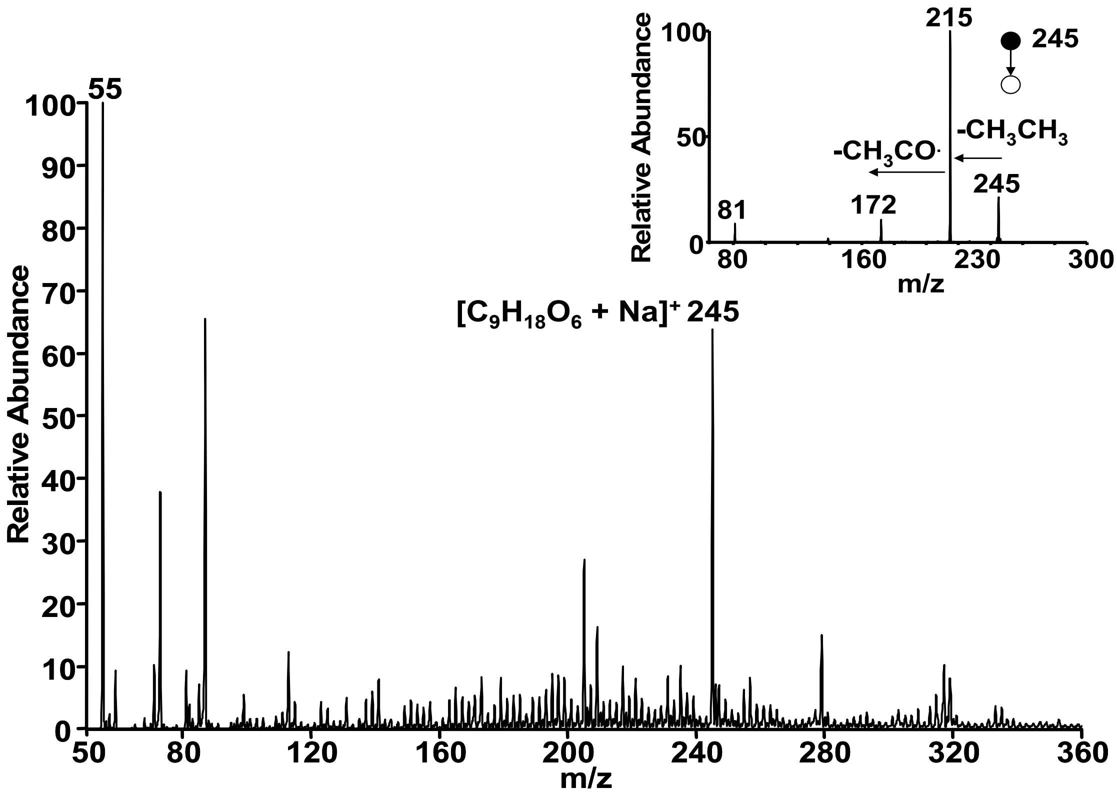

Figure S-1 Positive ion DESI spectrum of 10 ng TATP in a diesel matrix deposited on 1 cm^2 of paper. Methanol/water (70:30) doped with NaCl (10 mM) was used as the spray and a 4 mm^2 area was sampled. MS/MS product ion spectrum of m/z 245 is shown inset.

