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Laser sampling

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The review is devoted to the major advances in laser sampling. The advantages and drawbacks of the technique are considered. Specific features of combinations of laser sampling with various instrumental analytical methods, primarily inductively coupled plasma mass spectrometry, are discussed. Examples of practical implementation of hybrid methods involving laser sampling as well as corresponding analytical characteristics are presented.
The bibliography includes 78 references.

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I. Introduction

Laser sampling involves laser ablation of (usually) solid samples followed by transfer of atomic vapours (Fig. 1) and aerosol particles to a measuring device (atomizer, ionization chamber, excitation source). At present, laser sampling is used for both remote and fast analysis of samples of different nature. Since solid samples undergo rapid transition to the vapour phase, analytical methods with laser sampling do not involve preliminary sample preparation steps. A laser pulse causes ablation of a small amount of a material (less than 10^{-9} g); therefore, laser sampling is treated as quasi-nondestructive technique. The method enables *in situ* and layer-by-layer analysis of all materials, being compatible with many analytical methods, namely, inductively coupled plasma atomic emission spectrometry (ICP – AES), inductively coupled plasma mass spectrometry (ICP – MS), laser-enhanced ionization spectrometry (LEIS) and laser-induced fluorescence spectrometry (LIFS), laser-induced breakdown spectrometry (LIBS) and some other methods.

In this review, we restrict ourselves to the applications that involve sampling in the classical sense. Studies on the widely used LIBS method were left out of consideration for two reasons. First, the number of publications on the subject is so huge that a separate consideration is required. Next, laser radiation plays a dual role in LIBS, being utilized for sampling and as excitation source; this distinguishes LIBS from other methods with laser sampling. There is an excellent comparative study [1] which reviews LIBS in detail.† We also excluded studies on laser desorption – ionization mass spectrometry because in this case laser radiation can hardly be interpreted as being used for sampling.

† See also *Laser Ablation ICP MS in the Earth Sciences: Current Practices and Outstanding Issues*. *Mineralogical Association of Canada, Short Course Series* Vol. 40 (Vancouver, 2008).

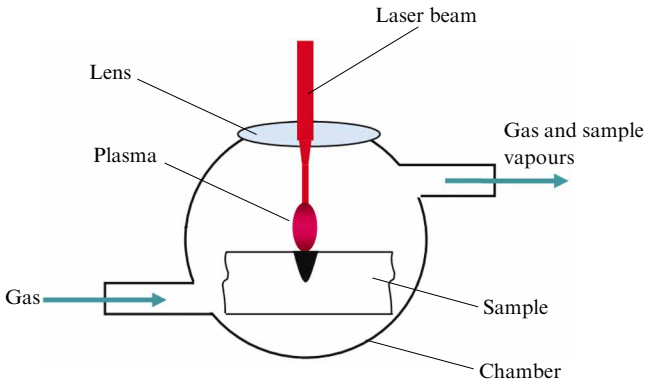


Figure 1. A schematic of laser sampling (simplified).

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Recently, a large number of reviews on different methods including methods with laser sampling as well as other sampling and transportation techniques have been reported. Mention may be made of regular publications on atomic spectrometry. For instance, publications [2, 3] are devoted to the determination of particular elements and to advances in atomic spectrometry, respectively. In this review, the emphasis is placed on common features of laser sampling that are not related to peculiarities of analytical techniques.

Laser sampling plays an important role in those analytical applications where high spatial resolution is required (analysis of particles, small inclusions or distribution of elements in tissues); therefore, the issues concerned with damaged surface area and efficient transport of particles to analyzers are of crucial importance.[3] Currently, laser sampling is integrated with many analytical methods, ICP – MS being ranked first.

II. Inductively coupled plasma mass spectrometry with laser sampling

Ultrahigh sensitivity and selectivity of determination makes ICP – MS one of the most powerful methods of analytical chemistry. The physical basis and trends in the development of the method have been documented in monographs ‡ and reviews. Among them, the review by Engelhard [4] should be noted first of all. The publication has a special focus on instrumental development and novel applications of the method including those with laser sampling that reduce the limits of detection to tens of femtogrammes. Also, the results of analysis depend strongly on the sample preparation techniques. Sample preparation for analysis of geological samples by ICP – MS was reviewed.[5] It was emphasized that laser sampling is suitable for ablation of any solid material irrespective of its physicochemical properties. The samples may represent small pieces of rocks, pressed pellets or fused glasses.

