

Practical application of lead triple spiking for correction of instrumental mass discrimination

S. J. G. Galer
W. Abouchami

Max-Planck-Institut für Chemie, Postfach 3060, D-55020 Mainz,
Germany

The external precision of Pb isotope ratio measurements by TIMS is currently limited to ~0.1% due to variations in instrumental mass discrimination. It was shown by Dodson (1963) that the unknown mass discrimination factor could be obtained from a second measurement on an aliquot of a sample to which a double spike has been added. From the three isotope ratios measured on the two runs it is straightforward to solve for the three unknowns – the respective fractionation factors of the two runs and the spike/sample ratio.

Practical applications of the Pb double spike technique have used a mixed ^{207}Pb - ^{204}Pb tracer in the ratio ~9:1 (e.g. Hamelin *et al.*, 1985; Woodhead *et al.*, 1995). These studies have demonstrated that a factor of up to ~3 improvement in external precision can be obtained compared with good conventional, uncorrected measurements. Further, any systematic errors arising from matrix effects are effectively eliminated using the technique (Woodhead *et al.*, 1995). Slightly more favourable results have been obtained by using a double spike composed of the non-natural isotopes ^{205}Pb - ^{202}Pb (Todt *et al.*, 1996), which has the added advantage that only one mass spectrometric run is required; a disadvantage, ignoring the cost of these spikes, though, is that isobaric interferences on these masses must be continually monitored and corrected for during measurement.

A systematic survey of stable isotope tracer compositions, axis combinations and mathematical solutions to this problem was recently undertaken by Galer (1997). From this study, there appears to be an optimal composition to use as a spike to correct samples of common Pb for instrumental mass fractionation. This spike composition (designated here as TS) is unusual in that it is a mixture of three stable isotopes of lead – ^{207}Pb - ^{206}Pb - ^{204}Pb – rather than just two, ^{207}Pb - ^{204}Pb , used in previous studies.

The error magnification factor γ on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio (i.e. the bias-corrected error relative to the measured, unspiked internal error) was estimated by Galer (1997) using a realistic error propagation

model based upon the ion statistical uncertainties on the two runs and the TS composition. For the optimized TS composition, γ lies at ~1.2 over a large range in spike/sample ratios, becoming larger than 2.0 only when the spike/sample ratio is less than 0.05 or greater than 3.8. This implies that when preparing the TS-sample mixture, the quantity of Pb in the sample need only be known to within a factor of ~40 either way to avoid an unfavourable $\gamma > 2$. This behaviour is in sharp contrast to that of the ^{207}Pb - ^{204}Pb double spikes that have been used previously, which never have $\gamma < 2$ for any spike/sample ratio. Such double spikes as these, even in the most favourable cases, require internal precisions on the individual runs a factor of ~2 better to achieve the same final precision as the TS – in effect, measurement times (or sample sizes) would need to be a factor of ~4 larger.

In order to see how such an optimal triple spike would perform in practise, a tracer of TS composition was prepared and subjected to a number of tests to evaluate its performance. All Pb isotopic measurements were performed in static multi-collection mode on a Finnigan MAT-261. Inter-cup efficiency biases were determined by simplex minimization from measurements of the NBS-982 equal-atom Pb standard. The TS itself was calibrated by joint runs of the triple spike alone and mixtures in varying proportions with the NBS-982 standard – the mass bias-corrected TS isotopic composition can then be obtained by solving the equations with the TS as the 'unknown' (cf. Hamelin *et al.*, 1985). Thus, any isotopic compositions determined using the TS are traceable to the NBS-982 Pb isotopic composition of Todt *et al.* (1996) which, in turn, was normalized to a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of 1.00016.

The first test of the triple spike was measurement of the NBS-981 common lead standard, whose isotopic composition has recently been redetermined by Todt *et al.* (1996). Samples of NBS-981 were mixed with TS in a large range of spike/sample ratios and combined with unspiked runs to yield fractionation-corrected ratios for NBS-981. To improve in-run

TABLE 1. Measurements of the NBS-981 Pb standard

$^{206}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$ (ppm)	$^{207}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$ (ppm)	$^{208}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$ (ppm)
Hamelin <i>et al.</i> (1985), N = 20 16.9403 \pm 0.0054 (319)	15.4956 \pm 0.0080 (516)	36.7176 \pm 0.0215 (586)
Woodhead <i>et al.</i> (1996), N = 109 16.937 \pm 0.0040 (236)	15.492 \pm 0.0048 (310)	36.708 \pm 0.0128 (349)
Todt <i>et al.</i> (1996), N = 11 16.9356 \pm 0.0024 (146)	15.4891 \pm 0.0030 (200)	36.7006 \pm 0.0114 (300)
This study, N = 60 16.9405 \pm 0.0015 (90)	15.4963 \pm 0.0016 (103)	36.7219 \pm 0.0044 (120)

All ratios normalized to $^{208}\text{Pb}/^{206}\text{Pb}$ of 1.00016 for NBS-982.

uncertainties, all data were normalized to the first block of data collected. Internal errors on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio were 0.0005–0.0009 and propagated errors on the bias-corrected ratios, following the matrix methodology of Hamelin *et al.* (1985), averaged 0.0009. Thus, the error magnification factors γ appear to be in good agreement with those estimated by Galer (1997). Importantly, the individual corrected data do not correlate with the spike/sample ratio of the mixtures used, indicating that there are no systematic errors associated with calibration of the TS. The unweighted means and 2σ of the population are reported in Table 1. External uncertainties on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio are ± 0.0015 absolute or 90 ppm in relative terms at the 2σ level, an order of magnitude superior to conventional, uncorrected data and a factor of ~ 2 better than has been achieved before using the double spike technique (Table 1). The corresponding errors for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are better still – 0.914750 \pm 35 (38 ppm) and 2.16771 \pm 10 (44 ppm), respectively – approaching the external reproducibility possible for conventional, normalized Sr and Nd isotope measurements. Given that the sample sizes used for the unspiked NBS-981 runs were 5–15 ng Pb, it appears that the principal source of residual error is internal, arising from measurement of the minor ^{204}Pb peak, and can probably be improved further by an increase in sample size.

So far, Pb isotopic compositions of approximately

sixty samples have been measured using the triple spike method (Abouchami *et al.*, 1997 and this volume). Since the technique can be seriously compromised by differential blank contribution between the unspiked and spiked aliquots, the sample-TS mixtures were prepared after chemical separation of the Pb, as suggested by Hamelin *et al.* (1985). Based upon duplicate runs for 16 samples, external reproducibilities on $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are ± 90 ppm, ± 120 ppm and ± 140 ppm, respectively, and are comparable to those obtained for the NBS-981 standard (Table 1). Thus, the triple spike technique seems to be a cheap, viable and relatively easy method of obtaining Pb isotopic data with external precisions of ~ 100 ppm.

References

- Abouchami, W., Galer, S.J.G. and Koschinsky, A. (1997) *Eos, AGU 1997 Fall Meeting*, **78** (46), F-378.
- Dodson, M.H. (1963) *J. Sci. Instrum.*, **40**, 289–95.
- Galer, S.J.G. (1997) *Terra Nova*, **9**, 441.
- Hamelin, B., Manhès, G., Albarède, F. and Allègre, C.J. (1985) *Geochim. Cosmochim. Acta* **49**, 173–82.
- Todt, W., Cliff, R.A., Hanser, A. and Hofmann, A.W. (1996) in: *Geophys. Monogr.* **95**, 429–437, American Geophys. Union.
- Woodhead, J.D., Volker, F. and McCulloch, M.T. (1995) *Analyst*, **120**, 35–39.