

Supporting Information

Simultaneous determination of chlorine and sulfur in geochemical reference samples by Wavelength Dispersive X-ray Fluorescence Spectrometry

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Sample preparation for total sulphur determinations by ICP-OES

0.2500g of the sample was placed in a 50mL Teflon beaker, 2.5 mL of nitric acid, 2.5 mL of hydrochloric acid, 5 mL of hydrofluoric acid, and 1 mL of perchloric acid were added. Close the lid, shake and leave it overnight. Place the beaker on a hot plate, remove the lid, rinse with a small amount of water, heat and decompose at 190 to 210 °C, and dry it until the white smoke is exhausted (If the sample is not completely decomposed, add nitric acid and hydrofluoric acid before evaporating to dry). 5mL of 50% hydrochloric acid was added and heated on a hot plate until the solid salts were completely dissolved. Remove the beaker for cooling, transfer the solution to a 25mL polyethylene colorimetric tube, Use pure water to make up the volume to 25mL, and measure after standing for 4h.

Sample preparation for total sulphur determinations by combustion-IR detection

0.4g of iron flux was placed in a porcelain crucible, 0.08 g of the sample was placed, cover the surface of the sample with 1.5g of tungsten flux. The crucible was placed on the crucible rack of the elemental infrared analyser. After the analysis heating was started, the sulfur release curve in the sample will be displayed in the data display area of the software.

Table S1 Repeated determination results for Cl and S

Reference samples	Elements	Reference value (mg/kg)	Repeat measured value (mg/kg) (n=10)									
			1	2	3	4	5	6	7	8	9	10
GSD23	Cl	46±8	49.3	127.4	215.9	250.2	291.1	300.8	370.6	403.5	425.6	470.1
	S	11700±900	11791	11365	11880	11895	11350	11664	11843	11611	11622	11867
GSD12	Cl	163±25	172.2	206.6	217.9	245.1	274.0	299.7	340.0	373.9	390.5	433.7
	S	940±54	927.4	938.0	943.3	989.9	935.6	942.4	915.5	944.5	926.5	968.1
GSS33	Cl	284±11	291.7	380.0	451.4	516.2	581.4	610.5	635.6	713.5	713.1	793.5
	S	268±19	263.3	258.3	245.2	252.8	260.2	249.6	247.6	255.1	244.8	268.5
GSS24	Cl	4800±300	4967	4877	4973	4990	4996	4744	4975	5064	4997	4991
	S	2000±300	2028	1942	1994	1986	1951	1879	2002	1989	1950	1978
GSS23	Cl	6300±600	6017	6200	6190	6214	6187	6166	6343	6180	6432	6177
	S	(420)	408.9	419.4	424.9	419.1	428.0	421.3	430.5	418.1	446.2	412.7

Table S2 Analysis results of chlorine in reference samples by WD-XRF

Analysis content	Reference samples									
	GSS32	GSS2	GSS34	GSS33	GSS23	GSD12	GSS24	GSD28	GSD21	GSD23
Concentrations determined of sulfur (mg/kg) (n=7)	35.8	67.7	927.4	298.3	6426	175.0	4905	86.2	2875	40.9
	32.5	63.8	917.7	297.4	6214	184.9	4745	91.6	3031	40.7
	29.6	61.3	941.9	292.6	6425	186.8	4563	93.0	2850	42.5
	34.7	64.4	898.4	319.2	6489	186.8	4256	92.1	3138	40.5
	30.3	66.5	980.5	271.7	6804	178.6	4623	89.3	2963	40.5
	32.6	61.2	941.9	306.3	6993	160.4	4469	91.8	3250	42.7
	32.2	62.8	937.0	293.6	6426	168.5	4549	92.4	2988	46.7
Average value (mg/kg)	32.5	63.9	935.1	297.0	6540	177.3	4587	90.9	3013	42.1
Reference value (mg/kg)	34	62	906	284	6300	163	4800	99	2800	46
Relative error (%)	-4.3	3.1	3.2	4.6	3.8	8.8	-4.4	-8.2	7.6	-8.6
Standard deviation (mg/kg)	2	2	25	14	266	10	205	2	142	2
Relative standard deviation (RSD) (%)	6.8	3.9	2.7	4.9	4.1	5.7	4.5	2.6	4.7	5.3
$\Delta \log C$	-0.019	0.013	0.014	0.019	0.016	0.036	-0.020	-0.037	0.032	-0.039

