

Strontium, Neodymium and Lead Isotope Analyses of NIST Glass Certified Reference Materials: SRM 610, 612, 614

Jon D. **Woodhead** and Janet M. **Hergt**

School of Earth Sciences, The University of Melbourne, Melbourne, VIC 3010, Australia.
e-mail: jdwood@unimelb.edu.au, jhergt@unimelb.edu.au

The NIST glass certified reference materials, SRM 610-617, have been widely adopted by the geological community as calibration samples for a variety of *in situ* trace element analytical techniques. There is now an urgent requirement for similar reference materials for *in situ* isotopic analytical techniques. We have analysed SRM 610, 612 and 614 for their Pb, Sr and Nd isotopic compositions using thermal ionisation mass spectrometry. Large differences in isotopic composition were observed between each CRM, suggesting a significant trace element content in the initial starting material (base glass). As a result, isotopic compositions for one CRM cannot be extrapolated to another, and each must be calibrated for use independently. We present the first compilation of working values for these glasses.

Keywords: NIST, SRM 610-614, glass, isotope analysis, compilation, working values.

Les matériaux de référence suivants, verres NIST, SRM 610-617, ont été largement adoptés par la communauté géologique comme standard pour un grand nombre de techniques analytiques in situ d'éléments en traces. Il y a maintenant un besoin urgent de matériaux de référence similaires pour les analyses isotopiques in situ. Nous avons analysé les compositions isotopiques du Pb, Sr et Nd dans SRM 610, 612 et 614 par spectrométrie de masse à thermoionisation. Des différences importantes ont été observées entre chaque matériau certifié de référence, suggérant une teneur en éléments traces significative dans le matériau de départ (verre). Les compositions isotopiques pour un matériau certifié de référence donné, en tant que résultats, n'ont pu être extrapolées à un autre matériau, chacun devant être étalonné indépendamment. Nous présentons la première compilation de données de travail pour ces verres.

Mots-clés : NIST, SRM 610-614, verre, analyse isotopique, compilation, données de travail.

In recent years the rapid proliferation of analytical techniques capable of *in situ* isotopic analysis (e.g. secondary ion mass spectrometry, SIMS and laser ablation, multi-collector inductively coupled plasma mass spectrometry, LA-MC-ICP-MS) has led to an urgent requirement for suitable standard reference materials. In the long-term, it is envisaged that many different “matrix matched” CRMs will be available. Such CRMs will need to be widely available, homogeneous within error of a typical analysis, and well characterized. As a first approach to this problem we have analysed the well-known NIST certified reference glasses SRM 610, 612, and 614 for Sr, Nd, Pb isotopic compositions, using well-proven thermal ionisation mass spectrometry (TIMS) techniques. The results of this study should also be directly applicable to the

complementary glass CRMs, SRM 611, 613, and 615, which were prepared from the same starting material (see below).

Although there are sporadic references in the literature to individual Pb isotope analyses of the NIST SRM 610 glass (e.g. Walder *et al.* 1993), it was decided to undertake a more detailed study using the “state-of-the-art” double spike analysis to provide the highest quality data possible. Furthermore, this technique provides direct traceability to the well known pure element standard NIST SRM 981, since the double spike is itself calibrated by reference to this material.

In addition to the Pb data, Sr and Nd isotope analyses are presented for each of these glasses as part of

the current study. While this may seem an unusual decision given the high concentrations of interfering elements (i.e. Rb, Sm etc.) present in these glasses, the philosophy behind this decision is straightforward. A number of new techniques (particularly MC-ICP-MS but also, for example, the accelerator-based AUSTRALIS project, Sie *et al.* 2000) have the potential to correct isotopic analyses for major isobaric interferences. In the case of MC-ICP-MS, this ability results from the fact that, to a first approximation, mass bias within the plasma source is a simple function of mass, hence instrument-induced isotopic fractionation measurements on one element can be used to correct the bias experienced by another (e.g. Halliday *et al.* 1995). While this initial assumption now appears to be oversimplified (i.e. there are significant elemental fractionation effects occurring in plasma instruments, e.g. Maréchal *et al.* 1999, White *et al.* 2000), it is entirely reasonable to expect that within the next few years, protocols will be developed for *in situ* Sr and Nd isotope analysis in the presence of high concentrations of Rb and Sm (indeed our own preliminary experiments with MC-ICP-MS suggest this is entirely possible). Since the determinations presented here were conducted on chemically separated Sr and Nd, the results provide an excellent control on the validity of interference corrections developed for MC-ICP-MS (and other) techniques. In this case, traceability to the well known NIST SRM 987 Sr and La Jolla Nd reference materials is provided.

