Ultratrace Analysis of ^{41}Ca by Resonance Ionization Mass Spectrometry

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Introduction:

The isotopic ratio determination of rare isotopes in the range below 10^{-10} is of great importance for a wide spectrum of applications. The required specifications concerning isotopic selectivity and isobaric suppression can only be reached by dedicated techniques [1]. Presently these methods are accelerator mass spectrometry (AMS), atomic trap trace analysis (ATTA) and high resolution resonance ionization mass spectrometry (RIMS) using continuous narrowband lasers.

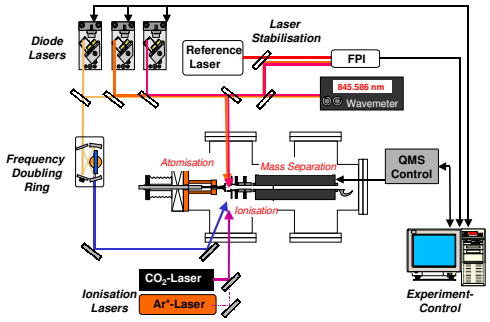
The ultratrace isotope ^{41}Ca has a lifetime of 1.03×10^5 y and a relative natural abundance of ^{41}Ca/^{40}Ca of only about 10^{-14}. High resolution RIMS measurements for ^{41}Ca determination in *environmental* and *bio-medical* samples as well as *calibration* studies to the complementary techniques are presented.

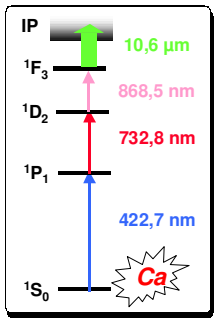
Ca 40	Ca 41	Ca 42	Ca 43	Ca 44	Ca 45	Ca 46	Ca 47	Ca 48
96.941	$1.03 \cdot 10^5$	0.647	0.135	2.086	163d	0.003	4.54d	0.187

K 39	K 40	K 41
93.258	0.0117	6.73

Stable and long-lived isotopes of calcium and dominant isobars in the mass 41 region

Experimental Method and RIMS Excitation Scheme for Calcium:





The setup for high resolution RIMS [2] consists of three major components:

- Sample atomization: electro-thermally heated graphite crucible for efficient and well collimated atomic beam production
- Laser ionization: 3 continuous narrowband diode laser systems for multi-step resonant excitation, ionization via CO_2 laser
- Mass separation: quadrupole mass spectrometer for subsequent mass analysis and low background ion detection.

An efficient laser excitation scheme is prerequisite for ultra trace analysis; it has been determined in previous spectroscopic studies [3]: the Ca-isotopes are excited with blue light from the $4s^2\,{}^1S_0$ ground state into the first excited $4s4p\,{}^1P_1$ state. From there the atoms are resonantly excited with two infrared photons via $4s4p\,{}^1P_1 \rightarrow 4s4d\,{}^1D_2 \rightarrow 4snf\,{}^1F_3$ (n=15 or 17). Afterwards they are ionized by a non resonant high-power CO_2-Laser at 10,6 µm.

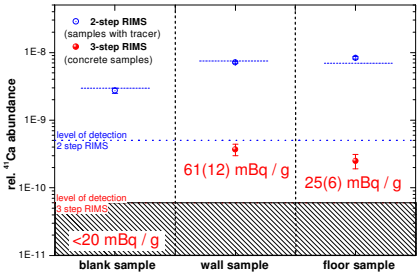
Environmental Investigations:

As a first demonstration of an analytical application, nuclear reactor components for environmental dosimetry have been measured.

Concrete samples from different places inside the biological shield have been taken. ^{41}Ca is produced in the concrete via neutron capture in ^{40}Ca by the high neutron flux. Ca is a 5-10% component of concrete. For clearance certification of this material in Germany, ^{41}Ca activities below 100 Bq / g must be determined.

For evaluation of the RIMS method, a known amount of ^{41}Ca has been spiked into a number of samples and measured with 2-step RIMS. The blue dotted lines show the expectations, while the blue symbols represent mean values of several individual measurements, showing good agreement.

