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Laser ablation inductively coupled plasma mass spectrometry for direct isotope ratio measurements on solid samples

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Abstract

Isotope ratio measurements have been increasingly used in quite different application fields, e.g., for the investigation of isotope variation in nature, in geoscience (geochemistry and geochronology), in cosmochemistry and planetary science, in environmental science, e.g., in environmental monitoring, or by the application of the isotope dilution technique for quantification purposes using stable or radioactive high-enriched isotope tracers. Due to its high sensitivity, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is today a challenging mass spectrometric technique for the direct determination of precise and accurate isotope ratios in solid samples. In comparison to laser ablation quadrupole ICP-MS (LA-ICP-QMS), laser ablation coupled to a double-focusing sector field ICP-MS (LA-ICP-SFMS) with single ion detection offers a significant improvement of sensitivity at low mass resolution, whereby isotope ratios can be measured with a precision to 0.1% relative standard deviation (R.S.D.). In LA-ICP-SFMS, many disturbing isobaric interferences of analyte and molecular ions can be separated at the required mass resolution (e.g., $^{40}Ar^{16}O^+$ and $^{56}Fe^+$ for iron isotope ratio measurements). The precision on isotope ratio measurements was improved by one order of magnitude via the simultaneous detection of mass-separated ion currents of isotopes using multiple ion collectors in LA-ICP-MS (LA-MC-ICP-MS).

The paper discusses the state of the art, the challenges and limits in isotope ratio measurements by LA-ICP-MS using different instrumentations at the trace and ultratrace level in different fields of application as in environmental and biological research, geochemistry and geochronology with respect to their precision and accuracy.

Keywords: Geochronology; Isotope ratio measurements; Laser ablation inductively coupled plasma mass spectrometry; Mass bias correction

1. Introduction

The determination of isotope ratios is becoming increasingly important, e.g., in geological research (geochronology) [1–11], in biology and life sciences [12–15], for the characterization of radioactive waste [16] or environmental control [17–20]. Besides the different mass spectrometric techniques such as inductively coupled plasma mass spectrometry, ICP-MS; glow discharge mass spectrometry, GDMS; thermal ionization mass spectrometry, TIMS; secondary ion mass spectrometry, SIMS; sputtered neutral mass spectrometry, SNMS; spark source mass spectrometry, SSMS; laser ionization mass spectrometry, LIMS; resonance ionization mass spectrometry, RIMS, ICP-MS is the method most frequently employed for isotope ratio measurements due to its excellent sensitivity, good precision and accuracy. Isotope ratios were studied more often by ICP-MS than laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [21]. However, laser ablation ICP-MS is becoming the method of choice for analysis of solid samples due to the advantage of direct solid sampling and its capability of providing micro-scale information. For a long time, TIMS was the most frequently used solid mass spectrometric technique for determining precise and accurate isotope ratios of metals with ionization potentials lower than 7 eV. Today TIMS is still used as a routine technique in many laboratories worldwide in geochemistry, geochronology,

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the nuclear industry and environmental research. Due to instrumental developments in LA-ICP-MS with single and multiple ion collectors and the advantages in comparison to TIMS, e.g., high sensitivity, comparable precision and accuracy, practically no restriction on the ionization potential of chemical elements, time-independent mass fractionation and the possibility of additional multi-element analysis at trace and ultratrace level, no complicate chemical sample preparation procedure, TIMS will be increasingly replaced in future by powerful LA-ICP-MS for direct isotope ratio measurements on solid samples without sample preparation.

Laser ablation ICP-MS, as a relatively new and powerful analytical mass spectrometric technique (introduced onto the commercial analytical market in 1990), was originally developed for direct multi-element analysis on solid samples at the trace and ultratrace level. The major limiting property for precise isotope ratio measurements has been observed in the instability of inductively coupled argon plasma and the laser ablation process itself. Instrumental developments therefore focused on improving the laser ablation regime, on increasing plasma stability, improving sample introduction of ablated material in the inductively coupled plasma and especially on developing multiple ion detection systems. With the introduction of the multiple ion collector (MC) instruments “Plasma 54” about 12 years ago, LA-ICP-MS has become an established method for high-precision isotope analysis with a performance comparable to MC-TIMS. The first work that demonstrates the potential of LA-MC-ICP-MS for very high-precision isotope ratio measurements performed directly on solid samples was done by Walder et al. [37] in case of lead isotope ratios measurements of NIST glass standard reference material 610. Already in this work it has been demonstrated that measured isotope ratios agree with those determined by TIMS and also the precision in LA-MC-ICP-MS is comparable to that obtained in TIMS.