Table S3 Analysis results of chlorine in reference samples by spectrophotometry

Analysis content	Reference samples									
	GSS32	GSS2	GSS34	GSS33	GSS23	GSD12	GSS24	GSD28	GSD21	GSD23
	29.1	60.5	948.6	279.9	5510	149.8	5168	110.3	2856	45.8
	33.5	64.1	831.0	310.5	6221	158.1	4844	101.8	3214	40.2
	30.7	71.2	843.5	278.1	6219	177.9	5419	108.6	3121	39.4
Concentrations determined of sulfur (mg/kg) (n=7)	33.4	61.7	911.1	306.3	5546	151.2	4123	91.0	2745	43.5
	32.6	68.7	893.6	271.8	6348	145.5	5512	99.1	2912	46.1
	37.0	58.1	861.0	300.9	6364	171.6	5100	99.6	2663	38.3
	32.8	61.7	843.5	293.4	5781	151.8	5092	109.7	3209	39.4
Average value (mg/kg)	32.7	63.7	876.1	291.6	5998	158.0	5037	102.9	2960	41.8
Reference value (mg/kg)	34	62	906	284	6300	163	4800	99	2800	46
Relative error (%)	-3.7	2.8	-3.3	2.7	-4.8	-3.1	4.9	3.9	5.7	-9.1
Standard deviation (mg/kg)	2	5	43	15	375	12	460	7	224	3
Relative standard deviation (RSD) (%)	7.6	7.3	4.9	5.2	6.3	7.7	9.1	6.9	7.6	7.8
$\Delta \log C$	-0.017	0.012	-0.015	0.011	-0.021	-0.014	0.021	0.017	0.024	-0.041

Table S4 Analysis results of sulfur in reference samples by WD-XRF

Analysis content	Reference samples									
	GSS32	GSS2	GSS34	GSS33	GSS23	GSD12	GSS24	GSD28	GSD21	GSD23
	73.1	208.5	416.5	269.7	439.1	918.1	2181	5213	7081	12611
	66.8	205.8	407.3	298.5	453.8	896.5	2218	5021	6915	12974
	75.0	197.2	408.9	298.8	431.7	901.8	1906	5305	7128	12650
Concentrations determined of sulfur (mg/kg) (n=7)	74.2	210.4	401.2	282.9	424.1	915.9	2117	5435	7732	12638
	70.5	202.7	389.1	291.0	445.5	916.0	1941	5547	7056	12391
	69.1	199.4	408.2	289.5	432.2	942.8	1956	4997	7155	12702
	69.3	196.0	417.8	278.1	456.3	899.7	2232	5208	7671	12357
Average value (mg/kg)	71.1	202.9	407.0	286.9	440.4	913.0	2079	5246	7248	12617
Reference value (mg/kg)	77	210	431	268	420	940	2000	5520	6700	11700
Relative error (%)	-7.6	-3.4	-5.6	7.1	4.9	-2.9	3.9	-5.0	8.2	7.8
Standard deviation (mg/kg)	3	6	10	11	12	16	141	202	319	206
Relative standard deviation (RSD) (%)	4.3	2.8	2.4	3.7	2.7	1.7	6.7	3.8	4.4	1.6
$\Delta \log C$	-0.034	-0.015	-0.025	0.030	0.021	-0.013	0.017	-0.022	0.034	0.033

Table S5 Analysis results of sulfur in reference samples by ICP-OES

Analysis content	Reference samples									
	GSS32	GSS2	GSS34	GSS33	GSS23	GSD12	GSS24	GSD28	GSD21	GSD23
	82.1	232.2	439.8	251.7	426.8	961.4	1867	5211	6311	12245
	83.6	236.8	396.3	246.0	427.3	969.2	1947	5369	6173	12081
	81.7	236.4	389.3	251.4	462.3	1017	1851	5267	6017	12149
Concentrations determined of sulfur (mg/kg) (n=7)	80.9	241.9	431.7	242.7	482.0	998.1	1927	5221	6304	11142
	81.8	238.5	420.8	245.4	474.0	1003	2032	5315	6251	12011
	79.9	238.3	395.5	258.3	489.3	995.2	2087	5296	6108	11537
	81.0	213.3	416.3	250.2	442.3	998.5	1942	5048	5966	13192
Average value (mg/kg)	81.6	233.9	412.8	249.4	457.7	991.8	1950	5247	6161	12051
Reference value (mg/kg)	77	210	431	268	420	940	2000	5520	6700	11700
Relative error (%)	5.9	11.4	-4.2	-6.9	9.0	5.5	-2.5	-5.0	-8.0	3.0
Standard deviation (mg/kg)	1	10	20	5	26	20	84	103	137	638
Relative standard deviation (RSD) (%)	1.4	4.1	4.7	2.1	5.6	2.0	4.3	2.0	2.2	5.3
$\Delta \log C$	0.025	0.047	-0.019	-0.031	0.037	0.023	-0.011	-0.022	-0.036	0.013

