

Original Article

Determination of rare earth elements, uranium and thorium in soil samples by microwave-assisted acid digestion and inductively coupled plasma mass spectrometry*

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Abstract

This paper presents a simple microwave digestion method for soil samples leading to correct determination of the rare earth elements (Ce, La, Nd, Sc), uranium (U) and thorium (Th) using inductively coupled plasma mass spectrometry (ICP-MS). Six soil samples were collected from different depths (0-0.1, 0.1-0.3, 0.3-1.0, 1.0-2.0, 2.0-3.0 and 5.0-8.0 m) in Phuket province, Thailand. The samples were decomposed using microwave-assisted acid digestion at four different acid conditions including (I) 20 mL concentrated nitric acid; (II) 20 mL concentrated hydrochloric acid; (III) mixture of 8 mL nitric acid and 12 mL hydrochloric acid; and (IV) mixture of 12 mL nitric acid and 8 mL hydrochloric acid. Instrumental neutron activation analysis (INAA) was also applied for determination of REEs, U and Th in those soil samples to compare the results. It was found that the concentrations of Ce, La, Nd, Sc, U and Th in all soil samples obtained by ICP-MS using concentrated nitric acid had acceptable agreement with INAA results. The measured concentrations of Ce, La, Nd, Sc, U and Th in the soil samples ranged within 260-461, 153-922, 87-632, 10-16, 33-134 and 156-323 mg/kg, respectively.

Keywords: rare earth elements, microwave-assisted acid digestion, inductively coupled plasma mass spectrometry, soil sample

1. Introduction

The market demand of rare earth elements (REEs) has been increasing over the recent years. They are used in many applications of high technology, in medical devices, and in military defense systems (Zhou, Li, & Chen, 2017). The REEs are separated into light REEs (LREE; La–Eu) and heavy REEs (HREE; Gd–Lu) (Zhou, Han, Liu, Song, & Li, 2020). In addition, scandium (Sc) and yttrium (Y) are considered REEs because their chemical properties are similar with the REEs (Verni *et al.*, 2017). Moreover, the REEs are

often rich in the natural radionuclides including thorium and uranium (Amaral, Sa, & Morais, 2018). The REEs can be found in soil, especially lanthanum (La) and cerium (Ce) (Ramos *et al.*, 2016). However, soil gives very complex heterogeneous environmental samples (Li, 2018). There are several techniques to quantify REEs, U and Th, including instrumental neutron activation analysis (INAA), X-ray fluorescence (XRF) spectrometry, isotope dilution mass spectrometry, inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) (Balaram, 2019).

INAA is an efficient nuclear analytical technique for determination of elemental composition, in which the elements in a sample to be analyzed are made radioactive by irradiation with neutrons and subsequent radioactivity is measured (Oliveira, Menezes, Jacomino, & Sperling, 2017). This technique provides sensitivity, accuracy, has capability

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for multi-elemental non-destructive analysis, and lowers the possibility of contaminating the sample (Razae, Saion, Wood, & Abdi, 2010). This technique can be applied to samples with various matrix effects (Frontasyeva, Vasiliev, Hristozova, & Evastatieva, 2017).

ICP-MS has successfully been applied to analyze elements in soil samples with complicated matrices. ICP-MS has low detection limit, high sensitivity and high dynamic linear range (Verni *et al.*, 2017). This technique is the most appropriate for quantification of REEs in soil extracts, either those obtained directly following an acid extraction or via an alkaline fusion of the materials to be analyzed (Ramos *et al.*, 2016). However, two latent problems may effect on the REE quantification by ICP-MS, especially in geochemical and environmental matrices: (i) the dissolution of siliceous material; and (ii) the occurrence of spectral interferences in the mass spectrum (Aurel *et al.*, 2020). The fusion is a versatile pretreatment for soil samples, but it does not guarantee accuracy of the analysis because of the use of large amounts of fusion reagents (Zhang & Hu, 2019). Microwave-assisted digestion is the most popular decomposition pretreatment technique for geological samples. Closed digestion provides both high temperature and pressure (Ramos, Almeida, Junior, Arruda, & Pastore, 2017). The radiating energy in a microwave-assisted system is absorbed by the digestion medium and the sample molecules, which accelerates the chemical reactions resulting in complete decomposition of the sample. In addition, localized internal heating taking place on individual sample particles can result in these particles to burst, which creates fresh surfaces for contact with reagents, leading to increased dissolution rate (Hu & Qi, 2014). Therefore, reaction kinetics are speeded up by this technique, while the operating temperature in open digestion is limited by the boiling point of the acid solution.

In the case of acid digestion, a wide variety of reagents are in use. Naturally, the selection of the reagent depends on the sample to be digested. Normally, HNO₃ is a strong oxidizing agent and the most widely used digestion reagent for decomposition of carbonate and sulfide minerals. It can liberate trace elements from many rock samples as highly soluble salts. Meanwhile, HCl is a weak reducing acid that can dissolve iron and manganese oxides better than HNO₃. It is also an excellent solvent for carbonates, phosphates, many metal oxides, and metals. Many silicates can form soluble salts when attacked by HCl at elevated temperatures and pressures (Hu & Qi, 2014). From the advantages of both HNO₃ and HCl mentioned above, synergetic effects of HNO₃ and HCl in the decomposition of soil samples should be studied. Although hydrofluoric acid (HF) can attack silicates and quartz particles and release silicon as volatile SiF₄, the REEs can be precipitated in digestion solutions containing an excess of fluoride, resulting in too low recoveries of the elements (Aldabe, Santamaria, Elustondo, Lasheras, & Santamaria, 2013). Boric acid (H₃BO₃) is added to the solution after digestion to re-dissolve the precipitated fluorides by forming BF₄. However, the addition of H₃BO₃ has two severe disadvantages: (i) a heavy matrix load is introduced into the ICP-MS, and (ii) H₃BO₃ contains relevant amounts of elemental impurities, which will lead to elevated detection limits for the elements investigated (Aurel *et al.*, 2020). While the digestion using HF shows the best results, there are numerous health risks, such as internal

organ damage, vision loss from fumes, and skin damage. HF is also corrosive for the nebulizing system and the plasma torch. Therefore, it is desired to create alternative methods of soil dissolution without using HF

There have been very few studies on the evolution of REEs, U and Th in soil samples collected from the different regions of Thailand. The analysis method for quantification of those elements needs to be developed for obtaining reliable and accurate values. The obtained data will promote the management of rare earth resources in the country. The objective of this study was to determine a microwave-assisted digestion procedure suitable for routine analysis of soil samples prior to ICP-MS measurement, by testing a variety reagents. The methodology was tested for soil samples collected from Phuket province, Thailand, from different depths to get different types of matrices. The soil samples were digested using several acid conditions. Comparison of the ICP-MS results with the baseline results of INAA analysis for benchmarking the performance on some REEs, namely Ce, La, Nd, Sc, U and Th, was also performed.

