

CHAPTER 3: ANALYTICAL INSTRUMENTS

3.1 INTRODUCTION

This chapter focuses on the analytical instruments used in this study for sample preparation and measurement. It provides a summary of the description of the instruments, the operating principles and techniques used by the instruments.

3.2 SAMPLE PREPARATION INSTRUMENTS

3.2.1 Multiwave 3000 (Anton Paar GmbH)

Multiwave 3000 is a new design of a micro-wave assisted sample preparation system. It consists of various rotors for fast and complete closed vessel digestion of organic or inorganic samples under high pressure and temperatures, figure 3.1.

Principle of operation

Microwaves are high-frequency electromagnetic radiation in the frequency range 300 MHz to 300 GHz that is between high frequency (30 kHz – 300 MHz) and infrared radiation. Only 4 microwave frequencies are permitted for industrial and scientific use. Of these, 2.45 GHz is the most frequently used. Microwave 3000 digestion instrument incorporates two microwave generators (magnetrons) that generate waves at this frequency of 2.45 GHz.

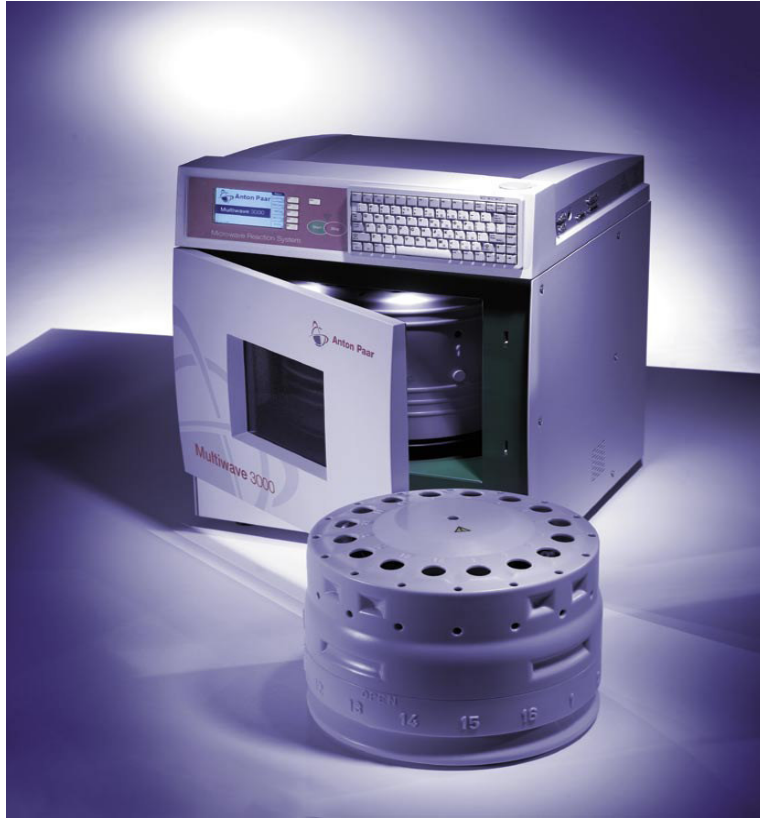


Figure 3.1 Microwaves 3000 (Anton Paar GmbH)

Electromagnetic waves are interconnected electric and magnetic fields which change over time and propagate at the speed of light through space. The electromagnetic field produced is described by the field strength vectors E and B .

$$E/B = C/\lambda \quad (3.1)$$

Where E is the electric field, B the magnetic field, c the speed of propagation and λ is the wavelength.

A magnetron is a metallic vacuum tube, consisting of a cathode and an anode, which is surrounded by a permanent magnet frame. High voltage is applied to a

heated rod (cathode) to emit electrons. These electrons are drawn into a circular path by the applied magnetic field. These electrons hit the outer wall of the tube (anode), which is cut at regular intervals radially to the chamber (resonator). Within these incisions the polarity of the electrical field reverses with the desired frequency and produces microwaves. These are emitted via an antenna like in the microwave oven.

