Supporting information for

CuFe$_2$O$_4$ magnetic nanocrystal clusters as a matrix for the analysis of small molecules by negative-Ion matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

Zian Lin,[ab]* Jiangnan Zheng,[b] Wei Bian,[a] and Zongwei Cai[a]*

a.Partner State Key Laboratory of Environmental and Biological Analysis, Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon Tong, Hong Kong, SAR, P. R. China

b. Ministry of Education Key Laboratory of Analysis and Detection for Food Safety, College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350116, China

- **Corresponding author:** Zian Lin, Zongwei Cai

- **Postal address:** Department of Chemistry, Hong Kong Baptist University

- Kowloon Tong, Hong Kong, SAR, P. R. China

- **Fax**: +852-34117348

E-mail: zianlin@fzu.edu.cn (Z.A. Lin); zwcai@hkbu.edu.hk (Z.W. Cai)
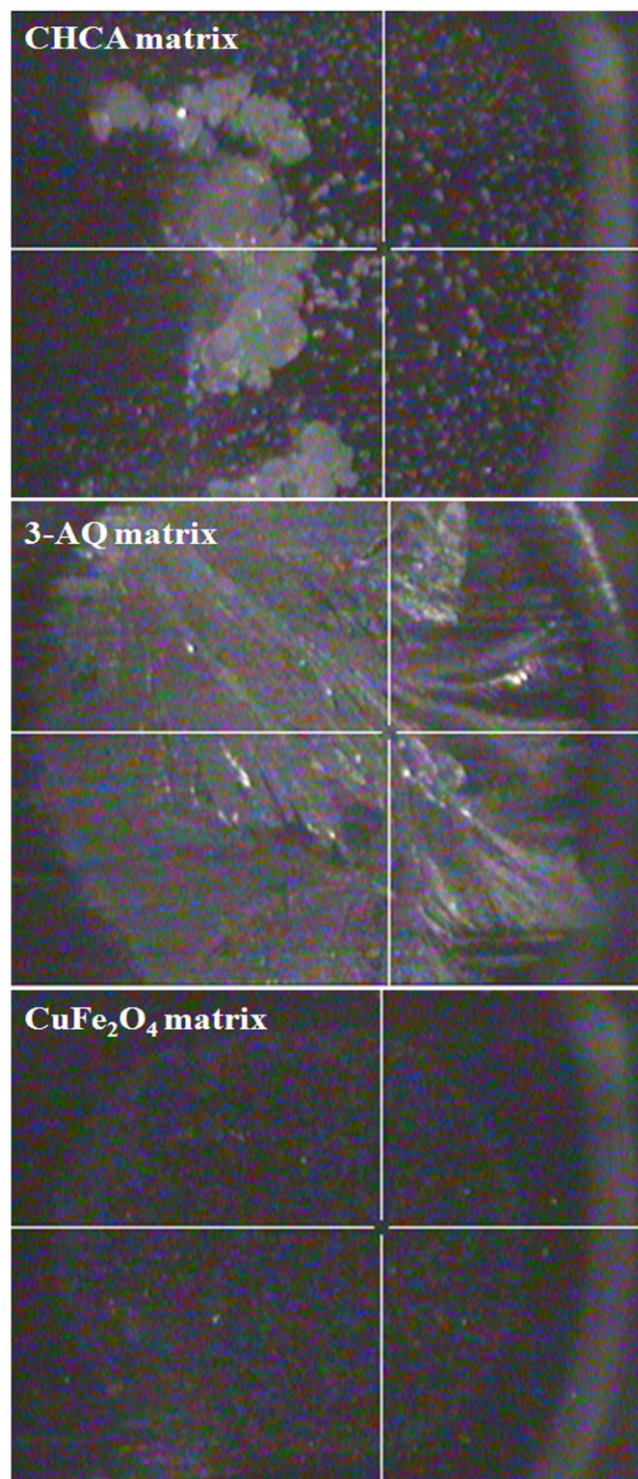
Supporting Information-Figures