Isotopic labeling experiments support the proposed fragmentation mechanism (Scheme 1 in the text). Fig. 2a (in the text) shows the DESI spectra obtained for labeled TATP (deuterium labeled terminal methyl groups). Labeled TATP (TATP-d_n, n = 6, 12, and 18) (0.7 µg total amount) was deposited on a metal surface in an area of 1 cm^2. The ions at m/z 245, 251, 257, and 263 correspond to $(C_9H_{18}O_6 + Na)^+$, $(C_9H_{12}D_6O_6 + Na)^+$, $(C_9H_6D_{12}O_6 + Na)^+$, and $(C_9D_{18}O_6 + Na)^+$ complexes, respectively. As observed in Fig. 2b, the CID product mass spectrum for the ion at m/z 251 $(C_9H_{12}D_6O_6 + Na)^+$ showed two main peaks, $(C_7H_9D_3O_6 + Na)^+$ at *m/z* 218 and $(C_7H_6D_6O_6 + Na)^+$ at *m/z* 221. This result is in agreement with the expected 2:1 ratio of losses of CH_3CD_3 and CH_3CH_3 from the $(C_9H_{12}D_6O_6 + Na)^+$ complex (Scheme 1b, in the text) and is consistent with the proposed fragmentation pathway shown in Scheme 1a. Ions observed at lower masses correspond to the losses of $CD_3CO^{\cdot}$ or $CH_3CO^{\cdot}$ from the ion at m/z 218 and to the loss of $CH_3CO^{\cdot}$ from the ion at m/z 221. These ions occur at m/z 172 $(C_5H_9O_5 + Na)^{+\cdot}$, m/z 175 $(C_5H_6D_3O_5 + Na)^{+\cdot}$, and m/z 178 $(C_5H_3D_6O_5 + Na)^{+\cdot}$, respectively, again in good agreement with the expected 1:1:1 ratio (Scheme 1b). Further fragmentation of these three ions gives products ions at m/z 81 and 87 corresponding to $(C_3H_6O + Na)^+$ and $(C_3D_6O + Na)^+$, respectively. Fig. 2c shows the CID mass spectrum for the ion at m/z 263 $(C_9D_{18}O_6 + Na)^+$. The loss of CD_3CD_3 from the ion at m/z 263 gives rise to a product ion at m/z 227 $(C_7D_{12}O_6 + Na)^+$ which subsequently fragments losing a $CD_3CO^{\cdot}$ group to give the product ion at m/z 181 $(C_5D_9O_5 + Na)^{+\cdot}$. Further fragmentation of the ion at m/z 181 produces the $(C_3D_6O + Na)^+$ at m/z 87.

Table 1. CID of deuterated mixtures of TATP and TrATrP adducted to Na^+, K^+, and NH_4^+ ions

TATP or deuterated TATPs	M.W.	Dopant		Precursor Ion	Product ions		Composition
			m/z		m/z	%	
$C_9H_{18}O_6$	222	NaCl	245	$[C_9H_{18}O_6 + Na]^+$	215	100	$[C_7H_{12}O_6 + Na]^+$
					172	11	$[C_5H_9O_5 + Na]^{+\cdot}$
					81	9	$[C_3H_6O + Na]^+$
$C_9H_{12}D_6O_6$	228	NaCl	251	$[C_9H_{12}D_6O_6 + Na]^+$	221	100	$[C_7H_6D_6O_6 + Na]^+$
					218	53	$[C_7H_9D_3O_6 + Na]^+$
					178	7	$[C_5H_3D_6O_5 + Na]^{+\cdot}$
					175	6	$[C_5H_6D_3O_5 + Na]^{+\cdot}$
					172	6	$[C_5H_9O_5 + Na]^{+\cdot}$
					87	8	$[C_3D_6O + Na]^+$
					81	9	$[C_3H_6O + Na]^+$
$C_9H_6D_{12}O_6$	234	NaCl	257	$[C_9H_6D_{12}O_6 + Na]^+$	224	100	$[C_7H_3D_9O_6 + Na]^+$
					221	47	$[C_7H_6D_6O_6 + Na]^+$
					181	7	$[C_5D_9O_5 + Na]^{+\cdot}$
					178	7	$[C_5H_3D_6O_5 + Na]^{+\cdot}$
					175	6	$[C_5H_6D_3O_5 + Na]^{+\cdot}$
					87	8	$[C_3D_6O + Na]^+$
					81	24	$[C_3H_6O + Na]^+$
$C_9D_{18}O_6$	240	NaCl	263	$[C_9D_{18}O_6 + Na]^+$	227	100	$[C_7D_{12}O_6 + Na]^+$
					181	13	$[C_5D_9O_5 + Na]^{+\cdot}$
					87	13	$[C_3D_6O + Na]^+$
$C_9H_{18}O_6$	222	KCl	261	$[C_9H_{18}O_6 + K]^+$	231	100	$[C_7H_{12}O_6 + K]^+$
					188	27	$[C_5H_9O_5 + K]^{+\cdot}$
					97	25	$[C_3H_6O + K]^+$
$C_9H_{12}D_6O_6$	228	KCl	267	$[C_9H_{12}D_6O_6 + K]^+$	237	45	$[C_7H_6D_6O_6 + K]^+$
					234	100	$[C_7H_9D_3O_6 + K]^+$
					194	10	$[C_5H_3D_6O_5 + K]^{+\cdot}$
					191	8	$[C_5H_6D_3O_5 + K]^{+\cdot}$
					188	11	$[C_5H_9O_5 + K]^{+\cdot}$
					103	4	$[C_3D_6O + K]^+$
					97	21	$[C_3H_6O + K]^+$
$C_9H_6D_{12}O_6$	234	KCl	273	$[C_9H_6D_{12}O_6 + K]^+$	240	100	$[C_7D_9H_3O_6 + K]^+$
					237	45	$[C_7H_6D_6O_6 + K]^+$
					197	8	$[C_5D_9O_5 + K]^{+\cdot}$
					194	7	$[C_5H_3D_6O_5 + K]^{+\cdot}$
					191	10	$[C_5H_6D_3O_5 + K]^{+\cdot}$
					103	21	$[C_3D_6O + K]^+$
					97	22	$[C_3H_6O + K]^+$
$C_9H_{18}O_6$	222	LiCl	229	$[C_9H_{18}O_6 + Li]^+$	199	100	$[C_7H_{12}O_6 + Li]^+$
					156	11	$[C_5H_9O_5 + Li]^{+\cdot}$
					65	1	$[C_3H_6O + Li]^+$
$C_9H_{12}D_6O_6$	228	LiCl	235	$[C_9H_{12}D_6O_6 + Li]^+$	205	53	$[C_7H_6D_6O_6 + Li]^+$
					202	100	$[C_7H_9D_3O_6 + Li]^+$
					162	1	$[C_5H_3D_6O_5 + Li]^{+\cdot}$
					159	1	$[C_5H_6D_3O_5 + Li]^{+\cdot}$
					156	1	$[C_5H_9O_5 + Li]^{+\cdot}$

