Supplementary Information

Experimental details

Chemicals and reagents. Graphene was purchased from Shanghai Boson Technology Co., Ltd. Ethanol was a analytical grade. Distilled water was purified ny a Milli-Q system (Milford, MA, USA). All the authentic standard compounds, berberine hydrochloride, curcumin, wogonin, scutellarin, luteoloside and chlorogenicacid were purchased from the Institute for the Control of Pharmaceutical and Biological Products of China (Beijing, China) and cotinine, cotinine nitrogen oxides and nicotine nitrogen oxides were purchased from Anpu Co., Ltd.

Synthesis of magnetic graphene. The magnetic graphene was prepared via a hydrothermal method reported by Jia et al.[1] Briefly, graphene (400mg) was dispersed into 50 ml concerntrated nitric acid at 60 ℃ with magnetic stirring for 7 hours. The graphene treated by HNO_3 was collected by washing with water for five times and then dired in vacuum at 50 ℃. Then the dried pretreated graphene (150mg) and $FeCl_3 \cdot 6H_2O$ (405mg) were dispersed into 40 ml ethylene glycol solution with trisodium citrate (0.15 g), sodium acetate (1.8 g) and poly(ethylene glycol)-20000 (1.0 g) by ultrasonication and magnetic stirring for 2 hours. The mixture was sealed in the autoclave to be heated at 200 ℃ for 10 hours. Finally the gained magnetic graphene was washed with water and collected by magnetic separation techniques.

Characterization. Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) operated at 200 kV. Scanning electronic microscope (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operating at 20 kV. Fourier transform infrared spectra (FT-IR) were collected on Nicolet Fourier spectrophotometer using KBr pellets (USA). The Raman spectra were recorded at room temperature on a LabRam-1B Raman spectrometer with a laser at an excitation wavelength of 632.8 nm.

Sample preparation for MALDI-TOF-MS. 1 mg of magnetic graphene was suspended in 1 ml of water/ethanol (1:1, v/v) with sonication. All the authentic standard compounds were weighed accurately and then dissolved in proper solvents and diluted with water by different ratios for proper concentrations of each analytes at 100ng/ml to 0.1mg/ml, respectively. Berberine hydrochloride and luteoloside was dissolved in water; curcumin, chlorogenicacid and wogonin were dissolved in ethanol; scutellarin was dissolved in acetic acid; cotinine, cotinine nitrogen oxides and nicotine nitrogen oxides were dissolved in methanol.

MALDI spotting. 1μl of the magnetic graphene suspension was pipette onto the MALDI target (Applied Biosystems, MDS SCIEX, Foster City, CA, USA). It was left in the air at room temperature to form a thin layer, and a 1 μl solution of analyte was then pipette onto the layer of matrix and left in the air for evaporation of the solvent and for further analysis by MALDI-TOF-MS.

Pre-enrichment step with magnetic graphene as the adsorbents and matrices prior to MALDI-TOF-MS analysis. 5 mg of magnetic graphene was suspended in 1ml of water/ethanol (1:1, v/v) with sonication. 10 μl of the suspension was pipetted immediately into 400μl of analyte

solution. The mixture was then vibrated for 30 min. After magnetic separation, about 1μl of the magnetic graphene suspension was pipetted onto MALDI sample target. The sample target was again left at room temperature for evaporation of the solvent. And then the substrates were subjected to MALDI-MS for further analysis.

MALDI-TOF-MS analysis. Mass spectra were acquired in reflection mode on a 5800 Proteomics Analyzer (Applied Biosystems, Framingham, MA, USA) with the Nd: YAG laser at 366nm, a repetition rate of 200Hz and an acceleration voltage of 20 kV.

