Electronic Supplementary Information

Paper Spray Mass Spectrometry for Discriminating the Quality of Commercial Gasolines

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Table S1. Comparison of the compositions of the observed peaks in the analysis of gasoline samples

series	observed peaks					
I	m/z	108	122	136		
	composition	$C_7H_{10}N^+$	$C_8H_{12}N^+$	$C_9H_{14}N^+$		
II	m/z	114	128	142	156	170
	composition	$C_7H_{16}N^+$	$C_8H_{18}N^+$	$C_9H_{20}N^+$	$C_{10}H_{22}N^+$	$C_{11}H_{24}N^+$
III	m/z	202	216	230	244	258
	composition	$C_{14}H_{20}N^+$	$C_{15}H_{22}N^+$	$C_{16}H_{24}N^+$	$C_{17}H_{26}N^+$	$C_{18}H_{28}N^+$
IV	m/z	374	388	402	416	
	composition	$C_{25}H_{46}N_2^+$	$C_{26}H_{48}N_2^+$	$C_{27}H_{50}N_2^+$	$C_{28}H_{52}N_2^+$	

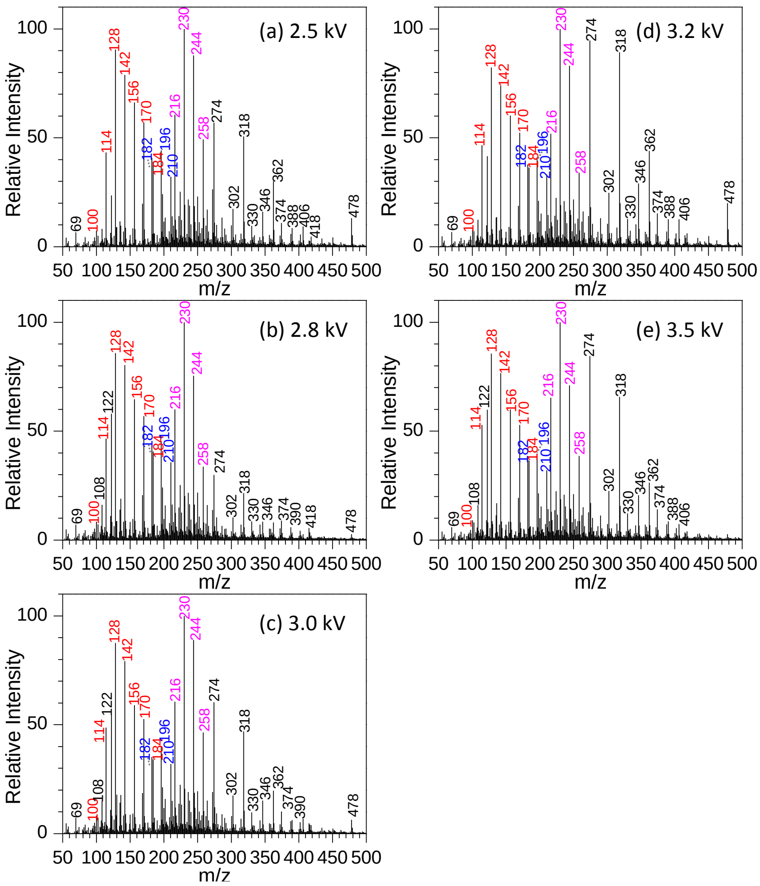

***Figure S1*.** Effect of spray voltage on the performance of gasoline analysis: **(a)** 2.5 kV; **(b)** 2.8 kV, **(c)** 3.0 kV, **(d)** 3.2 kV, and **(e)** 3.5 kV (Note: applied voltage: 3.5 kV; sample volume: 25 µL; percentage of gasoline in methanol: 70%).

