Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information for

"Organic Salt, NEDC (N-Naphthylethylenediamine Dihydrochloride) Assisted Laser Desorption Ionization Mass Spectrometry for Identification of Metal Ions in Real Samples"

by

Jian Hou, Suming Chen, Ning Zhang, Huihui Liu, Jianing Wang, Qing He, Jiyun Wang, and Zongxiu Nie

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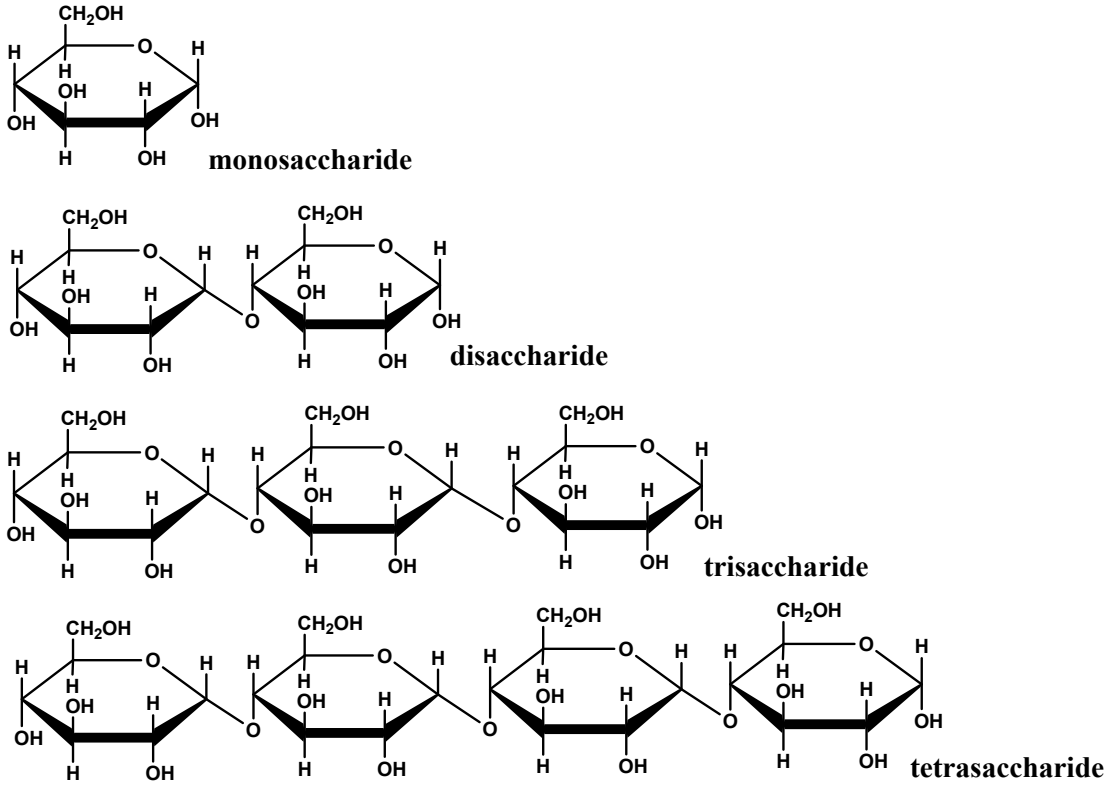
Table S1. Theoretical isotope abundance of $CuCl_2$, $MgCl_3$, $PbCl_3$ and $ZnCl_3$