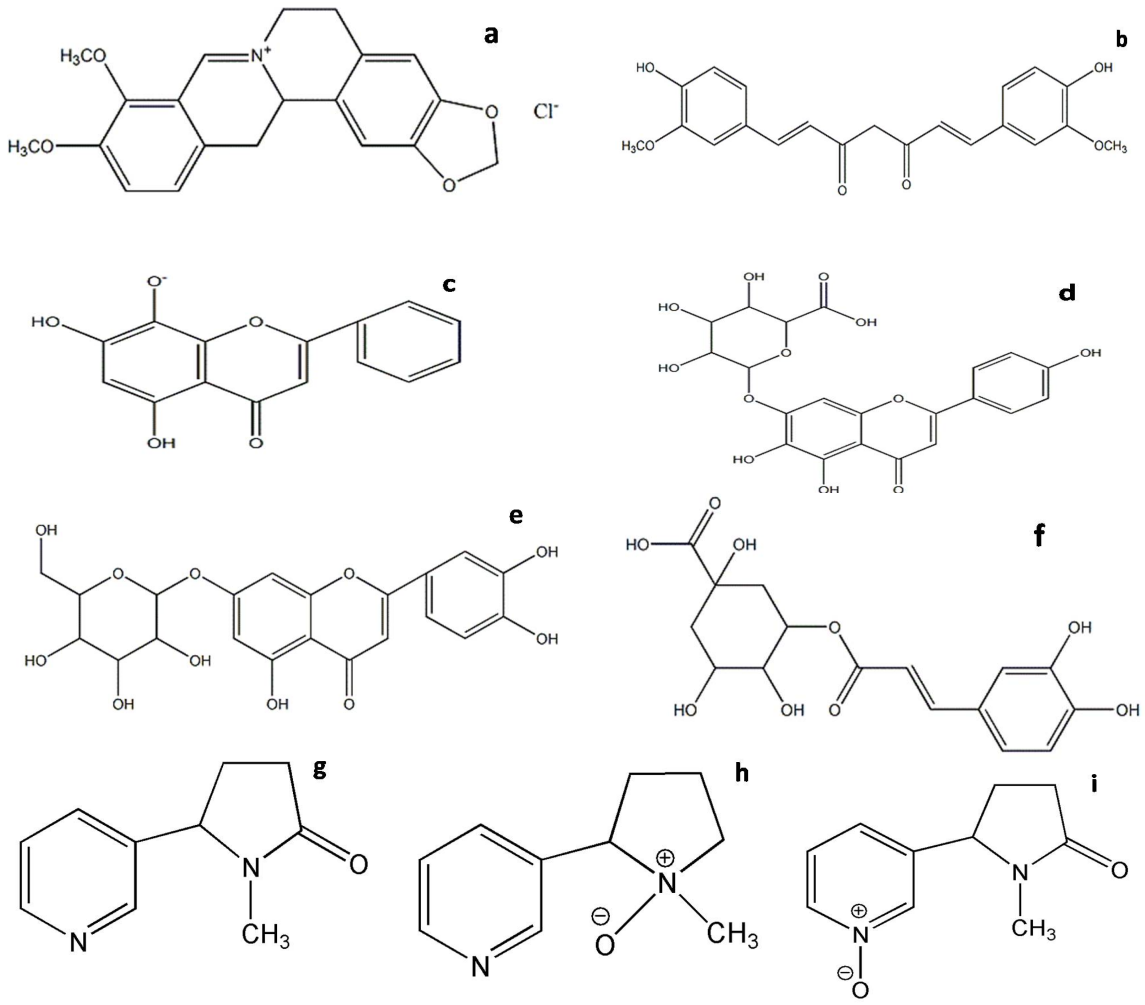

Fig. S1 The chemical structure of the analytes ((a) berberine hydrochloride; (b) curcumin; (c) wogonin; (d) scutellarin; (e) luteoloside; (f) chlorogenic acid; (g) cotinine; (h) nicotine nitrogen oxides; (i) cotinine nitrogen oxides)

