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Determination of trace and rare-earth elements in Chinese soil and clay reference materials by ICP-MS

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Abstract Inductively coupled plasma mass spectrometry (ICP-MS) has become a powerful tool for providing reliable analytical results in many laboratories around the word. In this study, the mixture of HF and HNO_3 acids in high-temperature and high-pressure closed-vessel digestion technique were used to decompose some Chinese reference materials, and thirty seven elements were determined by ICP-MS. Most of the results for Chinese soil reference materials were found to be in reasonable agreement with the reference values, except Cs, Ta, Li, Ge, Zn, Nd, Tb and Ta whose values need to be revised. Their precisions were typically lower than 5% RSD. However, the Precisions of Chinese clay reference materials, especially for GBW03102 and GBW03102a, were significantly different with reference values, probably reflecting the existence of a coarser-grained fraction (>70 μm) in samples, and the formation of fluorides in Al-rich samples during sample decomposition by using the mixture of HF and HNO_3 acids. Moreover, thirty-seven trace elements covering the mass range from Li to U in four Chinese clay reference materials were firstly provided with good precision and accuracy in this study.

Key words ICP-MS; Chines soil and clay reference materials; analytical uncertainty

1 Introduction

Since the birth of the first commercial instrument in 1983, ICP-MS has been widely applied in a variety of fields such as geology, environmental science, industry, medical science, and biology, owing to its advantages of high sensitivity, low detection limit, fast analysis, broad dynamic linear range, less spectral interference and simultaneous multi-element detection (Li Bing and Yang Hongxia, 2003; Li Bing and Yin Ming, 1995). In the past decade, along with the development of and the improvement in ICP-MS instrumentation for sensitivity and interference, the ICP-MS analytical method has become a standard method for various researches (Hu Zhaochu et al., 2010; Hu Shenghong et al., 2000; Liu Ye et al., 2007; Liu Ying et al., 1996).

In routine ICP-MS analysis of common geological samples, international reference materials and national reference materials have become indispensable tools for quality control to improve the data quality for trace element determination (Jenner et al., 1990). Nevertheless, some national reference materials, such as clay, only the contents of major elements were reported (Wang Yiming, 2003), and their trace and rare-earth elements were not reported in later literature. The high-temperature and high-pressure digestion bomb (Patent No. ZL03218713.01) used in this study is similar to what was reported by Qi Liang et al. (2000), which can effectively dissolve zircon, spinel, and chromite minerals in geological samples, and have the advantages of less pollution and low detection limits. In addition, the technique of abundance-matched calibration standard solution simulating the natural abundance ratios of geological samples can improve the precision and accuracy of the results (Liu Ye et al., 2007). Consequently, we contributed new data for trace and rare-earth elements in four

Chinese clay reference materials. Chinese soil reference materials were also analyzed to verify the reliability of our method.

2 Experimental

2.1 Instrument and reagents

The experiments were made using an Agilent 7500a ICP-MS instrument (Agilent Technologies, Tokyo, Japan). The RF power was fixed at 1350 W. A micro flow nebulizer (100 μL/min) and a double path spray chamber were used for sample introduction. The ICP-MS operating conditions were optimized to obtain maximum signal intensities for Li, Y, Ce and Tl, while the ratios of oxide ions (CeO^+/Ce^+) and doubly charged ions (Ce^{2+}/Ce^+) were routinely maintained at <1.5%. Details of the instrumental operating conditions and measurement parameters are summarized in Table 1.

Table 1 Operation parameters for ICP-MS

Item	Parameter
RF power	1350 W
Plasma gas flow rate	15 L/min
Carrier gas flow rate	0.94 L/min
Make up gas	0.15 L/min
Extract 1	–163.5 V
Extract 2	–93 V
Einzel1,3	–90 V
Einzel 2	7 V
Omega bias	–40 V
Omega (+)	4.4 V
Omega (–)	4.2 V
QP focus	3.9 V
Plate bias	–8 V
Sample uptake rate	100 μL/min
Sample depth	6.0 mm
Dwell time⁄mass	200 ms
Detector mode	On
Scan type	Peak hopping, three sweeps per reading and three readings per replicate
Scan number	3

Ultra-pure water (18 MΩ/cm) was obtained by using a Milli-Q Element Ultrapure Water System (Millipore Corporation, USA). The ultra-pure acids (nitric acid and perchloric acid) were prepared from commercially available reagents by sub-boiling distillation with a commercial available quartz still, while hydrofluoric acid was doubly distilled with a custom-made sub-boiling distillation device. The multi-element stock solution was made by using single element standard stock solutions (National Center for Analysis and Testing of Steel Materials, China). Three multi-element stock solutions were prepared by diluting 1.0 mg·mL^{-1} single-element standard solutions to span the concentration range from 0.1–500 ng·mL^{-1} in 3% v/v HNO_3 + 0.1% v/v HF. Data of multi-element mixed working standard solutions are listed in Table 2. Rhodium was used as an internal standard to make corrections for matrix effects and by repeatedly analyzing a calibration solution as a drift monitor over the duration of a run.

The test samples were soil reference materials (GBW07401, GBW07403, GBW07404, GBW07405, GBW07408, GBW07423, GBW07424, GBW07425, GBW07427, and GBW07429) developed by the Institute of Geophysical and Geochemical Exploration (IGGE) of the Chinese Academy of Geological Sciences (CAGS) and clay reference materials (GBW03101, GBW03102, GBW03102a, and GBW03103) were developed by the Institute of Geology, State Administration of Building Materials Industry, China.

