Trace element analysis of geological materials by ICP-MS I

DSP analytical geochemistry

C9067

Markéta Holá, MU Brno

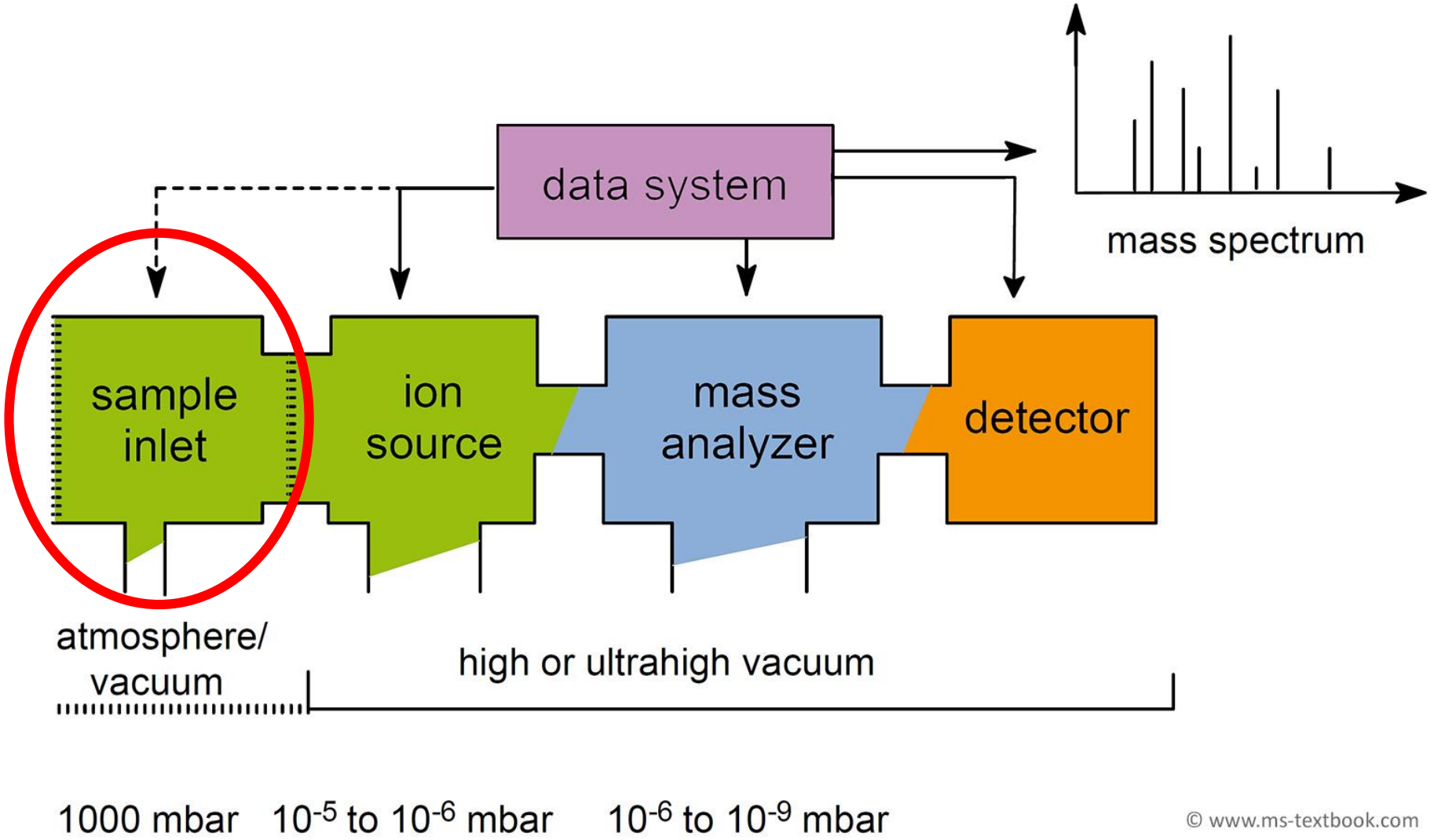
EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Outline

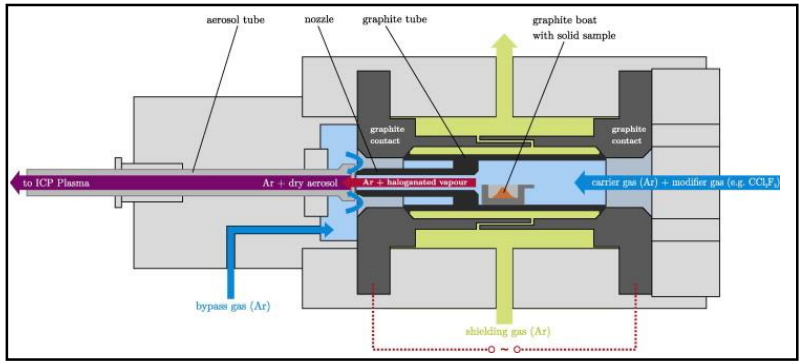
1. Mass spectrometry. General introduction and history.
2. Ion sources for mass spectrometry. Inductively coupled plasma.
3. Interface. Ion optics. Mass discrimination. Vacuum system.
4. Spectral interferences. Resolution, ion resolution calculations.
5. Mass analyzers. Elimination of spectral interferences.
6. Non-spectral interference.
7. Detectors, expression of results.
8. Introduction of samples into plasma.
9. Laser ablation for ICP-MS.
10. Excursion in the laboratory.

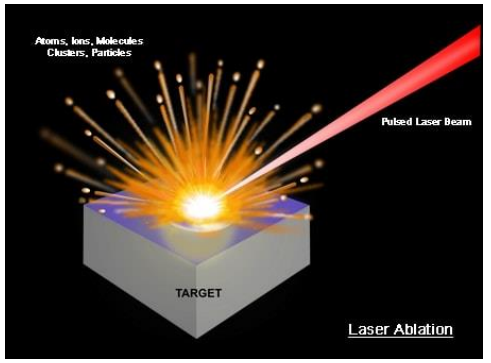

data system
mass spectrum
sample inlet
ion source
mass analyzer
detector
atmosphere/ vacuum
high or ultrahigh vacuum
1000 mbar
10-5 to 10-6 mbar
10-6 to 10-9 mbar
© www.ms-textbook.com

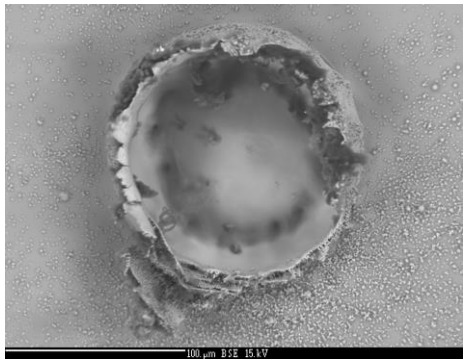
Sample introduction

The purpose of the sample introduction system is to transport the analyte to the ICP in a form that can be converted into elemental ions for ICP-MS.

In most cases, an aerosol is generated from the sample, which is transported into the plasma. One possibility is the nebulizing of liquid samples, where the nebulizer is connected to the plasma head or the wet aerosol passes through the desolvation unit. In the case of dry aerosol generation, for example by laser ablation or electrothermal vaporization, the aerosol is entrained by the carrier gas through the transport tube to the ICP. The sample can also be introduced into the plasma in the form of vapors and gases, for example when using the method of generating gaseous hydrides or in conjunction with ICP-MS with gas chromatography (GC-ICP-MS).







Sample introduction

A key parameter affecting the properties of the ICP-MS analytical result is the introduction of the sample into the plasma in a defined volume, form and time.

The sample is transported to the ICP discharge in the form of a wet or dry aerosol, or in the gas phase.

Fáze	Forma při vstupu do ICP	Technika
kapalná / suspenze	(polo)vlhký aerosol	pneumatický zmlžovač (standardní technika)
kapalná	vlhký aerosol	vysokotlaká tryska
kapalná	polosuchý aerosol	termosprej
kapalná	polosuchý aerosol	ultrazvukový zmlžovač (standardní technika)
kapalná	směs plynů a par	generace plynných hydridů
kapalná / suspenze	suchý aerosol	elektrotermické vypařování ETV
pevná / suspenze	suchý aerosol	elektrotermické vypařování ETV
pevná	suchý aerosol	laserová ablace
pevná	suchý aerosol	jiskrová ablace
pevná / suspenze	páry	přímé vnášení do speciální plazmové hlavice
plynná	směs plynů	GC-ICP-MS

Sample introduction

aerosol

The sample is transported to the ICP discharge in the form of a wet or dry aerosol.

