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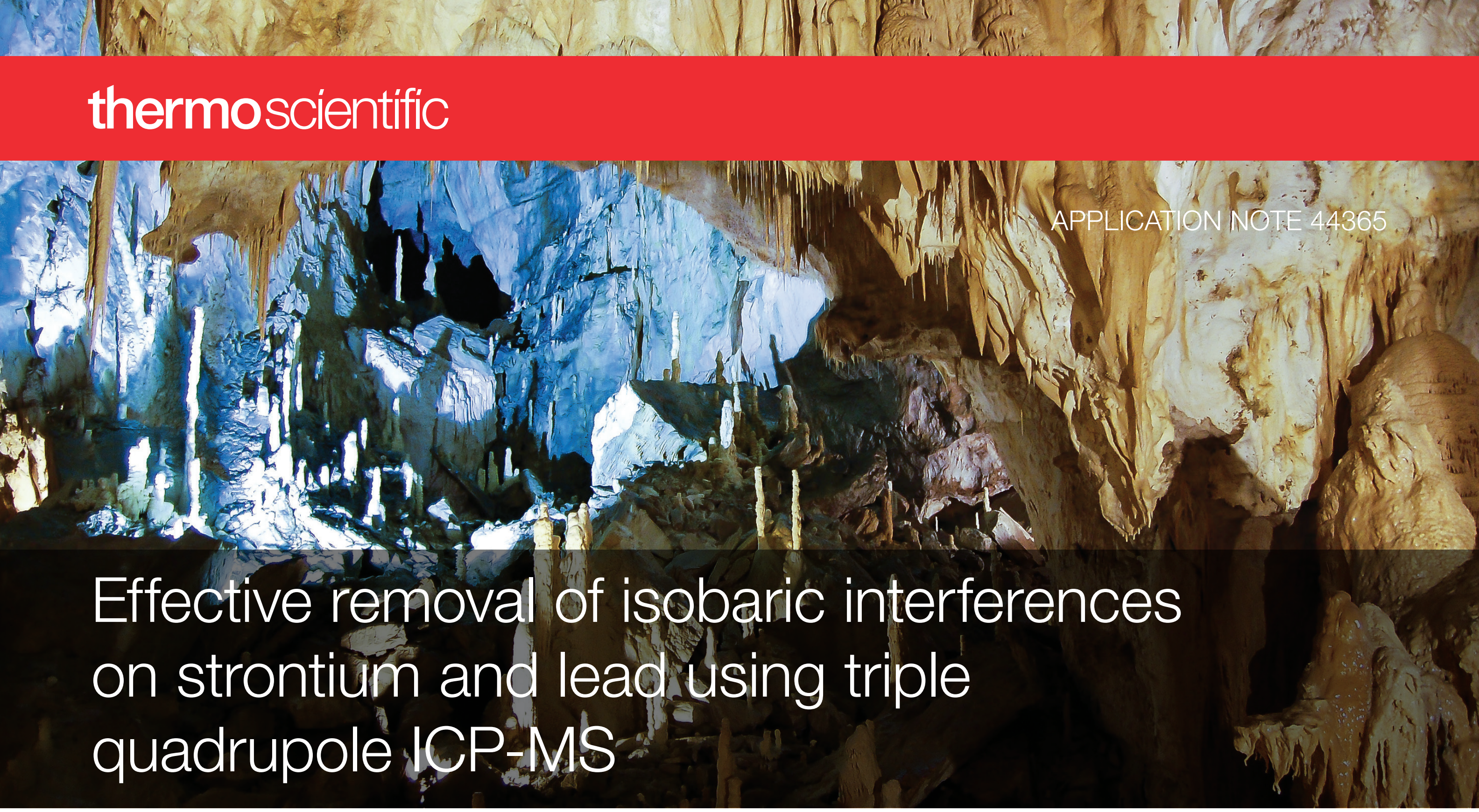

APPLICATION NOTE 44365

Effective removal of isobaric interferences on strontium and lead using triple quadrupole ICP-MS

Authors
Daniel Kutscher,
Simon Lofthouse,
Simon Nelms and
Shona McSheehy Ducos

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Goal

To show the complete removal of isobaric interferences such as ^{87}Rb on ^{87}Sr, or ^{204}Hg on ^{204}Pb utilizing the Thermo Scientific iCAP TQ ICP-MS.