2.2 Sample preparation

The procedures used for sample decomposition in our laboratory were described as follows: soil and clay reference materials were dried at 105℃. 50±1 mg of samples were accurately weighed and placed into a polytetrafluoroethylene (PTFE) bomb. 1.50 mL of HNO_3, 1.50 mL of HF, and 0.01 mL of $HClO_4$ were added and the bomb was heated with an electric hot plate at 140℃ until they turned into wet salt, and then 1.50 mL of HNO_3 and 1.50 mL of HF were added. The closed bombs were heated with an electronic oven at 190℃ for 48 hours. The cooled bombs were placed onto an electric hot plate to evaporate to dryness, 3.00 mL of HNO_3 was added and the solution was evaporated until it turned into wet salt; then 3.00 mL of 50% HNO_3 was added. The closed bomb was heated in an oven at 150℃ for 12 hours. After cooling, the solution was transferred into a clean polyethylene terephthalate (PET) flask, Rh was added as an internal standard with the concentrations of Rh in the solution as 10 ng/mL (ppb); afterwards, the solution was diluted to 80 g with 2% HNO_3 (with the corresponding dilution factor of 1600), and the diluted solution was kept under a sealed condition for ICP-MS measurement.

3 Results and discussion

3.1 Limits of detection and procedural blank

The limits of detection (LODs) of ICP-MS mainly depend upon instrumental sensitivity, spectral interferences, memory effects, cleanliness of digestion vessels and blank level of analytical reagents, and it is possible to define the lowest concentrations that can be reliably detected and quantified. The LODs are determined for each element calculated as the concentration equivalent of three times the standard deviation of the ion counts obtained from duplicate runs of reagent blank solutions (3% v/v HNO_3 including the internal standard spikes). As illustrated in Fig. 1, the LOD values of the 37 analyzed elements in this study are all within the range from 0.1 to 100 pg·g^{-1}, which are far below their lowest concentrations in most of the geological samples. Moreover, in order to evaluate the effect of procedural blank on the determination of 37 analyzed elements, five individual procedural blanks were prepared as the same as sample decomposition, and then measured as unknown. As shown in Fig. 1, total procedural blanks for the analyzed elements are mostly higher than 3–10 times the corresponding LOD, which are mainly caused by the blank level of analytical reagents and the environment for sample preparation.

3.2 Accuracy of the results for soil reference materials

Digestion with HF and HNO_3 acids has been widely used for the decomposition of geological samples. In order to evaluate the accuracy and precision of this conventional method, thirty-seven elements in ten Chinese soil reference materials were determined using ICP-MS and high-pressure HF/HNO_3 digestion technique. The results are presented in Table 3. The precisions of the measurements were shown as the relative standard deviation (RSD) in Fig. 2. The RSD in this study was lower than 10% for most elements and typically lower than 5% for the rare-earth elements (REE). The results exhibited reasonably good precisions for all studied elements.

The accuracy of this study was assessed by comparing our results with the recommended or suggested values (Table 3). The relative deviations (RD) are shown in Fig. 3. It can be seen from Fig.3 that the results obtained in this study for most of the elements are

Table 2 Multi-element working standard solutions

Element	ρ_B (ng·mL^{-1})		
	STD1	STD2	STD3
Ba, Sr	500	100	20
V, Rb, Zr, Ce	250	50	10
Cr, Cu, Zn, Nd, La	100	20	4
Co, Ni, Pb, Li	50	10	2
Sc, Th, Ga, Y, Pr, Sm, Gd, Nb	25	5	1
Cs, Hf	10	2	0.4
Dy, Er, Yb, U	5	1	0.2
Be, Lu, Tb, Ho, Tm, Eu, Ta	2.5	0.5	0.1

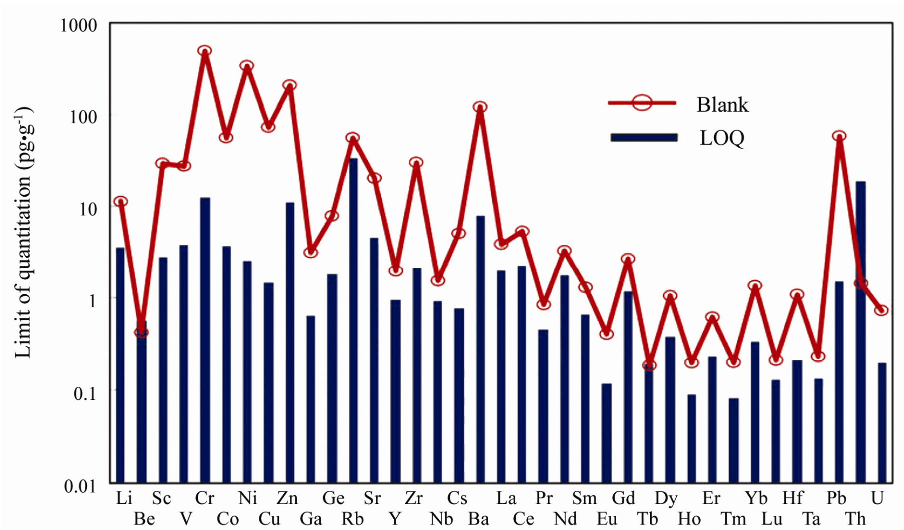

Fig. 1. Limits of quantitation (LOQs) and procedural blank.