History of development

The NIST (originally NBS) glass certified reference materials, SRM 610-617, were never intended as standards for *in situ* analysis, being instead developed as reference materials for bulk analysis in the glass industry. In the absence of other suitable CRMs, however, they are now almost universally employed for this purpose. The history of development and certification of the NIST glasses has been documented in some detail by Kane (1998a), and only a brief overview is presented here. The glasses were prepared by the Corning Glass Works from a single soda-lime glass support matrix. This base glass was prepared from high purity sand, alumina, soda ash and calcium carbonate, and then four additional glasses were manufactured by spiking the base with sixty one trace elements to nominal concentrations of 500, 50, 1.0, and 0.02 $\mu\text{g g}^{-1}$. These products are designated SRMs 610-611, 612-613, 614-615, 616-617 respectively (within each concentration range two CRMs are available, differing only in the thickness of the wafer supplied); the unspiked glass

was not issued as a reference material. For the two most concentrated glasses, appropriate masses of the base glass and spiking compounds were mixed and melted together (e.g. 97 kg base glass plus 3.05 kg trace components for SRMs 610-611) while, for the two lowest levels, spiking was achieved by serial dilution of base glass (e.g. 100 kg base glass with 6.1 g trace components for SRMs 614-615). As a result of this process, and the fact that trace components were added as oxides, carbonates and sulfates, the original support matrix composition changes considerably between the different series of glasses.

Initial certification was achieved for only a few of the original trace components of the glass (Reed 1991), although subsequent analyses by many groups have documented homogeneity for most elements at a variety of analytical scales and between wafers (e.g. Hinton 1999, Hinton *et al.* 1995, Kane 1998b, Norman *et al.* 1996, Rocholl *et al.* 1997). In contrast, isotopic measurements are much rarer, as discussed later.

Experimental

Individual glass buttons were crushed into small (ca. 1 mm) fragments using an agate pestle and mortar. From each glass crush, four aliquots of chips (ranging from 10 mg for the SRM 610 glass to 300 mg for the SRM 616 glass) were weighed and dissolved separately in closed Teflon vessels using a HF/HNO₃ mixture at 150 °C. After taking to dryness, samples were then refluxed with 6 mol l⁻¹ HCl at 150 °C, dried once again, and then taken up in 0.6 mol l⁻¹ HBr prior to loading on columns.

Lead was separated by conventional anion exchange procedures on micro-columns containing BioRad AG 1-X8 (200-400 mesh) resin and using 2 column passes in HBr/HCl media, with the column eluate being retained for subsequent separation of Sr and Nd. Strontium and a bulk REE fraction were separated by conventional cation exchange chemistry in HCl media using BioRad AG50W-X8 (200-400 mesh) resin. Neodymium was further separated from the bulk REE's using di-(2-ethylhexyl)-orthophosphoric acid (HDEHP) adsorbed on a Teflon substrate. Total procedural blanks measured concurrently with the samples were in all cases insignificant (e.g. Pb was always less than 100 pg); consequently no blank corrections have been made.

All samples were analysed on a Finnigan MAT 262 mass spectrometer operated in static multicollection

mode, with total ion currents typically in the range 3–6 volts, measured across a $10^{11} \Omega$ resistor. Samples for Pb were loaded on single rhenium filaments using a silica gel/phosphoric acid emitter, with Sr and Nd loaded on single tantalum and double rhenium-tantalum filaments respectively.