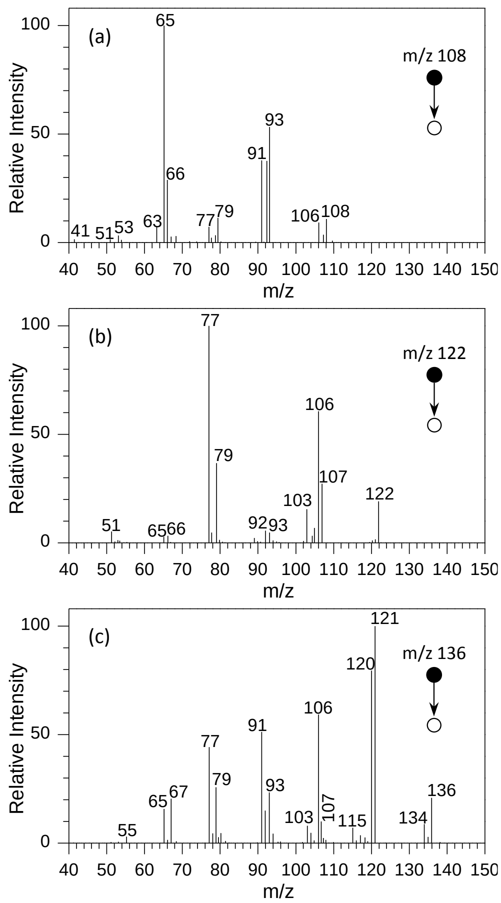

Figure S2. MS/MS mass spectra of the peaks occurred at **(a)** m/z 108, **(b)** m/z 122, and **(c)** m/z 136 (Note: The proportion of gasoline sample in different solvents was 40% (v/v), and 25 μL of spray solution and 3.5 kV DC voltage were applied for each analysis).

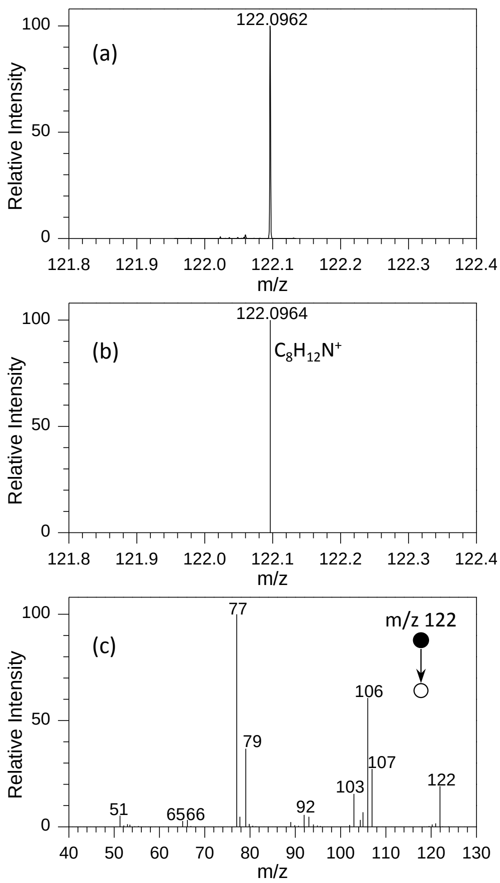

Figure S3**.** **(a)** Mass spectrum of m/z 122.0964 using a high-resolution Orbitrap mass spectrometer, and **(b)** theoretical mass spectrum of the product with a composition of $C_8H_{12}N^+$ from the Thermal Xcalibur software; **(c)** MS/MS spectra of the species occurred at m/z 122 (Note: The proportion of gasoline sample in different solvents was 40% (v/v), and 25 µL of spray solution and 3.5 kV DC voltage were applied for each analysis).