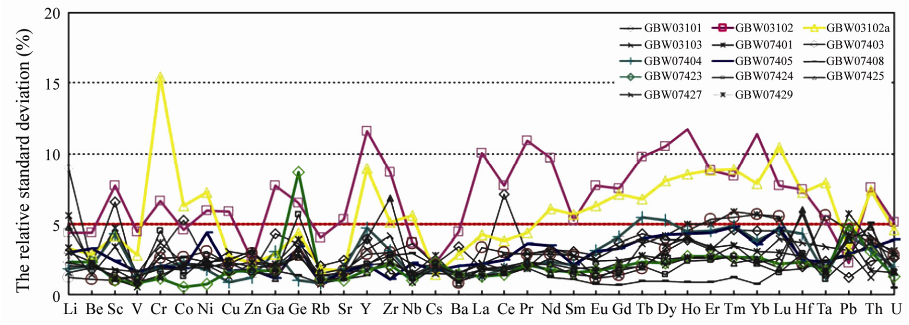

Fig. 2. Relative standard deviations (% RSD) of the determined average values.

in good agreement with the recommended or suggested values and their RDs are lower than 10% for most of the elements. Cs and Ta in GBW07403, Sc in GBW07404, Tb in GBW07405, Li in GBW07408, Y and U in GBW07423, and Ta in GBW07424 are the significant exceptions, which exhibited 10%–20% higher than the recommended or suggested values. However, The average measured values of Cs (2.62±0.05 $\mu g\cdot g^{-1}$) and Ta (0.64±0.04 $\mu g\cdot g^{-1}$) in GBW07403, Tb (0.56±0.02 $\mu g\cdot g^{-1}$) in GBW07405, and Li (40.5±0.9 $\mu g\cdot g^{-1}$) in GBW07408 obtained in this study agree very well with the reference values given by Qi Liang (2000) (Cs: 2.61±0.05 $\mu g\cdot g^{-1}$, Ta: 0.65±0.02 $\mu g\cdot g^{-1}$, Tb: 0.56±0.02 $\mu g\cdot g^{-1}$, and Li: 40.6±1.9 $\mu g\cdot g^{-1}$).

In addition, our Ta values of five Chinese soil reference materials are higher (11%–16%) than its recommended values. Since Nb and Ta have almost identical ionic radii and have long been regarded as behaving identically during geochemical fractionation processes, the ratios of Nb/Ta are thought to be constant in the same kinds of rocks. For example, the Nb/Ta ratio in the upper crust is 13.4 (Rudnick and Gao Shan, 2003). Soil, shale, mudstone and siltstone are fine-grained members of clastic sediments and sedimentary rocks, which can represent the composition of the upper continental crust. Hence, the Nb/Ta ratio of Chinese soil reference materials should be consistent with that in the upper continental crust. Therefore, we can evaluate the quality of the available data according to the Nb/Ta ratio. As shown in Fig. 4a, the Nb/Ta ratios of Chinese soil reference materials in this study are approximately in good agreement with that of the continental upper crust. However, most recommended values are significantly lower than the Nb/Ta ratio of 13.4 with bias up to 10%.

The above results indicate that the recommended values of Cs, Ta, Li, Ge, Zn, Nd, Tb and Ta in Chinese soil reference materials, which are given by Wang Yimin (2003) and the website of chemical metrology and analytical science division, national institute of metrology (http://www.ncrm.org.cn/English/Home/Index.aspx), should be revised.

3.4 The results of clay reference materials

As we have noted, the trace elements values for four clay national reference materials (GBW03101, GBW03102, GBW03102a, and GBW03103) are unavailable up to now. Thirty-seven trace elements covering the mass range from Li to U in these reference materials were also determined by ICP-MS with high-pressure HF/HNO_3 digestion in this study. The analytical results are presented in Table 3. The precision of measurements of RSD is shown in Fig. 2. Precision was lower than 10% for most elements and typically lower than 5% for the REE. For GBW03102 and GBW03102a, RSDs were significantly high, Cr, Y, Pr, Ho, Yb, and Lu exhibited RSDs slightly higher than 10%. Such high RSDs mostly reflect low element abundances [such as Ho (0.34 $\mu g\cdot g^{-1}$) and Yb (0.65 $\mu g\cdot g^{-1}$) in GBW03102 and Lu (0.15 $\mu g\cdot g^{-1}$) in GBW03102a] and/or sample heterogeneity. To investigate the relationship between RSD and the particle size, the particle size distribution of these reference materials was determined by using a laser particle-analyser (Malvern and Mastersizer, 2000). It can be seen from Fig. 5 that GBW03102 shows a wide distribution range of particle sizes and the existence of a coarser-grained fraction (>70 μm), which are thought to be the important sources for analytical uncertainty. GBW03102a shows a relatively narrow distribution range of particle sizes and a fine-grained fraction compared with GBW03102. In addition, the poor precision of measurements may be mainly attributed to the formation of fluorides during sample decomposition by using the mixture of HF and HNO_3 acids. AlF_3 can lead to the restoration of REE, Y, and Th, and a great loss of Nb and Ta (Takei et al., 2001; Zhang Wen et al., 2012). Previous studies revealed that the major elements, specifically Al, were incorporated into insoluble fluoride compounds, such as AlF_3 during sample decomposition (Takei et al., 2001). It was noticed that the concentrations of Al_2O_3 in GBW03102, GBW03102a are 36.74% and 31.32%, respectively, higher than those in GBW03101 and GBW03103. Therefore, AlF_3 was formed in those Al-rich samples when they were decomposed by a high-pressure digestion; the formation of insoluble residues (e.g. fluorides) makes RSDs of the analytical results become significantly high.