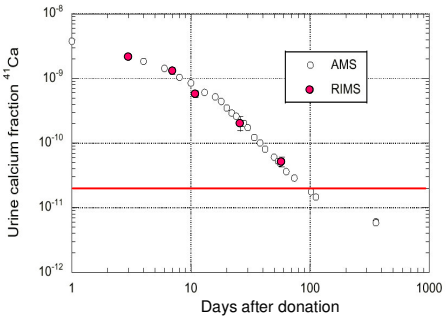
^{41}Ca content in all samples without spike were below the detection limit of 2-step RIMS, thus 3-step RIMS with a significantly higher selectivity has been used. In multiple measurements contamination of 25(6) mBq/g in the floor sample below the reactor core, 61(12) mBq/g in the wall sample and below 20 mBq/g in the blank sample taken outside of the biological shield were determined.



Bio-Medical Studies:

The OSTEODIET network of the Fifth Framework Project of the European Union investigates the use of ^{41}Ca as novel bio-medical tracer technology for osteoporosis therapy and prevention studies. After medication of 3,7 kBq = 100 nCi of ^{41}Ca, the urinary excretion in dependence of different dietary or medical treatments is monitored by RIMS or AMS.

In collaboration with the LLNL AMS facility we have measured relative ^{41}Ca concentration as function of time after medication for one individuum. Measurements down to isotopic ratios of 10^{-11} show good agreement between RIMS and AMS [4] and prove the applicability of both techniques for these studies.

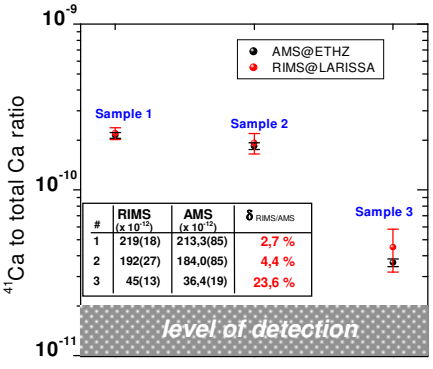


Intercomparison and Calibration of AMS to RIMS:

Laboratory intercomparison of the different mass spectrometric techniques RIMS and AMS have been performed as a basis for calibration of the results.

Therefore samples have been exchanged between the AMS-Group at the ETH Zürich, Switzerland and our RIMS setup. Several synthetically produced ^{41}Ca-samples from spallation of ^{56}Fe have been measured by RIMS and AMS.

Deviations of primary data on isotopic ratio measurements were below 5% even at a lower 10^{-10} level, giving confidence in both methods. Further decreasing isotopic ratios to a few times 10^{-11} increases the observed deviation increases up to 24%, which still is fulfilling expectations and requirements. Nevertheless, in all measurements, ratios measured by RIMS are slightly higher than those of AMS, which is not yet fully understood and will be subject to further investigations.



#	RIMS ($\times 10^{-15}$)	AMS ($\times 10^{-15}$)	$\delta_{RIMS/AMS}$
1	219(18)	213,3(85)	2,7 %
2	192(27)	184,0(85)	4,4 %
3	45(13)	36,4(19)	23,6 %

Summary and Outlook:

High resolution cw RIMS provides a versatile and powerful tool for ultratrace analysis. Isotopic ratios of ^{41}Ca/^{40}Ca from 10^{-8} down to 10^{-11} have been analyzed in various samples. With metallic samples we have determined ^{41}Ca down to a detection level of 3×10^{-13}, which is presently limited by the overall efficiency of about 5×10^{-5}. Progress is made towards a further increase of efficiency and a lowering of the detection level by installation of a new diode laser system and ion optics.

The performance of the tabletop RIMS setup has been compared with different AMS facilities, showing good agreement over at least three orders of magnitude. Using certified ^{41}Ca reference material with isotopic ratios of 10^{-4} to 10^{-13}, which will be provided by IRMM (Belgium), further calibration with AMS or other innovative approaches , e.g. ATTA, becomes feasible.

References:

[1] K. Wendt et. Al, *Resonant laser ionization mass spectrometry: An alternative to AMS?*, Nucl. Instr. Meth. B 172, 162 (2000)
[2] P. Müller et al., *^{41}Ca ultratrace determination with isotopic selectivity >10^{12} by diode-laser-based RIMS*, Fresenius J Anal Chem 370, 508 (2001)
[3] P. Müller et al., *Isotope shifts and hyperfine structure in calcium 4snp $^1D_1$ and 4snf F Rydberg states*, Eur. Phys. J. D 12, 33 (2000)
[4] S.P.H.T. Freeman et al., *The study of skeletal calcium metabolism with ^{41}Ca and ^{45}Ca*, Nucl. Instr. Meth. B 172, 930 (2000)

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