					71	2	$[C_3D_6O + Li]^+$
					65	1	$[C_3H_6O + Li]^+$
$C_9H_6D_{12}O_6$	234	LiCl	241	$[C_9H_6D_{12}O_6 + Li]^+$	208	100	$[C_7H_3D_9O_6 + Li]^+$
					205	46	$[C_7H_6D_6O_6 + Li]^+$
					165	1	$[C_5D_9O_5 + Li]^{+\cdot}$
					162	1	$[C_5H_3D_6O_5 + Li]^{+\cdot}$
					159	1	$[C_5H_6D_3O_5 + Li]^{+\cdot}$
					71	2	$[C_3D_6O + Li]^+$
					65	1	$[C_3H_6O + Li]^+$
$C_9D_{18}O_6$	240	LiCl	247	$[C_9D_{18}O_6 + Li]^+$	211	100	$[C_7D_{12}O_6 + Li]^+$
					165	2	$[C_5D_9O_5 + Li]^{+\cdot}$
					71	1	$[C_3D_6O + Li]^+$
$C_9H_{18}O_6$	222	NH_4OAC	240	$[C_9H_{18}O_6 + NH_4]^+$	223	8	$[C_9H_{18}O_6 + H]^+$
					97	2	$[C_3H_6O_2 + Na]^+$
					91	44	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$
					74	100	$[C_3H_6O_2]^{+\cdot}$
$C_9H_{12}D_6O_6$	228	NH_4OAC	246	$[C_9H_{12}D_6O_6 + NH_4]^+$	229	11	$[C_9H_{12}D_6O_6 + H]^+$
					97	27	$[C_3H_6O_2 + Na]^+$
					91	62	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$
					74	100	$[C_3H_6O_2]^{+\cdot}$
$C_9H_6D_{12}O_6$	234	NH_4OAC	252	$[C_9H_6D_{12}O_6 + NH_4]^+$	235	10	$[C_9H_6D_{12}O_6 + H]^+$
					97	29	$[C_3H_6O_2 + Na]^+$
					91	59	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$
					74	100	$[C_3H_6O_2]^{+\cdot}$

