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OPTICAL PROCEDURES FOR ANALYSIS*

**NOMENCLATURE, SYMBOLS, UNITS
AND THEIR USAGE IN
SPECTROCHEMICAL ANALYSIS—V
RADIATION SOURCES**

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Comments on these recommendations are welcome and should be sent within 8 months from October 1981 to the Secretary of the Commission:

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Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

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RADIATION SOURCES

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1. INTRODUCTION

Part V is a sequel to Parts I, II, III and IV of the Nomenclature for Spectrochemical Analysis issued by IUPAC. Parts I and II are concerned mainly with some general recommendations in the field of emission spectroscopic analysis. Part III deals with the nomenclature of analytical flame spectroscopy and associated procedures. Part IV concerns X-ray spectroscopy and Part V deals with the nomenclature classification and description of radiation sources.

Radiation sources (see Note a) are defined as those devices and their associated apparatus components which produce *electromagnetic radiation* for various purposes.

Radiation sources include sources used for optical emission spectroscopy (OES), atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), molecular absorption spectroscopy (MAS), molecular emission and luminescence spectroscopy (MES and MLS), X-ray emission spectroscopy (XRES) and X-ray fluorescence spectroscopy (XRFS).

There are essential differences between these sources and the ways in which they are used.

This section does not deal with sources used in X-ray spectroscopy and molecular spectroscopy (see Parts IV and VI).

The classification of radiation sources may be based on two general physical forms of radiation, viz. *coherent* and *non-coherent electromagnetic radiation*.

Coherent sources include those sources where the radiation has a constant phase relationship between wave fronts, spatially as well as temporally, e.g. *lasers*.

Non-coherent optical sources emit radiation which is randomly distributed in phase, spatially as well as temporally. Most sources which are used in spectroscopy and for spectrochemical analysis, conform to this latter group.

A broad classification of non-coherent optical sources may be made as follows: *gaseous discharges*, which include most known light sources; *chemical flames*, which are gases heated by *exothermic reactions* between two or more gases and which have been discussed in detail in Part III; *incandescent bodies* which give rise to *non-discrete* continuous radiation and other miscellaneous sources such as phosphorescent bodies, X-ray sources, etc.

Note a. The term radiation source is preferred to light source as the word light is understood to refer to the spectral region to which the human eye is sensitive.

The sources discussed in this part are tabulated in Table 1.1. Terms and symbols for general quantities and units published in Part III have been extended and are included in Table 1.2.

The selection of the sources listed in Table 1.1 was done on the grounds of their being the most commonly used for spectrochemical and spectroscopic analysis. Sources seldom used or sources of historical interest have not necessarily been included.

The terms, units and quantities used have been selected to agree with those of other International bodies dealing with radiation and physical phenomena, viz. Commission Internationale d'Eclairage (CIE), International Union of Pure and Applied Physics (IUPAP), Bureau Internationale des Poids et Mesures (BIPM) (SI units) and International Electrotechnical Commission (IEC).

TABLE 1.1. General classification of radiation sources (as discussed in this document)

| Type | Sort | Gas pressure range | Types of spectra radiated* |
|---|-----------------------------------|------------------------|----------------------------------|
| Arcs | dc | atmospheric (~100 kPa) | a,m,c |
| | ac | atmospheric | a,m,c |
| | current-carrying plasmas | atmospheric | a,m,c |
| | non-current-carrying plasmas | atmospheric | a,m,c |
| | high pressure | 100 - 600 kPa | c, broad a |
| | low pressure | 10 - 100 kPa | a,m,c |
| Sparks | high voltage | atmospheric | a,m,c |
| | medium voltage | atmospheric | a,m,c |
| | low voltage | atmospheric | a,m,c |
| | vacuum sparks | <10 Pa | a,m,c |
| Radiofrequency plasmas | inductively-coupled | atmospheric | a,m,c |
| | capacitively-coupled | atmospheric | a,m,c |
| Microwave | capacitive (electrode) | atmospheric | a,m,c |
| | induced (electrodeless) | <2 kPa or atmospheric | a,m,c |
| Lasers | continuous | - | a (primary) a,m,c (secondary) |
| | pulsed | - | a (primary) a,m,c (secondary) |
| Low pressure electrical discharges in gases | arc lamps | 1 - 100 kPa | a,c |
| | Geissler | 1 - 10 kPa | a,m,c |
| | Glow discharge: hollow cathode | 0.1 - 10 kPa | a,m,c |
| | plane cathode | 0.1 - 10 kPa | a,m,c |

*a - atomic and ionic

m - molecular

c - continuous (including unresolved band spectra)

TABLE 1.2. Terms, symbols and units for measurable quantities for radiation sources

| Term | Symbol | Practical unit |
|---|------------------|---------------------------------|
| mass | m | Kg |
| time | t | s |
| electric current | I | A |
| thermodynamic (absolute) temperature | T | K |
| ionization temperature | T_{ion} | K |
| electron temperature | T_e | K |
| gas temperature | T_g | K |
| excitation temperature | T_{exc} | K |
| radiant intensity | I_e | $W \cdot sr^{-1}$ |
| radiant flux | Φ | W |
| illumination | E | lx |
| frequency (in optical spectroscopy) | ν | Hz |
| frequency (electrical) | f | Hz |
| wavelength | λ | nm |
| wavenumber ($1/\lambda$) | σ | cm^{-1} |
| period | T | s |
| spark duration | θ | s |
| number of oscillations | \dot{p} | l |
| energy | E | J |
| power (E/t) | P | W |
| quantity of electricity | Q | C |
| potential difference, tension (voltage) | U | V |
| current density | j | $A \cdot m^{-2}$ |
| normal current density | j_n | $A \cdot m^{-2}$ |
| ion current density | j_+ | $A \cdot m^{-2}$ |
| electron current density | j_- | $A \cdot m^{-2}$ |
| glow current density | j_g | $A \cdot m^{-2}$ |
| charge density | ρ | $C \cdot m^{-3}$ |
| cathode fall tension (voltage) | U_c | V |
| breakdown tension (voltage) | U_{br} | V |
| re-ignition tension (voltage) | U_3 | V |
| capacitor tension (voltage) | U_{cap} | V |
| burning tension (voltage) | U_b | V |
| spark gap tension (voltage) | U_g | V |
| conductance (electrical) | G^s | $S \equiv \Omega^{-1}$ |
| capacitance | C | F |
| inductance | L | H |
| reactance | X | Ω |
| Avogadro constant | N_A | mol^{-1} |
| Boltzmann constant | k | $J \cdot K^{-1}$ |
| Planck constant | h | J.s |
| gas constant | R | $J \cdot K^{-1} \cdot mol^{-1}$ |
| mass number | A | l |
| atomic number | Z | l |
| mass number of species X | $A(X), A_x$ | l |
| atomic number of species X | $Z(X), Z_x$ | l |
| atomic mass (of nuclide ${}^B X$) | $m_a({}^B X)$ | g |
| atomic mass constant : $m_a({}^{12}C)/12$ | m_u | l |
| relative atomic mass (of nuclide ${}^B X$): $m_a({}^B X)/m_u$ (was called "atomic weight") | $A_r({}^B X)$ | l |
| relative molecular mass (ex. H_2O) (was called "molecular weight") | $M_r(H_2O)$ | l |
| elementary charge | e | C |
| electron mass | m_e | g |
| number of particles | N | l |
| number of particles of species X | $N(X), N_x$ | l |
| number density of particle per unit volume | n | cm^{-3} |
| number density of particles in state q | n_q | cm^{-3} |
| number density of element as free atom | n_{at} | cm^{-3} |
| number density of element as free ion | n_{ion} | cm^{-3} |
| number density of electrons | n_e | cm^{-3} |
| total number density of element in different forms (atom, ion, molecule) in the gaseous state | n_t | cm^{-3} |
| number density of ground state species X | $[X_0]$ | cm^{-3} |
| n_{at} for atoms of X | $[X], n_{at}(X)$ | cm^{-3} |