Introduction

Unresolved spectral interferences may lead to biased results in ICP-MS. Single quadrupole ICP-MS typically uses a comprehensive interference removal mechanism with an inert collision gas (helium) and kinetic energy discrimination (KED). This approach, is based on the difference in size between an analyte and polyatomic interference and as such is effective for removal of many common interferences. In some cases though, two elements may share isotopes with identical mass number. These isotope overlaps are commonly referred to in ICP-MS as isobaric interferences. As the elemental ions are of a similar size, KED is not able to resolve these interferences. In addition, as the difference in mass between overlapping isotopes is extremely low, they cannot be spatially resolved using either quadrupole based or high resolution ICP-MS. Often, correction of isobaric interferences is accomplished using mathematical methods, however this procedure may lead to increased measurement uncertainties. Isobaric interferences may be resolved using reactive gases (e.g. O_2 or NH_3), in the cases where one element forms a different product ion to the other. However, side reactions may create new unwanted interferences with other ions extracted from a sample, so that full interference removal may not be possible.

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The use of oxygen as a reactive gas leads to product ions which are fairly easy to interpret (mass shifts of mainly 16, but also 17 and 18 amu), whereas using ammonia as a reactive gas leads to the formation of a wide variety of product ions, as different cluster ions will be formed for each individual isotope of a given element. With ammonia, mass shifts from as low as 15 amu are observed, but also product ions with over 100 amu mass differences can be formed. Interpreting results from unknown or complex sample matrices may therefore be challenging. Using triple quadrupole ICP-MS, a dedicated mass filtering step ahead of the collision/reaction cell (CRC) overcomes the problem of uncontrolled side reactions, as only ions with the same mass to charge ratio (*m/z*) as the analyte may enter the cell and subsequently react with gas molecules. Method development for triple quadrupole ICP-MS may seem to be more complicated in comparison to single quadrupole ICP-MS, as the right combination of reactive gas used, scan setting (SQ vs. TQ) and product ion (where applicable) needs to be defined by the operator. Within the Qtegra ISDS Software for the Thermo Scientific™ iCAP™ TQ ICP-MS, this can all be determined easily even by unexperienced users using the Reaction Finder method development assistant. At the same time, experts can manually add other settings for flexibility in method development.

Instrumentation

All measurements were accomplished using a Thermo Scientific iCAP TQ ICP-MS system. The instrument was tuned daily using the autotune routines supplied with the operating software. All solutions were prepared gravimetrically from single element standards. The precision of the isotope ratios was calculated from 10 main runs with 30 sweeps each. The data displayed in this paper was not mass bias corrected, so that the isotope ratios may differ slightly from the true value. However, the effect of mass bias would affect all individual measurements in the same way, so that correction would not alter the fundamental findings. Generally, isotope ratios are noted together with the observed standard deviation (as an indication for the attainable precision of the measurement) throughout this work. Typically, the observed relative standard deviation of the isotope ratio was in the order of 0.1%. In order to compare the results obtained using conventional single quadrupole based ICP-MS analysis utilizing kinetic energy discrimination (SQ-KED), single quadrupole ICP-MS using reactive gases (SQ-O_2 and SQ-NH_3) and triple quadrupole ICP-MS with mass filtering and use of reactive gases (TQ-O_2 and TQ-NH_3), the iCAP TQ ICP-MS was configured to scan all samples in the three corresponding measurement modes. An overview of the instrument´s settings can be found in Table 1.

Table 1. Instrumental Parameters.

