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Lead Isotope Determinations by Mass Spectrometry and Its Application by Isotope Dilution Technique

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Abstract

A method for the determination of Lead isotope ratios by thermal ionization mass spectrometry (TIMS). This method also describes the application of isotope dilution mass spectrometry (IDMS) to the field of reference material (RM) characterization focusing on the approach. Emphasis is placed on IDMS measurements of highest analytical quality. Basic principles as well as the equation system are being recalled. The evaporation and ionization currents are determined for a measurement of isotopic ratios of head, employing double rhenium filament assembly in the ion source and Faraday cup as the detector using the presently available RM.

Introduction

Lead has four naturally-occurring isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. ^{204}Pb is not radiogenic. The isotopic composition of Pb is commonly expressed as the ratios ^{208}Pb/ ^{206}Pb or ^{206}Pb/ ^{207}Pb. The less abundant ^{204}Pb is often used as a reference in geochronological studies because it is stable and its abundance is constant [1]. The other three (^{206}Pb, ^{207}Pb and ^{208}Pb) are the end products of radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively[2]. The ^{207}Pb/ ^{206}Pb and ^{208}Pb/ ^{206}Pb values are commonly used in comparing environmental samples since the total lead concentrations are often low and the relative abundances of these three isotopes is much higher than that of 204Pb. The relative abundances of these isotopes vary with the type and geological ages of the rocks and ore deposits at different sites, and hence with geographic locations [3].

Thermal ionization mass spectrometry (TIMS) is still regarded as the definitive methodology for lead isotope measurements. A development of sample loading technique using silicagel drastically. Improved the ionization efficiency of Pb in TIMS, which allowed the Pb isotope analysis with significantly smaller sample size compared to the electron impact ionization method with gaseous methyl Pb [4].

The origin of the isotope dilution principle is not known exactly. Different assumptions can be found in the literature, where o most of them see the origin in zoology [5]. The isotope dilution principle first was used to count the population of rare birds on islands. M. Berglund found a clear reference that the isotope dilution principle has been applied in zoology [6]. The principle of IDMS is surprisingly simple. A sample with known isotopic composition of the analyte element, but unknown element content is mixed with a known amount of spike. This spike contains the analyte element in a different isotopic compositor. Ideally enriched in the rarest natural isotope. After complete mixing of sample and spike the so-called sample-spike blend or isotope diluted sample gained a new isotope ratio being between the isotope ratio of the sample and that of the spike [7]. As IDMS only requires isotope ratio determination and mass measurements, the advantage compared to other methods become apparent: After equilibration losses of analyte do not affect the accuracy of the analytical result, because the measure and, the blend isotope ratio, is equal in all sub-samples of the blend [8,9]. IDMS offers the possibility to determine major (%) to ultra-trace concentrations (< ng. Kg) of elements, species and compounds in various matrices. The factor that IDMS has the potential to produce analytical results of highest accuracy and precision, metrologically denoted to as smallest uncertainties, makes it most suitable as reference method for RM characterization [10]. In the last years the utility of inductively coupled plasma mass spectrometry (ICP-MS) in Pb isotopic studies has been explored and the development of sensitive and highly precise analytical techniques based on ICP-MS has allowed the determination of isotopic relations of Pb in environmental and geologic materials[11-13].

Experimental:

Apparatus

- Thermal ionization mass spectrometer (MAT 261), Finnigan Mat Co. (Germany). The characteristics of this instrument are as follow
- Single focusing.
- A multiple filament assembly.
- Varying magnetic field.
- The ion current is measured by either a Faraday cup or secondary electron multiplier.
- Angle of deflection 90°.
- Background determination after each scan.
- Ion accelerating voltage 10 KV.

— Masses (No. 23, K 39) are calibrated to measure the intensities of Lead isotopes.

Reagents

— NBS 981 standard reference material, common lead isotopic standard; this standard was purified to at least 99.9 + percent purity, and extruded into wire form.

Absolute Abundance Ratio, $^{204}Pb/^{206}Pb = 0.059042 \pm 0.00003$
Absolute Abundance Ratio, $^{207}Pb/^{206}Pb = 0.91464 \pm 0.00033$
Absolute Abundance Ratio, $^{208}Pb/^{206}Pb = 2.1681 \pm 0.0008$

^{204}Pb= 1.4255
^{206}Pb= 24.1442
^{207}Pb= 22.0833
^{208}Pb= 52.3470

— NBS 983, Radiogenic lead isotopic standard, this standard was purified to at least 99.9 + percent purity and extruded into wire form, it has been employed as a spike standard.