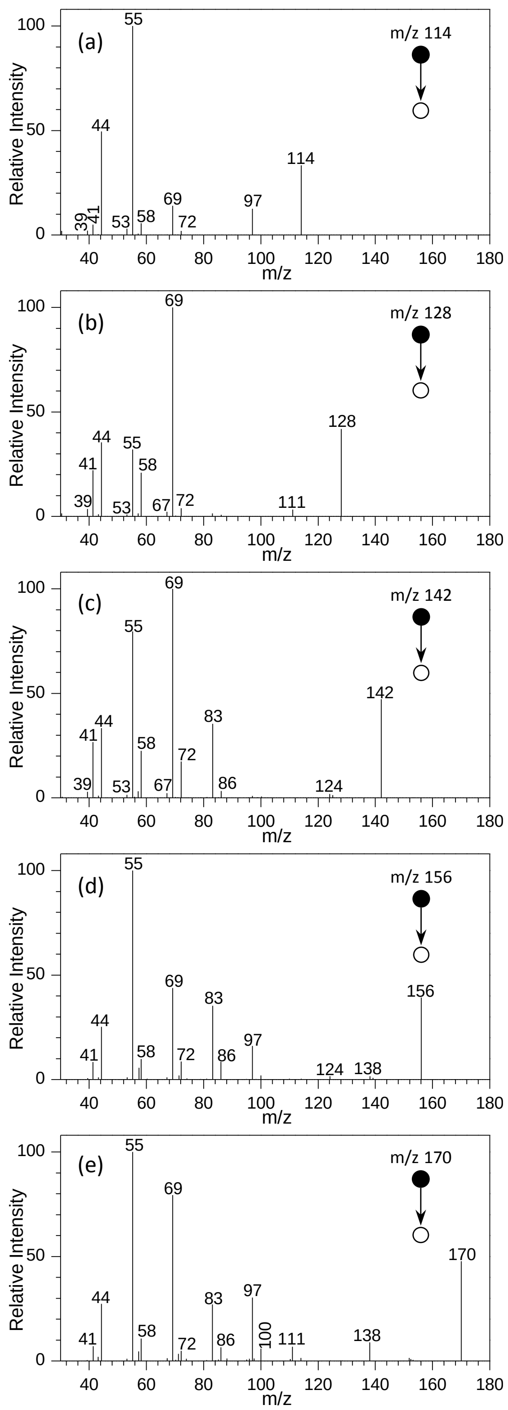

***Figure S4*.** MS/MS mass spectra of the peaks occurred at **(a)** m/z 114, **(b)** m/z 128, **(c)** m/z 142, **(d)** m/z 156, and **(e)** m/z 170 (Note: The proportion of gasoline sample in different solvents was 40% (v/v), and 25 µL of spray solution and 3.5 kV DC voltage were applied for each analysis).

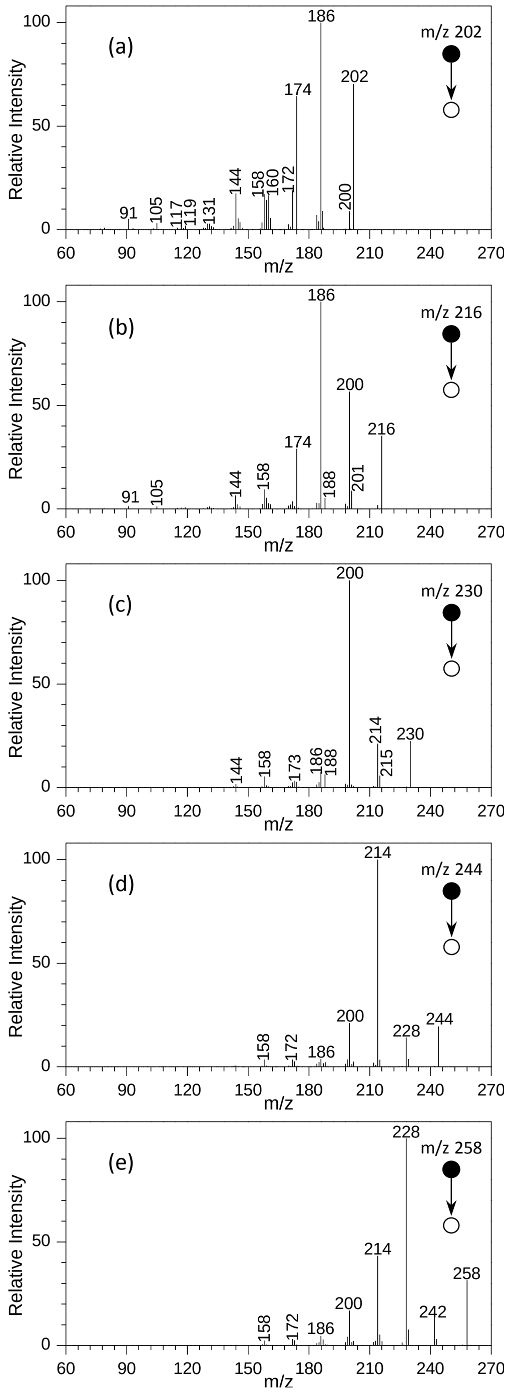

Figure S5. MS/MS mass spectra of the peaks occurred at **(a)** m/z 202, **(b)** m/z 216, **(c)** m/z 230, **(d)** m/z 244, and **(e)** m/z 258 (Note: The proportion of gasoline sample in different solvents was 40% (v/v), and 25 µL of spray solution and 3.5 kV DC voltage were applied for each analysis).

