

Further Evaluation for High-precision Isotopic Measurement of ^{205}Pb -spiked Pb by Dynamic Multiple Ion Counting

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ABSTRACT: A high-precision MIC-ID-TIMS (multiple ion counting-isotope dilution-thermal ionization mass spectrometry) Pb isotope ratio measurement method (using ^{205}Pb as spike) with a TRITON Plus TIMS, which is equipped with a ^{205}Pb -Pb MIC array, using a two-line multi-dynamic data collection method, was thoroughly re-set and re-evaluated, based on our previous work¹. After some vital modifications, better than 0.01% RSE internal precision on $^{207}\text{Pb}/^{206}\text{Pb}$ for a ^{205}Pb -spiked NIST981 with ~ 50 pg of Pb load was achieved with a measurement time of about 100 min. This is more precise compared to the traditional isotopic measurement method for the ^{205}Pb -spiked Pb, using a single secondary electron multiplier (SEM) with five peak jumps, provided with similar ion beam intensities and measurement time. The external precision on $^{207}\text{Pb}/^{206}\text{Pb}$ was better than 0.1% (2RSD, $n = 24$), which is much better than that achieved by the static MIC method as previously reported^{1, 2}. The present work indicates that the ^{205}Pb -Pb MIC array of the TRITON Plus TIMS can be successfully used for zircon ID-TIMS U-Pb dating with high precision, particularly is useful for samples containing extremely small amounts of Pb (down to several pico-grams).

INTRODUCTION

Multi-ion counting can be used for the determination of isotopic ratios for samples in ultra-small amounts. The Thermo Scientific™ TRITON Plus™ thermal ionization mass spectrometer (TIMS) can be configured with a multi-ion-counting (MIC) array designed for the collection of ^{205}Pb -spiked Pb isotopes, with the collector spacings fixed for ^{205}Pb -spiked Pb isotopes, using three Secondary Electron Multiplier (SEM) ion counters (IC1B, IC2, IC3A) and two Compact Discrete Dynode (CDD) multipliers (IC4, IC5).^{1,2} This design is mainly aimed at high-precision Pb isotopic analysis for zircon ID-TIMS U-Pb dating using a ^{205}Pb spike. For ID-TIMS U-Pb dating, commonly only several picogram quantities of Pb can be separated from a single zircon grain, especially after a chemical abrasion procedure is applied to remove the Pb loss.³ The simultaneous detection of

all of the Pb isotopes using the MIC array offers great increase in the total counts for each isotope and hence, potentially much better precision.⁴

Nevertheless, with data acquisition in a static mode using the MIC array, the quality of the analytical isotope data highly relies on the stability of the relative yields of different multipliers.^{1,2} Usually, sample/standard calibration (*i.e.* sample-standard bracketing, SSB) is used for correcting the yield effect of different multipliers.⁵⁻⁸ With the method, the cross-calibration factors are deduced from the measurement of a known standard prior to the measurement of the sample. This method is time-consuming, as extra standards are required to measure. More importantly, the relative yields of different multipliers may vary significantly between different filament loads,^{1,2} probably due to the problem that the multiplier yields are dependent on the source tuning

conditions to some extent. This is also reflected by the poor external precisions on $^{207}\text{Pb}/^{206}\text{Pb}$ (worse than 0.3%, 2RSD) with the static data acquisition using the Pb MIC array for replicate analyses of the NSIT 981 Pb standards.¹ Thus this means that Pb isotopic analysis using the Pb MIC array in static mode is not robust even with the sample/standard cross-calibration. Accordingly, Sarkar *et al.*² presented a method by measuring the relative yields of different ion counters before and after the sample measurement from the same filament/load using the ^{208}Pb signal, measured sequentially by each ion counter and the central Faraday cup. This means more sample consumption but even so, only 0.1–0.3% 2RSD precision can be achieved on $^{207}\text{Pb}/^{206}\text{Pb}$. Alternatively, an in-run method can be used for cross-calibration of the relative yields of the multipliers by sequential measurements of a single stable ion beam.^{4,9} However, with this method, similarly, more acquisition time is required for the in-run peak jump calibration and thus the ion beam collection efficiency is largely reduced. Amelin and Huyskens⁴ reported that the in-run cross-calibration method for the Pb MIC array can only achieve 0.05–0.1% uncertainty for Pb isotopic analysis.