TrATrP or deuterated TrATrPs	**M.W.**	**Dopant**		**Precursor Ion**	**Product ions**		**Composition**
			m/z		**m/z**	**%**	
$C_{12}H_{24}O_8$	296	NaCl	319	$[C_{12}H_{24}O_8 + Na]^+$	289	100	$[C_{10}H_{18}O_8 + Na]^+$
					246	28	$[C_8H_{15}O_7 + Na]^{+\cdot}$
					141	11	$[C_4H_6O_4 + Na]^+$
$C_{12}H_{18}D_6O_8$	302	NaCl	325	$[C_{12}H_{18}D_6O_8 + Na]^+$	295	100	$[C_{10}H_{12}D_6O_8 + Na]^+$
					292	91	$[C_{10}H_{15}D_3O_8 + Na]^+$
					252	27	$[C_8H_9D_6O_7 + Na]^{+\cdot}$
					249	13	$[C_8H_{12}D_3O_7 + Na]^{+\cdot}$
					246	12	$[C_8H_{15}O_7 + Na]^{+\cdot}$
					144	12	$[C_4H_3D_3O_4 + Na]^+$
					141	12	$[C_4H_6O_4 + Na]^+$
$C_{12}H_{12}D_{12}O_8$	308	NaCl	331	$[C_{12}H_{12}D_{12}O_8 + Na]^+$	301	27	$[C_{10}H_6D_{12}O_8 + Na]^+$
					298	100	$[C_{10}H_9D_9O_8 + Na]^+$
					295	24	$[C_{10}H_{12}D_6O_8 + Na]^+$
					258	8	$[C_8H_3D_{12}O_7 + Na]^{+\cdot}$
					255	13	$[C_8H_6D_9O_7 + Na]^{+\cdot}$
					252	13	$[C_8H_9D_6O_7 + Na]^{+\cdot}$
					249	7	$[C_8H_{12}D_3O_7 + Na]^{+\cdot}$
					147	3	$[C_4D_6O_4 + Na]^+$
					144	13	$[C_4H_3D_3O_4 + Na]^+$
					141	3	$[C_4H_6O_4 + Na]^+$
$C_{12}H_6D_{18}O_8$	315	NaCl	337	$[C_{12}H_6D_{18}O_8 + Na]^+$	304	100	$[C_{10}H_3D_{15}O_8 + Na]^+$
					301	93	$[C_{10}H_6D_{12}O_8 + Na]^+$
					261	14	$[C_8D_{15}O_7 + Na]^{+\cdot}$