Absolute Abundance Ratio, $^{204}Pb/^{206}Pb = 0.000371 \pm 0.00002$
Absolute Abundance Ratio, $^{207}Pb/^{206}Pb = 0.071201 \pm 0.00004$
Absolute Abundance Ratio, $^{208}Pb/^{206}Pb = 0.013619 \pm 0.000024$

^{204}Pb= 0.0342
^{206}Pb= 92.1497
^{207}Pb= 6.5611
^{208}Pb= 1.2550

— Analytical reagent grade nitric acid (Carlo Erba, Milan, Italy, No. 408015).
— Hydrochloric acid from (Merck, Darmstadt, Germany).
— Milli— Qwater (Millipore, Bedford, MA, USA).
— Lead (II) carbonate (Aldrich Company, ACS reagent 99.99 + %).

The lead metals of NBS standard (981; 983) were dissolved in a mixture of ($3HCl + 1 HNO_3$) for overnight then were added excess of HNO_3 to convert the lead chloride to lead nitrate.

Procedure of IDMS

In the IDMS, a series of lead mixtures were prepared by mixing a known aliquot of spike solution; NBS 983 with a certain portion of sample (unknown concentration of lead (II) carbonate) already prepared. The mixtures were chosen to represent a series of different ratios of spike to sample as shown in Table 4. Fig 1, shows the IDMS principle for lead. For profound discussion on IDMS the schematic diagram (Fig. 1) is not detailed enough and it is necessary to have a closer look at the equation system.

For the calculation of lead concentration in the sample (lead (II) carbonate taken as unknown), the following equation is used for IDMS [14].

$$Cx = Cs. \frac{m_s}{m_p} \cdot \frac{M_p}{M_s} \cdot \frac{Hs^{206}}{Hp^{208}} \cdot \frac{(1/\,Vmix.) - (1/\,Vs)}{1 - Vp\,/\,Vmix.}$$

Cx= Lead conc. in the unknown sample solution (mg/ml).
Cs= Lead conc. in the spike solution (mg/ml).
m_s= amount of spike solution weight in mg.
m_p= amount of unknown sample solution in mg.
Mp= mean atomic weight of lead in the unknown solution.
Ms= mean atomic weight of lead in the spike solution.
Hs^{206}= atom % ^{206}Pb in the spike.
Hp^{208}= atom % ^{208}Pb in the sample.
Vmix.= atomic ratio of $^{208}Pb/\,^{206}Pb$ in the mixture.
Vs.= atomic ratio of $^{208}Pb/\,^{206}Pb$ in the spike.

Vp = atomic ratio of $^{208}Pb/^{206}Pb$ in the sample.

Sample Loading:
The filament used for loading is a single filament made of Rhenium. The quantity of lead load on the evaporation filament (0.3 µg/ ml) as a Lead Nitrate solution followed by a drop of 10% NH_4OH solution to insure the formation of $Pb(OH)_2$ which enable the lead sample to stick on the filament during evaporation process [15]. The filament which is in the loading position is connected automatically via spring contact to the preparation heating. This unit provides facilities for reproducible, temperature programmed heating up of the loaded filaments, making possible to concentrate the sample on a small area in the mid of the filament.

Results and Discussion:
In the analysis of NBS standard, 981 (common lead isotopic standard) and NBS, 983 (Radiogenic lead isotopic standard). The ionizing filament current is set at 1 Amp and then the heating current for ionizing filament is slowly increased (about 0.2 Amp every 5 minutes), until the lead signal is detectable on the grid and then grow, as the higher temperature phase begins to be ionized. The best intensity of Pb (208, 206, 204, 207) signals required current of (2.3- 2.6 Amp), for the ionizing filament only at a temperature of (1100- 1500 °C). A small amount of isotopic fractionation generally occurs during on analysis, the $^{208}Pb/^{206}Pb$ ratio changes during the data taking period of an analysis (20 mins.). To minimize the effect of this fractionation, all analysis were in an identical manner. Usually, the data were always taken through the same time interval [15].

