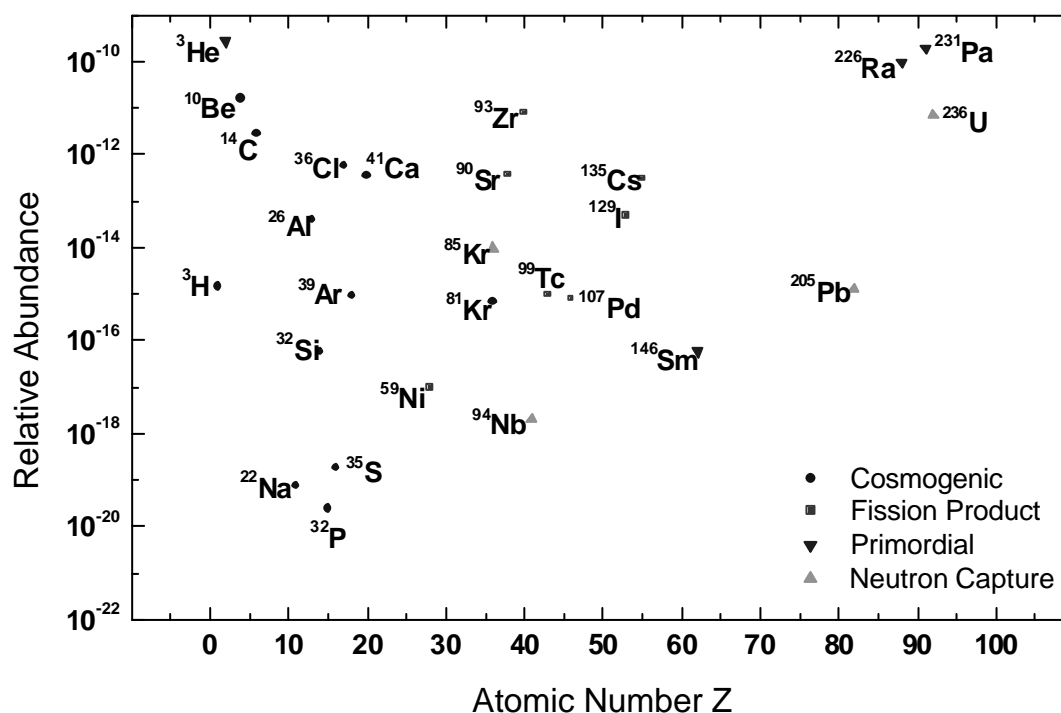


Resonance Ionization Mass Spectrometry for Sensitive and Selective Ultratrace Analysis

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High Resolution Laser Resonance Ionization Mass Spectrometry (RIMS) is developed and applied as a versatile tool for elemental trace analysis, in particular when highest elemental and isotopic selectivity is required. Through resonant excitation and ionization of atoms with lasers in general highest intrinsic elemental (=isobaric) selectivity is achieved by the uniqueness of optical atomic transition wavelengths. Using narrow bandwidth continuous wave lasers in a sequential multi-step excitation process, in addition very high optical isotopic selectivity is achieved by employing the isotope shifts in each atomic transition. Subsequent mass spectrometry on the produced photo-ions further increases isotopic selectivity and adds highest sensitivity and lowest detection limits to the technique by efficient and low background ion detection. The specifications realized in the Mainz LARISSA (Laser Resonance Ionization Spectroscopy for Selective trace Analysis) experiment by far exceeds conventional mass spectrometry and compares to the results of the well known and sophisticated technique of Accelerator Mass Spectrometry, but using table top equipment.

The interest in ultratrace determination of rare isotopes is multifold. Figure 1 shows a compilation of long-lived and stable isotopes with relative abundances below 10^{-10} of their neighboring isotope together with their class of origin. The determination of these isotopes is of highest interest for a wide variety of applications. The detection and analysis of these isotopes, both natural and man-made, yielded a wealth of information encoded in the production, transport, and decay processes of these isotopes. Many of them are well suited as sensitive probes in geochemistry and environmental studies concerning investigations in the atmosphere, the hydrosphere, the, and the lithosphere. Further applications concern cosmochemistry and astrophysics with analysis on extraterrestrial material, nuclear and particle physics. By the use of artificially enriched samples, numerous bio-medical studies and investigations in material sciences performed. For all these investigations, very high selectivity, far greater than 10^9 , is required and efficiency in the range of 10^{-3} or higher is preferred.