All Pb isotope analyses were corrected for instrumental mass fractionation effects by the use of a ^{207}Pb - ^{204}Pb double spike procedure, which effectively simulates the presence of a non-radiogenic isotope pair. Considerable literature now exists on the use of the double spike technique (e.g. Hamelin *et al.* 1985, Woodhead *et al.* 1995, Todt *et al.* 1996, Woodhead and Hergt 1997, Powell *et al.* 1997, Galer 1999, Thirlwall 2000) and these discussions will not be re-iterated here. Suffice it to say that the aforementioned studies have all demonstrated that considerable improvements in precision and accuracy over conventional analyses are obtained by the use of a double spike method. In addition, our double spike is itself calibrated by analysis of variable admixtures of spike and SRM 981 and, thus, provides direct traceability to the NIST reference materials. A slight complication in the latter arises since, in recent years, a number of new determinations of the composition of SRM 981 have been presented (e.g. Todt *et al.* 1996, Galer 1999, Thirlwall 2000). However, these determinations are not all in agreement and, in some cases involve a certain circularity of reasoning, being based upon an assumed composition for the NIST SRM 982. To a first approximation, all determinations appear to lie on a single (?mass fractionation) line but, until there is widespread agreement upon preferred values for the SRM 981, we have chosen not to adopt any particular preference. Consequently, all our analyses are reported relative to the following values for SRM 981, which were used in the calibration of our double spike (Woodhead *et al.* 1995): $^{206}\text{Pb}/^{204}\text{Pb} = 16.937$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.491$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.700$. These are the values of Catanzaro *et al.* (1968) but, in agreement with many other laboratories, we adopt a lower value for the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio (in this case from Richards 1986), rather than the certified value which appears too high in comparison with other measured ratios. These values are within error of those presented by Todt *et al.* (1996), but it is a relatively simple matter for the reader to renormalise our data to their own preferred values for SRM 981 if necessary. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ respectively.

When used optimally, the ^{207}Pb - ^{204}Pb double spike produces relative uncertainties (when propagated through the spike unmixing equations) on individual analyses of the order of 0.0001, (i.e. 0.01% (Powell *et al.* 1997). Errors reported for the Sr and Nd isotope determinations are ± 2 standard error within-run precision.

Results and discussion

Results for NIST glasses and isotopic reference materials run concurrently are provided in Table 1. Multiple analyses (including chemistry) of individual aliquots of each NIST SRM are extremely reproducible, demonstrating isotopic homogeneity at the scale of sampling, which is to be expected given the glassy nature of these reference materials, and literature studies suggesting trace element homogeneity (e.g. Hinton 1999). Whether the NIST SRMs are homogeneous on other scales, particularly the microscale, is a question beyond the scope of the present paper.

There are, however, significant differences in isotopic composition between each CRM. Arrays in isotope-isotope space suggest a simple mixing relationship exists between each CRM series. Assuming homogeneous (and identical) starting materials for each CRM, these observations are entirely consistent with the original starting material (base glass) containing a significant level of certain trace elements, being progressively doped with further trace elements to produce the final range in reference materials (Figure 1). The effect is most noticeable for the Pb and Sr systems; for Nd, there is some hint that the 614 CRM may have a lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, but this is still within error of the 610 and 612 results.

In this context, it is important to note that early attempts to obtain isotope dilution Sr analyses for these materials concluded that the original base glass must have contained approximately $50 \mu\text{g g}^{-1}$ of Sr (Moore *et al.* 1973). The results of our calculations (see caption to Figure 1) are consistent with this ($45 \mu\text{g g}^{-1}$ Sr) and would also suggest that the base glass in addition contained a significant concentration of Pb ($1.5 \mu\text{g g}^{-1}$). This is clearly illustrated by the mixing curves presented in Figure 1. While such a conclusion is not surprising, it does require that each CRM must be fully characterized independently before use.