Mass discrimination effects have been observed in measurements of isotopic ratios using TIMS. Several process contribute to this phenomenon. These are mainly space charge effects (Columbic repulsions) in the skimmer cone region, which results in preferential transmission of the heavier ions [16], and mass- dependent sensitivity of the mass spectrometer. The effect of mass bias should be monitored, and if necessary corrected, by using standard of known isotopic composition close to that of the unknown. The standard should be analyzed frequently during an analytical run to monitor changes in mass bias with time. Mean ratio, standard derivation and the correction factor. For the isotope ratios $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ are given in Table 1 and 2 for the two standard reference materials 981 and 983.

The results are shown in Fig. 2 and 3, The TIMS was optimized to maximize Pb signal intensity in the measurements of SRM 981 and 983 Pb solution. The resultants average values of SRM 981 and 983 are $^{208}Pb/^{206}Pb$ = 2.0682024 and 0.013424 respectively.

The correction factors to the certified value for SRM 981 and 983 are $^{208}Pb/^{206}Pb$ = 1.048302 and 1.014526, which shows an excellent reproducibility of our analysis. Fig. (4), Pb isotope composition of SRM 981, reported in literatures compared with our data. The relative differences obtained by TIMS data seem to be deviated from the expected straight linear mass dependent fractionation trends due to anomalous behavior of Pb as pointed out previously [15, 17, 18].

Table 3, shows the results of analysis of Pb isotope ratios, standard deviation and correction factor of the mean ratios, determined by TIMS for lead carbonate. From these analyses the stability of peak intensity for lead carbonate has the longer time of the ion current due to isotope fractionation occurred in the ionic emission process. If the signal starts to decay, the run should be rejected. Decaying singles generally show significant change in the observed ratio with time [19].

Performing IDMS with TIMS requires an analyte isolation step, as evaporation, ionization and thus fractionation in TIMS dramatically change with matrix. Because analyte isolation in mandatory for TIMS and thus an intrinsic component, the measurement procedure "TIMS" is largely unaffected by matrix [8]. IDMS has the potential to produce analytical results of highest accuracy and precision. The IDMS equation system is not discussed anymore as it seems well-known. But for a better understanding of all details and for following the comparison of different IDMS approaches it is helpful to recapitulate the IDMS equation system, which described in experimental. Data for the measurements of lead concentration by IDMS is given in Table 4, which shows the mixing ratios of ^{208}Pb and ^{206}Pb for the isotopic dilution analysis of ^{206}Pb. It is seen from this table that the ratio 1:5 gives better results in comparison with the other ratios (1:1 and 1:2).

This could be attributed to the difference in the peak height of these isotopes. Total error in the IDMS of Lead samples by isotopic dilution Analysis consists of the following errors [20-21]:

A- The error of weighing (buoyancy, electrostatic charge, moisture content, stability).
B- Isotope ratio determination (interferences, mass discrimination or fractionation effects, dead time effect, calibration effect, contamination, abundance sensitivity).
C- The error of sample preparation (incomplete digestion, incomplete isotopic mixture / exchange).

Conclusions
The experimental results reported in this work suggest that good precision and accuracy may be achieved by using

TIMS to determine lead isotopic ratios for NBS-981, NBS-983 and lead carbonate. Also the mean ratios of the lead isotope are corrected. The IDMS process is well understood and all sources of errors are known in principle. The identified errors or bias can be avoided or corrected by simple mathematics or additional measurements leading to the highest accuracy and precision in elemental analysis compared to other techniques. The IDMS has been together with ITMS, this combination established as international accepted reference method for elemental analysis. IDMS offers sufficient development potential to follow future needs in analytical chemistry and reference material characterization.

References

[1] M. T. Rodriguez- Salazar, O. Morton Bermea, E. Hernandez- Alvarez, M. E. Garcia- Arreola, M. T. Ortuno- Arzate, 2010, Development and Validation of on analytical method for the determination of lead isotopic composition using ICP- QMS, Geofisica Internacional 49(3), 113- 117.

[2] C. D. Judd and K. Swami, 2010, ICP- MS determination of lead isotope ratios in legal and counterfeit cigarette tobacco samples, Isotopes in Environmental and Health Studies Vol. 46, No.4, 484- 494.

[3] A. Dicken, 1995, Radiogenic Isotope Geology, Cambridge University Press, Cambridge.

