

Supporting Information

Determination of major and trace elements in plant samples by
inductively coupled plasma optical emission spectrometry with deep
eutectic solvent extraction based on choline chloride-carboxylic acids
Wenzhi Zhao^{a, b}, Yanfeng Sun^a, Xiaoyong Wei^a, Guangyuan Niu^a, Chuanfang Zhou^{a*}

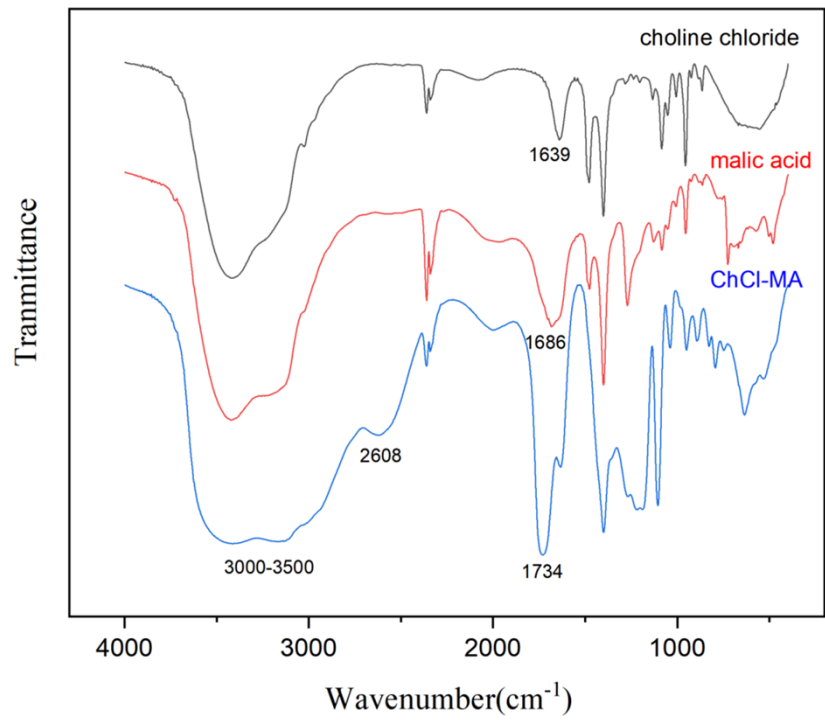


Fig. S1. FT-IR spectra of the synthesized DESs and the initial reagents

Table 1s. Effect of the hydrogen bond donor type (sample mass 0.1 g, DES mass 0.5 g, Ultrasound for 40 min, 1ChCl:1.5HBD).

Sample	Element	Certified (mg/kg)	ChCl-OX		ChCl-CI		ChCl-MA		ChCl-MAL	
			Measured (mg/kg)	R (%)	Measured (mg/kg)	R (%)	Measured (mg/kg)	R (%)	Measured (mg/kg)	R (%)
GSB2a	Ca	300±20	280±10aA	93	292±11bB	97	304±5.0cB	101	323±11dC	108
	Fe	25±2	22.6±1.4aA	90	27.8±0.6cC	111	25.7±0.8bB	103	28.4±1.4cC	114
	K*	0.22±0.01	0.23±0.01bB	105	0.24±0.01cC	109	0.21±0.01aA	95	0.24±0.01bcBC	109
	Mg*	0.62±0.04	0.63±0.02aA	102	0.66±0.03bAB	106	0.63±0.02aA	102	0.67±0.02bB	108
	Mn	10.0±0.4	10.8±0.3dD	108	9.1±0.3bB	91	9.7±0.3cC	97	8.5±0.3aA	85
	Na	37±5	34.5±0.9abAB	93	33.7±0.7aA	91	35.5±0.7bB	96	39.1±1.6cC	106
	P*	0.18±0.01	0.177±0.003bB	98	0.181±0.004cB	101	0.181±0.002cB	101	0.169±0.002aA	94
	S*	0.15±0.01	0.141±0.009aA	94	0.164±0.004bB	109	0.159±0.004bB	106	0.163±0.006bB	109
	Zn	12.3±1.5	13.0±0.6bbB	106	11.4±0.9aA	93	12.1±0.4aAB	98	11.3±0.7aA	92
GSB4	Ca*	0.153±0.008	0.145±0.005bBC	95	0.142±0.003bB	93	0.152±0.007cC	99	0.128±0.003aA	84
	Fe	139±4	141±7cC	101	131±9bB	94	143±4cC	103	102±6aA	73
	K*	1.86±0.09	1.83±0.05aA	98	1.81±0.05aA	97	1.92±0.05bB	103	1.79±0.06aA	96
	Mg*	0.23±0.014	0.232±0.006bB	101	0.225±0.007bB	98	0.233±0.005bB	101	0.197±0.011aA	86
	Mn	28.0±1	27.9±0.5cC	100	26.2±1.1bB	94	27.8±0.7cC	99	21.5±1.5aA	77
	Na	(15)	12.3±0.6bB	82	13.1±1cB	87	15.7±0.2dC	105	10.9±0.5aA	73
	P*	0.66±0.03	0.659±0.014bcB	100	0.645±0.023bB	98	0.67±0.01cB	102	0.6±0.017aA	91
	S*	0.364±0.027	0.322±0.01aA	88	0.344±0.014bB	95	0.367±0.003cC	101	0.358±0.009cBC	98
Zn	38.0±2	36.9±1.7aAB	97	36.7±1.1aAB	97	36±1.4aA	95	39.1±2.0bB	103	

