

Supporting Information

for

“Magnetic extractant with Fe₃O₄@SiO₂ core and aqueous ammonia coating for microextraction of petroleum acids”

Gang-Tian Zhu,^{*, a} Fei Liu,^a Sheng He,^a Xiao-Mei He,^b Shu-Kui Zhu,^c and Yu-Qi

Feng^b

^a Key Laboratory of Tectonics and Petroleum Resources (Ministry of Education),
China University of Geosciences, Wuhan 430074, P.R. China. E-mail:
zhugangtian@163.com

^b Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of
Education), Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China.

^c State Key Laboratory of Biogeology and Environmental Geology, China University
of Geosciences, Wuhan 430074, China

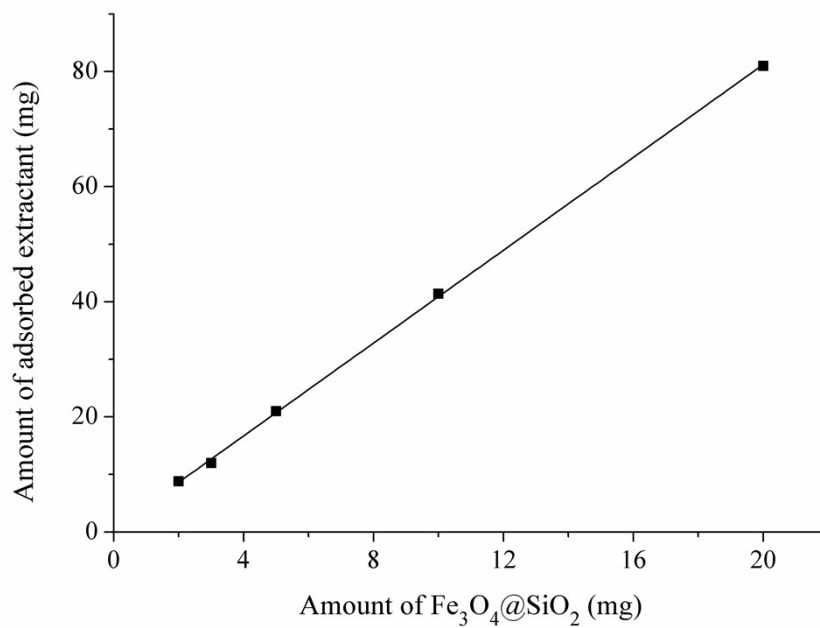


Figure S1. The relation between the weights of the adsorbed extractant and the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ support. The line is constructed by using average values in triplicate measurements. The extractant is 10 wt% $\text{NH}_3\cdot\text{H}_2\text{O}$ in H_2O .