The aim of this work is to review the advantages, the limits and new applications in environmental and biological science, geology and geochemistry of laser ablation ICP-MS using quadrupole-based or sector field ICP-MS with single and multiple ion collectors.

2. LA-ICP-MS instrumentation and capability for isotope analysis

LA-ICP-MS uses the ablation of sample material by a focused laser beam in an inert gas atmosphere (e.g., Ar) under normal pressure and transferring ablated material into an inductively coupled plasma ion source of an ICP-MS. The experimental arrangement of LA-ICP-MS using several types of mass spectrometers – as used in the author’s laboratory – is shown in Fig. 1. In LA-ICP-MS, different commercial laser ablation systems—mostly solid state Nd-YAG laser ablation systems, (e.g., CETAC LSX 200, LSX 500 and LSX 3000, Cetac Technologies, Omaha, NE, USA; Merchantek LUV 266 nm laser microprobe, UP 213, UP 266, UP 266 Macro from New Wave Research/Merchantek, Fremont, CA, USA; VG MicroProbe II, Thermo Finnigan, Bremen Germany; Ablascope 213 nm, Bioptic, Berlin, Germany) are coupled directly to several types of ICP-MS. Especially the new Nd-YAG laser ablation systems, which work at a wavelength of 213 nm at small laser spot and relatively high laser power density (e.g., Ablascope from Bioptic), as demonstrated in two other papers in this issue [12,50], are advantageous for a multitude of applications on isotope ratio measurements. Furthermore, a few commercial excimer laser ablation systems (e.g., UP 193H, New Wave Research/Merchantek; GeoLasArF, MicroLas, Göttingen, Germany) are available on the analytical market and several home-made laser ablations systems [2,22–24] are also in use in several laboratories. Application of excimer lasers in laser ablation ICP-MS is increasing because the shorter the wavelength, the less fractionation effects are in general observed [25]. Minimizing of fractionation effects is possible by performing laser ablation (independent of the laser ablation system used) with a laser power density of 10^9 W cm^{-2} and higher [26–28]. Elemental fractionation does not play an important role for the determination of inter-element isotope ratios, but in the case of geochronology where intra-element isotope ratios (e.g., ^{206}Pb/^{238}U, ^{208}Pb/^{232}Th, ^{187}Re/^{188}Os) are measured elemental fractionation has to be considered and minimized. Fractionation effects of Pb and U isotopes caused by defocusing of the laser beam during ablation on a crater have been avoided by using the active focusing mode [29] or linear scan mode of laser ablation [9].

The most frequently used LA-ICP mass spectrometers worldwide are quadrupole-based instruments (LA-ICP-QMS) without collision cells (PQ II, VG-Elemental; Elan 6000, Perkin-Elmer; Agilent 7500, Agilent; X Series, Thermo Elemental; Ultramass, Varian). LA-ICP-QMS allows isotope ratio measurements with an internal precision for short-term isotope ratio measurements from 0.2 to 1% relative standard deviation (R.S.D.). The precision in isotope ratio measurements for elements at the trace concentration level using LA-ICP-QMS is limited, for example, by counting statistics, which can be improved by increasing the integration time (number of laser shots, repetition frequency). Instrumental progress in isotope ratio measurements by quadrupole ICP-MS with a single ion detector has been achieved by the introduction of the collision cell (CC) interface in order to neutralize plasma gas ions (Ar^+) and to dissociate disturbing argon-based molecular ions (ArX^+, X = O, N, C, H or Ar) by ion–molecule reactions if, for instance, He/H_2 was introduced into the cell as the collision gas mixture. The application of the collision cell in LA-ICP-MS (LA-ICP-CC-MS) results in higher ion transmission by reducing the kinetic energy of ions, and in an improvement of the sensitivity and precision of isotope ratio measurements compared to LA-ICP-MS without the collision cell. In spite of the advantages LA-ICP-MS with collision cell is difficult to handle (requires careful time-consuming optimization procedure, and new molecular ions are formed

