Laser ablation technique

First laser ablation technique was invented in 1960. The history of laser ablation studies begins with the birth of the laser itself. Laser ablation is a technique of removing of material from superficial solid with the help of laser beam. The number of studies grows simultaneously in seventies and they got a great success but it was explored in the year 1985 with many applications for example laser medication, laser with mass spectrometry, laser with optical emission spectrometry and a thin film growth. Laser ablation-optical emission spectrometry (LA-OES) and laser ablation-mass spectrometry (LA-MS) had been investigated for quantitative and qualitative analysis of solid material. After this invention scientist has taken 20 years to explore the combination of laser sampling with a specific source capable of multi-element analysis laser ablation inductively coupled plasma atomic emission spectrometry. 3LA-ICP-OES/MS technique is a non-destructive quantification of large number of samples so elements with low detection limit. Applications of LA-ICP-OES/MS give a great contribution in many field like archaeological, geological, environmental, forensic investigation and semiconductor industrial fields. The primary goal of laser ablation technique is to quantify element. 2

There are many different pulse laser uses in ablation process. First laser which is used to ablate solid material for chemical quantify is ruby. This was achieved by Maiman of

the Hughes Research Laboratory using a ruby crystal as the active medium. 1 Now days Nd: YAG laser have been widely used in analytical science because it require little maintenance, easy to handle, and relatively cheaper. Basically ablation is affected by laser wavelength; there is a simple principal behind this technique, shorter the laser wavelengths gives higher the ablation rate and lower the fractionation. For Nd: YAGlasers, the fundamental wavelength is in the near-IR at 1064 nm.

Year of first report on the different laser types and wavelengths for micro-scale analysis with ICP-MS3

Year	Laser	Wavelength	Pulse duration
1985	Ruby	694	Ns
1992	Nd: YAG	1064	Ns
1993	Nd: YAG	266	Ns
1995	ArF	193	Ns
1996	KrF	248	Ns
1997	Nd: YAG	532	Ns

1997	XeCl	308	Ns
1998	Nd: YAG	213	Ns
2002	Ti: Sapphire	≈800	Fs
2003	F2	157	Ns
2003	Nd: YAG	193	Ns
2003	Ti: Sapphire	≈260	Fs

In past there were many techniques tried for the sample introduction such as spark ablation, electro thermal vaporisation, direct sample insertion and laser ablation began to be used with ICP-MS. Laser pulses is use for ablate of solid material and carriage of the released material to the ICP in a gas flow, mostly argon is a best alternative to the nebulisation of aqueous sample solution. In addition laser ablation has a great advantage over other technique like reduce sample preparation; reduce spectral interference and rapid sample exchange. 4 if we talk about the evolution of LA-ICP-MS in last few years many scientists work on a different field like geological applications of LA-ICP-MS, biological applications, metal, polymer, glass applications and they got a huge success. As we know that ruby was a first laser to ablate solid for introduction to ICP-MS. The main feature of ruby laser is ruby, flash tube, and elliptical reflector and trigger wire. Generally, crystal surface of one end is highly polished and silvered and the other end is partially polished. Ruby consists of aluminium oxide, Al2O3, to which has been added a small proportion (about 0. 05% by mass) of Cr2O3. The ruby laser is totally based on the energy level principle. When chromium ion is excited from the ground level, this process is known as optical pumping. This is produced by an intense flash of white light from the flash tube and transition may occur. Spontaneous transitions produce photons, which trigger further emission. Photon travel perpendicular to the one end of the rod accumulates and release form the other end of the ruby rod which is partially silver polished.