[4] M. Tanimizu and T. Ishikawa, 2006, Development of rapid and precise Pb isotope analytical technique using MC- ICP- MS and new results for GSJ rock reference samples, Geochemical Journal, Vol. 40, 121-133.

[5] E. Roth, 1997, Critical Evaluation of the use and Analysis of stable Isotopes, Pure Appl. Chem., 69, 1735- 1828.

[6] M. Berglund, 2004, Introduction to Isotope Dilution Mass Spectrometry (IDMS) in P. De Groot (ed.), Handbook of Stable Isotope Analytical Technique, 1, 820- 834.

[7] J. Vogel and W. Pritzkow, 2010, Isotope Dilution Mass Spectrometry- A Primary method of measurement and its role for RM Certification, Journal of Metrology Society of India, Vol. 25, No. 3, 135- 164.

[8] J. Diemer, C. R. Quetel and P.D.P. Taylor, 2002, comparison of Performance of Different ICP-MS Instruments on the Measurement of Cu in a water Sample by ICP- IDMS, J. Anal. At. Spectrom., 17, 1137- 1142.

[9] F. Wombcher, M. Rehkamper, Mezer and C. Munker, 2003, Stable Isotope Composition of Cadmium in Geological Materials and Meteorites Determined by Multiple_ Collector ICP_ MS, Geochim. Cosmochim. Acta., 67, 4639- 4654.

[10] H. Wei, Y. Xiao, A. Sun, C. Zhang and S. Li, 2004, Effective elimination of isobaric ions interference and precise thermal ionization mass spectrometer analysis for boron isotope, Int. J. Mass Spectrometry. 235 (2), 187–195.

[11] J. G. Farmer, L. J. Eades, A. B. Mackenzie, A. Kirika and T. E. Bailey- Watts, 1996,Stable Lead Isotope Record of Lead Pollution in Loch Lomond Sediments, Environ. Sci. Technol. 30, 3380- 3038.

[12] F. Monna, j. Lancelot, I. W. Croudace, A. B. Cundy and J. T. Lewis, 1997, Pb Isotopic Composition of Airborne Practical Material from France and the Southern United Kingdom: Implications for Pb Pollution Source in Urban Areas. Environ. Sci. Technol. 31, 2277- 2286.

[13] H. C. Moor, T. Schaller and M. Sturm, 1996, Recent changes in stable Lead Isotope Ratios in Sediments of Lake Zug, Switzerland, Environ. Sci. Techno. 30, 2928- 2933.

[14] A. Henrion, 1994, Reduction of Systematic- Errors in Quantitative- Analysis by Isotope- Dilution Mass- Spectrometry (IDMS). J. Anal. Chem., 350, 657- .658.

[15] E. J. Catonzaro, T. J. Murphy, W. R. Shieids, and E. L. Harner, 1968, J. of Research of the National Bureau of Standards, Physic and Chemistry, 72A, No. 3, 261- 267.

[16] I. T. Platzner, 1997, Modern isotope ratio mass spectrometry, Chemical Analysis, Vol. 145, 187- 189.

[17] W. Todt, R. A. Cliff, A. Hanserand, A. W. Hofmann, 1996, Evaluation of ^{202}Pb- ^{205}Pb double spike for high- precision lead isotope analysis, Earth Processing: Reading the Isotope Code, Geophysical monograph 95.

[18] M. F. Thirlwall, 2000, Inter- laboratory and other errors in Pb isotope analysis investigated using ^{207}Pb- ^{204}Pb double spike., Chem. Geol., 163, 299-322.

[19] W. R. Shields, 1966, Analytical mass spectrometry section, Instrumentation and procedures for Isotopic Analysis, NBS- 277.

[20] K. G. Kehl, K. Weirauch, S. Wunderli and V. R. Meyer, 2000, The Influence of Variations in Atmospheric Pressure on the Uncertainly Budget of Weighing Results, Analyst, 125, 959- 962.

[21] A. Reichmuth, S. Wunderli, M. Weber and V. R. Meyer, 2004, The Uncertainly of Weighing Data Obtained with Electronic Analytical Balances, Microchim. Acta., 148, 133-141.

Table 1. Mass Spectrometric Analysis of Lead isotopes standard NBS 981.