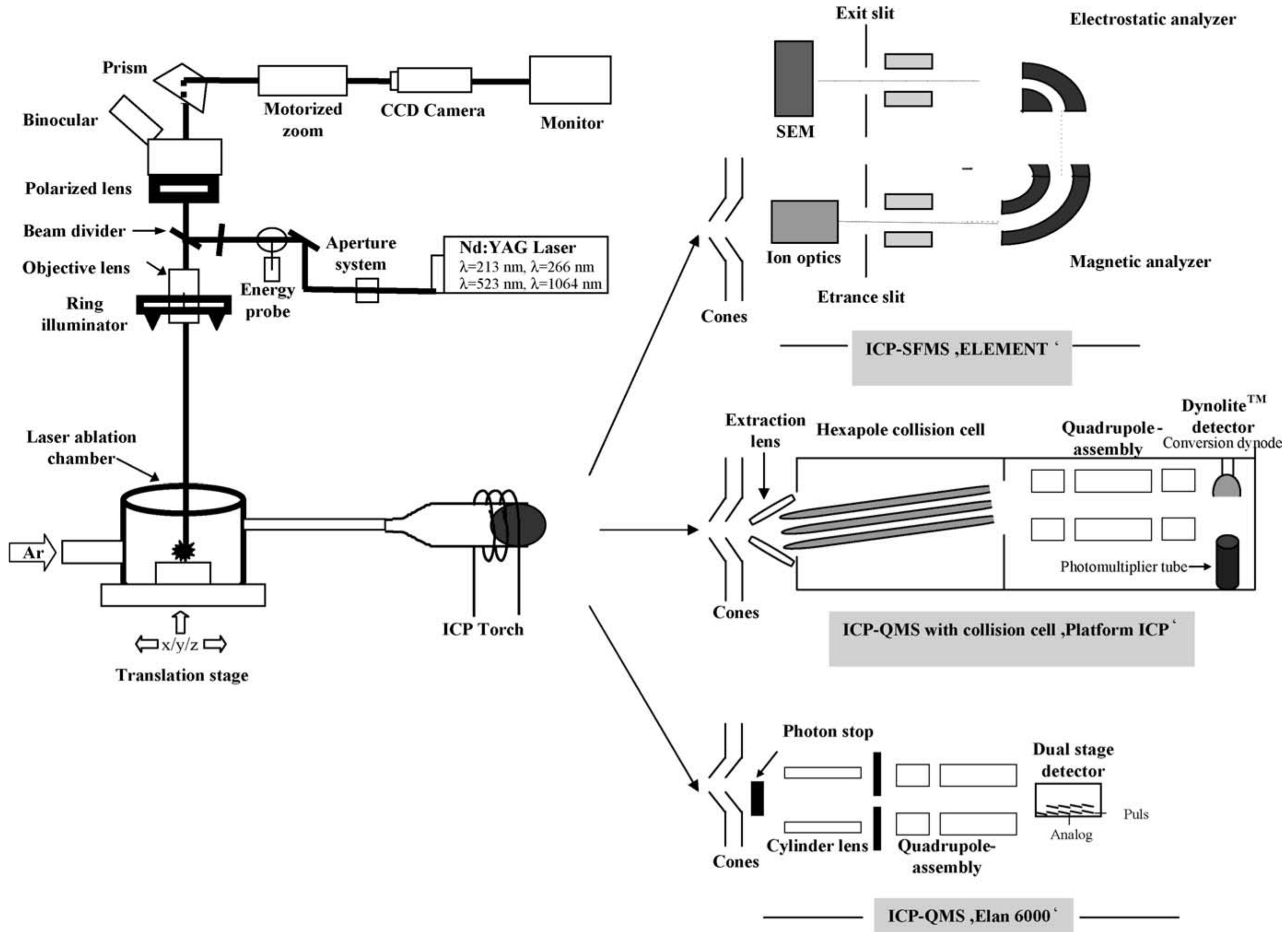

Fig. 1. Experimental arrangement of LA-ICP-MS using several types of mass spectrometers.

by collision-induced reactions) [30,31]. This is perhaps the reason why at present LA-ICP-MS with collision cell is not commonly used in isotope ratio measurements. Vanhaecke et al. [32] determined ^{106}Pd/^{108}Pd and ^{195}Pt/^{194}Pt isotope ratios in Pb buttons to be 1.02 ± 0.02 and 1.03 ± 0.03, respectively, by LA-ICP-CC-MS. In this work, no disturbing molecular ions had to be dissociated by ion–molecule reactions because Pt and Pd were considered as essentially interference-free. Likewise, without the activation of the collision cell ^{235}U/^{238}U isotopes have been measured by LA-ICP-CC-MS in soils contaminated with depleted uranium [17].

