10.3.1.4 Radiofrequency plasmas

Radiofrequency plasmas (rf plasmas) are formed in a flow of gas by an externally applied radio frequency field.

10.3.1.4.1 Inductively coupled plasmas (ICP)

In *inductively coupled plasmas* (inductively coupled rf plasmas or inductively coupled argon plasmas) energy transfer to the gas is achieved with the help of an *induction coil* or *inductor* (the terms coil, load coil and work coil are discouraged). It is recommended that the frequency at which the source operates is given, e.g., 27 or 12 MHz, and the gas type defined. The plasma is formed within and/or above a set of refractory tubes arranged coaxially with the induction coil, the whole forming a *plasma torch* (Fig. 10.3). The induction coil constitutes a part of an oscillating circuit of one of the following types:

The *tank circuit* of a *free running* oscillator is built up by capacitors and inductors for a specific frequency. This frequency may vary around its nominal value depending on the *plasma impedance*, the power and the *coupling efficiency*. The coupling efficiency is the ratio of power accepted by the plasma to the *incident power*, i.e. the output of the oscillator. *Reflected power* is the power reflected back to the oscillator.

A *crystal-controlled oscillator* makes use of a quartz crystal to provide a *fixed frequency* of oscillation. A series of other stages (circuits) can provide *frequency multiplication* (*doubling*, for instance) to achieve the required frequency and power.

Another type of oscillator is the *tuned-line oscillator*. This consists of two *quarter wavelength lines*, the length (l) of which accurately defines the frequency (f):

$$f = \frac{C}{4l}$$

where C is the capacitance of the *matching capacitor*. These lines constitute an *impedance-converter* which enables the circuit to match the load variations.

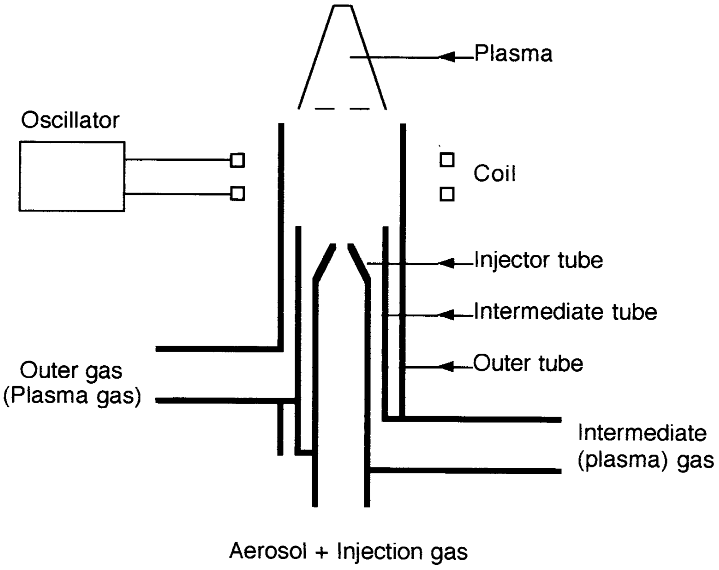

Fig. 10.3 Schematic diagram of a plasma torch

10.3.1.4.2 Plasma torch (Fig. 10.3)

The plasma torch consists of a tube assembly and the induction coil. It has the following functions: to confine the *plasma gas* axially in the induction coil where the plasma occurs and to ensure that it is self-sustained after initiation, to isolate the plasma from the induction coil and to feed the sample into the plasma by means of a *carrier gas*.

Two gas flows, the *outer* or plasma *gas* and the other the *injection gas* or *aerosol carrier gas*, are sufficient to operate an analytical plasma and the torch may therefore by constructed with two tubes, usually of fused silica. The torch tubes are concentric with the *injector* placed axially and opening at or below the level of the induction coil. The terms cooling gas and coolant gas are discouraged. A third gas flow, the *intermediate* (plasma) *gas,* is commonly used in order to push the plasma away from the injector.

The velocity of the aerosol carrier gas must be sufficiently high to pierce the plasma, but not so high as to reduce the *transit time*, i.e. the *residence time* of species in the excitation zone.

An ICP can be initiated either with the use of a conducting rod inserted in the torch at the inductor level or by means of an electrical discharge created by a *Tesla coil.*
In a complex matrix, the line intensities of all analyte elements are usually measured using the same operating parameters. This requires the selection of *compromise conditions* which may not be optimum for all elements.