Digestion

Digestion is the conversion of a solid sample into a liquid, homogeneous state. This makes the sample easier to aliquot and has all the prerequisites for an interference-free qualitative and quantitative determination of the elements or compounds of interest. After mechanical sample preparation, decomposition is the most time-consuming step in wet-chemical procedures. It is therefore very useful to optimize this step and reduce the required time while retaining or increasing the quality of the analysis.

Materials exposed to microwave behave differently depending on their dielectric constants. They may reflect microwave radiation (metals), be permeated by radiation without getting heated (glass, plastics), or absorb microwave energy (water). Polar molecules in the later cases are stimulated to oscillate and dissolved ions move through the electromagnetic field. To heat a substance, the material

must couple to the microwaves. In other words, the substance must absorb electromagnetic energy.

Generally speaking, two mechanisms are available; dipole rotation and ionic conduction. The former is the case with materials which have a pronounced dipole (water, acids and solvents). In the rapidly changing electric field, the molecules try to orient themselves in the direction of the field lines. This sets them in rotation-vibration. The energy absorption from the microwave field is more intensive the closer the resonance frequency of the molecule is to the frequency of the microwave. The latter occurs when there are free ions (electrolytes, glassy materials and ceramic materials).

The two processes of oscillation and movement due to the electromagnetic field by ions produces heat energy due to Ohmic effect. These properties ensures fast heating of samples by microwave radiation by the instrument in contrast to the conventional heating in heating blocks or ovens where heat transfer is necessary between media through metal parts, air or vessels in use.

Non-pulsed microwave power of up to 1400 W and improved vessel design allow temperatures and pressures of up to 300°C and 80 bar to be used at the same time. Closed vessel technique helps to speed up reactions by allowing higher temperatures while preventing the loss of volatile analytes, figure 3.2. The

resulting low reagent consumption saves time and money and also helps minimize exposure to corrosive gases and hazardous solvent vapour.



Figure 3.2 Multiwave 3000 (Anton Paar GmbH) reaction vessels

3.2.2 Fritsch GmbH Planetary Mono Mill Pulverisette 6

Fritsch GmbH Planetary mono mill “pulverisette 6” (figure 3.3) is used for quick dry and wet grinding of inorganic and organic samples for analysis, quality control, materials testing and mechanical alloying. It can also be used for mixing and homogenization of dry samples, emulsions and pastes



Figure 3.3 Fritsch GmbH Planetary Mono Mill “Pulverisette 6

Planetary mono mill “pulverisette 6” is driven by a maintenance-free three-phase alternating current motor, which is operated with a frequency converter. The instrument can be operated in two voltage ranges; single-phase alternating voltage of 100 - 120 V +/- 10% and 200 - 240 V +/- 10%.

Table 3.1 Technical and electrical data of Planetary Mono Mill “Pulverisette 6’

Electrical detail	100 - 120/200 – 240 V/L
Frequency	50 - 60 Hz
Input power	880 W
Working principle	Impact force
Interface	RS232
Timer	99 minute
Maximum speed	600 rpm
Over all dimensions (W x D x H)	370 x 530 x 500 mm
Weight net	63 kg
Weight gross	83 kg
Max feed size	10 mm
Feed quantity	Up to 1 x 225 mL

Principle of operation

The material is crushed and disintegrated in a grinding bowl by grinding balls. The grinding balls and the material in the grinding bowl are acted upon by the centrifugal forces due to the rotation of the grinding bowl about its own axis and due to the rotating supporting disc.

The grinding bowl and the supporting disc rotate in opposite directions, so that the centrifugal forces alternately act in the same and opposite directions. This results in, as a frictional effect, the grinding balls running along the inner wall of the grinding bowl, and impact effect, the balls impacting against the opposite wall of the grinding bowl.

Optimization of the grinding time and speed is done on the principle that a longer grinding time will increase the fine fraction and a higher speed will reduce the grinding time and increase the fine fraction. The use of many small balls increases the fine fraction with increased running times. Reversing operation improves homogenizing of the material.

Grinding bowl and balls

In order to prevent abrasion, the hardness of the grinding balls must be higher than that of the material used. Normally grinding bowls and grinding balls of the same material are used. The size of the grinding bowls and number of grinding balls are determined experimentally depending on the initial particle sizes of the samples. The choice of grinding bowls and grinding balls was made based on density and resistance to abrasion relative to the sample to be ground, table 3.2. It is also based on the premise that a higher mass (density) of the grinding balls will accelerate the grinding to fine fractions.

