

# Lead isotope determinations by inductively-coupled plasma mass spectrometry (ICP-MS): potential of sector field instruments

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Flem, B., Grimstvedt, A. & Cook, N.J. 2000: Lead isotope determinations by inductively-coupled plasma mass spectrometry (ICP-MS): potential of sector field instruments. *Norges geologiske undersøkelse Bulletin 436*, 203-207.

Lead isotope measurements have been carried out using a high-resolution inductively-coupled plasma mass spectrometer (Finnigan MAT ELEMENT, configured with CD-1 option). The method can be applied to all types of geological samples brought into solution form. Three common lead standards are used for documentation of the method. Detection limits for  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  lie between 0.124 and 2.86  $\text{pg ml}^{-1}$ . Optimisation of scanning conditions at a count rate of approximately 200,000 cps for  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$ , led to a relative standard deviation of 0.05% for the mean  $^{207}\text{Pb}/^{206}\text{Pb}$  isotope ratio, based on 15 consecutive measurements. The method can be routinely applied to gain geochronological and petrological data for genetic studies of mineral deposits, including deposits of industrial minerals. Because of space charge effects in the skimmer cone region and mass-dependent sensitivity of the mass spectrometer, the measured intensity ratio of samples must generally be calibrated using external or internal standards of known isotope ratios to correct for mass biases and mass fractionation.

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## Introduction

Geochronological, isotopic and petrological data are important elements in studies of mineral deposits. This is true for all types of mineral deposits, both metalliferous ores and deposits of industrial minerals. Alternatively, geochronological and isotope data are useful tools for prospecting, as they can help establish geological correlations on the basis of age and/or isotopic signature, and aid identification of formations offering economic potential. This paper describes development work carried out at the Geological Survey of Norway to use inductively-coupled plasma mass spectrometry (ICP-MS) as a method for lead isotope measurements. The possibility to use the technique in investigations of mineral deposits on a routine basis represents an important additional tool for unravelling the geological framework hosting economic deposits of industrial minerals such as limestone, dolomite, talc and other mineral products.

Lead isotopes can be measured in minerals whose U/Pb and Th/Pb ratios are sufficiently low such that the isotopic composition will not change appreciably with time. Examples include the commonest lead mineral, galena ( $\text{PbS}$ ). Pb-Pb isochrons for such minerals, and for whole rocks with similarly low ratios, can give an age of formation. Such methods have been in wide usage for several decades and have been applied to metalliferous ores (e.g., Bjørlykke et al. 1993, Billström & Vivallo 1994); to a broad range of igneous rocks, from granite to basalt; and also to various types of sedimentary rocks. Reliable ages can be obtained for rocks with a simple crystallisation history. However, because of the significant difference in geochemical behaviour and mobility of U and Pb, major problems can arise in interpretation of situations in

which the Pb isotope systematics have been reset. The application of Pb isotopes for geochronology has declined in popularity in recent years. However, studies of Pb isotope systematics are an increasingly used tool in petrogenetic studies in which the goal is to establish the lead source. Lead isotopes, and other radiogenic isotope ratios, are used to identify source regions in the crust as well as mixing and contamination processes. Modern reviews of Pb/Pb isotope methodology (Faure 1986, Rollinson 1993) show how Pb/Pb geochronology is applied to give ages of metamorphism (i.e. time of resetting), and more rarely to give ages of crustal formation.

Determination of lead isotope ratios in geological samples may be carried out using a variety of analytical methods, e.g., TIMS (thermal ionisation mass spectrometry). In the past decade or so, inductively-coupled plasma mass spectrometry (ICP-MS) has established itself as an excellent method for determination of Pb isotope abundances. Measurement of Pb isotope ratios with ICP-MS has been shown to be possible on all types of environmental samples. These can range from atmospheric aerosols (e.g., Surges & Barrie 1987), gasoline (e.g., Lord 1994), fresh and saline waters (e.g., Halicz et al. 1994) and digested samples (e.g. Widenbeck et al. 1995). If the ICP-MS is used in combination with a laser probe, the determination of Pb isotope ratios can also be carried out on solid samples, permitting *in situ* determination of Pb isotope systematics in individual mineral grains (e.g., Feng et al. 1993).