Laser ablation ICP-MS using the double-focusing sector field ICP mass spectrometer (ICP-SFMS) with a single ion collector are advantageous for precise and accurate isotope ratio measurements at a trace and ultratrace concentration level of the analyte in solid samples. LA-ICP-SFMS offers higher sensitivity and flat top peaks when operating in low mass resolution mode in comparison to LA-ICP-QMS, which results in better precision of measured isotope ratios (0.1% R.S.D.) [21]. At higher mass resolution, which is required for isotopes at given masses that are disturbed by isobaric interferences from molecular ions, a decrease in precision is observed due to lower sensitivity and loss of flat top peak shape. The best precision for isotope ratio measurements by LA-ICP-MS down to 0.005% R.S.D. is possible using sector field ICP-MS with multiple ion collectors (LA-MC-ICP-MS) for the simultaneous detection of mass-separated ion currents. At the present time, three double-focusing sector field instruments, Nu Plasma from Nu Instruments (Nu instruments, Wrexham, UK), Neptune from Thermo Electron, and the single-focusing sector field ICP-MS with collision cell, IsoProbe, from GV Instruments (GV Instruments, Manchester, UK) are on the analytical market. LA-ICP-MS with multiple ion collectors (MC-ICP-SFMS using Plasma 54 from VG Elemental as the first mass spectrometer developed or Nu Plasma from Nu Instruments as the most frequently used instrument of this type) has the best properties so far for direct high-performance precise isotope analysis on solid samples.

Recently, a new large-geometry high resolution multiple collector ICP-MS (Nu Plasma 1700, Nu instruments) for high precise and accurate determination of isotope ratios was introduced by Halliday et al. [33]. This instrument offers a laser software control, time-resolved analysis software and carrier gas control for Ar and He.

Instead of multiple Faraday detectors, another approach for improving isotope ratio measurements was proposed by Allen et al. [34], who used a twin quadrupole device for the simultaneous determination of isotopes by LA-ICP-MS. Using this experimental arrangement $^{52}Cr/^{53}Cr$ isotope ratios in steel standard reference material NIST 1263 were measured with a precision of 0.06–0.1% (R.S.D. of five averaged ratios).

3. Limiting effects and problems in isotope ratio measurements by LA-ICP-MS

Sources of uncertainty in isotope ratio measurements by LA-ICP-MS are mass interference problems, mass discrimination effects, dead time of ion detector, abundance sensitivity of mass spectrometer, interference problems due to instrumental background and memory effects or contamination during sample preparation or on the sample introduction system, plasma instabilities, matrix effects, fractionation effects (as discussed in Section 2) and others. The most serious limiting problem in laser ablation ICP mass spectrometry is the appearance of a multitude of different isobaric interferences of measured isotopes with singly or doubly charged atomic or molecular ions. For example, Boulyga et al. [43] measured $^{240}Pu/^{239}Pu$ isotope ratios of about 0.4 with a precision of 7–17% R.S.D. in Chernobyl soil samples by LA-ICP-SFMS at ultratrace level using a modified laser ablation system with a high ablation rate (LINA-Spark Atomizer system) in combination with a sector field ICP-MS at medium mass resolution ($m/\Delta m = 4000$) and dry plasma conditions in order to separate occurring $^{207}Pb^{16}O_2{}^+$ molecular ions from $^{239}Pu^+$ and to suppress the $^{238}UH^+$ formation as well as the peak tailing of $^{238}U^+$ on $m/z = 239$. However, determination of isotope ratios by LA-ICP-SFMS is more often performed in low-resolution mode ($m/\Delta m = 300$) [1,11,13,18] because by isotope ratio measurements at higher mass resolution the precision decreases due to significant lower ion intensities, no flat top peaks occur and the mass calibration is less stable.

