

Lead isotope analysis: Removal of ²⁰⁴Hg isobaric interference from ²⁰⁴Pb using ICP-QQQ in MS/MS mode

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Application note

Geochemistry and isotope analysis



Introduction

Lead (Pb) isotopic abundances exhibit the greatest natural variation of any element. This is because three of the four stable isotopes of lead (206Pb, 207Pb and 208Pb) are mainly derived from the radioactive decay of other elements (238U, 235U and 232Th respectively). As a result, the Pb isotopic abundances seen today are largely dependent upon the original concentration of U and Th in the rock, and the overall age of the deposit. The fourth stable isotope (204Pb) is the only "natural" or non-radiogenic isotope — i.e., it was formed entirely in a primordial supernova event rather than later as a decay product. The decay series and half-lives that lead to the different radiogenic Pb isotopes can result in markedly different relative isotope abundances, which vary with the geological location, chemical makeup and age of the material.



These variations can be used to trace the origin of materials in archaeology, environmental contamination, medicine, food etc., as well as geochronology (rock and mineral dating) studies. Other uses requiring access to Pb isotopic information include Isotope Dilution Analysis (IDA) and stable isotope tracer studies.

Being able to accurately measure all of the Pb isotopes is important for a number of investigations, of which geochronology is one of the most important. Two different approaches are used for such dating studies, based on measurement of the Pb/Pb or Pb/U ratios. Of the two approaches, Pb/U dating is probably utilized more frequently, and is generally replacing Pb/Pb measurement particularly for "younger" deposits. However, the Pb/Pb method is still very important for those very old or U-depleted deposits and for meteoritic dating.

Whichever methodology is selected, the natural or "common lead" ²⁰⁴Pb isotope is measured as a reference to calculate the original (primordial) level of the other (mainly radiogenic) Pb isotopes, so accurate measurement of ²⁰⁴Pb is essential. Unfortunately, for measurements made using inductively coupled plasma mass spectrometry (ICP-MS), ²⁰⁴Pb suffers an isobaric interference from ²⁰⁴Hg (an isobaric overlap is where isotopes of different elements occur at the same nominal mass) meaning that any mercury present as contamination or as a component of the sample would bias the measurement of ²⁰⁴Pb.

Techniques for removal or avoidance of interferences in ICP-MS can include sample preparation or separation approaches (often very time consuming), or instrumental/spectral resolution using a high resolution sector-field ICP-MS instrument (ICP-SF-MS). ICP-SF-MS is a useful technique for the avoidance of polyatomic interferences in ICP-MS, but the spectral resolution (M/ Δ M) required to separate the isobaric overlap from 204 Hg on 204 Pb is close to 500,000, which is around 50

times higher than the maximum resolution of ~10,000 that can be achieved on any commercial ICP-SF-MS:

Equation 1. Calculation of theoretical resolution needed to separate equal molar quantities of ²⁰⁴Hg from ²⁰⁴Pb

Accurate masses: 203.973481 Hg; 203.973037 Pb

$$R = \frac{203.973037}{203.973481 - 203.973037} \cong 459400$$

"Chemical resolution" (whereby an ion-molecule reaction is used to attenuate the interference and/or move the analyte to an interference-free mass) is an alternative approach that has become available more recently for ICP-MS instruments equipped with a collision/reaction cell (CRC). Chemical resolution involves introducing a reactive gas into the Collision Reaction Cell and utilizing ion-molecule chemistry to either a) react with the interfering ion to neutralize it (e.g. via a charge transfer reaction) or move it to a different mass, or b) react with the analyte to form a new product ion that can be measured at an alternative interference-free mass (e.g., via a molecular addition or cluster reaction).

In the case of the 204 Hg overlap on 204 Pb, ammonia gas can be used to separate the two ions. Mercury reacts very efficiently (essentially 100%) with ammonia gas; this reaction is by charge transfer — the Hg $^+$ ion is neutralized to Hg 0 transferring the charge to ammonia:

Equation 2. Mercury ion-molecule reaction scheme with ammonia gas

$$Hg^+ + NH_3 \rightarrow Hg^0 + "NH_3^+"$$

This efficient reaction means that the ²⁰⁴Hg isobaric interference can theoretically be removed from ²⁰⁴Pb, provided Pb is not also neutralized by reaction with the ammonia cell gas.

