Supplementary Material

Detection of Chemical Warfare Agent Simulants and Hydrolysis Products in Biological Samples by Paper Spray Mass Spectrometry

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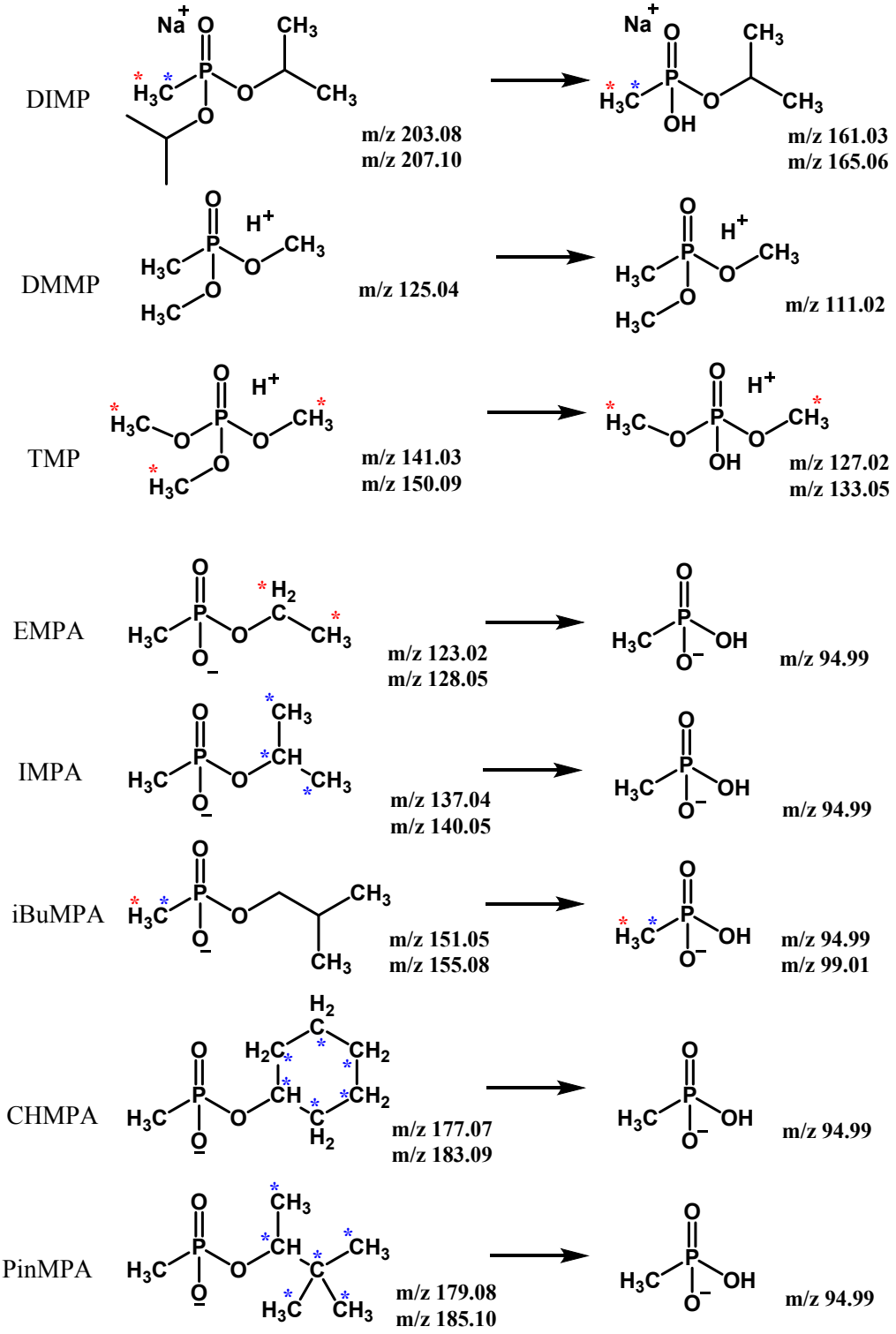
Supplementary Table 1. All monitored transitions for the intact CWA simulants, CWA hydrolysis products, and stable isotope labeled compounds used as internal standards as well as the collision energies (CEs) used for each. The CWA hydrolysis products were each run in both positive and negative ion modes, the latter of which is highlighted.