As known to all that REEs refer to lanthanides (La–Lu) in the periodic table; two adjacent REEs have different abundances, and their graph of lanthanide element abundance vs. atomic number shows a saw tooth curve. However, chondrite-normalized REE patterns can eliminate the saw tooth and form a smoothly curved trend from La to Lu, with no significant relative depletions or enrichments, except for elements Ce and Eu (Rollinson, 1993). Therefore, the accuracy of sample determination can be assessed by chondrite-normalized REE patterns. As shown in Fig.4b, the results of REE data for four Chinese clay national reference materials exhibit smooth chondrite-normalized REE patterns. These results indicate that the recommended values of trace elements and REE in clay reference materials by using the proposed ICP-MS analytical method in this study have excellent precision and accuracy. These results indicate that the analytical results for Chinese clay reference materials in this study have good accuracy and precision.

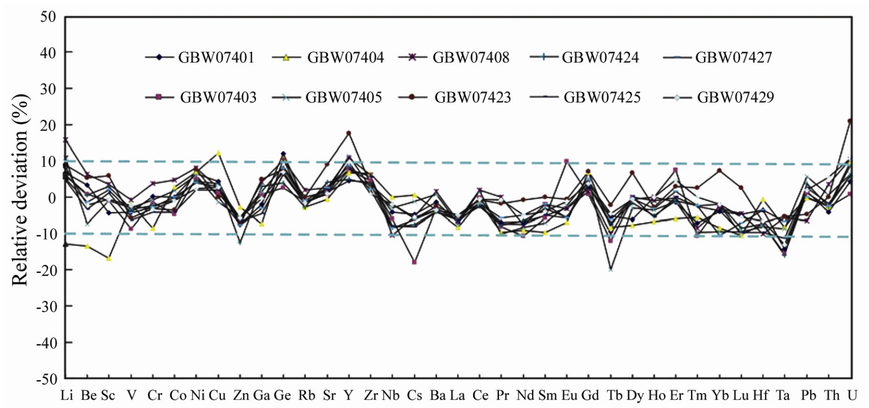

Fig. 3. Relative deviations of ten Chinese soil reference materials obtained in this study. The used reference values of the reference materials are outlined in Table 3.

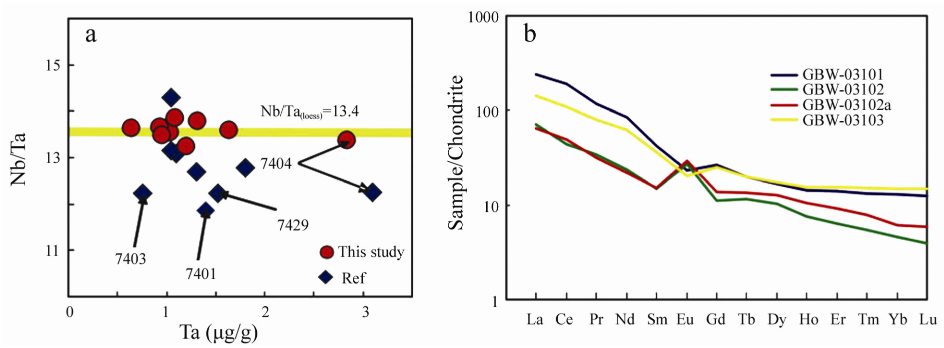

Fig. 4. Plots of Ta vs Nb/Ta for Chinese soil reference materials and chondrite-normalized REE patterns for Chinese clay standards samples.

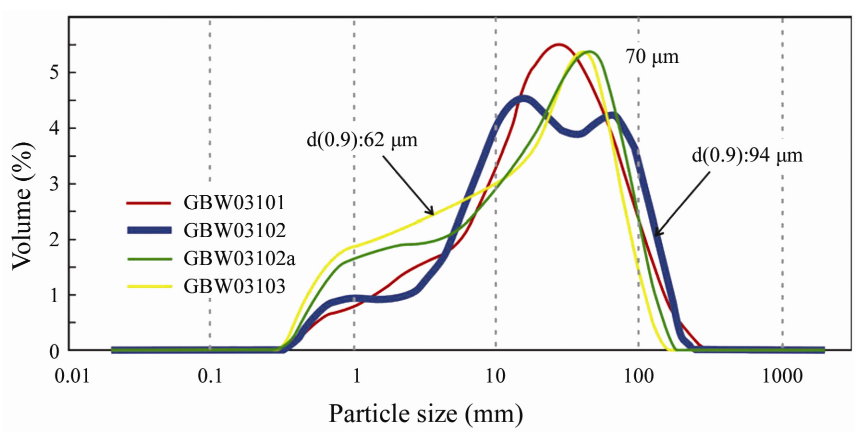

Fig. 5. Particle size distribution of Chinese clay reference materials.