A review [6] by researchers from Italy is devoted to analytical applications of ICP – MS with laser sampling in biology. Specific features of detection of short transient signals typical of laser sampling coupled with ICP – MS were analyzed [7] and it was concluded that consideration of Poisson statistics is necessary (often, this is ignored). In the case of very short signals, the background signal is usually very weak and the use of normal distribution may introduce significant errors when calculating the limits of detection (Fig. 2).

Fryer and co-workers [8] considered physical basis of the interaction of laser radiation with solid samples and reported parameters of various lasers used for laser sampling. It was shown that experiments with femtosecond lasers are characterized by significant reduction of matrix effects on the results of determination. Also, no composition-matching reference materials are needed in this case. This was explained by elimination (or minimization) of thermal heating, plasma shieldng and poor absorption of radiation by transparent materials due to high power density of femtosecond laser pulses.

‡ See, *e.g.*, a collective monograph *Laser Induced Breakdown Spectroscopy* (Eds J P Singh, S N Thakur) (Amsterdam: Elsevier, 2007).

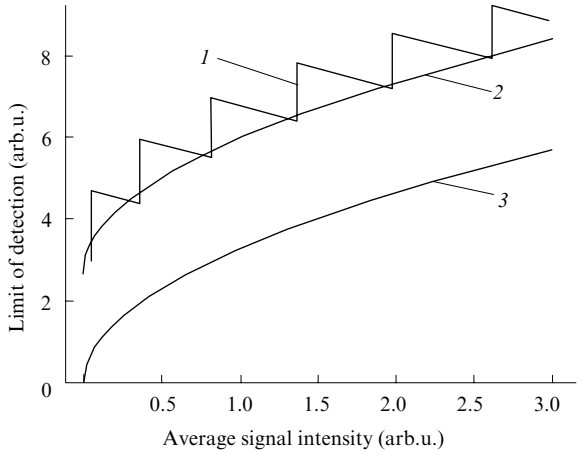


Figure 2. The limits of detection calculated using Poisson statistics and normal distribution.[7]
Exact solution for the limit of detection using Poisson statistics, the discrete distribution is visible (*1*), approximate solution for the limit of detection assuming Poisson statistics and the IUPAC approximation formula (*2*) and the limit of detection calculated using the IUPAC formula for normal distributed data (*3*).

Yet another useful review [9] is devoted to collection of ablated particles, their transportation and excitation in inductively coupled plasma.

Russo *et al.*[10] reported a comparative study of the influence of nanosecond and femtosecond laser radiation on the surface of solid samples and subsequent transportation of the ablated aerosol to ICP – MS. It was shown that experiments with femtosecond lasers give better accuracy in determination. The main difference between the two types of lasers consists in that the nanosecond laser is still illuminating the sample while the plasma is expanding, whereas the femtosecond pulse is over before any mass can leave the surface of the sample. Also, the heated region is larger for the nanosecond rather than femtosecond pulse. In addition, fractionation effects as well as extensions of crater rims and other undesired features are observed in the former case. In the case of femtosecond laser pulses, craters produced on the surface (Fig. 3) have a regular shape and smooth rims.

Laser sampling at different wavelengths was studied.[11, 12] It was shown that the decrease in the pulse duration from nano- to femtoseconds causes the matrix effects to reduce to a greater extent than after changes in the wavelength; however, the results obtained using shorter-wavelength radiation are more reliable, all things being equal.

The analytical signal in ICP – MS depends strongly on the nature [13] and humidity [14] of the carrier gas used for transportation of ablated particles. Experiments with helium under laminar flow revealed separation of aerosol particles into a disperse fraction and larger fragments; this may lead to poorer reproducibility of results. On the contrary, aerosol produced using argon as carrier gas has a higher degree of dispersion which is almost independent of the flow conditions.