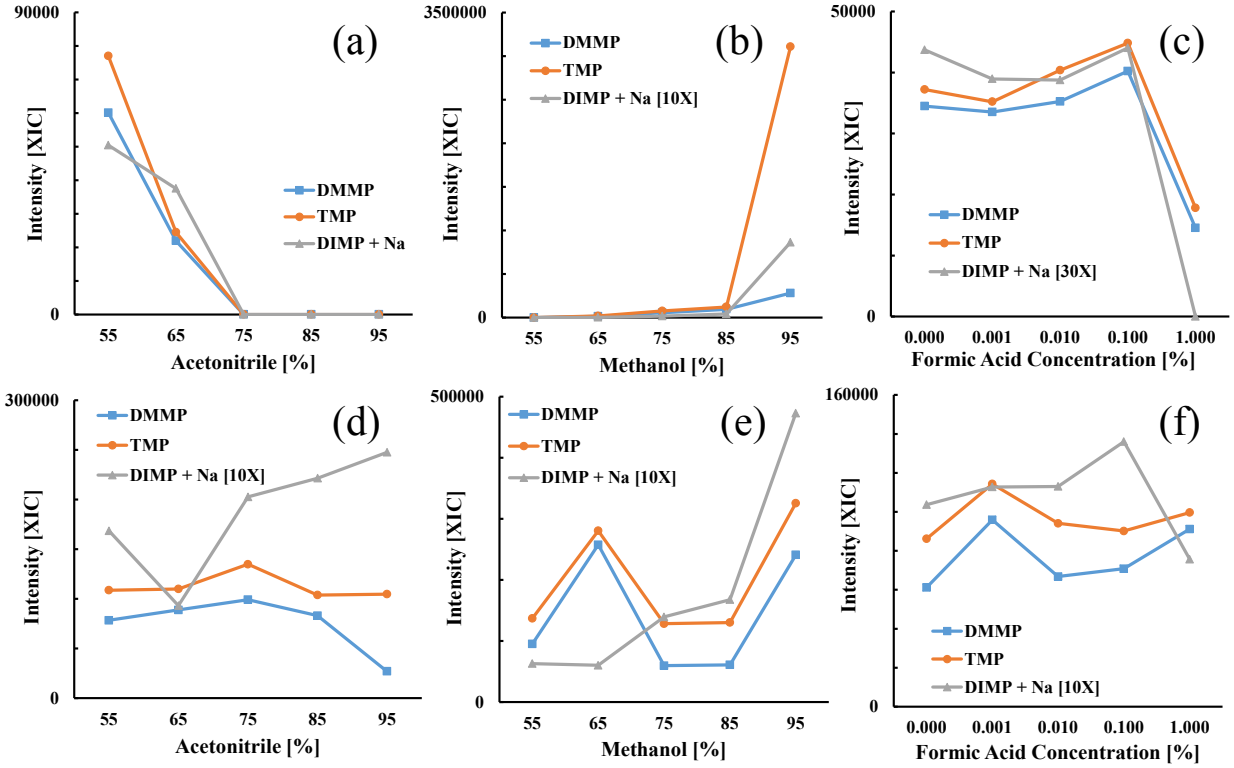
Compound	Adduct	Precursor Ion (*m/z*)	Fragment Ion (*m/z*)	CE (V)
TMP	+H	141.0311	127.0154	35
d_9TMP	+H	150.0877	133.0531	35
DMMP	+H	125.0362	111.0205	32
DIMP	+Na	203.0807	161.0338	30
$^{13}Cd_3$DIMP	+Na	207.1029	165.0560	30
EMPA	+H	125.0364	97.0055	10
	-H	123.0212	94.9896	12
d_5EMPA	+H	130.0679	98.0117	11
	-H	128.0529	94.9897	14
IMPA	+H	139.0506	97.0055	10
	-H	137.0371	94.9896	14
$^{13}C_3$IMPA	+H	142.0619	97.0055	12
	-H	140.0473	94.9896	14
iBuMPA	+H	153.0675	97.0055	16
	-H	151.0528	94.9895	16
$^{13}Cd_3$iBuMPA	+Na	179.0719	73.0292	13
	-H	155.0752	99.0118	15
CHMPA	+Na	201.0650	118.9872	13
	-H	177.0683	94.9896	23
$^{13}C_6$CHMPA	+Na	207.0851	118.9871	10
	-H	183.0885	94.9896	20
PinMPA	+Na	203.0808	118.9871	12
	-H	179.0840	94.9896	21
$^{13}C_6$PinMPA	+Na	209.1007	118.9871	10
	-H	185.1042	94.9896	19