Terms, symbols and units for measurable quantities for radiation sources (continued)

| Term | Symbol | Practical unit |
|---|--|--|
| n_{ion} for ions of X^+ | $[X^+], n_{\text{ion}}(X)$ | cm^{-3} |
| n_{t} for element X | $[X]_{\text{t}}, n_{\text{t}}(X)$ | cm^{-3} |
| number density of excited species X^* | $[X^*]$ | cm^{-3} |
| total gas pressure | p, p_{t} | Pa |
| partial pressure of species X | $p(X), p_{\text{x}}$ | Pa |
| excitation energy | E_{exc} | J, eV |
| excitation energy of state q of species X | $(E_{\text{q}})_{\text{x}}$ | J, eV |
| ionization energy | $E_{\text{ion}}, E_{\text{i}}$ | J, eV |
| excitation potential | V_{exc} | V, eV |
| ionization potential | $V_{\text{ion}}, V_{\text{i}}$ | V, eV |
| metastable excitation potential | V_{meta} | V, eV |
| work function | ψ | V, eV |
| kinetic energy of particle | E_{k} | J |
| statistical weight of state q | g_{q} | 1 |
| statistical weight of ground state | g_{o} | 1 |
| statistical weight of state q of species X | $g_{\text{q}}(X), (g_{\text{q}})_{\text{x}}$ | 1 |
| partition function | Z, Q | 1 |
| partition function of species X | $Z(X), Z_{\text{x}}$ | 1 |
| transition probability for spontaneous transition from upper state u to lower state l | A_{ul} | s^{-1} |
| transition coefficient for absorption transition from states l \rightarrow u | B_{lu} | $\text{s}^{-1} \cdot \text{J}^{-1} \cdot \text{m}^3$ or $\text{s}^{-1} \cdot \text{Pa}^{-1}$ |
| weighted transition probability | gA | s^{-1} |
| frequency of spectral line emitted due to transition u \rightarrow l | ν_{ul} | Hz |
| relative intensity of spectral line emitted by electron transitions from states u \rightarrow l | I_{ul} | 1 |
| oscillator strength for absorption by transitions from states l \rightarrow u | f_{lu} | 1 |
| weighted oscillator strength | gf | 1 |
| volumetric flow rate | F | $\text{l} \cdot \text{s}^{-1}$ |
| through (mass) flow rate | Q | $\text{Pa} \cdot \text{l} \cdot \text{s}^{-1}$ |
| sputtering yield | S_{sp} | $\text{atoms} \cdot \text{ion}^{-1}$ |
| sputtering rate | q_{sp} | $\text{g} \cdot \text{s}^{-1}$ |
| cathode removal rate | q_{c} | $\text{g} \cdot \text{s}^{-1}$ |
| sensitivity | S | |
| standard deviation (estimate) | s | |
| relative standard deviation | s_{r} | |
| analytical calibration function | $x=g(c)$ | |
| | or | |
| | $x=g(q)$ | |
| analytical evaluation function | $c=f(x)$ | |
| | or | |
| | $q=f(x)$ | |
| positive column current density | j_{a} | $\text{A} \cdot \text{m}^{-2}$ |
| electric field strength | E | $\text{V} \cdot \text{m}^{-1} = \text{N} \cdot \text{C}^{-1}$ |
| magnetic flux | Φ | Wb |
| magnetic flux density | B | T |

2. TERMS, UNITS AND SYMBOLS FOR THE DESCRIPTION OF PROCESSES COMMON TO ALL RADIATION SOURCES

The terms in this section are common to all sources and form the basis for the detailed description in the subsequent sections.

Most radiation sources perform one or more of the tasks of *volatilization*, *atomization*, *ionization* and *excitation* (see Note a). These processes are dependent on parameters such as the sample type and form, the pressure and the temperature.

The pressure within a *plasma* (see Section 2.3.3) affects the characteristics of the radiation significantly. Sources may therefore be classified into various groups depending on the *average gas pressure* at which they operate. They can also be classified according to the

Note a. Radiation is emitted when an electronic transition takes place resulting in an *exoenergetic condition* and is *absorbed* when an *impinging* photon or photons transfer their kinetic energy to the atom or molecule.

type of radiation (e.g. *continuous, molecular*), but for the purpose of this document the pressure criterion has been selected.

A *primary source* (see Note a) may be used when its radiation is required for other processes, e.g. in atomic absorption, atomic fluorescence or Raman spectroscopy.

A *sampling source* is one where the material to be analysed is easily introduced into the source.

2.1 Terms relating to volatilization, atomization and ionization of material

Volatilization is the process whereby the sample is converted into a gas. This may be by thermal means, in which case it can also be called *evaporation*, e.g. in a *direct current (dc) arc*, or by other physical means, such as bombardment by ions, e.g. *sputtering* in a discharge. Processes pertaining to the sample are the *transportation* of sample material, e.g. *diffusion, convection* and *migration*. Other associated processes include *distillation, dissociation, sublimation* and *cataphoresis*. *Selective volatilization* occurs when the *volatilization rate* of a constituent is greater or less than that of the bulk of the sample.

Atomization is the process whereby the sample material is converted to atoms. Atoms may occur in a ground state or they may be excited to higher energy levels by *collision processes*.

Energy transfer from another particle in a higher state of energy may occur. The *absorption* of energy from one or more photons is also possible.

An atom, because it has no resultant electrical charge, is *neutral*.

Ionization is a process leading to the formation of *ions*.

If the ion has a deficiency of electrons it is positively charged (*positive ion*) and if it has an excess of electrons it is negatively charged (*negative ion*).

Volatilization, transportation, atomization, ionization and excitation processes can be influenced by *matrix effects*. Matrix effects denote the influence of the *components* (concomitants) of the sample on the above processes, while *inter-element effects* (see Note b) are the influence of elements on each other.

2.2 Terms relating to types of radiation

2.2.1 Atomic and ionic spectral lines. *Atomic and ionic spectral lines* originate from quantified electronic transitions between *energy levels* of atoms and ions respectively (see Note c).

2.2.2 Molecular radiation. Molecular radiation results from the *rotational, vibrational* and *electronic energy transitions* of molecules (see Note d).

2.2.3 Band spectra. *Band spectra* are the combination of many different spectral lines resulting from vibrational, rotational and electronic transitions (see Note e).

2.2.4 Continuous radiation. Continuous radiation (*continuum*) arises from non-quantified *free-free transitions* of electrons in the fields of the ions, *free-bound transitions* or *radiative recombinations* of electrons and ions, *incandescent radiation* emitted by hot solids (when the radiation distribution conforms to that described by *Planck's law*, it is considered *black body radiation*) (see Note f) and *unresolvable band spectra*, i.e. where the *widths* of the spectral lines are wider than the spacings between them.

Note a. Where radiation sources are used as primary sources for other analytical methods, e.g. atomic absorption spectroscopy, one or more of these processes may not be relevant (see Part III).

Note b. The terms third-partner effect and third component are ambiguous and are discouraged.

Note c. In the past it has been common usage to denote atomic lines as arc lines and ionic lines as spark lines. This usage is now considered to be incorrect. The correct way to indicate that lines are due to atomic or ionic transitions is:

Element symbol I wavelength e.g. Cu I 324.7 nm; and
Element symbol II wavelength e.g. Cu II 213.6 nm

Note d. See IUPAP document 5.5

Note e. *Unresolved band spectra* may appear as a spectral continuum.

