B- Sample introduction:

Samples for trace element analysis are rarely in a form suitable for direct introduction to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). They are dissolved to form solutions for aspiration into the spectrometer excitation source. In many cases, it would be desirable to analyse solid samples directly, without lengthy sample preparation procedures, which sometimes leads to analytical problems. Many analytical methods have been developed for direct solids analysis, each with unique strengths and weaknesses. Most recently, laser sampling, used in conjunction with ICP-MS, has been shown to be promising for direct trace element determinations in solids.

B1- Solid analysis: Laser Ablation

* Principle of Laser

Laser is an acronym for Light Amplification by Stimulated Emission of Radiation. As a consequence of its light-amplifying property, a laser has spatially narrow and extremely intense beams of radiation having identical frequency, phase, direction and polarisation properties. According to the resonance condition (λE = hv) and to the rules of quantum mechanics, an atom can change its energy level, which leads to the absorption or emission of a photon. Stimulated emission is the basis of laser behaviour. Stimulated emission leads to the emission of a coherent radiation with the incoming radiation. In order to have light amplification in a laser it is necessary that the number of photon produced by stimulated emission exceed the number of photons lost by absorption. This light amplification is only achieved when a population inversion from the normal distribution of energy state exists. This population inversion (activation of a laser material) is created by an external pumping source (a flashlamp, an electric discharge), so that a few photons of proper energy will trigger the formation of a cascade of photons of the same energy. This cascade of photons is focussed on a sample. Interaction between the laser beam allows the conversion of photon energy into thermal energy, which is responsible for the vaporisation of most of the exposed solid surface. The material ablated is swept away with an argon stream to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and analysed.

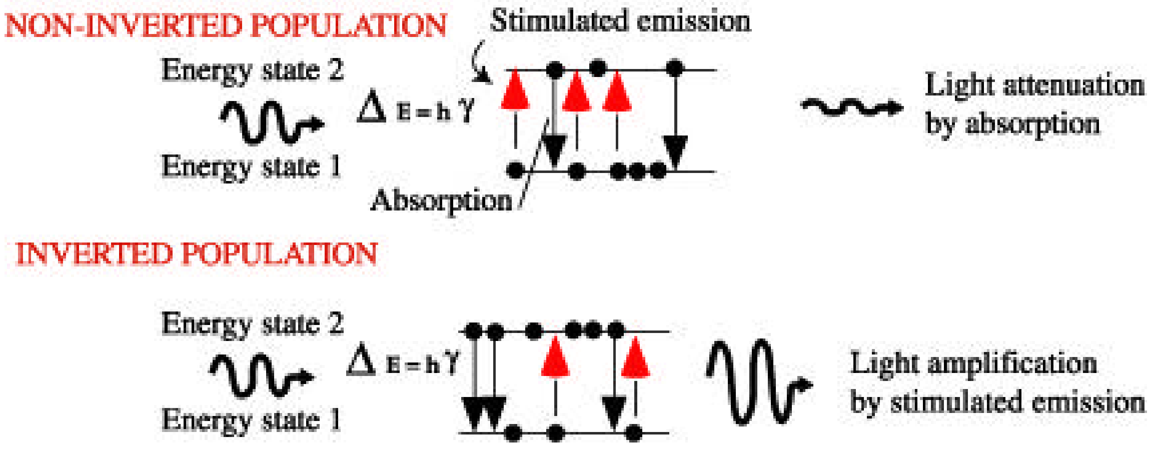


Figure 2.21: Principle of Light amplification: Passage of radiation through a non-inverted population and an inverted population. An incoming radiation is lost by absorption (top) or an inverted population is created by "external pumpping" (bottom). A few photon will trigger the formation of a cascade of photon of the same energy.

Two main types of UV lasers are widely used in Earth Sciences:

(1) **Excimer gas lasers** in which light is emitted by a short-lived molecule made up of one rare gas atom. This type of laser is beginning to be use in LA-ICP-MS. Its operation depends on electronic transitions in molecules.