2. Materials and Methods

2.1 Standards and materials

For ICP-MS analysis, HNO₃ (65% wt, Merck) and HCl (37% wt, Merck) were employed in sample digestion. To prepare analytical calibration solutions, a multi-element stock solution of 1000 mg/L (Inorganic Ventures, USA) in 1% nitric acid was diluted to the concentration range of 5-50 µg/L. In preparing solutions, ultrapure water from a milli-Q water purification system, Milipore (Cedex, France), with 18 MΩ/mL resistivity was used.

2.2 Soil sample preparation

Soil samples used in the experiments were collected from Phuket province, Thailand (latitude 7°51'24.22" N, longitude 98°19'19.49" E). The samples were taken from different depths (0-0.1, 0.1-0.3, 0.3-1.0, 1.0-2.0, 2.0-3.0, and 5.0-8.0 m) as shown in Figure 1. All samples were air dried, homogenized and passed through a 250 µm sieve. Finally, the samples were dried to constant weight at 110°C before INAA and ICP-MS analyses.



Figure 1. Soil samples from different depths.

2.3 Inductively coupled mass spectroscopy (ICP-MS) analysis

Soil samples were decomposed using a microwave assisted system (MAR6, CEM Corporation, Matthews, NC). One gram of soil sample was accurately weighed into Teflon high pressure digestion vessel. The acid solutions were added in the vessels. The studied acid mixtures were as follows: Condition I conc. HNO_3 : 20 mL concentrated nitric acid, Condition II conc. HCl : 20 mL concentrated hydrochloric acid, Condition III $2\text{HNO}_3:3\text{HCl}$: 8 mL conc. HNO_3 + 12 mL conc. HCl , Condition IV $3\text{HNO}_3:2\text{HCl}$: 12 mL conc. HNO_3 + 8 mL conc. HCl .

Each condition was tested with three replications. After the vessels were closed, the digestion was then run using the following two step heating program: 20 min ramp to 210 °C, 15 min holding at 210 °C. After the digests had cooled to room temperature, they were transferred to previously decontaminated 50-mL polypropylene flasks and the volume was made up with distilled-deionized water. The sample solutions were cooled and then filtered. The clear solutions were evaporated at 150 °C to near dryness on a hotplate. Then, the samples were diluted to a final volume of 10 mL using 1% wt HNO_3 . An Agilent Technology 7700 Series ICP-

MS was used in this study. A flow diagram for the analysis of REEs, U and Th in soil samples by ICP-MS is shown in Figure 2.

2.4 Instrumental neutron activation analysis (INAA)

Soil sample and certified geological reference material (igneous rock; JG-2), (each weighing about 0.10 g) were sealed in polyethylene bags. The bags were placed together into polyethylene rabbit prior to neutron irradiation. All samples were irradiated at the TRR-1/M1 swimming pool-type research reactor (Thailand). The irradiation was operated under 5×10^{11} neutrons $\text{cm}^{-2} \text{s}^{-1}$ neutron flux, 26 h irradiation time, 14 d decay time and 3,600 s counting time. The samples were irradiated with neutrons which generated radioactive nuclides. The radioactive nuclides emitted gamma rays with characteristic energies. After an appropriate decay time, the gamma-ray energies of samples were measured by a high purity germanium (HPGe) detector with 1.95 keV of resolution for ^{60}Co and 60% relative efficiency. The gamma-ray spectra were processed using the Gamma Vision computer program (GENIE 2000, EG & ORTEC and Canberra Industry, USA). A flow diagram for the analysis of REEs in soil samples by INAA is shown in Figure 2. The radionuclides, half-life, and γ -energies of REEs, U and Th isotopes are shown in Table 1.

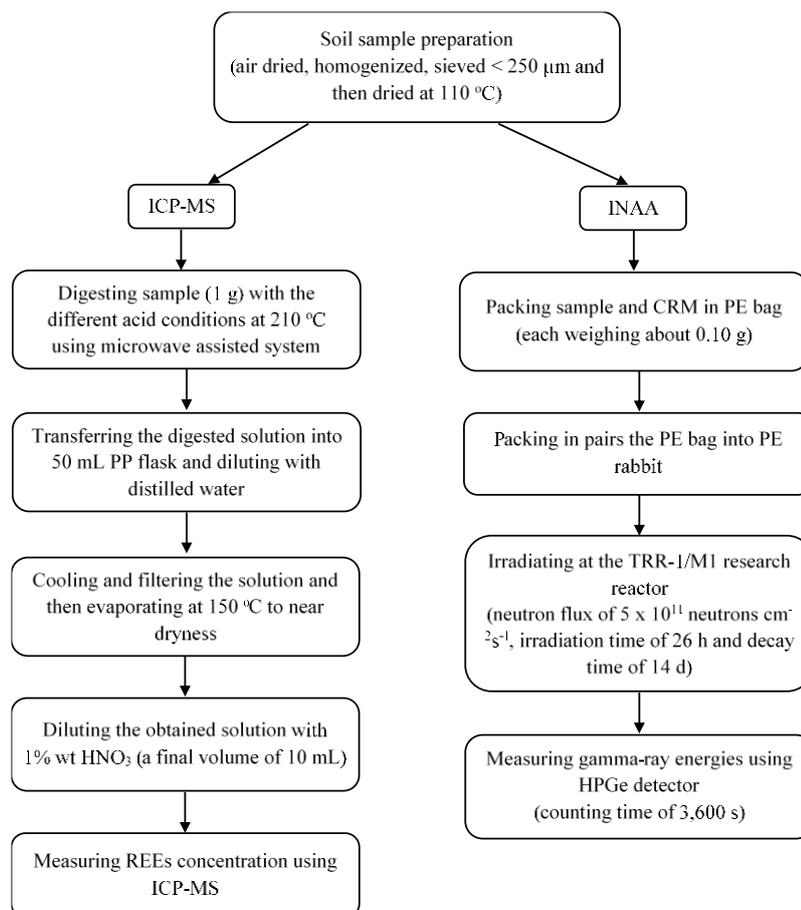


Figure 2. Flow diagram for the analysis of REEs, U and Th in soil samples by ICP-MS and INAA