Supplementary Table 2. Results for separately prepared calibration verification samples for calibration curves of the CWA simulants prepared in blood and urine. Data collected in positive ion mode with 95/5 methanol/water w 0.01% formic acid.

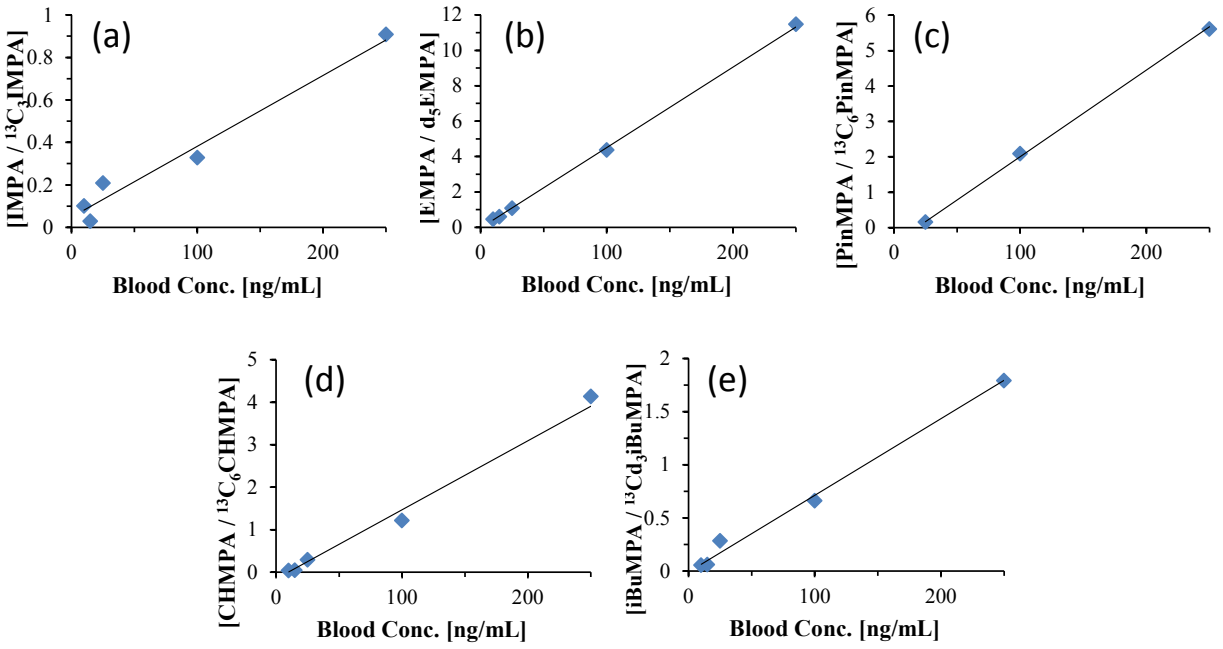
CCVs URINE				
	Ratio	Measured [ng/mL]	Prepared [ng/mL]	% Recovery
TMP	0.022	51.7	57.1	90.6
	0.143	163.7	160.2	102.2
DMMP	0.020	46.9	55.7	84.2
	0.123	148.7	156.3	95.1
DIMP	0.026	41.6	44.8	92.9
	0.233	294.0	298.2	98.6
CCVs BLOOD				
	Ratio	Measured [ng/mL]	Prepared [ng/mL]	% Recovery
TMP	0.065	67.0	56.1	119.4
	0.294	274.5	246.3	111.5
DMMP	0.064	71.5	60.9	117.5
	0.289	269.5	267.3	100.8
DIMP	0.041	59.5	59.0	100.8
	0.226	300.0	273.3	109.8