A large number of balls reduce grinding time, and the grinding result lies within a narrower grain band width. However, this is limited by the volume of the grinding bowl size and the sizes of the balls, table 3.3.

Table 3.2 Properties of various grinding bowls and grinding balls

Material (bowl and balls)		Density (g cm ⁻³)	Resistance to abrasion
Agate	99.9% SiO ₂	2.65	Good
Sintered corundum 1	99.7% Al ₂ O ₃	3.7	Fairly good
Sintered corundum 2	85% Al ₂ O ₃	3.5	Fair
Zirconium dioxide	95% ZrO ₂	5.7	Very good
Teflon balls with steel cores for polyamide bowls		3.0 1.4	Adequate
Chrome nickel steel		7.9	Fairly good
Hardened chrome steel		7.85	Good
Tungsten carbide	93% WC + Co	14.75	Very good
Silicon nitride (Syalon)	90% Si ₃ N ₄	3.2	Extremely good

Table 3.3 Number of balls per grinding bowl

Grinding bowl		500 mL	250 mL	80 mL
Balls Ø	10 mm	100	50	30
Balls Ø	20 mm	25	15	5
Balls Ø	30 mm	10	6	
Balls Ø	40 mm	4		

When filling the bowl, the grinding balls are placed in the empty bowl first and the material to be ground is then filled on the balls with volumes as described in table 3.4.

Table 3.4 Filling of the grinding bowl

Grinding bowl	Min. filling²	Max. filling
500 mL	80 mL	225 mL
250 mL	30 mL	125 mL
80 mL	1 mL	30 mL

3.3 SAMPLE MEASUREMENT INSTRUMENTS

3.3.1 Malverns Mastersizer S (Long Bench)

The Mastersizer S is a modular particle size analyzer offering measurement versatility, it can measure spray droplet size as well as wet and dry samples, figure 3.4. Two variants of Mavern Mastersizer S are available to measure samples in the range 0.05 μm to 900 μm and 0.05 μm to 3500 μm .



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Figure 3.4 Malverns Mastersizer S instrument

Principle of operation

The technique uses laser diffraction more correctly called Low Angle Laser Light Scattering (LALLS). The application range according to ISO 13320 is 0.1 – 3000 μm . the method relies on the fact that diffraction angle is inversely proportional to

the particle size. He-Ne gas laser source of coherent intense light and fixed wavelength ($\lambda = 0.63 \mu\text{m}$) is used. The detector consists of a slice of photosensitive silicon with a number of discrete detectors (16 – 32). Photon correlation spectroscopy technique (PCS) with a photomultiplier and a signal correlator is used in the range 1 nm - 1 μm when the intensity of light scattered is low. Particles are sprayed or blown through the beam for measurement by means of pressure and sucked into a vacuum cleaner. Particles in suspension are measured by recirculating the sample in front of the laser beam. The Mastersizer S detector array acquires light scattering data at the rate of 500 Hz (one measurement every 2 milliseconds).

The key to particle size measurement is the ability to present a well dispersed sample to the instrument optics at an appropriate concentration with a minimum of sample bias. Efficient sample dispersion is essential for achieving optimum measurements.

3.3.2 Inductively coupled plasma (ICP) spectrometry

Principle of operation

The ICP-OES uses the concept that light has a dual nature, that is, it can behave like a wave and also like a particle. Light consists of particles, their energy being proportional to the wavelength. Spectral analysis makes use of the fact that the occurrence of certain lines serves as proof of the presence of certain elements.

Atomic spectroscopy is based on the measurement of the amount of electromagnetic radiation that is absorbed or emitted by an analyte atom to determine its concentration in a sample (Bradford and Cook, 1997). When reverting to the ground state, an excited atom or ion releases absorbed energy as light (photons) of characteristic wavelengths, the positions and intensities of which can be measured. The energy transfer for electrons when they fall back to ground state is unique to each element as it depends upon the electronic configuration of the orbitals (Bauer *et al.*, 1978; Alcock, 1995). The energy transfer, E , is inversely proportional to the wavelength of electromagnetic radiation:

$$E = hc/\lambda \quad (3.2)$$

Where h is Planck's constant, c the velocity of light and λ is the wavelength, and hence the wavelength of light emitted is also unique (Skoog *et al.*, 1992).