Table 1. Nuclear parameters for the elements of interest

Element	Radionuclide	Half-life	Energy (keV)
Ce	¹⁴¹ Ce	32.50 d	145
La	¹⁴⁰ La	40.26 h	1596
Nd	¹⁴⁷ Nd	10.98 d	531
Sc	⁴⁶ Sc	83.8 d	889
U	²³⁹ Np	56.55 h	277
Th	²³³ Pa	27.0 d	312

The percentage difference in concentration (%difference) between ICP-MS and INAA was calculated as follows equation (1).

$$\% \text{difference} = \frac{(C_{\text{INAA}} - C_{\text{ICP-MS}})}{C_{\text{INAA}}} \times 100 \quad (1)$$

where C_{INAA} and $C_{\text{ICP-MS}}$ are the mean concentrations of REEs or U or Th obtained from INAA and ICP-MS, respectively.

3. Results and Discussion

3.1 REEs, U and Th concentrations measured by ICP-MS

The decomposition conditions are among the most important factors affecting accuracy of quantitative ICP-MS analysis of a geological sample. This is due to potentially incomplete dissolution of mineral phases and the loss of volatile compounds during sample digestion step. In this

study, alternative acid conditions including conc. HNO₃ (condition I), conc. HCl (condition II), 2HNO₃:3HCl (condition III) and 3HNO₃:2HCl (condition IV) were used to dissolve six soil samples from different depths for REEs, U and Th analyses by ICP-MS, in order to find suitable acid conditions for decomposition of each soil depth. The results are summarized in Table 2-7. The precision of analytical results was evaluated through the relative standard deviation (RSD), from analyses run in triplicates. As can be seen in Table 2-7, for soil sample at the depth of 0.0-0.1 m, the RSD values were better than 5% for almost all acid conditions. The acid condition III was found to achieve the highest mean concentration of REEs followed by condition I, condition II and condition IV. However, the concentrations of REEs obtained from condition III were slightly higher than those obtained from condition I. Meanwhile, the condition I could efficiently extract U and Th from the soil sample. In case of soil sample at the depth of 0.1-0.3 m, the precisions of analytical results obtained from conditions I and II (<5%) were better than those from conditions III (1-37%) and IV (5-36%). This might be attributed to the spectral interferences originating from contamination of organic matter contained in this soil layer, when conditions III and IV were applied. The acid conditions III are capable of leaching REEs from the soil sample, while condition I was favorable for the extraction of U and Th and acceptable for extraction of REEs.

At the depths of 3.0-1.0 and 1.0-2.0 m, most of the RSD values found were less than 10%. In these depth ranges (subsoil horizon), REEs, U and Th could be efficiently extracted by condition III. The concentrations of all elements obtained by condition III were considerable higher than those obtained using condition I. A poor extraction efficiency of all

Table 2. Concentrations of rare earths, uranium and thorium in soil samples collected at the depth of 0-0.1 m measured by ICP-MS after digestions at different acid conditions and INAA.

Element	INAA (mg/kg)	ICP-MS											
		Cond. I (conc. HNO ₃ *)			Cond. II (conc. HCl**)			Cond. III (2HNO ₃ :3HCl)			Cond. IV (3HNO ₃ :2HCl)		
		Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)
Ce	263.00	284.19	4.76	1.67	63.31	2.47	3.90	313.41	7.15	2.28	250.40	3.75	1.50
Dy		7.91	0.18	2.30	1.28	0.01	1.08	8.77	0.26	2.97	4.54	0.38	8.29
Er		3.52	0.06	1.56	0.56	0.00	0.47	3.99	0.15	3.76	2.04	0.08	4.06
Eu		1.14	0.03	2.40	0.19	0.00	2.03	1.44	0.05	3.59	0.62	0.02	2.97
Gd		23.57	0.53	2.26	3.79	0.06	1.71	27.09	0.68	2.52	13.60	0.68	5.03
Ho		1.39	0.03	2.41	0.22	0.00	0.86	1.54	0.06	3.62	0.75	0.02	3.15
La	96.00	153.48	2.27	1.48	28.44	1.43	5.04	174.04	3.57	2.05	126.39	1.12	0.89
Lu		0.37	0.00	1.25	0.08	0.00	0.77	0.41	0.01	3.64	0.21	0.01	3.75
Nd	56.60	86.78	1.13	1.30	25.01	0.49	1.96	110.02	3.14	2.85	98.64	2.18	2.21
Pr		42.92	0.58	1.35	7.22	0.18	2.43	54.30	1.40	2.59	28.69	0.53	1.83
Sc	8.70	11.45	0.45	3.96	1.79	0.07	3.69	13.81	0.46	3.35	6.85	0.11	1.63
Sm		28.40	0.45	1.59	4.04	0.02	0.43	35.57	0.86	2.42	15.81	0.76	4.80
Tb		2.23	0.04	1.62	0.36	0.01	2.00	2.51	0.07	2.79	1.21	0.03	2.41
Tm		0.46	0.00	0.76	0.09	0.00	0.79	0.51	0.02	3.45	0.25	0.00	1.45
Y		29.21	0.59	2.02	4.37	0.14	3.17	36.25	1.27	3.52	16.46	0.47	2.86
Yb		2.85	0.01	0.26	0.48	0.00	0.39	3.09	0.11	3.70	1.60	0.03	2.10
U	nd	52.58	0.52	0.99	8.54	0.02	0.21	43.17	1.00	2.31	31.18	1.10	3.52
Th	153.15	212.01	1.39	0.65	35.34	0.03	0.08	194.35	4.79	2.46	136.70	4.77	3.49

*conc. HNO₃ is concentrated HNO₃

**conc. HCl is concentrated HCl

Table 3. Concentrations of rare earths, uranium and thorium in soil samples in mg/kg collected at the dept of 0.1-0.3 m measured by ICP-MS after digestions at different acid conditions and INAA.