					258	14	$[C_8H_3D_{12}O_7 + Na]^{+\cdot}$
					255	26	$[C_8H_6D_9O_7 + Na]^{+\cdot}$
					147	13	$[C_4D_6O_4 + Na]^+$
					144	14	$[C_4H_3D_3O_4 + Na]^+$
$C_{12}H_{24}O_8$	296	KCl	335	$[C_{12}H_{24}O_8 + K]^+$	305	100	$[C_{10}H_{18}O_8 + K]^+$
					262	17	$[C_8H_{15}O_7 + K]^{+\cdot}$
					157	12	$[C_4H_6O_4 + K]^+$
$C_{12}H_{18}D_6O_8$	302	KCl	341	$[C_{12}H_{18}D_6O_8 + K]^+$	311	100	$[C_{10}H_{12}D_6O_8 + K]^+$
					308	94	$[C_{10}H_{15}D_3O_8 + K]^+$
					268	17	$[C_8H_9D_6O_7 + K]^{+\cdot}$
					265	14	$[C_8H_{12}D_3O_7 + K]^{+\cdot}$
					262	8	$[C_8H_{15}O_7 + K]^{+\cdot}$
					160	13	$[C_4H_3D_3O_4 + K]^+$
					157	12	$[C_4H_6O_4 + K]^+$
$C_{12}H_{12}D_{12}O_8$	308	KCl	347	$[C_{12}H_{12}D_{12}O_8 + K]^+$	317	27	$[C_{10}H_6D_{12}O_8 + K]^+$
					314	100	$[C_{10}H_9D_9O_8 + K]^+$
					311	22	$[C_{10}H_{12}D_6O_8 + K]^+$
					274	5	$[C_8H_3D_{12}O_7 + K]^{+\cdot}$
					271	9	$[C_8H_6D_9O_7 + K]^{+\cdot}$
					268	9	$[C_8H_9D_6O_7 + K]^{+\cdot}$
					265	4	$[C_8H_{12}D_3O_7 + K]^{+\cdot}$
					163	3	$[C_4D_6O_4 + K]^+$
					160	14	$[C_4H_3D_3O_4 + K]^+$
					157	3	$[C_4H_6O_4 + K]^+$
$C_{12}H_6D_{18}O_8$	315	KCl	353	$[C_{12}H_6D_{18}O_8 + K]^+$	320	100	$[C_{10}H_3D_{15}O_8 + K]^+$
					317	97	$[C_{10}H_6D_{12}O_8 + K]^+$
					277	9	$[C_8D_{15}O_7 + K]^{+\cdot}$
					274	9	$[C_8H_3D_{12}O_7 + K]^{+\cdot}$
					271	17	$[C_8H_6D_9O_7 + K]^{+\cdot}$
					163	13	$[C_4D_6O_4 + K]^+$
					160	13	$[C_4H_3D_3O_4 + K]^+$
$C_{12}H_{24}O_8$	296	LiCl	303	$[C_{12}H_{24}O_8 + Li]^+$	273	100	$[C_{10}H_{18}O_8 + Li]^+$
					230	18	$[C_8H_{15}O_7 + Li]^{+\cdot}$
					125	1	$[C_4H_6O_4 + Li]^+$
$C_{12}H_{18}D_6O_8$	302	LiCl	309	$[C_{12}H_{18}D_6O_8 + Li]^+$	279	100	$[C_{10}H_{12}D_6O_8 + Li]^+$
					276	91	$[C_{10}H_{15}D_3O_8 + Li]^+$
					236	11	$[C_8H_9D_6O_7 + Li]^{+\cdot}$
					233	9	$[C_8H_{12}D_3O_7 + Li]^{+\cdot}$
					230	7	$[C_8H_{15}O_7 + Li]^{+\cdot}$
					128	1	$[C_4H_3D_3O_4 + Li]^+$
					125	1	$[C_4H_6O_4 + Li]^+$
$C_{12}H_{12}D_{12}O_8$	308	LiCl	315	$[C_{12}H_{12}D_{12}O_8 + Li]^+$	285	32	$[C_{10}H_6D_{12}O_8 + Li]^+$
					282	100	$[C_{10}H_9D_9O_8 + Li]^+$
					279	26	$[C_{10}H_{12}D_6O_8 + Li]^+$
					242	5	$[C_8H_3D_{12}O_7 + Li]^{+\cdot}$
					239	9	$[C_8H_6D_9O_7 + Li]^{+\cdot}$
					236	9	$[C_8H_9D_6O_7 + Li]^{+\cdot}$
					233	4	$[C_8H_{12}D_3O_7 + Li]^{+\cdot}$
					131	1	$[C_4D_6O_4 + Li]^+$
					128	2	$[C_4H_3D_3O_4 + Li]^+$
					125	1	$[C_4H_6O_4 + Li]^+$

$C_{12}H_6D_{18}O_8$	315	LiCl	321	$[C_{12}H_6D_{18}O_8 + Li]^+$	288	99	$[C_{10}H_3D_{15}O_8 + Li]^+$
					285	100	$[C_{10}H_6D_{12}O_8 + Li]^+$
					245	10	$[C_8D_{15}O_7 + Li]^{+\cdot}$
					242	10	$[C_8H_3D_{12}O_7 + Li]^{+\cdot}$
					239	16	$[C_8H_6D_9O_7 + Li]^{+\cdot}$
					131	2	$[C_4D_6O_4 + Li]^+$
					128	4	$[C_4H_3D_3O_4 + Li]^+$
$C_{12}H_{24}O_8$	296	NH_4OAC	314	$[C_{12}H_{24}O_6 + NH_4]^+$	296	6	$[C_{12}H_{24}O_8 + H]^+$
					97	2	$[C_3H_6O_2 + Na]^+$
					91	100	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$
$C_{12}H_{18}D_6O_8$	302	NH_4OAC	320	$[C_{12}H_{18}D_6O_8 + NH_4]^+$	302	5	$[C_{12}H_{18}D_6O_8 + H]^+$
					97	100	$[C_3H_6O_2 + Na]^+$
					91	38	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$
$C_{12}H_{12}D_{12}O_8$	308	NH_4OAC	326	$[C_{12}H_{12}D_{12}O_8 + NH_4]^+$	308	6	$[C_{12}H_{12}D_{12}O_8 + H]^+$
					97	100	$[C_3H_6O_2 + Na]^+$
					91	5	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$
$C_{12}H_6D_{18}O_8$	315	NH_4OAC	332	$[C_{12}H_6D_{18}O_8 + NH_4]^+$	315	7	$[C_{12}H_6D_{18}O_8 + H]^+$
					97	100	$[C_3H_6O_2 + Na]^+$
					91	2	$[C_9H_{18}O_6 + NH_3]^{+\cdot}$