Values are for mean±standard deviation of seven replicate measurements (n=7); Values in parenthesis are reference value; * Concentration unit is %; Different lowercase letters indicate the significance of different hydrogen bond donor types for the same element at p <0.05; Different capital letters indicate the significance of different hydrogen bond donor types for the same element at p <0.01

Table S2 Analysis results of target analytes in GSB2a by ICP-OES under different DES mass

Elements	Certified (mg/kg)	0.1g		0.25g		0.5g		1g	
		Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)
Ca*	0.153±0.008	0.084±0.004aA	55	0.125±0.007bB	82	0.152±0.007cC	99	0.158±0.007cC	103
Fe	139±4	98.7±3.3aA	71	108.4±6.5bB	78	143±4.2dD	103	129.3±3.1cC	93
K*	1.86±0.09	1.14±0.04aA	61	1.34±0.04bB	72	1.92±0.05cC	103	1.90±0.03cC	102
Mg*	0.23±0.014	0.163±0.01aA	71	0.175±0.01bB	76	0.233±0.005cC	101	0.237±0.01cC	103
Mn	28.0±1	21±1.6aA	75	23.2±0.8bB	83	27.8±0.7cC	99	27.4±1.4cC	98
Na	(15)	10.4±0.7aA	69	12.9±0.7bB	86	15.7±0.2dD	105	14.6±0.9cC	97
P*	0.66±0.03	0.416±0.01aA	63	0.482±0.01bB	73	0.67±0.01cC	102	0.673±0.01cC	102
S*	0.364±0.027	0.24±0.01aA	66	0.288±0.01bB	79	0.367±0.003cC	101	0.397±0.01dD	109
Zn	38.0±2	28.5±1aA	75	33.4±1.2bB	88	36.0±1.4cC	95	39.5±0.8dD	104

Values are for mean±standard deviation of seven replicate measurements (n=7); Values in parenthesis are reference value; * Concentration unit is %; Different lowercase letters indicate the significance of different DES mass for the same element at p <0.05; Different capital letters indicate the significance of different DES mass for the same element at p <0.01

Table S3 Analysis results of target analytes in GSB2a by ICP-OES under different ultrasonic time