The mass discrimination effect in LA-ICP-MS as a result of space charge effects of ions (due to Coulomb repulsion of positively charged ions formed in the ICP and leaving the skimmer cone) [44] and nozzle separation effect in ICP-MS [45] is a further source of uncertainty in isotope ratio measurements and can be corrected measuring isotope standard reference materials. Internal correction in LA-ICP-MS is applied using either an internal standard element with well-known isotopic composition (e.g., Tl for lead isotope ratio measurement [7,37]) is added or a constant isotope ratio of the element under investigation (e.g., $^{86}Sr/^{88}Sr$ for strontium [3,5], $^{192}Os/^{188}Os$ or $^{192}Os/^{189}Os$ for osmium [4,38], $^{186}W/^{184}W$ for tungsten [8], $^{91}Zr/^{90}Zr$ for zirconium [42]) is used. Internal mass bias correction is commonly used in LA-ICP-MS, if no solid isotope standard reference materials are available for most element of interest. Therefore, a mass discrimination correction by simultaneous solution nebulization and laser ablation sample introduction seems to be advantageous. Horn et al. [2] nebulized a solution containing known amount of Tl and a ^{235}U spike simultaneously with laser ablation of solid samples in order to perform mass bias correction for of Pb/Pb and Pb/U. Introduction of thallium aerosol into the plasma during laser ablation of soil samples and continuous measurement of $^{203}Tl/^{205}Tl$ was performed in order to correct for mass bias of uranium isotope measurements by Seltzer [17]. Using a dual gas sample introduction system for this way of mass bias correction both introduction systems cannot be optimized to 100% efficiency [2]. In order to overcome this problem a mono gas sample introduction system can be used, whereby measurements with optimized gas flow rates for both sample introduction systems are possible [46]. The use of isotopic standard solution is applicable for internal mass bias correction (simultaneous nebulization of isotopic standard solution and laser ablation of solid sample). External mass bias correction using isotopic standard solution (successively nebulization of isotopic standard solution and laser ablation of solid sample) is not possible due to differences in mass bias factor values for laser ablation sampling and solution nebulization as, e.g., observed by Stirling et al. [40]. The reason for this phenomenon can be an additional contribution to space–charge effects caused by ionized laser-induced aerosols [40].

The dead time of the ion detector (channel electron multiplier, pulse counting systems) is a further source of uncertainty in isotope ratio measurements for counting rates higher than 10^6 cps because a lower number of counts are registered than actually occur. In order to determine the dead time of the detector isotope ratio is measured as a function of different element concentrations in the sample using fixed dead times. For example, Seltzer [17] prepared synthetic soil standards with a uranium concentration of 50 mg/kg and 100 mg/kg, respectively, and measured the $^{235}U/^{238}U$ isotope ratio as a function of dead time for both standards, whereby the convergence of the two data plots corresponds to the correct dead time of 148 ns.

The abundance sensitivity of the mass spectrometer used, which is the contribution of a neighboring peak to the intensity of a measured isotope, can influence the accuracy of isotope abundance measurements. High-abundance sensitivity is desirable for measurements of low-abundance isotopes in the presence of neighboring high-abundance isotopes, e.g., for the determination of ^{239}Pu or ^{236}U ultratrace in the presence of uranium [18,47,48,49]. In LA-ICP-SFMS abundance sensitivity was improved by Boulyga et al. [43] at medium resolution in order to directly measure ^{239}Pu in the presence of ^{238}U in contaminated soil samples. Precise $^{234}U/^{238}U$ isotope ratio measurements in geological samples have been performed by LA-MC-ICP-MS, whereby the abundance sensitivity has been determined to be 0.3 ppm by measuring the contribution of $m/z = 238$ to $m/z = 237$ [40].

4. Selected application of LA-ICP-MS

In Table 1 some selected applications of isotope ratio measurements using different LA-ICP-MS equipment are summarized. As demonstrated in Table 1, most applications of isotope ratio measurements by LA-ICP-MS are in the field of geology and geochronology. Further applications are in biology, life science and environmental research.

A major application for LA-ICP-MS in geochronology is age determination of zircons. Scott and Gauthier [36] compared TIMS and LA-ICP-QMS for age determination of detrital zircons, whereby both samples showed a similar distribution of ages from each sample and TIMS results were more precise (±0.1%) than LA-ICP-QMS analyses (±1–2%). Precision of ^{206}Pb/^{238}U age determination on zircons by LA-ICP-MS could be affected by elemental fractionation of Pb and U as already discussed in Section 2. Li et al. [9] successfully minimized Pb/U fractionation by linear scan ablation – instead of single point ablation whereby the laser beam is getting defocused within the measurement – and determined ^{206}Pb/^{238}U rations by LA-ICP-QMS on single zircons with a precision of 0.8–5% R.S.D. Likewise, with LA-ICP-QMS Hirata [39] performed Pb–U age determination on zircon and baddeleyite samples, which size (typically 20–40 μm) allows only a single point analysis (laser spot size 10–15 μm) with a single set of ^{206}Pb/^{238}U, ^{207}Pb/^{235}U and ^{207}Pb/^{206}Pb isotope ratios. Therefore, precision for Pb/U ratio measurements of 5% R.S.D. was estimated by 10-repeated analysis of NIST glass standard reference material 610. In this study, Hirata did not employ LA-MC-ICP-MS, which can provide more precise and accurate isotopic data, because due to poor sensitivity of the Faraday detectors used in MC-ICPMS (VG Plasma 54) isotopic analysis by LA-MC-ICPMS requires a two orders of magnitude larger sample volume than that required by QMS instruments. Nevertheless, LA-MC-ICP-MS is becoming the method of choice for in situ Pb isotope dating, which provides Pb ages identical to those determined by TIMS analysis and with a precision comparable to that obtained by TIMS as demonstrated by Willigers et al. [7]. But as also demonstrated in this study isobaric interferences on $m/z = 207$ as identified by LA-ICP-SFMS can attribute to differences of about 0.5–1.0% in calculated ages determined via LA-MC-ICP-MS to those obtained by TIMS. This result demonstrates that a double-focusing sector field instrument can also be advantageous when performing high-precision in situ dating studies. Besides double-focusing sector field ICP-MS with single ion detection is advantageous for in situ Pb geochronological studies on samples with small amount of radiogenic Pb because it offers a significant improvement of sensitivity at low mass resolution.