Parameter	Value		
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min^{-1}, pumped at 40 rpm		
Spraychamber	Quartz cyclonic, Peltier cooled to 2.7 °C		
Injector	2.5 mm id, Quartz		
Interface	High Sensitivity (2.8 mm) insert, Ni cones		
RF Power	1550 W		
Nebulizer Gas Flow	1.11 L·min^{-1}		
QCell settings	**SQ-KED**	**SQ-O_2, TQ-O_2**	**SQ-NH_3, TQ-NH_3**
Gas Flow	100% He, 4.5 mL·min^{-1}	100% O_2, 0.35 mL·min^{-1}	100% NH_3, 0.33 mL·min^{-1}
CR Bias	-21 V	- 7.5 V	- 7.5 V
Q3 Bias	-18 V	-12 V	-12 V
Scan Settings	0.1 s dwell time per analyte, 30 sweeps, 10 main runs		

Sample preparation

In order to evaluate the performance of the iCAP TQ ICP-MS for this application, the targeted isotope ratio was measured with and without the elements causing isobaric interferences (e.g. Sr in presence of Rb). All solutions were prepared gravimetrically in 2% nitric acid. Generally, no mass bias correction was applied, as only the potential effect of interfering elements was the objective of this study.

Method development and analysis

Two prominent examples for isobaric interferences are the detection of ^{87}Sr (7.00% abundant in nature) in the presence of Rb, which also has an isotope with mass number 87 (^{87}Rb is 27.84% abundant). Secondly, ^{204}Pb (1.40% abundant) is interfered by ^{204}Hg (6.85% abundant), which is of special concern for geological applications, where the ^{204}Pb isotope is often used as a reference isotope (as it is not affected by radioactive decay of U or Th).

Using single quadrupole ICP-MS, strontium is typically analyzed using KED to make sure polyatomic interferences are removed, but also standard mode (no interference removal) may be feasible depending on the sample. For removal of the isobaric interference of ^{87}Rb, oxygen can be used as a reactive gas in the CRC system. While Sr undergoes an oxidation reaction and hence forms product ions with *m/z* 103 ($^{87}Sr^{16}O^+$) and 104 ($^{88}Sr^{16}O^+$) respectively, ^{87}Rb does not react with oxygen. If the analyzing quadrupole of either a single or a triple quadrupole ICP-MS is set to scan *m/z* 103 and 104 under these conditions, only Sr will be detected. However, only triple quadrupole instruments can filter out ions potentially interfering at the new product ion mass of Sr, such as $^{103}Rh^+$, $^{104}Ru^+$ or $^{104}Pd^+$. Independent of the Rb content in a given sample, the isotope ratio measured for ^{88}Sr/^{87}Sr should vastly agree with the theoretical value of 11.7971.

Figure 1 demonstrates how the quadrupoles in TQ-ICP-MS are set for Sr isotopes in this application.

For Pb, similar experiments were conducted in order to estimate the effect of the isobaric interference caused by ^{204}Hg on ^{204}Pb. In order to judge how far the isobaric interference was eliminated, the isotope ratio ^{204}Pb/^{208}Pb (reference value 0.02672) was used as a reference.

Results

In order to evaluate the performance in different measurement modes for Sr, a calibration curve was acquired using SQ-KED as a reference, and using triple quadrupole technology in combination with oxygen as a reactive gas. The resulting detection sensitivity using oxygen and a mass shift reaction was about 30% in comparison to SQ-KED (14 kcps/µg·L^{-1} in comparison to 51 kcps/µg·L^{-1}), however, the instrumental detection limit was not affected (0.001 µg·L^{-1} for ^{88}Sr in both modes of analysis).

In a second experiment, solutions containing 10 µg·L^{-1} and varying concentrations of Rb were analyzed and the isotope ratio ^{88}Sr/^{87}Sr was evaluated. Furthermore, solutions containing equal amounts of Sr and Rb in a matrix containing either or both 1 mg·L^{-1} of Pd and 10 mg·L^{-1} of Ru (to account for lower abundance of the ^{104}Ru isotope in comparison to monoisotopic ^{103}Rh) were analyzed. Typically, considering the isotopic abundance of the strontium isotopes ^{87}Sr and ^{88}Sr, one would expect a theoretical isotope ratio of 11.7971. The results are displayed in Table 2.