species	High resolution			Low resolution		
	Isotopes	m/z	Abundance	Isotopes	m/z	Abundance
$CuCl_2$	$^{63}Cu\,^{35}Cl_2$	132.86731	100	$^{63}Cu\,^{35}Cl_2$	133	92.077
	$^{63}Cu^{35}Cl^{37}Cl$	134.86436	64.8	$^{63}Cu^{35}Cl^{37}Cl$,	135	100
	$^{65}Cu\,^{35}Cl_2$	134.8655	44.6	$^{65}Cu\,^{35}Cl_2$		
	$^{63}Cu^{37}Cl_2$	136.86141	10.5	$^{65}Cu^{35}Cl^{37}Cl$,	137	35.713
	$^{65}Cu^{35}Cl^{37}Cl$	136.86255	28.9	$^{63}Cu\,^{37}Cl_2$		
$MgCl_3$	$^{24}Mg\,^{35}Cl_3$	128.89161	100	$^{24}Mg\,^{35}Cl_3$	129	90.970
	$^{24}Mg^{35}Cl_2{}^{37}Cl$	130.88866	97.2	$^{24}Mg^{35}Cl_2{}^{37}Cl$,	131	100
	$^{26}Mg\,^{35}Cl_3$	130.88916	14.1	$^{26}Mg\,^{35}Cl_3$		
	$^{24}Mg^{35}Cl^{37}Cl_2$	132.88571	31.5	$^{24}Mg^{35}Cl^{37}Cl_2$,	133	40.110
	$^{26}Mg^{35}Cl_2{}^{37}Cl$	132.88621	13.7	$^{26}Mg^{35}Cl_2{}^{37}Cl$		
$PbCl_3$	$^{206}Pb^{35}Cl_2{}^{37}Cl$	312.87807	44.7	$^{206}Pb^{35}Cl_2{}^{37}Cl$,	313	100
	$^{208}Pb\,^{35}Cl_3$	312.8832	100	$^{208}Pb\,^{35}Cl_3$,		
	$^{206}Pb^{35}Cl^{37}Cl_2$	314.87512	14.5	$^{208}Pb^{35}Cl_2{}^{37}Cl$,	315	76.017
	$^{208}Pb^{35}Cl_2{}^{37}Cl$	314.88025	97.2	$^{206}Pb^{35}Cl\,^{37}Cl_2$		
$ZnCl_3$	$^{64}Zn^{35}Cl_3$	168.83571	100	$^{64}Zn^{35}Cl_3$	169	64.958
	$^{66}Zn^{35}Cl_3$	170.8326	57.4	$^{64}Zn^{35}Cl_2{}^{37}Cl$,	171	100
	$^{64}Zn^{35}Cl_2{}^{37}Cl$	170.83276	97.2	$^{66}Zn^{35}Cl_3$		
	$^{66}Zn^{35}Cl_2{}^{37}Cl$	172.82965	55.8	$^{66}Zn^{35}Cl_2{}^{37}Cl$,	173	81.690
	$^{64}Zn^{35}Cl^{37}Cl_2$	172.82981	31.5	$^{64}Zn^{35}Cl^{37}Cl_2$,		
	$^{68}Zn^{35}Cl_3$	172.83141	38.7	$^{68}Zn^{35}Cl_3$		

Red isotopes are used to determine the limits of detection.



Scheme S1. The chemical structures of calibrants used in the experiment.

