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Review

Recent developments in isotope ratio measurements by resonance ionization mass spectrometry

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Abstract

Resonance ionization mass spectrometry (RIMS) has become a sensitive and highly selective technique for the determination of extremely low elemental or isotopic abundances, involving isotope ratio measurements with dynamical ranges of 10^9 and beyond. The experimental detection limits are as low as 10^6 atoms per sample, and isotopic selectivities of up to 10^{13} have been achieved under optimal conditions. The potential of RIMS using different experimental systems is outlined in the determination of lowest abundances and isotope ratios of long-lived radioisotopes of general importance like $^{238-244}$Pu, ^{41}Ca, and ^{236}U for studies in geosciences, environmental, bio-medical or fundamental research.

Keywords: Resonance ionization spectroscopy; Mass spectrometry; Long-lived radionuclides; Isotope ratio measurements; Ultratrace detection

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Contents

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1. Introduction

The development of lasers as strong and quasi-monochromatic light sources with a good tunability has brought tremendous progress into various fields, among others in spectroscopy, analytical spectrochemistry, and laser mass spectrometry. The optical excitation of atoms and molecules by resonant absorption of laser light, realized in a step-wise process followed by the photo-ionization of the species, has nowadays become feasible in a rather efficient way. Combined with selective and nearly background free detection of the resulting photo-ions in conventional mass spectrometers this technique forms the basis of resonance ionization mass spectrometry (RIMS) [1,2]. Apart

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from fundamental investigations in the fields of atomic structure, quantum optical studies or the determination of the first ionization potential of the actinides, RIMS has been applied in numerous analytical fields such as molecular trace gas detection, solid state surface analysis, determination of explosives and chemical warfare agents as well as for the sensitive determination of rare isotopes involving lowest isotope ratio measurements [1–5].

In this review, the focus will be put on isotope ratio measurements of long-lived radioisotopes by RIMS, especially with respect to recent developments. These radioisotopes are investigated for a wide range of tasks [4,5]. The individual radioisotopes have various sources and origins [6]: they can be ascribed either to natural radioactivity, including primordial and cosmogenic species, or anthropogenic radioactivity, e.g., dispersed into nature by nuclear explosions, releases from nuclear power stations, medical applications, etc. Many of these isotopes are well suited for geochemical and environmental studies in the atmosphere (cosmic ray flux, origin and chemistry of trace gases), the hydrosphere (circulation studies, dating of oceanic and groundwater), the cryosphere (radiodating and climatology), and the lithosphere (geomorphologic studies, characterization of volcanism). Further applications cover cosmochemistry and astrophysics, nuclear and particle physics as well as bio-medical and material sciences.

For quite a number of the long-lived radioisotopes, the detection by radiometric techniques is not very efficient due to the low specific radioactivity or the application of complicated chemical separation procedures before the measurement. Therefore, direct counting of the radioactive isotopes becomes favorable even though it is often hampered by an extremely high surplus of neighboring stable isotopes as well as elemental or molecular isobars. The abundances of many of the long-lived radioisotopes of interest lie in the range of 10^{-8} to 10^{-12} or even lower of the total sample or the neighboring isotope content with the consequence that only detection methods with a high efficiency, an excellent isotopic selectivity, and a good background suppression are applicable. For a few radioisotopes of importance like ^{99}Tc or ^{239}Pu no stable isotopes are present, and in these cases only a moderate selectivity in the range of a few thousand is required. Thus, to reach lowest detection limits combined with high selectivity, mass spectrometric techniques are used in general.

Conventional mass spectrometric methods for isotope ratio determination [7] are thermal ionization mass spectrometry (TIMS) [8] or inductively coupled plasma mass spectrometry (ICP-MS) [9–12]. They use non-selective ionization processes which often lead to isobaric interferences. For dedicated applications requiring exceptional high isotopic selectivities and/or good isobaric suppressions accelerator mass spectrometry or RIMS can be used. Accelerator mass spectrometry (AMS) provides isotopic selectivities up to 10^{15} by combining different selection stages and yields detection limits down to 10^4 atoms [13], but is hampered by its high experimental expense. Since more than 30 years RIMS has been employed for the isotope-selective ultratrace analysis of long-lived radioisotopes [1,2,14–21]. Advantages of the laser-based technique RIMS include:

- Almost complete suppression against all elemental and molecular isobars caused by the uniqueness of the optical transitions.
- High to ultra-high isotopic selectivity achieved by combination of the two isotope specific properties of the method, namely the selection of one individual isotope through utilization of isotope shifts in the optical excitation process and of one mass in the mass separation process. The isotope shift can further be increased by applying collinear optical excitation on fast moving atoms.
- Very good efficiency originating from the high cross-sections of the optical excitation and ionization processes, high transmission of the mass spectrometer and efficient ion detection.

However, there are also some disadvantages: RIMS is a strict one element technique, adaptation to a new element requires elaborate development and up to now no commercial support for routine operation is available. A laser-based determination system as realized by RIMS is very desirable as a competitive and/or complementary technique to AMS. As presented below, this has already been reached by now and RIMS has shown its usefulness and outstanding specifications in a number of analytical studies. In contrast to other mass spectrometric methods RIMS and AMS are dedicated to single element determination and are not suitable for multi-element analysis.

2. Background of RIMS

Adapted to a broad range of isotopes under investigations and the specific requirements of the analytical tasks various experimental versions of RIMS have been set up by a number of groups worldwide, each one being specifically tailored for one or a few individual applications. Nevertheless, these are all based on one concept. After a simple chemical separation, the isolated fraction is thermally evaporated from an atomic beam source. Single or multi-step resonance excitation and subsequent ionization is carried out by irradiation of the atoms with tuned laser light and the resulting ions are accelerated within an electric field, transmitted through a mass spectrometer and subsequently detected by ion counting. Quantification involves precise determination of isotope ratios to a known reference value or standard.

2.1. Resonance excitation and ionization process

For the optical resonance excitation from the atomic ground state or from a thermally populated low-lying excited state up to final ionization usually a number of different pathways are required. Possible excitation ladders are indicated in Fig. 1. Optical excitation along the first steps of all these channels can be carried out very efficiently: typical atomic

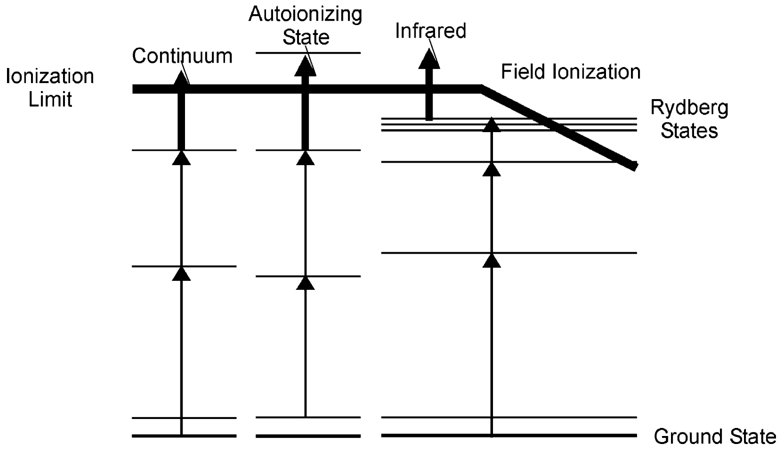


Fig. 1. Excitation schemes for multi-step resonance ionization mass spectrometry.