Experimental

An Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) instrument was used to investigate whether this chemical resolution application can offer a reliable and practical solution to the problem of the ²⁰⁴Hg/²⁰⁴Pb overlap in the presence of matrix elements typical of geological sample types.

The 8800 ICP-QQQ offers a very flexible means of investigating and utilizing ion-molecule reactions. The instrument can be operated under conditions that simulate conventional quadrupole ICP-MS instruments (with the CRC operated in either ion guide or bandpass mode), as well as utilizing MS/MS modes which are unique to the ICP-QQQ's tandem MS configuration. For further information on the operating modes of the 8800 ICP-QQQ see the Agilent 8800 ICP-QQQ Application Handbook (Pub No. 5991-2802EN).

For the preliminary experiments, the 8800 ICP-QQQ was setup using the standard sample introduction system consisting of a Micromist nebulizer, quartz spray chamber and 2.5 mm injector torch; standard Ni interface cones were fitted and solutions were sampled from an Agilent I-AS autosampler. Instrumental conditions are presented in Table 1. In order to minimize peristaltic pump "noise", the isotope analysis was performed using free aspiration.

Table 1. 8800 ICP-QQQ operating conditions

Parameter	Value
RF power (W)	1550
Carrier as flow rate (L/min)	1.05
Sampling depth (mm)	10
Extraction lens 1 (V)	0
Extraction lens 2 (V)	-170
Octopole bias (V)	-8
Energy discrimination (V)	-8
NH ₃ flow (10% in He) (mL/min)	0.0 or 1.7

All solutions were prepared from high purity single element standards (Spex, USA). Ultrapure water (Merck Millipore, Germany) and acids (Merck, Germany) were used throughout. An acid matrix consisting of 1% HNO $_3/0.5\%$ HCl (v/v) was used for all working solutions and rinses.

Results and discussion

To confirm that Pb does not undergo a charge-transfer reaction (and to check if any cluster ions are formed) a 1 μg/L (ppb) Pb solution was aspirated and a Product Ion Scan (ProIS) performed. A ProIS fixes the first quadrupole (Q1) at a selected mass, thereby only allowing the target precursor ions into the cell. The analyzer quad (Q2) is then scanned over the entire spectrum or a user-defined mass region to measure any reaction product ions that are formed. In this case, Q1 was set to 208 amu (the most abundant isotope of lead — ²⁰⁸Pb), and Q2 was scanned across the mass range 200-260 amu. Small peaks were observed at 225 and 242 amu indicating the formation of minor cluster ions — Pb(NH₃) and Pb(NH₃)₂ respectively. The sum of the signal for these clusters amounted to <0.5% of the total Pb signal (the sum of the unreacted precursor and reacted product Pb ions); at this level the product ions can be considered negligible and ignored. Pb did not appear to undergo any charge transfer reaction, as the Pb signal with ammonia gas in the cell remained at practically the same level as with no reaction gas.

To assess the effectiveness of the removal of the 204 Hg signal in NH $_3$ mode, and to check whether a bias may be introduced when operating in ammonia reaction mode, the Pb isotopic pattern was checked for a 1 µg/L lead solution spiked with 10 µg/L Hg; Tl at 1 µg/L was also included to confirm that no hydrogen donation occurs (i.e., Tl-H interference) from a non-Pb source. Figure 1 displays the Pb and Tl peaks under MS/MS ammonia reaction mode. The overlay of the theoretical natural abundance templates demonstrates that the Hg contribution at m/z 204 was completely removed, and the measured Pb and Tl peaks match the theoretical templates well, indicating that no bias or new interferences are introduced.

As a comparison of the potential impact of the isobaric ^{204}Hg interference and the method applicability, the same 1 µg/L Pb and Tl solution spiked with 10 µg/L of Hg was also measured in no gas mode. Figure 2 displays the spectrum for the spiked solution without reaction gas, demonstrating that, in no gas mode, the

Hg ions appear at their natural masses, including the ^{204}Hg isotope which contributes a severe overlap on ^{204}Pb . From the comparison of Figures 1 and 2, it can clearly be observed that the Hg from the 10 µg/L spike contributes the vast majority of the total signal at m/z 204 in no gas mode.