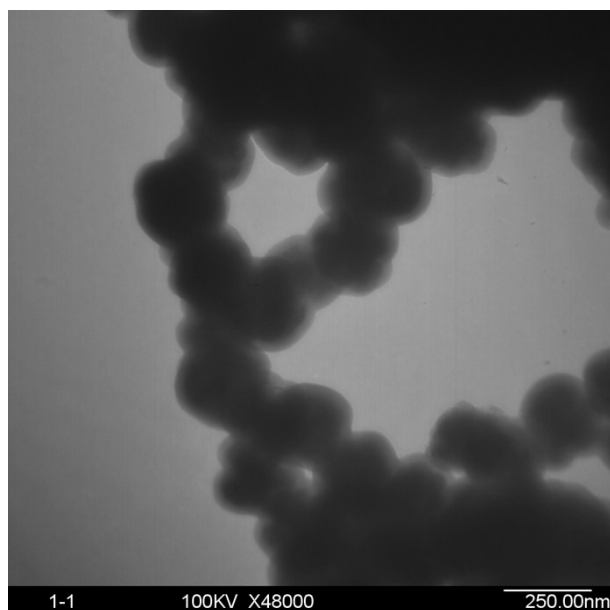


Figure S2. The TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

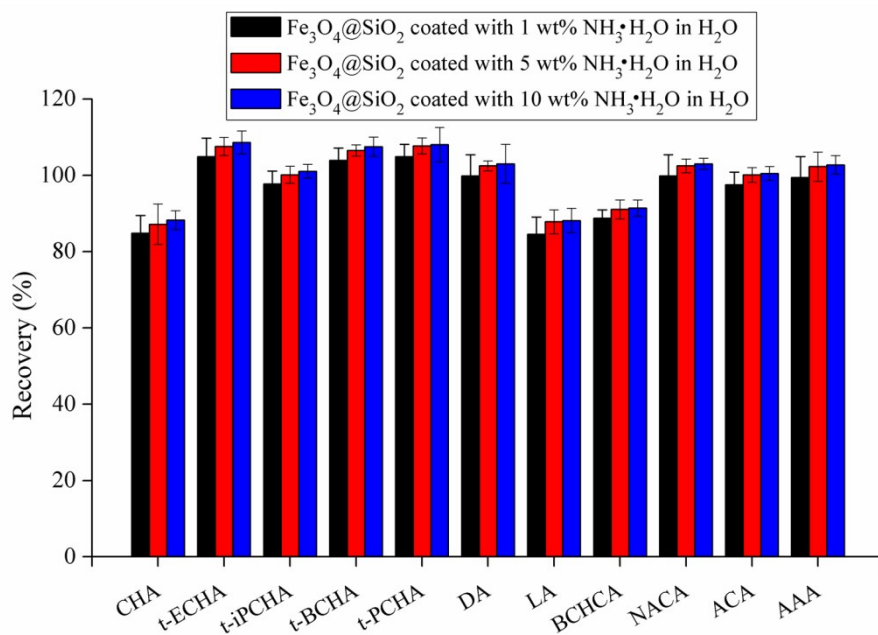


Figure S3. Effect of the type of extractant to coat $\text{Fe}_3\text{O}_4@SiO_2$ on extraction efficiency.

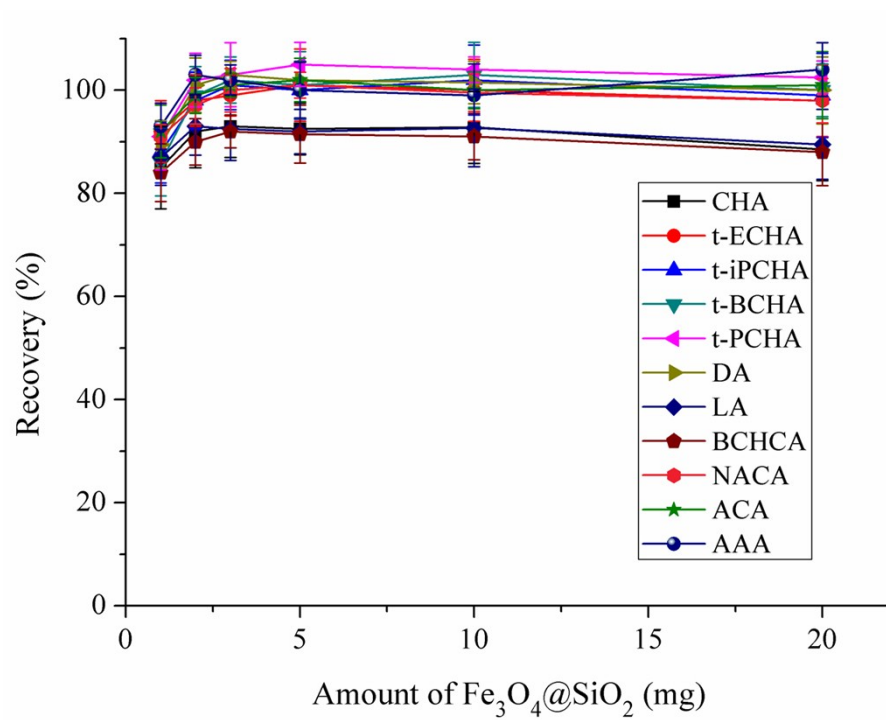


Figure S4. Effect of the amount of Fe₃O₄@SiO₂ on extraction efficiency.