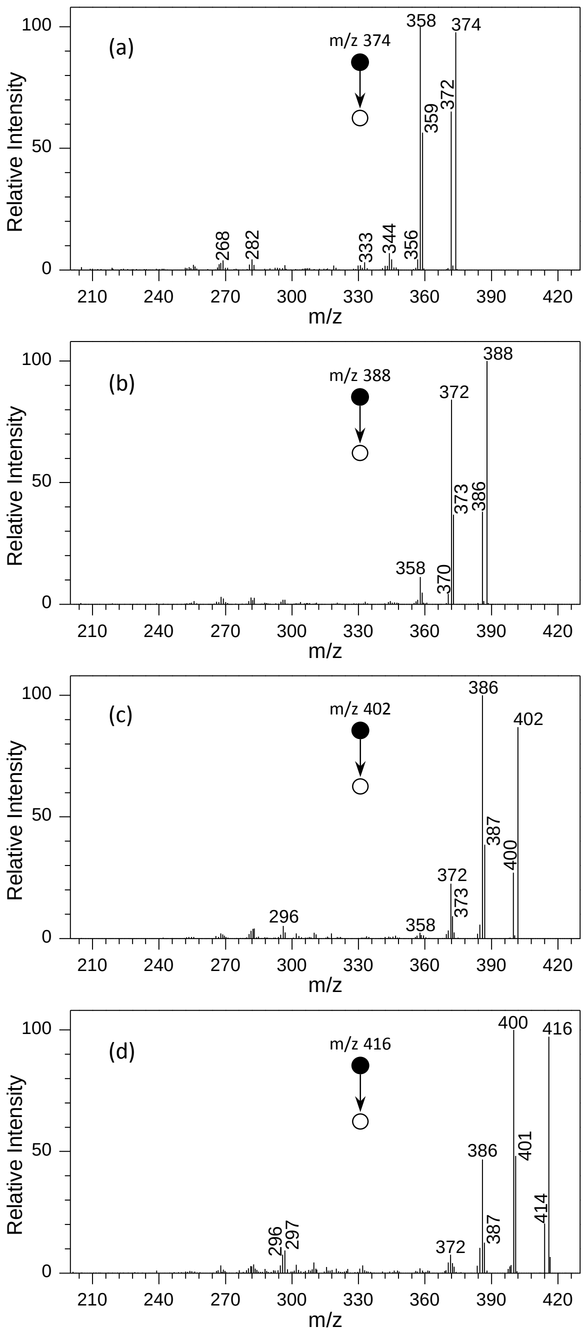

***Figure S6*.** MS/MS mass spectra of the peaks occurred at **(a)** m/z 374, **(b)** m/z 388, **(c)** m/z 402, and **(d)** 416 (Note: The proportion of gasoline sample in different solvents was 40% (v/v), and 25 µL of spray solution and 3.5 kV DC voltage were applied for each analysis).

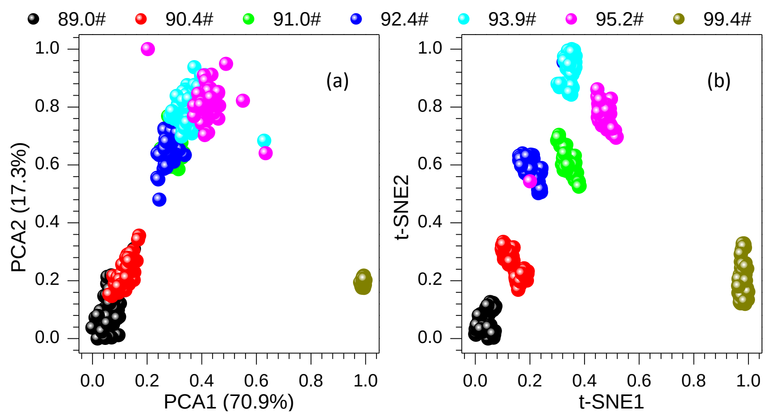

Figure S7**.** Comparison of PCA analysis with t-SNE analysis in distinguishing different types of standard gasoline samples: **(a)** PCA analysis, and **(b)** t-SNE analysis. [Note: Different types of standard gasoline samples were collected from PetroChina Changqing Petrochemical Company (Xianyang, China)].