lifetimes for the strong transitions between most bound atomic states are of the order of 10 ns while the cross-section for absorption of a photon is given by $\sigma = \lambda^2/2\pi \approx 10^{-10}\,\mathrm{cm}^2$ for the idealized case of an atom at rest. As the excitation probability is determined by $\mathrm{d}W(t) = \sigma J(t)\,\mathrm{d}t$, a flux of about $J(t) \approx 10^{18}$ photons/(cm^2 s), corresponding to a power of only about 100 mW/cm^2 of the tunable laser, is sufficient for the saturation of such a transition. Due to the different velocities of the moving atoms in real experiments an effective cross-section for individual velocity classes has to be used, which is lowered by about a factor of 10–100, depending on the collimation of the atomic beam. Nevertheless, this value is still easily reached by today's state-of-the-art continuous (cw) as well as pulsed laser systems. Direct non-resonant ionization into the continuum, as shown on the left-hand side of Fig. 1 is rather unfavorable as it is characterized by a low cross-section of only about $10^{-17}\,\mathrm{cm}^2$. This "bottle-neck" of the process can be avoided for elements with a complex atomic spectrum, like, e.g., the lanthanides and actinides, by populating a low-lying autoionizing state, a doubly excited atomic state, which converts energy rapidly and decays within a lifetime of less than 1 ns into an ion and an electron. Furthermore, excitation into high-lying Rydberg states with subsequent efficient field or far infrared ionization can be used. For these processes the ionization probability is easily increased by two to three orders of magnitude compared to non-resonant ionization into the continuum but nevertheless very intense laser light sources are needed for saturation of the ionization step, provided most easily by powerful pulsed laser systems.

2.2. Laser systems for RIMS

The choice of the laser system for a particular RIMS application depends on the experimental specifications. In any case, tunable lasers must be used to precisely match the resonance lines of the element under study. Pulsed tunable lasers, which utilize laser dyes or crystals as active media can cover broad tuning ranges and deliver sufficient laser power for the saturation of optical transitions as well as for the extension of their spectral range via non-linear optical processes of frequency doubling, tripling or mixing. A drawback is the spectral profile which usually lies in the GHz range. Thus, even in multi-step processes pulsed lasers very often do not provide sufficient isotopic but only elemental resolution. Additionally, the duty cycle affects the efficiency. Therefore, high repetition rate lasers in the 10 kHz range are required for a good efficiency. Alternatively, pulsed laser desorption or sputtering, well synchronized to an ionizing laser system can be employed.

Solid state lasers based on titanium–sapphire crystals are now state-of-the-art for high repetition rate tunable laser systems [22] and replace dye laser systems, which are more inconvenient to handle, require frequent maintenance and are therefore not ideally suited for routine measurements.

Continuous wave lasers have a much narrower spectral bandwidth in the MHz region. Hence, they are useful for high-resolution studies and give access to effects in the optical spectra like isotope shifts and hyperfine structures, which are used to increase the isotopic selectivity up to extremely high values. They also avoid any losses due to "laser off" periods. Unfortunately, the power of cw-lasers as well as the accessible spectral range is much smaller than pulsed lasers and often limits efficiency and overall performance. Moreover, the narrow experimental linewidth of the cw-lasers requires high experimental effort on laser frequency adjustment and control. In the last years compact and tunable diode lasers have appeared on the market for some spectral regions.

2.3. Mass spectrometer and ion detection

The second selective part of the RIMS system is the mass spectrometer. For the determination of lowest concentrations as well as for precise isotope ratio measurements, the quantity of interest is the suppression of neighboring masses, given by the isotopic abundance sensitivity, which is the reciprocal value of the mass selectivity S_{MS} of the system. The characteristic quantity of the mass spectrometer is its resolution, defined as $\Re = \frac{M}{\Delta M}$, where ΔM is the width of the mass peak at position M. This quantity is correlated to S_{MS} in a complex non-analytical manner. Ab initio calculations of the selectivity require the precise knowledge of individual mass peak shapes. For each mass spectrometer this must be obtained numerically by extensive ion trajectory calculations, taking into account the complete spectrometer field geometry as well as laser ionization and ion beam parameters. Neighboring mass suppressions as high as 10^6 to 10^8 can be realized experimentally for a mass spectrometer. The limiting factors are very different for the individual spectrometers: TOF-systems are limited by inhomogenities in the acceleration field and the time resolution of the detector; critical for magnetic sector field spectrometers are gas-kinetic collisions with residual gas molecules demanding for a very high vacuum, while quadrupole mass spectrometers can be tuned to selectivities $>10^8$ if highest driving radio-frequencies and low velocity and velocity spread of the initial ions are maintained. For all the spectrometer types the transmission amounts to values up to 80%, provided the emittance of the laser ionization process is well matched to the acceptance of the mass spectrometer. Additionally, resonant laser excitation and ionization results in very narrow energy spread of the initial ion below 1 eV, which positively influences the specifications of the mass spectrometer and allows widely background free ion detection with a standard channeltron or channelplate detector [23].