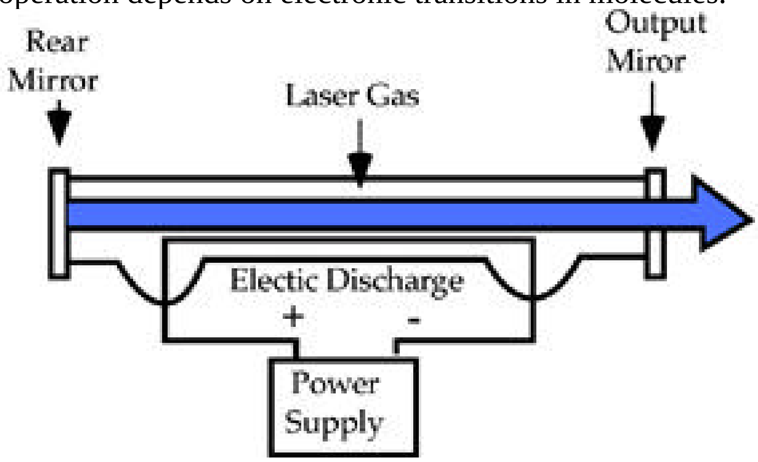


Figure 2.22: Schematic of an excimer laser head (Hecht, 1988).

(2) **Solid state lasers** such as the frequency-quadrupled Nd:YAG in which the atoms that emit light are fixed within a crystal or a glassy material. Lasers are characterised mainly by their wavelength (1064 nm for a Nd:YAG), output power and pulse length fixed by the design of the laser (nanosecond or picosecond)

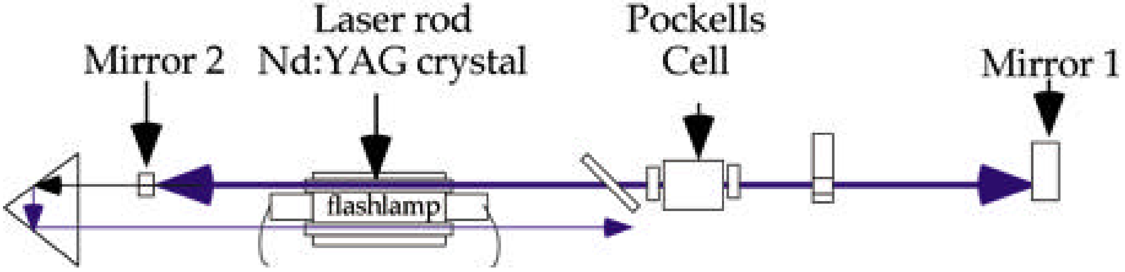


Figure 2.23: Schematic of a Nd:YAG laser head.

Wavelengths (nm)

Figure 2.24: Schematic relations between wavelengths and photon energy for excimers and Nd:YAG.

Solid interaction:

Laser - material interaction is a complex process resulting in (1) vaporisation or ablation; (2) ejection of atoms, ions, molecular species and particulate; (3) shock waves. Power density is a critical parameter which allow the separation of two different process; (1) vaporisation and (2) ablation.

Laser ablation of a solid sample consists of several stages, in which different kinds of 'vapour-products' are ejected. The initial stage is electronic excitation inside the solid, accompanied by the ejection of electrons at the sample surface, due to photoelectric and thermo-ionic emission. During this time, the energetic electrons in the bulk of the solid transfer energy to the lattice through a variety of scattering mechanisms; the sample target then undergoes melting and vaporization, followed by ionization and the formation of a plasma plume consisting of the sample constituents. The expanding plume interacts with the surrounding gas to form a shock wave, causing the ambient gas to become further ionised. The expanding high-pressure plasma exerts a force back to the target, which flushes out the melted volume. This recoil pressure and flushing mechanism can produce large-sized particles (several micrometers). The transport efficiency to the ICP is typically low for small diameter particle <5nm, which tend to be lost by diffusion, and is also low or large particles > 3mm, which will settle out owing to gravity. Particles with diameters between these extremes are carried with an efficiency of >80%.