An energy source is needed in order to atomize and ionize the samples to allow radiation emission. In the ICP-OES, plasma is used as an energy source, producing heat of 5500 K - 8000 K and up to 10 000 K in some regions, enough to ionize and excite most analyte atoms. Molecular interferences are greatly reduced with this excitation source but are not eliminated completely.

ICP sources are used to excite atoms for atomic-emission spectroscopy and to ionize atoms for mass spectrometry. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the ray's intensity (Alcock, 1995). Argon gas is supplied to the torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube in order to generate plasma. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. Solution samples are introduced into the plasma in an atomized state (Boumans, 1996).

The apparatus for the ICP-OES is composed of three main sections: the nebulizer, the torch and the detection system (Tyler and Horiba, 2000. ICP-OES) as shown in figure 3.5.

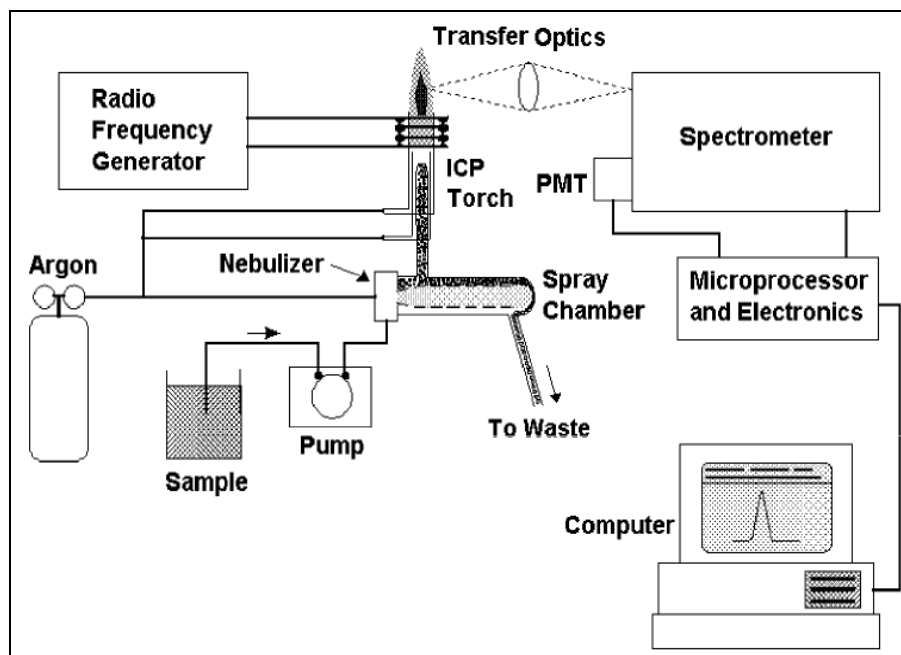


Figure 3.5 ICP-OES schematic diagram (Arcinus, 2000)

Nebulizer

The ICP-OES operates by introducing an aqueous sample into an energy source, plasma in this case. The sample is picked up by a peristaltic pump, and passed through a nebulizer, using inert argon gas as a carrier. This reduces the liquid sample to a fine aerosol, which is more effectively ionized by the plasma. Various types of nebulizers are available, including cross-flow, concentric, Babington, and its variations. Although the resulting mists of these nebulizers generally contain small and consistent droplets, the nebulized samples are passed through a spray chamber, which filters out larger droplets to ensure consistency in drop size. The aerosol is then injected through the torch and into the plasma for ionization (Tyler and Horiba, 2000). ICP-OES; Interactive Training, 2004. ICP Spectroscopy)

Plasma

The primary component of the ICP-OES is the plasma source, which is formed and maintained using a torch and a load coil. Plasma is defined as anything that contains >1% electrons and positive ions in mixture, conducts electricity and is affected by a magnetic field (Interactive Training, ICP Spectroscopy, 2004.). Because of these properties, plasma can be safely produced and contained using electric and magnetic fields (Montaser *et al.*, 1998).

