Comparison of calibration methods to estimate chemical concentrations using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) ; mean count rate vs integrated signal intensity

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Running title : Comparison of calibration methods to estimate chemical concentrations using LA-ICP-MS

Abstract : Laser Ablation - Inductively Coupled Plasma - Mass Spectrometer (LA-ICP-MS) provides quick and simple experimental procedures for multi-elemental analyses of little amount of samples without complex pretreatments or preparation. Two methodologies, which are the mean count rate method (MCRM) and the integrated signal intensity method (ISIM), are compared to obtain the NET signal, which is then incorporated into the equation to obtain chemical concentration. The effects of repetition frequency in laser setting and choice of internal standard, and a detection limit are investigated. The repetition frequency and the choice of internal standard give no significant effect on concentration obtained by LA-ICP-MS. All concentrations by the ISIM show good agreement with the reference values of Pearce et al., (1997). The detection limit of ISIM is one-fifth of that of the MCRM. Therefore, to measure small quantity of radioisotopes, such as ^{234}U and ^{230}Th, the ISIM can be the effective method.

Introduction

Laser Ablation - Inductively Coupled Plasma - Mass Spectrometer (LA-ICP-MS) provides quick and simple experimental procedures for the multi-elemental analyses of little amount of samples without complex pretreatments or preparation. Because of its advantages, the LA-ICP-MS has been successfully applied to geochemistry of solid materials (e.g., Jarvis and Williams, 1993, Pickhardt et al., 2005, Spears, 2004, Pearce et al., 1999). The signals are acquired by peak hopping, one point per isotope during each mass spectrometer sweep, producing the time-intensity profile for each analyte (Figure 1). In this study, two methodologies to calculate representative signals of each isotope are compared to obtain chemical concentrations : the mean count rate method and integrated signal intensity method. In the mean count rate method (MCRM,
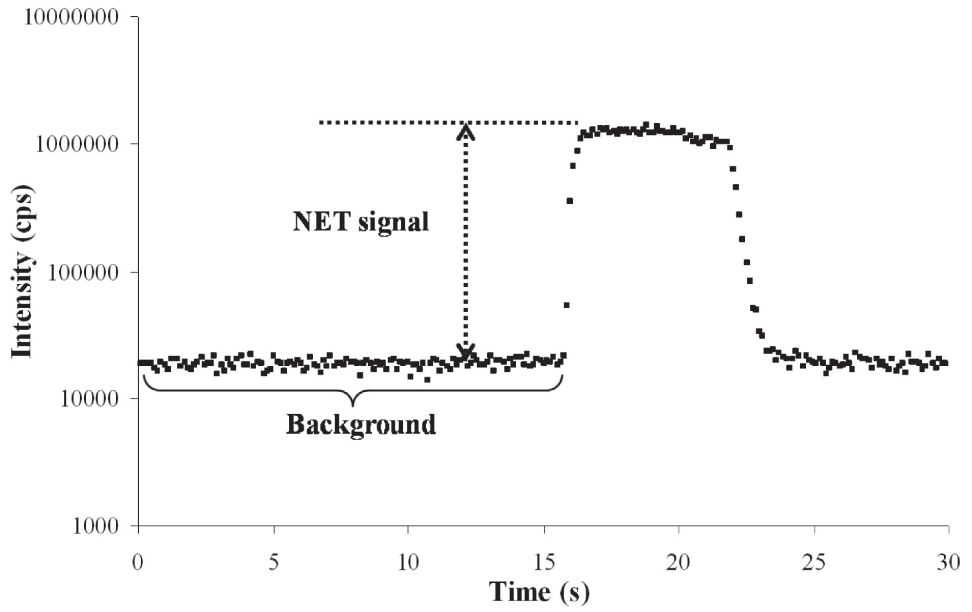
Figure 1. Time − signal intensity profile to estimate the NET signal by MCRM.
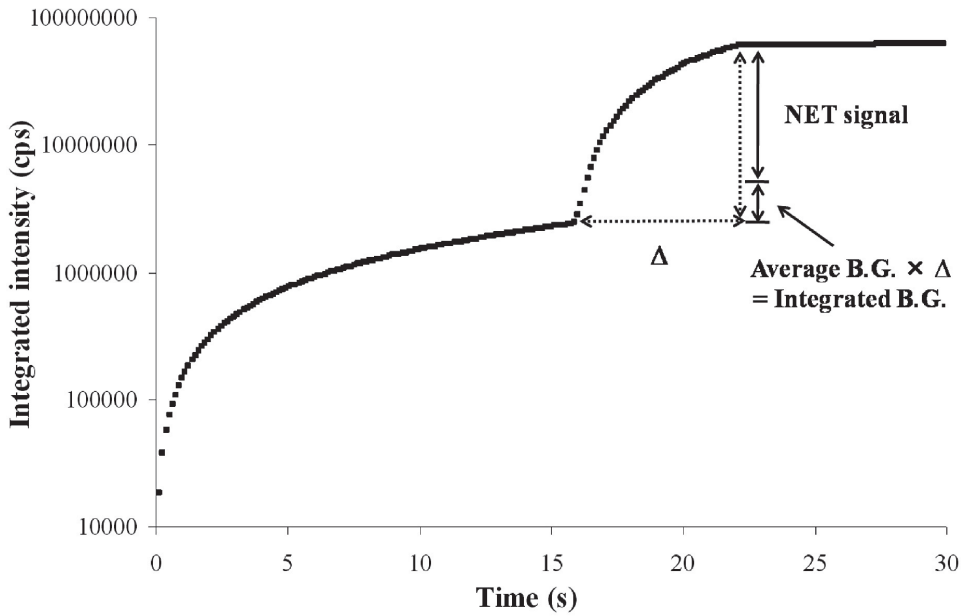