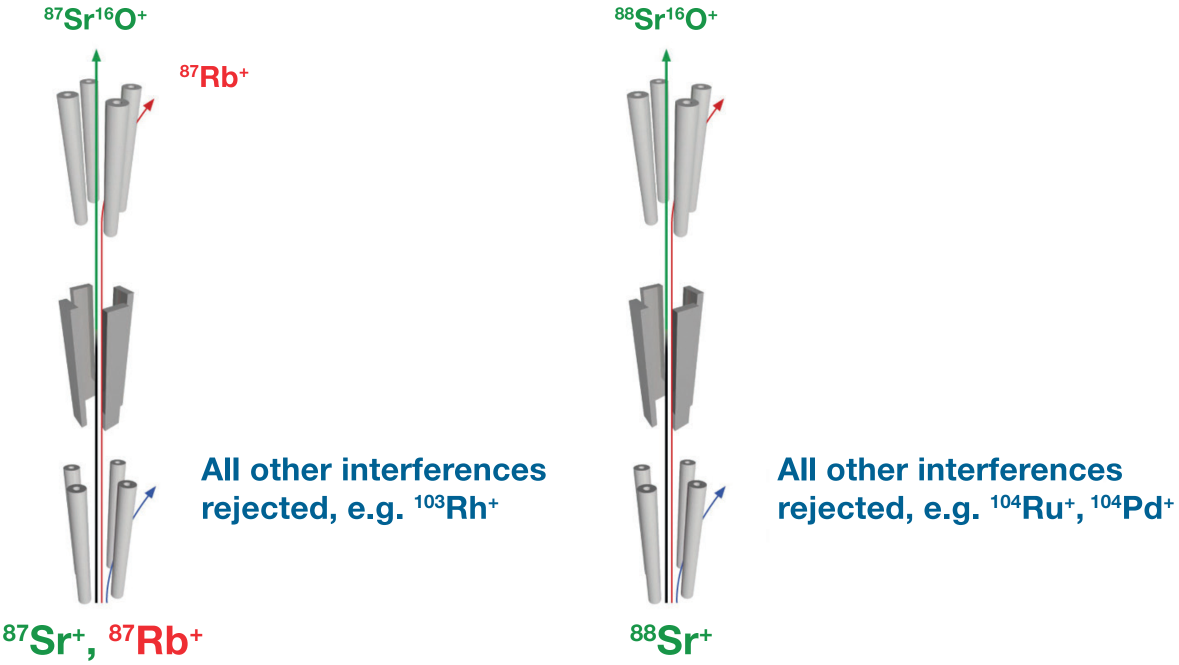

Figure 1. Schematic illustrating the analysis of strontium isotopes in presence of Rb using triple quadrupole ICP-MS operated with oxygen as reaction gas.

Table 2. Isotope ratio for ^{88}Sr/^{87}Sr in solutions containing varying amounts of Rb (*no mass bias correction applied).

Sample	Isotope Measured isotope ratio ^{88}Sr/^{87}Sr using SQ-KED mode*	Isotope measured isotope ratio ^{88}Sr^{16}O/^{87}Sr^{16}O using SQ-O_2 mode*	Measured isotope ratio ^{88}Sr/^{87}Sr using TQ-O_2 mode *TQ-O2*
10 µg·L^{-1} Sr	12.6280 ± 0.1097	9.0228 ± 0.0550	12.1175 ± 0.1447
10 µg·L^{-1}Sr, 10 µg·L^{-1} Rb	2.6572 ± 0.0122	N/A	12.0635 ± 0.0877
10 µg·L^{-1} Sr, 100 µg·L^{-1} Rb	0.3216 ± 0.0158	N/A	12.1053 ± 0.1123
10 µg·L^{-1}Sr, 1 mg·L^{-1} Rb	0.0311 ± 0.0003	N/A	12.1183 ± 0.1160
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb	0.0032 ± 0.00004	N/A	12.0741 ± 0.0907
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb, 1 mg·L^{-1} Rh	2.5832 ± 0.0157	0.0038 ± 0.000005	12.0464 ± 0.0970
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb, 10 mg·L^{-1} Ru	2.5992 ± 0.0205	10,634.0766 ± 848.20	12.1338 ± 0.1094
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb, 1 mg·L^{-1} Rh; 10 mg·L^{-1} Ru	2.6338 ± 0.0158	2.0209 ± 0.0059	12.0003 ± 0.1074