REMAINING

Nd: YAG is widely uses in advance analytical practical's. Basically its work on different energy levels like ground level, meta stable level and pumping levels. In this system lasing occurs between the metastable levels. As the terminal level is essentially empty at room temperature, the population of E1 can be increased by a relatively small pump power above that of the E3 level. This is a significant advantage over the ruby system4. There is few influence of physical and chemical property of sample occurs because of aerosol particles generated by nanosecond laser ablation at 213 nm. The main problem of LA-ICP-MS is calibration strategy for a specific quantitative analysis. Different material have different matrix and when laser is introduce for ablation it may produce matrix " effect". Matrix effect cause changes in volume and composition of the generated particles during thelaserbeam interaction with the different sample surfaces. To solve this problem we need to calibrate the matrix match5.

Principal of laser ablation

A typical laser ablation system consists of laser, ablation process and detection system. Usually in this type of practical we use pulsed lasers. Argon or other inert gases typically carry the ablated sample into the ICP. Thermal and non- Thermal mechanism is involved in the ablation process but it's depending on the wavelength of the laser. Test sample absorbed the laser light (thermal process) and transfer this energy into atomic lattice. Then outer layer of the sample breakdown and melting and vaporisation process may occur. Different chemical required different latent heat of vaporisation, researchers says that if the level of photon energy is more than the bounding energy between two atoms in a solid sample. The electromagnetic laser radiation breaks the atomic lattices and ejects ion and atoms without producing any heat. 8

The following are the basic principle of laser ablation. 6

- Solid sample of a specific size is set up in a special design laser ablation chamber.
- Optical lens can be used for the investigation of solid specimen surface and select region to be analysed.
- The parallel radiation of solid state laser, gas laser or excimer laser with specific energy and time duration. Then introduce laser light directly onto the small region of sample with the help of optical lens.

- Ablated sample material range from nanogram to milligram produced by one or more laser shots consist of vaporised ions, small solid particles, solidified liquid droplets, free atoms and few clusters. If the vapours contain significant population of excited or ionized atoms, direct LA-AES and LA-MS for element analysis is possible.
- We can introduce ablated material in ICP as an aerosol by the flow of carrier gas; generally we use argon gas as a carrier. In second step ablated material is completely atomized, excited and ionised. The radiation of the atomic emission or the masses of isotopes species can be recorded with the help of different kind of detectors in spectrometers of LA-ICP-MS and LA-ICP-OES6.

Principal of laser action remain. diagram

An ideal solid sampling method should include the following features. 6

- Handle small and large sample size.
- Accurate measurement.
- Simple operation.
- Reproducible sampling.
- Simultaneous multi element analysis.
- Applicable to wide range of sample composition.
- Wide dynamic range.
- Variability from micro analysis to macro analysis.
- Acceptable cost of instrument and maintenance.
- Suitable method for quantification.

Ablation stage. 2

As we know the main feature of laser ablation lens, ablation chamber, and adjustable platform. Lens is fixed into optical microscope so that optical and visual focusing coincides and sample surface can be seen by CCD camera. Analytical sample is placed in a chamber which is made up of fused silica window. The adjustable chamber directly connected with computer and controls the position of sample in x, y, z directions. Few micron of displacement is achieved by this technique without any hindrance. Depending on the timing between individual laser pulses and platform movement, different tasks such as depth profiling, spatial profiling, surface and bulk analyzes are possible. If we applies laser ablation with inductive couple plasma, it require inert gas to transport the ablate sample to ICP. Argon and helium is widely use as a carrier gas. These gases provide better transportation and ablation rate. To improve transport efficiency, the sample or chamber is placed directly under the ICP torch.

Detection system. 2

ICP-MS

Quadrupole mass analysers are used in inductive couple plasma mass spectrometry. However, time of flight, double focusing electro static-magnetic sector, multiple faraday

Analogue detector instruments, ion trap mass analyser have been used with ICP-MS. Quadrupole mass analyser has a ability to scan between two different masses. We can measure 1000 masses in only one second. There is one disadvantage of using quadrupole mass analysers, if ablated vapour contains large particles so, it may produce some spatial changes such as enhancements or depressions in the signal level and chemistry. Double focusing electrostatic-magnetic sector instruments produce high resolution and very low background levels. For isotopes ratio applications usually we can use multiple faraday analogue detectors because it’s give a very high precision and time of flight instruments are better suited for laser ablation sampling ICP-MS. This system is able to remove the specific errors due to large particles in ICP. 2

