Supplementary Material

Development of an Automatic Linear Calibration Method for High Resolution Single Particle Mass Spectrometry: Improved Chemical Species Identification for Atmospheric Aerosols

Shengqiang Zhu[1], Lei Li[2], Shurong Wang[1], Mei Li[2], Yaxi Liu[1], Xiaohui Lu[1], Hong Chen[1],

Lin Wang[1, 3], Jianmin Chen[1, 3], Zhou Zhen[2], Xin Yang*[1, 3] and Xiaofei Wang*[1, 3]

[1] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

[2] Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou, 510632, China

[3] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

Atmospheric Measurement Techniques Discussions

*To whom correspondence should be addressed.

Correspondence to:

Xiaofei Wang

Email: xiaofeiwang@fudan.edu.cn Tel: +86-21-31242526

Xin Yang

Email: yangxin@fudan.edu.cn Tel: +86-21-31245272

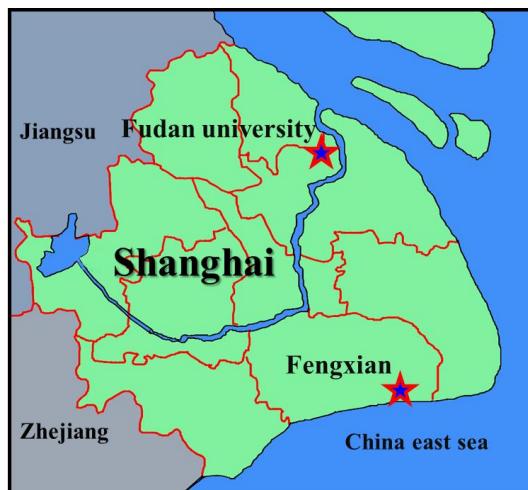



Fig.S1 the location of the Fengxian and Fudan university

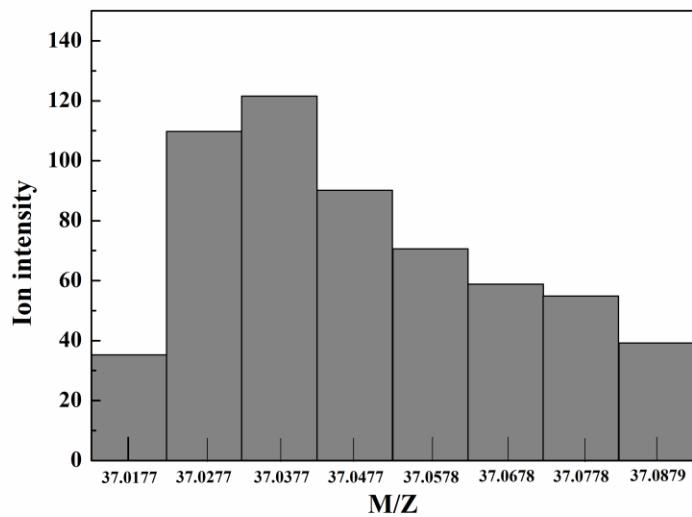
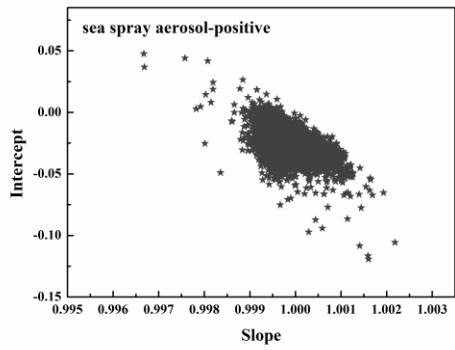
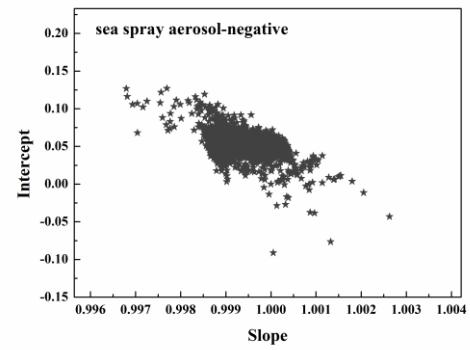
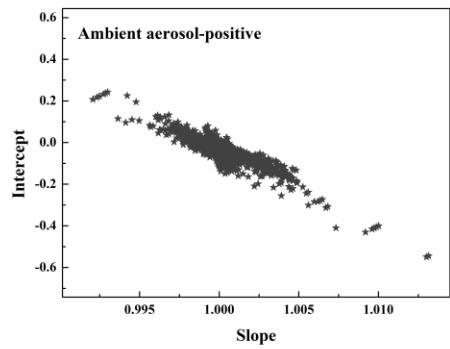
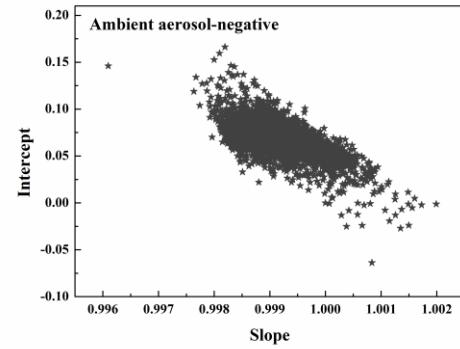