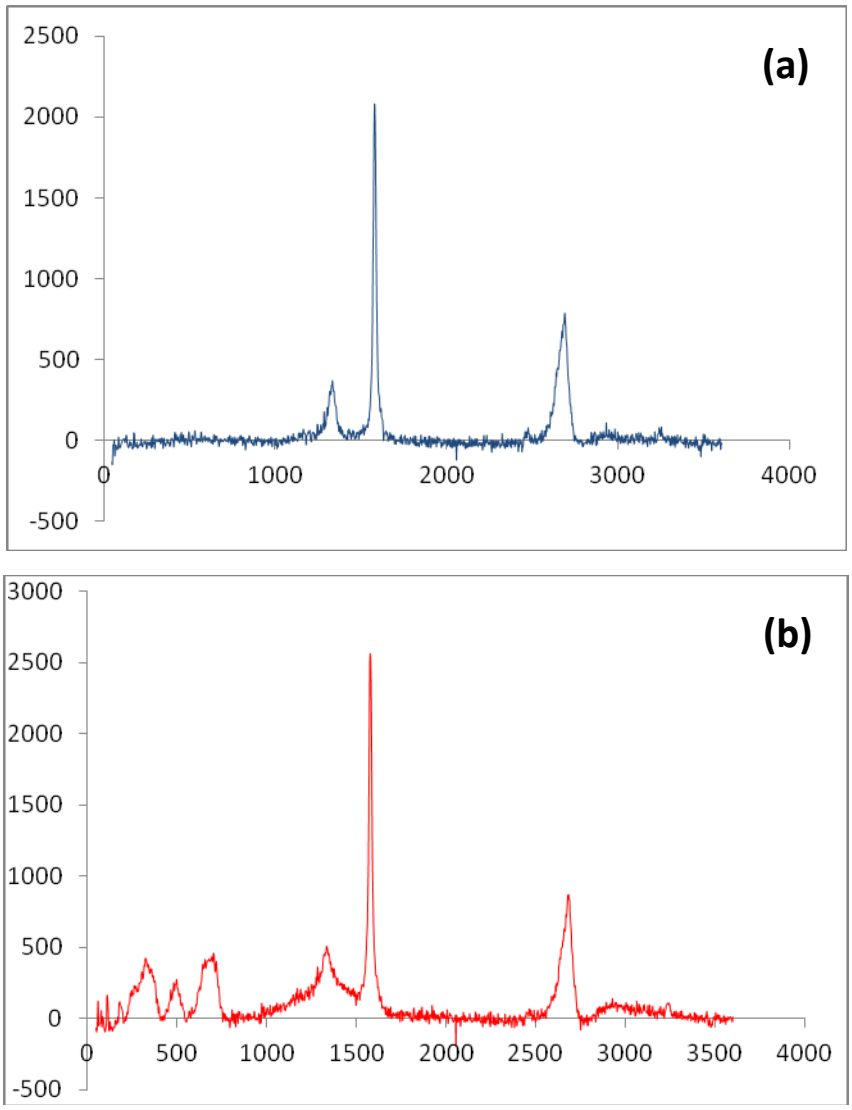

Fig. S2 The Raman spectra of graphene treated by HNO_3 (a) and magnetic graphene (b)