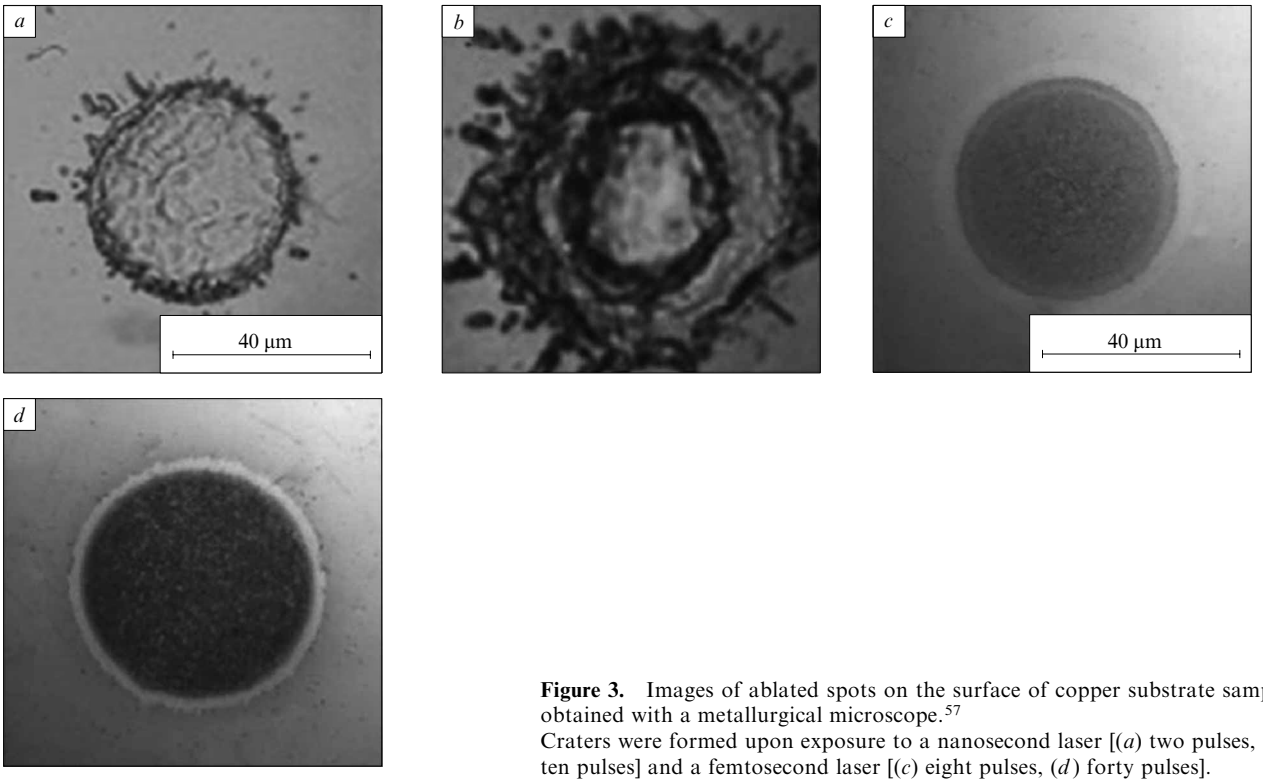


Figure 3. Images of ablated spots on the surface of copper substrate sample obtained with a metallurgical microscope.[57]
Craters were formed upon exposure to a nanosecond laser [(*a*) two pulses, (*b*) ten pulses] and a femtosecond laser [(*c*) eight pulses, (*d*) forty pulses].

II.1. Inductively coupled plasma mass spectrometry with laser sampling: applications

ICP – MS with laser sampling has numerous applications and can be used to analyze a wide variety of systems. For instance, determination of rare-earth elements in carbonates was reported.[15] Argon or helium was used as carrier gas; the addition of small amounts of nitrogen improved the sensitivity. The system was calibrated using synthetic carbonates doped with rare-earth elements and NIST glass standards. The difference between the results of determination for carbonate and glasses was 25% – 40% for argon atmosphere *vs*. less than 10% for helium atmosphere (*cf*. 25% for La).

ICP – MS with laser sampling has found an interesting application in forensics. In particular, the method was utilized[16] to detect gunshot residue particles including those collected from skin surfaces using ^{121}Sb, ^{137}Ba and ^{208}Pb as the characteristic elements. The method is much less time-consuming and may be suggested as an alternative to scanning electron microscopy.

Examples of applications of ICP – MS with laser sampling to analysis of particular systems are collected in Table 1.