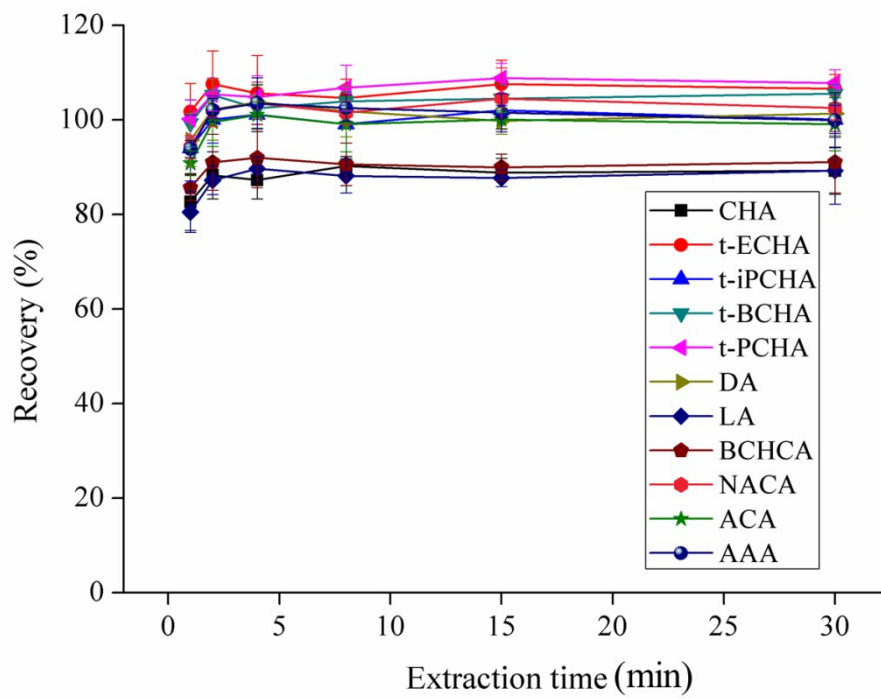


Figure S5. Effect of the extraction time on extraction efficiency.

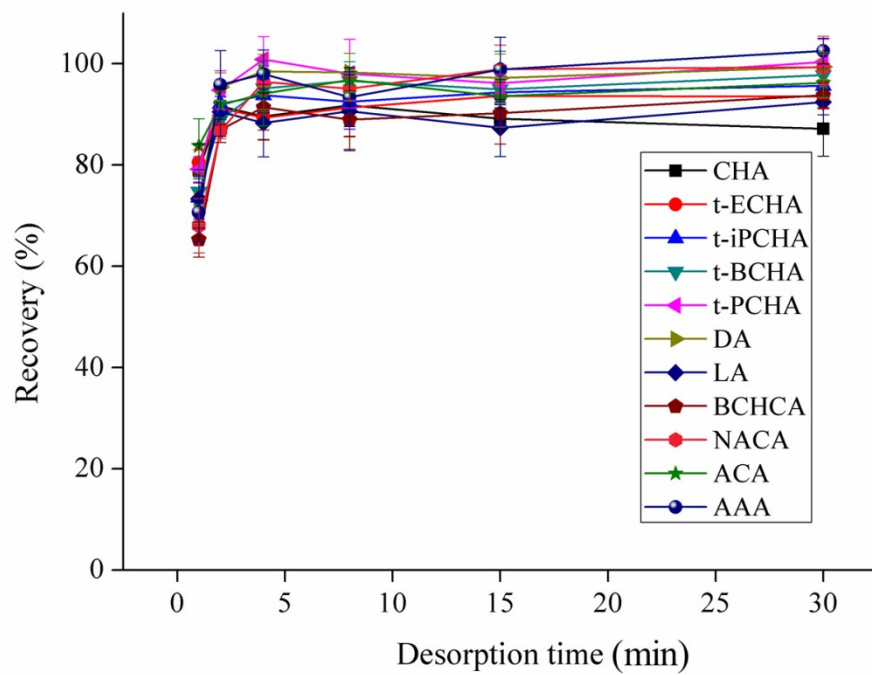


Figure S6. Effect of the desorption time on extraction efficiency.