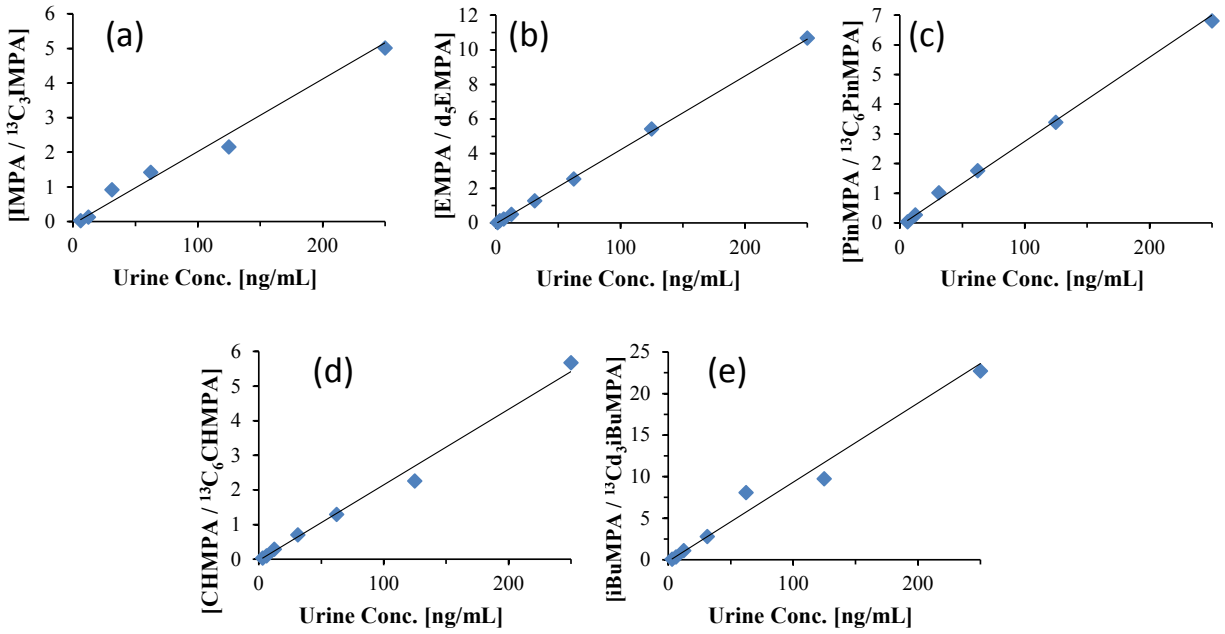
Supplementary Figure 1. Structures of the molecular ions and the most intense fragment ions for the CWA simulants and hydrolysis products. Asterisks are used to denote the location of ^{2}H and ^{13}C in the stable isotope labeled analogs.