Element	INAA (mg/kg)	ICP-MS											
		Cond. I (conc. HNO ₃ [*])			Cond. II (conc. HCl ^{**})			Cond. III (2HNO ₃ :3HCl)			Cond. IV (3HNO ₃ :2HCl)		
		Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)
Ce	261.00	368.19	1.51	0.41	124.16	0.67	0.54	314.84	38.24	12.15	240.09	11.11	4.63
Dy		10.14	0.29	2.84	2.53	0.00	0.08	12.26	1.33	10.86	5.17	0.75	14.47
Er		4.53	0.13	2.90	1.08	0.01	0.66	5.48	0.60	10.92	1.75	0.31	17.94
Eu		1.65	0.06	3.40	0.36	0.00	0.88	2.16	0.22	10.41	0.65	0.16	24.47
Gd		31.78	0.76	2.39	7.67	0.04	0.52	35.93	4.08	11.36	13.93	1.10	7.89
Ho		1.77	0.05	2.61	0.40	0.00	0.22	2.11	0.23	10.72	0.68	0.15	21.55
La	153.00	200.67	5.26	2.62	62.37	0.87	1.40	297.63	110.34	37.07	120.93	5.81	4.80
Lu		0.46	0.01	2.77	0.11	0.00	1.64	0.55	0.05	9.69	0.22	0.08	35.70
Nd	139.39	128.07	3.32	2.59	56.10	0.03	0.05	166.38	18.17	10.92	108.55	5.15	4.74
Pr		62.88	1.91	3.04	16.22	0.07	0.41	81.46	9.31	11.43	31.99	1.94	6.06
Sc	10.26	13.96	0.04	0.30	3.24	0.02	0.67	10.69	1.02	9.59	6.94	0.85	12.23
Sm		40.83	1.05	2.58	8.73	0.02	0.25	54.80	5.95	10.86	17.20	1.34	7.77
Tb		2.94	0.09	3.22	0.67	0.00	0.62	3.51	0.36	10.21	1.12	0.23	20.44
Tm		0.57	0.02	2.95	0.14	0.00	1.09	0.69	0.08	11.40	0.31	0.09	27.10
Y		38.23	0.72	1.88	8.90	0.00	0.04	46.81	4.78	10.21	17.15	1.41	8.25
Yb		3.52	0.10	2.80	0.87	0.00	0.34	4.22	0.43	10.27	1.39	0.26	18.98
U	54.16	54.40	1.71	3.15	13.22	0.01	0.09	32.77	3.28	10.02	24.11	1.25	5.20
Th	190.00	247.34	10.10	4.08	61.58	0.57	0.93	155.68	2.11	1.35	119.42	6.03	5.05

*conc. HNO₃ is concentrated HNO₃

**conc. HCl is concentrated HCl

Table 4. Concentrations of rare earths, uranium and thorium in soil samples in mg/kg collected at the dept of 0.3-1.0 m measured by ICP-MS after digestions at different acid conditions and INAA.

Element	INAA (mg/kg)	ICP-MS											
		Cond. I (conc. HNO ₃ [*])			Cond. II (conc. HCl ^{**})			Cond. III (2HNO ₃ :3HCl)			Cond. IV (3HNO ₃ :2HCl)		
		Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)
Ce	428.00	333.10	15.68	4.71	115.25	5.94	5.15	461.12	10.67	2.31	315.88	29.66	9.39
Dy		12.38	0.68	5.53	3.36	0.17	5.20	53.39	2.32	4.34	8.79	0.84	9.51
Er		5.48	0.33	5.97	1.36	0.03	2.54	25.75	1.08	4.18	3.76	0.39	10.49
Eu		2.17	0.11	5.23	0.50	0.00	0.29	4.66	0.23	5.00	1.42	0.21	14.48
Gd		35.84	2.07	5.79	9.26	0.44	4.80	95.29	4.27	4.48	27.32	1.61	5.89
Ho		2.33	0.13	5.39	0.51	0.02	3.73	10.28	0.43	4.22	1.47	0.08	5.19
La	297.00	252.79	12.43	4.92	76.32	1.21	1.59	705.14	15.32	2.17	235.67	9.71	4.12
Lu		0.56	0.03	5.16	0.13	0.00	2.17	2.61	0.12	4.44	0.39	0.02	6.25
Nd	347.16	178.19	9.34	5.24	77.73	2.46	3.17	298.48	6.40	2.14	211.91	20.05	9.46
Pr		86.55	4.59	5.31	22.32	0.66	2.94	158.76	7.52	4.74	61.11	5.70	9.32
Sc	12.98	10.16	0.67	6.57	2.21	0.01	0.43	10.98	0.42	3.85	7.32	0.44	6.06
Sm		58.23	2.90	4.99	12.62	0.49	3.86	109.79	5.06	4.61	39.43	1.94	4.93
Tb		3.86	0.24	6.12	0.88	0.04	4.81	12.73	0.54	4.26	2.26	0.22	9.60
Tm		0.76	0.04	5.84	0.17	0.01	4.22	3.27	0.14	4.42	0.48	0.02	4.60
Y		48.76	2.72	5.59	11.06	0.72	6.55	296.37	6.05	2.04	31.86	1.83	5.73
Yb		4.64	0.28	6.10	1.05	0.02	2.32	18.55	0.78	4.21	3.04	0.13	4.36
U	105.90	37.14	2.05	5.51	8.41	0.01	0.12	134.01	2.76	2.06	24.86	1.07	4.30
Th	219.81	169.48	10.86	6.41	40.24	1.17	2.91	322.64	7.28	2.26	137.76	14.79	10.73

*conc. HNO₃ is concentrated HNO₃

**conc. HCl is concentrated HCl

Table 5. Concentrations of rare earths, uranium and thorium in soil samples in mg/kg collected at the dept of 1.0-2.0 m measured by ICP-MS after digestions at different acid conditions and INAA.