More recently, Faraday cups with 10^{13} ohm amplifier has been applied for Pb isotope analysis of small samples.^{2,9,10} However, with this method, the ^{204}Pb , which is a very small signal for zircon Pb analysis but important for common/blank Pb correction, cannot be measured by the Faraday cup connected to a 10^{13} ohm amplifier. Thus, the ^{204}Pb still has to be measured by a SEM ion counter. Consequently, in-run correction of the yield of the SEM relative to the Faraday cup is required and hence, extra analysis time and sample consumption.^{9,10}

Recently, we have presented a two-line dynamic multi-ion counting method for the measurement of ^{205}Pb -spiked Pb for the application of zircon U-Pb dating.¹ With this method, the yield effect of the multiple ion counters is eliminated. Nevertheless, in this earlier work,¹ some key parameters for the multipliers were not thoroughly set up, particularly the peak-alignments for the ion counters in different mass steps, the deflection and RPQ (retard potential quadrupole) parameters for the RPQ-SEM ion counter (IC1B), and the peak-centering setup during the Pb isotopic measurements. As a consequence, the internal analytical precision (RSE) for $^{207}\text{Pb}/^{206}\text{Pb}$ in a ^{205}Pb -NIST 981 mixture (containing ~50 pg of total Pb) can only achieve ~0.03% – 0.07%.¹ Collectively, the presented method is not very robust.

In this study, some key issues for the two-line dynamic multi-ion counting method using the ^{205}Pb -Pb MIC array were profoundly revisited. Consequently, better than 0.01% internal precision (RSE) on $^{207}\text{Pb}/^{206}\text{Pb}$ for 50 pg ^{205}Pb -spiked Pb loads was achieved, with ~100 min measurement time. Thus, the time-normalized internal precision is significantly improved compared to the traditional single SEM peak-jumping measurement method. Meanwhile, the external precision on $^{207}\text{Pb}/^{206}\text{Pb}$ was better than 0.1% (2RSD, $n = 24$). Therefore, the present work shows that the

^{205}Pb -Pb MIC array of the TRITON Plus TIMS can be used for high-precision zircon ID-TIMS U-Pb dating with great advantages, particularly is useful for samples containing extremely small amounts of Pb (down to several picograms).

INSTRUMENTATION

A Thermo Scientific Triton Plus thermal ionization mass spectrometer (TIMS), installed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), was employed for this study. The instrument was equipped with a multi-ion-counting (MIC) array, spaced for the simultaneous collection of ^{205}Pb -spiked Pb isotopes.¹ In this study, we named it the ^{205}Pb -Pb MIC array. The MIC system is configured with three SEM multipliers (IC1B, IC2-L5, IC3A) and two CDD ion counters (IC4, IC5). Among the ion counters, only the IC5, which is bonded to the Faraday Cup L4, can be slightly moved along with Faraday Cup L4. Other ion counters are fixed. In this study, only three SEMs and one CDD ion counter, IC5, were applied to determine the Pb isotopes of a ^{205}Pb -spiked Pb through a two-line dynamic collection method (Table 1). The dark noise of the ion counters is less than 5 counts/min.

Instrument setup. Primarily, the yield and dead time of the ion counters was set up using the method similar to that described in detail by Wang *et al.*¹ In brief, the yield of the ion counters was measured by switching a stable ~8 mV ^{208}Pb ion beam sequentially into the central Faraday cup, IC5, IC1B, IC2 and IC3A. Through the ratios of the ^{208}Pb measured by each ion counter to that determined by the center cup, the yield of each ion counter was obtained. In order to obtain optimum performance, it is necessary to ensure that the yield of each ion counter is greater than 90%. If the yield is smaller than 90%, the high voltage applied for the ion counter is ramped accordingly. Again, similar to that described in detail by Wang *et al.*,¹ dead time was determined by measuring the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of the NIST 981 standard for each ion counter by a peak jumping method at different intensities (e.g., ^{208}Pb ion beam at ~1, 2, 4, 8, 10 mV, respectively) to check the linearity. Accordingly, the dead time of each ion counter was obtained. The dead time was set to 16 ns for IC1 B, 15 ns for IC2, 15 ns for IC3 and 60 ns for IC5. In addition to the primary yield and dead time setup for the multipliers, in this study, some key issues were revisited for the instrument setup compared to Wang *et al.*¹ and is described in the following paragraphs.