II.2. Figures of merit

The use of ICP – MS with laser sampling for quantification is limited by fractionation of elements as a result of ablation, transportation, efficient atomization and ionization in argon plasma. This can increase errors if the compositions of analytes and standard samples differ appreciably. Vaporization of aerosol produced by laser sampling and the diffusion losses of the elements being determined in the inductively coupled plasma was studied using optical and mass spectroscopic detection.[40] It was shown that the ion extraction efficiency prior to mass spectrometry depends on the form (atomic or molecular) in which the elements of interest are present in the system. The dependences of analytical signal and fracionation of elements on various parameters of laser radiation (focal spot diameter, laser power density and repetition rate of laser pulses) were studied.[41] These parameters were shown to have a strong effect on fracionation and analytical characteristics of the method. An increase in the focal spot diameter from 20 to 120 μm leads to signal enhancement. A similar effect was observed with increasing pulse repetition rate because the mass being ablated increases. Smaller size of the focal spot leads to manifestation of fractionation effects, probably, due to a change in the character of ablation of the material, formation of deeper craters, and changes in the size distribution of aerosol particles and the mass of the sample being introduced into an inductively coupled plasma.

Difficulties in plotting calibration curves are due to the absence of reference samples of necessary composition; in this case, one can use matrix-matching reference samples.[36] Differences in ablation rates between different samples should be corrected using internal standards (normalizing elements).[42] However, this is useless for the hybrid method under consideration[43] because the detemination of both low-volatility elements (rare-earth elements, Zr, U, Th) and high-volatility elements (Zn, Sb) is not improved. In some cases, the calibration problem can be solved using the standard addition method.[18]

The results of analysis of meteorite samples produced by laser ablation using nanosecond pulses were compared with the results of direct analyses of solutions of the same samples and determination of platinum group elements after chromatographic separation using isotope dilution[44] by ICP – MS. The results obtained appeared to be in good agreement; pronounced matrix effects were observed in the case of laser sampling due to the absence of standard samples whose composition should match that of analytes.

Table 1. Results of analysis of samples by ICP – MS with laser sampling.

Samples	Elements to determine	Laser ablation system			Concentration of element to determine /mg kg^{-1}	Ref.
		laser type	λ /nm	t /ns		
Standard Reference Materials: sediments and soils	Zn, Sr, Ba, Gd, Pb	Excimer ArF	193	4	Tens	17
Standard Reference Materials: sediments, a soil, a rock material, Allende meteorite sample	Pb, Sr, Ba, Ni, Cu, Zn	The same	193	4	Tens and hundreds	18
Minerals and fluid inclusions	Br Cl	"	193	–	8 > 500	19
Fluid inclusions into minerals (fluorites, carbonates)	Mn, Fe, Cs, Pb, Na, K, Ca	"	193	–	From a few units to thousands	20
Fluid inclusions into Alpine quartz veins, Trimouns talc deposit and Athabasca Basin uranium deposits	Cl, Na, Ca, K, Mg	"	193	–	8 – 500	21
Frozen fluid inclusions	Be, B, K, Co, Zn, Ga, Sr, Cd, Te, Ba, Pt, Au, Tl, Pb, Bi	Ti-Sapphire	194	–	From a few units to tens	22
Roman glasses and late Iron Age glass beads	Li, B, P, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr, Ag, Sn, Sb, Ba, Bi	Excimer ArF Nd : YAG	193 213	– –	From a few units to thousands	23
Whole rocks	14 rare-earth elements, Sc, Y, Zr, Nb, Hf, Ta	Excimer ArF	193	–	From 0.05 (Lu) to 260 (Ce)	24
Fused whole-rock glass samples	Cr, Mn, Fe, Ni, Cu, Zn, Ga, Rb, Pb, Y, Zr, Nb, Th, *etc*.	Nd : YAG	266	4.9	From a few hundredths to a few thousands	25
Aragonites	Rare-earth elements, Y	Excimer ArF	193	–	From 0.5 (Lu) to 51 (Ce)	26
Gem-quality diamonds	La, Ce – Lu	Nd : YAG	213	–	From 0.1 to 9	27
Diamonds	~40 elements	"	266	–	From 0.02 to 56	28
Rocks	Y, La, Ce – Lu	"	1064	–	From a few tenths to a few tens	29
Geological samples	Y, La, Ce – Lu	"	193	–	From a few tenths to a few tens	30
Basalt, fluorite	Mg, Mn, Co, Ni, Cu, Zn, Sr, Ce, Pb, Th, U	Excimer ArF	193	–	From 0.8 to 52	31
Lake Baikal sediments	^{87}Rb, ^{232}Th, ^{234}U, ^{238}U	The same	193	–	From a few units to tens	32
Inclusions into minerals	Sc, Ti, V, Mn, Sr, Y, Zr, Nb, Ba, La, Nd, Sm, Eu, Gd, Dy, Ho, Yb, Hf, Pb	"	193	–	From 0.03 (Nb) to 523 (V)	33
Soils, sediments	Be, Si, Ca, V, Cr, Fe, Ni, Cu, Zn, Ge, As, Y, Rh, Ag, Cd, Sn, Sb, Tl, Pb, Th, U	Nd : YAG	266	–	From 0.67 (Tl) to 45000 (Fe)	34
Soils	Cr, Cu, Zn, Cd, Pb	"	266	–	From 0.38 (Cd) to 350 (Zn)	35
Basalts and shales	> 30 elements	"	266	–	From a few tenths to a few hundreds	36
Geological reference materials	Rare-earth elements, Sc, Ti, V, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, Hf, Ta, Pb, Th, U	Excimer ArF	193	–	From 0.001 (Ta) to 13000 (Ti)	37
Lanthanum gallium silicate	54 impurity elements	Nd : YAG	213	–	From $n \times 10^{-1}$ (Mg, Ti, V, Cr, Mn, Ni, Cu, Zn) to 2×10^{-3} (U)	38
Herbal supplements	Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd	"	213	–	From a few hundredths to a few hundreds	39