Table 2 shows the comparison between our new data and existing literature analyses for the NIST SRMs. Of these, Sr isotope data are available for all

Table 1.
Isotope data for NIST glasses SRM 610, 612, 614

Measured/calculated ratios					
Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$
610-1	17.047	15.509	36.976	0.709698 ± 14	0.511925 ± 8
610-2	17.048	15.509	36.974	0.709709 ± 14	0.511925 ± 7
610-3	17.046	15.509	36.975	0.709688 ± 13	0.511929 ± 8
610-4	17.046	15.510	36.973	0.709702 ± 13	0.511927 ± 8
612-1	17.092	15.508	36.995	0.709066 ± 15	0.511932 ± 8
612-2	17.094	15.511	37.001	0.709064 ± 15	0.511928 ± 7
612-3	17.095	15.509	36.998	0.709073 ± 15	0.511929 ± 6
612-4	17.094	15.512	37.006	0.709049 ± 15	0.511930 ± 8
614-1	17.842	15.536	37.484	0.708370 ± 15	0.511918 ± 8
614-2	17.829	15.533	37.471	0.708373 ± 14	-
614-3	17.827	15.528	37.458	0.708348 ± 13	0.511923 ± 8
614-4	17.833	15.533	37.473	0.708361 ± 14	0.511920 ± 6
Calibration standards*	16.935	15.492	36.703	0.710262 ± 14	0.511888 ± 8
	16.935	15.492	36.701	0.710291 ± 17	0.511864 ± 6
Recommended values					
Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$
610-1	17.047	15.509	36.975	0.709699	0.511927
610-2	(0.0018)	(0.0010)	(0.0026)	(0.000018)	(0.000004)
610-3	-	-	-	-	-
610-4	-	-	-	-	-
612-1	17.094	15.510	37.000	0.709063	0.511930
612-2	(0.0026)	(0.0036)	(0.0094)	(0.000020)	(0.000004)
612-3	-	-	-	-	-
612-4	-	-	-	-	-
614-1	17.833	15.533	37.472	0.708363	0.511920
614-2	(0.0134)	(0.0066)	(0.0214)	(0.000022)	(0.000006)
614-3	-	-	-	-	-
614-4	-	-	-	-	-

Pb-isotope data are calculated values after double spike deconvolution. Errors on individual Sr and Nd isotope data are ± 2 SE within-run precision. Figures in brackets represent 2 SD of the recommended (mean) values.

* Calibration standards are NIST SRM 981 (Pb), SRM 987 (Sr) and La Jolla (Nd).

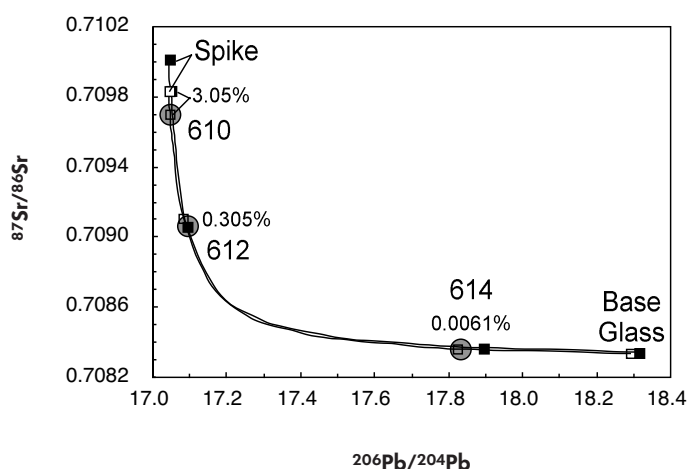


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ isotope diagram illustrating compositional relationships between SRMs 610, 612 and 614 determined from this study (shaded circles) relative to hypothetical mixing trajectories between the original base glass and trace element spike. The two mixing curves were calculated using our own isotope data, concentration data reported by Reed (1991) and the base glass/trace element spike mixing proportions reported by Kane (1998a) for these CRMs. Unfortunately, these data are not perfectly internally consistent, possibly reflecting variable loss of spike or base glass during manufacture. Consequently we show two slightly different mixing curves; one assumes that the mixing proportions for SRMs 610 (3.05%) and 614 (0.0061%) are correct (open squares), and the other that those reported for SRMs 612 (0.305%) and 614 are correct (filled squares). Calculations combining SRMs 610 and 614 produce negative Pb concentrations in the base glass and thus are not reproduced here.