Tiepolo [11] demonstrated that age determination in zircons with less than 1 ppb of radiogenic Pb is possible with a spatial resolution down to 20 μm in LA-ICP-SFMS if operating the instrument in the low mass resolution mode.

At the present time, LA-ICP-MS is the most powerful analytical technique for solving a lot of analytical tasks in the routine mode, e.g., control of radioactive samples in nuclear power plants for the final storage of radioactive waste, which requires fast analytical methods, or environmental monitoring at ultralow concentration levels due to fallout from nuclear weapons testing, nuclear power plants or nuclear accidents [16]. The advantage of LA-ICP-MS in comparison to radioanalytical methods was demonstrated by the analysis of mosses from the Alps [18]. After separation of long-lived radionuclides and electroplating on steel targets detection limits are in general better than in α spectrometry. The Pu concentrations were determined in moss samples at the $2.5 \times 10^{-13}\,\mathrm{g\,g^{-1}}$ to $5 \times 10^{-14}\,\mathrm{g\,g^{-1}}$ level, whereby the detection limits for ^{239}Pu and ^{240}Pu isotopes by LA-ICP-MS are about $4\,\mathrm{fg\,g^{-1}}$. The ^{240}Pu/^{239}Pu isotope ratio of 0.212 ± 0.003 was constant for all moss samples investigated. This result indicates that the Pu contamination in mosses was mainly caused by global fallout after nuclear weapon tests (from 1960 to 1965).

Precise and accurate isotope ratio measurements by LA-ICP-MS are possible only if no disturbing interferences occur. Waight et al. [5] demonstrated significant deviations of strontium isotope ratios for ^{84}Sr/^{86}Sr and ^{87}Sr/^{86}Sr measured in geological samples by LA-MC-ICP-MS compared to those obtained by the analysis of Sr separated from matrix, what indicates that disturbing interferences (e.g., Ca dimers, Ca argides and doubly charged rare earth elements) occur in LA-MC-ICP-MS. Measurements on Cameroon feldspar megacryst by LA-MC-ICP-MS yielded a ^{87}Sr/^{86}Sr isotope ratio of 0.703106, which is in perfect agreement with TIMS measurements and the obtained precision of 0.004% compare favorably with the precision of TIMS [3]. In contrast to geological applications, LA-ICP-SFMS for ^{87}Sr/^{86}Sr isotope ratio measurements in bone and teeth tissue were used by Prohaska et al. [13] in order to assess prehistoric human migration. In this study, ^{87}Sr/^{86}Sr isotope ratio measurements were performed on skeletal samples from three selected individuals after liquid digestion with and without Rb matrix separation by ICP-SFMS and by laser ablation ICP-SFMS (with mathematical Rb correction), whereby the results of all three approaches show a good agreement within the estimated uncertainty of 0.15%. But it was also found that if the ^{87}Rb signal is more than 1% of the ^{87}Sr signal the total combined uncertainty is increased for less than 10% in case of mathematical correction. For investigations of Sr isotope ratios in prehistoric human bones and teeth LA-ICP-MS proved to be the method of choice due to only small sample pieces are necessary to analyze ratios (very important when dealing with very valuable sample material from old ancestral specimens) and the possibility to provide lateral and therefore also time resolved data as stored in tooth samples.