* Description of the New Wave Research™ Laser ablation System

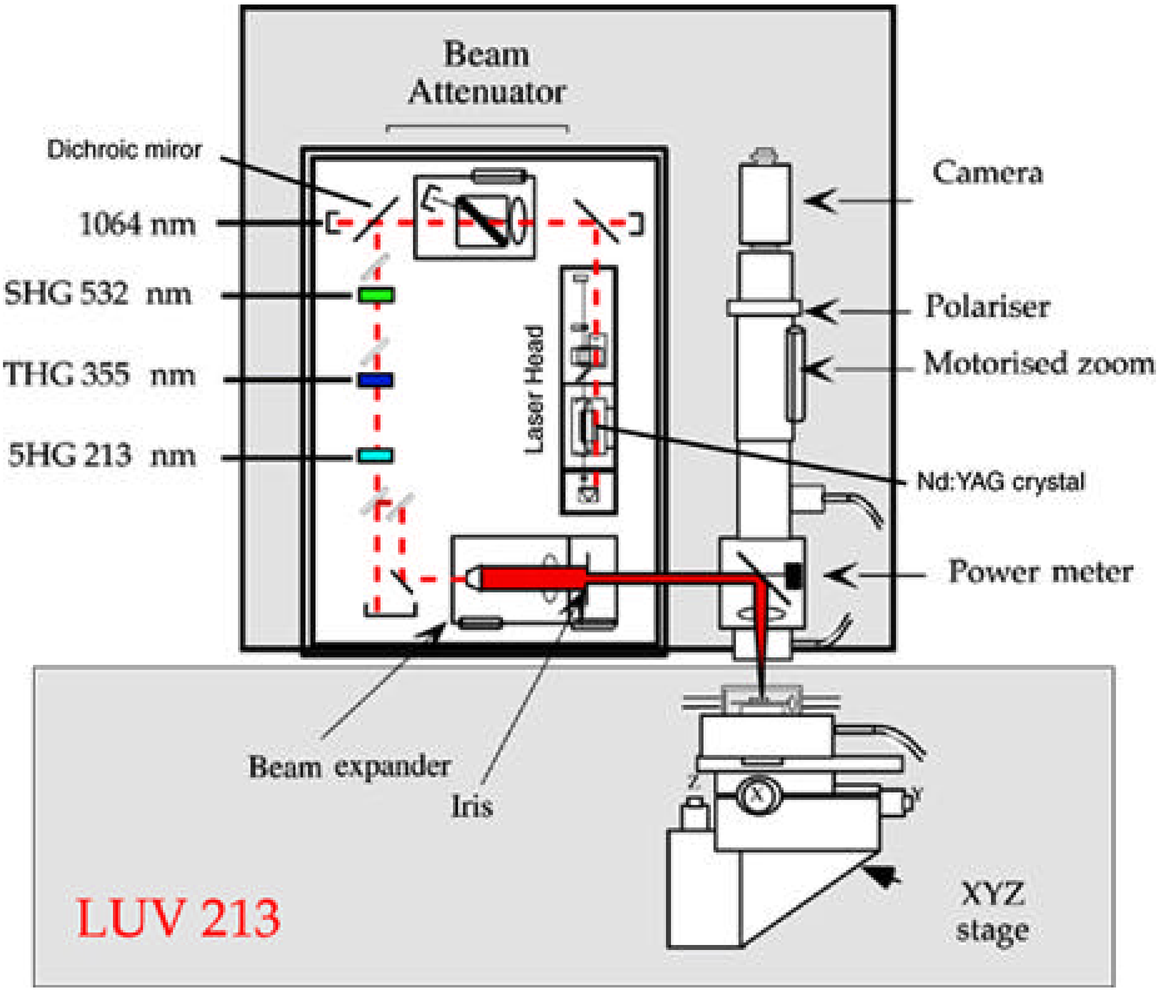


Figure 2.25: Sketch of the fifth harmonic generator of the petrographic laser ablation system from New Wave Research™.