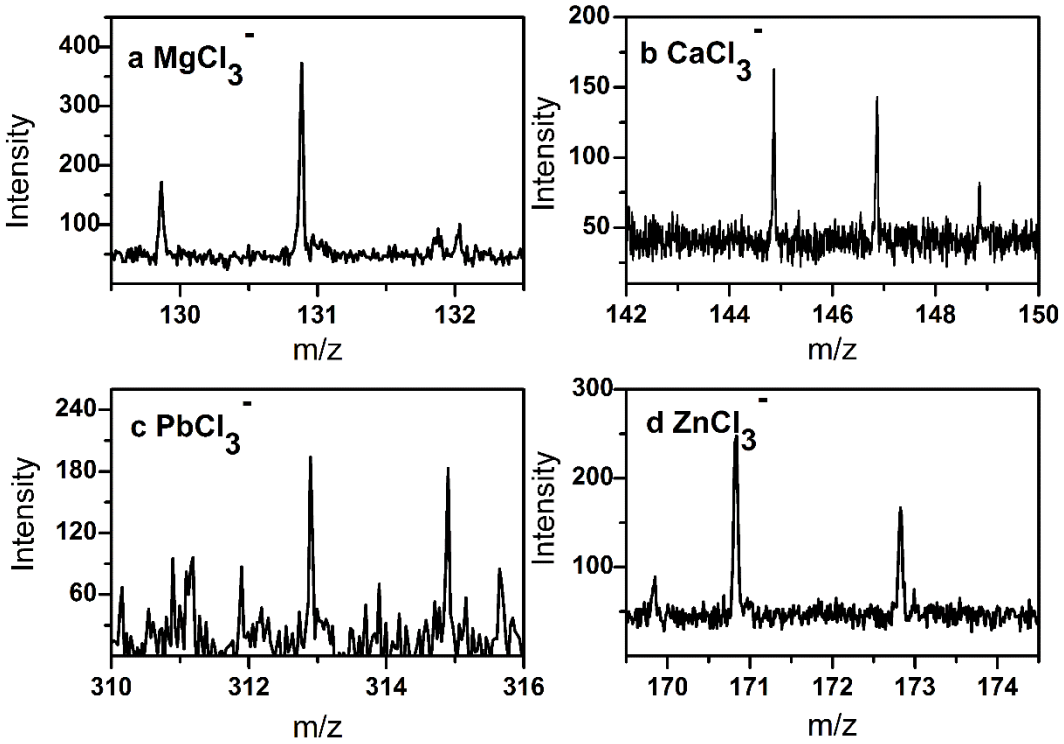


Figure S1. The mass spectra of 500fmol Ca^{2+}, Mg^{2+}, Pb^{2+} and Zn^{2+} on the steel targets, respectively.

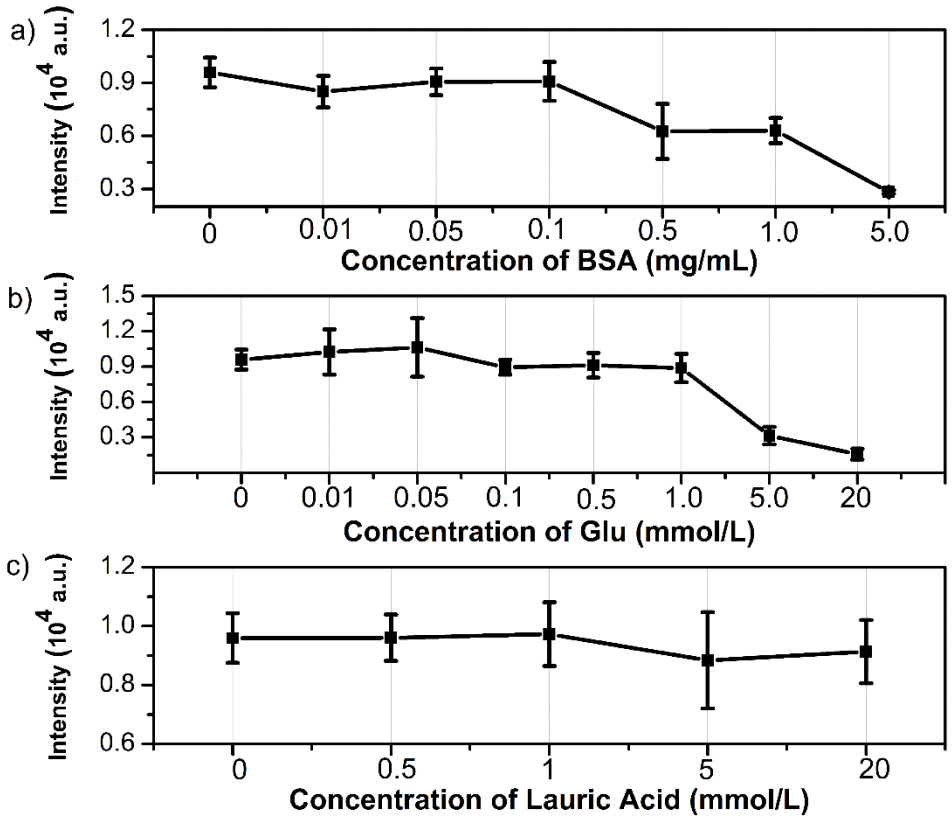


Figure S2. The interference effects of gradient concentrations of BAS a), Glu b) and Lauric acid c) to 100 μmol/L Mg^{2+} solution.