Figures S-2a and S-2c show the DESI mass spectra for labeled tetracetone tetraperoxide (TrATrP) (0.7 µg total amount) complexes with Na^+ and K^+ respectively, deposited on metal surfaces in a total area of 1 cm^2. From Figure S-2a we can observe several ions at m/z 319, 325, 331, and 337 corresponding to $(C_{12}H_{24}O_8 + Na)^+$, $(C_{12}H_{18}D_6O_8 + Na)^+$, $(C_{12}H_{12}D_{12}O_8 + Na)^+$, and $(C_{12}H_6D_{18}O_8 + Na)^+$ complexes respectively. Figure S-2b is the CID spectrum for the ion at m/z 331, showing losses of 30, 33, and 36 mass units corresponding to CH_3CH_3, CH_3CD_3, and CD_3CD_3 respectively, and giving products ions at m/z 301 $(C_{10}H_6D_{12}O_8 + Na)^+$, m/z 298 $(C_{10}H_9D_9O_8 + Na)^+$, and m/z 295 $(C_{10}H_{12}D_6O_8 + Na)^+$ respectively. The ions at m/z 301, m/z 298, and m/z 295 fragment further to give the ions at m/z 258 $(C_8H_3D_{12}O_7 + Na)^{+\cdot}$, m/z 255 $(C_8H_6D_9O_7 + Na)^{+\cdot}$, m/z 252 $(C_8H_9D_6O_7 + Na)^{+\cdot}$, and $(C_8H_{12}D_3O_7 + Na)^{+\cdot}$ by loss of the radical species $CH_3CO^\cdot$, $CH_3CO^\cdot$, $CD_3CO^\cdot$, and $CD_3CO^\cdot$, respectively. Further fragmentation produces the ions at m/z 141, m/z 144, and m/z 147 corresponding to $(C_4H_6O_4 + Na)^+$, $(C_4H_3D_3O_4 + Na)^+$, and $(C_4D_6O_4 + Na)^+$, respectively.

Figure S-2d shows the CID spectrum for the ion at m/z 347, the $(C_{12}H_{12}D_{12}O_8 + K)^+$ complex. Upon CID, this ion produces the same characteristic losses of 30 (CH_3CH_3), 33(CH_3CD_3), and 36 (CD_3CD_3), corroborating the same fragmentation pathway as for the $(C_{12}H_{12}D_{12}O_8 + Na)^+$ complex and giving the product ions at m/z 317 $(C_{10}H_6D_{12}O_8 + K)^+$, m/z 314 $(C_{10}H_9D_9O_8 + K)^+$, and m/z 311 $(C_{10}H_{12}D_6O_8 + K)^+$ respectively. Several ions corresponding to $(C_8H_3D_{12}O_7 + K)^{+\cdot}$, $(C_8H_6D_9O_7 + K)^{+\cdot}$, $(C_8H_9D_6O_7 + K)^{+\cdot}$, and $(C_8H_{12}D_3O_7 + K)^{+\cdot}$ complexes are observed at m/z 274, m/z 271, m/z 268, and m/z 265, respectively. They fragment further giving the product ions at m/z 163 $(C_4D_6O_4 + K)^+$, m/z 160 $(C_4H_3D_3O_4 + K)^+$, and m/z 157 $(C_4H_6O_4 + K)^+$.