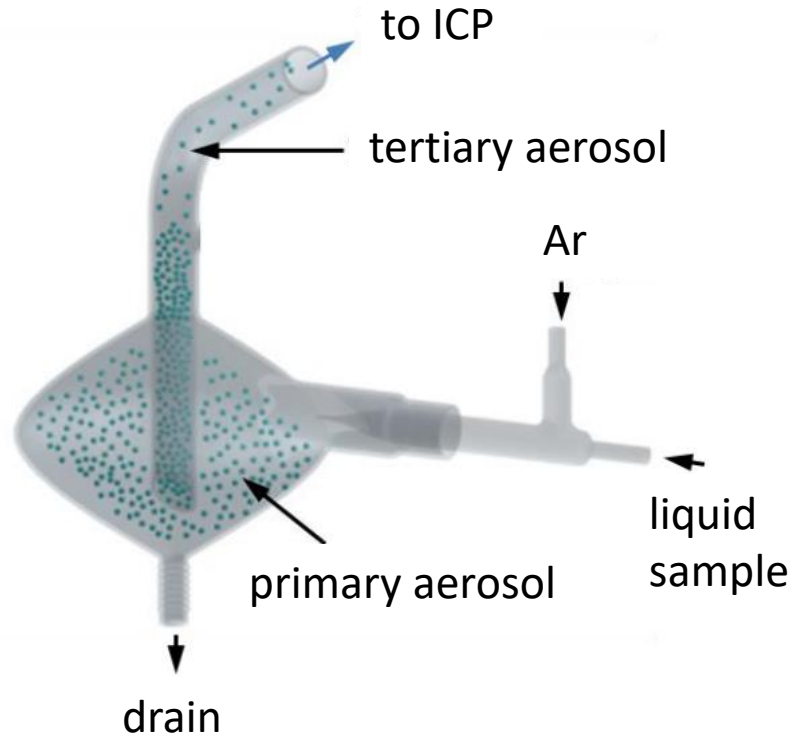
To obtain reliable analytical results, you need a generation technique aerosol exhibited the following properties:

- independence of aerosol generation efficiency from sample properties,
- the same chemical composition of the aerosol and the sample,
- dominant proportion of small aerosol particles (<1 µm),
- stability of aerosol generation and transport into the plasma,
- good aerosol transport efficiency,
- minimal interference with the sample matrix.

Aerosol generation

The process of aerosol generation from solutions and transport to the ICP can be divided into three phases, which follow each other or partially overlap.

1. **Primary aerosol generation by the nebulizer** – by acting against the surface tension of the nebulized liquid, a polydisperse aerosol is created with a primary particle size distribution dependent on the properties and operating conditions of the nebulizer, the properties of the solution and the energy source
2. **Secondary aerosol modification** – reduction of mean particle diameter by loss or shattering on a solid barrier or interaction with another energy source, e.g. a gas stream
3. **Tertiary modification of the aerosol** – during transport, particles exceeding the limiting aerodynamic cross-section are lost depending on the mechanism limiting the passage of particles along the transport route: gravitational losses, centrifugal losses, impacts on walls, turbulence. Further, the particles are reduced by natural or controlled evaporation in the carrier gas stream.



Pneumatic nebulizers

They are the most commonly used devices for generating aerosols from solutions.

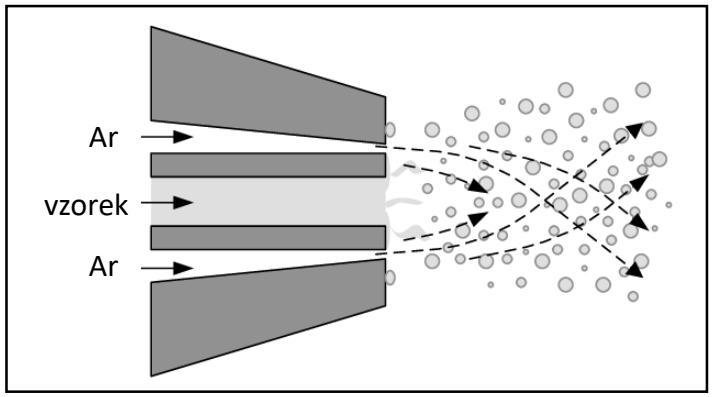
Nebulizing is dependent on the carrier gas flow rate.

The aerosol is created by kinetic energy through the interaction of the carrier gas with the liquid flow. The gas flow must have a sufficient speed to break the flow of liquid, which is transported to the mouth of the nozzle either by force (peristaltic or other pump) or by the suction effect.

- **capillary nebulizers**
  - concentric (with suction) – Meindhard
  - cross-flow (with/without suction) – Kniseley
- **Babingtonova type nebulizers**
  - V-groove
  - grid (Hildebrand)
  - fritted disc

Material

- glass
- polymers (resistant to HF)