3. Application of RIMS

3.1. Pulsed RIMS with high repetition lasers and a time-of-flight mass spectrometer

RIMS with pulsed laser excitation and a time-of-flight (TOF) mass spectrometer is used now for ultratrace determination of actinides, mainly plutonium, in the environment [24]. For such determinations an extreme selectivity is not required. A sketch of the experimental arrangement as used for Pu determination is shown in Fig. 2; the experimental procedure is the following: after chemical separation of plutonium, the isolated sample is electrolytically deposited on a tantalum backing, which is afterwards covered with a thin layer of titanium by sputtering for enhancement of the atomization probability. By electrothermal heating of this sandwich filament, a continuous atomic beam is evaporated which is superimposed perpendicularly by three laser beams for ionization of the atoms by three-step, three-color laser excitation [22]. The resulting photo-ions are accelerated by 3 kV, transmitted through either a linear or a reflectron TOF mass spectrometer and finally detected with a channelplate detector. As the laser pulse serves as trigger for the TOF, for each individual laser pulse a full mass spectrum can be recorded. The mass resolution of the TOF spectrometers of $R \approx 600$ is sufficiently high to yield isotopic selectivities of $S \approx 1000$ without using isotope-selective optical excitation.

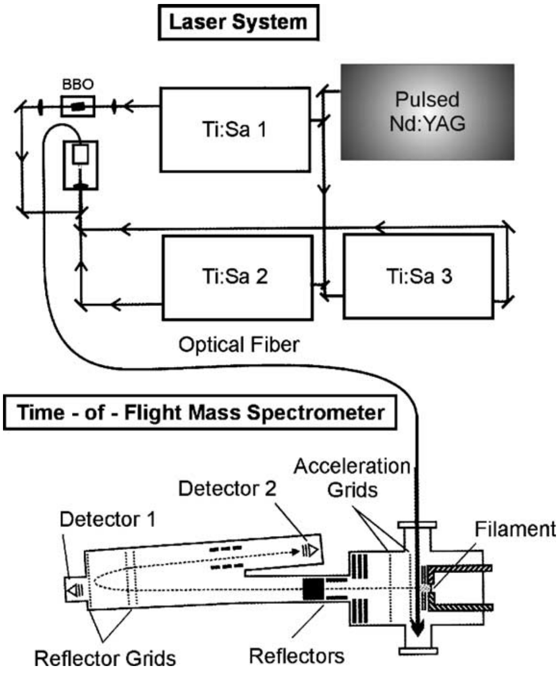


Fig. 2. Sketch of the experimental set-up for pulsed laser resonance ionization mass spectrometry with a time-of-flight mass spectrometer.

With this set-up an overall efficiency of $\varepsilon \approx 3 \times 10^{-5}$ has been obtained, which can be explained by considering the different experimental steps involved: chemical separation (50%), atomization during evaporation (50%), ground state population (40%), spatial overlap of atomic beam and lasers beams (7%), temporal overlap of the beams (4%), TOF-transmission (60%), and detector efficiency (30%). Multiplying these quantities leads to a theoretical expectation for the overall efficiency of $\approx 5 \times 10^{-5}$, which is in rather good agreement with the experimental value. A detection limit of $\approx 10^6$ atoms (0.4 fg) for a signal/noise ratio of 3 and for a single isotope with a 3σ-confidence level is extracted, which, e.g., is about two orders of magnitude better than the detection limit for ^{239}Pu by α-spectroscopy. For exact isotope ratio measurements the isotope shifts of the individual plutonium isotopes 238, 239, 240, 241, 242, and 244 must be taken into account for the excitation scheme in use. As can be seen from Table 1a the isotope ratios measured with RIMS for the NIST standard SRM 996 are in excellent agreement with the certified ratios. Table 1b gives the isotopic composition of plutonium in a uranium penetrator as used during the Balkans conflict in comparison with weapon-grade plutonium [25]. The measured plutonium composition can be explained by the fact that the depleted uranium for the penetrators was produced in a machinery in which recycled reactor fuel was processed earlier resulting in a contamination with trace amounts of plutonium.