The New Wave™ laser is a Nd:YAG laser, which comprises a rod of Yttrium aluminium garnet ($Y_3 Al_5O_{15}$) doped with approximately 3wt% Nd_2O_3, providing a wavelength of 1064 nm. The wavelength of the beam generated by the laser within the resonator cavity is frequency quadrupled to the Ultra Violet (UV) range using 3 harmonic crystals (SHG 532nm, THG 355nm, 5HG 213nm). The maximum output energy is about 10 mJ with a pulse length of 4 ns with the first design of the laser system. The output energy can be changed by varying the voltage applied to the flashlamp of the cavity resonator (figure 2.23) or by using a beam attenuator. The size and shape of the beam is also monitored by a beam expander. The beam is finally focussed on a sample through the objective lens of a microscope. The sample is observed through a microscope using three different light sources (incident, transmitted and reflected). The sample is contained within a sample cell and connected to an XYZ motorised stage. This laser sampling use electronic stepper motors to move the stage on which the sampling cell is mounted. Remote control X, Y and Z axes stages allow you to move the sample under the laser beam in different manners: single point, along a line or within an area (raster).

laser cavity: When a discharge occurs in the xenon flashlamp, the atoms Nd^{3+} of the Nd:YAG laser are raised from the ground state to the pumping level. This optical pumping produces an overpopulation of excited-state Nd. The system becomes unstable and a photon will stimulate the emission of a cascade of photons. The light pulse is reflected from the two mirrors and is amplified each time it passes through the laser rod. Because of the design of the cavity resonator, light produced is amplified until it reaches a threshold and emission can occur. By placing an optical switch (Pockells Cell) between the laser rod and one of the mirrors, the laser run in a Q-switched mode, which leads to the formation of a single large output pulse.

Harmonic Crystals:The large output pulse generated within the cavity resonator has a fundamental wavelength of 1064 nm (Infra Red) characteristic of the Nd:YAG laser rod. The Infra Red wavelength can be frequency-quintupled to 213 nm using 3 harmonic generating crystals, which provide second, fourth and fifth harmonics in the ultraviolet (213 nm). Dichroic mirrors are also necessary to reflect the initial wavelength of the laser toward the beam attenuator.

Beam Attenuator: The initial output energy is reduced using a half wave retardation plate and a calcite polarising prism. By rotating the half wave plate with angular velocity ω (the output polarisation rotates at an angular velocity of 2_ω) the polarised light emerges from the prism with different irradiance Is and Ip. Depending the orientation of the prism, the laser beam can be reflected by the prism to a trap (ω = 45°, Is ~ 100%) or pass through the prism without any attenuation (ω = o°, Ip ˜ 100%)