Table 2.
Comparative isotope data for NIST glasses SRM 610, 612, 614

	SRM 610	SRM 612	SRM 614
²⁰⁶Pb/²⁰⁴Pb			
This study	17.047 ± 0.0018	17.094 ± 0.0026	17.833 ± 0.0134
Walder <i>et al.</i> (1993)	17.049 ± 0.012	-	-
Machado and Gauthier (1996)	17.064 ± 0.007	-	-
²⁰⁷Pb/²⁰⁴Pb			
This study	15.509 ± 0.0010	15.510 ± 0.0036	15.533 ± 0.0066
Walder <i>et al.</i> (1993)	15.506 ± 0.010	-	-
Machado and Gauthier (1996)	15.525	-	-
²⁰⁸Pb/²⁰⁴Pb			
This study	36.975 ± 0.0026	37.000 ± 0.0094	37.472 ± 0.0214
Walder <i>et al.</i> (1993)	36.989 ± 0.024	-	-
Machado and Gauthier (1996)	37.046	-	-
⁸⁷Sr/⁸⁶Sr			
This study	0.709699 ± 0.000018	0.709063 ± 0.000020	0.708363 ± 0.000022
Reed (1991)	0.7094 ± 0.0002	0.7089 ± 0.0002	0.7083 ± 0.0002
Reed (1991) re-normalised*	0.7095	0.7090	0.7084

* NIST values re-normalised to the standard value (⁸⁷Sr/⁸⁶Sr = 0.710275) reported in this paper. Assumes a NIST value of ⁸⁷Sr/⁸⁶Sr = 0.71014 for SRM 987, from Moore *et al.* (1973). Errors quoted on the literature Pb data are reported as 2s, although it is not clear from either publication whether this represents internal or external precision.

CRMs from the certification sheets (Reed 1991), and Pb isotope analyses only for SRM 610 (there are no previous Nd isotope data for any of these materials). Our Sr isotope analyses show reasonable agreement with values provided by Reed (1991) in the NIST certification sheets, although the new data are characterized by a much higher level of precision and accuracy, being the product of multi-collector TIMS analysis. Furthermore, our Pb isotope analyses are also in excellent agreement with the data presented by Walder *et al.* (1993), based upon analyses by N. Belshaw (personal communication, 1991). The data of Machado and Gauthier (1996) are just outside the reported analytical errors of our analyses but the differences observed between the two are consistent with instrumental mass fractionation effects. Since the double spike technique generally provides a more efficient control of mass bias than conventional TIMS procedures, we recommend the values reported in this publication be adopted as preferred values.

Conclusions

We report Pb, Sr and Nd isotopic analyses of the NIST glass CRMs, as a first approach to providing suitable reference materials for *in situ* isotopic analysis by a variety of analytical techniques such as SIMS and MC-ICP-MS. All appear to be homogeneous at the

sampling volumes and levels of analytical precision obtainable with current TIMS instrumentation but significant differences in isotopic composition were observed between each series of reference samples. This observation is easily explained by a significant (non-zero) abundance of Sr, Pb (and possibly Nd) in the original base glass starting product. As a result, it is not possible to extrapolate, for example, isotopic values for SRM 610 to SRMs 612 and 614. Based upon these analyses, working values are provided for the Pb, Sr, and Nd isotopic compositions of the NIST SRM 610, 612, and 614 glasses.

References

Catanzaro E.J., Murphy T.J., Shields W.R. and Garner E.L. (1968)

Absolute isotopic abundance ratios of common, equal-atom, and radiogenic lead isotopic standards. *Journal Resources of the National Bureau of Standards*, 72A, 261-267.

Galer S.J.G. (1999)

Optimal double and triple spiking for high precision lead isotope measurement. *Chemical Geology*, 157, 255-274.



references

Halliday A.N., Lee D.-C., Christensen J.N., Walder A.J., Freedman P.A., Jones C.E., Hall C.M., Yi W. and Teagle D. (1995)

Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes*, 146/147, 21-33.

Hamelin B., Manhès G., Albarède F. and Allègre C.J. (1985)

Precise lead isotope measurements by the double spike technique: A reconsideration. *Geochimica et Cosmochimica Acta*, 49, 173-182.

Hinton R.W. (1999)

NIST SRM 610, 611 and SRM 612, 613 multi-element glasses: Constraints from element abundance ratios measured by microprobe techniques. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 23, 197-207.