With no standards, the results of analysis can be interpreted incorrectly because the interaction of laser radiation with the surface is different for samples of different composition.

Often, the matrix effects can be eliminated or minimized using ICP – MS with laser sampling. In particular, a study of geological samples [30] revealed almost no fractionation, which is of great importance for obtaining reliable data.

It was found that ICP – MS using a quadrupole mass spectrometer and an excimer laser ablation system (λ = 193 nm) makes it possible to obtain correct results in the determination of rare-earth elements in various glass standards with a surface resolution of 24 μm;[45] the limits of detection varied from 0.003 to 0.030 μg g^{-1}.

Yet another problem accompanying laser sampling is associated with fluctuations of the energy of a laser pulse and with changes in the state of the surface at the focal spot. The action of these factors can lead to changes in the mass ablated per pulse and thus to poorer reproducibility of results. Various methods for correction of analytical signals were proposed to take into account the ablated mass. The simplest method is to use the photoacoustic signal produced upon laser ablation as reference signal.[46] The signal is due to the emergence of a shock wave upon ablation of the material from the surface, the signal amplitude being proportional to the ablated mass.

III. Other instrumental analytical methods with laser sampling

ICP – AES with laser sampling was used to analyze milk powder for Ca, Mg, Zn and Na.[47] In addition, these elements were determined by LIBS and ICP – AES using samples in the form of solutions. Matrix effects on the temperature, electron density (n_e) and other parameters of inductively coupled plasma were reported. In particular, vaporization of different samples causes n_e to vary between 8.9 and 13.8×10^{14} cm^{-3} and the rotational temperature to vary from 3400 to 4400 K. LIBS measurements showed that problems in laser sampling/ICP – AES experiments are due to ablation of solid samples.

A new method of determination of heavy metals in high-salt samples is based on electrodeposition of elements followed by laser sampling to inductively coupled plasma with atomic emission detection.[48]

Laser ablation assisted spark-induced atomic emisison spectrometry was proposed [49] as alternative to LIBS. For most elements studied (Si, Fe, Mg, As, Al, Co, Ca, Ti, Sr, V, Ba), the analytical signal is 10 – 220 times more intense than the LIBS signal, the accuracy in determination being also higher; this was explained by more appropriate conditions for spectra acquisition in the case of spark discharge compared to laser plasma.

Laser atomic absorption spectrometry and LIFS with laser sampling were used to determine trace amounts of nonmetals in steels.[50] LIFS with laser sampling was employed [51] to analyze toners for laser printers. Namely, a third-harmonic pulse of a Nd:YAG laser (λ = 355 nm, t = 9 ns) was focused on the surface of a printed toner to form a plume. A few microseconds later, the plume was intercepted by an excimer ArF laser pulse (λ = 193 nm, t = 10 ns). The ArF laser pulse vaporized the toner particles in the plume to produce analyte atoms (Ti, Sr, V, Cu, Fe). The trailing edge of the same 193 nm laser pulse excited fluorescence of various atoms. This research group also reported an application of this method to multi-element analysis of ceramics and polymers.[52]

The authors of a review [53] on diode laser atomic absorption spectrometry considered a combination of the method with laser sampling and described the determination of chlorine in polymers and the isotope ratio for uranium.