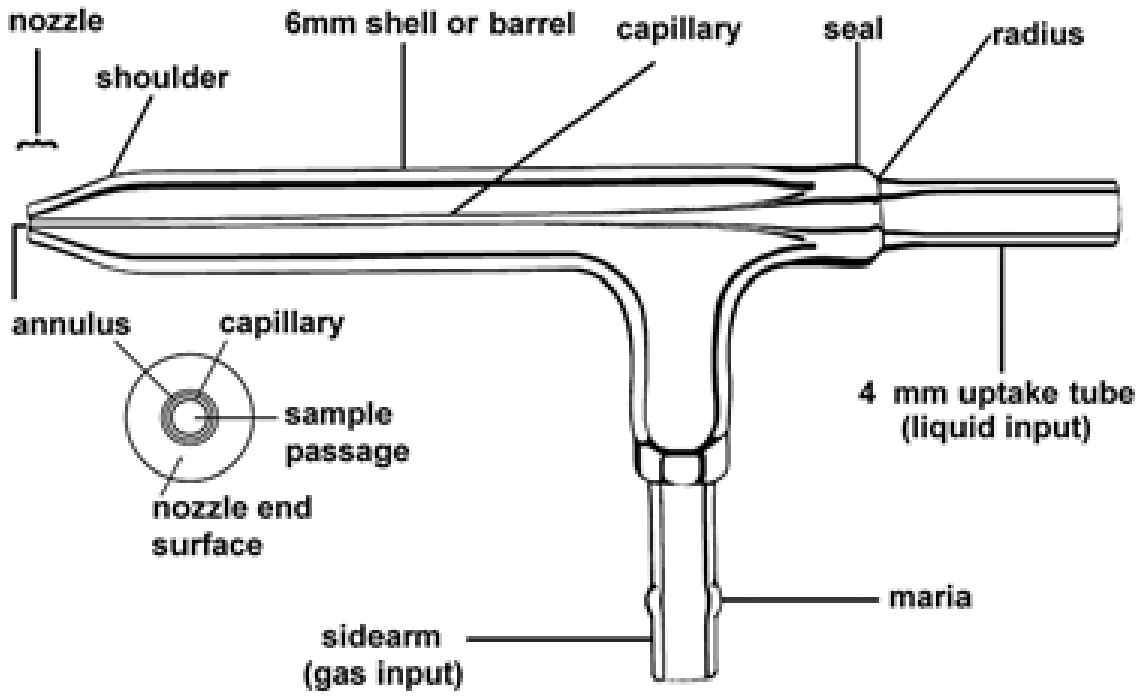


Sample introduction

nebulizers

Concentric nebulizers

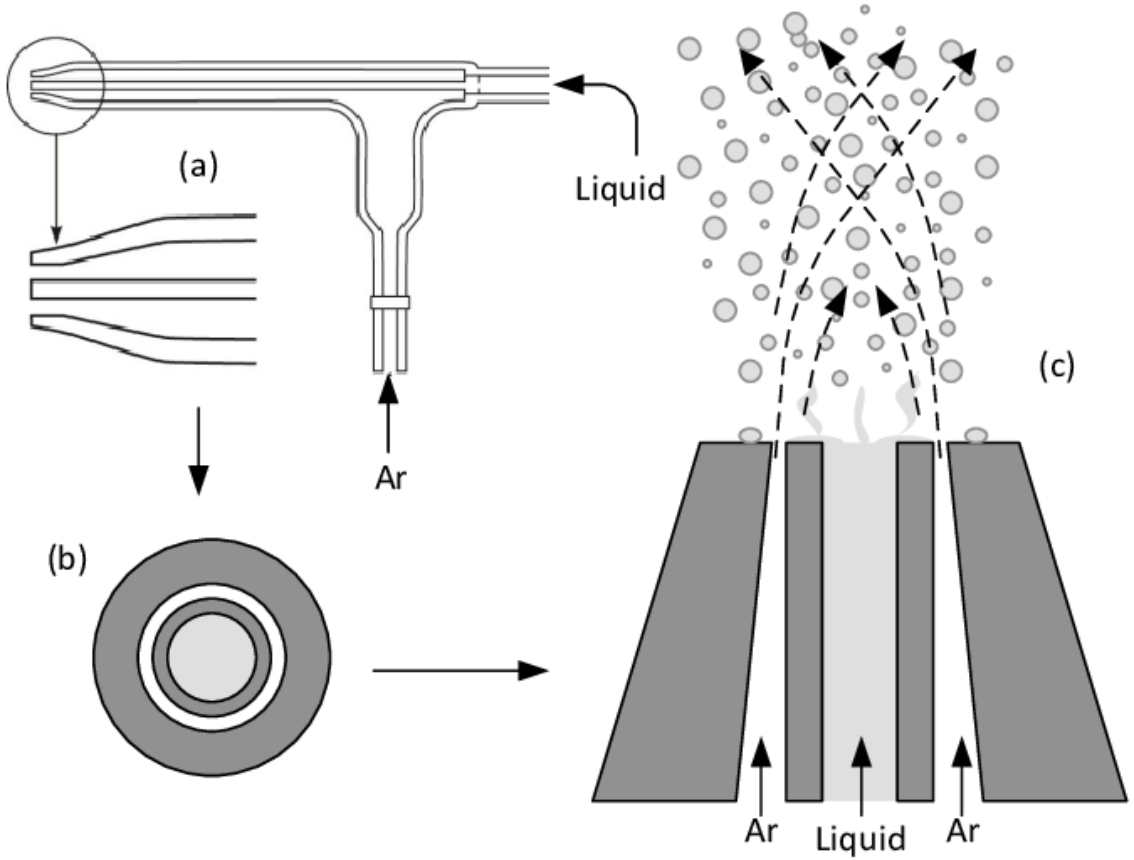
Concentric nebulizers have a central capillary with the liquid and an outer capillary with the gas. The gas draws the liquid into the gas stream through induction, and the liquid is broken into a fine mist as it moves into the gas stream.



Sample introduction

nebulizers

Meinhard concentric glass nebulizer (CGN)



(a) Schematic diagram of a typical pneumatic concentric nebulizer with the tip geometry under magnification, (b) front view of the nebulizer tip geometry, and (c) scheme of the nebulization process.

Sample introduction

nebulizers

Microconcentric nebulizers

10 – 100 µl/min (concentric ~ 1 ml/min)

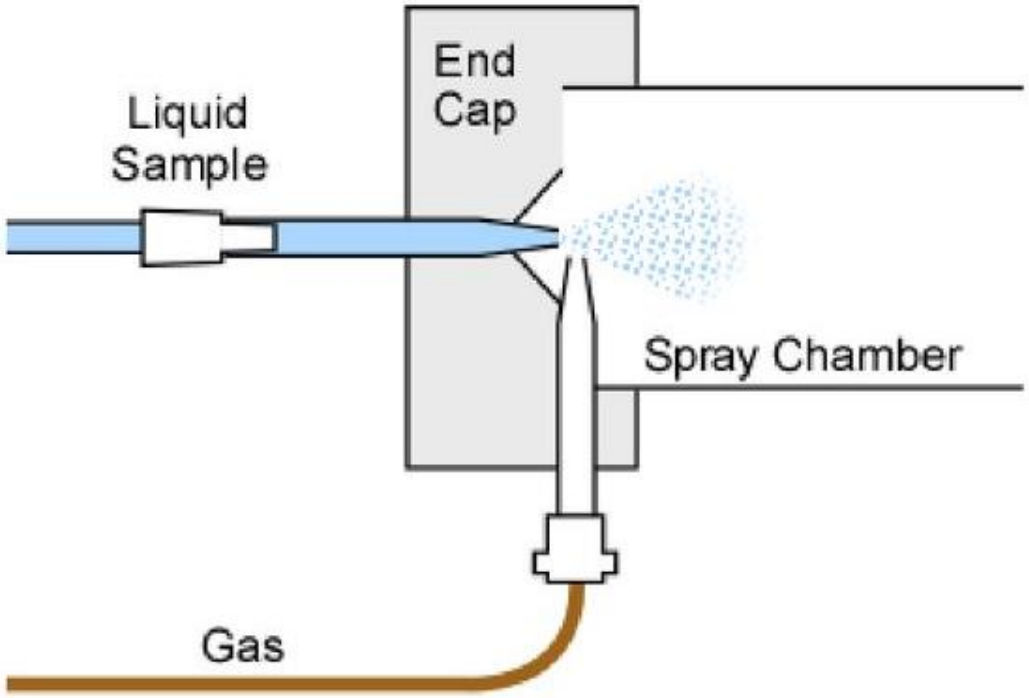
Microconcentric nebulizers use the principle of concentric nebulizer, but use higher gas pressures at low flow rates of liquid solution. This makes them ideal for cases where only a small amount of sample is available.

Sample introduction

nebulizers

Cross flow nebulizers

Cross flow nebulizers have a gas capillary set at right angles to the liquid capillary. The gas is blown across the liquid capillary and this produces a low pressure that draws the liquid into the gas stream. Generally the suction is similar to what is produced in a concentric nebulizer. The benefit of a cross flow is that the liquid capillary have a larger inside diameter allowing for more particles to pass through without plugging the nebulizer. The disadvantage is that the mist is usually not as fine or as consistent.



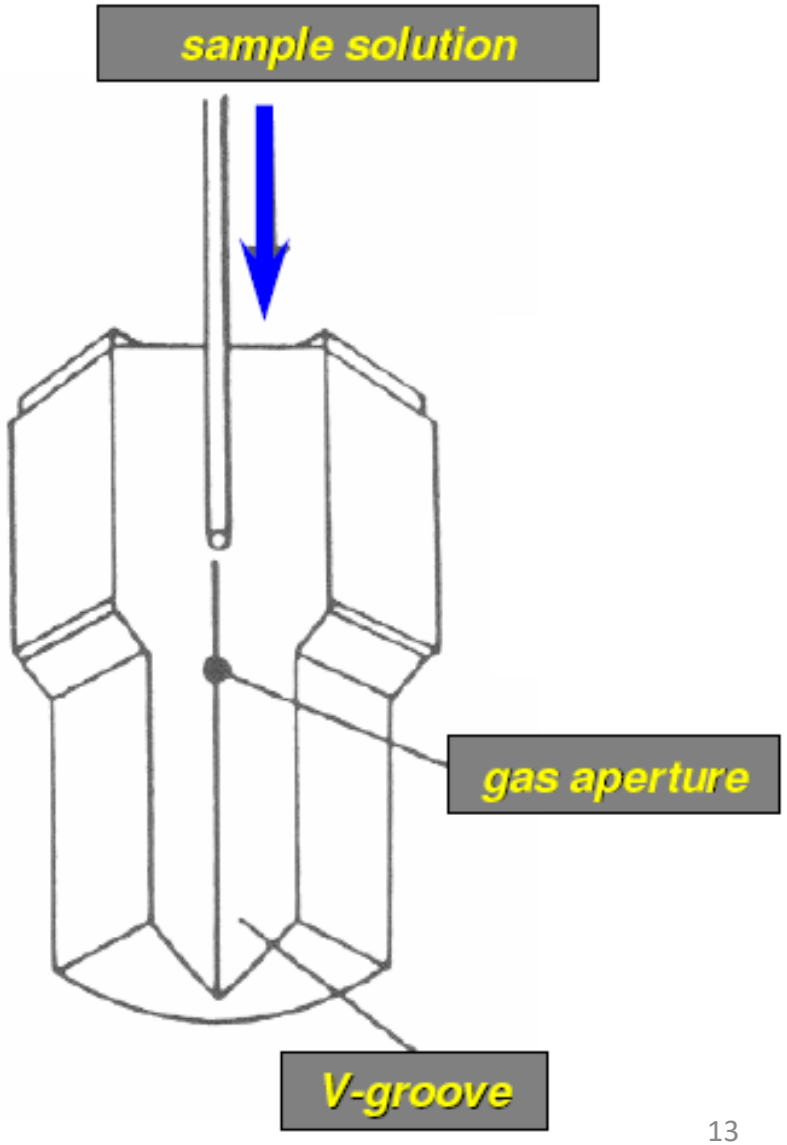
Sample introduction

nebulizers

V-groove nebulizers

The liquid is delivered in a capillary at right angles to the gas capillary, but the liquid is poured down a vertically orientated groove that flows past a gas orifice. The gas pulls the liquid into the gas flow and forms a fine mist.