10.3.1.4.3 Spectral characteristics

When argon is used as a plasma gas, the emitted radiation is comprised mainly of lines of the argon atomic spectrum (Ar I). Molecular bands (e.g. OH, C_2, N_2, CN, $N^+{}_2$) are observed if a compound containing these species is injected into the plasma. The intensity of the spectral lines observed in a defined *observation zone* depends on the plasma parameters.

Local thermal equilibrium does not usually exist in these plasmas. This implies that the *excitation mechanism* of the analytes is not purely thermal. Argon atoms excited to metastable levels seem to be of particular importance for all relevant processes in the plasma.

Electrons (up to ~30 eV), argon ions (argon *ionization energy* 15.76 eV) and excited argon atoms play a major role in the processes taking place in an argon ICP.

Only atomic spectra are produced for elements which are difficult to ionize or elements for which the ionic *excitation levels* are high.

Elements for which the sum of the ionization energy and the *excitation energy* of the relevant ion is moderate, produce spectra of the *singly ionized element* (II lines).

10.3.1.4.4 Analytical procedures

The ICP is used mainly for the analysis of liquid samples. *Sample solutions* and *reference solutions* are aspirated into the continuously running source, and measurements are recorded after a sufficient delay after the start of aspiration. This delay is usually 4-5 times the *time constant* of the whole measuring system. The emitted intensities being constant, *instantaneous measurements* may be made or the signal may be integrated. Once the radiation intensity is constant the system is said to be in a *steady state*. The atomic radiation intensity is affected by the residence time of atoms in the *excitation region* of the plasma. In *simultaneous analytical systems*, the signals from several elements may be integrated simultaneously for a predetermined time.

Most important techniques for determining the analyte concentration make use of the *analytical curve technique* or a *bracketting technique*. It is also possible to refer to an *internal reference line* after adding a *reference element* to the sample solutions in a specified concentration or to use an *analytical addition technique*.

Because of the *background (molecular and continuous) radiation*, it is common practice to apply *background correction techniques*. The background can also be used for reference purposes.

10.3.1.4.5 Capacitively coupled plasmas (CCP)

A *capacitively coupled plasma* may be obtained by energy transfer through capacitive coupling to a plasma torch. Greater departure from local thermal equilibrium is observed than with the ICP and, while electron temperatures may be high, gas temperatures are low. The *atomization efficiency* of this type of plasma is relatively poor. Spectral characteristics and analytical procedures are similar to those described for the ICP. The residence time of atoms in the CCP is generally longer.

10.3.1.4.6 Microwave plasmas

The initiation, sustaining, thermal and excitation properties of *microwave plasmas* are different from those of radiofrequency plasmas. The frequency range of these sources is above 300 MHz with a frequency of 2450 MHz being the most common.

10.3.1.4.7 Capacitive microwave plasmas (CMP)

When a single electrode is used, the source is called a *one-electrode microwave plasma*. *Microwaves* generated by a *magnetron* are conducted to a tunable cross-shaped *coaxial cavity via* a *coaxial waveguide*. The plasma torch constitutes one area of the cross containing a pointed hollow cathode. Sample aerosol is conducted up the open electrode and emerges from the tip. Plasma formation at atmospheric pressure takes place at the tip as a *brush* discharge. Only one gas or aerosol carrier is thus necessary.

10.3.1.4.8 Microwave induced plasmas (MIP)

Several cavity configurations exist, of which the transverse 1/4 or 3/4 wavelength configurations and the *tapered cavity* are the most commonly used. Other cavities are classified according to their *transverse electromagnetic mode* (TEM) configurations. With the MIP and CMP, an adjustable *tuning stub* is used to assist the initiation of the plasma and to compensate for the load.

In the *atmospheric pressure microwave induced plasma* the microwaves are concentrated by means of a tunable *resonant cavity* into a fused silica tube through which a gas or an aerosol at or near atmospheric pressure is flowing.

In the *low pressure microwave induced plasma* a sealed fused-silica tube is operated at reduced pressure and contains a small portion of the sample to be analysed.

Spectral characteristics and analytical procedures for MIPs are similar to those described for the ICP. Solute volatilization and *spatial distribution interferences* occur. In order to reduce them, *matrix matching* is used.

The low pressure MIP is of value for *isotopic analysis* using molecular band emission (e.g., compounds of ^{15}N).