Table 3 Analytical results for ten Chinese soil reference materials (n=6; Data are in μg·g^{-1})

Element	GBW07401			GBW07403			GBW07404			GBW07405			GBW07408		
	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)
^{7}Li	35.0	37.3±2.1	5.59	18.4	19.5±0.2	1.23	55.00	47.9±0.9	1.85	56.0	62.0±1.9	2.99	35.0	40.5±0.9	2.27
^{9}Be	2.50	2.58±0.05	1.88	1.40	1.41±0.02	1.09	1.85	1.60±0.03	2.03	2.00	1.85±0.06	3.26	1.90	2.02±0.04	1.99
^{45}Sc	11.2	10.7±0.5	4.69	5.00	4.95±0.05	1.00	20.00	16.6±0.7	4.30	17.0	16.8±0.4	2.37	11.7	12.1±0.2	1.76
^{51}V	86.0	82.4±1.2	1.50	36.0	32.8±0.4	1.28	247.00	242±3	1.34	166	161±2.6	1.62	81.0	80.3±1.3	1.67
^{53}Cr	62.0	62.1±2.3	3.66	32.0	31.5±0.8	2.62	370.00	338±6	1.92	118	117±2.4	2.05	68.0	70.5±1.4	1.99
^{59}Co	14.2	14.2±0.3	2.23	5.50	5.23±0.14	2.69	22.00	22.6±0.5	2.27	12.0	12.2±0.2	1.85	12.7	13.3±0.4	2.67
^{60}Ni	20.4	21.7±0.5	2.11	12.0	12.6±0.4	3.06	64.00	68.4±1.2	1.80	40.0	42.4±1.9	4.39	31.5	34±0.8	2.32
^{65}Cu	21.0	21.9±0.3	1.27	11.4	11.5±0.3	2.21	40.00	44.9±0.4	0.89	144	142±2.4	1.69	24.3	24.9±0.6	2.54
^{66}Zn	680	628±14	2.28	31.0	29.2±0.9	2.95	210.00	204±3	1.25	494	466±8	1.79	68.0	63.4±2.0	3.10
^{71}Ga	19.3	18.9±0.4	2.00	13.7	13.8±0.3	1.86	31.00	28.7±0.8	3.08	32.0	32.5±0.4	1.14	14.8	15.4±0.3	1.72
^{74}Ge	1.34	1.50±0.04	2.95	1.17	1.20±0.03	2.79	1.90	2.10±0.02	1.05	2.60	2.82±0.10	3.39	1.27	1.40±0.02	1.38
^{85}Rb	140	138±1	0.75	85.0	83.9±0.8	0.94	75.00	72.9±0.6	0.85	117	117±1	0.84	96.0	97.8±0.8	0.83
^{88}Sr	155	157±3	1.67	380	383±7	1.70	77.00	76.5±1.4	1.86	42.0	42.6±0.7	1.63	236	242±3	1.09
^{89}Y	25.0	26.1±0.5	1.73	15.0	16.1±0.5	2.84	39.00	41.6±2.0	4.73	21.0	23.4±0.5	2.09	26.0	28.8±0.4	1.34
^{90}Zr	245	255±6	2.38	246	257±8	3.02	500.00	532±17	3.12	272	279±3	1.12	229	243±7	2.83
^{93}Nb	16.6	15.9±0.2	1.48	9.30	8.73±0.32	3.63	38.00	38.0±0.5	1.29	23.0	22.3±0.5	2.24	15.0	13.4±0.4	2.95
^{133}Cs	9.00	8.57±0.24	2.80	3.20	2.62±0.05	2.09	21.40	21.5±0.4	1.75	15.0	14.8±0.3	1.73	7.50	7.09±0.15	2.05
^{135}Ba	590	581±6	1.03	1210	1174±10	0.81	213.00	205±3	1.53	296	298±6	2.08	480	487±5	0.97