In the ICP-OES, plasma is formed in the torch, which is composed of three concentric tubes of glass or quartz. The innermost tube provides nebulizer flow of the sample into the plasma, the middle tube, called the intermediate gas flow, prevents the plasma from getting too close to the nebulizer flow, and makes nebulizer injection easier. The outer tube, called the outer flow, provides argon for initial plasma ignition, as well as keeping the load coil cool from the immense heat (Tissue, 1996. ICP excitation source; Montaser *et al.*, 1998).

The load coil consists of a liquid-cooled conductive metal, which provides an alternating current of 700 to 1500 watts oscillating at 27 or 40 MHz. This current sets up an annular magnetic field region within the coil and above the torch, where the plasma is maintained (figure 3.6). Ignition of the plasma occurs by first swirling argon gas in the outer flow, then producing a magnetic field within the load coil (Jarvis *et al.*, 1992).

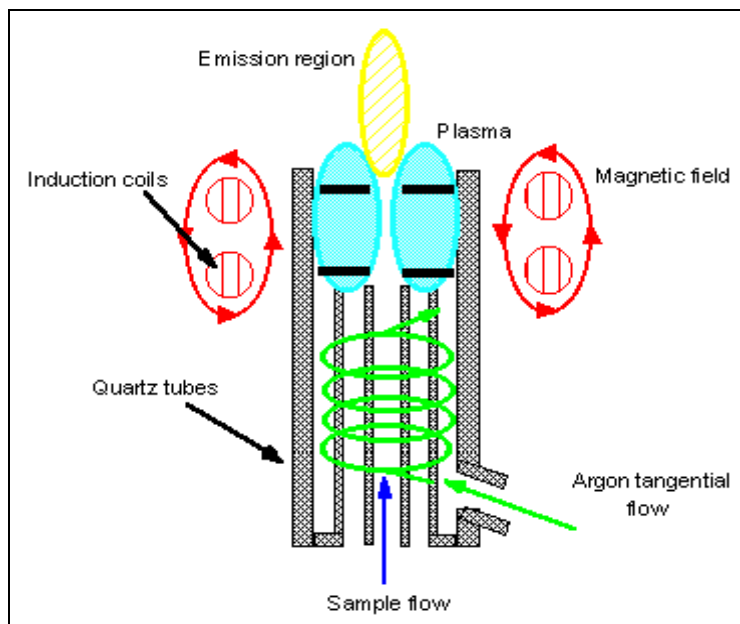


Figure 3.6 Formation of plasma in the torch (Tissue, 1996. ICP excitation source)

The Tesla coil produces a spark which seeds the system and strips some of the argon atoms of their electrons. Being confined within the magnetic field, this electron collides with other argon atoms, producing a chain reaction, which ionizes argon within the field creating plasma. An argon cross flow which shears the top of the plasma further confines its expansion. A notch on the torch side provides an emission viewing window for the detector (Bradford and Cook, 1997).

Argon is the preferred plasma gas because it is inert and therefore does not readily react chemically with samples; it has a high first ionization energy of 15.75 eV, causing effective ionization of, and emission by, almost all other elements; it is optically transparent and it has a relatively low thermal conductivity, so that heat

is retained in the plasma fireball enabling stable operation at moderate power inputs. Nitrogen has been investigated as an alternative to Argon, but produces increased spectral and isobaric interferences when used alone (Jarvis I and Jarvis, K, 1992).

The combination of torch, induction coil and gas flows are designed to support stable colloidal plasma centered at the open end of the quartz glass coolant tube. The plasma has three discrete regions: the fireball, secondary region and tail flame, each of which has very different physical and chemical characteristics (Boulos and Barnes, 1981 & 1987).

The fireball or induction region is a doughnut-shaped area into which energy is transferred into the plasma by the interaction between the Argon flow and the RF magnetic field. The highest temperatures (10,000 K) are produced in this region which contains large populations of highly excited Argon ions. It is an intense light source dominated by Argon emission lines and a broad background continuum, making it unsuitable for use as an analytical source.