Element	INAA (mg/kg)	ICP-MS											
		Cond. I (conc. HNO ₃ *)			Cond. II (conc. HCl**)			Cond. III (2HNO ₃ :3HCl)			Cond. IV (3HNO ₃ :2HCl)		
		Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)
Ce	355.00	278.69	11.74	4.21	75.59	1.22	1.62	332.65	67.67	20.34	222.05	2.54	1.14
Dy		30.26	2.34	7.74	5.87	0.09	1.47	34.47	6.81	19.75	14.23	0.26	1.85
Er		13.89	1.16	8.36	2.46	0.01	0.36	15.87	3.16	19.89	5.94	0.21	3.53
Eu		4.60	0.58	12.54	0.75	0.00	0.12	4.98	1.03	20.72	2.65	0.18	6.97
Gd		68.99	5.03	7.29	12.27	0.00	0.04	78.97	15.90	20.14	31.06	0.10	0.32
Ho		5.60	0.63	11.19	0.93	0.00	0.27	6.25	1.23	19.73	2.30	0.14	6.20
La	349.00	433.25	30.88	7.13	104.43	1.19	1.14	501.62	100.41	20.02	260.73	2.49	0.96
Lu		1.26	0.13	10.63	0.25	0.01	2.55	1.63	0.33	20.04	0.77	0.20	26.59
Nd	370.87	281.71	22.13	7.86	96.52	0.08	0.08	324.39	65.17	20.09	241.06	2.19	0.91
Pr		135.94	10.55	7.76	27.58	0.00	0.01	157.15	31.87	20.28	68.93	0.68	0.98
Sc	10.33	8.50	0.62	7.27	1.87	0.04	2.05	13.46	2.69	19.97	4.23	0.39	9.12
Sm		102.92	8.03	7.81	17.36	0.01	0.07	118.05	23.57	19.97	45.14	0.47	1.04
Tb		8.21	0.81	9.83	1.40	0.00	0.18	9.19	1.87	20.31	3.48	0.22	6.45
Tm		1.57	0.17	11.04	0.31	0.01	2.42	1.99	0.40	20.15	0.80	0.12	15.52
Y		127.03	8.67	6.82	21.66	0.16	0.75	153.10	30.45	19.89	54.63	2.51	4.59
Yb		10.68	0.91	8.52	1.88	0.01	0.34	12.03	2.45	20.40	4.53	0.20	4.49
U	68.96	49.33	4.52	9.17	9.23	0.34	3.67	60.77	0.21	0.34	22.62	0.59	2.63
Th	205.99	194.50	13.54	6.96	37.81	0.58	1.53	210.22	41.13	19.56	104.17	13.31	12.77

* conc. HNO₃ is concentrated HNO₃

** conc. HCl is concentrated HCl

Table 6. Concentrations of rare earths, uranium and thorium in soil samples in mg/kg collected at the dept of 2.0-3.0 m measured by ICP-MS after digestions at different acid conditions and INAA.

Element	INAA (mg/kg)	ICP-MS											
		Cond. I (conc. HNO ₃ *)			Cond. II (conc. HCl**)			Cond. III (2HNO ₃ :3HCl)			Cond. IV (3HNO ₃ :2HCl)		
		Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)
Ce	332.00	259.83	20.69	7.96	137.05	1.05	0.77	264.25	10.43	3.95	170.94	17.97	10.51
Dy		33.65	2.90	8.63	14.06	0.03	0.21	33.81	1.45	4.28	15.37	1.42	9.26
Er		15.03	1.28	8.54	5.72	0.03	0.47	15.25	0.70	4.59	6.21	0.40	6.48
Eu		4.75	0.41	8.68	1.71	0.01	0.33	4.75	0.20	4.22	2.95	1.50	50.82
Gd		76.18	6.61	8.67	29.62	0.22	0.75	77.42	3.71	4.79	32.85	2.76	8.39
Ho		6.10	0.56	9.19	2.21	0.00	0.02	6.08	0.29	4.84	2.42	0.12	4.83
La	534.00	526.42	41.52	7.89	267.26	1.31	0.49	535.40	20.83	3.89	398.94	113.39	28.42
Lu		1.51	0.12	8.03	0.56	0.00	0.35	1.50	0.07	4.37	0.64	0.02	3.20
Nd	434.98	296.29	24.86	8.39	215.60	1.11	0.52	299.80	11.73	3.91	241.71	19.12	7.91
Pr		144.80	11.96	8.26	62.19	0.05	0.07	147.35	5.47	3.71	70.20	5.63	8.02
Sc	12.34	9.02	1.03	11.42	4.15	0.02	0.58	11.68	0.51	4.33	4.18	0.04	1.07
Sm		107.59	9.17	8.52	40.58	0.14	0.35	109.42	4.49	4.11	45.29	3.59	7.94
Tb		8.94	0.77	8.58	3.30	0.02	0.76	8.99	0.41	4.56	3.74	0.27	7.14
Tm		1.89	0.17	8.87	0.70	0.00	0.17	1.88	0.10	5.54	0.80	0.01	1.75
Y		146.54	14.12	9.63	53.41	0.06	0.12	151.54	5.89	3.89	60.06	3.70	6.16
Yb		11.23	1.02	9.12	4.29	0.03	0.61	11.20	0.57	5.08	4.64	0.27	5.86
U	130.26	62.78	5.60	8.92	23.92	0.11	0.45	60.86	2.85	4.68	26.43	2.10	7.95
Th	239.67	198.32	18.10	9.13	79.08	0.39	0.49	188.84	9.33	4.94	130.20	35.04	26.91

* conc. HNO₃ is concentrated HNO₃

** conc. HCl is concentrated HCl

Table 7. Concentrations of rare earths, uranium and thorium in soil samples in mg/kg collected at the dept of 5.0-8.0 m measured by ICP-MS after digestions at different acid conditions and INAA.