Table S6 Analysis results of sulfur in reference samples by combustion-IR detection

Analysis content	Reference samples									
	GSS32	GSS2	GSS34	GSS33	GSS23	GSD12	GSS24	GSD28	GSD21	GSD23
Concentrations determined of sulfur (mg/kg) (n=7)	88.9	209.3	403.2	251.7	435.8	996.1	1767	4986	6150	11145
	72.1	239.5	472.4	236.9	415.6	1028	1930	5144	7145	10899
	73.5	239.4	466.7	231.6	426.4	987.2	1856	5321	5899	11062
	80.2	218.7	444.7	277.8	375.8	894.2	2211	5747	7125	11754
	75.7	218.1	408.7	270.9	373.2	1025	1935	5661	5986	9684
	77.3	248.7	469.1	265.8	361.9	984.1	1988	5277	6678	9927
	91.2	245.4	481.7	255.6	439.8	1021	1921	4897	6211	9788
Average value (mg/kg)	79.8	231.3	449.5	255.8	404.1	990.8	1944	5290	6456	10608
Reference value (mg/kg)	77	210	431	268	420	940	2000	5520	6700	11700
Relative error (%)	3.7	10.1	4.3	-4.6	-3.8	5.4	-2.8	-4.2	-3.6	-9.3
Standard deviation (mg/kg)	7	16	32	17	33	46	137	320	525	805
Relative standard deviation (RSD) (%)	9.4	6.7	7.1	6.7	8.1	4.7	7.1	6.1	8.1	7.6
$\Delta \log C$	0.016	0.042	0.018	-0.020	-0.017	0.023	-0.012	-0.018	-0.016	-0.043

Table S7 The description of the reference samples

Reference samples	category	Sampling area	Cl content (mg/kg)	S content (mg/kg)
GSS2	Soil	Chestnut soil in siziwang banner inner mongolia, China	62±10	210±43
GSS3	Soil	Yellow brown soil, ye county, shandong province, China	57±11	123±14
GSS7	Soil	Basalt red soil in xuwen, guangdong province, China	100±6	250±36
GSS9	Soil	Hongze lake deposits, China	45±9	241±22
GSS14	Soil	Sichuan basin, China	50±4	173±21
GSS17	Soil	Sandy soil in wulatehou banner, inner mongolia, China	38±6	108±14
GSS18	Soil	Saline-alkaline soil in hangjinhou banner, inner mongolia, China	7800±500	7000
GSS19	Soil	Brown desert soil in haiyan county, qinghai province, China	758±78	816
GSS20	Soil	Lushan saline-alkali soil, xinjiang province, China	40000±3000	27000±2900
GSS21	Soil	Grey calcareous soil in shihezi, xinjiang province, China	152±12	167
GSS22	Soil	Sediment of yellow beach in rizhao city, shandong province, China	5100±300	440±42
GSS23	Soil	Sediments on the beach of xiangshan, zhejiang province, China	6300±600	420
GSS24	Soil	Sediment from the south beach of yangjiang city, guangdong province, China	4800±300	2000±300
GSS26	Soil	Wuhe huaihe sediments, anhui province, China	75±9	162±10
GSS28	Soil	Sediment of xiangjiang river, yiyang city, hunan province, China	41±6	281±21
GSS31	Soil	Hanshui river basin, hanchuan city, hubei province, China	65±5	180±8
GSS32	Soil	Huaihe river basin, chuzhou city, anhui province, China	34±4	77±9
GSS33	Soil	Yellow river basin, binzhou city, shandong province, China	284±11	268±19
GSS34	Soil	Haihe river basin, tanggu district, tianjin, China	906±33	431±22
GSD12	Stream Sediment	Yangchun polymetallic mining area, guangdong province, China	163±25	940±54
GSD16	Stream Sediment	Langshan metamorphic rock area, inner mongolia, China	33±3	87±10
GSD18	Stream Sediment	Mudanjiang granite district, heilongjiang province, China	30	66±10
GSD21	Stream Sediment	Copper mining area, xinjiang province, China	2800±200	6700±600
GSD22	Stream Sediment	North slope of tianshan mountain, xinjiang province, China	298±39	6200
GSD23	Stream Sediment	Polymetallic mining area, dexing city, jiangsu province, China	46±8	11700±900
GSD27	Stream Sediment	Copper mining area, tibet autonomous region, China	476±22	1060±60
GSD28	Stream Sediment	Lead and zinc mine in lanping county, yunnan province, China	99±7	5520±170