High content of dissolved contents (up to 20 %)
Poor stability



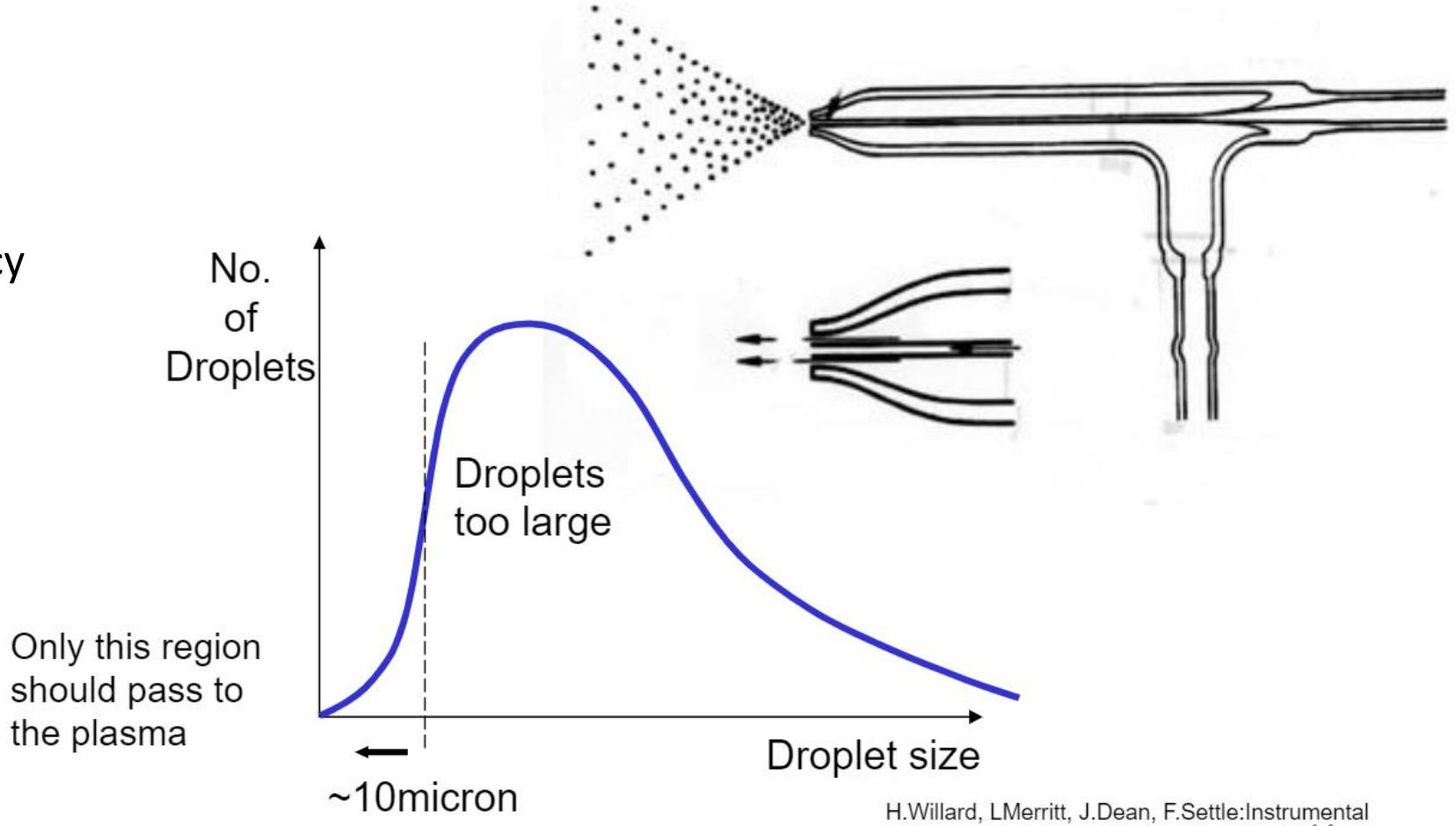
Sample introduction

nebulizers

Droplet size

Sample introduction efficiency varies between 1 – 80 %
(Concentric nebulizer < 5%)

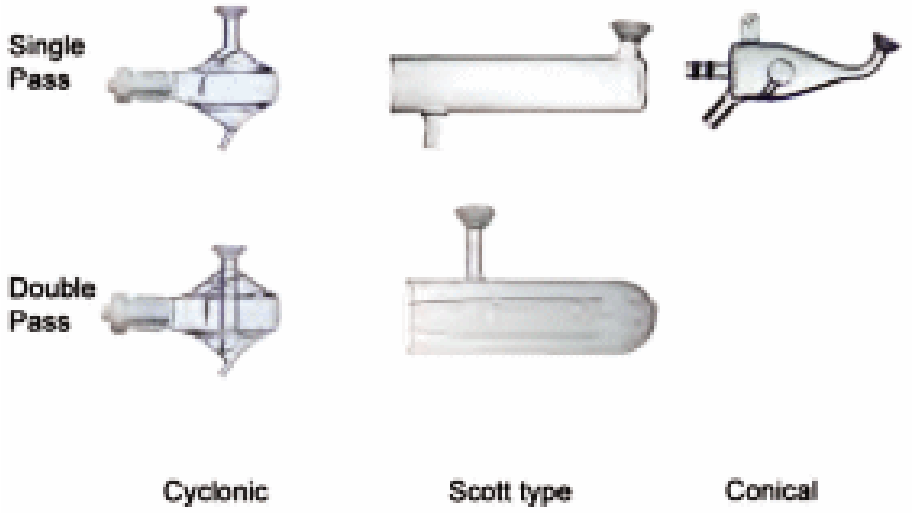
Spray Chamber



H.Willard, LMerritt, J.Dean, F.Settle:Instrumental Methods of Analysis; Wadsworth Publishing Company

Spray chambers

The spray chamber is part of the system for introducing the liquid sample into the plasma. Its task is to filter the aerosol produced by the nebulizer (primary/secondary aerosol) so that only the smallest droplets reach the source (tertiary aerosol). Cyclonic, cylindrical (Scott type) and conical spray chambers are most often used in plasma spectrochemistry.

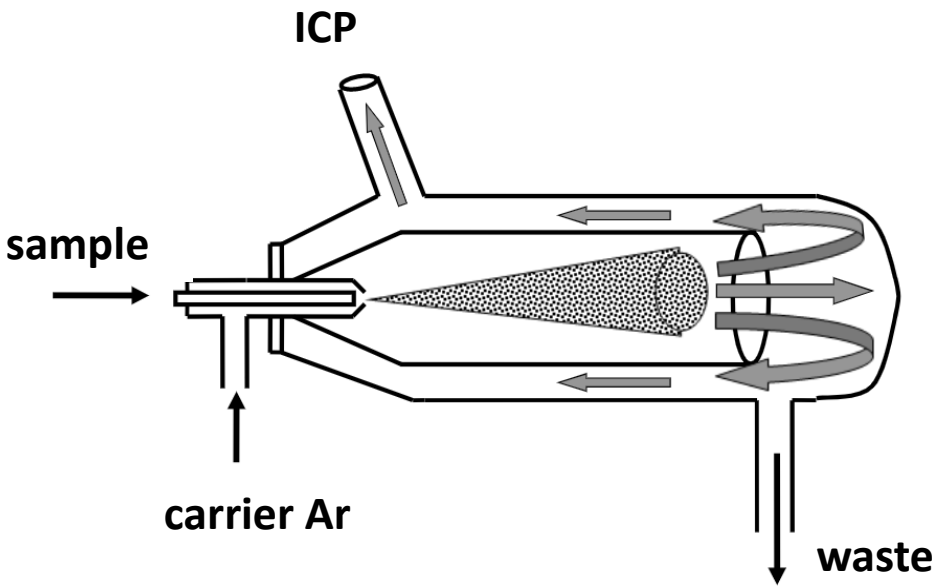


The spray chamber controls not only what proportion of the analyte is transported to the ICP, but also the amount of aerosol and solvent vapor that reaches the plasma. If too much aerosol or solvent vapor enters the plasma, the temperature of the plasma in the central channel will decrease or the plasma will switch off. The spray chamber also reduces the pulses during aerosol formation.

Spray chambers

Scott type

It is the most used type of spray chamber. It consists of two concentric tubes. The aerosol enters the spray chamber through the inner tube and at its end is forced to change its flight path by 180˚ towards the outer tube, at the end of which there is a supply to the plasma. Due to the influence of gravity, impact of droplets on the walls and coagulation between them, larger droplets on the walls of the chamber are eliminated on the way to the exit to the plasma, and only a fine aerosol enters the plasma. This spray chamber is most often associated with a concentric nebulizer.