Element	INAA (mg/kg)	ICP-MS											
		Cond. I (conc. HNO ₃ *)			Cond. II (conc. HCl**)			Cond. III (2HNO ₃ :3HCl)			Cond. IV (3HNO ₃ :2HCl)		
		Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)	Mean (mg/kg)	SD (mg/kg)	RSD (%)
Ce	360.00	440.93	9.51	2.16	242.13	0.24	0.10	444.29	118.20	26.61	271.56	42.38	15.61
Dy		30.32	0.20	0.68	12.37	0.04	0.35	36.44	1.07	2.93	13.38	1.93	14.40
Er		13.87	0.05	0.35	5.26	0.05	1.04	16.98	0.51	3.02	5.68	0.71	12.59
Eu		5.74	0.08	1.41	2.03	0.00	0.11	6.95	0.26	3.68	2.32	0.18	7.69
Gd		88.27	1.59	1.80	33.97	0.10	0.30	109.01	3.90	3.57	37.29	5.49	14.74
Ho		5.33	0.04	0.81	1.91	0.00	0.06	6.42	0.21	3.22	2.12	0.16	7.67
La	644.00	747.65	10.41	1.39	372.90	0.44	0.12	921.90	33.41	3.62	415.74	62.85	15.12
Lu		1.31	0.00	0.07	0.50	0.00	0.40	1.57	0.05	2.90	0.59	0.05	9.24
Nd	766.67	514.48	9.91	1.93	366.17	0.02	0.00	632.45	22.08	3.49	409.69	59.93	14.63
Pr		246.17	5.40	2.19	103.46	0.04	0.03	303.75	9.90	3.26	115.81	16.93	14.62
Sc	8.97	9.79	0.01	0.15	4.70	0.15	3.13	15.52	0.78	5.03	4.30	0.47	10.92
Sm		158.68	2.93	1.84	57.98	0.25	0.42	194.52	7.34	3.77	64.64	9.40	14.55
Tb		8.99	0.14	1.54	3.28	0.03	0.83	11.00	0.32	2.88	3.75	0.51	13.73
Tm		1.68	0.01	0.47	0.62	0.00	0.07	1.98	0.06	2.89	0.74	0.03	3.72
Y		118.90	1.34	1.13	43.42	0.18	0.41	149.31	6.79	4.55	47.25	6.70	14.18
Yb		9.98	0.08	0.85	3.80	0.02	0.59	11.90	0.35	2.94	4.02	0.45	11.17
U	122.04	72.93	0.38	0.53	28.80	0.04	0.13	85.45	2.99	3.50	30.02	4.76	15.84
Th	153.26	227.77	0.79	0.35	92.70	4.29	4.62	268.71	3.70	1.38	102.39	16.05	15.67

*conc. HNO₃ is concentrated HNO₃

**conc. HCl is concentrated HCl

elements can be observed when the conditions II and IV were used. For soil samples from the depths 2.0-3.0 m and 5.0-8.0, the RSD values for conditions I, II and III were below 10%, while those for condition IV ranged in 5-50%. The concentrations of all elements had the same trend as for the depth of 0.1-0.3 m. From the results above, it can be seen that conditions I and III were promising for the extraction of REEs, U and Th from all soil sample depths. The concentration ranges of the elements obtained by both methods were Ce (260-461 mg/kg), Dy (8-53 mg/kg), Er (3-26 mg/kg), Eu (1-7 mg/kg), Gd (23-109 mg/kg), (1-10 mg/kg), La (153-922 mg/kg), Lu (0.5-3 mg/kg), Nd (87-632 mg/kg), Pr (43-304 mg/kg), Sc (10-16 mg/kg), Sm (28-195 mg/kg), Tb (2-13 mg/kg), Tm (0.5-3 mg/kg), Y (29-296 mg/kg), Yb (2-19 mg/kg), U (33-134 mg/kg) and Th (156-323 mg/kg).

3.2 Concentration measurements by ICP-MS and INAA compared across some REEs, U and Th

Some REEs, U and Th concentrations as measured by ICP-MS were compared with those measured by INAA. There have been reports indicating that INAA is one of the most powerful techniques for quantitative analysis of REEs, U and Th (Yavar, Sarmani, Khalafi, Wood, & Khoo, 2015). This is due to its exceptional sensitivity to many trace elements, including REEs, in a wide variety of rocks and minerals (El-Taher, 2012), with fairly low detection limits. This analytical method does not necessarily require chemical decomposition of the sample (Machado, Pereira-Filho, & Nogueira, 2016). In this study, the accuracy of INAA method was evaluated using certified geological reference material, igneous rock (JG-2).

The measurement was performed for five replicates (n=5). The difference between the certified values and the measured values of some REEs (Ce, La, Nd and Sc), U and Th, as well as the uncertainties are summarized in Table 8. As can be seen the INAA technique showed good precision with the RSD ranging within 0.47-5.22 except for Nd (15.07). A good agreement between the measured values and the certified values of CRMs, JG-2 was observed. The deviation of the obtained values from certified data ranged within 0.28-3.28%.

The concentrations of some REEs— Ce, La, Nd and Sc, U as well as Th in soil samples from different depths when measured by INAA are summarized in Table 2-7 and a comparison of the results obtained by ICP-MS and INAA at different depths is shown in Figure 3. Meanwhile, the differences in concentrations of Ce, La, Nd, Sc, U and Th as measured by INAA from those measured by ICP-MS are presented in Figure 4. An acceptable difference in concentrations of Ce as measured by ICP-MS using the acid condition I as well as condition III and those obtained by INAA can be observed for almost all soil depths (less than 23%). The acid conditions II and IV were found to be not efficient for extraction of Ce from soil samples. As shown in Table 2-7, the concentrations of Ce from using the acid conditions II and IV, measured by ICP-MS, were lower than the INAA values, especially for condition II. The concentrations of Ce measured by ICP-MS using conditions II and IV deviated significantly from those obtained by INAA. The differences ranged in 32-79% and in 5-49% for the acid conditions II and IV, respectively. For La, the differences exceeded 20% for the whole range of soil depths and all acid conditions, except for the depth 2.0-3.0 m and using acid condition I (1.42%) or III (0.26%). Similarly, in the case of

Table 8. Concentrations of rare earths, uranium and thorium in certified geological reference material, igneous rock (JG-2) in mg/kg measured by INAA.