*run No.	Mean ratio $^{208}Pb/^{206}Pb$	St. dev	Mean ratio $^{207}Pb/^{206}Pb$	St. dev	Mean ratio $^{204}Pb/^{206}Pb$	St. dev
1	2.061904	2.8×10^{-3}	0.834336	1.2×10^{-3}	0.055079	8.7×10^{-5}
2	2.069436	5.9×10^{-3}	0.83516	2.1×10^{-3}	0.055227	1×10^{-4}
3	2.069036	2.8×10^{-4}	0.833371	2.3×10^{-4}	0.055226	1.2×10^{-4}
4	2.069564	1.8×10^{-3}	0.834791	1.3×10^{-3}	0.054718	1.7×10^{-4}
5	2.070028	2.2×10^{-3}	0.834810	2.6×10^{-3}	0.054968	3.1×10^{-4}
6	2.069617	4.2×10^{-3}	0.834754	2.2×10^{-3}	0.055279	3.8×10^{-4}
7	2.069308	3.1×10^{-3}	0.834529	1.1×10^{-3}	0.055090	9.9×10^{-5}

*each one is a mean of five measurements.

Mean ratio $^{208}Pb/^{206}Pb = 2.069442$

Mean ratio $^{207}Pb/^{206}Pb = 2.069442$

Mean ratio $^{204}Pb/^{206}Pb = 2.069442$

$$^{208}Pb / ^{206}Pb = \frac{2.1681}{2.069442} = 1.047674$$ Correction factor.

$$^{207}Pb / ^{206}Pb = \frac{0.91464}{0.834599} = 1.095903$$ Correction factor.

$$^{204}Pb / ^{206}Pb = \frac{0.059042}{0.055084} = 1.071854$$ Correction factor.

Table 2. Mass Spectrometric Analysis of Lead isotopes standard NBS 983.

*run No.	Mean ratio $^{208}Pb/^{206}Pb$	St. dev	Mean ratio $^{207}Pb/^{206}Pb$	St. dev	Mean ratio $^{204}Pb/^{206}Pb$	St. dev
1	0.013435	1.0×10^{-4}	0.053919	1.8×10^{-4}	0.000602	3.2×10^{-5}
2	0.013274	3.6×10^{-5}	0.051515	4.4×10^{-4}	0.000535	1.3×10^{-5}
3	0.013327	4.8×10^{-5}	0.051522	1.7×10^{-4}	0.000559	1.6×10^{-5}
4	0.013431	4.6×10^{-5}	0.054413	1.6×10^{-4}	0.000607	2.1×10^{-5}
5	0.013579	1.2×10^{-4}	0.054332	3.8×10^{-4}	0.000542	2.9×10^{-5}
6	0.013498	2.3×10^{-5}	0.052109	1.6×10^{-3}	0.000531	1.2×10^{-5}

*each one is a mean of five measurements.

Mean ratio $^{208}Pb/^{206}Pb = 0.013424$

Mean ratio $^{207}Pb/^{206}Pb = 0.052968$

Mean ratio $^{204}Pb/^{206}Pb = 0.000562$

$$^{208}Pb / ^{206}Pb = \frac{0.013619}{0.013424} = 1.014526$$ Correction factor.

$$^{207}Pb / ^{206}Pb = \frac{0.071201}{0.052968} = 1.344226$$ Correction factor.

$$^{204}Pb / ^{206}Pb = \frac{0.000371}{0.000562} = 0.660142$$ Correction factor.

Table 3. Results of the determination of lead isotope ratios for Lead (II) Carbonate by TIMS.

*run No.	Mean ratio $^{208}Pb/^{206}Pb$	St. dev	Mean ratio $^{207}Pb/^{206}Pb$	St. dev	Mean ratio $^{204}Pb/^{206}Pb$	St. dev
1	2.069319	5.4×10^{-3}	0.835778	2.5×10^{-3}	0.054759	1.7×10^{-4}
2	2.070312	3.7×10^{-3}	0.835340	1.2×10^{-3}	0.054445	1.6×10^{-4}
3	2.073254	2.7×10^{-3}	0.836196	2.0×10^{-3}	0.054879	1.2×10^{-4}
4	2.067917	2.0×10^{-3}	0.836271	2.1×10^{-3}	0.055077	1.6×10^{-4}
5	2.068996	1.9×10^{-3}	0.835883	8.1×10^{-4}	0.054956	9.5×10^{-5}
6	2.071430	2.8×10^{-3}	0.835584	9.1×10^{-4}	0.054637	1.7×10^{-4}
7	2.073815	2.7×10^{-3}	0.835296	7.4×10^{-4}	0.054587	9.7×10^{-5}
8	2.073197	1.6×10^{-3}	0.836101	4.8×10^{-4}	0.054587	1.3×10^{-4}
9	2.071097	3.0×10^{-3}	0.835478	1.3×10^{-4}	0.055144	2.8×10^{-4}

*each one is a mean of five measurements.