Setup of the deflection and RPQ parameters for IC1B. First, the parameters for the SEM IC1B ion counter with RPQ were re-set up to improve peak flatness/width. In the first step, under a condition without the RPQ connection (i.e., removing RPQ by disconnecting the RPQ cables), the deflection voltage for IC1 B was fully tuned with a stable ^{207}Pb ion beam (~3 mV) to optimize the peak shape (peak width) and ion beam intensity. Subsequently, after re-connecting the RPQ to the SEM IC1, the suppressor

Table 1. TRITON PLUS TIMS MIC Configuration for ²⁰⁵Pb-spiked Pb Isotopic Measurement

Line	Axial masses*	IC4	IC3-A SEM	IC2-L5 (SEM)	RPQ/IC1-B (SEM)	IC5-L4 (CDD)	Integration time (s)	Idle time (s)	Dispersion Quad (V)	Peak-center control**
1	223.3	²⁰⁴ Pb	²⁰⁵ Pb	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	4.194	1	+16	²⁰⁶ Pb
2	222.3	²⁰³ Tl	²⁰⁴ Pb	²⁰⁵ Pb	²⁰⁶ Pb	²⁰⁷ Pb	4.194	1	+20	²⁰⁶ Pb

*Virtual masses corresponding to the center of the multi-collector system; **Ion beams used for inter-block peak centering during a sample measurement: in Line 1, the ion beam is centered using ²⁰⁶Pb detected by IC2; in Line 2, the ion beam is centered using ²⁰⁶Pb detected by IC1 B.

voltage of the RPQ was slightly tuned to further optimize the peak flatness. *Note: The 10 kV high voltage applied to the ion source must be powered off before connecting and disconnecting the RPQ cables.* After this modification, it was found that the IC1B peak shape significantly improved. After the deflection voltage and RPQ parameters of the IC1B are correctly set up, in general, it is unnecessary to re-tune it during the analytical sessions.

Setup of peak alignments for the MIC. Second, the peak alignment is particularly critical for the performance of the MIC system. In our primary work¹, the zoom dispersion quad voltage was set to zero, compromising for the multi-static collection data acquisition. Under this condition, however, the IC5, IC1B, IC2, IC3A were not aligned perfectly (not shown).

In this study, the peak alignment for the MIC, including IC1B, IC2, IC3A, was re-optimized by tuning the voltage of the Dispersion Quad of zoom optics using a stable ion beam obtained from a ²⁰⁵Pb-spiked NIST 981, with a ²⁰⁸Pb intensity of about 6 – 7 mV, for both Lines 1 and 2 sub-configurations. Subsequently, the IC5 peak alignment was optimized by slightly moving the L4 cup position. Finally, after the Dispersion Quad of zoom optics was set to 16 V for Line 1 and 20 V for Line 2 (Table 1), and the L4 cup position was set to 84.20 mm, a perfect peak alignment for the IC5, IC1B, IC2-L5 and IC3A ion counters was obtained for both Lines 1 and 2, as illustrated in Fig. 1.

Under such zoom optics settings, IC4 is not perfectly aligned (not shown), but it does not matter since IC4 was not used in the analytical protocol for this study.

In addition, the peak shape of the IC5 CDD multiplier is imperfect (Fig. 1), which is common for the CDD ion counter.⁴ Nevertheless, it is not important since IC5 just involves in the ²⁰⁸Pb/²⁰⁶Pb measurement, which is not critical, because ²⁰⁸Pb/²⁰⁶Pb is only used for Th/U estimation in the zircon for the ID-TIMS zircon U-Pb dating technique.

Peak-centering setup during the dynamic MIC Pb isotopic measurements. Third, since the ²⁰⁵Pb-Pb MIC ion counters are far from the center of the multi-collector system for the instrument, *i.e.* strongly off-axis, the MIC method is sensitive to mass calibration stability. Therefore, it is necessary to make sure that the ion beams of the Pb isotopes for each line can be fully placed into the corresponding ion counters. Consequently, peak centering must be performed prior to each block for using the ²⁰⁶Pb signal detected by IC2-L5 for Line 1 and IC1B for Line 2, respectively, during a measurement run, as shown in Table 1.