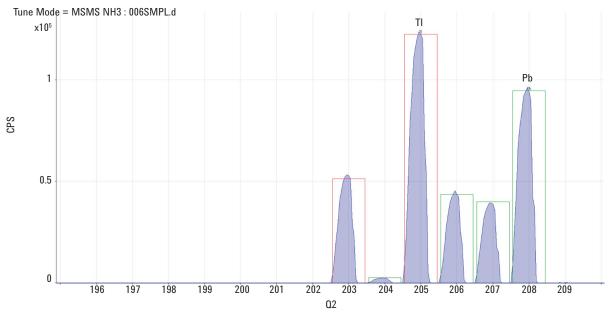


Figure 1. Ammonia MS/MS reaction mode spectrum for a solution with 1 ppb Pb and Tl and 10 ppb Hg — the Hg has been completely removed from the mass spectrum. Isotopic abundance (with the theoretical template overlaid) for Pb and Tl under ammonia reaction mode — pattern fits the theoretical template.

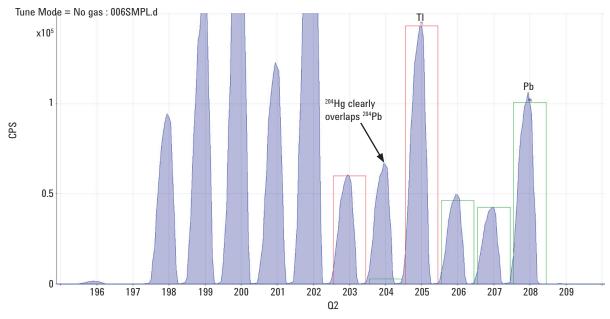


Figure 2. No gas spectrum for a solution with 1 ppb Pb and Tl and 10 ppb Hg — a clear overlap from the 204Hg isotope can be observed on 204Pb

As the charge transfer reaction that is used to remove the Hg⁺ ions is very efficient, it could reasonably be argued that this application could be performed on a conventional quadrupole ICP-MS using NH₃ reaction gas. This may indeed be the case for simple, pure standards; but natural materials, especially geological samples, contain a very complex mix of major and trace elements. Combined with this, ammonia is a very reactive gas and can form complex clusters and reaction product ions from many coexisting elements including Ti, Y and the REE elements. If these clusters form at the same mass as one or more of the lead isotopes then the use of ammonia cell gas without MS/MS mode would introduce further bias and errors. To test this hypothesis a solution of NIST 981 Pb isotope standard $(1 \mu g/L)$ was spiked with 10 $\mu g/L$ Hg and 50 $\mu g/L$ REE mix (to keep the experiment relatively simple no other potential matrix elements were added). The standard was measured using the 8800 ICP-QQQ operated in

single quadrupole "bandpass" mode (where Q1 allows a "window" of masses covering a range above and below the Q2 set mass into the cell) and the resulting spectrum is displayed in Figure 3. From this spectrum, the complexity of the reaction product ions generated in ammonia reaction gas mode is apparent; all of the masses in the range measured are affected by reaction product ions, and the isotopes for lead are all interfered. Table 2 displays some of the possible interferences from REE-ammonia cluster ions, but it is clear that many different REE-ammonia clusters could affect the Pb isotopes. It is worth noting that other matrix and analyte elements could also contribute product ions at these masses, and the only way to be sure of avoiding these overlaps is to prevent these parent ions from entering the cell. Once the REE ions have entered the cell, reaction with the ammonia cell gas proceeds very quickly, and the resulting product ions have the same m/z as the target Pb isotopes so cannot be selectively removed using a bandpass filter in the cell.