Application of ICP-MS methods to Pb isotope determinations is advantageous in studies of mineral resources and metallogeny in that rapid, reliable analysis of samples is permitted at relatively low cost. Furthermore, if the technique

can be used in conjunction with a laser probe, analyses could be performed *in situ* on samples prepared for mineralogical or petrographical study, thus further reducing preparation and analysis time. The method offers, therefore, significant promise for the future.

In this paper, the application of inductively-coupled plasma mass spectrometry (ICP-MS) to direct determination of Pb isotope ratios in aqueous or digested samples is investigated. Three common lead standards with different concentrations of Pb isotopes have been studied in order to show the suitability of the technique for routine determination of Pb isotopes.

### Instrumental details

A standard, double focusing, sector field, ICP-MS (Finnigan MAT, ELEMENT) instrument is used (Feldmann et al. 1994, Giessmann & Greb 1994). The configuration included the CD-1 option from Finnigan, consisting of a torch insert module which replaces the standard Element ICP torch holder. A grounded Pt electrode (GuardElectrode™) is inserted between the quartz ICP torch and the RF load coil to prevent

capacitive coupling from the load coil into the ICP. The ICP is then sustained by 'pure' inductive coupling; secondary discharge between the ICP and mass spectrometer is eliminated. The CD-1 option is used for the widest range of sample matrices and instrumental operating conditions, including cold plasma ICP-MS. The most important operating parameters are given in Table 1. The Finnigan MAT ELEMENT is a sector field, high-resolution ICPMS, but all measurements were carried out at a mass resolution of 300 (mass of isotope M / mass difference of isotopes, ΔM). The high resolution (mass resolution 8000-9000) was only used for checking of isobaric interference. The instrument operating parameters were tuned on a 1 ng ml<sup>-1</sup> solution of NBS-981 to give a peak height of approximately 700,000 cps for <sup>208</sup>Pb.

Three common lead isotope standards have been used (NBS-981, NBS-982 and NBS-983). A specific amount of each standard was digested in an autoclave at 200 kPa for 30 minutes with 7 N HNO<sub>3</sub>. After cooling to room temperature, the solution was diluted to the concentrations given in Table 2. Nitric acid was added to a concentration of 0.24 M for solution conservation. A sample blank was prepared in the same way to check and correct for contamination during digestion and dilution. The blank solution was also used to estimate the limits of detection (LOD).

The limits of detection (LOD) for all Pb isotopes were established from the sensitivity data given in Table 2 and 15 successive measurements on the blank sample. LOD determination is here based on 3 times the standard deviation multiplied by 2<sup>0.5</sup>, divided by the sensitivity, S; equation [1].

$$LOD = \frac{3\hat{\sigma}}{S} \sqrt{2} \quad [1]$$

### Results and discussion

Mass discrimination effects have been observed in measurements of isotopic ratios using ICP-MS. Several processes contribute to this phenomenon. These are mainly space charge effects (Columbic repulsions) in the skimmer cone region, which result in preferential transmission of the heavier ions (Platzner 1997), and mass-dependent sensitivity of the mass spectrometer. The effect of mass bias should be monitored, and if necessary corrected, by using a standard of known isotopic composition close to that of the unknown. The standard should be analysed frequently during an analytical run to monitor changes in mass bias with time. Mass bias is also

Table 1. Operating conditions of the ICP-MS.