A combination of LEIS with laser sampling made it possible to carry out *in situ* analysis of aircraft-grade aluminium alloys. Methods for normalization of analytical signal to one or more reference signals were developed.[54, 55] This significantly improves the calibration because one can take into account fluctuations of laser power, amount of ablated sample material and plasma temperature by measuring the laser pulse energy, opto-acoustic signal and atomic emission signal, respectively.

There is considerable literature on laser sampling assisted mass spectroscopic analytical methods that do not use inductively coupled plasma. For instance, a high-resolution time-of-flight mass spectrometer was used to analyze aerosols whose particles were vaporized upon illumination with a c.w. laser (λ = 1064 nm).[56] The method was used [57] for rapid layer-by-layer analysis of multilayered copper and plastic samples using a femtosecond laser as ablation system.

Electrospray ionization mass spectrometry (EI MS) with laser sampling was used [58] for the determination of drugs in solutions, human hair and plant tissues. The technique involves no hydrolysis, extraction or derivatization or

Table 2. Results of analysis of samples using different methods with laser sampling.

Sample	Elements to determine	Method	Nd:YAG laser ablation system		Concentration of element to determine	Ref.
			λ /nm	t /ns		
Steel	P	LIFS	1064 and 532	20	From 37 to 350 mg kg^{-1}	66
	P	LIFS	532	6 ns	From 3.9 to 720 mg kg^{-1}	67
Fish scale	Hg	LIFS	213	–	From 6 to 10 pg	68
Uranium oxide	^{235}U, ^{238}U	Diode laser atomic adsorption spectrometry	1064	–	–	69
Milk powder	Ca, Mg, Zn, Na	ICP AES	355	–	From a few tens to a few thousands mg kg^{-1}	47
Working electrode after electrodeposition from KCl solution (32 g $litre^{-1}$)	Cd, Cu, Cr	ICP AES	1064	–	A few mg $litre^{-1}$	48

separation of drugs. A similar method was utilized [59, 60] for the determination of lipids, polypeptides and proteins in living cells and tissues.

A combination of HPLC with electrospray ionization mass spectrometry used for detection was developed.[61] A laser was used for vaporization of the sample, particles from the laser plume were collected using a liquid-phase collector and introduced into the chromatographic column. The analytical potential of the method was demonstrated taking analysis of a thin ink film containing a mixture of rhodamine dyes as an example. Yet another example of a complicated hybrid method of analysis is provided by a combination of capilary electrophoresis with electrospray ionization mass specrtometry. The ablated materials were captured in the exposed sampling solvent and then delivered to the inlet of a capillary column for separation and analysis of components using a mass spectrometer. The system was used to analyze mixtures of polypeptide/protein standards.[62]

A new approach in surface-enhanced Raman spectroscopy utilizes laser sampling to significantly improve the sensitivity and spatial resolution (it was 5 μm).[63]

A miniature mass analyzer with laser sampling was designed for extraterrestrial planetary exploration, in particular, *in situ* analysis of planetary materials.[64, 65]

Other analytical applications of laser sampling combined with various methods are exemplified in Table 2.

IV. Isotopic analysis

Laser sampling extends the potential of methods for isotopic analysis (first of all, mass spectrometry). Indeed, it enables analysis of small samples, *e.g.*, hair, cell structures or surfaces covered with various spatially confined components.

The isotope ratios were measured using laser ablation sampling in air with ICP–MS.[70] The samples, copper and two minerals, were laser ablated and aerosol thus produced was transported into a gas exchange chamber to replace the air by argon and then into a mass spectrometer. The results obtained in these experiments were compared with those obtained using ICP–MS with laser sampling in helium in a closed chamber. The reproducibility and trueness in both cases were comparable, but the atmospheric sampling technique was characterized by weaker peaks (up to a factor of five), which points to losses of the material in the gas transport system. Nevertheless, the method can be used to analyze samples that should not be destroyed or are too large to be accommodated within the gas exchange chamber. A combination of laser sampling with ICP–MS was used to measure the isotope ratios for copper,[71] uranium,[72, 73] lead,[70, 74] zinc and hafnium.[70]

In geochronology, the isotope ratio is necessary to date rocks. For instance, Kostitsyn with co-workers [75, 76] used laser ablation by the fifth harmonic of a Nd:YAG laser and ICP–MS to date rocks in the Northern Baikal region and Kamchatka.