Fig. 1 Pb peak overlap using TRITON Plus TIMS ²⁰⁵Pb-Pb MIC array for mass step 1 (a) (zoom dispersion quad = 16 V) and mass step 2 (b) (zoom dispersion quad = 20 V). Mass scale is related to the center of the multi-collector system. Counter intensities are normalized to IC5 (~400 kcps) for (a) and IC1B (~200 kcps) for (b).

Mass spectrometric determination of Pb isotopes by MIC. The mass spectrometric determination method is also similar to that reported by Wang *et al.*¹ In brief, the sample was loaded onto a high-purity, zone-refined, single Re filament (0.77 mm wide and 0.038 mm thick; 99.999% purity; H. Cross) with silica-gel as an ion emitter.^{11,12} The Re filament was pre-degassed in a degas machine at 4.5 A for 40 min prior to use. The filament temperature for Pb ionization was about 1050 –1150 °C during the mass spectrometric measurements. Data were acquired in 10 blocks with 50 cycles per block (total of 500 cycles). The integration time was set to 4 s for each line, and the settling time between the mass steps was 1 s. A peak-center program was run for both mass steps using ²⁰⁶Pb as a pilot signal before each block to re-locate the ion beams into the ion counters (Table 1). In addition, the ion beam was fully re-focused every 5 blocks, using ²⁰⁶Pb⁺ ion beam

detected by the IC2 ion counter as a pilot signal. The filament current might be gently increased to maintain the signal intensity between blocks. Generally, the $^{208}\text{Pb}^+$ ion beam intensity was maintained to about 200–300 kcps for 50 pg NIST 981 throughout a sample measurement run. The total measurement time for a sample analysis is about 105 min.

Data reduction. Again, the data reduction protocol was similar to that reported by Wang *et al.*¹ as follows:

(1) The $^{207}\text{Pb}/^{206}\text{Pb}$ was calculated from ^{207}Pb measured by IC1 B in mass step 1 and ^{206}Pb measured by IC1 B in mass step 2, *i.e.*:

$$^{207}\text{Pb}/^{206}\text{Pb} = (^{207}\text{Pb})_{\text{Line1}} / (^{206}\text{Pb})_{\text{Line2}}$$

(2) The $^{205}\text{Pb}/^{206}\text{Pb}$ was calculated from ^{205}Pb measured by IC2 in mass step 2 and ^{206}Pb measured by IC2 in mass step 1, *i.e.*:

$$^{205}\text{Pb}/^{206}\text{Pb} = (^{205}\text{Pb})_{\text{Line2}} / (^{206}\text{Pb})_{\text{Line1}}$$

(3) The $^{208}\text{Pb}/^{207}\text{Pb}$ was calculated from ^{208}Pb measured by IC5 in mass step 1 and ^{207}Pb measured by IC5 in mass step 2, *i.e.*:

$$^{208}\text{Pb}/^{207}\text{Pb} = (^{208}\text{Pb})_{\text{Line1}} / (^{207}\text{Pb})_{\text{Line2}}$$

(4) The $^{208}\text{Pb}/^{206}\text{Pb}$ was calculated by the following equation:

$$^{208}\text{Pb}/^{206}\text{Pb} = (^{208}\text{Pb})_{\text{Line1}} / (^{207}\text{Pb})_{\text{Line2}} \times (^{207}\text{Pb})_{\text{Line1}} / (^{206}\text{Pb})_{\text{Line2}}$$

(5) The $^{204}\text{Pb}/^{205}\text{Pb}$ was calculated from ^{204}Pb measured by IC3A in mass step 2 and ^{205}Pb measured by IC3A in mass step 1, *i.e.*:

$$^{204}\text{Pb}/^{205}\text{Pb} = (^{204}\text{Pb})_{\text{Line2}} / (^{205}\text{Pb})_{\text{Line1}}$$

(6) The $^{204}\text{Pb}/^{206}\text{Pb}$ was calculated by the following equation:

$$^{204}\text{Pb}/^{206}\text{Pb} = (^{204}\text{Pb})_{\text{Line2}} / (^{205}\text{Pb})_{\text{Line1}} \times (^{205}\text{Pb})_{\text{Line2}} / (^{206}\text{Pb})_{\text{Line1}}$$

With this data reduction protocol, all of the isotopic ratios were determined by the same ion counter, thus yield calibration of the ion counters is not required during the mass spectrometric measurements.