Mean ratio	Mean ratio	Mean ratio
$^{208}Pb/^{206}Pb = 2.071039$	$^{207}Pb/^{206}Pb = 0.835769$	$^{204}Pb/^{206}Pb = 0.054753$
After corection (AC)	AC	AC
2.169774	0.915922	0.058687

$^{208}Pb = 52.3545$

$^{207}Pb = 22.1003$

$^{206}Pb = 24.1290$

$^{204}Pb = 1.4161$

Table 4. Lead concentration measurements of the Lead Carbonate by IDMS

Mixture No.	Spike (mg.)	Sample (Lead Carbonate) (mg.)	Mixing Ratio spike: sample	Lead conc. taken (mg/ml)	Lead conc. found (mg/ml)
1	1.0706	1.0997	1:1	62.5112	62.1051
2	0.5298	1.0966	1:2	62.5112	62.2913
3	0.5258	2.7043	1:5	62.5112	62.4833

Known quantities:-
- Sample mass or spike mass.
- Isotopic composition.

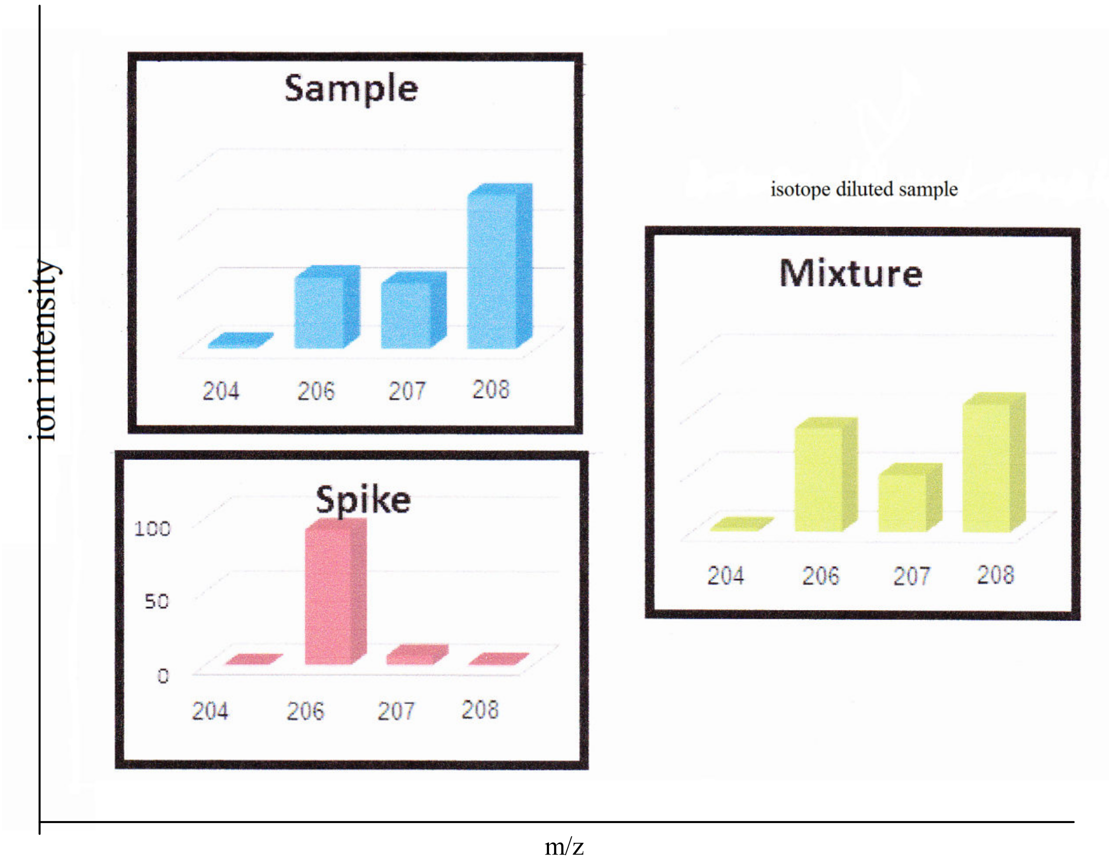

Fig. 1 Schematic IDMS principle demonstrated for Pb when 2.7043 mg. of sample mixed with 0.5258 mg. of spike