	Ce	La	Nd	Sc	U	Th
1	46.24	19.90	32.10	2.42	11.33	33.76
2	48.30	19.30	26.40	2.39	11.30	30.48
3	48.30	19.90	21.62	2.40	11.30	31.60
4	48.30	20.59	29.81	2.41	11.77	32.95
5	49.70	22.01	26.40	2.40	11.58	31.60
Mean (mg/kg)	48.17	20.34	27.27	2.40	11.46	32.08
SD (mg/kg)	1.24	1.04	3.98	0.01	0.21	1.28
RSD (%)	2.56	5.22	15.07	0.47	1.85	4.06
Certified values	48.30	19.9	26.40	2.42	11.30	31.60
Error (%)	0.28	2.21	3.28	0.71	1.38	1.51

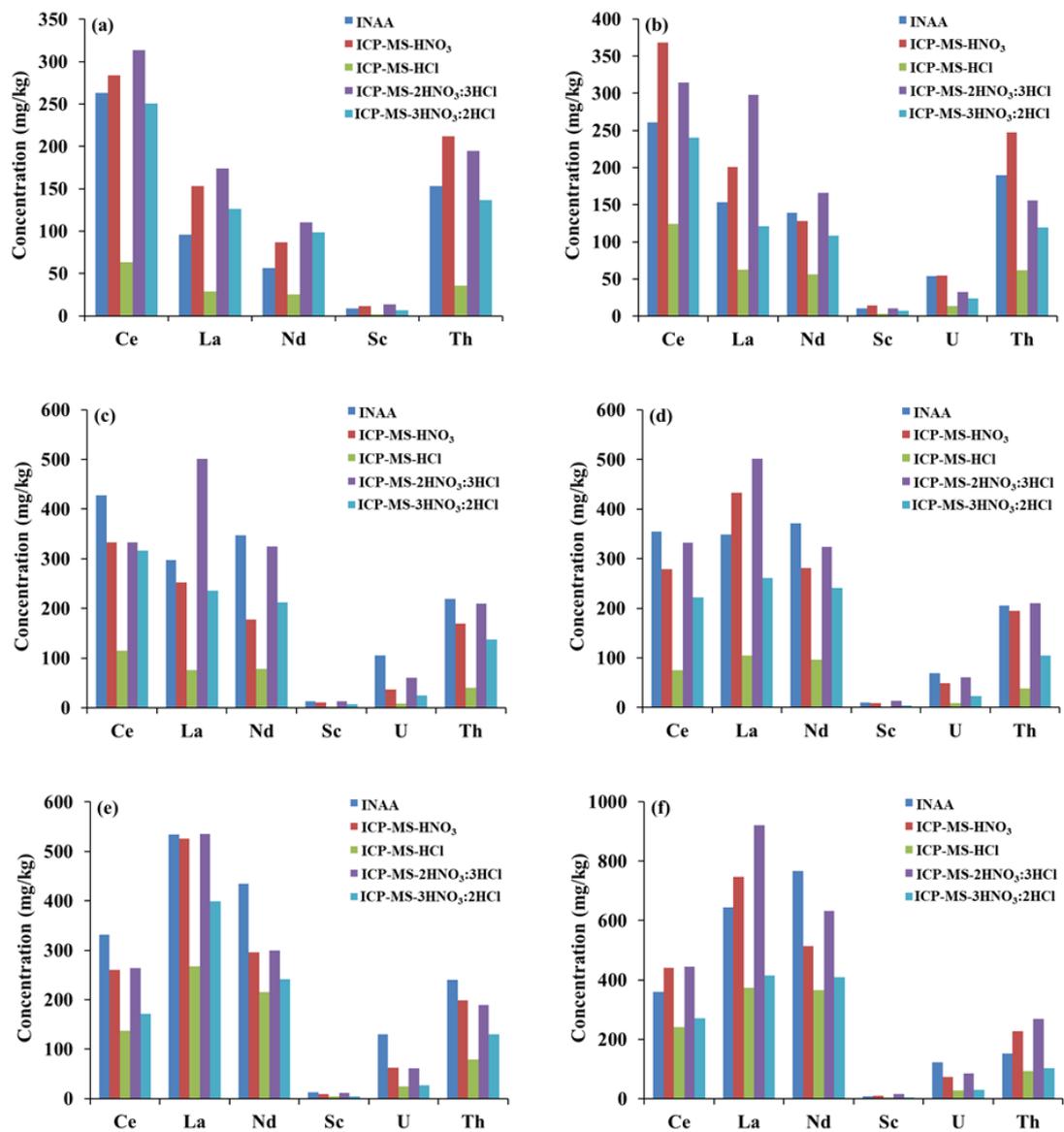


Figure 3. Comparison between ICP-MS and INAA results for the concentrations of Ce, La, Nd, Sc, U and Th in soil samples from different depths: (a) 0.0-0.1 m, (b) 0.1-0.3 m, (c) 0.3-1.0 m, (d) 1.0-2.0, (e) 2.0-3.0 and (f) 5.0-8.0 m, prepared at different acid conditions