A mandatory basis for the development of the technique is the development and refinement of laser sources and mass spectrometers, as well as extensive laser spectroscopic studies of excitation and ionization path ways. Analytical studies presently concern the ultra trace isotope ^{41}Ca with a terrestrial abundance of about 10^{-14} . Here scientific interest is manifold:

1. Environmental: ^{41}Ca is produced in significant quantities in shielding concrete of nuclear facilities by neutron capture and is the highest long-lived contamination in this material. Due to the long half-life and unfavourable decay properties, sensitive radiometric determination of this specific activity is not easily possible and selective atom counting using high resolution RIMS is the method of choice in activity quantification, depth profiling for environmental protection and classification of nuclear waste. Development and analysis is carried out in close collaboration with the nuclear chemistry department.

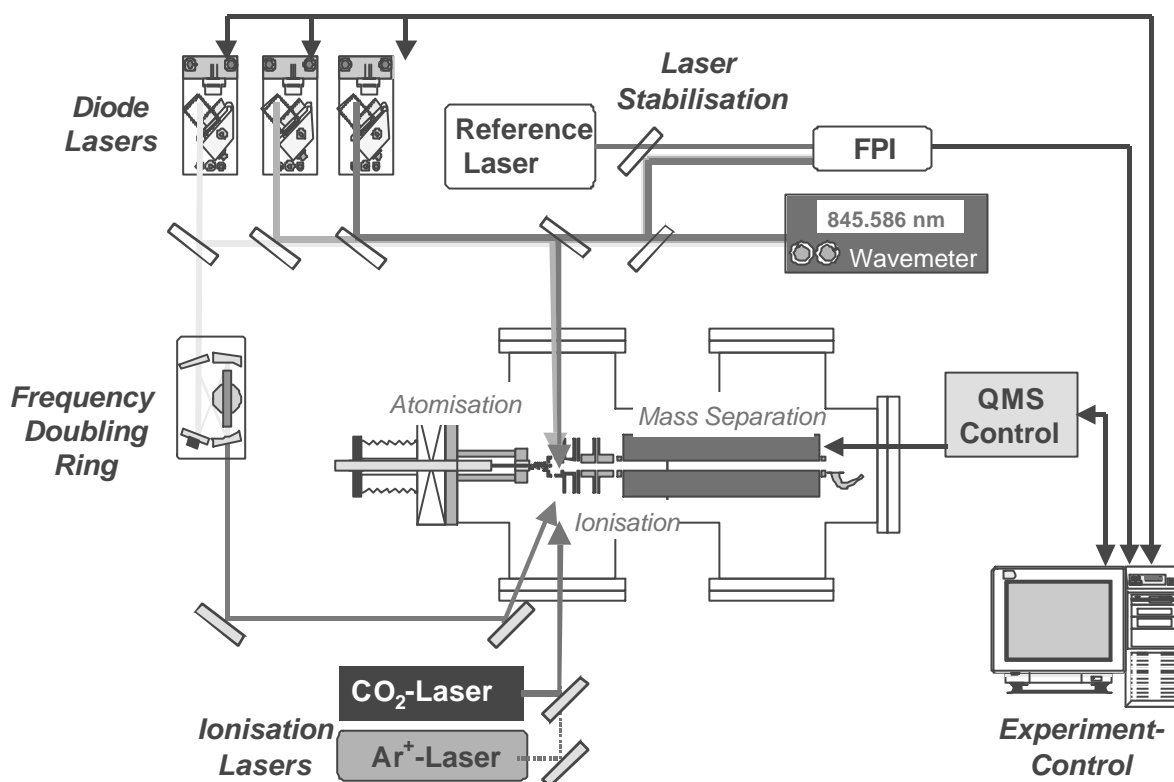
2. Cosmochemistry: In the cosmos ^{41}Ca is dominantly produced by proton induced spallation reactions on iron, e.g. in iron-rich meteoroids. Relative ^{41}Ca -abundance in extraterrestrial material hence differs from terrestrial value and can be as high as 10^{-11} . The sensitive determination of ^{41}Ca in artificially irradiated material as well as meteoritic sample contributes to the understanding of competing production mechanisms as well as to classification and analysis of this material, often carried out in combination with determination of isotope ratios and anomalies of isotope of various other elements. Measurements in collaboration with the Max-Planck Institut für Chemie, Abteilung Kosmochemie.