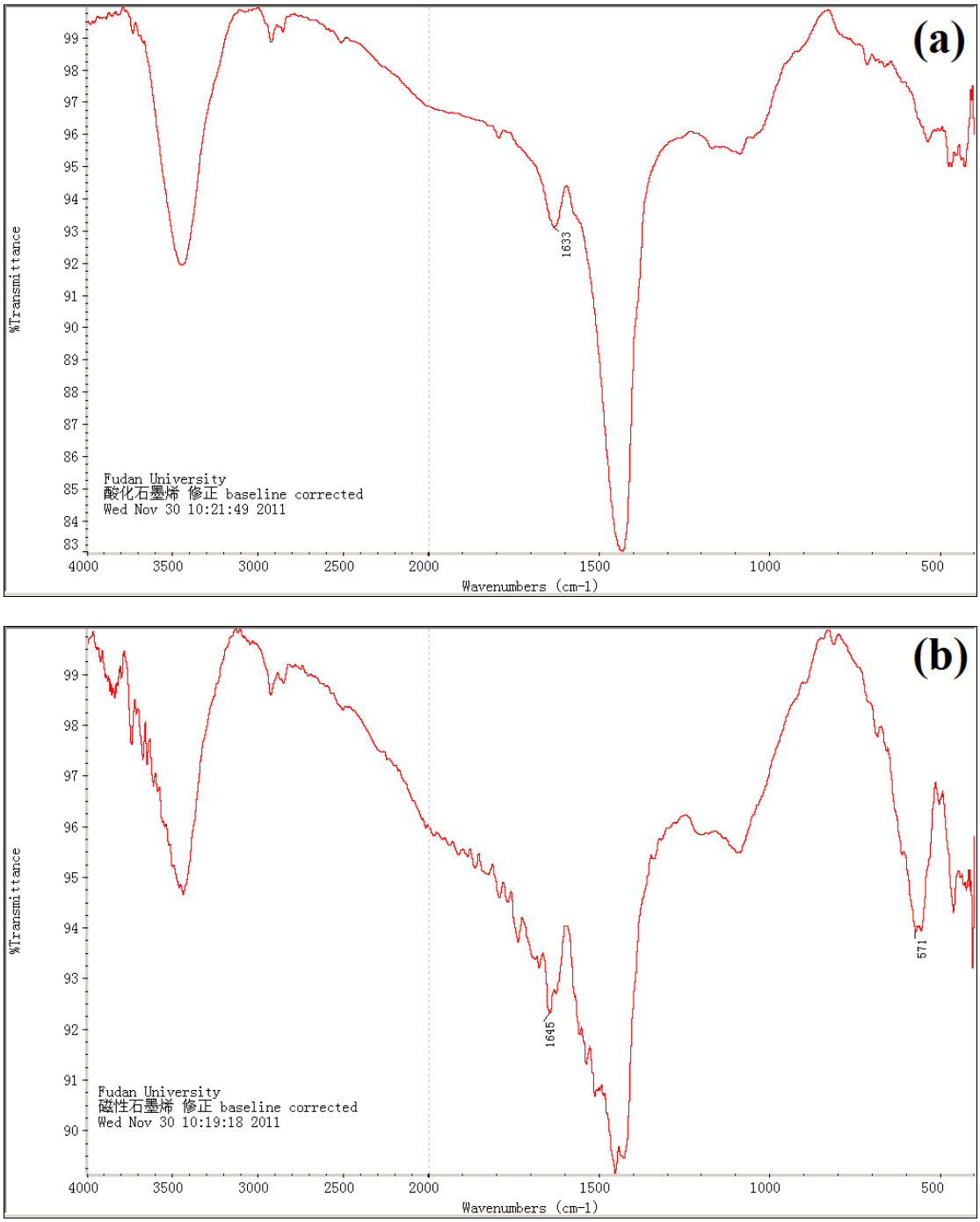

Fig. S3 The FTIR spectra of graphene treated by HNO_3 (a) and magnetic graphene (b)

