Supporting Information

Simple and sensitive determination of sulfite in Chinese herbal teas by ultrahigh-performance liquid chromatography tandem mass spectrometry

Leiwenxuan Yang[a,c], Gaohua Hu[a,c], Yali Huang[a,c], Chen Wang[a,c], Xin Liu[a,b], Chengyin Lu[a,b], Hongping Chen[a,b], Jianyang Zhang[a]* and Guicen Ma[a,b]*

[a]*Tea Research Institute, Chinese Academy of Agricultural Sciences, Hangzhou, 310008, China*

[b]*Laboratory of Quality and Safety and Risk Assessment for Tea Products (Hangzhou), Ministry of Agriculture and Rural Affairs, Hangzhou, 310008, China*

[c]*Graduate School of Chinese Academy of Agricultural Sciences, Beijing, China*

E-mail: mgc1314@tricaas.com; xianyu20082003@tricaas.com.

Phone:+86-571-8665-1650, Fax:+86-571-8665-2004

Address: Tea Research Institute, Chinese Academy of Agricultural Sciences, 9 Meiling South Road, Hangzhou, Zhejing Province,310008, China.

1.1 Preparation of extraction solution

A 2% formaldehyde buffer solution was prepared by weighing 0.77 g ammonium acetate in ultrapure water, adding 10.8 mL of 37% formaldehyde solution in a 200 mL volumetric flask and diluting to 200 mL with water. The pH of the solution was adjusted at 4.5 by dropwise addition of acetic acid. The working 0.2% formaldehyde extraction solution was diluted the 2% formaldehyde solution with ultrapure water. The 0.2% and 2% formaldehyde solutions were stored at 4°C for at least one week and one month.

1.2 Standard Preparation

Stock standard solution of HMS was prepared at 1000 mg L^{-1} by accurately weighing 10 mg of sodium sulfite (Na_2SO_3) and dissolving in 2% formaldehyde solution into 10 mL volumetric flask. On the day of analysis, further dilutions with 0.2% formaldehyde solutions were obtained different concentrations of 1, 5,10 and 100 mg L^{-1} of Na_2SO_3 working standard solutions.

1.3 Statistical Analysis

Determination of sulfite concentration of herbal tea samples were compared between UPLC-MS/MS and IT method using a two-sample independent t-test ($p < 0.05$). All the analysis were done employing SPSS version 26 (SPSS, Inc., Chicago, IL, USA)

Table S1 The MS/MS parameters for the analysis of HMS

Q1 Mass (m/z)	Q2 Mass (m/z)	dwell time (ms)	DP(V)	EP(V)	CE (V)
111.0	80.8	300	-42.0	-10.0	-16.0
111.0	79.9	300	-42.0	-10.0	-35.0

Table S2 Matrix effects of different adsorbents

Adsorbents	ME (%)
Crude	-81.1
CS/prGO/DM	-63.5
GCB	-67.6
C18	-70.9
PVPP	-79.1
SAX	-81.5
PSA	-80.1

Table S3 The corrected calibration equation of sulfite in three types of herbal teas.

Matrix	Corrected calibration equation
Chrysanthemum	$y = 6.727 \times 10^6 x + 7.211 \times 10^3$
Rose	$y = 1.467 \times 10^7 x + 1.075 \times 10^4$
Wolfberry	$y = 1.137 \times 10^7 x + 3.913 \times 10^4$

Table S4 The proposed method was compared with other previous reported LC-MS/MS methods for determination of sulfites in food

Method	Matrix	Extraction procedure	Clean-up procedure	Organic solvent(mL)	Recovery (%)	Reference
LC-MS/MS	Chrysanthemum Rose Wolfberry	Once extraction	dSPE(CS/prGO/DM composites)	0	84-103	This work
LC-MS/MS	white grape juice molasses dried potatoes crystallized ginger dried apricots frozen raw shrimp	Multiple extraction	SPE (C18 SPE cartridge)	6	86-114	US FDA Method C-004.03