RESULTS AND DISCUSSION

Analytical results for ^{205}Pb -spiked NIST 981. The MIC analytical protocol was first validated by analyses of the ^{205}Pb -spiked NIST 981. The use of ^{205}Pb -spiked NIST 981 is to demonstrate that the method is can be applied for Pb isotopic analysis of a ^{205}Pb -spiked Pb, as zircon ID-TIMS U-Pb isotopic analysis does. In the meantime, because $^{204}\text{Pb}/^{206}\text{Pb}$ is obtained through the formula $^{204}\text{Pb}/^{206}\text{Pb} = (^{204}\text{Pb})_{\text{Line2}} / (^{205}\text{Pb})_{\text{Line1}} \times (^{205}\text{Pb})_{\text{Line2}} / (^{206}\text{Pb})_{\text{Line1}}$, the method is only applicable to a ^{205}Pb -Pb mixture if $^{204}\text{Pb}/^{206}\text{Pb}$ is required to measure.

Under the operating conditions for this study, the Pb isotopic compositions of the ^{205}Pb -NIST 981 mixture as in Wang *et al.*¹ was re-determined. In brief, the mixture was produced by mixing 50 μL of 290 ng/g NIST981 solution and 500 μL of 9.22 nmol/g highly enriched ^{205}Pb spike. The isotopic abundances of ^{204}Pb ,

Table 2. Analytical Results for Pb Isotope Ratio of ^{205}Pb -spiked NSIT 981 Using MIC Multi-dynamic Method

	^{208}Pb (cps)	$^{207}\text{Pb}/^{206}\text{Pb}$	RSE (%)	$^{205}\text{Pb}/^{206}\text{Pb}$	RSE (%)	$^{208}\text{Pb}/^{206}\text{Pb}$	RSE (%)	$^{204}\text{Pb}/^{206}\text{Pb}$	RSE (%) ^a
1	1.68E+05	0.91396	0.012	0.23069	0.018	2.1705	0.018	0.05911	0.043
2	2.23E+05	0.91278	0.007	0.23016	0.012	2.1696	0.010	0.05917	0.025
3	3.35E+05	0.91411	0.006	0.23096	0.011	2.1719	0.010	0.05914	0.023
4	3.56E+05	0.91385	0.006	0.23104	0.010	2.1728	0.010	0.05915	0.022
5	4.31E+05	0.91379	0.008	0.23119	0.011	2.1753	0.013	0.05926	0.026
6	3.19E+05	0.91337	0.007	0.23134	0.011	2.1716	0.011	0.05925	0.023
7	2.39E+05	0.91343	0.007	0.23104	0.012	2.1720	0.010	0.05915	0.026
8	3.08E+05	0.91333	0.006	0.23129	0.010	2.1779	0.010	0.05920	0.023
9	2.03E+05	0.91291	0.007	0.23124	0.011	2.1668	0.010	0.05925	0.027
10	2.28E+05	0.91353	0.007	0.23170	0.015	2.1738	0.013	0.05934	0.027
11	2.52E+05	0.91383	0.007	0.23097	0.011	2.1724	0.011	0.05919	0.024
12	3.41E+05	0.91305	0.006	0.23101	0.009	2.1775	0.009	0.05928	0.021
13	1.83E+05	0.91362	0.008	0.23059	0.013	2.1707	0.012	0.05915	0.029
14	2.65E+05	0.91290	0.007	0.23106	0.011	2.1804	0.012	0.05924	0.025
15	2.14E+05	0.91352	0.007	0.23092	0.012	2.1688	0.010	0.05923	0.029
16	2.92E+05	0.91402	0.007	0.23086	0.010	2.1719	0.010	0.05916	0.023
17	2.58E+05	0.91307	0.007	0.23068	0.011	2.1703	0.011	0.05911	0.026
18	2.82E+05	0.91386	0.006	0.23110	0.010	2.1708	0.010	0.05922	0.025
19	3.44E+05	0.91413	0.006	0.23095	0.009	2.1697	0.009	0.05920	0.021
20	2.25E+05	0.91372	0.007	0.23084	0.012	2.1704	0.012	0.05918	0.025
21	2.43E+05	0.91419	0.007	0.23065	0.012	2.1688	0.011	0.05932	0.025
22	1.74E+05	0.91289	0.008	0.23056	0.013	2.1702	0.013	0.05912	0.029
23	1.23E+05	0.91382	0.009	0.23039	0.016	2.1731	0.014	0.05914	0.035
24	2.32E+05	0.91317	0.007	0.23032	0.013	2.1784	0.014	0.05916	0.026
Mean		0.91354		0.23090		2.1723		0.05920	
2SD ^b		0.00088		0.00070		0.0068		0.00013	
2RSD ^c		0.097		0.30		0.31		0.22	