Ablation cells ref 3

Direct solid micro-analysis using Laser ablation – Inductive couple plasma mass spectrometry has been used in many applications such as forensic, art, geo-sciences, material science, bio- science and cultural heritage. During the LA-ICP-MS measurement ablation cell plays an important role because it allows a quantitative transport aerosol and lead to a rapid transport from the ablation site to the ICP source. The guiding criteria were maximization of both aerosol extraction efficiency and transport speed. Usually there are two type of ablation cell is use in ablation system, open cell and a closed cell. The first open cell was invented in the year 1970 for flame atomic absorption spectrometry or microwave discharges. The cell size was a compromise between signal dispersion and minimization of aerosol spattering on the walls (so-called wall reaction), which is enhanced in reduced size cells.

Dittrich and Wennrich first introduced fully enclosed ablation cell chamber. This system has many advantages like no sample preparation is required for ablation such as surface polishing, and at atmospheric pressure that permitted the direct analysis of pressed pellets, clearly unstable under vacuum conditions. ref 3

Sample prepration

Calibration strategy

There is no universal method of calibration for all of solid-sample types. There are three general groups of calibration strategies

Calibration can then be achieved by comparing the response for the internal standard element in a reference material and the unknown. ref 5

Matrix-matched direct solid ablation ref 1

Matrix match is very popular technique for LA-ICP-MS. Matrix matching is necessary because the ablation rate varies with the sample matrix. Matrix matched standard consist of mixture of an appropriate matrix material with the analyte.

Dual introduction (sample-standard)

This method does not require the reference standards to be introduced by laser ablation. In this technique we use two sample introduction channels. One channel is for ablated material and another for nebulizer aqueous solution standards. Usually this method is used for semi-quantitative analysis with LA-ICP-MS.

Direct liquid ablation

Gunther et al. First demonstrate direct liquid ablation technique for LA- ICP-MS. Na (all elements) and Yb (rare earth elements only) were used as internal standards. To explain the similar ablation behaviour of liquids and solids, particle size distributions were measured and the contribution to the total ablation volume was calculated. ref 1

Sample introduction for LA-ICP-OES/MS ref 4

In many fields like clinical analysis, forensic, and biological the volume of sample available can be lower than 1 millilitre. The low sample consumption systems improve the analyte transport efficiencies afforded by conventional setups, some time solvent system may cause may type of interferences. It can be reduced by working at very low very low liquid flow rates. It can be observed that, in some cases, the sample volume is below 100µl. Usually, when liquid sample is analyse with the help of inductive couple plasma mass spectrometry or optical emission spectrometry. Nebulizers is use to transform liquid solution into an aerosol. A typically nebulizer deliver the solution with a specific rate on the order of 0. 5-2ml/min. There are many different type of nebulizer is available such as, micro nebulizer, high efficiency nebulizer, micro concentric nebulizer, micro mist nebulizer, sonic spray nebulizer etc. Basic reason to use a nebulizer is to generate aerosol. Micro nebulizer is very popular used in ICP-OES/MS. A micro nebulizer is used to generate stable aerosols at liquid flow rates below 100-200µl/min.

Aerosol generation.

Micro nebulizer provides finer aerosols, higher ICP sensitivities and lower limits of detection low liquid flow rates. A typical concentric nebulizer has lower capillary inner diameters and wall thickness than conventional ones. For conventional pneumatic nebulizers, the dimensions of liquid capillaries or the wall thickness and inner diameter are not appropriate for the generation of fine aerosols at low flow rates. It has been claimed that it is difficult to generate stable aerosols with conventional nebulizers at liquid flow rates below 300µl/min. In transport of liquid, if the flow rate is below then

100µl/min. So, solvent evaporation is enhanced and, on the other hand, droplet coalescence is dampened in the former situation.