Figure S1. Optical images of CHCA, 3-AQ and CuFe$_2$O$_4$ MNCs dispersed on the stainless steel target. Matrix concentration: CHCA and 3-AQ (each of them, 10 mg/mL) and CuFe$_2$O$_4$ MNCs (1 mg/mL).
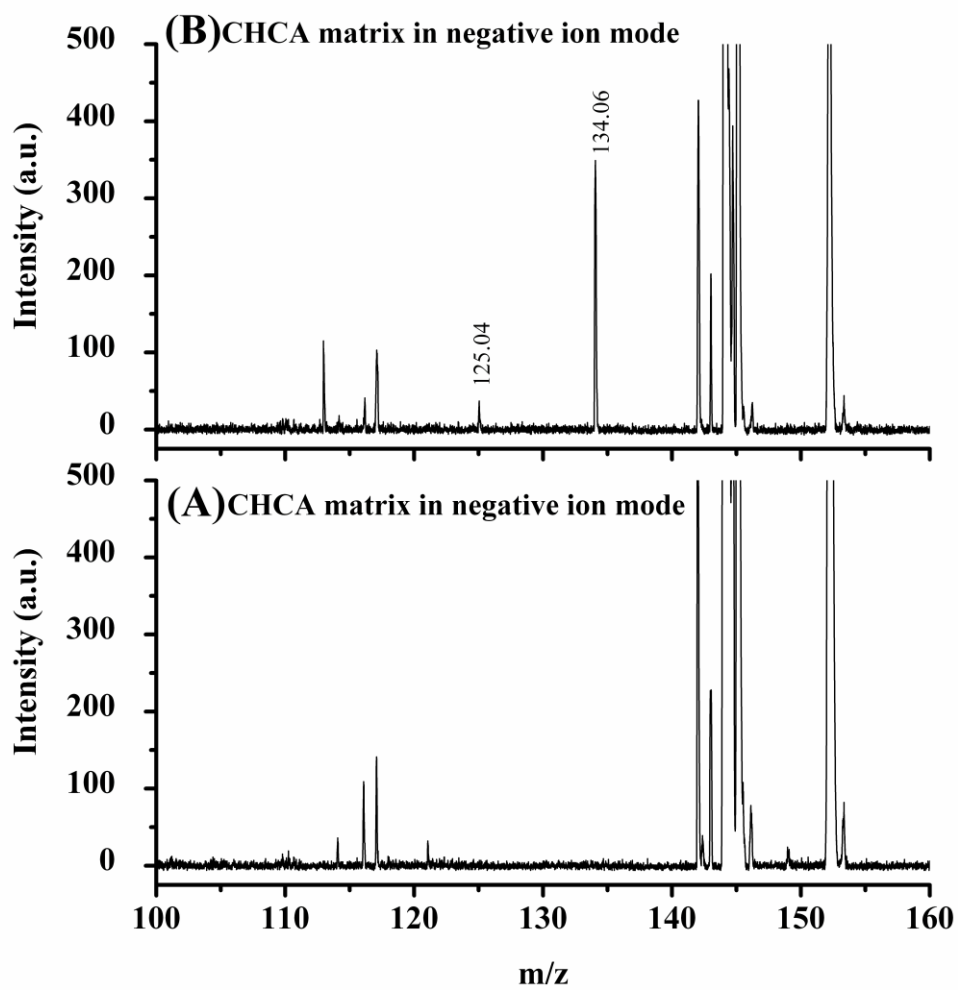
Figure S2. Mass spectra of four nucleobases by using CHCA matrix. (A) CHCA matrix; (B) CHCA matrix + nucleobases. Other experimental conditions is same as Figure.5