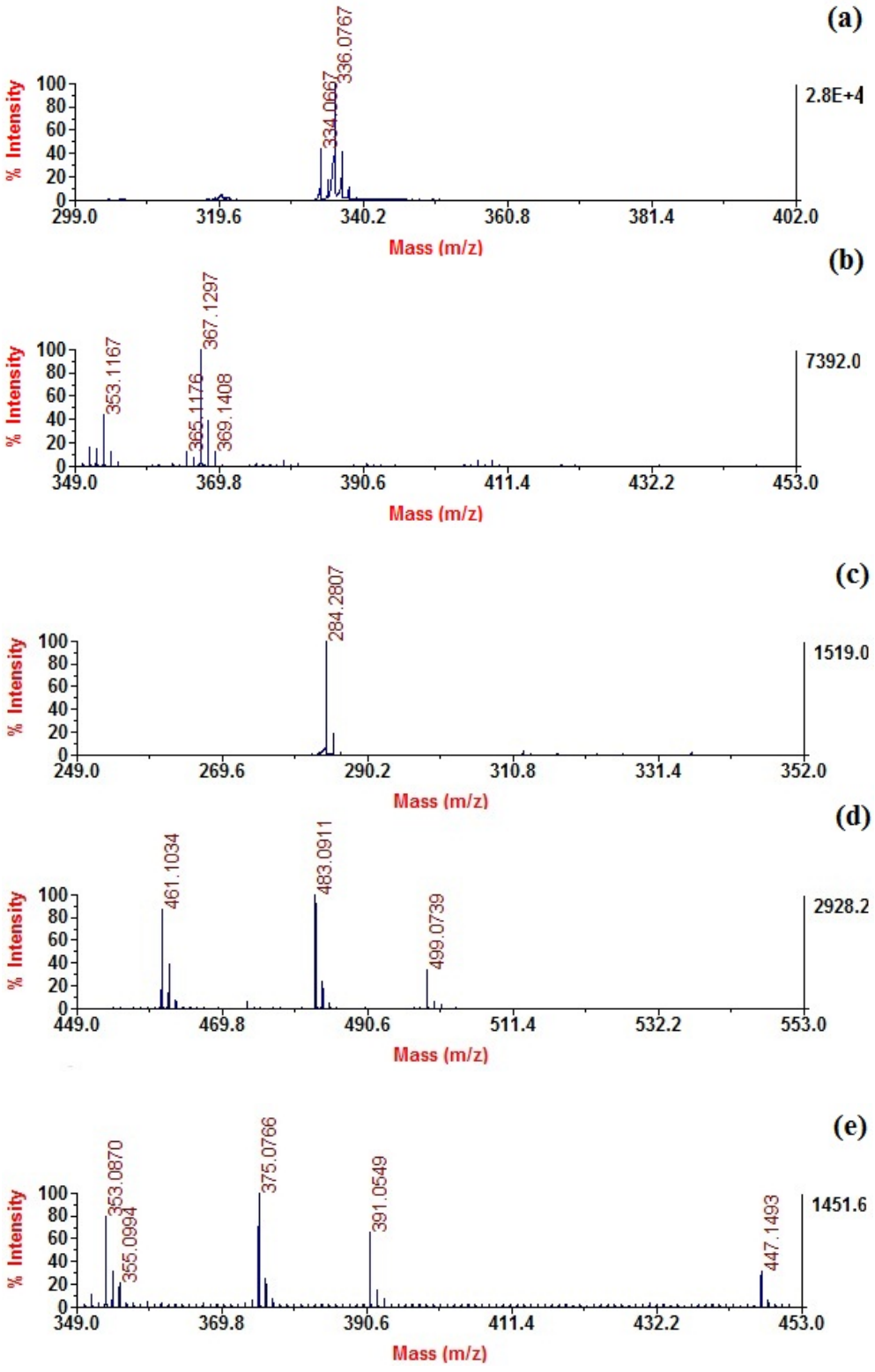

Fig.S4 The mass spectra of small molecules analyzed by MALDI-TOF-MS with magnetic graphene composites as a matrix ((a) berberine hydrochloride (m/z = 336 [M]); (b) curcumin (m/z = 367 [M - H]-); (c) wogonin (m/z = 284 [M]); (d) scutellarin (m/z = 461 [M - H]-); (e) chlorogenicacid (m/z = 353 [M - H]-)).