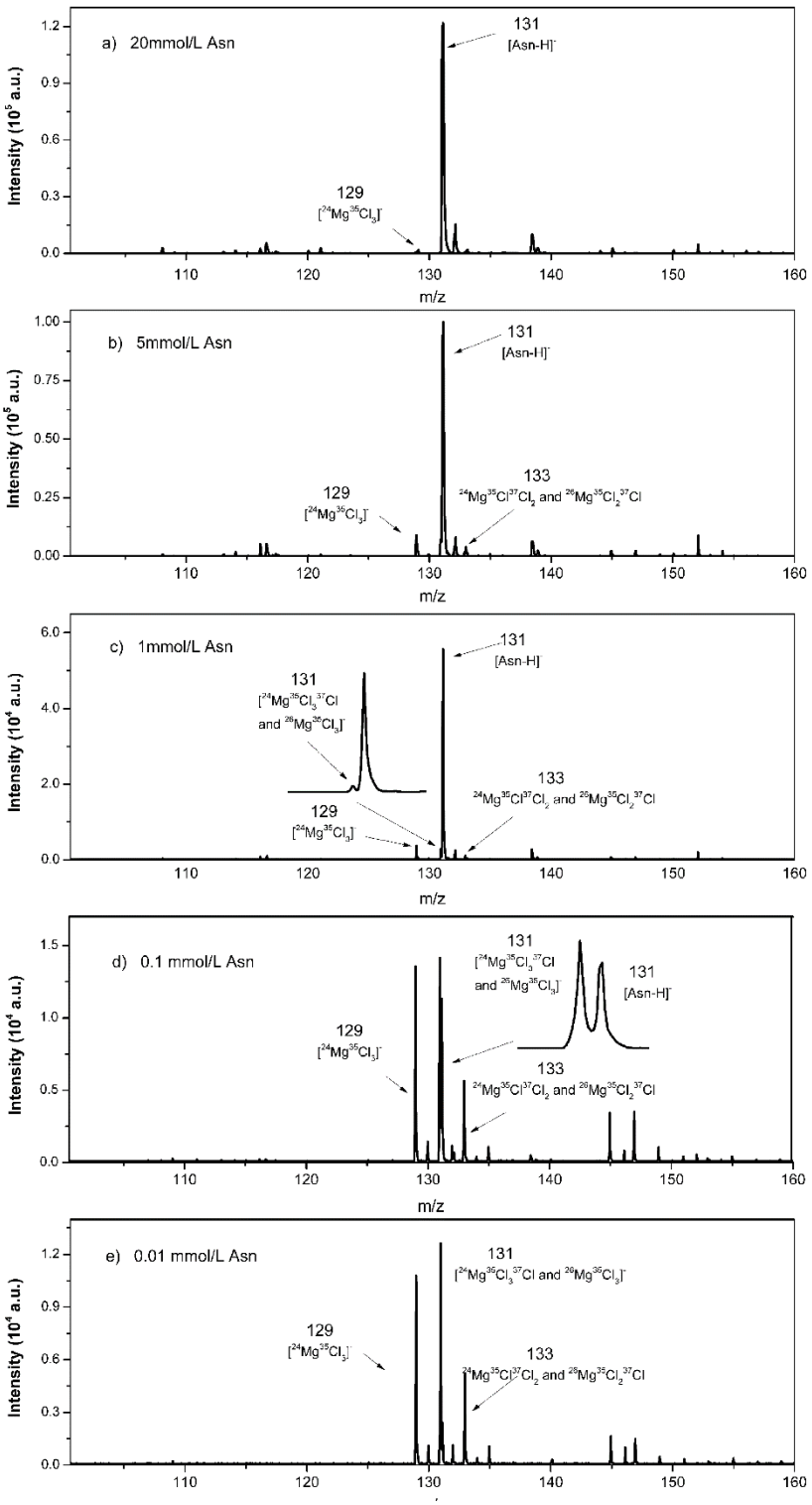


Figure S3. The interference of Asn at 20 mmol/L a), 5 mmol/L b), 1 mmol/L c), 0.1 mmol/L d) and 0.01 mmol/L e) to 100 μmol/L Mg^{2+} solution.

Both $[CuCl_2]^-$ and $[CuCl_3]^-$ peak in the spectra with no regard of original state of copper. There is analogous phenomenon in the analysis of Fe^{2+}, Fe^{3+}, Sn^{2+} and Sn^{4+} as well. Mechanisms for reduction of Cu^{2+} to Cu^+ in MALDI and ESI have been delineated[1, 2]. We suppose that this mechanism is rational in the situation of NEDC assisted metal analysis. Besides that, our results indicated oxidation in MALDI ionization. The stability of metal-chloride clusters may play a vital role to mass spectrum.