Figure 2. Time − integrated signal intensity profile to estimate the NET signal by ISIM.
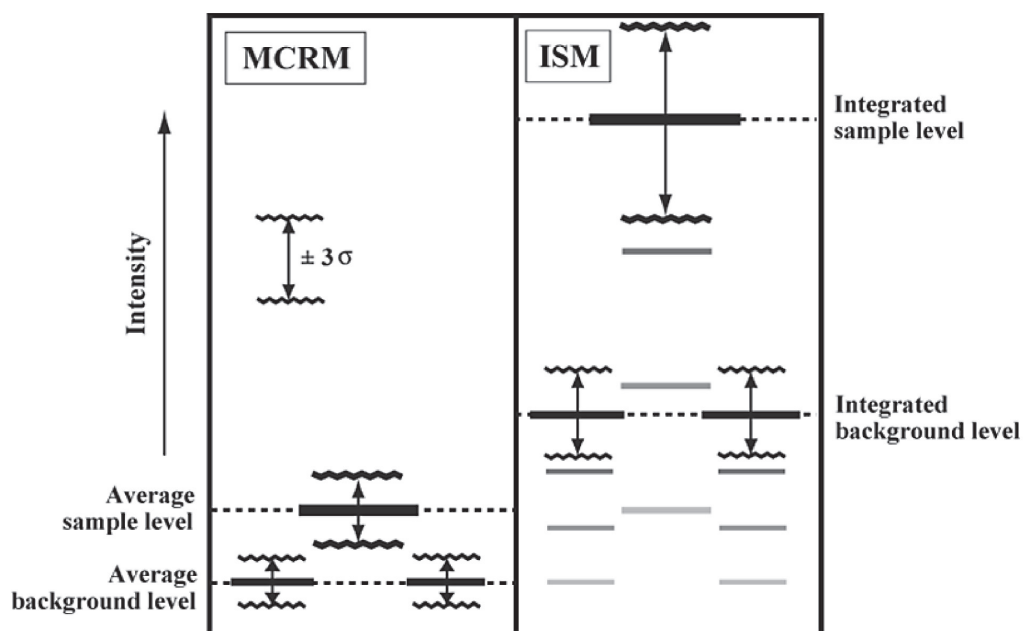
Figure 3. Theoretical advantage of ISIM to MCRM. In the schematic figure for the ISIM, the color change in lines represents the growth of signal through time. Integrated signal grows more over the background, therefore the detection limit is expected to become less.