As can be seen from the table, the increasing amount of Rb (and hence the abundance of ions with *m/z* 87) has no effect on the Sr isotope ratio when using the TQ-O_2 mode. In contrast, the single quadrupole approach using KED reveals a strong effect of the increasing amount of Rb in the sample solution, as the isobaric interference is not resolved. When utilizing oxygen as a reactive gas in single quadrupole based analysis, the obtained isotope ratio is mainly affected by the interfering ions on the product ion mass of 87 (^{103}[^{87}Sr^{16}O]) which are not removed and remain as interferences, since neither Rh nor Ru react with oxygen. Even the observed isotope ratio for a solution containing only Sr is strongly biased by other ions of unknown identity formed in the cell.

For elimination of the isobaric interference from Hg on Pb, a reaction with ammonia can be used. Hg undergoes a chemical reaction with ammonia molecules and forms product ions, which will have a different *m/z* ratio. At the same time, Pb does not react with ammonia, so it can be detected free from interferences when the analyzing quadrupole (Q3) is set to the same mass as the first quadrupole (i.e. mass 204 in this case). It is therefore important to avoid other reactions in the cell that could lead to the formation of a product ion with *m/z* 204, so lower mass ions that could generate additional interferences need to be removed in the first quadrupole. Again, the objective was to investigate how far traditional single quadrupole approaches in comparison to triple quadrupole operation may be suitable for this application. For the single quadrupole mode tests, ammonia was also used as the reactive gas, but with Q1 acting as an ion guide only, so that other ions originating from the sample could also enter the CRC system.

Table 3 clearly shows that, again, KED does not enable the removal of isobaric interferences, as the measured isotope ratio changes with increasing concentration of Hg added to the solution. In contrast, the use of NH_3 as a reactive gas in single quadrupole mode is capable of eliminating the isobaric ^{204}Hg interference from ^{204}Pb. Since no other ions are present in the ion beam when analyzing a solution containing only Hg and Pb, there is no drawback in not using an additional mass filter or just using Q1 as an ion guide. However, for real sample analysis this is almost never the case. If for example rare earth elements are present in the sample solution (which is likely in geological samples such as soils or rock digests), other cluster ions may be formed with NH_3, so that *m/z* 204 is again interfered. To test this, 1 mg·L^{-1} of ytterbium was added to the measured solution to introduce ^{170}Yb$(NH_3)_2$ as a potential interference on ^{204}Pb in SQ-NH_3 mode. Again, a biased ^{204}Pb/^{208}Pb isotope ratio is observed, clearly showing that there is an effect from ^{170}Yb$(NH_3)_2$ interference on ^{204}Pb in SQ-NH_3 mode. In order to visualize this newly formed polyatomic interference, a full mass spectrum was acquired using NH_3 as reactive gas (Figure 2).

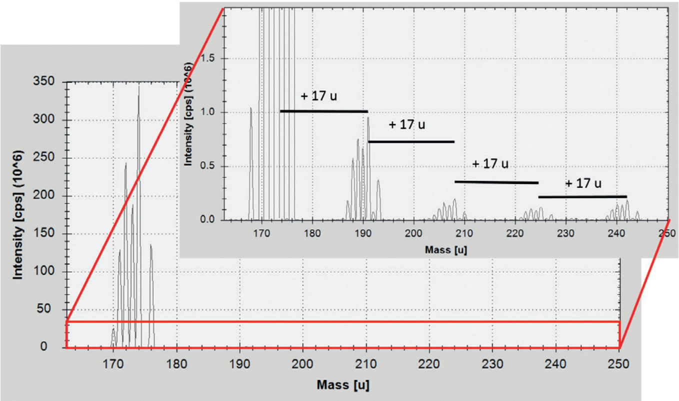

Figure 2. Full mass spectrum illustrating the formation of Yb derived product ions acquired using single quadrupole operation and ammonia as reaction gas.