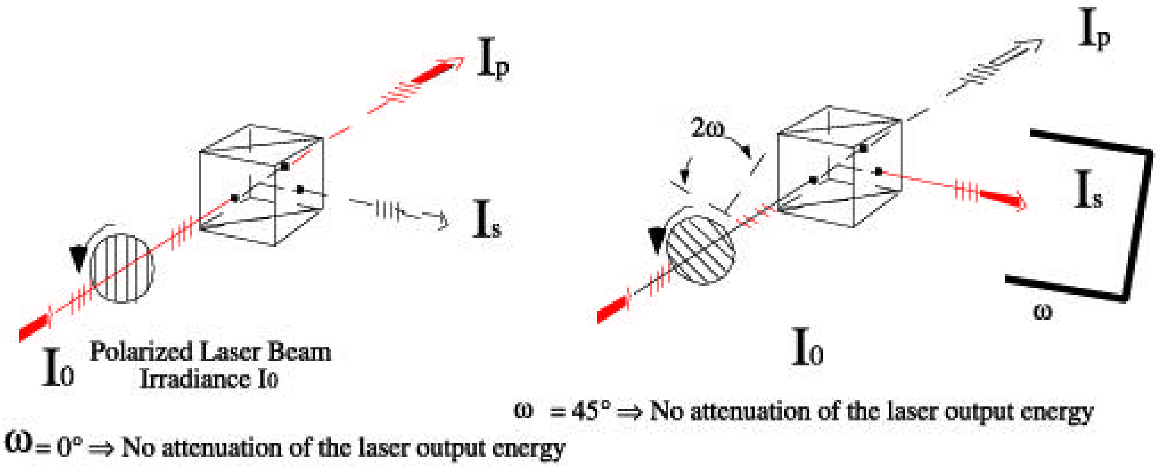


Figure 2.26: Schematic of the beam attenuator showing the effect of the half-wave plate rotation on the output energy (irradiance) after the calcite polarising prism.

Beam Expander: By moving the beam expander lenses from one to another, the beam size can be changed from 400 _m to 10 _m. An aperture can also change the energy profile of the beam from gaussian to a "top hat" beam profile.

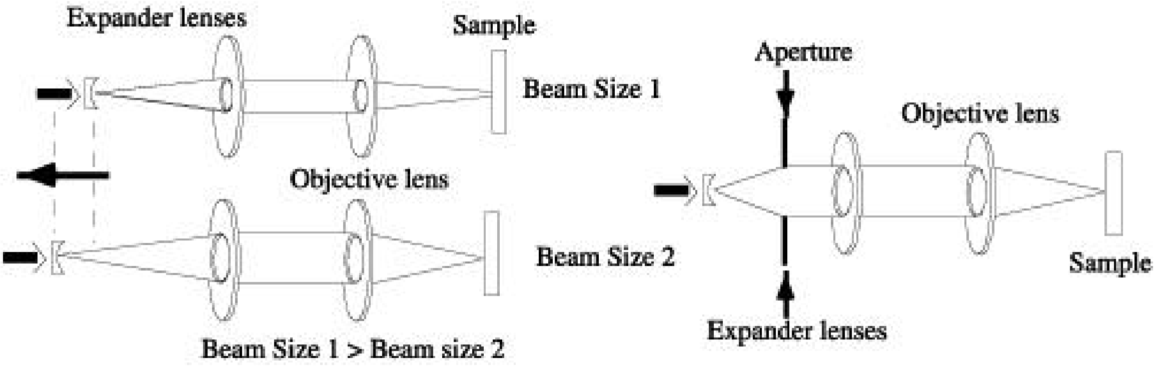
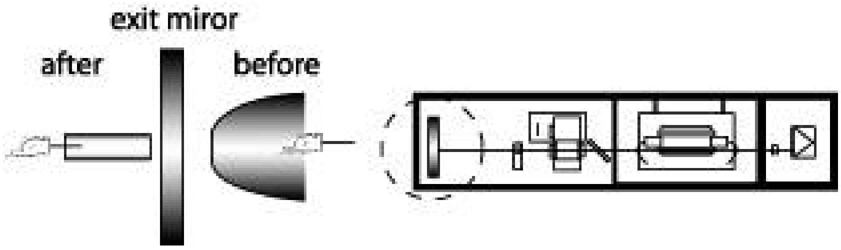


Figure 2.27: Schematic of the beam expander. The movement of the two lenses from the expander from one to an other is responsible for the modification of the spot size and the closure of the aperture is responsible for the change in the energy beam profile.