^{139}La	34.0	31.6±0.6	1.83	21.0	19.6±0.7	3.32	53.00	48.5±0.6	1.30	36.0	33.3±0.7	2.19	36.0	33.6±0.5	1.40
^{140}Ce	70.0	68.9±1.4	1.98	39.0	38.9±1.2	2.98	136.00	134±2.5	1.83	91.0	92.6±2.3	2.49	66.0	67.2±0.9	1.35
^{141}Pr	7.50	6.97±0.16	2.29	4.80	4.41±0.13	2.89	8.40	7.57±0.16	2.05	7.00	6.28±0.23	3.63	8.30	7.730.15	1.89
^{146}Nd	28.0	26.1±0.6	2.17	18.4	16.4±0.5	2.90	27.00	24.5±0.6	2.30	24.0	22.0±0.8	3.48	32.0	29.5±0.4	1.26
^{147}Sm	5.20	4.93±0.09	1.87	3.30	3.11±0.09	2.77	4.40	3.97±0.08	2.09	4.00	3.71±0.08	2.12	5.90	5.78±0.06	1.07
^{151}Eu	1.00	0.97±0.02	1.99	0.72	0.79±0.01	1.17	0.85	0.79±0.02	3.12	0.82	0.80±0.02	3.09	1.20	1.16±0.01	0.75
^{157}Gd	4.60	4.72±0.06	1.35	2.90	2.92±0.04	1.36	4.70	5.02±0.21	4.10	3.50	3.68±0.12	3.31	5.40	5.48±0.04	0.68
^{159}Tb	0.75	0.71±0.03	3.59	0.49	0.43±0.01	1.84	0.94	0.86±0.05	5.45	0.70	0.56±0.02	3.94	0.89	0.80±0.01	0.94
^{161}Dy	4.60	4.31±0.18	4.18	2.60	2.58±0.08	3.26	6.60	6.08±0.32	5.28	3.70	3.59±0.15	4.24	4.80	4.80±0.05	0.95
^{165}Ho	0.87	0.87±0.04	4.96	0.53	0.53±0.02	4.52	1.46	1.36±0.06	4.41	0.80	0.77±0.03	4.27	0.97	0.96±0.01	0.89
^{166}Er	2.60	2.56±0.13	4.98	1.50	1.61±0.09	5.34	4.50	4.23±0.19	4.49	2.40	2.37±0.10	4.38	2.80	2.79±0.02	0.87
^{169}Tm	0.42	0.39±0.02	5.85	0.28	0.25±0.01	5.47	0.70	0.66±0.03	4.86	0.41	0.37±0.02	4.79	0.46	0.42±0.01	1.24
^{172}Yb	2.70	2.59±0.15	5.66	1.70	1.66±0.09	5.67	4.80	4.39±0.17	3.79	2.80	2.53±0.09	3.58	2.80	2.71±0.02	0.77
^{175}Lu	0.41	0.39±0.02	5.30	0.29	0.26±0.01	5.50	0.75	0.67±0.03	4.55	0.42	0.38±0.02	4.68	0.43	0.41±0.01	1.73
^{178}Hf	6.80	6.55±0.19	2.90	6.80	6.30±0.14	2.26	14.00	13.9±0.6	4.30	8.10	7.43±0.18	2.43	7.00	6.29±0.12	1.87
^{181}Ta	1.40	1.20±0.02	1.42	0.76	0.64±0.04	5.61	3.10	2.84±0.04	1.42	1.80	1.64±0.04	2.31	1.05	0.99±0.02	2.42
^{208}Pb	98.0	99.5±5.7	5.74	26.0	26.3±1.2	4.55	58.00	57.8±2.4	4.18	552	583±17	2.92	21.0	19.6±0.5	2.70
^{232}Th	11.6	11.1±0.4	3.74	6.00	5.83±0.21	3.63	27.00	26.3±0.8	3.19	23.0	23.1±0.8	3.33	11.8	12.2±0.6	5.05
^{238}U	3.30	3.44±0.11	3.11	1.30	1.31±0.04	2.82	6.70	7.34±0.14	1.95	6.50	6.90±0.27	3.89	2.70	2.98±0.01	0.46