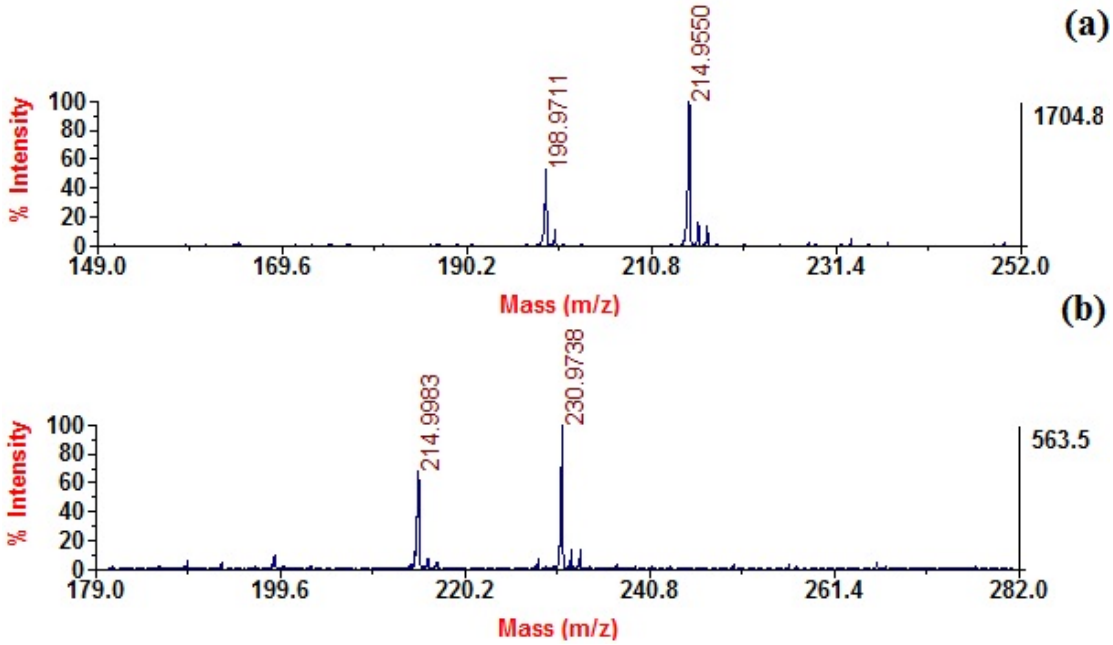

Fig.S5 The mass spectra of small molecules analyzed by MALDI-TOF-MS with magnetic graphene composites as a matrix ((a) cotinine (m/z = 215 [M + K] +); (b) cotinine nitrogen oxides (m/z = 231 [M + K] +)).