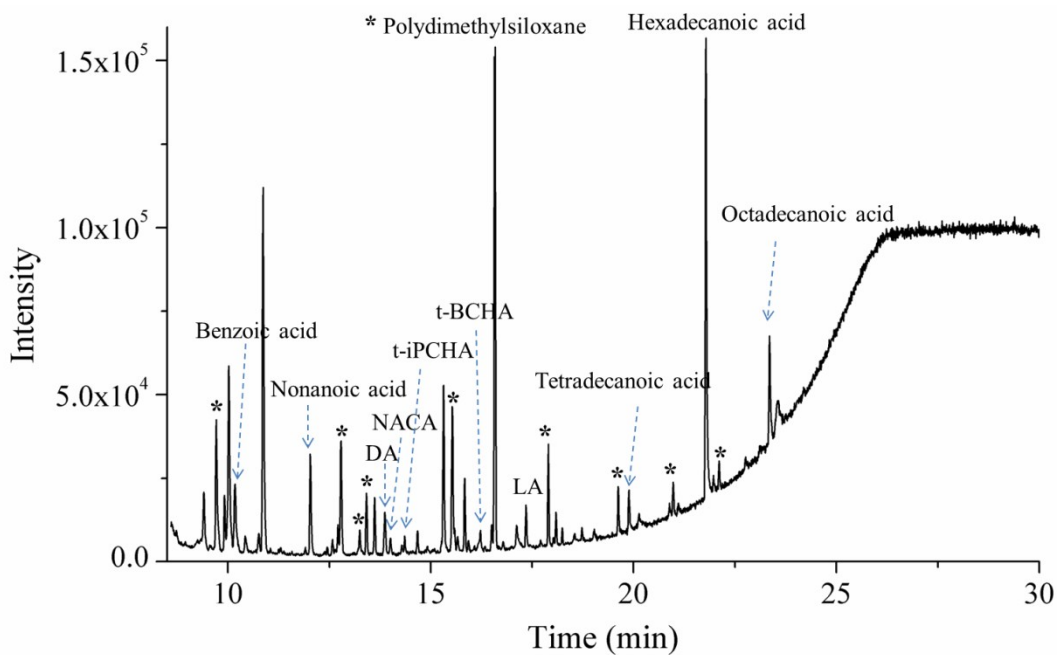


Figure S7. The total ion chromatogram of a crude oil after extraction with MAA followed by GC-MS analysis in full-scan mode. The mark “*” represents the signal of polydimethylsiloxane, which might come from the column bleeding or the injection port septum. The acid signals were identified based on the comparison with standards and library searching.

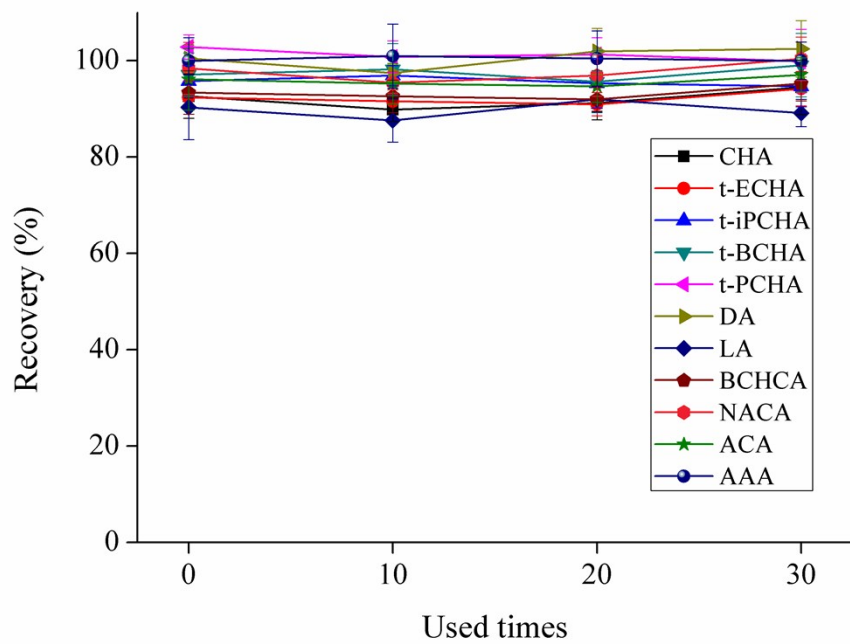


Figure S8. The extraction efficiency for the same $\text{Fe}_3\text{O}_4@\text{SiO}_2$ after used for 0, 10, 20 and 30 times.

Table S1. Calibration curves, LODs and LOQs of petroleum acids.

Analytes	Linear dynamic range (ng/g)	Regression line			LODs (ng/g)	LOQs (ng/g)
		Slope	Intercept	<i>R</i> value		
CHA	10-5000	0.0207	-0.0546	0.9994	1.9	6.2
t-ECHA	5-5000	0.0221	-0.0740	0.9994	1.0	3.4
t-iPCHA	5-5000	0.0224	-0.0401	0.9988	1.0	3.2
t-BCHA	5-5000	0.0176	-0.0518	0.9988	1.3	4.2
t-PCHA	5-5000	0.0204	-0.0460	0.9984	1.1	3.6
DA	5-5000	0.0388	-0.0580	0.9973	0.8	2.6
LA	5-5000	0.0144	0.0691	0.9954	1.2	4.1
BCHCA	5-5000	0.0412	-0.0917	0.9991	0.9	2.9
NACA	5-5000	0.0286	-0.0459	0.9995	1.0	3.3
ACA	5-5000	0.0279	-0.0332	0.9986	0.7	2.5
AAA	5-5000	0.0240	-0.0259	0.9971	0.8	2.8

Table S2. Precisions and recoveries of petroleum acids spiked into crude oil samples at three different concentrations.