Fig.S2 the explanation of the m/z bin value in the single particle mass spectra

(a)positive ions   (b)negative ions
Fig.S3 slope-intercept of the sea spray aerosol calibration

(a)positive ions   (b)negative ions
Fig.S4 slope-intercept of the ambient aerosol calibration

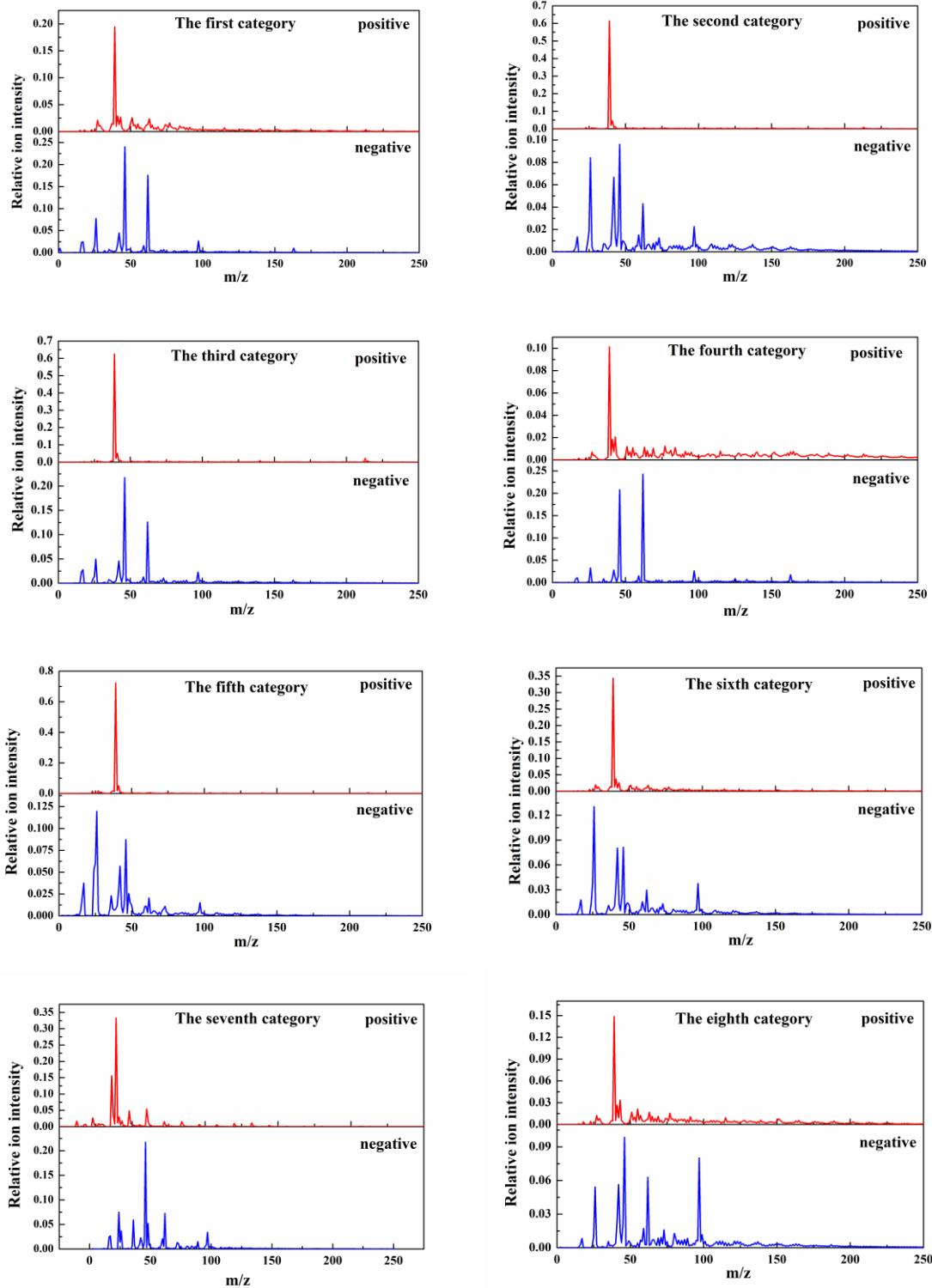