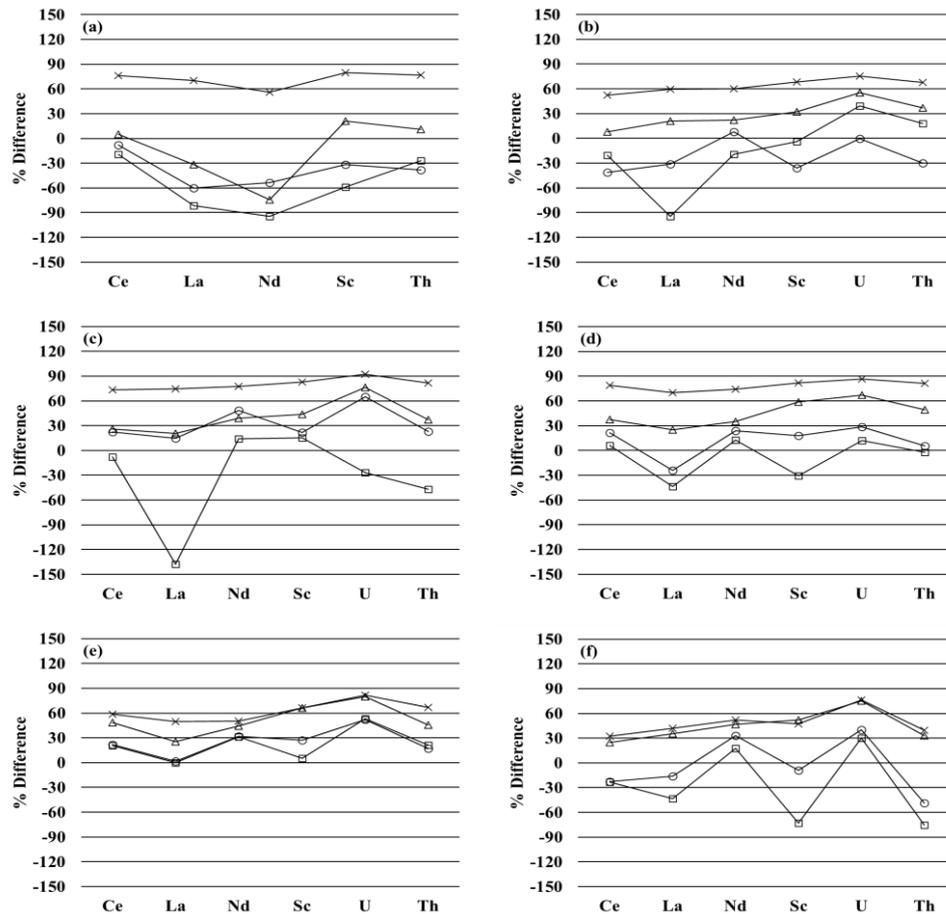


Figure 4. Percentage differences between ICP-MS and INAA results for soil samples from different depths: (a) 0.0-0.1 m, (b) 0.1-0.3 m, (c) 0.3-1.0 m, (d) 1.0-2.0 m, (e) 2.0-3.0 m and (f) 5.0-8.0 m. ICP-MS run after digestion at Condition I-conc. HNO_3 (circle), Condition II-conc. HCl (cross), Condition III- $2\text{HNO}_3:3\text{HCl}$ (square) and Condition IV- $3\text{HNO}_3:2\text{HCl}$ (triangle)

Nd, Sc, U and Th, the differences between ICP-MS and INAA were significant (20-94%). However, there were some acceptable differences between ICP-MS and INAA on using conditions I and III (better than 20%).

From all results, it can be concluded that the acid conditions I and III in the microwave assisted system seemed suitable for quantifying concentrations of REEs, U and Th in soil samples, even though there was a significant bias when compared with INAA in some cases. The results of elemental concentrations obtained from the acid conditions I and III also reveal that conc. HNO_3 and $2\text{HNO}_3:3\text{HCl}$ are adequate for extraction of REEs, U and Th from the whole range of soil depths. The error might have been caused by organic matter contents in each soil depth, causing matrix interference in ICP-MS measurement. A benefit of microwave digestion is the relatively short time of the procedure that does not require nuclear facilities while INAA does (Papaefthymiou & Papatheodorou, 2011). For the extraction processes, the choice of an individual acid or combination of acids (HNO_3 , HCl , $\text{HNO}_3\text{-HCl}$, etc.) depends on the nature of the matrix to be decomposed. The hydrochloric acid for wet digestion is useful for salts of carbonates, phosphates and some oxides. The nitric acid is a strong oxidizing agent and makes an oxidizing attack on many samples not dissolved by HCl (Güven & Akinci,

2011). In our case, although both conc. HNO_3 and $2\text{HNO}_3:3\text{HCl}$ were efficient acid conditions for the decomposition of soil samples, conc. HNO_3 was the best condition. This is because most differences between INAA and ICP-MS using conc. HNO_3 were lesser than when using $2\text{HNO}_3:3\text{HCl}$. Normally, the best acid medium for ICP-MS analysis is HNO_3 . The presence of HNO_3 matrix is not increasing polyatomic ions, which interfere with the determinations. Meanwhile, HCl can cause chloride-bearing polyatomic ions which have major interference in ICP-MS analysis (Hu & Qi, 2014). The fractions of REEs in soil samples from different depths are shown in Figure 5.

4. Conclusions

This study illustrated how soils can be digested for the analysis of REEs, U and Th. Acid digestion was required for the quantification of these elements in the samples. The study sought to find the most accurate methods for proper extraction of chosen elements without using HF. The results for alternative reagents (HNO_3 , HCl , $2\text{HNO}_3:3\text{HCl}$ and $3\text{HNO}_3:2\text{HCl}$) in soil dissolution by microwave-assisted system show that, overall, HNO_3 was the best one for soil digestion. The results from ICP-MS after acid digestion were

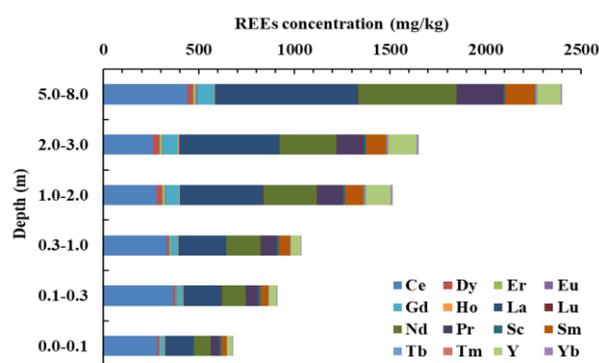


Figure 5. Fraction of REEs at different depths of soil samples

compared with INAA analysis for benchmarking. The results from this study can be applied to evaluate concentrations of REEs, U and Th in samples from other regions of Thailand. In future work, further matrix effects and mass interference will be studied to improve the quantitative analysis by ICP-MS with HNO_3 and $2\text{HNO}_3:3\text{HCl}$ digestion.

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