Solvent evaporation and aerosol characteristics at low liquid flow rate can be evaluated by this equation:

D3 = d30 – Et

Where d is the drop diameter at a given time t, d0 is the initial drop diameter and E is the so-called evaporation factor.

There are many different devices used for the introduction of liquid micro samples in ICP techniques. It can be classified into three different groups.

1. A nebulizer coupled to a spray chamber;
2. A nebulizer coupled to a desolvation system;
3. A direct injection nebulizer.

Micro nebulizers coupled to spray chambers:

Usually in the analysis of micro samples, pneumatic concentric micro nebulizers are widely used with ICP-MS as well as ICP-OES/AES.

High efficiency nebulizer {HEN}:

First high efficiency nebulizer was invented in the year 1992. HEN is totally made up of glass. Its design is similar to a Meinhard® but the critical dimension is less than the other one. It has many advantages like because of the reduced inner diameter of the capillary, even clean aqueous solutions must be filtered to avoid tip blockage caused by the presence of fibres or small particles. And due to the low cross section area of the gas exit, pressure of the gas is rather high.

Micro concentric nebulizer (MCN)

The micro concentric nebulizer can be easily introduced with double pass or cyclonic spray chambers by means of special end caps. MCN consist of polyamide narrow capillary and a t-shaped plastic body. The cross section area of the gas exit is very less. This gives a huge drawback because the aerosol is generated at the exit of the nebulizer where the gas stream has lost a fraction of its kinetic energy. MCN can be considered as a rather fragile nebulizer. This type of nebulizer is very popular in the application of inductive couple mass spectrometry and optical emission spectrometry because it provides great sensitivities than conventional pneumatic nebulizers.

Micro mist nebulizer (MMN):

The MMN is a modified glass conventional concentric nebulizer. Micro mist nebulizer has an ability to recess the liquid capillary with respect to the nebulizer tip. This important feature allows to working with high salt content solutions without suffering from nebulizer tip blockage.

PFA micro nebulizer (PFAN):

The PFA (tetrafluoroethylene-per-fluoroalkyl vinyl ether copolymer) micro nebulizer is an HF resistant. Basically this nebulizer is used for the analysis of samples containing high concentrations of organic solvents and dissolved solids. The PFA nebulizer has been extensively used under free aspiration mode. Usually this nebulizer is used for the analysis for extremely diluted samples without contamination from pump tubing and, at the same time, reduces the signal noise.

Multi micro spray nebulizer (MMSN):

The Multi micro spray nebulizer (MMSN) enhances the interaction efficiency between the gas and liquid streams. This is a modified version of the SSN. In this system the sample solution is divided into 3 parts, each one of the three capillaries employed is centred with three respective gas exit orifices and it has three aerosol generation points like three micro nebulizers. That's why is called as multi micro spray nebulizer.

Figures of merit & demerit of LA-ICP-OES and LA-ICP-MS ref 8

The figures of merit are depending on the operating condition, instrumentation and applications of laser ablation inductive couple plasma mass spectrometry. The best advantage of LA-ICP-MS is sensitivity, detection efficiency, direct sampling multi element quantification at the surface and bulk for elemental composition of solids, Reduced risks of analyte loss or cross-contaminations, Determination of spatial distribution of elemental compositions, Independent of sample geometry, No chemical procedures and Analysis of very small samples. ref 8

The disadvantage of this technique is very less. Some time the common matrix and molecular species can interact with the active analyte or some double charged molecular species create difficulty in quantification.

Applications of ICP-OES/MS

1) Recent applications on isotope ratio measurements by LA-ICP-MS (ref 9)

LA-ICP-MS is a powerful and sensitive technique for analysing stable and radioactive isotopes in different application fields because of their low good accuracy, detection limits and precision. ICP-MS can be use for isotope ratio measurements of Mg, Ca and K in plants, soils and nutrient solutions. Serious difficulties were encountered during the analysis of K and Ca isotope by ICP-MS. The problem is rise because of the interferences.