Examples for the isotope-selective determination of plutonium in environmental samples are presented in Fig. 3. Fig. 3a shows an RIMS-TOF spectrum of a water sample from the Irish Sea in which the isotopes Pu-238, Pu-239, Pu-

Table 1
Isotope ratios for plutonium as obtained with RIMS for the NIST standard SRM 996 (a) and isotopic composition of plutonium in a depleted uranium penetrator (b)

Pu isotopes	Measured ratios	Certified ratios
(a) NIST standard SRM 996		
238	0.00004(3)	0.0004(1)
239	0.00039(9)	0.00035(2)
240	0.0065(4)	0.0069(1)
241	0.00054(10)	0.00037(2)
242	0.0137(5)	0.0135(1)
244	1	1

Pu isotopes	Measured	Weapon-grade [25]
(b) Isotopic composition in % of plutonium in a depleted uranium penetrator		
239	93.6(59)	93.5
240	6.2(7)	6.0
242	0.06(1)	0.015

Errors given in brackets are 3σ standard deviations.

240, Pu-241, and Pu-242 could be determined. In Fig. 3b a mass spectrum from a dust sample containing plutonium from the reprocessing plant at the Research Center Karlsruhe is given. The isotope ratios are characteristic for reactor plutonium.

A novel approach for ultratrace analysis with pulsed RIMS may be an ion guide laser ion source [26]. Here the atoms produced are stored in a buffer gas cell at an argon pressure of 35 mbar within the interaction volume with the laser light for about 40 ms. The created ions are guided to a nozzle by an electric field, flushed out of the gas cell, mass separated in a quadrupole mass spectrometer and counted by a channeltron detector. This system has facilitated very recently the first spectroscopic studies on fermium with ~10^{10} atoms of Fm-255 [27].

3.2. High-resolution RIMS with continuous wave lasers

The first proposal to apply RIMS for significantly enhancing the isotopic abundance sensitivity of a conventional mass

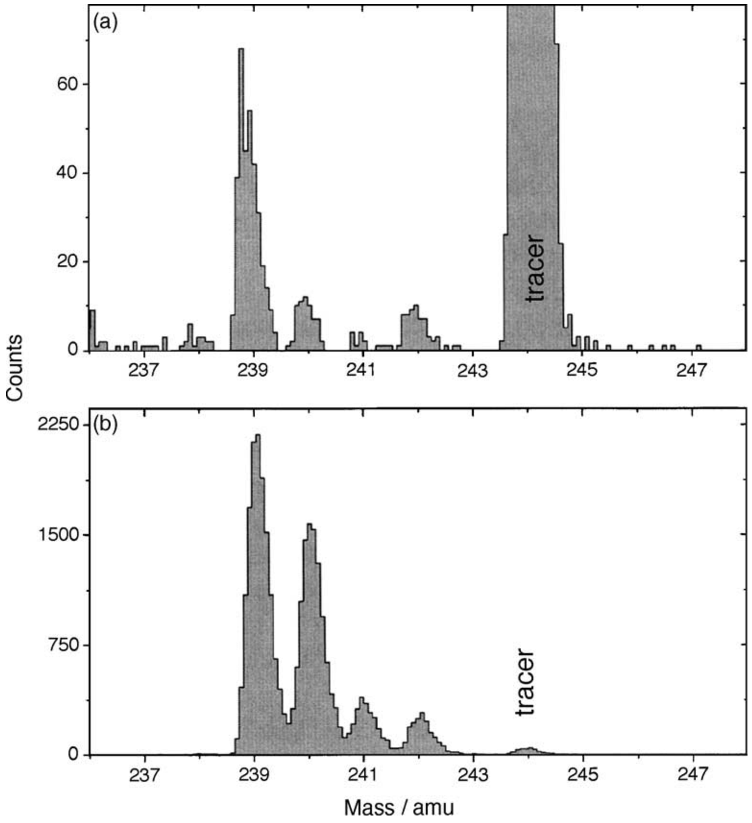


Fig. 3. Time-of-flight mass spectra of plutonium after pulsed laser ionization for (a) a water sample from the Irish Sea and (b) a dust sample contaminated with reactor plutonium.

spectrometer was made by Letokhov [1]. Two different experimental schemes have been realized afterwards: (i) collinear RIMS on a beam of fast moving atoms, being pioneered by Kudryavtsev et al. [28] and (ii) high-resolution multi-step resonance ionization mass spectrometry (HR-RIMS) in perpendicular geometry on a thermal atomic beam, which can be primarily accredited to Bushaw [29].