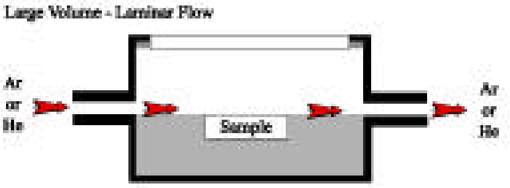
A new technique to improve the beam energy profile and to image the aperture involve the modification of the exit mirror of the laser head:

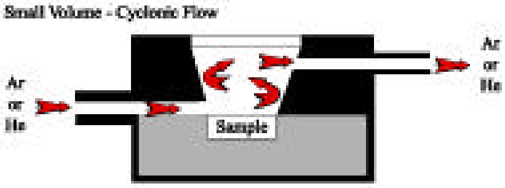


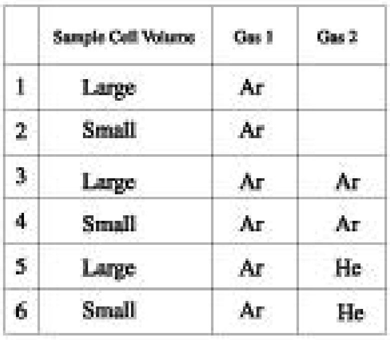
Sample cell: The sample cell must let the laser light pass through a sample cell window. The Ar or He gas pass though it and carry the ablated sample to the ICP. A series of purge the air from the cell to switch off the plasma after changing the sample. The sample cell window must either be coated for UV light or formed and angle in order to avoid reflection back to the objective lens and damage. Design of sample cells have evolved over the last few years in order to improve transport efficiency and potentially reduce fractionation during ablation.

Frankfurt (NewWave)

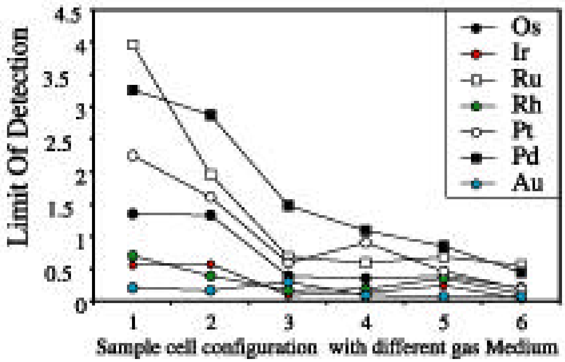
Monash





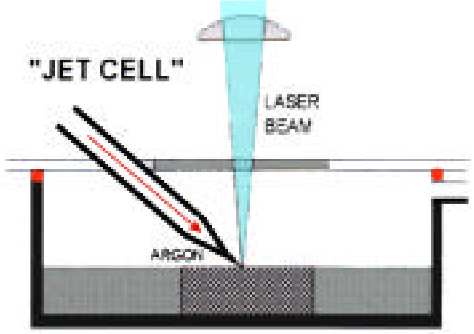


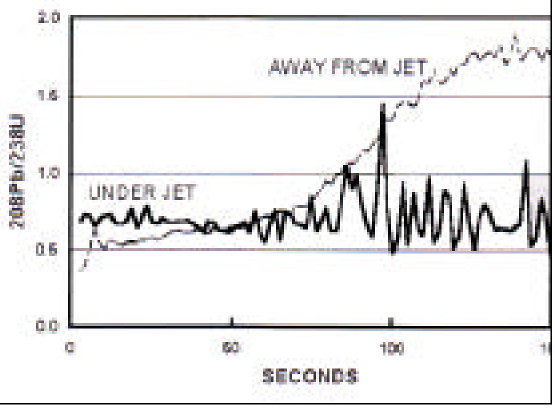
	Sample Cell Volume	Gas 1	Gas 2
1	Large	Ar	
2	Small	Ar	
3	Large	Ar	Ar
4	Small	Ar	Ar
5	Large	Ar	He
6	Small	Ar	He



Two different sample cell designs have been tested using two different gas medium (Ar and He). The design, using a sample cell with small volume and aerodynamically shaped for laminar flow in an argon atmosphere, give the poorest sensitivity. The design, using a sample cell with a large volume for a cyclonic-gas circulation, is accompanied by a two to four-fold increase in sensitivity when ablating in a He atmosphere. The development of surface deposit is greatly reduced by ablating in an ambient atmosphere of He instead of Ar. The sensitivity improvement of cyclonic versus laminar sample cell suggests that the plasma extend much further in heights in a He atmosphere rather than in an Ar atmosphere.