Elements	Certified (mg/kg)	10 min		20 min		30 min		40 min	
		Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)
Ca*	0.153±0.008	0.087±0.01aA	57	0.109±0.01bB	71	0.139±0.01cC	91	0.152±0.007dD	99
Fe	139±4	97.3±6.6aA	70	115.4±4bB	83	146±3.9cC	105	143±4.2cC	103
K*	1.86±0.09	1.14±0.03aA	61	1.40±0.06bB	75	1.77±0.05cC	95	1.92±0.05dD	103
Mg*	0.23±0.014	0.136±0.01aA	59	0.173±0.01bB	75	0.237±0.003cC	103	0.233±0.005cC	101
Mn	28.0±1	15.1±0.6aA	54	22.7±1.3bB	81	28.8±1cC	103	27.8±0.7cC	99
Na	(15)	8.55±0.5aA	57	12.9±0.3bB	86	14.4±0.6cC	96	15.7±0.2dD	105
P*	0.66±0.03	0.436±0.02aA	66	0.528±0.014bB	80	0.647±0.007cC	98	0.67±0.01dD	102
S*	0.364±0.027	0.197±0.007aA	54	0.288±0.006bB	79	0.368±0.005cC	101	0.367±0.003cC	101
Zn	38.0±2	22.0±1.6aA	58	33.8±1.4bB	89	36.9±0.9cC	97	36.0±1.4cC	95

Values are for mean±standard deviation of seven replicate measurements (n=7); Values in parenthesis are reference value; * Concentration unit is %; Different lowercase letters indicate the significance of different ultrasonic time for the same element at p <0.05; ; Different capital letters indicate the significance of different ultrasonic time for the same element at p <0.01

Table S4 Analysis results of target analytes in GSB4 by ICP-OES under different DES composition

Elements	Certified(mg/kg)	1:1		1:1.5		1:2		1:2.5	
		Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)	Measured (mg/kg)	R(%)
Ca*	0.153±0.008	0.122±0.01bAB	80	0.152±0.007cC	99	0.125±0.004bB	82	0.115±0.003aA	75
Fe	139±4	145±3.7aA	104	143±4.2aA	103	141±3.9aA	101	142±3.8aA	102
K*	1.86±0.09	2.05±0.1cC	110	1.92±0.05bB	103	1.74±0.1aA	94	1.71±0.1aA	92
Mg*	0.23±0.014	0.234±0.005aA	102	0.233±0.005aA	101	0.229±0.009aA	100	0.227±0.008aA	99
Mn	28.0±1	29.7±1.8bB	106	27.8±0.7aAB	99	27.2±1.2aA	97	26.7±1.2aA	95
Na	(15)	11.9±0.7aA	79	15.7±0.2cC	105	13.2±0.9bB	88	12.8±0.8bAB	85
P*	0.66±0.03	0.71±0.01cC	108	0.67±0.01aA	102	0.69±0.01bB	105	0.72±0.01dC	109
S*	0.364±0.027	0.314±0.01aA	86	0.367±0.003cB	101	0.355±0.02bB	98	0.351±0.01B	96
Zn	38.0±2	39.4±1.2bB	104	36.0±1.4aA	95	36.7±1.8aA	97	35.4±1.8aA	93

Values are for mean±standard deviation of seven replicate measurements (n=7); Values in parenthesis are reference value; * Concentration unit is %; Different lowercase letters indicate the significance of different DES composition for the same element at p <0.05; ; Different capital letters indicate the significance of different DES composition for the same element at p <0.01

Table S5 Analysis results of target analytes in GSB1a by ICP-OES

Analysis content	GSS 1																	
	Ca		Fe		K		Mg		Mn		Na		P		S		Zn	
	Value s	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)
Concentrations determined of target analytes (mg/kg) (n=7)	70.7	1.0	4.88	22.0	916	1.8	128	-1.5	10.3	-6.4	12.0	1.7	751.2	-3.7	913	-8.7	14.1	6.0
	71.5	2.1	4.59	14.8	860	-4.4	140	7.7	11.9	8.2	12.7	7.6	744.0	-4.6	863	-13.7	14.6	9.8
	72.1	3.0	4.41	10.3	883	-1.9	128	-1.5	10.7	-2.7	13.4	13.6	763.6	-2.1	814	-18.6	13.9	4.5
	68.7	-1.9	4.63	15.8	887	-1.4	140	7.7	11.8	7.3	12.8	8.5	728.0	-6.7	880	-12.0	14.4	8.3
	73.5	5.0	4.79	19.8	876	-2.7	136	4.6	12.2	10.9	12.8	8.5	795.7	2.0	869	-13.1	14.0	5.3
	74.8	6.9	4.40	10.0	921	2.3	135	3.8	11.5	4.5	12.4	5.1	763.6	-2.1	836	-16.4	14.9	12.0
	69.0	-1.4	4.52	13.0	872	-3.1	138	6.2	10.8	-1.8	12.9	9.3	760.1	-2.6	884	-11.6	13.0	-2.3
Average value (mg/kg)	71.5		4.6		888		135		11.3		12.7		758.0		866		14.1	
Reference value (mg/kg)	70		4		900		130		11.0		11.8		780.0		1000		13.3	
Relative error (%)	2.1		15.1		-1.3		3.7		2.7		7.6		-2.8		-13.4		6.2	
Standard deviation (mg/kg)	2.2		0.2		22.7		5.0		0.7		0.4		20.9		32.5		0.6	
Relative standard deviation (RSD) (%)	3.1		3.9		2.6		3.7		6.3		3.5		2.8		3.8		4.5	
$\Delta \log C$	0.009		0.061		-0.006		0.016		0.012		0.032		-0.012		-0.063		0.026	