Note f. See IUPAP document 5.5

2.3 Terms relating to the excitation and radiation of spectra

2.3.1 Plasmas. A plasma of the type occurring in spectrochemical radiation sources may be described as a gas which is at least partly ionized and contains particles of various types, viz. electrons, atoms, ions and molecules. The plasma as a whole is electrically neutral.

2.3.2 Plasma temperature. *Plasma temperature* may be described according to the types of temperature measurement used, e.g. when using atomic radiation, excitation temperature is obtained and when using molecular radiation, *rotational* or *vibrational temperatures* are obtained.

Several types of temperatures may be defined in a plasma on a *macroscopic scale*, viz.

Radiation temperature, which is defined by Planck's law,

Electron temperature, which is related to the kinetic energy of electrons,

Gas temperature, which is related to the kinetic energy of atoms, molecules, etc. and has a *Maxwellian distribution*,

Excitation temperature, which is related to the *population* of the energy levels and described by the *Boltzman law*, and

Ionization temperature, which is related to the *ionization equilibrium* described by the *Saha-Eggert equation*.

If a plasma is in *complete thermal equilibrium* (CTE) all these temperatures should be equal.

Practically no plasma fulfils these conditions and spectrochemical sources are generally not in complete thermal equilibrium.

On a *microscopic scale*, i.e. where the volume of gas under consideration is of the order of the *mean free path* of the radiating or absorbing particles, a condition of thermal equilibrium can nearly be fulfilled. The plasma is then said to be in *local thermal equilibrium* (LTE). In local thermal equilibrium, at least the electron, gas, ionization and excitation temperatures are equal in a part of the plasma and radiation temperature cannot be defined.

Norm temperature is the temperature indicated by the maximum radiance of a spectral line under the conditions prevailing in a plasma and is the result of competing effects of excitation and ionization.

2.3.3 Pressure effects. The *pressure* (see Note a) within a plasma influences the characteristics of the radiation, in that it affects the mean free path of the particles and their *collisional cross-sections*. Pressure thus affects the number of *collisions per unit of time*. Sources may broadly be classified into 4 different groups depending on the average gas pressure at which they operate, viz.

Low pressure (<10 kPa)

Medium pressure (10 - 100 kPa)

Atmospheric pressure (~100 kPa)

High pressure (>100 kPa)

2.3.4 Collisional processes. An atom can undergo a change in its state of excitation as a result of collisional processes with other particles. In an *elastic collision*, a change of kinetic energy alone between the colliding species takes place; in an *inelastic collision* (collisions of the first kind), kinetic energy is converted to internal energy of the atom. A form of this type of collision may be due to collision with a neutral particle in which kinetic energy is imparted to the atom to raise it to a higher energy level; in *super-elastic collisions* (collisions of the second kind), the internal energy of the impinging particle is converted to kinetic energy and in *quenching*, an atom in an excited state may lose its energy by a *collisional de-excitation* process. Terms "radiationless collision" and "thermal de-excitation" are considered unsatisfactory.

A *metastable state* (level) is any excited state which in principle by virtue of the selection rules, cannot combine with any lower state. These metastable states usually have considerably longer lifetimes than ordinary excited states.

2.3.5 Radiative processes. The change in the energy of an atom may be due to the *radiative processes*, i.e. the emission or absorption of radiation.

Note a. The unit mm of mercury (mmHg) or Torr is no longer acceptable. Pascal (Pa) is the SI accepted unit (1 Torr \approx 1.3 x 10² Pa and 1 atmosphere \approx 1 Bar \approx 100 kPa).

An atom in an *excited state* can emit a photon when the electron undergoes a transition from a higher to a lower energy level in the atom. This is known as *radiative de-excitation*. If such a transition occurs spontaneously, the rate at which atoms undergo transitions between two particular energy levels is proportional to the number of atoms in the excited level. The *proportionality constant* is called the *transition probability for spontaneous emission*.

An atom in a ground or excited state can absorb a photon, resulting in the atom going to a higher excited state. This is known as *photoabsorption*. A *transition probability for absorption* relates the rate of absorption to the *number density* of atoms in the lower level and the *radiation density*. A downward transition may be induced, by the same *radiation density*, between the same energy levels, which is termed *stimulated emission*. A *transition probability for stimulated emission* relates the rate of emission to the number density of atoms in the upper or higher level and the radiation density.

The *oscillator strength* (see Note a) for absorption f_{lu} is often used instead of the transition probability for emission to which it is proportional.

2.4 Terms relating to the shape and shift of spectral lines

The shape of a spectral line is described by the *line profile function*. The width of a spectral line is defined by its full width at half maximum intensity (*peak intensity*) (FWHM). The *physical line shape* is due to the combined effects of the different *broadening processes* (see Note b). *Line shift* is the displacement of the central wavelength of the spectral line by similar effects.

2.4.1 Natural broadening. *Natural broadening* has its origin in the finite lifetime of an excited state.

2.4.2 Doppler broadening. *Doppler broadening* is due to the random motion of the emitting atoms, and the *Doppler halfwidth* is proportional to the square root of the temperature. A Doppler broadened line has a *Gaussian shape*.

2.4.3 Doppler shift. The preferential motion of the radiating atoms relative to the observer cause *Doppler shift*.

2.4.4 Collisional broadening or pressure broadening. Collisions of the emitting particles with either neutral or charged particles cause *collisional* or *pressure broadening*. A line shift can also occur.

Collisions with neutral particles. *Van der Waals broadening* occurs when upper and lower levels are broadened by collisions with OTHER (like or unlike) neutral particles (see Note c). *Resonance broadening* results when a resonance level (either upper or lower level of the transition) is broadened by collisions with like atoms.

Collisions with charged particles. *Stark broadening* results when the collisions are with charged particles or the radiating or absorbing atoms are in a strong electrical field.

2.4.5 Self-absorption. Photons emitted in one region of a source are partly absorbed in their passage through the plasma. Because of the fact that the *absorption profile* is of the same shape as the *emission profile*, energy is selectively absorbed from the emission line, i.e. the *absorption coefficient* is a maximum at the centre of the line or central wavelength. The actual line profile is changed as a result of the lowering of the maximum intensity accompanied by a corresponding increase in apparent *halfwidth*. This is termed *self-absorption broadening*.

2.4.6 Self-reversal. *Self-reversal* is a case of self-absorption, when a line is self-absorbed to such an extent that the peak or central wavelength intensity is less than at the wings or non-central wavelengths.

Note a. Oscillator strength is the historical term relating to the Rutherford atomic model.

Note b. The physical shape is often described by the *Voigt function* and it takes into account natural broadening, Doppler broadening and pressure broadening. The shape of the line described by the Voigt function is known as the *Voigt profile*.

Note c. The term Lorentz broadening was used for neutral particle collision broadening and Holtzmark broadening for cases of Van der Waals broadening when collisions took place with like particles. Both terms are discouraged.

2.4.7 Zeeman effect. The *Zeeman effect* arises when atoms are exposed to a magnetic field. Such a field perturbs the energy levels resulting in a splitting of the spectral lines, i.e. the energy levels from which the transition arises are split up into different levels.

2.5 Further terms relating to special characteristics of spectral radiation

2.5.1 Polarization. Radiation from sources may be *polarized* or *unpolarized*. This radiation may be *plane*, *circularly* or *elliptically polarized*.