Table 1

Experimental parameters of LA-ICP-MS

ICP-MS

Model	Agilent 7500s
Forward power	1200 W
Reflected power	1 W
Carrier gas flow	1.1 l min^{-1} (Ar)
	0.30 l min^{-1} (He)
Auxiliary gas flow	1.0 l min^{-1}
Plasma gas flow	15 l min^{-1} (Ar)
Cones	Pt (sampler and skimmer)

Laser ablation system

Model	GeoLas Q + (MicroLas)
Wavelength	193 nm (Excimer ArF)
Repetition frequency	4, 5 Hz
Energy density at target	8 J cm^{-2}
spot diameter	20 μm

Table 2

(a) Comparison of ^{232}Th and ^{238}U concentrations (μg/g) of NIST 612 obtained by MCRM and ISIM at repetition frequency of 5 Hz.

Method	MCRM				ISIM			
Internal standard	^{29}Si		^{43}Ca		^{29}Si		^{43}Ca	
Measured isotope	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U
1	36.81	36.94	37.71	37.85	36.49	36.83	37.71	38.06
2	38.31	38.49	37.97	38.16	38.48	38.59	38.11	38.21
3	37.37	38.02	37.99	38.65	37.58	38.16	37.92	38.51
4	37.68	37.73	37.87	37.92	37.73	37.70	38.16	38.13
5	37.58	37.64	37.75	37.82	37.66	37.63	38.05	38.02
6	37.24	38.25	37.70	38.72	37.33	38.21	38.02	38.92
7	36.58	36.92	37.16	37.50	36.64	37.09	36.95	37.41
8	35.95	38.16	36.16	38.38	35.79	37.83	36.47	38.55
9	37.97	37.49	38.03	37.54	37.73	37.44	38.13	37.84
10	37.61	37.18	37.91	37.48	37.52	37.39	37.85	37.72
11	37.58	36.76	37.62	36.80	37.37	36.73	37.88	37.23
12	38.41	37.54	37.88	37.03	38.08	36.83	38.26	37.01
13	38.37	37.01	37.49	36.16	37.97	36.94	37.41	36.39
14	37.93	37.29	38.12	37.48	37.77	37.16	38.29	37.67
15	37.48	36.42	37.41	36.36	37.27	36.64	36.80	36.17
16	38.31	36.99	38.02	36.71	38.29	37.33	38.04	37.08
Average	37.57	37.43	37.68	37.53	37.48	37.41	37.75	37.68
Standard deviation	0.66	0.57	0.46	0.74	0.67	0.56	0.54	0.74
Standard error	0.17	0.14	0.12	0.19	0.17	0.14	0.13	0.19

(b) Comparison of ^{232}Th and ^{238}U concentrations (μg/g) of NIST 612 obtained by MCRM and ISIM at repetition frequency of 4 Hz.