Memorial (Jackson, GacMac short course, 2001)





This design offer 3 advantages (1) The gas flow dynamic is the same everywhere in the cell; (2) it shift the redeposition blanket and avoid the re-ablation of this blanket (3) it also reduce inter-element fractionation (U/Pb ratio). This design was also originally created to cool the sample and reduce fractionation. Water spray together with the jet has been tested but without much success yet.

Others: At ETH, a very efficient sample cell has been developed while studying the particle size distribution in different sample cell configuration (Bleiner and Günther, 2001). Other spray chambers are cooled in order to ablate ice core (Reinhardt, 2001). Finally, a special sample cell has been built in order to facilitate the ablation of large artefacts (Devos et al, 1999).

B2- Liquid analysis:

Nebulizer – Spray Chamber – Desolvator unit.

Usually sample introduction for plasma spectrometry is generally accomplished using solution nebulization. Sample is aspirated by a nebulizer (the most common type is a Meinhardt, Figure 2.28), using a peristaltic pump, into a typical Scott type spray chamber (Figure 2.29). The spray chamber limits the size of the droplets (<10 micron) that reach the plasma. Solutions may be swept with a flow of argon into the plasma.

The main drawbacks of pneumatic nebulizers are their low efficiency. Only 2-3% of the aspirated solution reaches the plasma. New micro-nebulizers (made of PTFE from Cetac^{TM}) with sample uptake down to 20 _m per minutes have very similar transmission than basic Meinhardt nebulizer and therefore improve efficiency up to 35%. Using a desolvator unit, about 40% of the solution is converted to an aerosol (Figure 2.30). The plasma must be set at higher power in order to prevent plasma extinction because of the high amount of sample to the torch. The plasma will also turn off since the amount of water vapour is too high. In order to reduce the amount of aerosol droplet to an aerosol particle, the aerosol generated by the nebulizer is rapidly heated to approximately 130°C. The vapour and aerosol droplets are transferred by the nebulizer gas flow into a condenser for solvent removal. The remaining dry aerosol is then directed to the ICP torch for atomisation and ionisation. The overall benefit is a 10 folds increase in sensitivity and a reduction in polyatomic interference. However a 2-5 min wash time is require between samples. Memory effect could also be significant. Recent studies on f isotopes by Collerson et al (2002) have showed that up to 6% of the sample remain and might cross-contaminate the following sample. Unusual isotopic composition (e.g. spike) should be avoided.