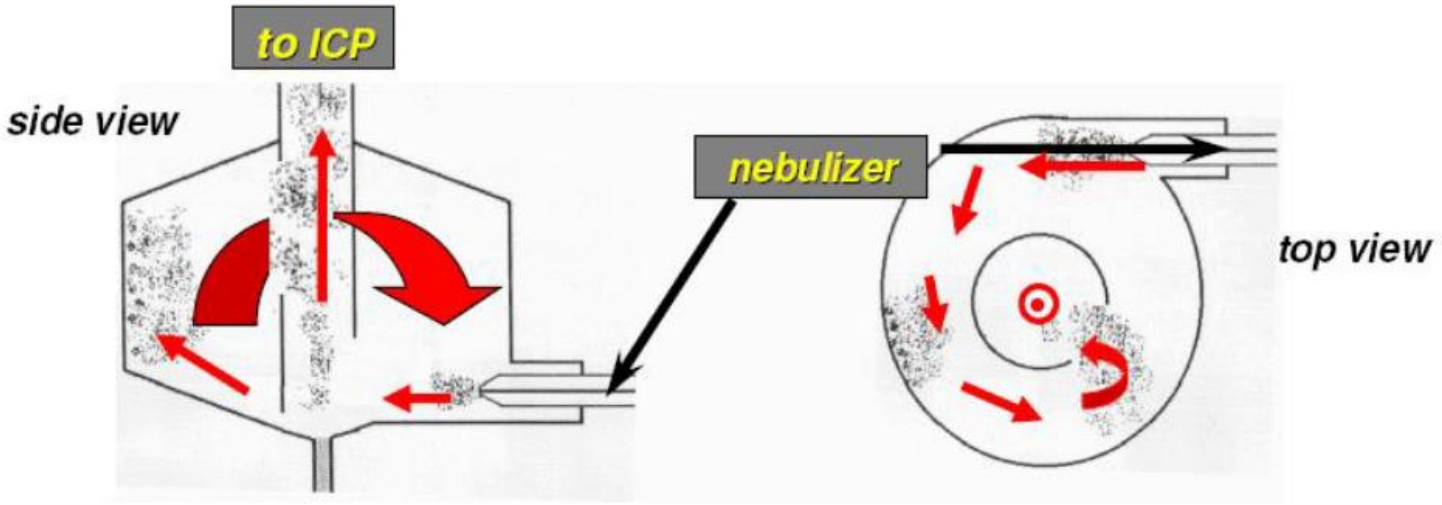


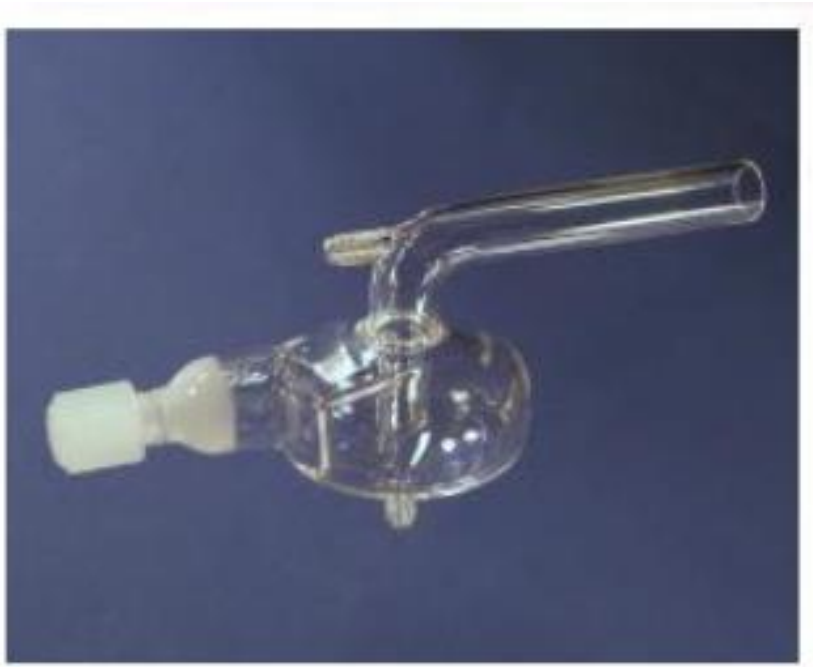
- Removal of large droplets
- Often with waterjacket for cooling

Spray chambers

Cyclonic type

- Higher sample introduction efficiency





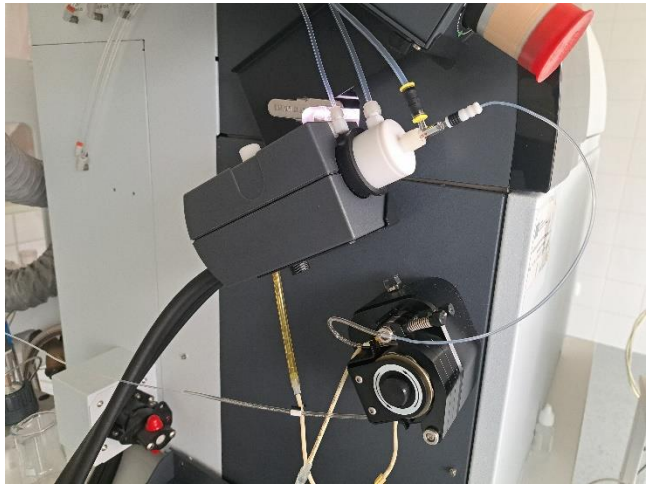
Efficiency of nebulization

The most common arrangement for nebulization the solution is a pneumatic nebulizer + spray chamber.

Efficiency:

1 – 4 % at sample flow rate > 0.5 ml min^{-1}
The low efficiency is a prevention for unwanted cooling of the plasma and its switching off
Chamber cooling is usually necessary

60 – 100 % at sample flow rate < 10 µml min^{-1}
Without spray chamber heating



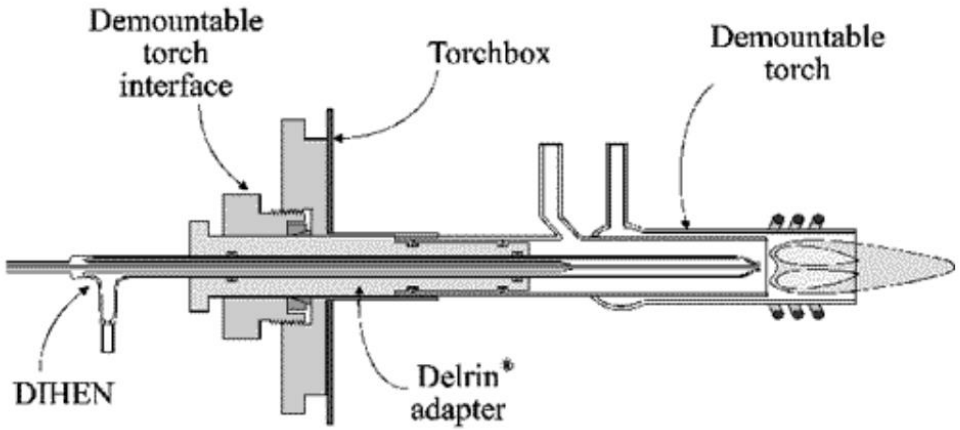
Micronebulizers

The limiting factor for elemental analysis can be the available sample volume.
Recently, sample introduction systems used in plasma spectrometry (ICP-MS) have evolved to expand the applicability of these techniques to the analysis **of micro- and nano-samples**. Another reason for introducing a small amount of sample is to minimize matrix or solvent sampling into the plasma.

Common nebulizers: flow rate 0.5 – 1.0 ml min^{-1}
Micronebulizers: flow rate < 200 µl min^{-1}

Princip:
- Miniaturizace běžně používaných zmlžovačů
- Direct Injection High Efficiency Nebulizer –
  bez mlžné komory, 100% účinnost, 1-100 µl min^{-1}

DIHEN MEINHARD® Nebulizer



(US Patent #6166379)

Nebulizers independent of gas flow

Jet impact

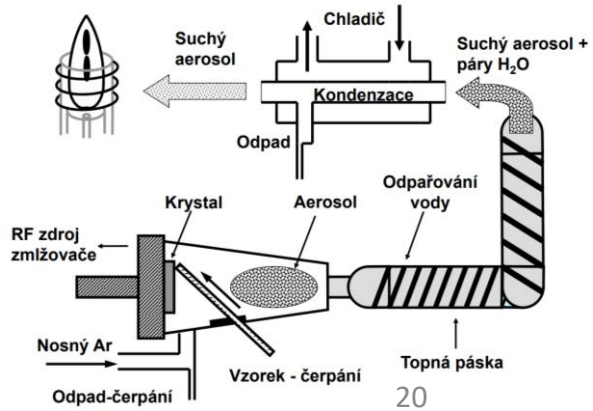
The aerosol is formed from a solution flowing at high speed from a capillary into the headspace of a spray chamber or against an impactor due to inertial effects that are greater than the surface forces in the liquid. The nebulizer requires the supply of the solution by a high-pressure pump under a pressure of 10 - 40 MPa into a capillary with a diameter of 10 - 30 µm. The resulting aerosol is transported by the carrier gas independently of the operation of the nebulizer.