Collinear RIMS utilizes the strong and mass dependent Doppler shift as well as the significant reduction in Doppler width. This happens by superimposing a laser beam collinearly on a beam of atoms accelerated to velocities of 10^5 m/s and beyond [30]. In this way a large artificial isotope shift and a narrow spectral width is produced enabling the suppression of neighboring isotopes already within only one selective optical excitation step. The collinear RIMS approach was first demonstrated for the selective determination of the rare ultratrace noble gas isotope ^{3}He in environmental samples, demonstrating selectivities of 10^9 in the suppression of ^{4}He and an overall efficiency of 4×10^{-5} [31]. Subsequently the technique has been applied for the fast and sensitive determination of the radiotoxic isotopes ^{89,90}Sr in environmental samples [32,33]. An overall efficiency of about 1×10^{-5} and a selectivity of $\sim 10^{11}$ in the suppression of the dominant stable isotope ^{88}Sr have been determined. The main limitation occurs by background from various unselective collisional ionization processes. This background and the high instrumental expense are the major drawbacks of collinear RIMS, and have so far prevented routine operation of such a system.

In the last decade the alternative technique of using multistep narrow bandwidth laser excitation in perpendicular geometry on a thermal atomic beam has found more and more application. A simple sketch of such an experimental arrangement as applied for the determination of ^{41}Ca is shown in Fig. 4. Up to three tunable cw-lasers are used for isotope-selective step-wise excitation on a thermal atomic beam, which is delivered from an electrothermally heated furnace. The laser beams are directed in a counter propagating way and perpendicular to the atomic beam in order to minimize Doppler broadening. Ionization is carried out directly in the ionization region of the mass spectrometer, either by population of an autoionizing state in the third step or a high-lying state with subsequent non-resonant ionization by a powerful far infrared laser. Quadrupole mass spectrometers (QMS), which permit for very high isotopic abundance sensitivity and lowest background ion detection – if used in combination with resonant laser ionization – are favorable [34]. Alternatively, also the use of magnetic sector field spectrometers has been reported [35].

Three-step narrow bandwidth excitation requires a broad set of spectroscopic studies on precise level positions, isotope shifts and hyperfine structures before this method can be used for isotope ratio measurements. After these data have been collected, often commercial diode lasers, offering some limited tunability via an extended laser cavity, can be used and thus simplify the experimental effort. However, a rather sophisticated laser control system, which enables stabilization and precise tuning of the different lasers with a precision of about 1 MHz is required for generation of highest selectivity and efficiency. Thus far, this technique has been applied successfully for selective ultratrace determination of ^{210}Pb [36], ^{135,137}Cs [35], ^{90}Sr [37], ^{41}Ca [38], and ^{152}Gd [39].

For the selective ultratrace determination of ^{41}Ca triple-resonance excitation is used to reach highest selectivity. In the interaction region, the atoms are excited along the optical transitions $4s^2\ ^1S_0 \rightarrow 4s4p\ ^1P_1 \rightarrow 4s4d\ ^1D_2 \rightarrow 4s\ 15f\ ^1F_3$ Rydberg state with laser light of 422.8, 732.8, and 868.5 nm, respectively. For this purpose three precisely tuned but weak diode lasers with powers in the range of only a few milliwatts are employed, already enabling the saturation of the strong transitions. Finally, efficient photo-ionization is carried out