| Method	MCRM				ISIM			
Internal standard	^{29}Si		^{43}Ca		^{29}Si		^{43}Ca	
Measured isotope	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U
1	37.22	38.93	36.65	38.33	35.84	37.79	36.44	38.42
2	37.95	39.57	37.57	39.18	37.65	39.44	37.25	39.03
3	37.31	38.14	37.04	37.85	36.54	37.20	37.34	38.02
4	37.82	38.61	37.49	38.27	37.64	38.90	37.22	38.47
5	37.74	38.48	37.41	38.14	37.76	38.96	37.14	38.33
6	36.74	37.88	36.34	37.47	36.89	38.18	36.43	37.71
7	37.81	38.16	37.20	37.54	37.34	38.03	37.14	37.83
8	36.92	37.83	37.10	38.01	36.15	37.49	36.54	37.89
9	38.50	37.97	38.15	37.61	38.98	38.47	38.31	37.81
10	38.80	38.04	37.26	36.53	38.84	38.23	37.29	36.71
11	39.09	37.58	37.39	35.95	39.11	38.02	37.11	36.08
12	37.79	37.14	37.47	36.83	38.11	37.55	37.43	36.89
13	37.53	37.77	36.94	37.18	37.46	37.67	36.74	36.94
14	37.83	36.40	37.25	35.84	37.75	36.25	37.61	36.12
15	38.17	36.70	37.84	36.39	38.64	37.49	38.06	36.92
16	37.75	37.36	38.15	37.76	38.22	37.46	38.54	37.78
Average	37.81	37.91	37.33	37.43	37.68	37.95	37.29	37.56
Standard deviation	0.60	0.77	0.47	0.89	0.95	0.75	0.60	0.83
Standard error	0.15	0.19	0.12	0.22	0.24	0.19	0.15	0.21
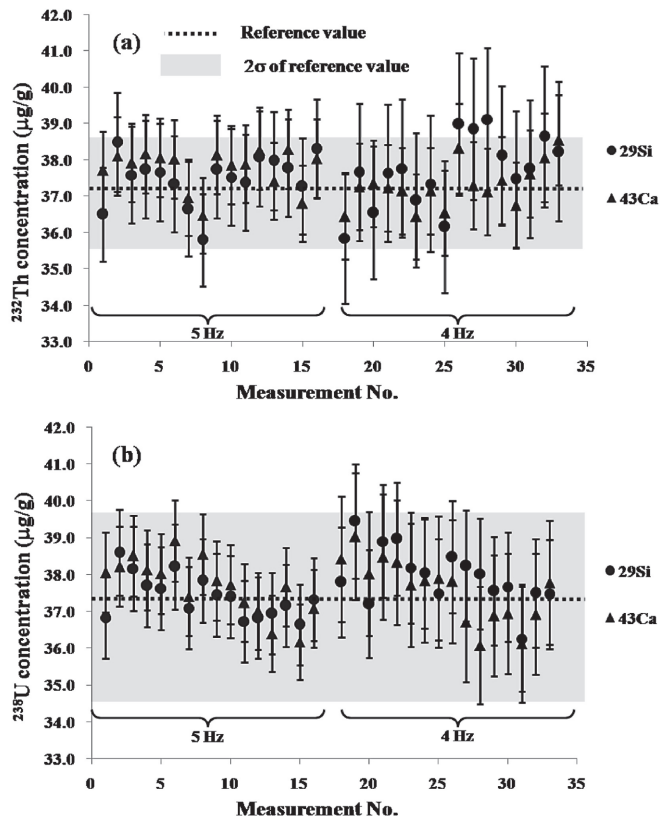
Figure 4. Concentrations (μg/g) of NIST 612 obtained by ISIM. The repetition frequencies are 5 Hz or 4 Hz, the internal standards are [29]Si or [43]Ca and the error bars represent ± 2 σ. (a) [232]Th (b) [238]U
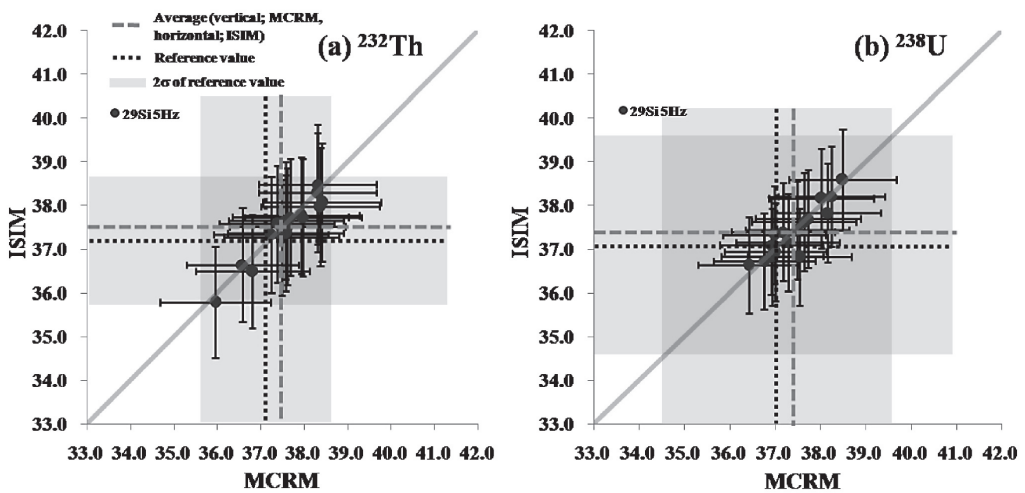

Figure 5. Comparison of concentrations (μg/g) of NIST 612 obtained by MCRM and ISIM. The repetition frequency and internal standard are 5 Hz and [29]Si, respectively. Solid line represents one-to-one correlation line, (a) [232]Th (b) [238]U

Tabel 3

(a) Comparison of ^{232}Th and ^{238}U detection limit (μg/g) of NIST 612 obtained by MCRM and ISIM at repetition frequency of 5 Hz.