Hinton R.W., Harte B. and Witt-Eichschen G. (1995)

Ion probe measurements of National Institute of standards and technology standard reference material SRM 610 glass, trace elements. *The Analyst*, 120, 1315-1319.

Kane J.S. (1998a)

A history of the development and certification of NIST glass SRMs 610-617. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 22, 7-13.

Kane J.S. (1998b)

An assessment of the suitability of NIST glass SRM literature data for the derivation of reference values. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 22, 15-31.

Machado N. and Gautier G. (1996)

Determination of $^{207}\text{Pb}/^{206}\text{Pb}$ ages on zircon and monazite by laser-ablation ICP-MS and application to a study of sedimentary provenance and metamorphism in southeastern Brazil. *Geochimica et Cosmochimica Acta*, 60, 5063-5073.

Maréchal C.N., Télouk P. and Albarède F. (1999)

Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, 156, 251-273.

Moore L.J., Moody J.R., Barnes I.L., Gramlich J.W., Murphy T.J., Paulsen P.J. and Shields W.R. (1973)

Trace determination of rubidium and strontium in silicate glass standard reference materials. *Analytical Chemistry*, 45, 2384-2487.

Norman M.D., Pearson N.J., Sharma A. and Griffin W.L. (1996)

Quantitative analysis of trace elements in geological materials by laser ablation ICP-MS: Instrumental operating conditions and calibration values of NIST glasses. *Geostandards Newsletter*, 20, 247-261.

Powell R., Woodhead J.D. and Hergt J.M. (1997)

Uncertainties on lead isotope analyses: Deconvolution in the double spike method. *Chemical Geology*, 148, 95-104.

Reed W.P. (1991)

Certificates of analysis for SRMs 610-611; 612-613; 614-615; 616-617 (revised). National Institute of Standards and Technology (Gaithersburg, USA).

Richards J.R. (1986)

Lead isotopic signatures: Further examination of comparisons between South Africa and Western Australia. *Transactions of the Geological Society of South Africa*, 89, 285-304.

Rocholl A.B.E., Simon K., Jochum K.P., Bruhn F., Gehann R., Kramar U., Luecke W., Molzahn M., Pernicka E., Seufert M., Spettel B. and Stummeier J. (1997)

Chemical characterisation of NIST silicate glass certified reference material SRM 610 by ICP-MS, TIMS, LIMS, SSMS, INAA, AAS and PIXE. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 21, 101-114.

Sie S.H., Sims D.A., Niklaus T.R., Bruhn F. and Suter G.F. (2000)

AUSTRALIS: A new tool for isotope geology. In: Woodhead J.D., Hergt J.M. and Noble W.P. (eds), *Abstracts and Proceedings of the Beyond 2000: New Frontiers in Isotope Geoscience conference*, Lorne, Australia. Eastern Press (Melbourne, Australia).

Thirlwall M.F. (2000)

Inter-laboratory and other errors in Pb-isotope analyses investigated by using a ^{207}Pb - ^{204}Pb double spike. *Chemical Geology*, 163, 299-322.

Todt W., Cliff R.A., Hanser A. and Hofmann A.W. (1996)

Evaluation of a ^{202}Pb - ^{205}Pb double spike for high-precision lead isotope analysis. In: A. Basu and S.Hart (eds), *Earth Processes: reading the isotopic code*. American Geophysical Union Geophysical Monograph, 95, 429-437.

Walder A.J., Abell I.D., Platzner I. and Freedman P.A. (1993)

Lead isotopic measurement of NIST 610 glass by laser ablation inductively coupled plasma-mass spectrometry. *Spectrochimica Acta*, 48B, 397-402.

White W.M., Albarède F. and Télouk P. (2000)

High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. *Chemical Geology*, 167, 257-270.

Woodhead J.D. and Hergt J.M. (1997)

Application of the "double spike" technique to Pb-isotope geochronology. *Chemical Geology*, 138, 311-321.

Woodhead J.D., Volker F. and McCulloch M.T. (1995)

Routine lead isotope determinations using a ^{207}Pb - ^{204}Pb double spike: A long-term assessment of analytical precision and accuracy. *The Analyst*, 120, 35-39.