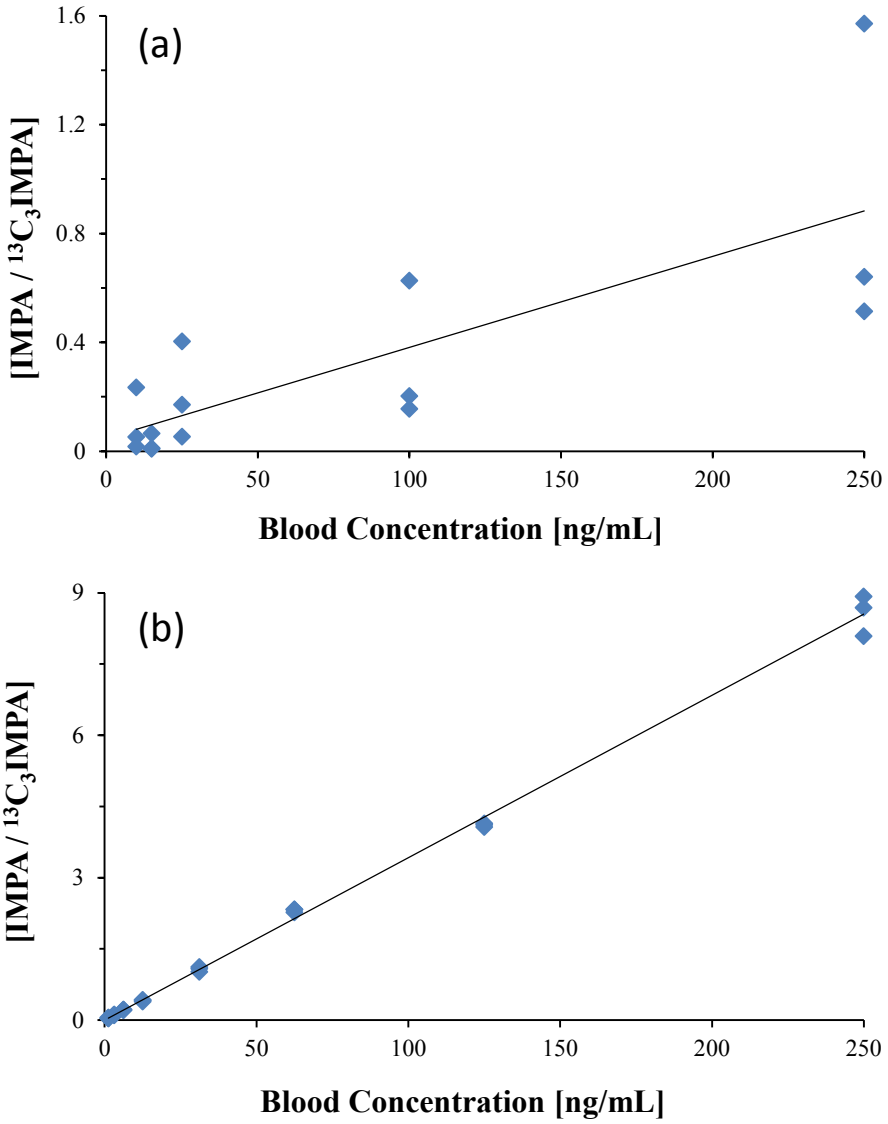
Supplementary Figure 2. Solvent and solvent modifier optimization for analysis of the CWA simulants in blood (a-c) and urine (d-f). Figures c and f were collected in positive ion mode using 95/5 methanol/water.



Supplementary Figure 3. Positive ion calibration curves for IMPA (a), EMPA (b), PinMPA (c), CHMPA (d), and iBuMPA (e) from 12 µL of blood using their corresponding SIL compound as the internal standard, generated using PS-MS. The molecular and fragment ions used to generate the curves are indicated in supplementary table 1. Each data point is an average of 3 replicates. The solvent used to collect the data was 95/5 methanol/water w 0.01% formic acid.



Supplementary Figure 4. Positive ion calibration curves for IMPA (a), EMPA (b), PinMPA (c), CHMPA (d), and iBuMPA (e) from 12 µL of urine using their corresponding SIL compound as the internal standard, generated using PS-MS. The molecular and fragment ions used to generate the curves are indicated in supplementary table 1. Each data point is an average of 3 replicates. The solvent used to collect the data was 95/5 methanol/water w 0.01% formic acid.



Supplementary Figure 5. (a) Positive ion using 95:5:0.01 methanol:water:formic acid and (b) negative ion using 90:10:0.01 methanol:CCl_4: ammonium hydroxide calibration curves for IMPA from 12 µL of blood using PS-MS, showing each individual analyte/ISTD measurement against its known concentration.