Method		MCRM				ISIM		
Internal standard		^{29}Si		^{43}Ca		^{29}Si		^{43}Ca	
Measured isotope	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U
1	0.0869	0.0839	0.0890	0.0859	0.0278	0.0120	0.0287	0.0124
2	0.1157	0.0834	0.1147	0.0827	0.0200	0.0123	0.0198	0.0122
3	0.0887	0.0903	0.0902	0.0918	0.0190	0.0240	0.0191	0.0242
4	0.1296	0.0809	0.1303	0.0813	0.0367	0.0099	0.0371	0.0100
5	0.1293	0.0807	0.1299	0.0811	0.0367	0.0099	0.0370	0.0100
6	0.1015	0.0979	0.1027	0.0991	0.0138	0.0139	0.0141	0.0142
7	0.0982	0.0935	0.0998	0.0950	0.0168	0.0105	0.0170	0.0106
8	0.0971	0.0757	0.0976	0.0762	0.0129	0.0171	0.0132	0.0174
9	0.1264	0.0841	0.1266	0.0842	0.0235	0.0154	0.0237	0.0156
10	0.1316	0.1073	0.1326	0.1081	0.0274	0.0289	0.0277	0.0291
11	0.0993	0.1157	0.0994	0.1158	0.0235	0.0252	0.0238	0.0256
12	0.1467	0.0962	0.1447	0.0949	0.0185	0.0119	0.0186	0.0120
13	0.1234	0.1289	0.1206	0.1259	0.0275	0.0235	0.0271	0.0231
14	0.1302	0.0928	0.1309	0.0933	0.0445	0.0186	0.0451	0.0189
15	0.1195	0.1069	0.1193	0.1067	0.0184	0.0185	0.0182	0.0182
16	0.1282	0.1091	0.1273	0.1082	0.0317	0.0288	0.0314	0.0286
Average	0.1158	0.0954	0.1160	0.0956	0.0249	0.0175	0.0251	0.0176
Standard deviation	0.0174	0.0143	0.0167	0.0137	0.0087	0.0065	0.0088	0.0064
Standard error	0.0043	0.0036	0.0042	0.0034	0.0022	0.0016	0.0022	0.0016

(Measurement No.)

(b) Comparison of ^{232}Th and ^{238}U detection limit (μg/g) of NIST 612 obtained by MCRM and ISIM at repetition frequency of 4 Hz.

| Method		MCRM				ISIM		
Internal standard		^{29}Si		^{43}Ca		^{29}Si		^{43}Ca	
Measured isotope	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U	^{232}Th	^{238}U
1	0.1207	0.1076	0.1188	0.1059	0.0251	0.0217	0.0255	0.0221
2	0.1172	0.1259	0.1160	0.1247	0.0236	0.0140	0.0234	0.0139
3	0.1413	0.1144	0.1403	0.1135	0.0318	0.0324	0.0325	0.0331
4	0.1559	0.0992	0.1545	0.0983	0.0202	0.0252	0.0200	0.0249
5	0.1556	0.0989	0.1542	0.0980	0.0203	0.0253	0.0200	0.0249
6	0.1299	0.1012	0.1285	0.1001	0.0189	0.0257	0.0187	0.0254
7	0.1284	0.1174	0.1263	0.1155	0.0251	0.0242	0.0249	0.0241
8	0.1248	0.1055	0.1254	0.1061	0.0183	0.0169	0.0185	0.0170
9	0.1248	0.1015	0.1236	0.1005	0.0240	0.0238	0.0236	0.0234
10	0.1424	0.1281	0.1367	0.1230	0.0309	0.0267	0.0297	0.0256
11	0.1428	0.1313	0.1366	0.1256	0.0332	0.0214	0.0315	0.0203
12	0.1430	0.0977	0.1418	0.0969	0.0394	0.0204	0.0387	0.0200
13	0.1756	0.1537	0.1729	0.1513	0.0406	0.0252	0.0399	0.0247
14	0.1623	0.1094	0.1598	0.1078	0.0401	0.0141	0.0400	0.0140
15	0.1396	0.1047	0.1384	0.1038	0.0229	0.0244	0.0225	0.0241
16	0.1348	0.1149	0.1362	0.1161	0.0304	0.0283	0.0306	0.0285
Average	0.1399	0.1132	0.1381	0.1117	0.0278	0.0231	0.0275	0.0229
Standard deviation	0.0156	0.0147	0.0152	0.0139	0.0074	0.0048	0.0072	0.0048
Standard error	0.0039	0.0037	0.0038	0.0035	0.0018	0.0012	0.0018	0.0012