Figure.S5 Classification results of the LR-SPAMS by ART-2a

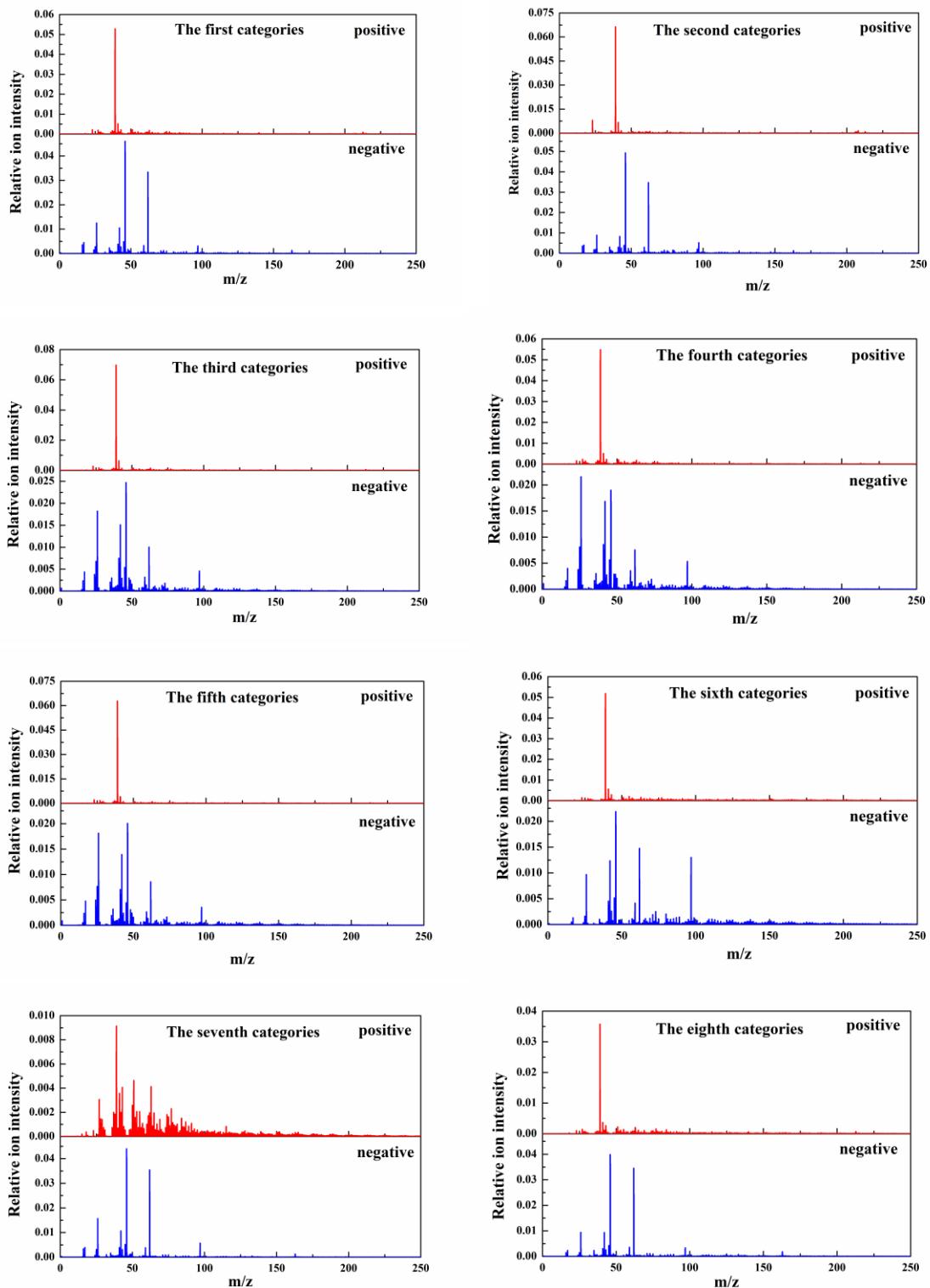



Figure.S6 Classification results of the HR-SPAMS by ART-2a

Table S1 deviation comparison between the averaged positive and negative mass spectra of calibration and non-calibration for sea spray aerosol