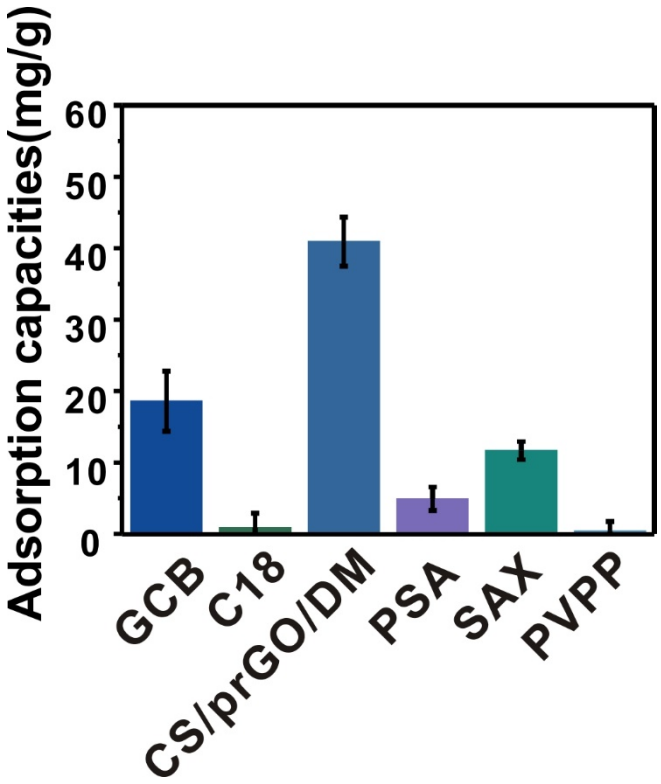

Fig. S1 Adsorption capacities of different adsorbents from chrysanthemum extracts.

Fig. S2 The photographs of chrysanthemum sample extract after purification by different dSPE adsorbents.

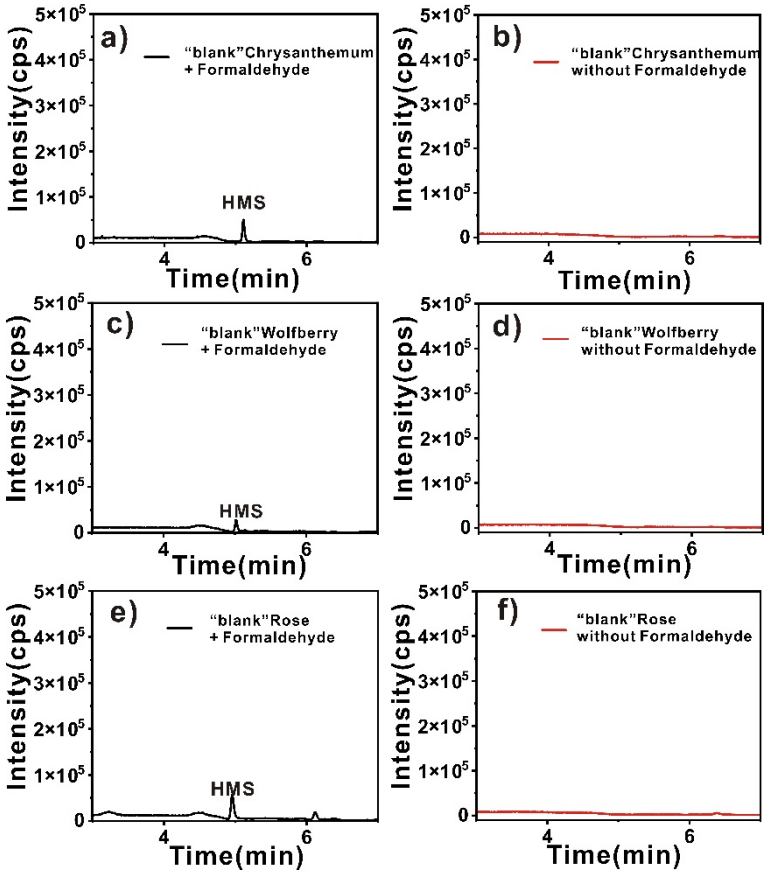

Fig. S3 UPLC-MS/MS chromatograms of sulfites from "blank" Chinese herbal tea samples with and without formaldehyde. a) and b) "blank" chrysanthemum sample with and without formaldehyde; c) and d) "blank" wolfberry sample with and without formaldehyde; e) and f) "blank" rose sample with and without formaldehyde.

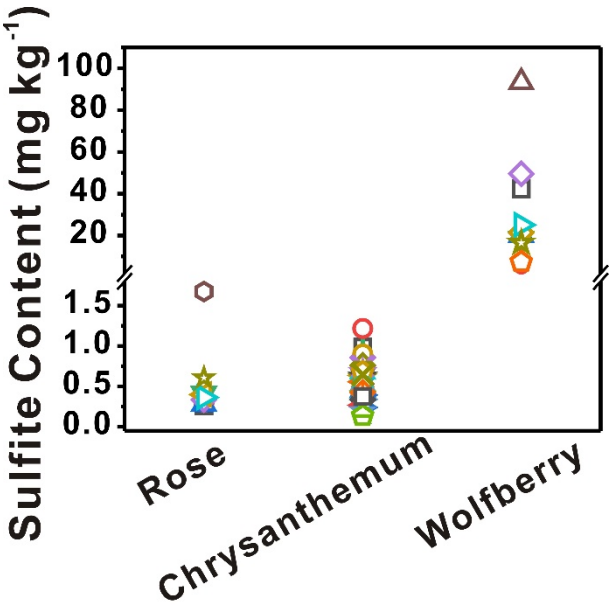

Fig. S4 The distribution of sulfite concentration in real Chinese herbal tea samples.