(Measurement No.)
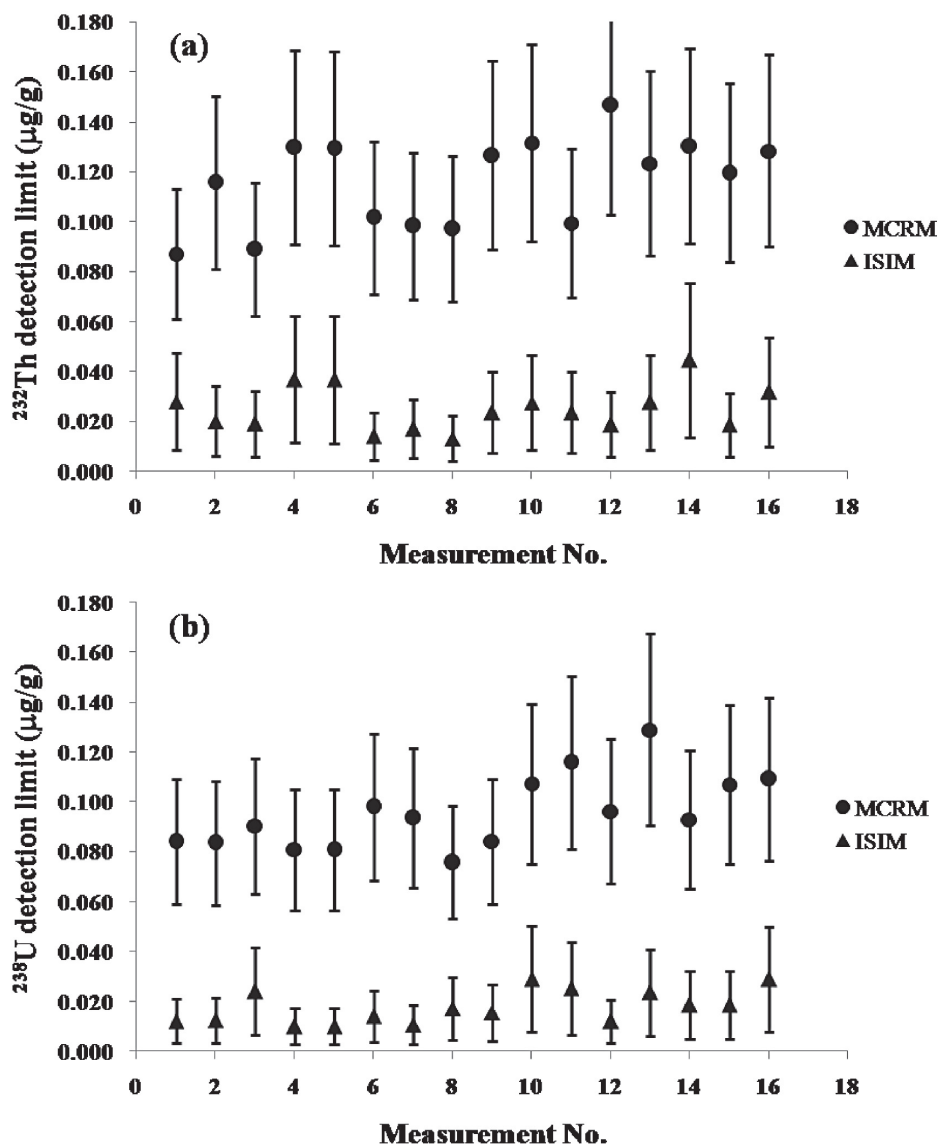
Figure 6. Comparison of detection limits (µg/g) of NIST 612 obtained by MCRM and ISIM. The repetition frequency and internal standard are 5 Hz and ^{29}Si, respectively. (a) ^{232}Th (b) ^{238}U