^aRSE: relative standard error; ^bSD: standard deviation; ^cRSD: relative standard deviation.

^{205}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb in the ^{205}Pb spike are about 0.0046%, 99.85%, 0.0384%, 0.0308% and 0.0731%, respectively. The mixture was put into a clean Teflon beaker and thoroughly fluxed to ensure isotopic equilibration. About 2 μL of the ^{205}Pb -spiked NIST 981, corresponding to ~ 50 pg NIST 981, was loaded for the determinations. The analytical results are given in Table 2. It can be seen that better than 0.01% (RSE) internal precision and 0.1% external precision ($n=24$, 2RSD) on $^{207}\text{Pb}/^{206}\text{Pb}$ can be achieved. The internal and external analytical precision on $^{207}\text{Pb}/^{206}\text{Pb}$ by the MIC system used in this study is much better than that obtained in our previous work¹. This may be because some key issues were revisited for the instrument setup as described above. Therefore, we concluded that the thorough setup of the deflection voltage and the RPQ parameters of IC1B, peak-alignments for the multiple ion counters for the two mass steps, and peak-centering prior to each block during the mass spectrometric measurements are critical for the MIC system to obtain accurate and precise Pb isotopic data.

The internal precision on $^{205}\text{Pb}/^{206}\text{Pb}$ is $< 0.02\%$ (RSE), mostly around 0.01% (RSE), but the external precision is greater than 0.2% (close to 0.3%), which is much worse than that of $^{207}\text{Pb}/^{206}\text{Pb}$ ($< 0.1\%$). This is probably due to the loading blank effect, which could lead to the slight variability of the $^{205}\text{Pb}/^{206}\text{Pb}$ for different loads of the ^{205}Pb -spiked NIST 981. The loading blank was measured by a ^{205}Pb spike in this study. It is about 0.2-0.5 pg.

Better than 0.01% RSE internal precision on $^{207}\text{Pb}/^{206}\text{Pb}$ and close to 0.01% RSE internal precision on $^{205}\text{Pb}/^{206}\text{Pb}$, and better than 0.1% external precision (2RSD, $n=24$) on $^{207}\text{Pb}/^{206}\text{Pb}$ for 50 pg loads of ^{205}Pb -spiked NIST981 were achieved, indicating that the two-line dynamic MIC method has great potential for application to high-precision zircon ID-TIMS U-Pb isotopic analysis using a ^{205}Pb spike, for samples containing pg level Pb.

Comparisons of the MIC and the traditional single SEM method. In this study, the ^{205}Pb -spiked Pb was also analyzed with the traditional single SEM peak jump method for comparison, using an ion beam intensity and total measurement time similar to that for the MIC method. In brief, a measurement run for the single SEM method consisted of 8 blocks of data, and each block contained 25 cycles of data. The integration time was 8 s for ^{204}Pb and 4 s for the other Pb isotopes (^{205}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb). The settling time (idle time) between peak jumps was set to 1 s. A peak-center program was run every 4 blocks to relocate the ion beams of ^{204}Pb , ^{205}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb into the center ion counter, respectively. The ion current during sample analysis was kept at 90% to 110% of the intensity at the beginning of the data acquisition, using ^{208}Pb as the pilot signal through an inter-block filament heating action. The ^{208}Pb ion beam intensity was normally about 200 – 300 kcps throughout a measurement run. The ionization temperature during the SEM measurements was about 1100 – 1150 $^{\circ}\text{C}$. The total measurement time for each sample was about 108 min. The comparison of the analytical