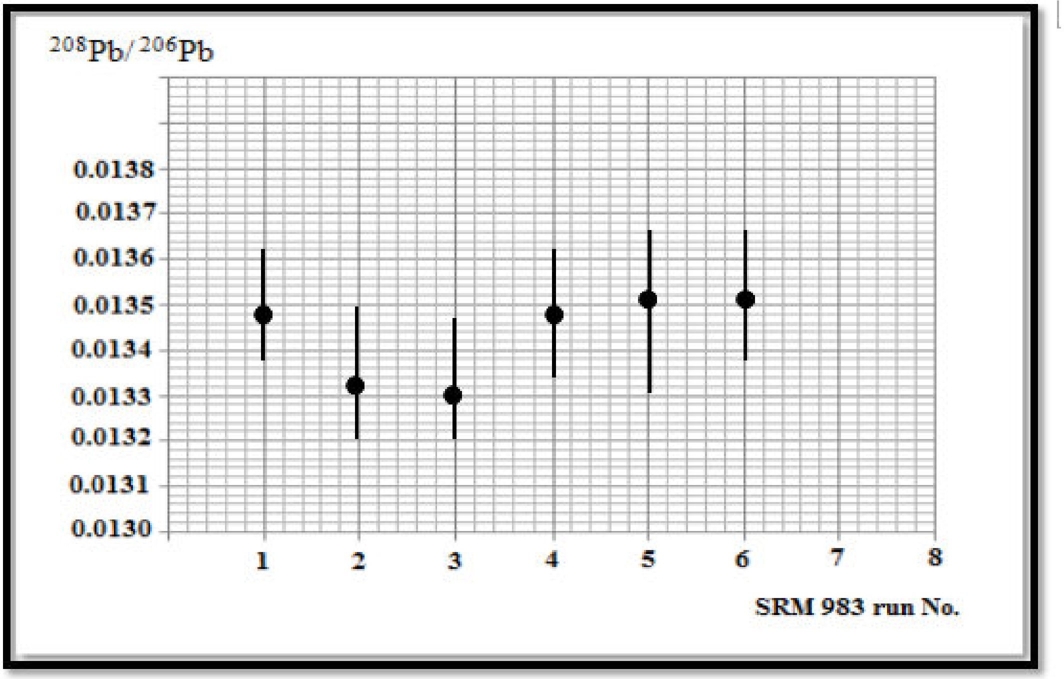

Fig. 2 Result of repeated analysis of a 0.3 µg/ml SRM 983 Pb solution, each ^{208}Pb/ ^{206} Pb and run No. is a mean of five measurements.