2.5.2 Scatter. Radiation originating from a part of the source may be scattered in a different part of the source (or in another source). The radiation may be scattered in all directions, depending on its wavelength and the nature and the inhomogeneity of the medium causing the *scatter*. If the scatter results in no change of the wavelength relative to the primary radiation, it is called *Rayleigh (elastic) scattering*. If the scattering process causes a wavelength change, the scatter is called *Raman (inelastic) scattering*.

3. ELECTRICAL ARCS

An *electrical arc* is a self-sustaining electrical discharge between at least two electrodes and is characterized by a comparatively small *cathode fall voltage*, a low *burning voltage* and a relatively high *current density*. The burning voltage of an arc is the voltage across the *electrode gap* during an arc discharge.

Based on the *operating current*, one has the *low current arc* (below 10 A), the *medium current arc* (10 - 30 A) and the *high current arc* (above 30 A). For spectrochemical purposes mainly low current and medium current arcs are used. The temperatures of the low and medium current arc plasmas considered in this document range between 3000 and 7000 K according to the *ionization potential* of the elements present.

3.1 Current-carrying arc plasma

A distinction may be made between *free burning arcs* and *stabilized arcs* according to the form of the *current-carrying arc plasma*.

Electrical arcs can be operated either with direct or with *alternating current*. The plasma can be *current-carrying* and *non-current-carrying (current free)*. The dependence of the voltage and current on time is called the *voltage-time* and *current-time relationship* of the arc.

3.1.1 Free-burning arcs. A free-burning arc operates mainly in the surrounding gas and partly in the vapour which it generates. The plasma of such an arc is formed freely in space. Its shape depends only upon the type and form of the electrode material, the electrode gap, the electrical parameters of the discharge and the chemical composition and convection properties of the discharge gas.

The direct current arc (dc arc). The most basic type of electrical arc is the dc arc. The dc arc is fed by a source having a total available voltage of between 100 and 300 V and a power of some kW. A resistor or some other stabilizing device must be used in the circuit of the dc arc to compensate for the negative *voltage-current characteristics*.

The alternating current arc (ac arc). The alternating current arc is fed by an ac supply normally having the mains network voltage and frequency but without an energy storing capacitor (see Note a) in the arc circuit (see Note b). Sometimes voltages of up to some thousands of volts are used. The ac arc can sometimes be operated as a *thermally ignited arc* without external ignition. When no ignition is used the arc is said to be an *uncontrolled ac arc*. The size of the electrode gap, however, usually necessitates reignition of the arc for each half cycle. The *ignition* can be done by a high frequency discharge, also known as an *ignition spark*. When the ignition is triggered electronically, one has an *electronically ignited* or a *controlled ac arc*.

In the *rectified ac arc* (see Note c) only one half cycle of the current phase of the arc flows. The arc must be reignited after each phase.

Note a. The word "condenser" (e.g. spark condenser) although still widely used is discouraged and should be replaced by capacitor. (Ref I.E.C.)

Note b. For exception, see Section 3.5.1.

Note c. The terms unipolar, unidirectional and uni-arc are discouraged in connection with arc nomenclature. Unidirectional spark is used in spark nomenclature (see Section 4.4).

3.1.2 Stabilized arcs. *Temporal and spatial stabilization* of the arc plasma may lead to an improvement in detection limits and/or precision of measurements (stabilized arc).

Magnetically stabilized arcs. Stabilization may be achieved by the influence of both *homogeneous and non-homogeneous magnetic fields*.

Gas-stabilized arcs. The arc plasma may be stabilized by a gas stream (gas-stabilized arc plasma), e.g. by a flow of gas around the arc which prevents radial wandering of the plasma.

Wall-stabilized arc (see Note a). Stabilization may be achieved by allowing the arc to burn through one or several *orifices* consisting of cooled metal or graphite discs (*stabilization rings*), thus fixing the position of the *arc column*. A cooled tube made from fused silica may achieve the same purpose. An arc burning through such a tube is called a wall-stabilized arc. The ring or wall stabilization diminishes the diameter of the plasma which then has a higher temperature in the constricted part (see Note b).

3.1.3 Interrupted arcs. All of the arcs mentioned may be operated as interrupted arcs. The interruption may be done periodically by electrical or mechanical means. The ratio of the burning period to the non-burning period (*on-off ratio*) is called the *duty cycle*. The number of burning periods per unit time is the repetition rate of the interrupted arc.

3.2 Non-current-carrying plasmas (current-free arc plasmas)

When a dc arc operating between electrodes in an enclosure is blown through an orifice from its normal discharge passage by a stream of gas, a non-current-carrying plasma is produced. The flow of gas may be parallel or perpendicular to the direction of the electrical current. In some configurations this orifice is in one of the electrodes (often the cathode). The *plasma plume* emerging from the orifice has good temporal and spatial stability. This type of arc is called a *plasma jet*.

3.3 Transferred plasmas

In some configurations of plasma jets a third electrode may be introduced, so that the plasma is transferred from one of the original electrodes to this third (external) electrode. The resulting *transferred plasma* also has good spatial and temporal stability. A *three-electrode plasma* generated between two anodes and one cathode belongs to this category of plasmas.

3.4 Transport of the sample into the discharge (see Note c)

3.4.1 General properties. If the sample is electrically conductive (metallic) it may be used directly as one (or both) of the electrodes (*self-electrode*). For electrically non-conductive samples, powders or liquids, the sample is introduced into the different types of discharge, as required for a *sample electrode* or analytical electrode. A graphite or an amorphous carbon sample electrode (*analytical electrode*) is generally used. The non-sample-carrying electrode is called the *counter electrode* (see Note d) and may be of carbon, graphite or metal, e.g. tungsten. The characteristics and operation of the arc depend on the material and shape of the electrodes and on the *analytical gap (arc gap)* as well as on the *polarity* of the sample electrode. If the sample electrode is positive, *anodic vaporization* takes place. If the sample electrode is negative, *cathodic vaporization* ensues. If radiation from only a thin layer near the cathode is utilized, the technique is known as the *cathode layer arc*. For this technique the sample electrode is usually the cathode, but this need not necessarily be the case.

3.4.2 Discontinuous procedures. During a given arcing period a given amount of the sample is evaporated completely (*complete evaporation*) or partially (*partial evaporation*) and the vapour products enter the plasma where they are excited as atoms or ions. The different vapour pressures of volatile components of a sample influence the time sequence of their evaporation and this *fractional distillation* or *burning-off effect* may cause systematic errors in the results of an analysis. While evaporation of the sample takes place, different chemical reactions called *thermochemical reactions* occur.

Note a. The use of terms such as constricted arcs, pinched arcs, etc. are discouraged.

Note b. At high current densities the magnetic effect of the current may cause a *pinch effect* resulting in a further *constriction* of the arc column.

Note c. Some of the processes considered for ac arcs in this section also apply to spark discharges discussed in Section 4.

Note d. Graphite and carbon electrodes differ in their *electrical and thermal conductivity*. Carbon counter electrodes with high electrical and thermal resistance are often used because of their inverse resistance characteristics and to avoid the *climbing of the arc*.

Electrically conductive samples used directly as self-electrodes are often evaporated in an interrupted ac arc to avoid their rapid melting and evaporation.

It is sometimes possible to form the conductive sample into a small sphere on the tip of a supporting electrode (usually carbon) in a dc arc. This type of arc is known as the *globule arc*.

Metallic filings or drillings may be analysed by compacting them into *pellets* which may be used as self-electrodes or contained in a supporting electrode.

Non-conducting powder samples have to be mixed with a conductive metal powder or graphite and placed directly or in the form of a pellet in hollow or *cup electrodes*.