Analytes	Intra-day precision (RSD, %; n=5)			Inter-day precision (RSD, %; n=3)			Recovery (%)		
	Low	Medium	High	Low	Medium	High	Low	Medium	High
	10 ng/g	100 ng/g	1000 ng/g	10 ng/g	100 ng/g	1000 ng/g	10 ng/g	100 ng/g	1000 ng/g
CHA	10.2	4.7	6.5	12.3	9.6	10.4	86.0±5.8	87.6±4.6	83.6±3.5
t-ECHA	7.5	2.2	2.7	6.9	6.7	4.7	99.4±5.3	103.4±3.1	102.6±2.6
t-iPCHA	6.8	3.2	5.1	4.8	5.8	3.9	102.9±4.5	106.3±2.4	107.8±5.7
t-BCHA	6.9	6.0	4.2	6.9	7.8	5.4	103.3±6.1	112.1±4.3	102.5±5.8
t-PCHA	4.8	2.5	4.4	7.2	8.2	2.1	101.3±3.2	107.3±3.6	105.0±5.2
DA	5.3	2.6	3.8	8.4	11.1	3.2	94.4±4.5	105.4±1.9	98.0±3.4
LA	3.7	1.3	2.7	6.5	10.5	6.1	91.4±2.7	107.9±6.5	89.7±1.4
BCHCA	11.3	6.1	8.9	13.4	12.8	9.4	88.8±6.2	92.1±4.8	84.7±3.1
NACA	5.8	2.5	5.3	5.8	9.5	4.7	79.1±2.5	103.4±2.9	86.4±3.5
ACA	6.2	4.0	5.1	7.3	5.8	2.0	96.0±4.3	99.3±3.3	101.6±4.2
AAA	4.9	2.5	4.2	6.2	5.8	3.1	97.4±3.2	100.2±3.1	100.9±4.5

Uncertainty estimation:

The estimation of uncertainties for the determined contents of PAs in crude oil samples were adopted from a previous review.¹ The calculation was done according to the Guide to the Expression of Uncertainty in Measurement (GUM) using the formula:

$$U = kc \sqrt{((u_r(\text{sample}))^2 + ((u_r(\text{cal}))^2 + ((u_r(\text{true}))^2 + ((u_r(\text{rep}))^2 + ((u_r(\text{LOD}))^2$$

where U is expanded uncertainty, k is coverage factor (usually two), c is average concentration of the analyte, $u_r(\text{sample})$ is relative standard uncertainty of crude oil sample mass determination, $u_r(\text{cal})$ is relative standard uncertainty of calibration step, $u_r(\text{true})$ is relative standard uncertainty of recovery determination, $u_r(\text{rep})$ is relative standard uncertainty of repeatability, $u_r(\text{LOD})$ is relative standard uncertainty of LOD determination.

The detailed values of the above uncertainties for the determination of PAs in crude oil 1 were shown in Table S3. The uncertainties for the analytical results in the other three crude oil samples were calculated by the same method and the final expanded uncertainty results were shown in Table 2 in the text.

References:

(1) Konieczka, P.; Namiesnik, J. *J. Chromatogr. A* **2010**, *1217*, 882-891.

Table S3. Calculated values of relative standard uncertainties, combined standard uncertainties and expanded uncertainties for the determination of PAs in crude oil 1.

Parameter	Value							
Analyte	t-ECHA	t-iPCHA	t-BCHA	t-PCHA	DA	LA	ACA	AAA
Concentration (ng/g)	24.6	34.2	48.4	55.7	182.5	290.2	41.3	38.1
LOD (ng/g)	1.0	1.0	1.3	1.1	0.8	1.2	0.7	0.8
Repeatability–RSD (%)	3.5	4.6	2.5	5.6	8.6	4.9	3.8	5.9
Trueness – recovery (%)	99.4±5.3	102.9±4.5	103.3±6.1	101.3±3.2	105.4±1.9	107.9±6.5	96.0±4.3	97.4±3.2
Uncertainty								
Mass of sample – $u_r(sample)$	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
Calibration – $u_r(cal)$	0.0095	0.0103	0.0089	0.0085	0.0120	0.0098	0.0056	0.0063
Recovery – $u_r(true)$	0.027	0.022	0.030	0.016	0.009	0.030	0.022	0.016
Repeatability – $u_r(rep)$	0.020	0.027	0.014	0.032	0.050	0.028	0.022	0.034
LOD – $u_r(LOD)$	0.041	0.029	0.027	0.020	0.004	0.004	0.017	0.021
Combined uncertainty	5.4%	4.6%	4.4%	4.2%	5.2%	4.2%	3.6%	4.4%
Expanded uncertainty (k = 2)	10.8%	9.2%	8.8%	8.4%	10.4%	8.4%	7.2%	8.8%
Result								
Concentration±U (ng/g)	24.6±2.7	34.2±3.1	48.4±4.3	55.7±4.7	182.5±19.0	290.2±24.4	41.3±3.0	38.1±3.4