<b>Plasma conditions</b>	
Plasma Power	900 Watt
<b>Data collection</b>	
Mass resolution (m/ΔM)	300
Scan type	Escan
No of scans	600
Counting time on each isotope per scan	0.05 s
Total counting time on each isotope	30 s
Detection mode	Counting
<b>Measured mass range</b>	
<sup>204</sup> Pb	203.905-204.041
<sup>206</sup> Pb	205.906-206.043
<sup>207</sup> Pb	206.907-207.045
<sup>208</sup> Pb	207.907-208.046

Table 2. Detection limits (LOD) obtained from 15 successive measurements on the blank sample and sensitivities obtained from calibration together with the concentrations of the digested NBS standards.

	Sensitivity [cps (ng ml <sup>-1</sup> ) <sup>-1</sup> ]	St. dev. of intensities Blank [cps]	Detection limit (LOD) [pg ml <sup>-1</sup> ]	NBS-981 [pg ml <sup>-1</sup> ]	NBS-982 [pg ml <sup>-1</sup> ]	NBS-983 [pg ml <sup>-1</sup> ]
Pb204	905094.7	26.4	0.124	15.70	17.3	0.503
Pb206	903388.7	305	1.43	266	635	1356
Pb207	926895.3	264	1.21	243	297	96.5
Pb208	933902.1	631	2.86	577	635	18.5

Table 3. Measured isotope ratios and relative standard deviation of the mean of 15 consecutive measurements.

		$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
NBS-981	Mean measured value	0.057925	0.92135	2.1987
	Certificate value	0.059042	0.91464	2.1681
	Bias %	-1.89 %	+0.733	+1.41
	Experimental %RSD	0.08	0.05	0.07
NBS-982	Mean measured value	0.026576	0.46783	1.00973
	Certificate value	0.027219	0.46707	1.00016
	Bias %	-2.36	+0.163	+0.957
	Experimental %RSD	0.06	0.04	0.05
NBS-983	Mean measured value	0.000298	0.070906	0.013095
	Certificate value	0.000371	0.071201	0.013619
	Bias %	-19.7	-0.414	-3.85
	Experimental %RSD	0.68	0.05	0.19

strongly dependent upon the day-to-day tuning of the Y-deflection lenses; the mass bias will reflect how well the Y-deflection lenses were tuned on the actual day. Mass bias for the isotope ratios  $^{204}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  are given in Table 3 for the three standard materials. The values are quite high, possibly suggesting that insufficient time was spent on instrumental tuning and that this must be borne in mind when unknown samples are analysed. A typical run procedure would include multiple determination of reagent blanks and reference standards alongside the unknown samples.

To correct systematic deviations, correction factors are determined using external or internal standards, which allow the conversion of intensity ratios into isotope ratios. External calibration uses certified standards with known isotope ratios, as the one used in this paper. The measured intensity ratios of the samples to be examined are corrected according to the following formula:

$$\frac{ax}{bx} = \frac{I_{ax \text{ sample}}}{I_{bx \text{ sample}}} \cdot Z \cdot \frac{I_{bx \text{ standard}}}{I_{ax \text{ standard}}} \quad [2]$$

where Z is the certified isotope ratio and I is the measured intensity. Elements with known isotope ratios, whose mass neighbours the mass of the element to be determined, can be used for internal standardisation (e.g.  $^{203}\text{Tl}/^{205}\text{Tl}$  can be used to determine the isotope ratio  $^{206}\text{Pb}/^{207}\text{Pb}$ ). The known isotope ratio is then used to correct for mass bias in the ratio to be determined.

The basic disadvantage of internal standardisation is linked to the condition that the mass discrimination effect for the internal standard must correspond to the mass discrimi-

nation effect of the isotope to be determined. This has to be checked in each individual case. External calibration is therefore normally used in preference to internal standardisation (Finnigan 1998).

It may happen that a value appears in a ratio determination which departs considerably from other values in that measurement series. If the number of values is small, such an outlying value can affect the standard deviation to such an extent that it is reasonable to conclude that the mean ratio recalculated without the outlying value would better express the true mean. Several statistical criteria for rejection of outlying values exist, e.g., the Chauvenet rejection criteria (Platzner 1997). In the present study, however, no rejection of measurements has been made, since the aim is to develop a method for Pb isotope measurements to be used on a routine basis.