Element	GBW07423			GBW07424			GBW07425			GBW07427			GBW07429		
	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)	Ref.	Mean	RSD (%)
^{7}Li	39.0	42.4±1	2.34	30.6	32.4±0.7	2.04	30.0	31.4±1.5	4.75	31.5	33.1±1.0	3.03	44.0	47.6±1.6	3.34
^{9}Be	2.10	2.21±0.05	2.35	2.40	2.41±0.05	1.98	2.25	2.17±0.05	2.17	1.90	1.87±0.04	2.31	2.70	2.64±0.04	1.45
^{45}Sc	12.0	12.7±0.1	1.05	10.2	10.5±0.1	1.37	10.0	10.1±0.1	1.15	10.5	10.7±0.1	1.11	14.8	14.7±0.5	3.42
^{51}V	90.0	84.7±0.7	0.81	74.0	71.4±0.6	0.83	74.0	69.2±0.9	1.32	74.0	70.7±0.4	0.56	119	116±1	0.89
^{53}Cr	75.0	72.6±0.8	1.13	58.0	56.6±2.6	4.50	59.0	56.5±1.0	1.87	65.0	63.1±1.7	2.73	87.0	84.0±1.2	1.37
^{59}Co	14.0	13.5±0.1	0.58	11.7	11.6±0.2	1.32	11.6	11.1±0.2	1.75	11.3	11.3±0.2	1.91	17.6	17.4±0.4	2.12
^{60}Ni	33.0	35.5±0.3	0.76	26.0	27.1±0.7	2.72	25.4	25.9±0.6	2.32	28.5	29.6±0.6	1.89	41.0	41.9±0.9	2.04
^{65}Cu	26.0	26±0.4	1.62	19.0	19.7±0.4	2.22	21.4	21.8±0.5	2.47	21.6	22.2±0.5	2.31	37.0	38±0.8	2.04
^{66}Zn	61.0	56.3±1	1.72	64.0	55.9±0.9	1.57	65.0	60.5±1.9	3.16	65.0	59.9±1.2	2.00	94.0	88.6±2.1	2.34
^{71}Ga	16.3	17.1±0.3	1.74	17.0	17.5±0.3	1.42	17.2	16.4±0.2	1.18	15.0	14.5±0.3	1.99	20.5	20.4±0.5	2.20
^{74}Ge	1.30	1.40±0.12	8.67	1.31	1.36±0.08	5.66	1.30	1.38±0.04	3.25	1.27	1.37±0.04	2.68	1.63	1.74±0.07	3.86
^{85}Rb	102	102±1	1.07	108	105±1	1.48	110	108±1	1.02	91.0	90±1.2	1.35	116	114±1	1.04
^{88}Sr	165	180±2	1.02	226	235±4	1.83	182	186±2	1.26	195	200±3	1.56	115	116±1	1.25
^{89}Y	25.0	29.4±0.5	1.79	26.5	27.8±0.6	2.17	23.6	25.4±1.0	3.93	24.5	26.6±0.8	3.18	33.0	36.2±0.8	2.09
^{90}Zr	234	242±5	2.09	350	362±10	2.83	270	285±20	6.86	257	262±11	4.18	272	274±6	2.22
^{93}Nb	14.4	14.1±0.1	1.00	16.5	15.1±0.2	1.17	13.8	12.7±0.2	1.30	14.0	12.8±0.1	0.89	18.6	18.2±0.3	1.51
^{133}Cs	8.10	7.61±0.18	2.30	6.50	6.01±0.13	2.17	6.00	5.51±0.11	2.06	6.00	5.62±0.11	1.96	8.90	8.40±0.13	1.52
^{135}Ba	520	506±7	1.45	613	588±8	1.35	634	607±5	0.79	500	482±7	1.49	716	690±10	1.42
^{139}La	38.0	36.0±0.5	1.30	35.5	33.3±0.6	1.76	34.0	31.8±0.6	1.83	34.0	32.3±0.7	2.16	47.0	44.6±0.6	1.28
^{140}Ce	74.0	73.3±1.1	1.43	70.0	68.1±1.2	1.73	65.0	63.4±1.2	1.85	66.0	64.8±1.8	2.85	93.0	92.3±1.4	1.55
^{141}Pr	8.50	8.34±0.18	2.11	8.50	7.83±0.18	2.25	7.90	7.31±0.17	2.40	7.90	7.44±0.22	2.95	10.3	10.2±0.2	1.85
^{146}Nd	32.0	31.7±0.6	1.75	32.0	29.9±0.6	2.12	30.0	27.7±0.4	1.55	30.0	28.5±0.9	3.09	41.0	38.9±1.0	2.61
^{147}Sm	6.20	6.19±0.10	1.58	6.00	5.80±0.08	1.46	5.50	5.22±0.09	1.75	5.60	5.48±0.15	2.72	7.80	7.49±0.15	2.01
^{151}Eu	1.27	1.26±0.02	1.70	1.25	1.18±0.02	1.30	1.18	1.11±0.01	1.12	1.18	1.11±0.03	2.51	1.56	1.54±0.03	1.74
^{157}Gd	5.40	5.78±0.11	1.95	5.20	5.36±0.09	1.73	4.70	4.85±0.09	1.93	4.90	5.13±0.17	3.40	6.80	7.05±0.16	2.25
^{159}Tb	0.86	0.84±0.02	2.29	0.84	0.78±0.02	2.05	0.76	0.70±0.01	1.97	0.80	0.75±0.03	3.99	1.08	1.03±0.03	2.79
^{161}Dy	4.70	5.01±0.11	2.26	4.70	4.62±0.07	1.46	4.20	4.20±0.13	3.07	4.50	4.48±0.16	3.50	6.20	6.16±0.15	2.50
^{165}Ho	1.03	1.00±0.03	2.71	0.97	0.92±0.02	2.37	0.89	0.84±0.03	3.95	0.92	0.89±0.04	4.03	1.23	1.23±0.03	2.69
^{166}Er	2.80	2.88±0.08	2.76	2.75	2.72±0.07	2.48	2.46	2.46±0.08	3.44	2.57	2.61±0.09	3.35	3.40	3.56±0.10	2.67
^{169}Tm	0.42	0.43±0.01	2.66	0.42	0.41±0.01	2.73	0.38	0.37±0.01	2.28	0.40	0.39±0.01	3.55	0.53	0.53±0.02	3.47
^{172}Yb	2.60	2.79±0.07	2.68	2.81	2.75±0.06	2.19	2.54	2.44±0.06	2.50	2.90	2.59±0.06	2.26	3.50	3.43±0.11	3.06
^{175}Lu	0.41	0.42±0.01	2.19	0.46	0.42±0.01	1.58	0.41	0.37±0.01	1.94	0.41	0.38±0.01	2.58	0.54	0.51±0.02	3.00
^{178}Hf	6.60	6.13±0.14	2.35	9.50	8.80±0.26	2.95	7.70	6.94±0.42	6.03	7.00	6.74±0.38	5.65	7.60	7.09±0.19	2.75
^{181}Ta	1.10	1.04±0.02	1.71	1.30	1.09±0.01	1.10	1.05	0.93±0.02	1.61	1.02	0.95±0.02	1.59	1.52	1.32±0.02	1.73
^{208}Pb	25.0	23.8±1.2	4.93	22.0	22.8±0.6	2.67	24.7	25.3±1.0	3.90	21.6	21.6±0.9	4.21	38.0	38.7±1.6	4.19
^{232}Th	12.8	12.8±0.4	3.09	11.3	11.0±0.4	3.69	10.8	10.6±0.5	4.81	11.0	10.7±0.4	4.15	14.5	15.3±0.3	1.72
^{238}U	2.10	2.54±0.03	1.30	2.25	2.38±0.04	1.61	2.20	2.33±0.04	1.66	2.19	2.38±0.07	2.90	3.00	3.32±0.05	1.54