Furthermore, LA-ICP-MS will have an increasing bearing upon tracer experiments in life science due to its capability for fast, precise and accurate isotope ratio measurements on solid biological samples. ICP-MS has been already successfully applied for investigation of transport phenomena of nutrient solutions in plants by tracer experiments using

Table 1
Instrumentation and precision for selected application in isotope ratio measurements by LA-ICP-MS

Sample	ICP-MS	Laser system/wavelength	Measured isotope ratio	R.S.D. (%)	Application	Reference
Zircons	ICP-QMS	LSX 100/266 nm	^{206}Pb/^{238}U	0.4–5.0	Geochronology	[9]
	Elan 6000		^{207}Pb/^{206}Pb	0.4–1.7		
Zircons	ICP-QMS	Compex 100/193 nm	^{208}Pb/^{206}Pb	0.2–0.9	Geochronology	[2]
	PQ II		^{206}Pb/^{238}U	0.2–0.9		
			^{207}Pb/^{235}U	0.4–1.4		
			^{207}Pb/^{206}Pb	0.2–1.1		
			^{208}Pb/^{232}Th	0.6–3.0		
NIST glass SRM minerals	ICP-QMS	Surelite I Continuum/266 nm	^{206}Pb/^{207}Pb	0.2–0.4	Geology	[35]
	X-7		^{208}Pb/^{207}Pb	0.3–0.4		
Zircons	ICP-QMS PQ II	Laser Probe/1064 nm	^{207}Pb/^{206}Pb	0.5–13.6	Geochronology	[36]
Soil	ICP-CC-QMS PQ ExCell	UP 266/266 nm	^{235}U/^{238}U	Not given	Environmental	[17]
Pb buttons	ICP-CC-QMS	GeoLas ArF/193 nm	^{106}Pd/^{108}Pd	2.0	Geology	[32]
	Elan 6100		^{195}Pt/^{194}Pt	2.9		
Steel alloy	ICP-MS	Model NY 82-30 Continuum/532 nm	^{52}Cr/^{53}Cr	0.06–0.1	Fundamental studies	[34]
	Twin quadrupole device		^{206}Pb/^{208}Pb	0.7		
Molybdenite	ICP-SFMS Element I	UV laser probe/266 nm	(^{187}Re+^{187}Os) /^{185}Re	0.2	Geochronology	[1]
Zircon	ICP-SFMS	Brilliant Quantel/266 and 213 nm	^{206}Pb/^{238}U	0.099–0.021	Geochronology	[11]
	Element I		^{207}Pb/^{235}U	0.71–19.8		
			^{207}Pb/^{206}Pb	0.65–1.98		
			^{208}Pb/^{232}Th	0.41–18.3		
Human bones	ICP-SFMS Element I	Ablascope/213 nm	^{87}Sr/^{86}Sr	0.1–0.2	Biology and life science	[13]
Flower leaves	ICP-SFMS	Ablascope/213 nm	^{235}U/^{238}U	0.4–1.3	Biology and life science	[50]
	Element I		^{234}U/^{238}U	1.6–2.0		
			^{236}U/^{238}U	1.0–2.1		
Separated protein spots in 2D gels	ICP-SFMS	Ablascope/213 nm (cooled laser ablation chamber)	^{67}Zn/^{64}Zn	5	Metallomics (tracer experiments)	[12]
	Element I		^{65}Cu/^{63}Cu	5		
			^{54}Fe/^{56}Fe	5		
Geological and environmental samples	ICP-SFMS	LINA-Spark/1064 nm	^{37}Cl/^{35}Cl	3	Environmental, geology	[51]
	Element II		^{81}Br/^{79}Br	3		
			^{129}I/^{127}I	3		
Geological glasses	ICP-SFMS	New Wave UP/213 nm	^{208}Pb/^{206}Pb	0.1–0.2	Earth science, geochemical research	[52]
	Element II		^{207}Pb/^{206}Pb	0.1–0.2		
			^{208}Pb/^{204}Pb	0.5–1		
			^{207}Pb/^{204}Pb	0.5–1		
			^{206}Pb/^{204}Pb	0.5–1		
Basalt, feldspar, gastropod shell	MC-ICP-MS	Fisions Laser Probe/1064 nm	^{87}Sr/^{86}Sr	0.003	Geology	[3]
	VG Plasma 54					
Mantle sulfides	MC-ICP-MS	Merchantek LUV/266 nm	^{187}Os/^{188}Os	0.05–1	Geochronology	[4]
	Nu Plasma		^{187}Re/^{188}Os			
Geological and biological samples	MC-ICP-MS	LSX 200/266 nm	^{87}Sr/^{86}Sr	0.002–0.09	Geochronology	[5]
	Axiom	New Wave LUV/213 nm	^{84}Sr/^{86}Sr	0.01–0.8		
Glasses	MC-ICP-MS Axiom	LSX 200 266 nm	^{11}B/^{10}B	0.1	Geology	[6]