Vanhaecke et al. (1996) reported  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios with relative standard deviation (RSD) of 0.1% in a 20-40  $\mu\text{g l}^{-1}$  solution of Pb or when the signal intensity exceeds 200,000 cps. The standard NBS-981 has a Pb concentration of 1.1  $\mu\text{g l}^{-1}$  and by tuning the instrument to an optimal signal intensity, nearly 200,000 cps were obtained for the nuclides  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$ . Values of precision obtained in the present work are comparable with those of Vanhaecke et al. (1996), although the isotopic concentrations are 20-40 times lower. Percentage RSD values are in the same order of magnitude; 0.2% RSD for single measurements and 0.05% RSD for the mean (Table 3). The reported precision is thus fully acceptable for routine application.

The detection limits for the isotopes are estimated to be between 0.124 and 2.86  $\text{pg ml}^{-1}$  (Table 2). The lowest detection limit (0.124  $\text{pg ml}^{-1}$ ) is obtained for  $^{204}\text{Pb}$ , the isotope which usually has the lowest abundance. In the NBS-983 solution,  $^{204}\text{Pb}$  is present at a concentration of 0.503  $\text{pg ml}^{-1}$ , i.e. 4 times higher than the detection limit. The experimental RSD for the ratio  $^{204}\text{Pb}/^{206}\text{Pb}$  in NBS-983 solution is, at 0.68%, quite high. However, since the instrumental intensity for  $^{204}\text{Pb}$  is approaching the lower limit of detection, RSD may be limited by counting statistics.

The standard deviation on the count rate, based on counting statistics given by Jenkins and De Vries (1970) is:

$$\sigma_R = \sqrt{\frac{R}{T}} \Leftrightarrow \text{Var}(R) = \sigma_R^2 = \frac{R}{T} \quad [3]$$

where R is the counting rate and T is the counting time. The net intensity for  $^{204}\text{Pb}$  ( $R_{204}$ ) is the peak intensity ( $I_{204}$ ) minus the background intensity ( $I_{Bk}$ ). The isotope ratio is then given by:

$$Z = \frac{R_{^{204}\text{Pb}}}{R_{^{206}\text{Pb}}} = \frac{I_{204} - I_{Bk}}{R_{^{206}\text{Pb}}} \quad [4]$$

The uncertainty in the isotope ratio, Z, can be expressed as a combination of the individual contributions. Expressing

the uncertainties as variance and by the differential of the dependent variable yields:

$$Var(Z) = Var\left(\frac{I_{204} - I_{Bk}}{R_{206}}\right) \approx \left(\frac{\partial Z}{\partial I_{204}}\right)^2_{I_{Bk}, R_{206}} \sigma_{I_{204}}^2 + \left(\frac{\partial Z}{\partial I_{Bk}}\right)^2_{I_{204}, R_{206}} \sigma_{I_{Bk}}^2 + \left(\frac{\partial Z}{\partial R_{206}}\right)^2_{I_{Bk}, I_{204}} \sigma_{R_{206}}^2 \quad [5]$$

The relative uncertainty (expressed as standard deviation) can be obtained from equation [5] when each partial derivative and the counting error given in equation [3] are introduced:

$$\frac{\sigma_z}{Z} = \sqrt{\frac{Var(Z)}{Z^2}} = \sqrt{\frac{1}{T} \left[ \left( \frac{1}{R_{204}} + \frac{2I_{Bk}}{R_{204}^2} \right) + \frac{1}{R_{206}} \right]} \quad [6]$$

Table 4. Measured intensities for <sup>204</sup>Pb and <sup>206</sup>Pb. T is the total counting time pr. isotope, R<sub>i</sub> are net intensities (as count rates), I<sub>i</sub> are peak intensities, and Z is the isotope ratio.