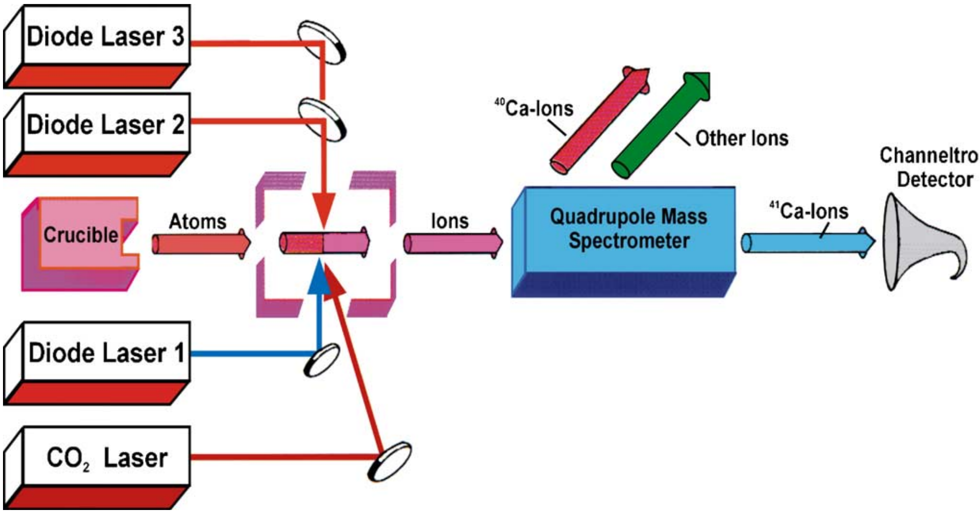
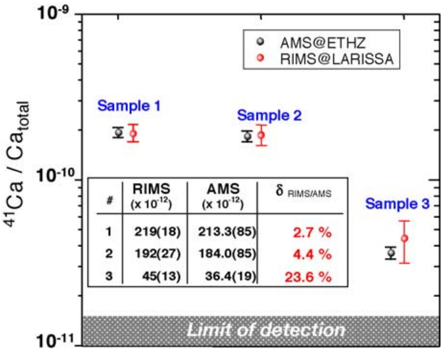


Fig. 4. Lay-out of the experimental set-up for high-resolution resonance ionization mass spectrometry with continuous wave lasers and a quadrupole mass spectrometer as applied for the determination of ^{41}Ca.

by a non-resonant high power CO_2-laser at 10.6 μm. The maximum isotopic selectivity of $\sim 5 \times 10^{12}$ for ^{41}Ca obtained so far is limited by several sources of background: photo-induced dimers, hydride formation, surface ionized isobars, like ^{41}K, and contributions from highly excited neutral atoms [40]. For suppressing this background sources and thus for reaching higher specifications different modifications will be adapted in the near future. For elements with complex atomic spectra, like Gd and Sm or U, ionization via autoionizing levels by means of a diode laser can be used. This approach is even more favorable, because resonance enhancements up to 10^6 with respect to non-resonant processes have been realized [41].



#	RIMS ($\times 10^{-12}$)	AMS ($\times 10^{-12}$)	$\delta_{RIMS/AMS}$
1	219(18)	213.3(85)	2.7 %
2	192(27)	184.0(85)	4.4 %
3	45(13)	36.4(19)	23.6 %

Fig. 5. Comparison of isotopic ratios of $^{41}Ca/Ca_{total}$ in the 10^{-10} range, as measured with high-resolution resonance ionization mass spectrometry (RIMS) and accelerator mass spectrometry (AMS).