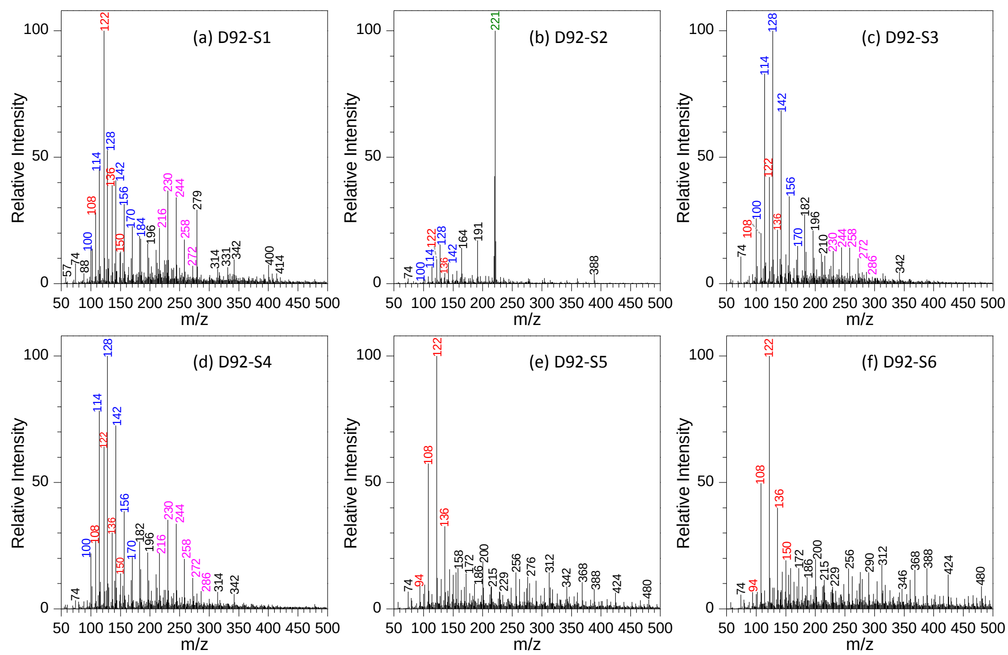

Figure S8**.** Typical mass spectra of the 92# gasoline samples from different gas stations of company D: **(a)** D92-S1, **(b)** D92-S2, **(c)** D92-S3, **(d)** D92-S4, **(e)** D92-S5, and **(f)** D92-S6 (Note: The proportion of gasoline sample in methanol solution was 70% (v/v), and 25 μL of spray solution and 3.5 kV DC voltage were applied for each analysis. Different series of peaks were marked with various colors, namely series I with red color, ●, series II with blue color, ●, series III with magenta color, ●, the peak at m/z 221 with olive color, ●, and the background peaks with black color, ●).

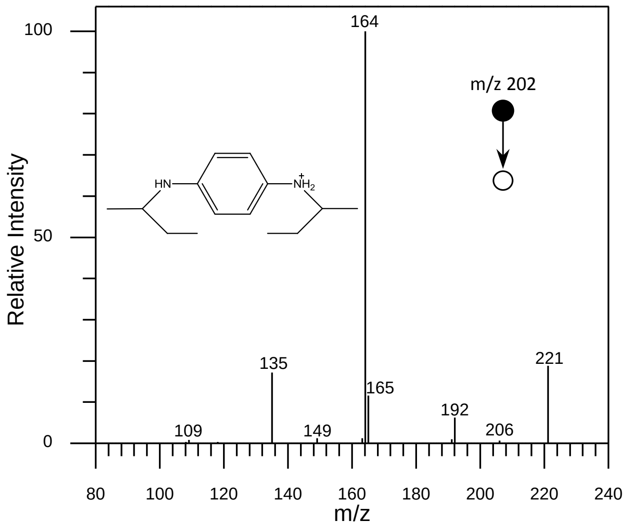

Figure S9. MS/MS mass spectrum of the peak occurred at m/z 221 (Note: The proportion of gasoline sample in different solvents was 70% (v/v), and 25 µL of spray solution and 3.5 kV DC voltage were applied for each analysis).

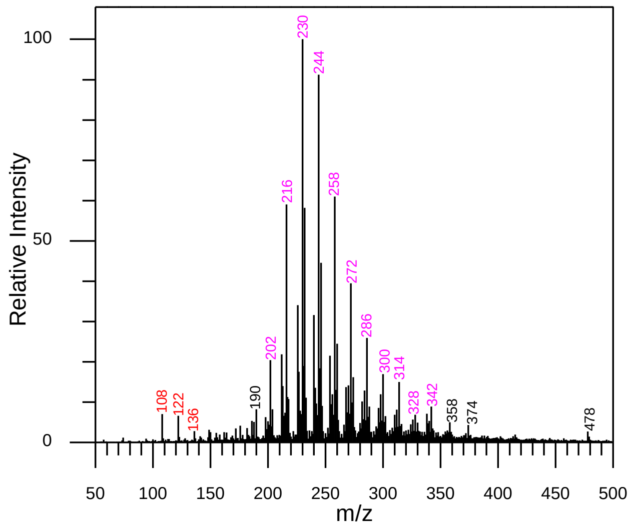

Figure S10. Mass spectrum of diesel solution by mixing diesel with methanol with a ratio of 7:3 (v/v) (Note: 25 µL of spray solution and 3.5 kV DC voltage were applied for each analysis).