Liquid samples (solutions) may be analysed as evaporated residues on the top surface of plane flat *carrier* or sample electrodes. Metal samples are sometimes dissolved and analysed as liquids.

Liquid sample injection enables a *limited volume* of a solution to be converted into an *aerosol* by means of a *nebulizer* and introduced into one of the various plasmas for analysis.

3.4.3 Continuous procedures. The *continuous supply* of new quantities of sample ensures uniform or *stationary radiation conditions* in the arc plasma over a relatively long arcing period. The influence of fractional distillation of various constituents is thus reduced.

For the continuous supply of a powdered sample into the discharge a hollow *sifter electrode* may be used. The acoustical shock-wave at the beginning of each discharge of an ac arc causes a small portion of the sample powder to fall from an upper sifter electrode through small holes in its base into the plasma where vaporization, dissociation, atomization and excitation occur. This is called the *acoustical shock-wave sifter system*.

In a similar fashion powdered samples may be introduced into the arc plasma between two *horizontal electrodes* by means of a *gravity-fed powder sifter system*. In this case the powdered sample falls into the discharge directly from a vibrating funnel, or it can continuously be fed into the discharge by a band or conveyer belt transporter.

For the transport of a powdered sample into the discharge from below the arc, different *blow-in procedures* are possible. A high frequency discharge may be used to prevent *agglomeration* of the powder.

The sample can be mixed with a binding medium, e.g. cellulose, and pressed to form a rod. The rod is then continuously fed into the discharge through an electrode bored to the diameter of the rod to give a *piston electrode*.

Liquid samples or solutions can be injected directly into the arc discharge through a *drilled electrode*. In *capillary electrodes* the sample is supplied from a reservoir and drawn into the discharge by capillary action. The whole capillary electrode can be made from graphite and the reservoirs made from a non-reactive material, e.g. polytetrafluoroethylene (PTFE). An example of this is the *vacuum-cup electrode*.

Porous cup electrodes (porodes) are hollow electrodes with porous bases. They are filled with the solution which penetrates through the bottom into the discharge. Rotating disc electrodes (*rotrodes*) can be used to provide a continuous supply of liquid sample into the discharge. The vertical disc electrode rotates continuously and is partially immersed in the sample solution. The discs can be made from metal, but normally crystalline graphite discs are used. An arrangement with two discs gives a more uniform sample supply and also enables the analysis of inflammable liquids. The *supply disc* is wetted by the sample and brings it into contact with the analytical *disc electrode*, which in turn rotates in the opposite direction. Arcing takes place between the rotating analytical electrode and a counter electrode.

Liquid samples or solutions can be dried to leave a residue on the upper surface of a *rotating platform (platrode)*. In the latter case fresh material is continuously brought into the discharge, i.e. providing the total exposure time is less than the time taken for one complete rotation of the platform.

Liquid samples or solutions may also be analysed by first creating an aerosol (see Note a) which can be introduced into various types of current-carrying or non-current-carrying arc plasmas. This technique enables a constant and uniform supply of the sample to be maintained.

Note a. See Part III, 3.1.1.1.

3.4.4 Erosion techniques. *Erosion techniques* are the formation of aerosols by means of *laser erosion* (see Lasers) or by *electro-erosion*, e.g. by arcs or sparks. The aerosol so formed may be conducted to an analysing plasma. An example of this type of source is the *capillary arc* which is essentially a wall-stabilized arc.

3.5 Operation

3.5.1 Electrical parameters. Many of the properties of an arc which make it suitable for spectrochemical analysis depend on the *electrical source parameters*.

A dc arc may be energized by a *rectified source* operating from the mains. In this case a *load resistor* is used to establish the current to a predetermined value and an *inductor* may be used to smooth it.

In other instances a power supply, also operating from the mains may provide an output of *constant voltage*. Electronic circuits may provide *constant current* to the arc under widely varying conditions. Sources of this type are called *electronically stabilized voltage* or *stabilized current supplies*.

As with dc arcs, ac arc circuits must have a load resistor to limit current. Other means such as *thyristor control* are also used to stabilize the supply voltage and the current. Sometimes additional current is supplied to the arc by means of a repeatedly charged capacitor thus giving a *condensed arc*. Where a low voltage arc must be ignited, an *ignitor circuit* is used consisting of a high voltage pulse operating through a *Tesla coil*. A *high frequency shorting capacitor* prevents high voltage from feeding back and damaging components in the lower voltage arc circuit.

Ignition after every half cycle of an applied ac voltage results in an *ignited ac arc*. Ignition at every full cycle results in a rectified ac arc which is a special kind of interrupted dc arc. The electrodes are held in a suitable arc stand (see Note a).

3.5.2 Arc atmospheres. An arc may operate in air, or in an atmosphere (*arc atmosphere*) created by providing a pure gas such as argon or carbon dioxide or a mixture of gases such as argon and oxygen at atmospheric or other pressures. When a carbon arc burns in air, nitrogen reacts with the carbon to form cyanogen which emits intense *cyanogen molecular bands*. These bands often mask spectral lines. By choosing a suitable *controlled atmosphere* free of nitrogen, this may be prevented and the arc stability improved. This *shielded electrical discharge* can be achieved by arcing in a relatively large *arc chamber* producing a free burning arc or by using a small cuvette with tangential or laminar flow.

When the gas emerges as a *laminar sheath* from openings (or a slit) around the lower electrode it prevents air from reaching the arc and a chamber is thus not required.

Inert gases, e.g. argon, and mixtures of inert gases with oxygen are the most widely used gases for controlled atmospheres.

3.6 Spectrochemical properties and applications

The arc has a relatively high operating temperature and as such is suitable for the evaporation, dissociation, atomization, ionization and excitation of a wide variety of materials. The radiation thus consists of *molecular bands*, *atomic* and *ionic spectra* and also continuous radiation due to *radiant particles*. Samples may be mixed with or introduced together with additives (see Part I, Section 7.7) for controlling volatilization, transport into the discharge region, excitation, *background suppression*, etc. These techniques include *buffered arcs*, *constant temperature arcs*, *carrier distillation arcs*, *seeded arcs*, etc.

The free-burning dc arc consumes relatively large amounts of electrode material. It is suited for determining trace elements in conductive samples and in non-conductive powder samples. For larger quantities of sample, as is often necessary for the analysis of *non-homogeneous material* or for the determination of traces of volatile elements, the *double arc* is useful. With this method the sample is heated by one arc and evaporated material excited by a second arc.

The ac arc is used mainly for metallic samples, pelleted powder samples and solutions.

Various dc arc plasmas are also successfully used for the analysis of solutions (see Sections 3.2 and 3.3).

Note a. See Section 4.5.

4. ELECTRICAL SPARKS (SPARK DISCHARGES)

Electrical sparks are defined as discontinuous *electrical discharges* across a gap between at least two electrodes constituting the *analytical gap (spark gap)*. The *discharge current* (see Fig. 4.1) is supplied by a cyclically charged capacitor C. After *spark ignition* the voltage across the analytical gap drops from the initial *capacitor voltage* U_{cap} to the low burning voltage U_b of an arc within a time that is short compared to the *spark duration* θ . Therefore basically, sparks can be considered as interrupted arcs of higher *initial current* I_0 or peak current and of a lower duty cycle than those treated in Section 3.1.1

4.1 Characterization of sparks

4.1.1 Charging circuit (Fig. 4.2). The spark capacitor C is charged through the *charging circuit*, a rectifier, a *charging resistor* and electronic or other devices for the control of *charging current*, *peak capacitor voltage* $U_{\text{cap}}(0)$ and the phase. If the capacitor is always charged at the same polarity a *dc spark* will result and in the case of an alternating charging voltage, an *ac spark*.