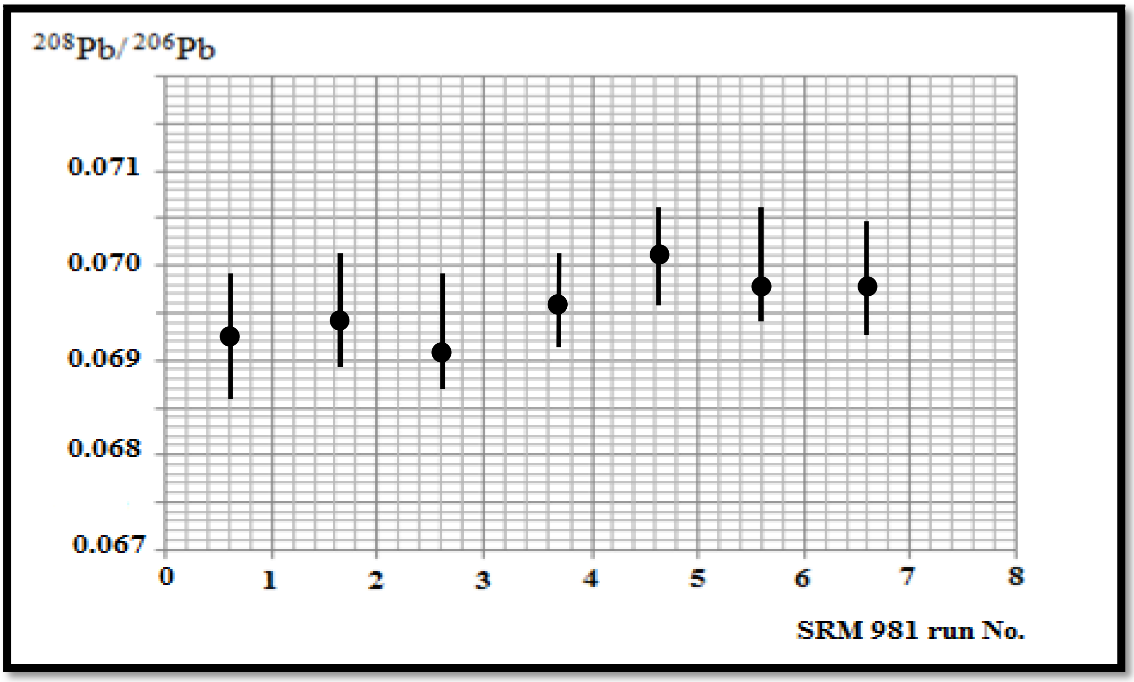

Fig. 3 Result of repeated analysis of a 0.3 µg/ml SRM 981 Pb solution, each result of ^{208}Pb/ ^{206} Pb and run No. is a mean of five measurements.

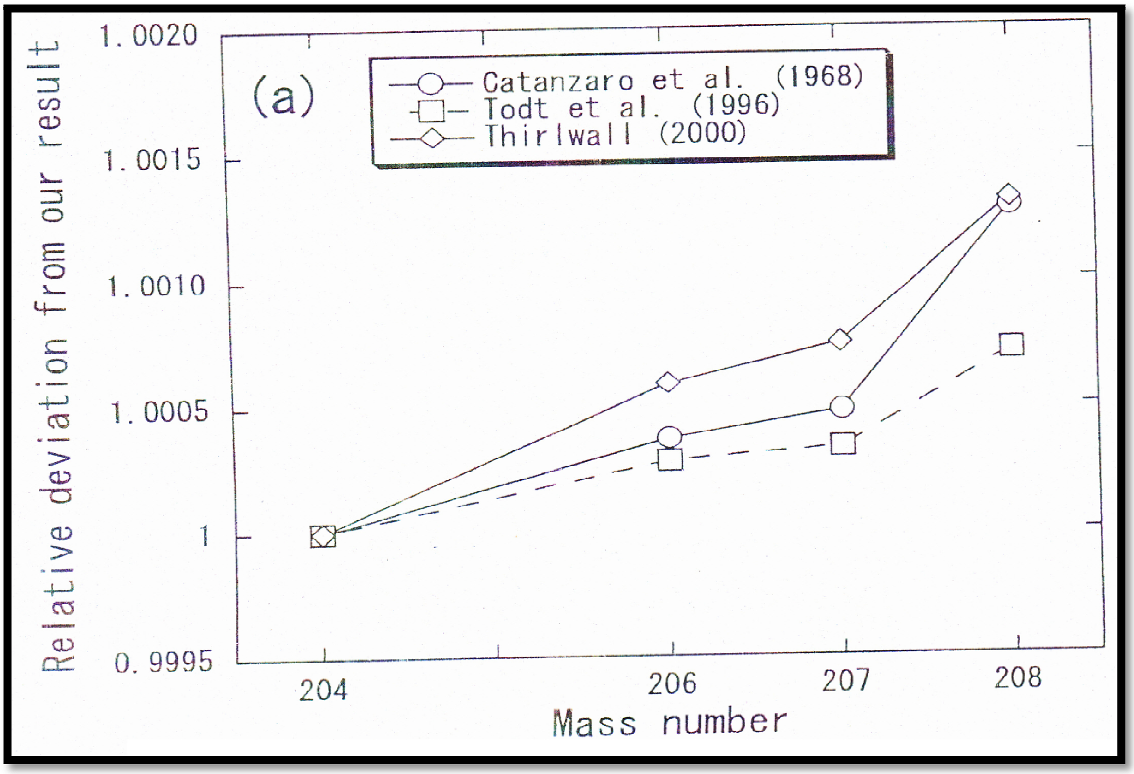

Fig. 4 Pb isotope composition of NBS 981 reported in literates by TIMS compared with our data.

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