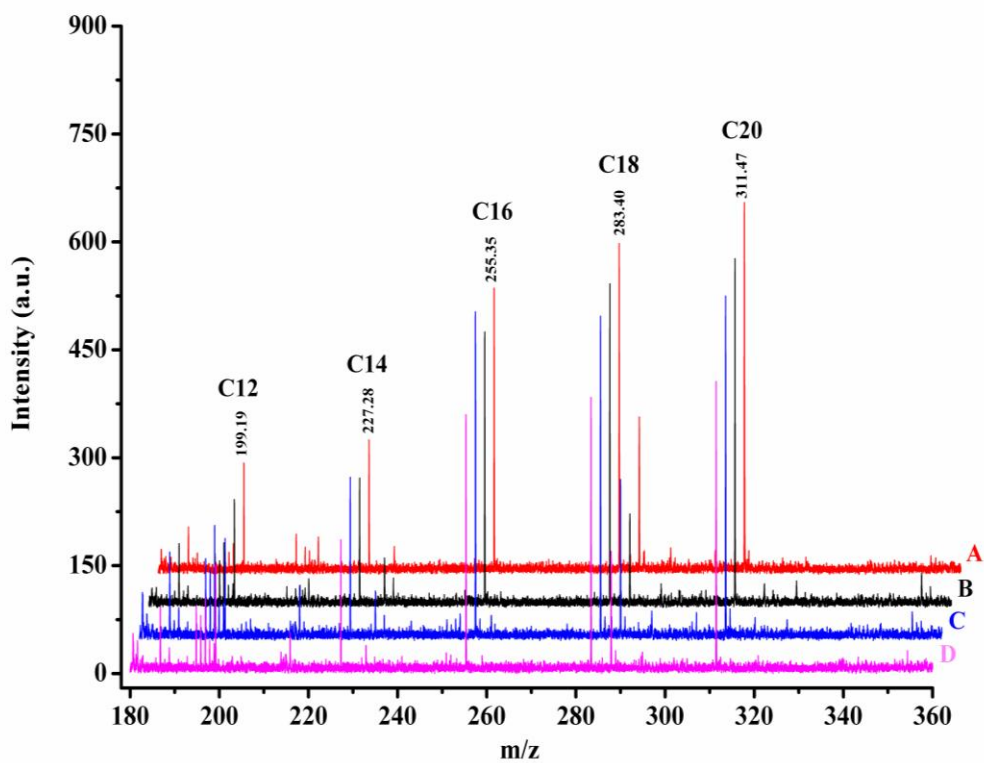
Figure S3. Mass spectra of fatty acids by using $CuFe_2O_4$ MNC matrix in negative ion mode with no additional salt (A); 10 mM NaCl (B); 100 mM NaCl (C); 1000 mM NaCl (D). The concentration of each fatty acid was 0.1 mM. All the analysis was performed under the same experimental condition (laser intensity of 60%)