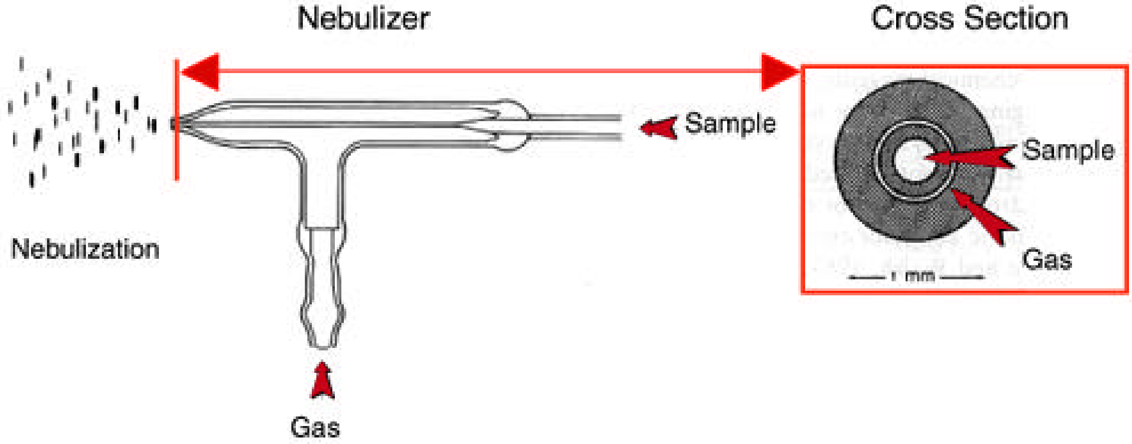


Figure 2.28: Schematic of a Meinhardt nebulizer

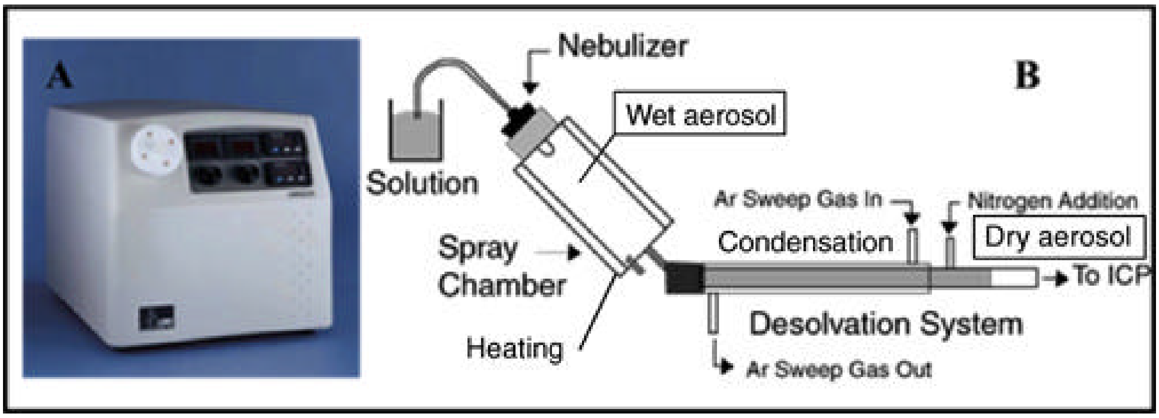


Figure 2.29: Schematic of a desolvator unit (the Aridus from Cetac^{TM})

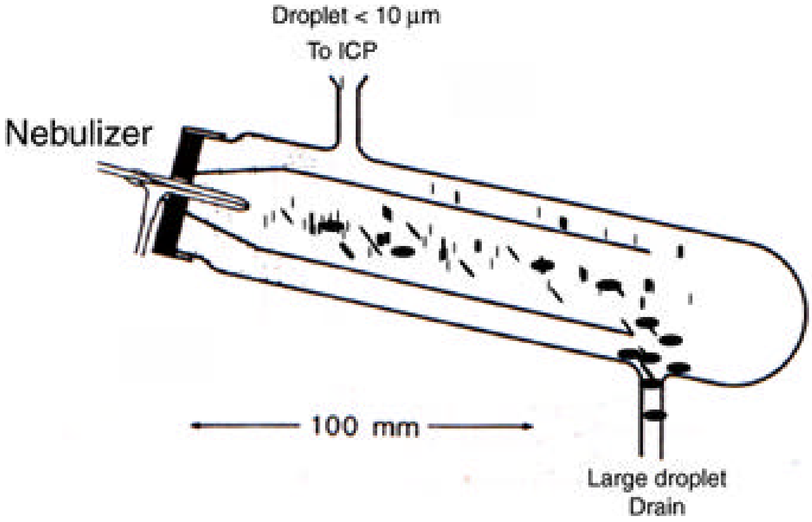


Figure 2.30: Schematic of a classical Scott-type spray chamber.

Suggested reading:

HechtJ. (1988) Understanding lasers, Howard W. Sams & Company.

Robert Thomas Spectroscopy tutorial available on pdf format at http://www.scientificsolutions1.com/icpmstutorial.htm.