Table 3. Isotope ratio for ^{204}Pb/^{208}Pb in solutions containing varying amounts of Hg and Yb.

Sample	SQ-KED	SQ-NH_3	TQ-NH_3
1 µg·L^{-1} Pb µg·L^{-1}	0.0258 ± 0.0001	0.0258 ± 0.0001	0.02581 ± 0.0001
1 µg·L^{-1} Pb + 5 µg·L^{-1} Hg	0.4301 ± 0.0025	0.0258 ± 0.0001	0.02591 ± 0.0001
1 µg·L^{-1} Pb +10 µg·L^{-1} Hg	0.8941 ± 0.0055	0.0258 ± 0.0001	0.02589 ± 0.0001
1 µg·L^{-1} Pb + 20 µg·L^{-1} Hg	1.8270 ± 0.0051	0.0258 ± 0.0001	0.02589 ± 0.0001
1 µg·L^{-1} Pb + 1 mg·L^{-1} Yb	0.0469 ± 0.0011	0.0721 ± 0.0002	0.02592 ± 0.0001

It can be seen that there are numerous cluster molecules formed from Yb and NH_3. While unreacted Yb still shows the highest abundance in the mass spectrum between *m/z* 168 and 176 (indicating that the reaction is not quantitative), the characteristic isotope pattern for Yb can be repeatedly found also at higher mass, with an equal distance of 17 amu between corresponding isotopes. This mass difference reveals the successive addition of one molecule of NH_3 per precursor ion and is characteristic for reactions of this gas. The main interference now found on *m/z* 204 corresponds to $^{170}\text{Yb}(^{14}\text{N1H}_3)_2^+$, but since all of the seven Yb isotopes react in the same way, the other Pb isotopes would be similarly interfered. In SQ-NH_3 mode, these newly formed polyatomic ionsare transmitted with the isotope mass of interest and so introduce a new interference on the target isotope. In contrast, when switching to a triple quadrupole based measurement mode (TQ-NH_3), all other ions with lower mass (such as ^{170}Yb) are removed from the ion beam before they enter the CRC system and so are not able to generate these new interferences. The side reaction of Yb with NH_3 therefore does not lead to the formation of new interferences on Pb, and in turn, the ^{204}Pb/^{208}Pb measured isotope ratio is not affected at all through the presence of either Hg or Yb. Furthermore, other rare earth elements that may lead to the formation of new interferences on ^{204}Pb due to their reactivity towards ammonia, for example cerium ($^{136}\text{Ce}(^{14}\text{N}^{1}\text{H}_3)_4^+$, 0.19% abundant) or europium ($^{153}\text{Eu}(^{14}\text{N}^{1}\text{H}_3)_3^+$, 52.20% abundant), are also removed by Q1 in triple quadrupole mode.

Conclusion

The removal of isobaric interferences using reactive gases has been demonstrated in two examples, ^{87}Rb/^{87}Sr and ^{204}Hg/^{204}Pb. Leveraging different reactivity towards oxygen and ammonia respectively allows a chemical separation of the isobars inside the CRC. Although single quadrupole instruments are also capable of utilizing reactive gases, unwanted side reactions with other elements present in the sample may lead to the formation of new interferences, as has been shown in the case of Yb and Pb. The importance of controlling the ions entering the CRC is a key factor with respect to obtaining analytical accuracy. Triple quadrupole ICP-MS using a dedicated mass filter in front of the CRC is the only definitive way of achieving this required ion transmission control and obtaining accurate data.

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