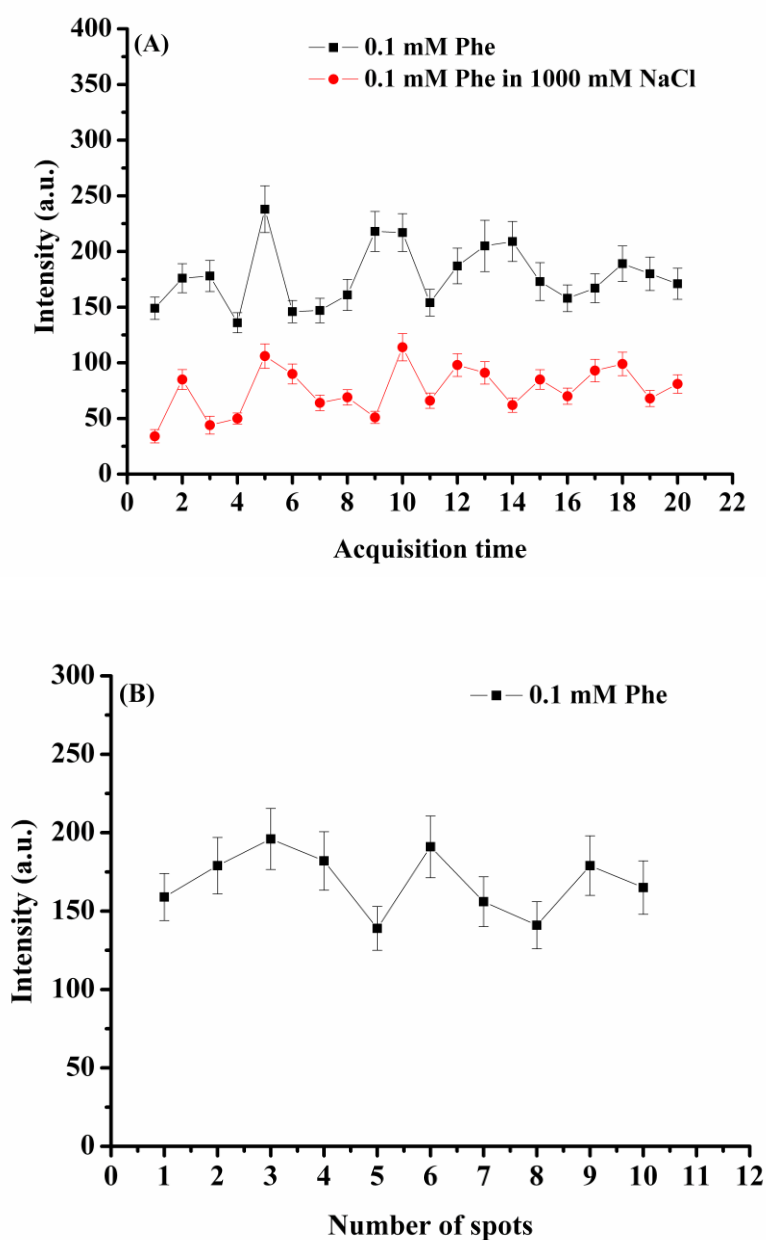
Figure S4. MS signal intensity of Phe repeatedly acquired from one sample spot (A) and 10 different sample spots (B) by using $CuFe_2O_4$ MNC matrix in negative ion mode. Continuous 20 spectra were obtained by applying laser shots on random positions uniformly