Table 1 (*Continued*)

Sample	ICP-MS	Laser system/wavelength	Measured isotope ratio	R.S.D. (%)	Application	Reference
Apatite, monazite, sphene, NIST glass SRM	MC-ICP-MS Axiom	LSX 200/266 nm	$^{206}Pb/^{204}Pb$	0.006–0.08	Geochronology	[7]
			$^{207}Pb/^{204}Pb$	0.006–0.08		
			$^{208}Pb/^{204}Pb$	0.01–0.09		
Wolframite	MC-ICP-MS	UV Microprobe 1/266 nm	$^{182}W/^{183}W$	0.015	Geochronology	[8]
	Nu Plasma 500		$^{184}W/^{183}W$	0.031		
			$^{186}W/^{183}W$	0.039		
Metallic reference material, Fe-bearing, geochemical samples	MC-ICP-MS	UV Microprobe 1/266 nm	$^{54}Fe/^{56}Fe$	0.1	Biology and geology	[10]
	VG Plasma 54		$^{57}Fe/^{56}Fe$	0.1		
NIST glass SRM 610	MC-ICP-MS	VG LaserProbe/1064 nm	$^{208}Pb/^{204}Pb$	0.05	Fundamental studies	[37]
	VG Plasma 54		$^{207}Pb/^{204}Pb$	0.06		
			$^{206}Pb/^{204}Pb$	0.05		
			$^{206}Pb/^{204}Pb$	0.04		
			$^{207}Pb/^{206}Pb$	0.04		
Iridosmines	MC-ICP-MS	UV Microprobe 1/266 nm	$^{187}Os/^{188}Os$	0.05	Earth science	[38]
	VG Plasma 54					
Zr-bearing minerals	MC-ICP-MS	UV Microprobe 1/266 nm	$^{92}Zr/^{90}Zr$	0.005–0.01	Geochronology	[39]
	VG Plasma 54		$^{94}Zr/^{90}Zr$	0.01–0.02		
			$^{96}Zr/^{90}Zr$	0.02		
NIST SRM 611, zircon, opal	MC-ICP-MS	LSX 100/266 nm	$^{234}U/^{238}U$	0.02–0.04	Geochronology	[40]
	VG Plasma 54		$^{230}Th/^{238}U$	0.05		
NIST Cu SRM 976	MC-ICP-MS	GeoLas 200CQ/193 nm	$^{65}Cu/^{63}Cu$	0.04	Fundamental	[41]
NIST Fe SRM 665	Nu Plasma 500		$^{56}Fe/^{54}Fe$	0.05		
Zircon	MC-ICP-MS	UV Microprobe 1/266 nm	$^{92}Zr/^{90}Zr$	0.005–0.01	Geochronology	[42]
	VG Plasma 54		$^{94}Zr/^{90}Zr$	0.01–0.02		
			$^{96}Zr/^{90}Zr$	0.02		

highly enriched ^{25}Mg, ^{26}Mg, ^{41}K, ^{42}Ca and ^{44}Ca isotopes, whereby in this study SIMS was employed to measure lateral distribution of different stable isotopes in cross sections of plants [53]. It has been demonstrated by Zoriy et al. [50] that LA-ICP-SFMS allows $^{235}U/^{238}U$ isotope ratio measurements on plant tissues with a precision of 0.4–1.3% R.S.D. depending on the diameter of laser ablation crater (15, 25 and 50 μm, respectively) if a cooled laser ablation chamber is used. A momentous application of LA-ICP-SFMS for tracer experiments in life science is the systematically screening of two-dimensional gels of separated Alzheimer-diseased brain proteins doped with isotopic-enriched tracers (^{54}Fe, ^{65}Cu and ^{67}Zn) after 2D gel electrophoresis in order to study the formation of proteins containing Cu, Zn and Fe in a human brain sample [12].

5. Conclusions

LA-ICP-MS can be applied as a fast analytical technique for precise and accurate isotope ratio measurements in solid samples. Due to the excellent sensitivity and very low detection limits, isotope ratio measurements are possible with very small sample amounts and for solid samples, and in general no or only simple preparation steps are required. The determination of isotope ratios with precisions of down to 0.1% R.S.D. is possible with double-focusing sector field LA-ICP-MS (with single ion collector), which allows the determination of isotope ratios with extremely low detection limits. The precision of LA-ICP-MS is improved to 0.005% by multiple ion collection.

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