4.1.2 Discharge circuit (Fig. 4.2). The *discharge circuit* connects the capacitor of capacitance C with the analytical gap. It may contain inductors, of induction L, a *resistor*, of resistance R, and devices for triggering the spark for control and synchronization purposes, e.g. a *control spark gap (control gap)*.

The *peak spark current* is called I_0 (Fig. 4.3A). Spark current I and burning voltage U_b may oscillate with the *spark frequency* f, resulting in an *oscillating spark* (see Note a). Suitable combinations of the *discharge impedances* as derived from the relation $R \approx 2\sqrt{L/C}$, lead to *critically damped*, $R=2\sqrt{L/C}$ (Fig. 4.3B) or *overcritically damped*, $R>2\sqrt{L/C}$ (Fig. 4.3C) *discharges*.

If determined by the *natural impedances* of the discharge circuit, an oscillating discharge current periodically passes through zero with consecutive reignition at the *reignition voltage* U_z (Fig. 4.1) which may be a few hundred volts. By securing a dc bias current, oscillating discharges can be prevented from being extinguished during part or during the full length of the spark duration (*dc biased oscillating discharge* (see Note b) (Fig. 4.3D). Discharges of the types shown in Fig. 4.3B, C and D are also called *unidirectional discharges*. With a *controlled duration spark* (see Note c) the spark current is terminated by additional means. The amplitude of an oscillating spark current decreases with time, showing a *linear* or *logarithmic decrement* depending on the prevailing impedance.

In spectrochemical analysis either a *single spark* or a sequence of sparks (train of sparks) can be used. *Spark repetition rates* are of the order of 50 to 100 s^{-1} . Repetition rates in excess of 100 s^{-1} are called *high repetition rate sparks* (HRRS).

The analytical gap is bridged by the electrically conducting *spark channel* through the *discharge atmosphere*. Electrode material is removed in the form of a *vapour jet* from the cathode. In the case of an *inert discharge atmosphere* electrode material is similarly removed from the cathode and, in other discharge atmospheres, from the anode too. Due to the randomly distributed direction of the vapour jet the *vapour cloud* produced in this way may be a current-carrying or a non-current-carrying plasma depending on whether it penetrates into the current-carrying spark channel or not.

4.2 High voltage sparks

A *high voltage spark* is a *self-ignited spark discharge* characterized by an initial capacitor voltage $U_{\text{cap}}(0)$ exceeding the *breakdown voltage* of the analytical gap or of a control gap. Typical capacitor voltages range from 10 to 20 kV (see Note d). *Spark energies* range from some tenths of a joule to a few joules. Only oscillating discharges are practically feasible. Due to the possible short spark duration time several *sparks per half cycle* of the mains supply are possible.

A high voltage spark generator is called an *uncontrolled high voltage spark generator* if the breakdown of the analytical gap determines the initiation of the discharge. In this case the *charging time constant* of the charging circuit determines the number of breakdowns per half cycle. In a *controlled high voltage spark generator* initiation of the discharge is governed by mechanical or electrical means. Either the voltage or the *breakdown time* can be controlled. The voltage control may be achieved by the defined breakdown voltage of a stationary

Note a. The number of oscillations per spark (p) are given by $p = \theta \cdot f$.

Note b. The term, controlled waveform spark, is discouraged.

Note c. Mono-alternance is a trade term for a similar source, but this term is discouraged.

Note d. Other operating conditions may be as follows: $500 < C < 20\,000 \text{ pF}$, $5 < L < 5\,000 \text{ }\mu\text{H}$, $50 \text{ kHz} < f < 1 \text{ MHz}$, $10 \text{ }\mu\text{s} < \theta < 1 \text{ ms}$.

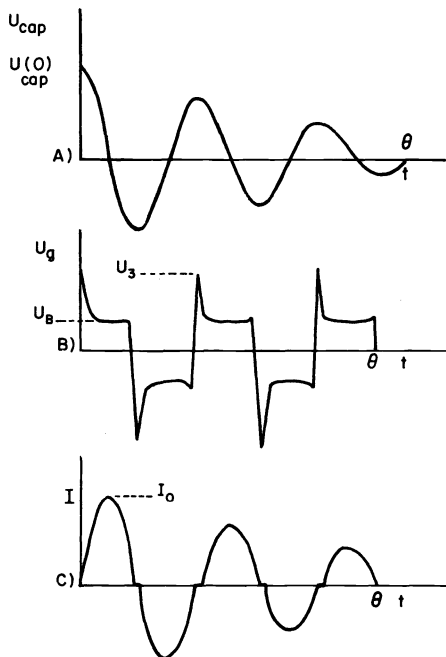


FIG. 4.1 : SPARK VOLTAGES AND SPARK CURRENT

- A : Capacitor voltage : U_{cap}
- B : Voltage across spark gap
- C : Current through spark gap

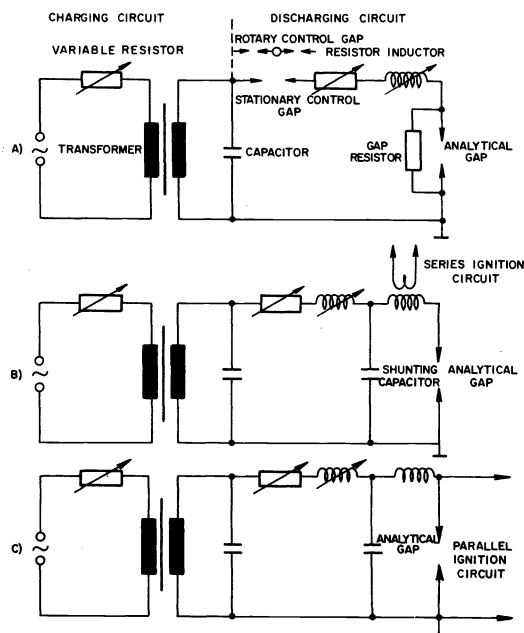


FIG. 4.2 : SPARK GENERATORS

- A : Controlled high voltage spark generator
- B : Medium or low voltage spark generator with series ignition circuit
- C : Medium or low voltage spark generator with parallel ignition circuit

(open or closed) control gap (*auxiliary spark gap* or *tandem gap*) in series with the analytical gap. The time control is achieved by a *triggerable stationary gap* or by the phase adjustment of a *synchronously rotating gap* (see Note a). Irradiation of the spark gaps by UV radiation obtained from an *ionization needle* or a discharge lamp and a high ohmic *gap resistor* (Fig. 4.2A) helps to overcome *breakdown jitter*.

4.3 Medium voltage sparks

Spark discharges have to be externally initiated if the capacitor voltage $U_{\text{cap}}(0)$ is lower than the breakdown voltage of the analytical gap. If this voltage is still significantly higher than the reignition voltage U_z of the analytical gap, one speaks of a *medium voltage spark* (see Note b). They are *externally-ignited spark discharges*. Ignition is accomplished by means of a high voltage *ignition pulse*, also called an ignition spark. Critical damping occurs at resistances of a few ohms. Therefore, a choice of discharges can be made, i.e. *undercritically damped oscillating discharges*, critically damped short lasting high current *sparklike discharges*, and *overcritically damped* long lasting low current *arc-like discharges* (see Note c). Apart from their different range of operating parameters, *medium voltage spark generators* require an *ignition circuit*. The igniting high voltage pulse can be introduced in series with the applied medium voltage across the gap by means of a *high frequency step-up transformer* (Tesla coil) to give *series ignition* (Fig. 4.2B). It can also be introduced in parallel with the gap voltage to give *parallel ignition* (Fig. 4.2C).