located on the spot. The concentration of Phe was 0.1 mM. All the analysis was performed under the same experimental condition (laser intensity of 55%)
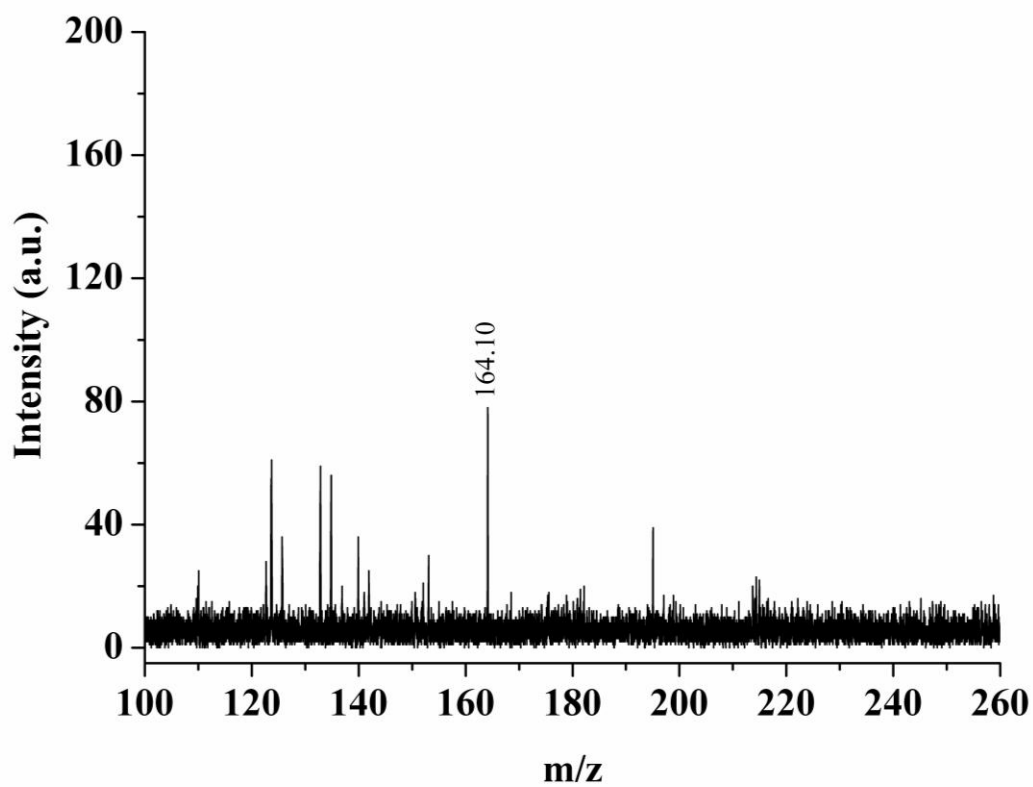
Figure S5. Mass spectrum of Phe by using $CuFe_2O_4$ MNC matrix in negative ion mode. The concentration of Phe was 0.1 mM and laser intensity of 70%