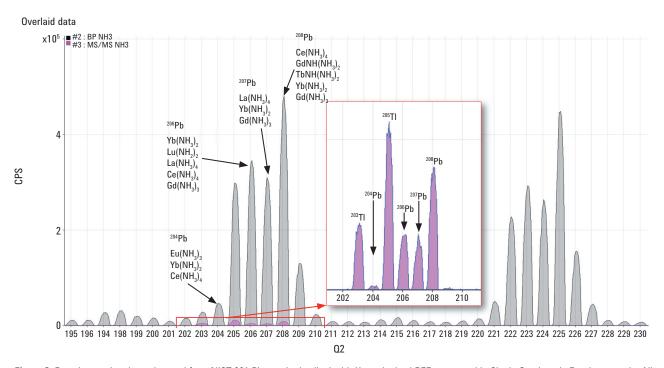


Figure 3. Reaction product ions observed for a NIST 981 Pb standard spiked with Hg and mixed REE, measured in Single Quadrupole Bandpass mode. All masses measured have peaks from the REE-ammonia clusters and the Pb isotopes are swamped by the interferences. Under MS/MS mode (overlay and inset) the cluster interferences are completely removed and the true Pb and Tl signal can be observed.

 Table 2. Examples of some possible interferences from REE-ammonia

 clusters on lead isotopes

Mass	Cluster
²⁰⁴ Pb	Eu(NH ₃) ₃ ; Yb(NH ₃) ₂ ; Ce(NH ₃) ₄
²⁰⁶ Pb	Yb(NH ₃) ₂ ; Lu(NH ₂) ₂ ; La(NH ₃) ₄ ; Ce(NH ₃) ₄ ; Gd(NH ₃) ₃
²⁰⁷ Pb	La(NH ₃) ₄ ; Yb(NH ₃) ₂ ; Gd(NH ₃) ₃
²⁰⁸ Pb	Ce(NH ₃) ₄ ; GdNH(NH ₃) ₂ ; TbNH(NH ₃) ₂ ; Yb(NH ₃) ₂ ; Gd(NH ₃) ₃

Many other sample types contain REEs at appreciable levels, including geological, food, soil and other environmental samples. The formation of REE-ammonia cluster ions therefore limits the applicability of reaction mode with ammonia cell gas, unless adequate control of the reaction chemistry is provided by using MS/MS mode on the ICP-QQQ. The Hg/REE spiked NIST 981 Pb sample was also measured using the exact same cell conditions as above, but with the 8800 ICP-QQQ

operated in MS/MS mode (shown in the overlay and inset spectrum in Figure 3). In MS/MS mode, all ions apart from the selected Pb masses are rejected by Q1, so the REE ions do not enter the cell and therefore cannot form reaction product ions that would overlap Pb. The NIST standard was also spiked with 1 ppb uranium to test the possibility of simultaneous U/Pb measurements and Figure 4 shows the same spiked NIST 981 standard measured under MS/MS mode peak jumping for the masses of interest (TI, Pb and U) using on-mass as well as mass-shift measurement, within the same acquisition. Although uranium partially reacted with ammonia it can be monitored using both the U(NH) adduct ion and directly on its original mass. This does mean that both Pb and U can be monitored under the same analytical conditions.

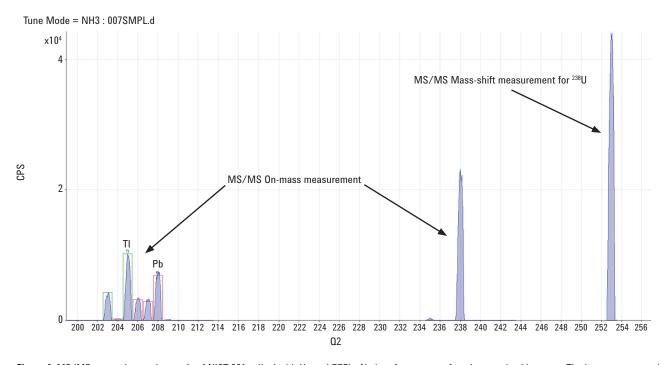


Figure 4. MS/MS ammonia reaction mode of NIST 981 spiked with Hg and REE's. No interferences are found on any lead isotopes. The instrument was also operated simultaneously for on-mass and mass-shift measurement for uranium.

Figure 5 displays the schematic for the MS/MS mode measurement of ^{204}Pb (the same principle applies to measurement of the other Pb isotopes): Q1 is set to m/z 204 rejecting all ions greater or less than 204 amu (<> ^{204}X); only the remaining ions (^{204}Hg and ^{204}Pb) enter the cell, which is pressurized with ammonia. The Hg $^+$ ions undergo a charge transfer reaction to form Hg 0 and, as neutral particles are not focused by the electrostatic fields at the cell exit, the Hg 0 is rejected before Q2.