Note: Recommended values by Wang Yimin (2003) and the website of chemical metrology and analytcial science division, National Institute of Metrology (http://www.ncrm.org.cn/English/Home/Index.aspx).

Table 4 Analytical results for four Chinese clay reference materials (*n*=6; Data are in μg·g^{-1})

Element	GBW03101		GBW03102		GBW03102a		GBW03103	
	Mean±S	RSD (%)	Mean±S	RSD (%)	Mean±S	RSD (%)	Mean±S	RSD (%)
^{7}Li	25.8±2.3	8.95	101±4	4.39	131±4	3.31	36.5±0.6	1.55
^{9}Be	3.46±0.07	2.12	4.90±0.21	4.38	10.6±0.3	2.85	2.12±0.04	1.94
^{45}Sc	16.2±1.1	6.52	0.51±0.04	7.71	0.56±0.02	4.19	11.7±0.2	1.78
^{51}V	154±1	0.84	1.19±0.05	4.43	2.45±0.07	2.78	78.3±0.8	0.95
^{53}Cr	69.4±2.1	3.09	14.3±0.94	6.59	3.06±0.47	15.42	62.3±0.7	1.16
^{59}Co	15.3±0.8	5.24	0.96±0.04	4.60	0.90±0.06	6.29	13.0±0.3	2.25
^{60}Ni	42.0±1.0	2.27	1.59±0.09	5.94	8.71±0.63	7.23	31.6±0.7	2.04
^{65}Cu	249±4	1.69	4.67±0.27	5.88	2.10±0.06	2.76	25.6±0.8	3.08
^{66}Zn	528±8	1.59	10.8±0.26	2.44	10.7±0.2	2.26	64.3±1.8	2.77
^{71}Ga	31.7±1.4	4.32	21.6±1.66	7.69	18.1±0.5	2.87	16.6±0.3	1.96
^{74}Ge	2.15±0.08	3.62	3.07±0.20	6.47	2.64±0.12	4.39	1.50±0.05	3.34
^{85}Rb	87.2±1.8	2.03	2.24±0.78	4.00	55.8±1.0	1.83	98.0±1.3	1.36
^{88}Sr	79.5±2.0	2.47	14.6±0.78	5.32	119±2	1.72	167±2	1.28
^{89}Y	22.6±0.9	3.96	11.0±1.27	11.58	17.51.6±	8.95	26.2±0.6	2.12
^{90}Zr	155±2	1.53	13.9±1.21	8.65	32.6±1.7	5.14	227±7	3.15
^{93}Nb	16.1±0.2	1.43	2.2±0.08	3.68	2.80±0.16	5.61	13.0±0.3	2.13
^{133}Cs	11.3±0.3	2.17	32.4±0.73	2.26	39.6±0.6	1.42	6.55±0.13	2.04
^{135}Ba	206±7	3.40	252±11.3	4.47	211±6	2.87	512±8	1.60
^{139}La	57.1±1.1	1.93	13.0±1.30	10.01	15.2±0.7	4.24	33.5±0.8	2.25
^{140}Ce	114±8	7.12	20.4±1.57	7.71	30.4±1.2	3.83	66.5±1.2	1.80
^{141}Pr	11.1±0.3	2.89	2.41±0.26	10.95	3.03±0.13	4.35	7.62±0.15	1.91
^{146}Nd	39.2±1.3	3.18	8.06±0.78	9.70	10.2±0.6	6.08	29.1±1.0	3.32
^{147}Sm	6.49±0.20	3.10	1.72±0.09	5.26	2.32±0.13	5.64	5.58±0.15	2.77
^{151}Eu	1.36±0.04	2.82	0.96±0.07	7.73	1.69±0.11	6.29	1.17±0.03	2.36
^{157}Gd	5.44±0.20	3.67	2.34±0.18	7.52	2.86±0.20	7.11	5.15±0.13	2.45
^{159}Tb	0.75±0.03	4.33	0.42±0.04	9.77	0.51±0.03	6.74	0.75±0.02	2.76
^{161}Dy	4.25±0.17	3.90	1.92±0.20	10.51	3.23±0.26	8.06	4.45±0.09	2.09
^{165}Ho	0.81±0.03	3.90	0.34±0.04	11.75	0.60±0.05	8.55	0.88±0.02	2.56
^{166}Er	2.32±0.07	3.19	0.89±0.08	8.82	1.53±0.14	8.80	2.57±0.07	2.59
^{169}Tm	0.34±0.02	4.60	0.12±0.01	8.43	0.20±0.02	8.87	0.39±0.01	2.63
^{172}Yb	2.20±0.10	4.49	0.65±0.07	11.40	1.05±0.08	7.82	2.51±0.06	2.54
^{175}Lu	0.32±0.01	4.52	0.09±0.01	7.68	0.15±0.02	10.41	0.38±0.01	3.98
^{178}Hf	4.33±0.08	1.96	0.45±0.03	7.42	0.96±0.07	7.22	5.73±0.21	3.67
^{181}Ta	1.10±0.03	2.42	0.75±0.04	5.24	0.82±0.06	7.94	0.95±0.03	3.39
^{208}Pb	994±12	1.23	113±3	2.28	101±3	3.23	22.9±0.7	3.16
^{232}Th	17.1±0.4	2.39	4.71±0.36	7.57	6.45±0.48	7.37	11.3±0.1	1.24
^{238}U	5.38±0.14	2.60	4.47±0.23	5.09	3.54±0.16	4.55	2.09±0.06	2.98

4 Conclusions

Our results show that analytical uncertainty probably reflects the existence of a coarser-grained fraction (>70 μm) in samples, but also is mainly due to the formation of fluorides in Al-rich samples during sample decomposition by using the mixture of HF and HNO_3 acids.

The results for Chinese soil reference materials determined in this study are in good agreement with the recommended or suggested values, except the values for Cs, Ta, Li, Ge, Zn, Nd, Tb and Ta which need to be revised. Moreover, thirty-seven trace elements covering the mass range from Li to U in four Chinese clay reference materials were firstly provided with good precision and accuracy.

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