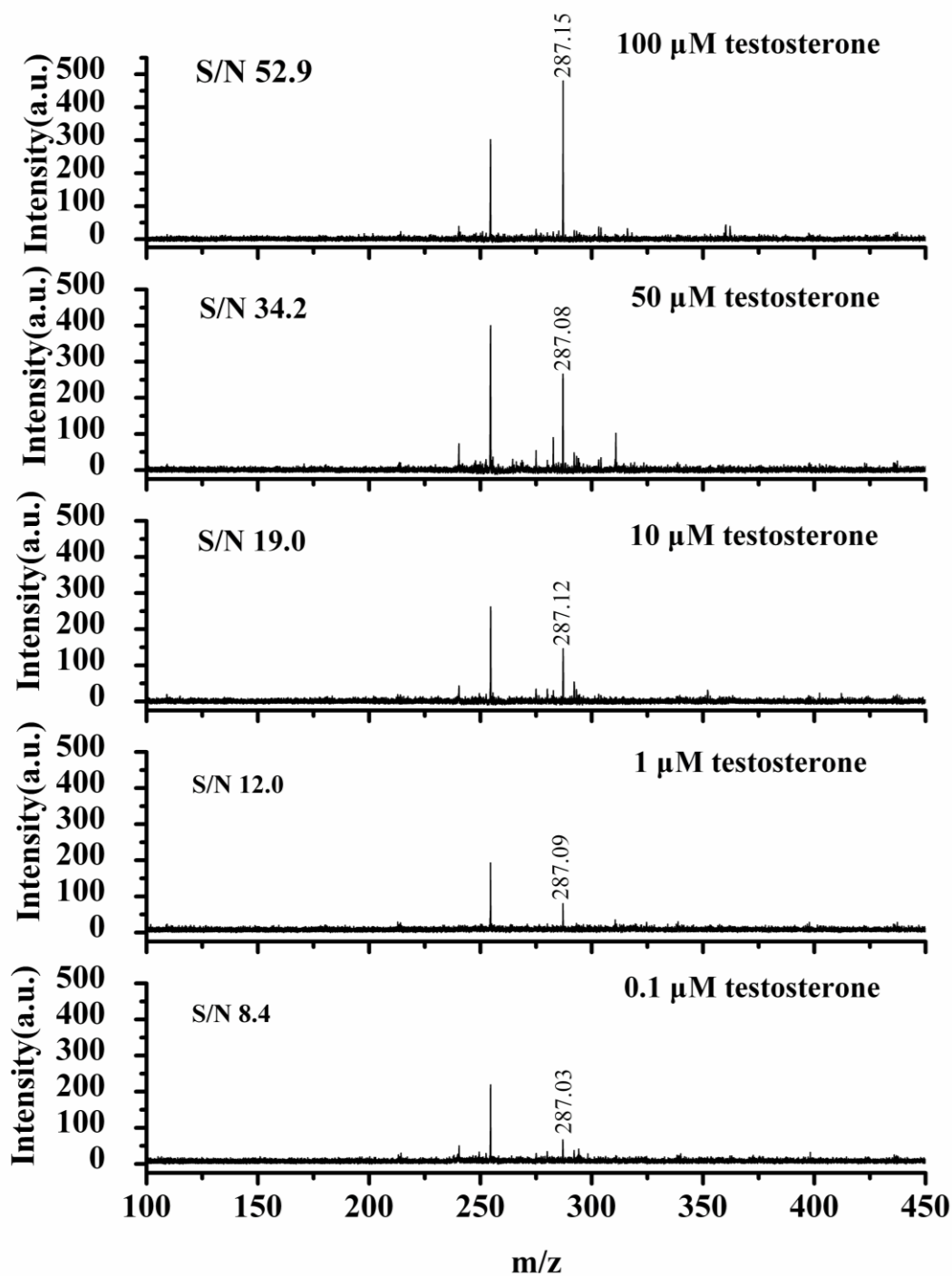
Figure S6. Mass spectra of Te at different concentrations (0.1μM, 1μM, 10 μM, 50 μM and 100 μM) by using $CuFe_2O_4$ MNC matrix in negative ion mode. The same laser intensity of 70% was applied for all.
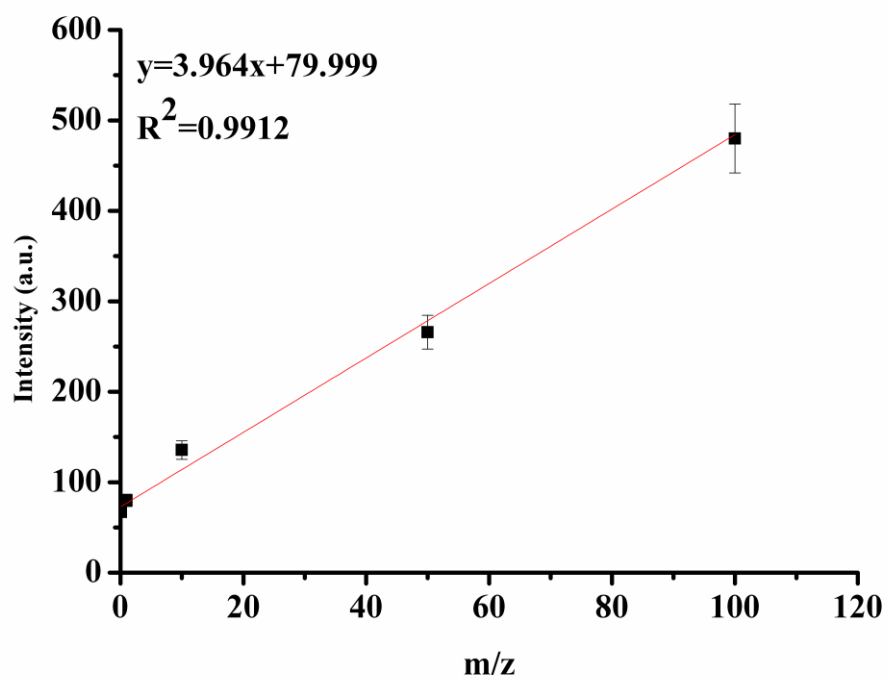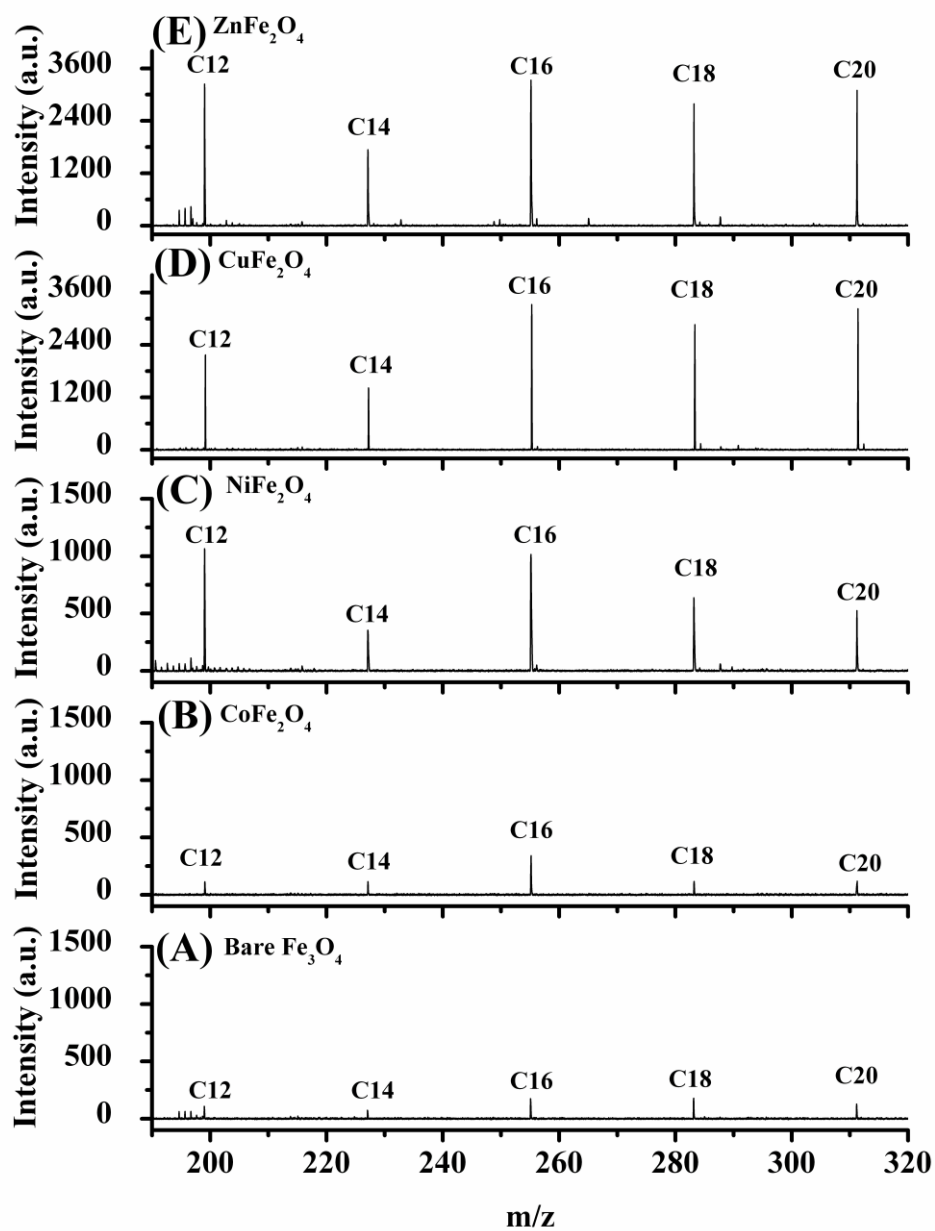
Figure S7. The calibration curve of Te.