Fig. 2 Comparison of analytical results for $^{207}\text{Pb}/^{206}\text{Pb}$ of ^{205}Pb -spiked NIST981 with different measurement methods using TRITON PLUS TIMS. MIC means determination by MIC method; Center SEM PJ means determination by the single center SEM with a peak jumping method. The solid line represents the mean, and the dotted lines represent a range of mean $\pm 2\text{SD}$

results of $^{207}\text{Pb}/^{206}\text{Pb}$ with the single SEM and MIC is illustrated in Fig. 2. It can be seen that the internal analytical precision on $^{207}\text{Pb}/^{206}\text{Pb}$ with the MIC method is about 2 times better than that obtained by the single SEM peak-jump method, provided with similar ion beam intensity and measurement time for the two kinds of measurement methods. This is because the ion beam collection efficiency with the MIC method improved ~ 2.5 times compared to the single SEM peak-jumping method.

However, it was found that the external precision on $^{207}\text{Pb}/^{206}\text{Pb}$ with the MIC method is not significantly improved compared to that obtained by the single SEM (IC1 C) peak jumping method. The reason remains unclear, but is probably due to the fact that the external precision is mainly controlled by the isotope fractionation effect for the Pb isotope analysis.^{13,14} As known, the Pb isotope fractionation effect cannot be corrected by an internal normalization method due to the lack of two non-radiogenic isotope ratios (only ^{204}Pb is un-radiogenic), unless a double spike is used.¹³⁻¹⁷ Since no internal isotope fractionation correction can be made, we will further optimize the measurement conditions (e.g., sample loading, filament heating) to control the degree of fractionation to improve the external analytical precision in the future.

Nevertheless, no significant improvement of the external precision is also likely because the MIC system is strongly off-axis, and thus too many ion beam deflections are involved with the MIC method, particularly for the ion counter IC1B. This problem needs to be further addressed in the future.

In addition, it was found that a good positive correlation between the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for the single SEM (not shown), indicating an isotope fractionation effect. Nevertheless, no such correlation can be observed from the results obtained by the MIC method. This is probably due to the problem that the ^{208}Pb

was measured by the CDD-IC5, which has a poor peak shape (Fig. 1) and thus gives less precise data for $^{208}\text{Pb}/^{206}\text{Pb}$.

The internal precision on $^{205}\text{Pb}/^{206}\text{Pb}$ for the MIC method is about 2 times better than that of the single SEM peak jumping method. Nevertheless, the external precision for the two kinds of determination methods is similar. This is likely, because the $^{205}\text{Pb}/^{206}\text{Pb}$ is slightly variable for different loads due to the loading blank effect, as mentioned above.

CONCLUSIONS

Isotopic analysis for ^{205}Pb -spiked Pb with the ^{205}Pb -Pb MIC array in TRITON Plus TIMS, using a two-line dynamic data collection method to completely eliminate the yield effect for the multiple ion counters, was thoroughly re-evaluated. After the critical parameters for the ^{205}Pb -Pb MIC array were fully re-setup, the analytical precision on $^{207}\text{Pb}/^{206}\text{Pb}$ for 50 pg ^{205}Pb -spiked Pb improved to better than 0.01% RSE. This is much better than that we obtained in our previous work¹, which gave ~ 0.02-0.03% RSE analytical precision. Meanwhile, the external precision on $^{207}\text{Pb}/^{206}\text{Pb}$ was better than 0.1% (2RSD, n = 24). The critical parameters mainly include zoom dispersion quad voltages for the peak alignments in the two-line data collection, the deflection voltage and RPQ parameters for the IC1B SEM ion counter, and the peak-centering setup during the mass spectrometric measurement. Compared to the traditional single SEM peak jumping measurement method, the time-normalized internal analytical precision on $^{207}\text{Pb}/^{206}\text{Pb}$ for ^{205}Pb -spiked NIST 981 improved ~ 2 times with the two-line dynamic MIC method; however, the external precision on $^{207}\text{Pb}/^{206}\text{Pb}$ for ^{205}Pb -spiked NIST 981 is not significantly improved, and the reason still needs to be further addressed. Our results indicate that the two-line dynamic MIC method has great potential for application to high-precision Pb isotopic analysis for ID-TIMS U-Pb dating, particularly for zircons containing only several picograms of Pb.

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Notes

The authors declare no competing financial interest.

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