In *multipurpose spark sources* (see Note d) the ignition may be achieved by using the high voltage spark generator.

4.4 Low voltage sparks

These discharges are similar to medium voltage spark discharges. The capacitor voltage U_{cap} is of the same order as the *mains supply voltage*. To compensate for the low voltage capacitors are accordingly large so as to provide the required spark energy. The number of oscillations per spark is small and unidirectional discharges are easily obtainable.

4.5 Spark stands

The *spark stand* contains the electrode holders, usually watercooled, for one or more electrode configurations (see Section 4.9). Provision is made optically or mechanically to align the electrodes and to adjust the electrode gap. Universal spark stands usually have an illumination system with a *projection screen*. For discharges at pressures other than normal or in atmospheres other than air a *spark chamber* is employed. Such a chamber may also have a *spark confiner plate* or disc made of a non-conductive material such as boron nitride to confine the spark to a definite area of a sample surface. In order to remove the evaporated electrode material the spark chamber is flushed by the continuous flow of the *working gas*.

4.6 Discharge atmospheres

The most common discharge atmospheres are air and argon. The latter is transparent to parts of the UV-spectral region where air is not. It does not react with the electrodes and permits the application of unidirectional discharges which do not evaporate material from the anode. Small quantities of other gases may be mixed with the *principal gas*, e.g. hydrogen with argon.

4.7 Discharges in vacuum

High excitation energies may be achieved by means of spark discharges at very low pressures. These sparks are called *vacuum sparks*. To overcome the high breakdown voltage, a very high capacitor voltage is necessary. Breakdown can be achieved at lower voltage by means of a *sliding spark*, which is essentially a spark along a non-conducting surface (*surface spark*).

4.8 Spectral characteristics

Due to the short *interaction time* of the sparks with the electrodes these generally remain cool. The high current density in the *burning spot* at the electrodes produces such a high local temperature that fractional distillation is significantly reduced in comparison with arc discharges. The plasma is usually considered to be in local thermal equilibrium (LTE) as soon as the initial voltage across the gap has dropped to the arc burning voltage. The temperatures and *electron pressure* in this period are of the same order as those of arc

Note a. Terms such as interrupters or synchronous interrupter are discouraged.

Note b. Typical operating conditions for medium voltage sparks are: $500 < U_{\text{cap}} < 1500$ V, $1 < C < 25$ μ F, $50 < L < 200$ μ H, $0.5 < R < 50$ Ω .

Note c. Spark frequencies of the oscillating discharges may be $2 < f < 20$ kHz with a spark duration of $0.2 < \theta < 2$ ms. With undercritically damped sparks the number of oscillations p will be $1 < p < 5$.

Note d. The word multisource is not recommended.

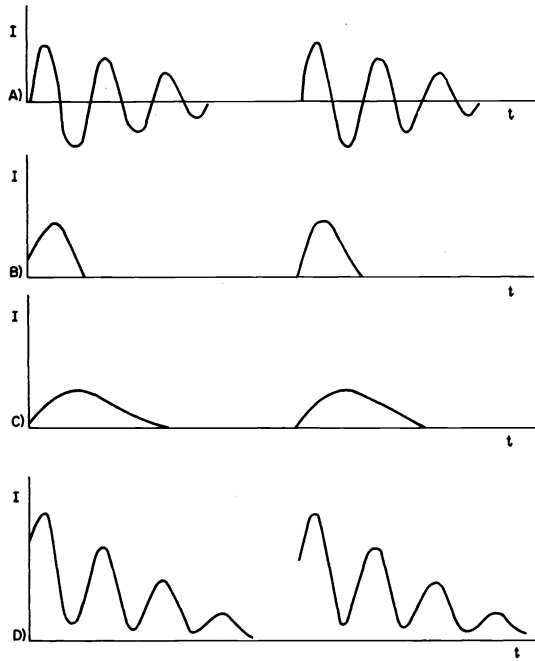


FIG. 4.3 : VARIOUS CURRENT WAVEFORMS

- A : Undercritically damped discharge
- B : Critically damped discharge
- C : Overcritically damped discharge
- D : DC-biased oscillating discharge

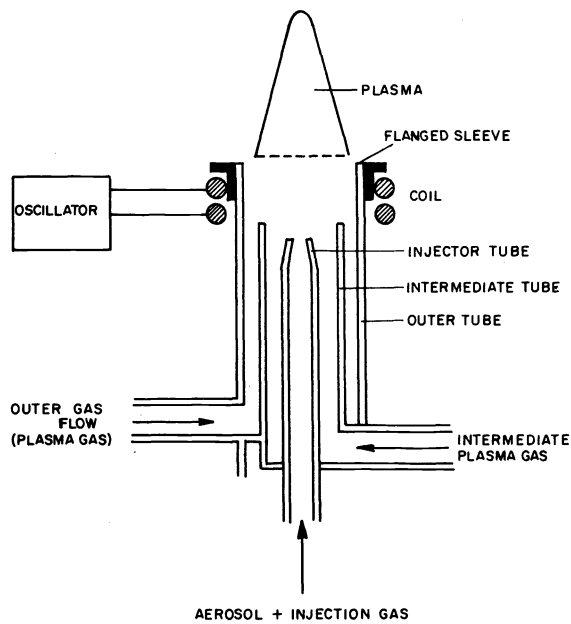


FIG. 5.1 : SCHEMATIC DIAGRAM OF PLASMA TORCH

discharges. Soon after breakdown the plasma is characterised by high temperatures and high electron pressure which are responsible for a pronounced *continuous spectral background*. By separating these two phases, with the help of *time-resolved spectroscopy*, it is possible to improve the line to background intensity ratios and correspondingly, the *power of detection*.

4.9 Analytical procedures

Small quantities of the sample are removed sequentially from the many burning spots produced by the numerous sparks. Although the removal of material is by *thermal evaporation*, matrix effects, due to the composition and physical properties of the surface, can significantly be reduced by a suitable choice of operating conditions.

The surface is first conditioned during the *prespark period*. This is established with the aid of a *prespark curve* (see Note a), also called *time-of-wait curve* or *intensity-time curve* (see Part I, Section 7.6.4). The intensity-time curve is aimed at determining *optimum spark conditions* for the *measurement period*. In many cases these conditions coincide with *sparkling equilibrium* and *evaporation equilibrium*. High energy presparking or *high repetition rate presparking* may be favourable in achieving this goal by enabling sampling from a liquid (molten) or a freshly solidified surface.

Spark sources, because of their relatively high precision and accuracy, are suitable sources for the routine analysis of metals, e.g. for production control purposes.

Metals can be analysed with the *point-to-point* configuration using two sample electrodes (self-electrodes) of the same material. The most common technique uses the *point-to-plane* configuration, i.e. a plane electrode made from the sample material with a pointed counter electrode made from another material, which does not contain the analytical elements. Various types of samples can be analysed in the form of solutions with the help of supporting electrodes (see Note b), carrier electrodes, rotating disc or rotating platform electrodes, vacuum cup or porous cup electrodes.

Electrically non-conductive samples can also be analysed with the help of *powder techniques*. Powders are prepared by grinding, sometimes after *fusion (isoformation)* and mixing with a conductive material, e.g. graphite or metal powder. From the mixture pellets are compressed which then serve as self-electrodes for spark excitation. Conductive pellets may be made by pressing metal filings, drillings and shavings.

5. RADIOFREQUENCY PLASMAS

Radiofrequency plasmas (rf plasmas) are formed in a flow of gas or gases, by an externally applied radio frequency field (see Note c) resulting in a *radiant plume*.