Table S6 Analysis results of target analytes in GSB4 by ICP-OES

Analysis content	GSS 1																	
	Ca		Fe		K		Mg		Mn		Na		P		S		Zn	
Concentrations determined of target analytes (mg/kg) (n=7)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)	Values	RE (%)
	1509.6	-1.3	143.0	2.9	19744	6.2	2289	-0.5	27.7	-1.1	15.3	2.0	6919	4.8	3583	-1.6	36.4	-4.2
	1591.2	4.0	150.1	8.0	18304	-1.6	2336	1.6	26.9	-3.9	15.5	3.3	6868	4.1	3779	3.8	38.7	1.8
	1559.2	1.9	141.6	1.9	20192	8.6	2406	4.6	28.8	2.9	16.0	6.7	6828	3.5	3674	0.9	36.7	-3.4
	1536.8	0.4	145.1	4.4	18489	-0.6	2419	5.2	27.8	-0.7	15.8	5.3	6861	4.0	3757	3.2	36.0	-5.3
	1482.4	-3.1	142.1	2.2	19184	3.1	2277	-1.0	27.1	-3.2	16.2	8.0	6828	3.5	3637	-0.1	35.3	-7.1
	1473.6	-3.7	140.4	1.0	19050	2.4	2312	0.5	28.2	0.7	16.0	6.7	6505	-1.4	3539	-2.8	34.3	-9.7
	1509.6	-1.3	147.4	6.0	19568	5.2	2335	1.5	27.8	-0.7	14.9	-0.7	6661	0.9	3782	3.9	36.3	-4.5
Average value (mg/kg)	1523.2		144.3		19218.7		2338.8		27.8		15.7		6781.1		3678.4		36.2	
Reference value (mg/kg)	1530.0		139.0		18600		2300		28.0		15.0		6600.0		3640.0		38.0	
Relative error (%)	-0.4		3.8		3.3		1.7		-0.8		4.5		2.7		1.1		-4.7	
Standard deviation (mg/kg)	42.0		3.5		676.3		54.8		0.7		0.5		146.0		97.7		1.4	
Relative standard deviation (RSD) (%)	2.8		2.4		3.5		2.3		2.3		3.1		2.2		2.7		3.7	
$\Delta \log C$	-0.002		0.016		0.014		0.007		-0.004		0.019		0.012		0.005		-0.021	

Table S7 Quantitative characteristics of the proposed method for the target analytes

Analytes	LOD ^a (mg kg ⁻¹)	LOQ ^b (mg kg ⁻¹)	LR ^c (mg kg ⁻¹)	r ^{2d}
Ca	0.476	1.570	50–4000	0.9998
Fe	0.141	0.470	5–600	0.9997
K	0.285	0.950	200–20000	0.9996
Mg	0.151	0.503	50–4000	0.9998
Mn	0.036	0.120	5–200	0.9999
Na	0.088	0.293	5–200	0.9995
P	1.296	4.320	200–20000	0.9996
S	2.113	7.043	50–5000	0.9995
Zn	0.137	0.457	5–200	0.9998

^a Limit of detection; ^b Limit of quantification; ^c Linear range; ^d Coefficient of determination;