A mandatory step for the determination of lowest isotopic abundances is the precise determination of isotope ratios with a very high dynamical range. In the case of ^{41}Ca determination, the low abundance (0.135%) stable isotope ^{43}Ca is used as reference and the analytical method determines relative count rates at three positions: mass spectrometer and all lasers are tuned to ^{41}Ca; mass spectrometer and all lasers are tuned to ^{43}Ca, and finally a background position is chosen. Background can be kept as low as 10 mHz, thus the maximum permitted count rate of the channeltron ion detector of $>10^6$ Hz gives a direct accessible range of up to 10^{-13} with respect to overall calcium, which can be further enhanced by controlled reduction of the ionization efficiency of the reference isotope. The measuring sequence is repeated until the whole sample is evaporated or the statistics of the result is good enough. It must be ensured that the ionization probability for the individual isotopes is identical or well known and that the mass spectrometer does not exhibit any mass discrimination. This is verified by calibration measurements of stable calcium with the known isotopic composition as a preparatory step before and during each analytical measurement. In this way environmental [42], cosmochemical [43], and bio-medical samples [44] have been analyzed for their ^{41}Ca isotopic abundance over a range of 3×10^{-6} down to $<3 \times 10^{-11}$ with an average isotopic ratio precision of better than 5% and a typical overall efficiency of $\leq 5 \times 10^{-5}$. Comparisons with accelerator mass spectrometry [43,44] and atomic trap trace analysis [45] have yielded very good agreement. An example of such an intercomparison measurement between HR-RIMS and AMS, carried out on cosmochemical ^{41}Ca samples, is illustrated in Fig. 5. ^{41}Ca has been produced artificially by proton induced nuclear spallation reaction of Fe at an accelerator. The determination of the isotopic abundance is important for the understanding of astrophysical cross-sections of cosmic ray absorption. With an abundance limit of 3×10^{-11} arising from potassium contaminations in the sample, a perfect agreement between both techniques has been obtained for $^{41}Ca/Ca_{total}$ ratios around 10^{-10}, while close to the detection limit the deviation increases up to 25%. A second example on the applicability of HR-RIMS is connected to bio-medical studies for prevention of osteoporosis. For the determination of excretion curves of ^{41}Ca in the urine of doped test persons, lowest abundances in the range of 10^{-9} and below have been measured. A typical excretion curve is presented in Fig. 6. The excretion can be described in an analytical form and ends up in a plateau in the 10^{-10} abundance range, where drug-related or nutritional intervention studies can be carried out, leading either to a significant increase or decrease of the level. Further investigations on this topic are in progress.

The isotope-selective ultratrace analysis of ^{236}U is also of great interest. This isotope, which is produced by neutron capture in ^{235}U at high neutron fluxes, i.e., in a nuclear reactor or during a nuclear bomb explosion, serves as a probe whether fissionable material is anthropogenic or from natural sources. ^{236}U can also be used for migration and speciation studies of uranium introduced into the environment, e.g., by the Chernobyl accident or by the use of uranium ammunition. Relative abundances in the range of 10^{-7} down to 10^{-11} must be determined. To explore the capabilities of HR-RIMS, extensive spectroscopic studies within the atomic spectrum of uranium are presently carried out to ascertain the best suited optical three-step excitation scheme for sensitive ultratrace determination.

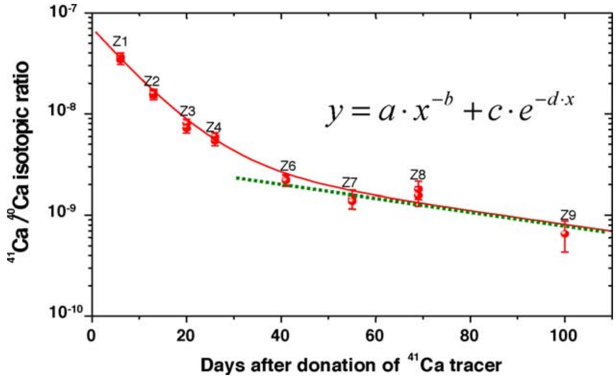


Fig. 6. Excretion curve of ^{41}Ca-concentration in human urine after donation of ^{41}Ca tracer at day 1, investigated by high-resolution resonance ionization mass spectrometry.

4. Conclusion and outlook

RIMS in different experimental arrangements has proven to be well suited for ultratrace analysis and isotope ratio measurements of long-lived radioisotopes. The major advantages of RIMS are the short measuring time, the high isotopic and isobaric selectivity and the low detection limits. So far, the analytical application is restricted to a few specialized laboratories, due to the relatively high experimental expenditure, especially on the side of the tunable lasers and their frequency control and adjustment. Nevertheless, it is expected that the advent of easy-to-use and reliable solid state laser systems, based, e.g., on titanium:sapphire and other crystals as active laser material or alternatively on novel laser diodes will simplify RIMS systems and allow automated routine analysis in the near future.

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