Figure S8. MALDI-TOF MS spectra of fatty acids by using different matrixes in negative ion mode. (A) Bare Fe_3O_4 MNCs; (B) $CoFe_2O_4$ MNCs; (C) $NiFe_2O_4$ MNCs; (D) $CuFe_2O_4$ MNCs; (E) $ZnFe_2O_4$ MNCs;. The concentration of all matrixes was 1 mg/mL. The same laser intensity of 60% was applied for all.

Supporting Information – Tables

Table S1 MS signal intensities of amino acids obtained in 3-AQ matrix and CuFe$_2$O$_4$ MNC matrix under negative ion mode (Figure 3B and 3D)

Compounds	Signal intensity obtained in 3-AQ matrix	Signal intensity obtained in CuFe$_2$O$_4$ MNC matrix
Gly	N[*]	620
ASP	818.33	5911.2
Gln	115.71	1738.8
His	728.6	2380.8
Phe	248.8	607.2
Tyr	84	326.4
Trp	293.33	441.6

*N represents not observed

Table S2 Peak identification of peptides for positive-ion LDI using CuFe$_2$O$_4$ MNCs (Figure 4B)

Compounds	M	[M+H]$^+$	[M+Na]$^+$	[M+K]$^+$	[M+Na+K-H]$^+$
Tyr-Gly-Gly	295.12	N*	318.08	334.00	N
Tyr-Phe	328.14	N	351.03	366.99	N
Glu-Val-Phe	393.19	N	416.11	432.07	N
Phe-Gly-Phe-Gly	426.19	N	449.14	465.12	487.20
Tyr-Gly-Gly-Phe-Leu	555.27	N	578.30	594.28	N
Arg-Ser-Gly-Phe-Tyr	628.69	N	N	N	N

*N represents not observed

Table S3 MS signal intensities of peptides obtained in 3-AQ matrix and CuFe$_2$O$_4$ MNC matrix under negative ion mode (Figure 4D and 4F)

Compounds	Signal intensity obtained in 3-AQ matrix	Signal intensity obtained in CuFe$_2$O$_4$ MNC matrix
Tyr-Gly-Gly	N[*]	1063.2
Tyr-Phe	N[*]	1357.2
Glu-Val-Phe	113	691.2
Phe-Gly-Phe-Gly	N[*]	699.6
Tyr-Gly-Gly-Phe-Leu	356	652.8
Arg-Ser-Gly-Phe-Tyr	216	117.6

*N represents not observed

Table S4 Peak identification of nucleobases for positive-ion MALDI using CHCA matrix (Figure 5A)

Compounds	M	[M+H]$^+$	[M+Na]$^+$	[M+K]$^+$	[M+Na+K-H]$^+$
C	111.04	112.05	134.00	150.00	172.00(**)
T	126.04	N	N	N	N*
A	135.05	136.06	158.02	174.02	196.00
G	151.05	152.05	174.02	190.00(**)	211.99

*N represents not observed

** Fragment peaks of CHCA overlapped with that of analytes

Table S5 Peak identification of nucleobases for positive-ion LDI using CuFe$_2$O$_4$ MNCs (Figure 5C)

Compounds	M	[M+H]$^+$	[M+Na]$^+$	[M+K]$^+$	[M+Na+K-H]$^+$
C	111.04	N*	134.04	150.00	172.00
T	126.04	N	149.00	N	N
A	135.05	N	158.03	174.02	196.00
G	151.05	N	174.02	190.00	212.00

*N represents not observed