2) LA-ICP-MS on biological samples and single particles (ref 9)

New trend focus on isotope dilution technique together with neon flow injections. Today, LA-ICP-MS is very popular method for determination of metals, for example on protein bands in gels after the gel electrophoresis of protein mixtures. In future LA-ICP-MS could be able to improve in the resolution of sub-micrometer range for isotope ratio measurements in biological and medical samples.

3) LA-ICP-MS for the elemental analysis of bone and teeth samples for discrimination purposes (ref 10)

Human bone and teeth is useful evidence when found in crime scenes because it consists of isotopic property. Usually LA-ICP-SF-MS method is applied for analysis of bone and teeth. In this method non-matrix calibration is required and it’s only required micro gram of sample for analysis. This is a fast and easy elemental analysis technique using LA-ICP-SF-MS for the intra-inter human discrimination of skeletal remains.

4) LA-ICP-MS for surface analysis (ref 6)

LA-ICP-MS is also used for the determination of lateral element distribution has also been described for ceramic layers and for profiling of metal layers. With the help of this technique we can measure the size of Al2O3, MgO and complex CaO, MgO and Al2O3.

5) Environmental applications and Geological applications (ref 1)

LA-ICP-MS has a excellent capacity to determined chemical content present in tree samples because of the high spatial resolution provided by a focused laser beam. The excellent sensitivity of LA-ICP-MS allows measurements of very low detection limit and multiple quantitative analyses. Geochronology is one of the basic principles in earth sciences. Age can be determined by measuring the 206Pb/238U, 207Pb/235U, and 207Pb/206Pb ratios. LA-ICP-MS has the ability to do spatially resolved in-situ determination of U_Pb isotopic compositions in zircons.

6) The emerging role of ICP-MS in proteomic analysis {ref 11}

ICP-MS stands now as a new tool in the field of quantitative proteomics. The system to be analysed may be very small e. g. a single cell, with 0. 5 pL volume and ca. 50 pg total protein content. The below diagram describe the emerging role of mass spectroscopy.

Recent trends and developments in laser ablation-ICP-mass spectrometry

Now, laser technology is not a new thing in any field. Laser is widely used in different programs such as for medical applications, for micro-machining, in CD-players, light shows and in analytical chemistry. As we know that laser is used for direct analysis of the elemental composition of solids, mostly solid state lasers, such as Nd: YAG laser with at 1064 nm wavelength is very popular in the determination of many things. But the trend moves towards the shorter wavelengths 1064 nm to 157 nm. In laser ablation set up we can use excimer lasers with different wavelength like XeCl 308 nm, KrF 248 nm, ArF 193 nm, and F2 157 nm. Laser ablation inductive couple plasma is one of the flexible and powerful technique in analytical field for isotope ratio measurement and direct determination of solids. A variety of calibration techniques have been developed and successfully applied to LA-ICP-MS. There is a great development with respect to calibration strategies.

Intensively study is going on the matrix-independent calibration procedures using external reference materials and/or internal standardization. Ref 12

Determination of boron in silicon wafers with the help of on-line isotope dilution laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method. This is a new and successful method. In this technique ablated aerosol sample was mixed on-line with enriched boron and conventional nebulizer system is used for continuous supply. By the mixing of two different aerosols, isotope ratio of boron has been changed and it is recorded by ICP-MS system. In this system accurately quantifies boron concentrations in silicon wafers without the need for an internal or external solid reference standard material. On-line solution-based isotope dilution in laser ablation ICP-MS is an accurate, simple, precise and quantification procedure.

Below the process diagram of on-line isotope dilution LA-ICP-MS

There is a still study and research on the new calibration method combine with IDA and LA-ICP-MS without using standard reference materials. In future we will focus on the applicability of this on-line LA-ICP-IDMS quantification concept to the determination of trace analytes in various other matrices. ref 13

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