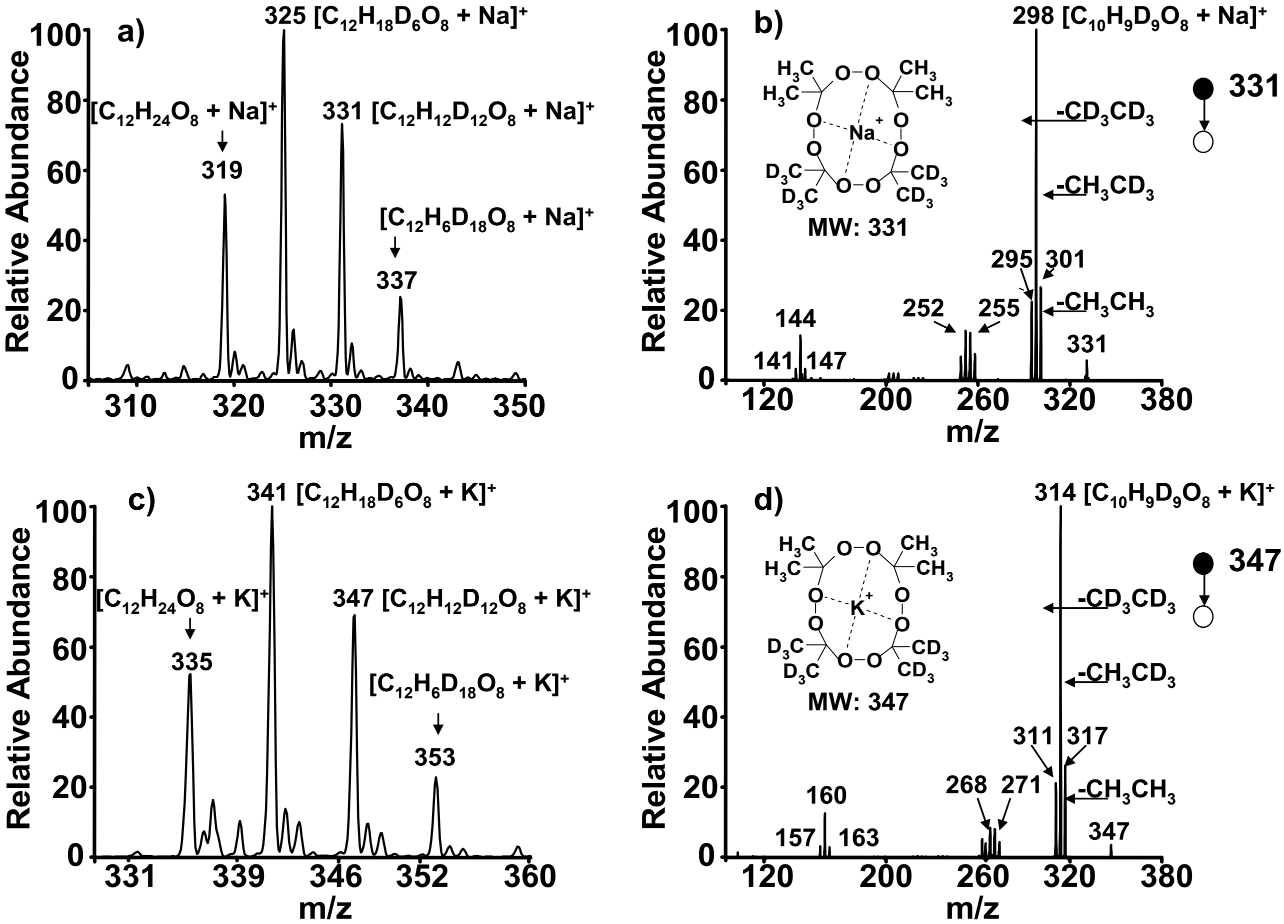

Figure S-2. Positive ion DESI spectra of a mixture of labeled 0.7 µg TrATrP (d_6 up to d_{18}) deposited on 1 cm^2 of metal surface. Methanol/water (70:30) doped with (a) NaCl (10 mM) or (c) KCl (10 mM) was used as the spray and a 4 mm^2 area was sampled. The corresponding MS/MS product ion spectrum of the (TrATrP-d_{12} + Na)$^+$ complex, m/z 331, and the (TrATrP-d_{12} + K)$^+$ complex, m/z 347 are shown in figures S-2b and S-2d respectively.