NBS 983				
I <sub>bk, 204</sub> [c/s]	I <sub>204</sub> [c/s]	I <sub>bk, 206</sub> [c/s]	I <sub>206</sub> [c/s]	T [s]
284	649	2774	1229270	30
R <sub>204</sub> [c/s]	R <sub>206</sub> [c/s]	Z=R <sub>204</sub> /R <sub>206</sub>		
365	1226497	0.000298		

If n replicates are run, the standard deviation of the mean is obtained by dividing by the square root of n. Using the data for sample NBS-983 given in Table 4 and equation [6], the relative standard deviation of the isotope ratio <sup>204</sup>Pb/<sup>206</sup>Pb can be estimated as:

$$\frac{\sigma_z}{Z} = \frac{\sigma_z}{Z\sqrt{n}} = \frac{1}{\sqrt{15}} \cdot \sqrt{\frac{1}{30} \cdot [(0.00027 + 0.00043 + 0.82 \cdot 10^{-6})]} = 0.0040 \quad [7]$$

This shows that the relative uncertainty from counting error is 0.40% (59% of the experimental RSD; Table 3). The experimental value of the relative standard deviation is then mainly limited by the counting error when considering the isotope ratio <sup>204</sup>Pb/<sup>206</sup>Pb in the NBS-983 solution. The contribution from counting error to total experimental RSD increases as the isotope concentration approaches the lower limit of detection. The relative standard deviation can be improved by increasing the counting time for <sup>204</sup>Pb.

Blank correction for <sup>204</sup>Hg on <sup>204</sup>Pb was not needed in this case since the standards did not contain Hg and because a blank solution treated in the same way as the standard is analysed and subtracted from the analytical result of the standards. However, when dealing with normal samples such correction is frequently required. The presence of Hg may either derive from the sample material itself or from the acids used for dissolution. In such cases, the abundance of <sup>202</sup>Hg can be used to calculate the contribution from Hg at 204 m/z.

## Conclusions

The isotope ratios of Pb in NBS-981, NBS-982 and NBS-983 were measured by sector field ICP-MS. The levels of precision obtained are sufficiently good to allow meaningful interpretation in isotope studies of mineral deposits. The method is easy, fast, relatively inexpensive and can be performed *in situ*. Age determinations based solely on calculated Pb isotope models are generally somewhat conjectural if they are not supported by independent geochronological information. However, if standard materials are available, it should be easy to extend this method to include the determination of Th and U isotopes, thus permitting U-Pb and Th-Pb dating methods to be developed using the same instrumentation.

Significant mass fractionation of Pb isotopes is observed. It is thus important to run standards of known isotopic composition which is close in isotopic composition to that of the unknowns, regularly throughout the sample series to correct for mass bias, which appears to be strongly dependent on the day-to-day tuning of the instrument.

Optimisation of scanning conditions led to a relative standard deviation (based on 15 consecutive measurements) for <sup>207</sup>Pb/<sup>206</sup>Pb which was 0.05% of the mean, a value comparable with the best values reported in the literature. Compared to a Finnigan ICP-MS without the CD-1 electrode, the new CD-1 option allows the same precision for the determination of isotope ratios in solutions in which the concentration of Pb is 20-40 times lower (Vanhaecke et al. 1996).

Using the CD-1 option, detection limits for Pb isotopes are extremely low. The <sup>204</sup>Pb isotope, which usually has the lowest abundance, has the best limit of detection (0.124 pg ml<sup>-1</sup>).

## Acknowledgements

The authors wish to thank Bjørn Sundvoll, Mineralogisk-Geologisk Museum, University of Oslo, for supplying the three common lead standards. Colleagues in the NGU laboratory, and especially Eli Høybråten and Siv H. Dundas, are thanked for their contributions to development work. Constructive reviews by Bernard Bingen and Joakim Mansfeld helped to significantly improve the paper.

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