Thermospray

The aerosol is formed by shock heating the solution above the boiling point in stainless steel or quartz capillaries. During the expansion of superheated vapors in a capillary with an internal diameter of 150 µm with an outlet opening of a diameter of 20-150 µm, an aerosol is created with an efficiency of up to 60%.

Utrasonic nebulizer

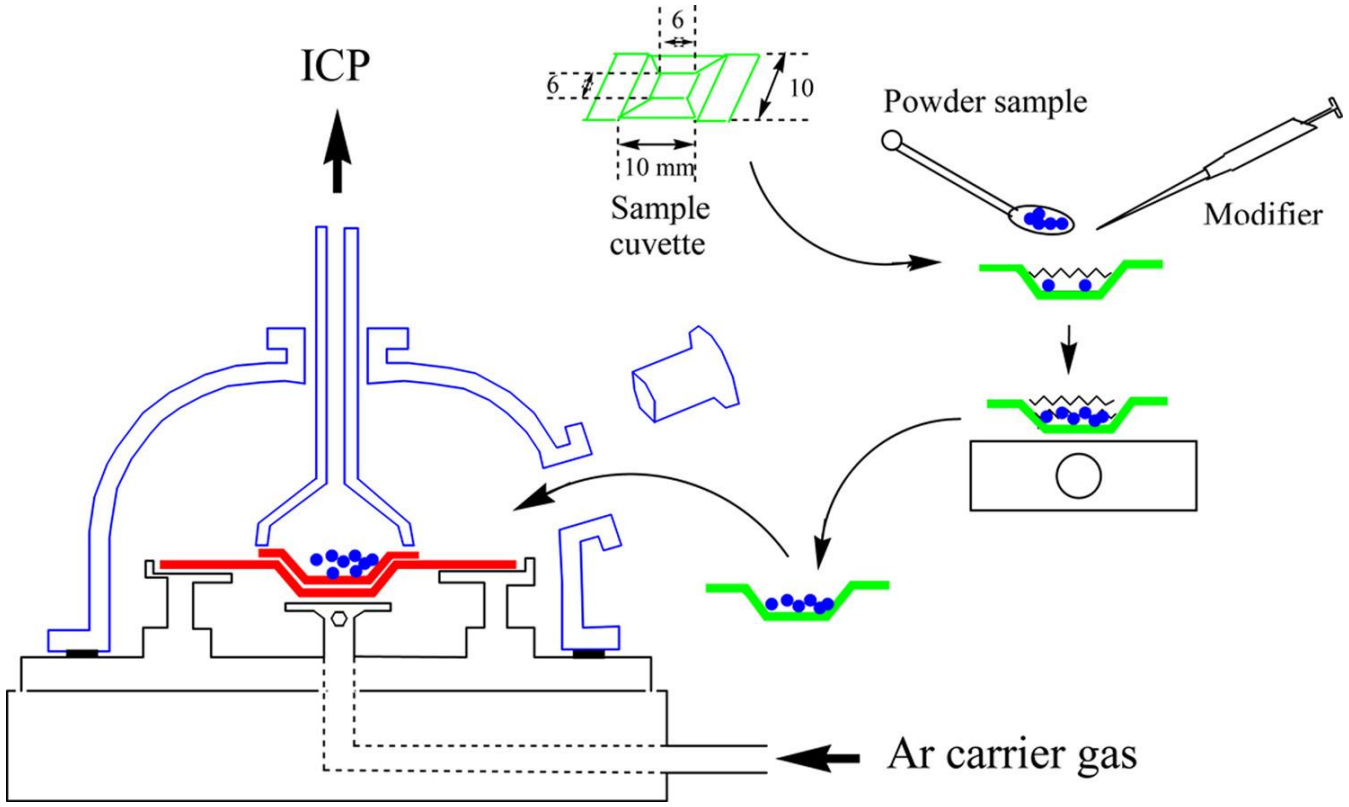
The aerosol is formed from a film of solution using acoustic energy generated by the vibration of the piezoelectric plate of the transducer. The sample is taken from the flowing carrier gas and introduced into the spray chamber. Due to their high efficiency (~10x higher than pneumatic nebulizer), ultrasonic nebulizers are coupled to the ICP through a desolvation stage, as it is necessary to reduce the load of the discharge with solvent and its vapors.



Sample introduction

Electrothermal vaporization ETV

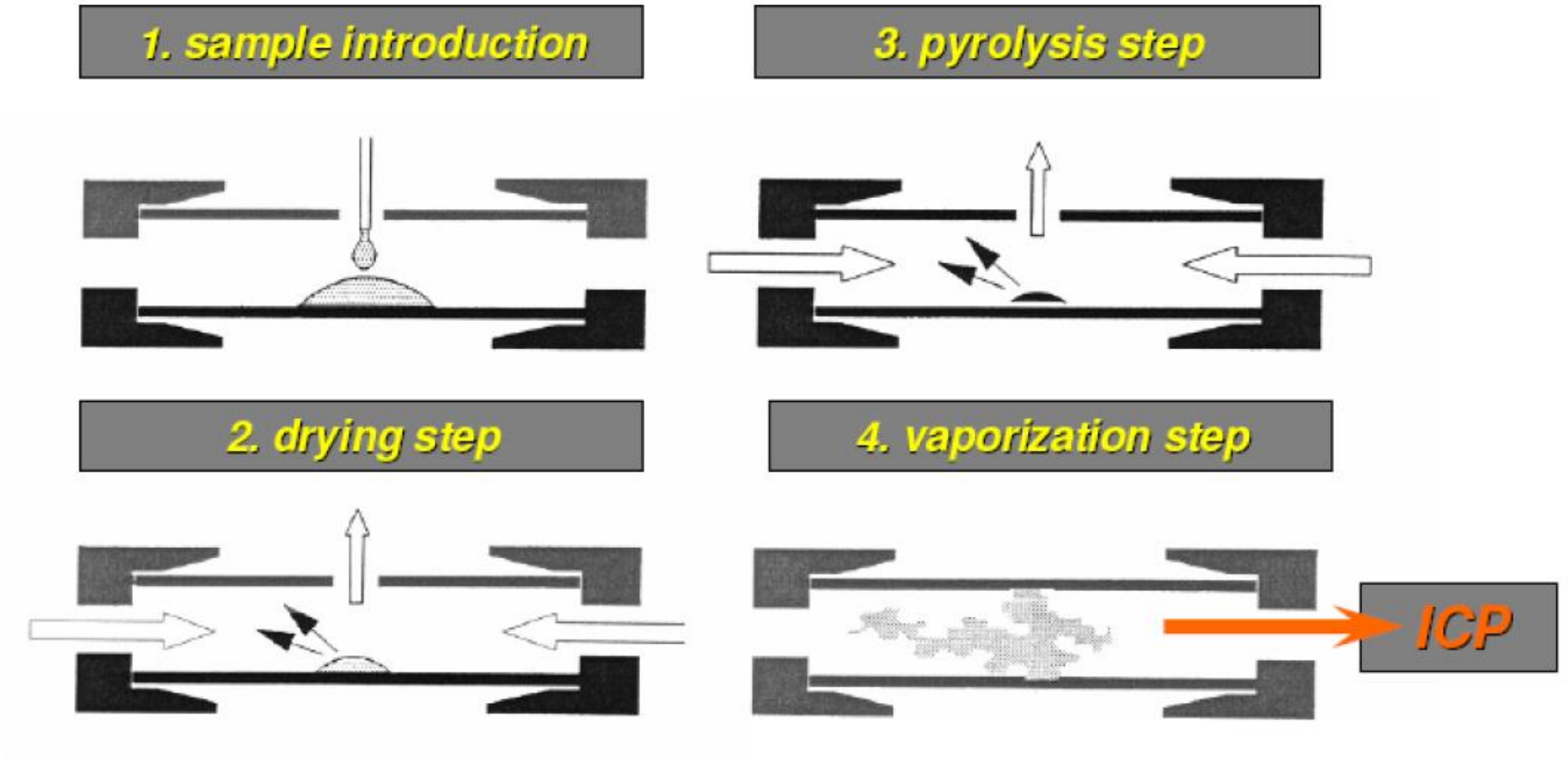
- Introduction of small volume – liquid, solid
- Sample subjected to multi-step t° programme
  - drying step
  - pyrolysis step (removal of matrix components)
  - vaporization step
  - high t° cleaning step
- Sample vapours transported to ICP (Ar)