3. Bio-medical: ^{41}Ca is an ideal tracer isotope for bio-medical investigations on calcium kinetics and malfunctions in the living organism. Due to the long half-life radioactive doses on test persons are well below any radiation hazard and a permanent labelling of the skeleton can be realized by one single medication. Isotope selective determination of ^{41}Ca excretion in blood or urine, using RIMS or alternatively AMS techniques, gives access to important bio-medical quantities, e.g. the bi-directional calcium flux from bone to soft tissue, which governs diseases like osteoporosis. For this purpose the technique is prepared for precise isotope ratio measurement on bio-medical samples in the range of 10^{-6} to 10^{-13} , working in close collaboration to nutritionists and physicians in a European Community network.

4. Radiodating: The long half-life of ^{41}Ca makes it an ideal candidate for developing a technique of radiodating, somewhat analogous to the one of radiocarbon-dating via ^{14}C , but accessing the range of 10^5 to 10^6 years before present. For these measurements an isotopic selectivity of about 10^{15} and an overall efficiency of about 10^{-3} must be realized to resolve the natural ^{41}Ca -abundance of $\sim 10^{-14}$. This value so far has not been reached with any technique and the realization of these extreme specification with a table-top set-up of RIMS is a true challenge for the experimentalist.

The experimental approach for RIMS uses atomization of the analytical sample in a electrothermally heated graphite furnace. The resulting atomic beam is overlapped perpendicularly with the beams of up to three narrow bandwidth continuous lasers for stepwise resonant excitation and a powerful far-infra-red laser for final ionisation. For resonant excitation compact extended cavity diode lasers have been developed, which are stabilized and controlled via fringe offset locking from a PC with highest precision. For realizing optical isotopic selectivities as high as 10^8 an extensive analysis and understanding of the coherent excitation process and the atomic parameters involved is mandatory. Photo-

ions are transmitted by a specially adapted ion optics into a commercial quadrupole mass spectrometer for further selection and background reduction. Experimental specifications obtained include an isobaric suppression $> 10^8$, an overall isotopic selectivity of 5×10^{13} and an efficiency of 2×10^{-5} . Presently all values are limited by non-specific background and ultimate limitations of the technique have not yet been explored. For this purpose further optimization concerning efficiency of atomization, power and stability of the different lasers, overlap and geometry of the ionization region are in progress. Successful analytical investigations so far have been carried out on numerous samples including irradiated concrete from a nuclear test reactor, artificial meteorite material and bio-medical samples. Perfect agreement with AMS results has been demonstrated in laboratory intercomparison measurements.



Based on this experiences the technique is presently extended for other applications. Elemental selective trace determination of isotopes from rare earths and actinide elements is of high interest. While analysis of gadolinium has already been demonstrated successfully on bio-medical samples, ultra trace determination of the isotope ^{236}U for the purpose of detection of reactor fuel in the environment is presently under development. Both studies include extensive spectroscopic investigations of high fundamental interest on the rich atomic spectra of these elements, in particular concerning unknown highly excited Rydberg and autoionizing configurations and their structures.

As a powerful alternative to high resolution continuous lasers system, high repetition rate solid state lasers are developed for use in trace analysis and suppression of isobars in isotope production at on-line mass separator facilities like ISOLDE, CERN. Here isotopic selectivity is of minor concern and can be achieved by pure magnetic sector-field or time-of-flight mass separation, while laser ionization only has to deliver isobaric selectivity.