To check the accuracy of the NH₃ MS/MS mode for Pb isotope analysis, two NIST lead standards were measured under isotope analysis mode. The Pb standards were spiked with Hg and REE's at 10 ppb and 50 ppb respectively along with individual Hg and REE spikes and unspiked. The instrument was set to measure the samples using three different cell conditions: single quadrupole mode without cell gas, single quadrupole bandpass with ammonia cell gas and MS/MS mode with ammonia cell gas. The NIST 982 standard was used as the reference standard to correct for Mass Bias (i.e., to calibrate the isotope ratio accuracy). Table 3 displays the data for the 204/206 isotope ratio measured in NIST 981 run as an unknown sample, together with the certified values and

deviation/recovery against the certified values. Data for NIST 982 with the Hg/REE spike additions is also included, with all ratios being mass bias corrected using the unspiked NIST 982. It is clear that interferences from Hg and the REE's cause significant error in the isotopic measurement of between 2 and ~300x in all modes apart from ammonia reaction mode with MS/MS.

The data presented in Table 3 confirm that the Agilent 8800 ICP-QQQ operating in MS/MS mode with ammonia reaction gas offers a powerful solution to the ²⁰⁴Hg isobaric interference on ²⁰⁴Pb.

The same reaction chemistry has also been applied to laser ablation (dry plasma) analysis using the 8800 ICP-QQQ, with data acquisition using time resolved analysis (TRA). The removal of the ²⁰⁴Hg overlap on Pb at mass 204 was also effective under these measurement conditions, indicating that the 8800 ICP-QQQ MS/MS method with ammonia reaction gas can also be applied to direct in situ Pb/Pb dating of minerals and other samples such as archaeological artefacts, where bulk measurement or sample digestion is not an option.

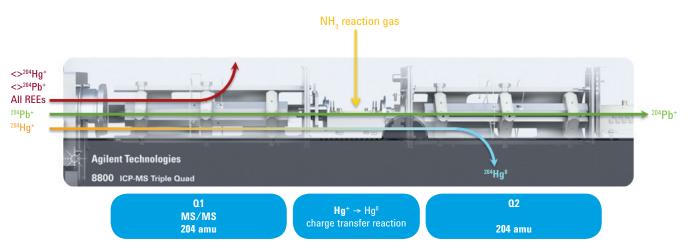


Figure 5. Schematic representation of MS/MS reaction mode for Hg interference removal . Q1 is set to m/z 204 rejecting all ions at masses other than 204 amu (<> ^{204}X).

Table 3. Analysis of 204/206 Pb ratio in certified NIST lead isotope standard with and without Hg and REE matrix spikes (982 material used for mass bias correction). *This 981 solution had some Hg contamination which biased the results in no gas mode.

204/206	No gas		NH ₃ bandpass		NH ₃ MS/MS			
	IR	Deviation	IR	Deviation	IR	Deviation		
Certified	0.059042							
NIST 981*	0.1403	2.376	0.0605	1.025	0.0591	1.001		
NIST 981 + Hg	22.0480	373.429	0.0589	0.998	0.0588	0.997		
NIST 981 + REE	0.1489	2.522	0.1192	2.019	0.0582	0.986		
NIST 981 + Hg REE	17.0132	288.155	0.1192	2.018	0.0611	1.034		
Certified	0.027219							
NIST 982	0.0272	1.000	0.0272	1.000	0.0272	1.000		
NIST 982 + Hg	0.8851	32.517	0.0273	1.003	0.0278	1.022		
NIST 982 + REE	0.0292	1.072	0.0989	3.633	0.0275	1.012		
NIST 982 +Hg REE	0.7251	26.639	0.0989	3.635	0.0276	1.013		

Conclusions

Chemical resolution using the Agilent 8800 ICP-QQQ offers exciting possibilities for the removal of difficult interferences that otherwise would require cumbersome sample preparation, and opens application areas that cannot be addressed using high resolution sector-field ICP-MS. In situations where sample preparation is not possible, such as direct analysis by laser ablation ICP-MS, chemical resolution in conjunction with MS/MS technology provides reliable interference removal without the need for complex and often unreliable mathematical correction.

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