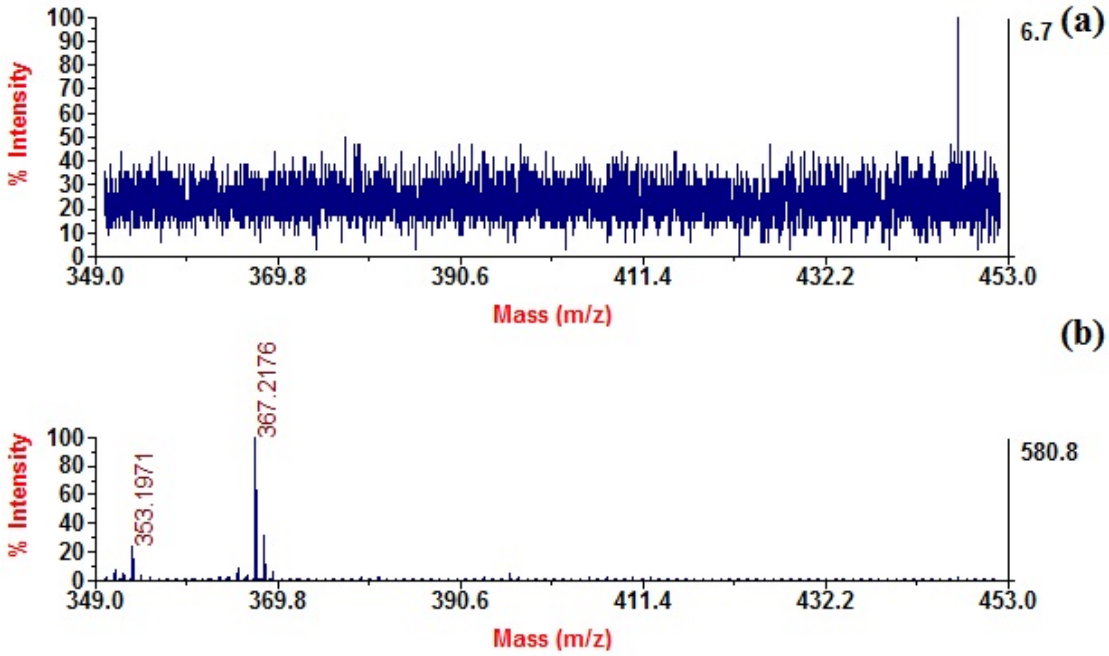

Fig. S6 The mass spectra of curcumin (m/z = 367 [M - H]-) analyzed by MALDI-TOF-MS with magnetic graphene composites as adsorbents ((a) before enrichment; (b) after enrichment).

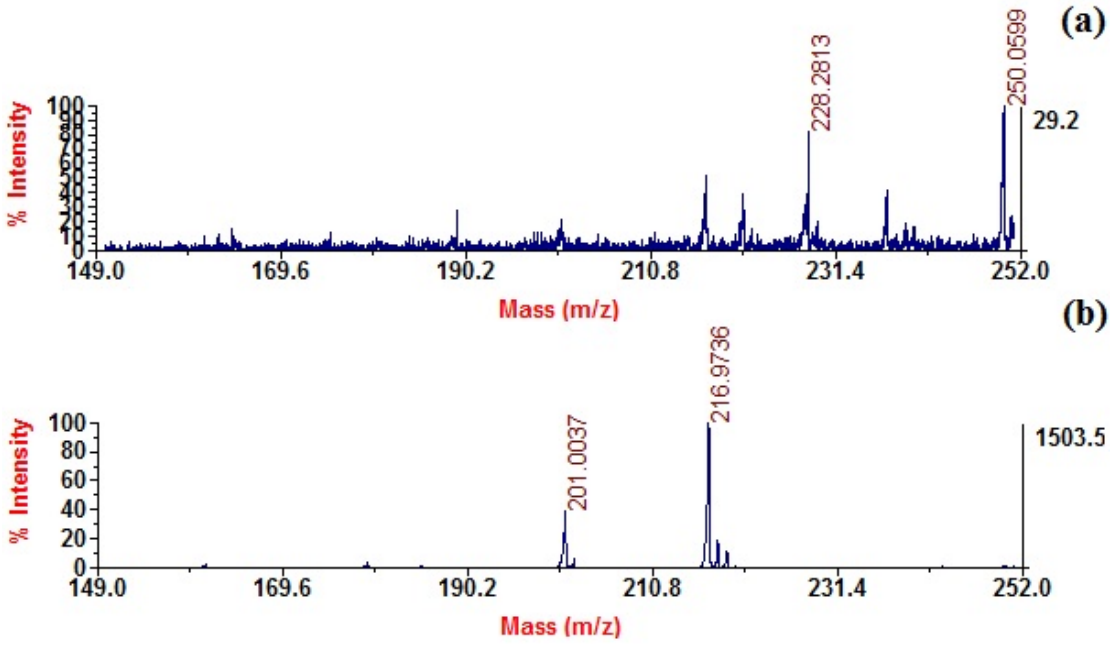

Fig. S7 The mass spectra of nicotine nitrogen oxides (m/z = 217 [M + K] +) analyzed by MALDI-TOF-MS with magnetic graphene composites as adsorbents ((a) before enrichment; (b) after enrichment).

Reference

1. B. P. Jia, L. Gao and J. Sun, Carbon, 2007, 45, 1476.