Nakata K., Talanta vol. 138, Pages 279-284

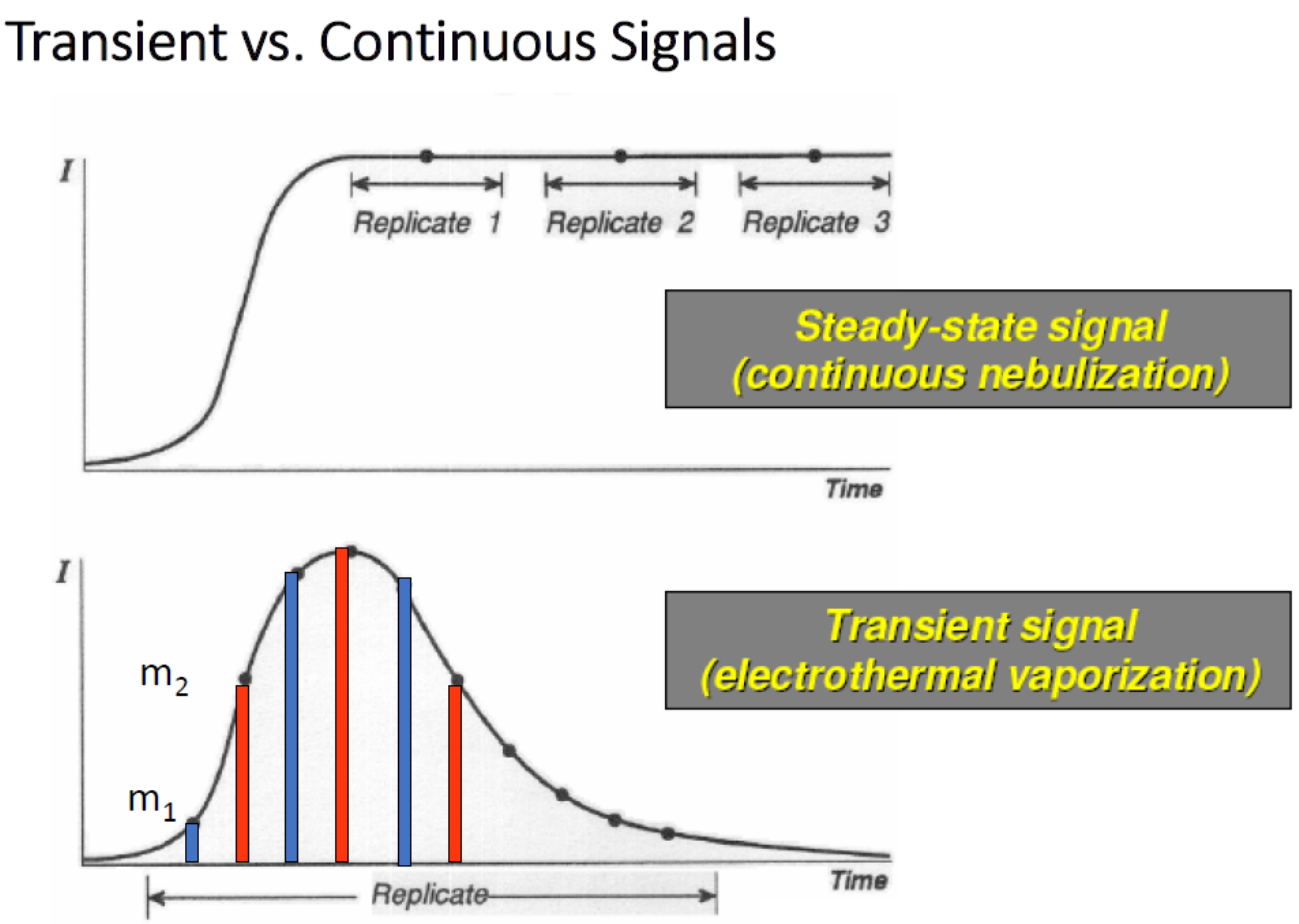
Sample introduction

Electrothermal vaporization ETV



Sample introduction

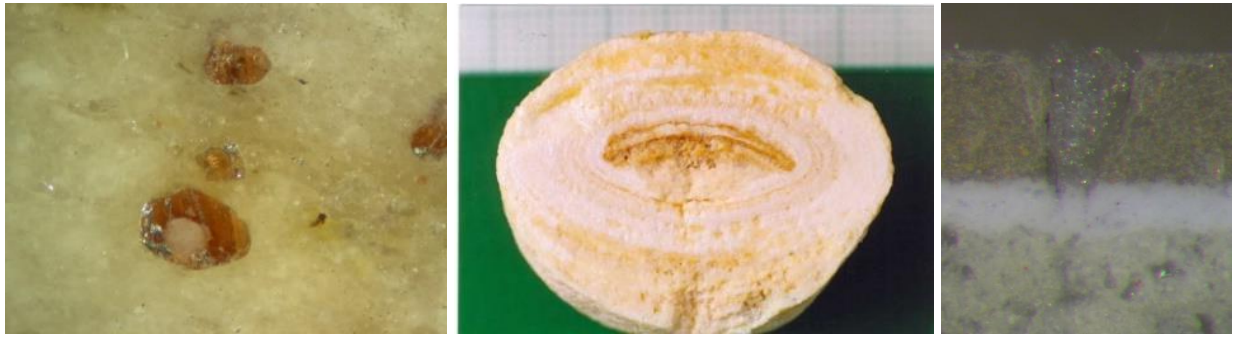
Electrothermal vaporization ETV

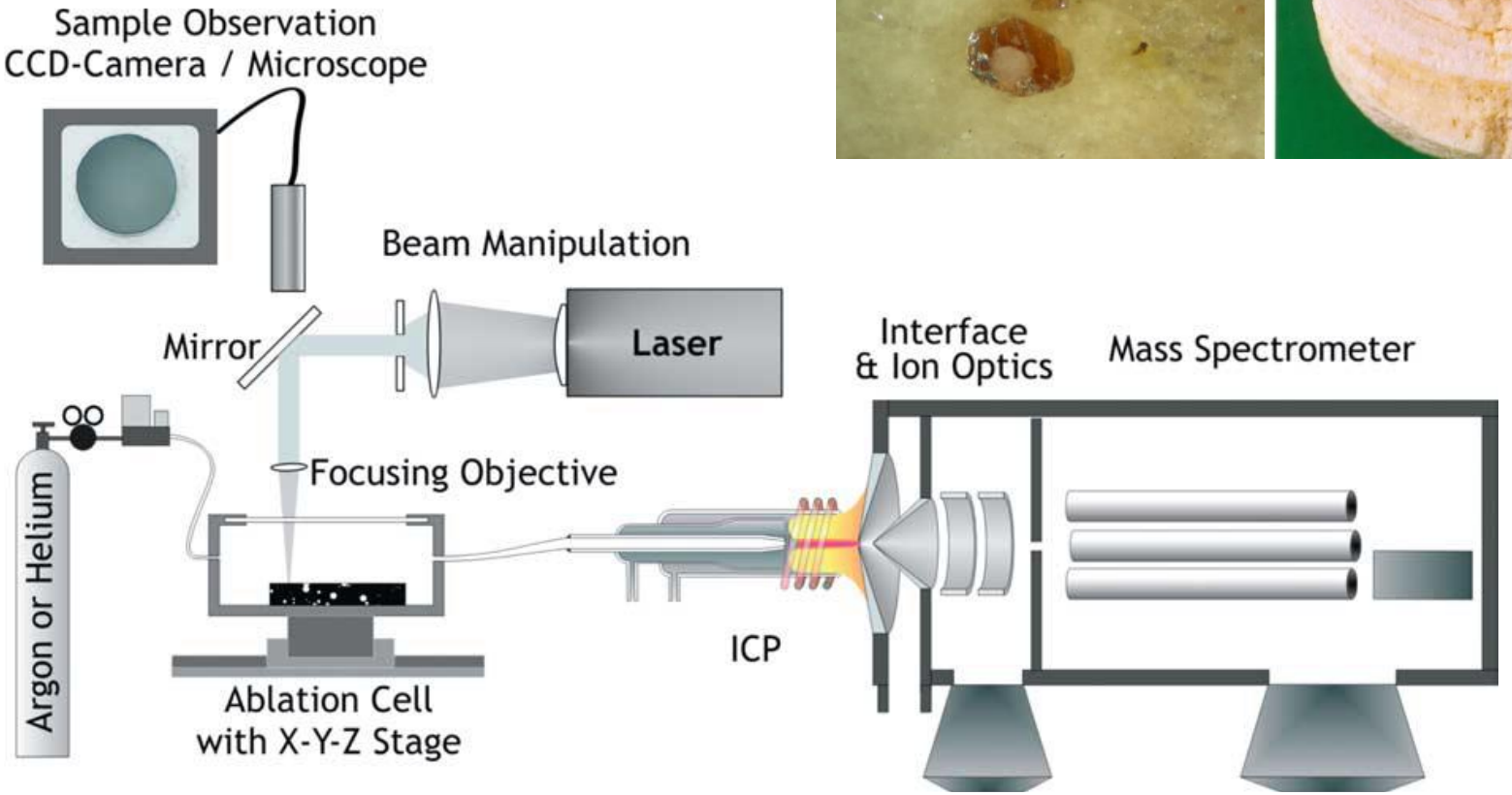


Problem: Spectral skew – fast acquisition

Sample introduction

Laser ablation LA

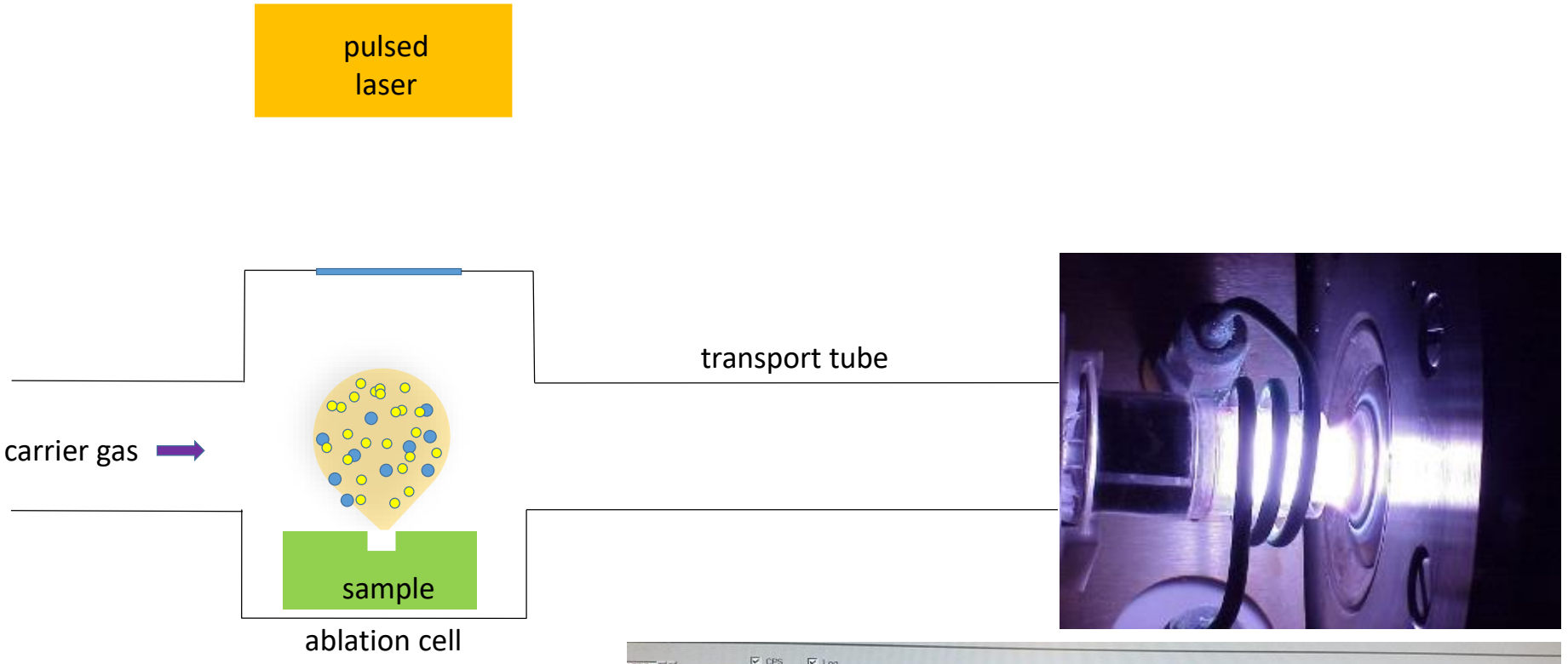


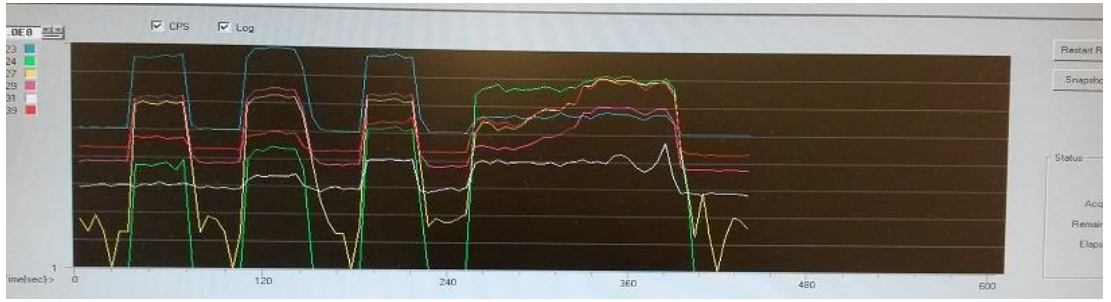


Günther, D., Hattendorf, B., 2005, Trends in Analytical Chemistry, vol. 24, no. 3, p. 255-265.

Sample introduction