The fireball is surrounded by a secondary region with temperatures of approximately 8000k, which is also luminous but slightly transparent. Beyond this, the tail flame or normal analytical zone is characterized by an incredibly low intensity of background emission and is consequently nearly invisible until a

sample is injected. Here, the emission spectrum exhibits a continuum with a relatively small number of discrete lines produced predominantly by Argon atoms. At the normal observation height for spectroscopic measurement of 12 - 18 mm above the induction coil, tail flame temperatures remain between 6200 and 6500k.

Samples are injected into the centre of the plasma toroid, and so pass through the centre of what is effectively a very high-temperature tube furnace. There is little inter-mixing of the sample with gases in the plasma fireball. The sample is heated rapidly to approximately 8000k by conduction, convection and radiation effects, and sample molecules undergo nearly instantaneous desolvation, vaporization, dissociation, ionization and excitation.

Detection

There are three types of detectors, namely sequential, simultaneous multi-channel and Fourier transform. Sequential instruments are usually programmed to move from the line for one element to that of a second, pausing long enough at each to obtain a satisfactory signal-to-noise ratio. In contrast, multi-channel instruments are designed to measure the intensities of emission lines for a large number of elements (up to 50 or 60) simultaneously, or nearly so (Goodfellow, 2003). Multi-channel instruments normally use a Rowland circle in a Paschen-Runge arrangement (figure 3.7).

Spectral dispersion of polychromatic radiation and focusing is achieved simultaneously through a grating scratched in a concave surface. The focusing takes place on the Rowland circle (with a radius which is half the curvature of the grating).

There are two types of multi-channel instruments: polychromators and array-based systems. The former apply a series of photomultiplier tubes for detection, whereas the latter use two dimensional charge-injection devices or charge-coupled devices as detectors (Boss and Freedden, 1997; Schwedt, 1997).

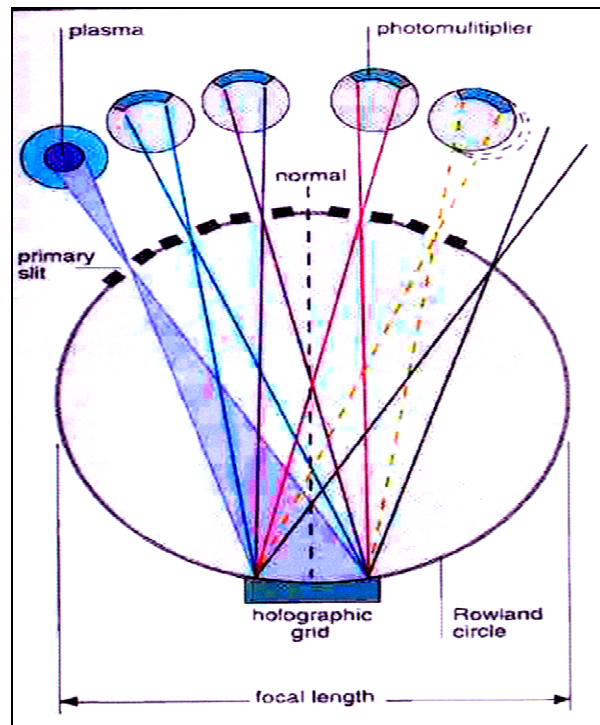


Figure 3.7 Multi-channel instrument with a Rowland circle (Schwedt, 1997)

The Spectro Ciros coupled charge detector (CCD) is the first solid-state detector based ICP-OES with continuous first order wavelength coverage from 125 nm to 770 nm. The CCD detectors do not require on-chip cooling and produce the fastest throughput of any solid-state detector ICP. The detectors have a pixel resolution of 9 pico-meters and are well suited for more complex matrices like the flue gas.

A complete 125 nm to 770 nm overview (more than 10000 emission lines) is available after a single 2.5 seconds measurement. Spectro's own patented technology, which uses an inert gas that is re-circulated through a filter, is integrated into the unit to promote efficient transmission of the lower wavelengths and hence, ensures analytical stability for the wavelengths below 180 nm (Goodfellow, 2003).

The success of Argon ICP-OES as analytical techniques stems mainly from the following important capabilities: very low detection limits; good precision [0.2 - 3% relative standard deviation (RSD)]; detection of nearly all elements; and broad dynamic concentration ranges (4 - 11 orders of magnitude) for many elements (Montaser, 1992).