In a separate experiment, the performance of the DESI method to selectively detect TATP by forming stable complexes with multiple dopants was examined. The spray solvent (methanol/water) was doped with the alkali metals Na^+, K^+, Li^+ and also with NH_4^+ and sprayed onto a metal surface containing TATP. The concentration ratios were 1:1:1:1 (10 mM each) for the alkali metal mixture and ammonia in the spray solution while 0.7 μg TATP was deposited on 1 cm^2 metal surface. From Figure S-3 we can observe several ions at m/z 229, 240, 245, and 261 corresponding to $(C_9H_{18}O_6 + Li)^+$, $(C_9H_{18}O_6 + NH_4)^+$, $(C_9H_{18}O_6 + Na)^+$, and $(C_9H_{18}O_6 + K)^+$ complexes respectively.

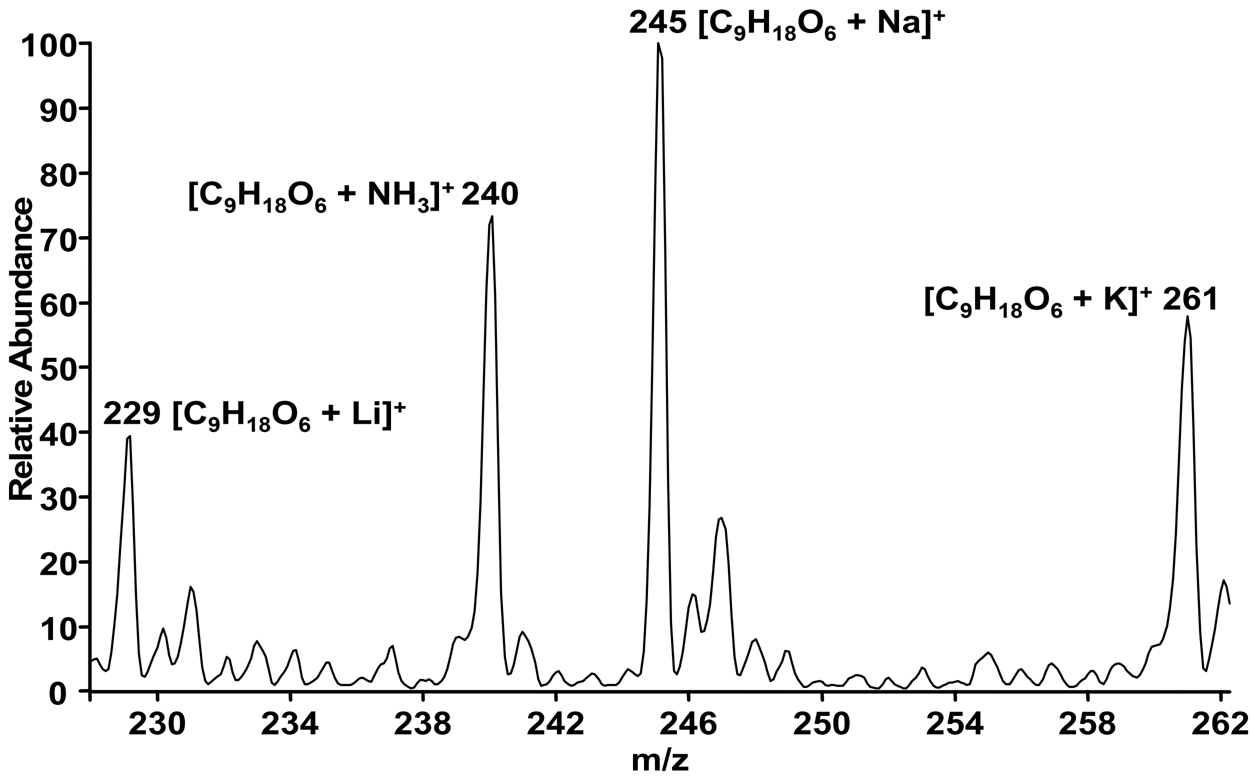

Figure S-3 Positive ion DESI spectrum of 0.7 μg TATP deposited in 1 cm^2 of paper surface. Methanol/water (70:30) doped with NaCl, CH_3COONH_4, LiCl, and KCl at the (1:1:1:1) concentrations ratios for the alkali metal mixture and ammonia (the concentration of each metal ion and ammonia components was 1 x 10^{-3} M) was used as the spray and a 4 mm^2 area was sampled.