positive species	Theo (m/z)	Theo-bin(m/z)	Noncal-bin(m/z)	Δm/z	Cal-bin(m/z)	Δm/z	negative species	Theo-(m/z)	Theo-bin(m/z)	Noncal-bin(m/z)	Δm/z	Cal-bin(m/z)	Δm/z
Na^+	22.98977	22.993	23.0167	0.0237	22.993	0	CN^-	26.00307	25.9994	25.9658	-0.0336	26.0078	0.0084
Mg^+	23.98505	23.9829	24.0072	0.0243	23.9829	0	Cl^-	34.96885	34.9641	34.9349	-0.0292	34.9641	0
K^+	38.96371	38.9672	38.998	0.0288	38.9672	0	Cl^-	36.9659	36.9622	36.9321	-0.0301	36.9622	0
Na_2Cl^+	80.94839	80.9438	80.9883	0.0445	80.9438	0	CNO^-	41.99799	41.9971	41.965	-0.0321	41.9864	-0.0107
Na_2Cl^+	82.94544	82.9421	82.9871	0.045	82.9421	0	$NaCl^-$	57.95862	57.9574	57.9448	-0.0126	57.9574	0
K_2Cl^+	112.89627	112.898	112.951	0.053	112.898	0	$MgCl_3^-$	128.89161	128.883	128.939	0.056	128.901	0.018
K_2Cl^+	114.89332	114.885	114.938	0.053	114.885	0	$MgCl_3^-$	130.88866	130.894	130.932	0.038	130.894	0
							$MgCl_3^-$	132.88571	132.884	132.941	0.057	132.884	0

Table S2 deviation comparison between the averaged positive and negative mass spectra of calibration and non-calibration for ambient aerosol

positive species	Theo (m/z)	Theo-bin(m/z)	Noncal-bin(m/z)	Δm/z	Cal-bin(m/z)	Δm/z	negative species	Theo (m/z)	Theo-bin(m/z)	Noncal-bin(m/z)	Δm/z	Cal-bin(m/z)	Δm/z
C^+	12	11.9991	12.0105	0.0114	12.0048	0.0057							
							CN^-	26.00307	25.9994	25.9658	-0.0336	26.0078	0.0084
Na^+	22.98977	22.993	23.0167	0.0237	22.993	0	Cl^-	34.96885	34.9641	34.9349	-0.0292	34.9641	0
C_3^+	36	36.0023	36.032	0.0297	35.9925	-0.0098	NO_2^-	45.99291	45.9897	45.9673	-0.0224	45.9897	0
K^+	38.9672	38.9672	38.998	0.0308	38.9672	0	NO_3^+	61.98783	61.9938	61.9678	-0.026	61.9808	-0.013
Fe^+	55.93494	55.932	55.9813	0.0493	55.9443	0.0123	SO_4^-	95.95175	95.9502	96.031	0.0808	95.9663	0.0161
Pb^+	207.97664	207.967	208.014	0.047	207.967	0	HSO_4^-	96.95958	96.9546	96.9709	0.0163	96.9546	0
Pb^+	205.97446	205.976	206.023	0.047	205.976	0							
Pb^+	206.97589	206.97	207.018	0.048	206.994	0.024							

Table S3 deviation comparison between the averaged positive and negative mass spectra of calibration and non-calibration for ambient aerosol with additional marker ions

positive species	Theo (m/z)	Theo-bin(m/z)	Noncal-bin(m/z)	Δm/z	Cal-bin(m/z)	Δm/z	negative species	Theo (m/z)	Theo-bin(m/z)	Noncal-bin(m/z)	Δm/z	Cal-bin(m/z)	Δm/z
C^+	12	11.9991	12.0105	0.0114	11.9877	-0.0094	CN^-	26.00307	25.9994	25.9658	-0.0336	26.0078	0.0084
Na^+	22.98977	22.993	23.0167	0.0237	22.993	0	Cl^-	34.96885	34.9641	34.9349	-0.0292	34.9641	0
C_3^+	36	36.0023	36.032	0.0207	36.0023	0	NO_2^-	45.99291	45.9897	45.9673	-0.0224	45.9897	0
K^+	38.9672	38.9672	38.998	0.0308	38.9672	0	NO_3^+	61.98783	61.9938	61.9678	-0.026	61.9808	-0.013
Fe^+	55.93494	55.932	55.9813	0.0493	55.9566	0.0246	SO_4^-	95.95175	95.9502	96.0148	0.0646	95.9663	0.0161
Pb^+	207.97664	207.967	208.038	0.071	207.967	0	HSO_4^-	96.95958	96.9546	96.9709	0.0163	96.9546	0
Pb^+	205.97446	205.976	206.047	0.071	205.976	0							
Pb^+	206.97589	206.97	207.041	0.071	206.994	0.024							

Notes: Theo(m/z): Theoretical m/z value; Theo-bin(m/z): Theoretical m/z bin value;
Noncal-bin(m/z):Non-calibration m/z bin value. Cal bin(m/z): Calibration m/z bin value.