Laser ablation isotope ratio mass spectrometry was used for stable isotopic analysis taking the determination of ^{13}C as an example.[77] The results of these experiments were comparable with the data obtained using traditional techniques; however, the new method enables *in situ* dtermination with a spatial resolution of 50 μm.

Laser ablation molecular isotopic spectrometry is a novel method of isotopic analysis. Since isotopic shifts in the molecular optical spectra are much larger than in the atomic spectra, no high-resolution spectrometers are needed for analysis in the former case. Molecular emission spectra are recorded at much longer time delays relative to the laser ablation pulse; this makes it possible to detect the formation of excited molecules in plasma. The method was used to study the formation of C_2 molecules using the molecular Swan system upon laser ablation of samples containing different amounts of ^{13}C isotope (Fig. 4).[78] The $^{12}C:^{13}C$ ratios were measured under different laser ablation conditions.

* * *

Our analysis of studies involving laser sampling for introduction of samples into analytical instruments showed that ICP–MS is still high on the list of instrumental methods. Moreover, the proportion of ICP–MS studies increases. This allows one to predict with certainty that the method will hold leading positions. At the same time, problems

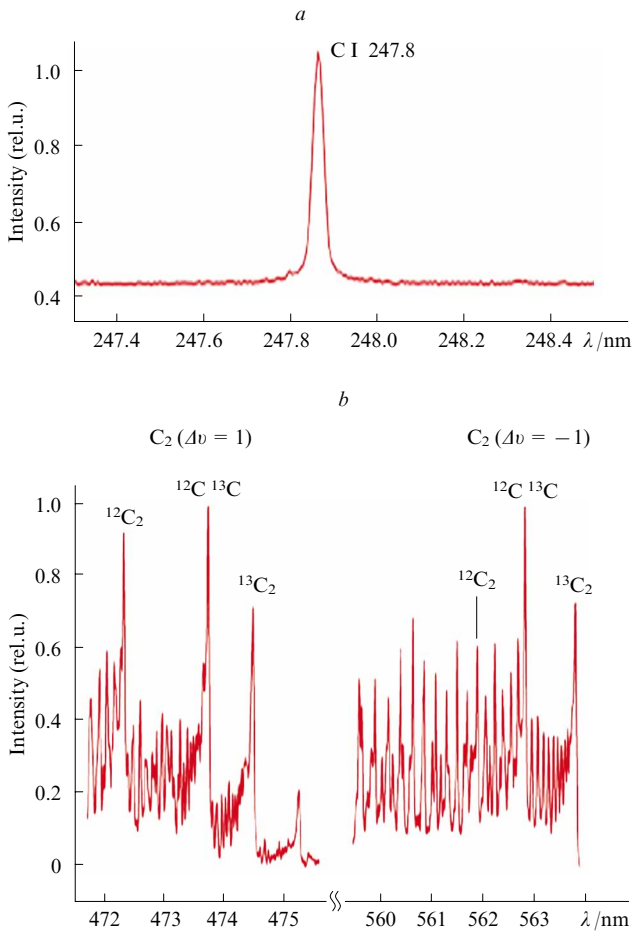


Figure 4. Emission spectra of atomic carbon (*a*) and molecular isotopic bands (*b*) during laser ablation of ^{13}C isotope samples (gate delay and width are 4 and 2 μs, respectively).[78]
$\Delta\upsilon = 1$ and $\Delta\upsilon = -1$ are the vibrational quantum number differences between the upper and lower states of C_2 molecule corresponding to transitions observed as spectral bands.

related to the use of laser ablation, such as insufficiently wide range of reference samples, fractionation effects, as well as matrix effects on the results of analysis, remain open despite the fact that ever-growing use of femtosecond lasers in the last decade in some cases led to significant reduction of the influence of the sample properties and fractionation. In the nearest future, one can expect complete replacement of nanosecond lasers by more advanced, although still expensive ones.

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