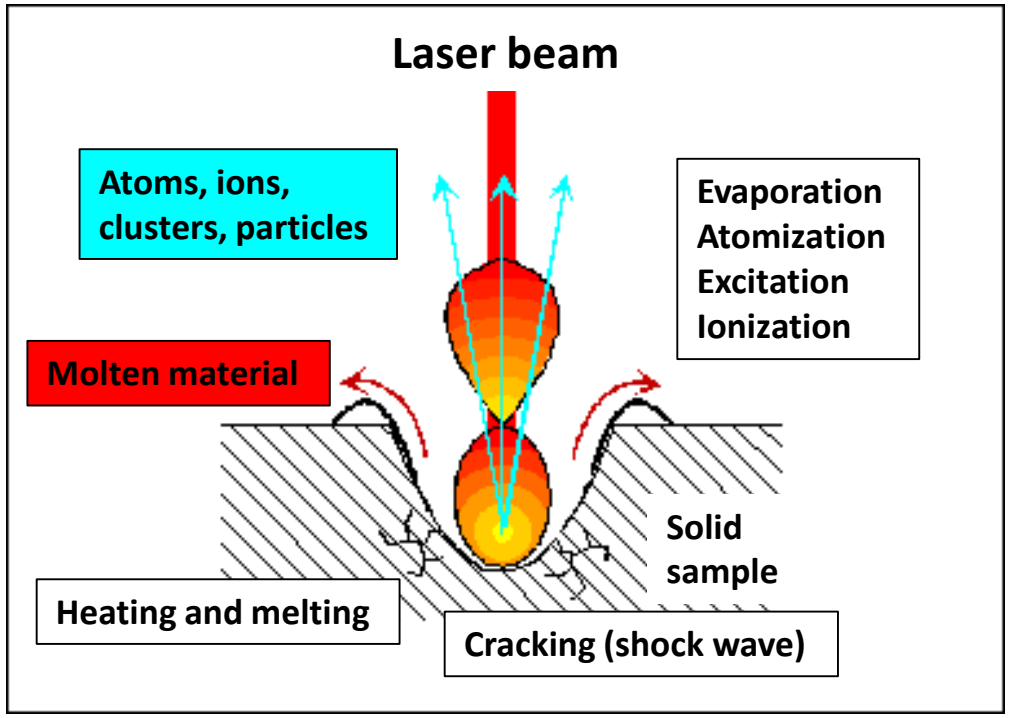
Laser ablation LA





Sample introduction

Laser ablation LA



Ablation process is influenced by:

Laser wavelength, pulse energy, **pulse duration**, repetition rate…

Sample introduction

Laser ablation LA

Advantages

- Solid sampling approach
  - no (minimal) sample pre-treatment (disslolution) required
  - high sample throughput
- Broad application range
- Spatially resolved analysis

Disadvantages

- Quantification complicated
- Purchase price
- Small ablation craters
  - higher LOD
  - problems with microheterogeneity