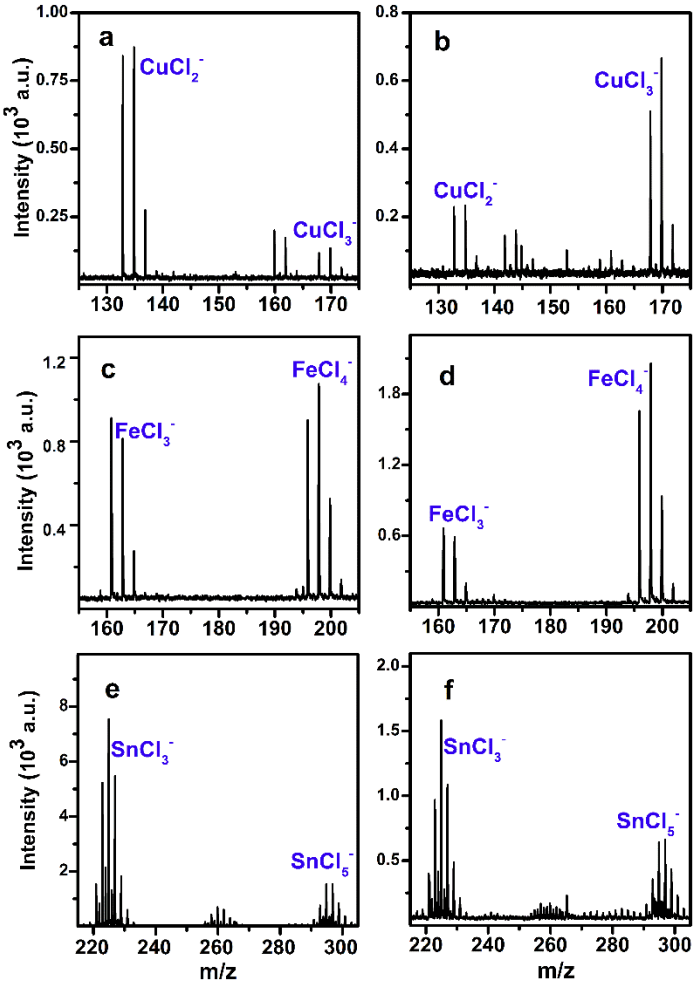


Figure S4. MALDI mass spectra of a) CuCl b) $CuCl_2$ c) $FeCl_2$ d) $FeCl_3$ e) $SnCl_2$ f) $SnCl_4$. Doubly charge states can be seen in each case.

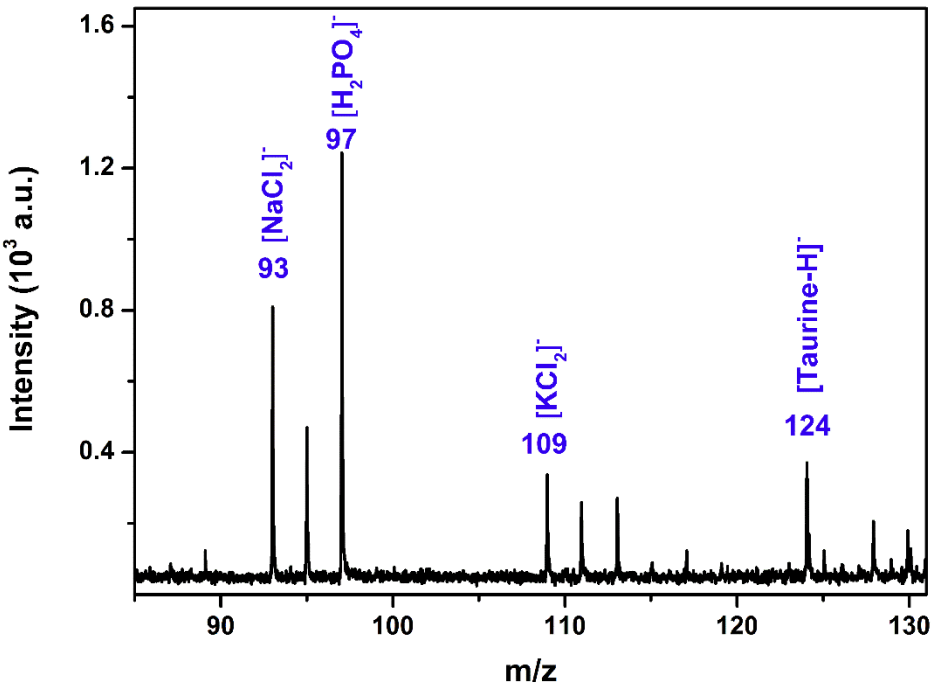


Figure S5. Mass spectrum of a 10 μm thick normal mouse brain slice on ITO glass by NEDC assisted laser desorption/ionization.

References

1. J. Zhang, V. Frankevich, R. Knochenmuss, S. D. Friess and R. Zenobi, *J. Am. Soc. Mass Spectrom.*, 2003, **14**, 42-50.
2. S. Mollah, A. D. Pris, S. K. Johnson, A. B. I. Gwizdala and R. S. Houk, *Anal. Chem.*, 2000, **72**, 985-991.