Figure 1), the average of signal intensity, after background (blank) correction, is incorporated into the equation to calculate the concentrations. The background is calculated as an average of signal intensities before laser ablation (Figure 1). The detection limit is estimated as 3σ (σ, standard deviation) of background signals. In the integrated signal intensity method (ISIM, Figure 2), signals are summed up for a given time slices during laser ablation. For the blank

correction, the average of background intensity measured before the laser ablation is summed up for the same duration with that to obtain an integrated signal (integrated background), and subtracted from the integrated signal (Figure 2). The detection limit is calculated as 3σ of integrated background. By sliding the calculation window through the sequence of background measurement, several integrated backgrounds are obtained and the standard deviation is calculated. In theory, the ISIM has an advantage to reduce the detection limit (Figure 3). In this study, concentration of radioisotopes and detection limits are calculated using above two methods and compared for the purpose of radiometric age determination.

Sample and experimental setting

^{238}U and ^{232}Th concentrations, which are useful for radiometric dating, are measured by LA-ICP-MS, Kanazawa University (Agilent 7500s equipped with GeoLas Q+). The synthetic glass from National Institute of Standards and Technology (NIST), NIST SRM 612, whose concentration is well known (Pearce et al., 1997, ^{232}Th ; 37.23 ± 0.72 µg / g, ^{238}U ; 37.15 ± 1.23 µg / g), is analyzed to compare two calibration methods and precisions are evaluated. NIST SRM 610 is used as an external standard (Pearce et al., 1997, Horn et al., 2000). ^{29}Si and ^{43}Ca are adapted as the internal standards, because silicate or calcium bearing minerals are often suitable for dating. Instrumental setting is listed in Table 1 and the detail of the equipment is described in elsewhere (Ishida et al., 2004, Morishita et al., 2005). Two laser repetition frequencies, 5 Hz and 4 Hz, are tested.

Results and discussion

Concentrations and detection limits of each isotope under a certain repetition frequency are listed in Table 2 and 3, and plotted in Figure 4 - 6.

Effect of repetition frequencies and internal standard

Hasebe et al. (in press) discussed that repetition frequency in laser shot and the choice of internal standard have no systematic effect on the results by the MCRM. In Figure 4, concentrations of ^{232}Th and ^{238}U by the ISIM are shown along with a reference value of NIST SRM 612 (Pearce et al., 1997). The error of each ablated spot is calculated as the percentage same with the standard deviation against the average of 16 measurements. The concentrations of each ablated spot, using the internal standard of ^{29}Si or ^{43}Ca, show little discrepancies among ± 2σ error range. When they are compared to the reference value, they are overlapped within ± 2σ error. An average value for each experimental setting agrees very well for all settings (Table 2). There is no clear evidence that, in the ISIM, both repetition frequencies and choice of internal standards give a systematic effect on the obtained concentrations.

Concentration ; MCRM vs ISIM

Based on the above discussion that there is no systematic effect of both repetition frequencies and the choice of internal standards on concentrations obtained by both MCRM and

ISIM, the concentrations obtained under the experimental condition of 5 Hz repetition frequency and ^{29}Si internal standard are compared between MCRM and ISIM. In Figure 5, concentrations of the ISIM are compared with those of the MCRM. All concentrations by the ISIM show good agreement with the MCRM and the preferred values of Pearce et al. (1997). Since the ISIM / MCRM ratios show one-to-one correlation relationship, choice of calculation methods cause no significant influence on the estimated chemical concentration.

Effect on detection limit

In Table 3, detection limits that are 3σ of background intensities or integrated background intensities, are listed. In Figure 6, the detection limits at repetition frequency of 5 Hz with internal standard ^{29}Si are shown. The detection limit of the ISIM is one-third ~ one-seventh (one-fifth on average) of that of the MCRM. This result indicates that the ISIM is the effective method for calculating a very small quantity ($< 10^{-4}$ µg/g) of radioisotope, say ^{234}U and ^{230}Th, concentrations.

Conclusion

1. The ISIM provides reliable concentrations of ^{232}Th and ^{238}U, concordant with the reference value of NIST SRM 612.
2. Repetition frequency in laser setting and choice of internal standard give no significant effect on concentration calculated by LA-ICP-MS.
3. Since the detection limit of ISIM is one-fifth of that of MCRM, ISIM is more effective method for the purpose of calculating an isotope concentration with very small quantity ($< 10^{-4}$ µg/g).

Acknowledgements

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