5.1 Inductively coupled plasmas (ICP)

In *inductively coupled plasmas (inductively coupled rf plasmas or inductively coupled argon plasmas)* (see Note d) energy transfer to the gas is achieved with the help of an *induction coil* or *inductor* (see Note e). A set of refractory tubes, called the *tube assembly*, is arranged coaxially with the induction coil and the plasma is formed within and/or above them.

5.1.1 Oscillators. The induction coil constitutes a part of an oscillating circuit of one of the following types:

A free running *oscillator* where the *tank circuit* (or *lump circuit*) is built up by capacitors and induction coils to give a specific frequency which depends on the values of the components. This frequency may vary (*floating frequency*) around its nominal value depending on the *plasma impedance* (or *plasma load*), the power and the *coupling efficiency* (see Note f).

Note a. The terms *spark-off*, *spark-off effects* and *spark-off curve* are discouraged.

Note b. The *copper spark* and *graphite spark* are specific cases of supporting electrode techniques.

Note c. Certain requirements regarding electrical interference must be obtained. These conditions may be less severe for certain frequencies.

Note d. It is recommended that the frequency at which the source operates be given, e.g. 27,12 MHz ICP, and the gas type may be defined.

Note e. The terms *coil*, *load coil*, *work coil* are discouraged.

Note f. 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* has a quartz crystal inserted to obtain a *fixed frequency* of oscillation at a constant *base frequency*. A series of other stages (circuits) permits *frequency multiplication* (doubling for instance) to get the fixed frequency required and power amplification.

The induction coil may be *remotely coupled*. Adaptation to load variation, for instance during *plasma initiation*, is obtained by a *coupling unit* (see Note a). It facilitates the maximum *incident power* in the induction coil and minimizes the *reflected power*. This can be obtained automatically with the help of servomechanisms.

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

$$f = \frac{C}{4l} \text{ where } C \text{ is the capacitance of the matching capacitor}$$

These lines constitute an *impedance-converter* which enables the circuit to match the load variations and the work coil to have more than 2 or 3 turns.

5.1.2 Plasma torch. The *plasma torch* consists of the 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, one the *outer or plasma gas* flow (see Note b) and the other the *injection gas* or *aerosol carrier gas* flow, are sufficient to operate an analytical plasma and the torch may therefore be constructed with two tubes. Due to the plasma's axial symmetry the torch tubes are concentric. The *injection tube* or *injector* is placed axially and opens at or below the level of the induction coil. The insulating refractory outer tube ends at a specific distance from the induction coil. If this distance is short, it may be useful to separate the plasma and the induction coil by using a flanged sleeve (see Fig. 5.1) (see Note c).

Some users have considered it necessary to use a third gas flow in order to push the plasma away from the injector. This third gas inlet necessitates the use of a third tube or *intermediate tube* which is also concentric and opens near the level of the injector. This gas operates as an *intermediate plasma gas*.

In certain torch configurations, even when only two gas flows are used, this intermediate tube has been retained in order to increase the plasma gas velocity without changing its flow rate.

The velocity of the aerosol carrier gas must be sufficiently high to pierce the plasma, but not too high to reduce the *transit time*, i.o.w. it is better to increase the *resident 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.

5.1.3 Plasma parameters. The type and intensity of spectral lines observed in a defined *observation zone* of the plasma depend on several *plasma parameters*: the height, width and position of the observation zone, usually related to the top of the induction coil, the outer gas and aerosol carrier gas flow rates, the intermediate gas flow rate (if any), the incident power of the plasma generator and the coupling efficiency, the physical state of the sample (gas or aerosol particles), the sample *uptake rate* (or rate of liquid consumption), the efficiencies of nebulization, aerosol transport, desolvation, volatilization and atomization (see Part III, Section 3.1.2) and the characteristics of the spectral lines chosen.

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.

5.1.4 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, C₂, N₂, CN, N₂⁺) are observed if a compound containing these species is injected into the plasma.

Note a. The use of the term *match box* is discouraged.

Note b. In many torches, the tubes are made of fused silica and constructed as one piece. Demountable torches are also used in which the tubes may be assembled by glueing them together or using O-rings in a machined base.

Note c. The terms cooling gas and coolant gas are discouraged.

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 of 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).

5.1.5 Analytical procedures (see Note a). The ICP is used mainly for the analysis of liquid samples. *Sample* 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 *bracketing 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* (see Part III, 4.2).

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.

5.2 Capacitively coupled plasmas (CCP)

A *capacitively coupled plasma* may be obtained by energy transfer through capacitive coupling. Coupling is obtained by applying a high frequency voltage to a capacitor which consists of a cylindrical (or coiled) electrode and a coaxial conductive (sometimes pointed) electrode. The torch consists of a fused silica tube, placed concentrically between the two electrodes. The carrier gas emerges from the inner electrode. The plasma forms at the tip of this central electrode giving rise to what has been called a *brush discharge* (see Note b).

It is possible, especially when using higher radiofrequencies, to remove the outer electrode and to have the central electrode discharge into air. Only the carrier gas flow is necessary. The aerosol (nebulized sample and carrier gas) is supplied to the torch through the *axial electrode* and is excited directly.

CCP sources are used mainly for the analysis of liquid samples. Helium, argon, hydrogen, nitrogen, oxygen or air may be used as carrier gases.

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.

Molecules in the CCP are less dissociated than in the ICP and molecular bands may overlap spectral lines.

Spectral characteristics and analytical procedures are similar to those described for the ICP. The residence time of atoms in the CCP is generally longer.

6. MICROWAVE PLASMAS

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

Note a. Most of these terms have already been defined in Part I (Section 6) and in Part II (Section 4) including the performance of an analysis. Terms relating to data interpretation are listed in Part II.

Note b. This term is historical and also applies to the single electrode microwave discharge source. (See Section 6.1).

6.1 Capacitive microwave plasmas (CMP) (See Note a) (*Electrode resonant cavity plasmas*)
Microwaves generated by a magnetron are conducted to a tunable cross-shaped cavity via a *coaxial wave guide*. The plasma torch constitutes one arm of the cross containing a pointed hollow electrode. 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.

6.2 Microwave induced plasmas (MIP) (*Electrodeless resonant cavity plasmas*)
 Several cavity configurations exist of which the transverse 1/4 or 3/4 wavelength configurations and the tapered cavity are most commonly used. Other cavities are classified according to their *transverse electromagnetic mode* (TEM) configurations.

6.2.1 Atmospheric pressure MIP. 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. A plasma generated in the tube is called the *atmospheric pressure microwave induced plasma*.

6.2.2 Low pressure MIP (<2 kPa). A sealed fused-silica container (tube) at reduced pressure and containing a small portion of the sample to be analysed is introduced into the resonant cavity.

Alternatively, the silica tube may contain an element or elements such that the source can be used as a primary source (e.g. for AAS and AFS).

6.3 Operating parameters and usages

Microwave plasmas at atmospheric pressures are used for the analysis of nebulized liquid samples and of solute vapours emerging with the carrier gas from chromatographs. Hydrogen, helium, nitrogen and argon are the plasma gases usually used.

These sources are very sensitive to plasma impedance variations, e.g. to sample quantities and the ionization potentials of the species introduced (plasma load). With the MIP and the CMP, an adjustable *tuning stub* is used to assist the initiation of the plasma and to compensate for the load.

Molecules in the MIP are dissociated less than in the ICP and molecular bands may interfere with spectral lines. Deviation from LTE is more pronounced than with the ICP.

Spectral characteristics and analytical procedures are similar to those described for the ICP. Solute volatilization and *spatial distribution interferences* occur. In order to reduce them, *matrix matching* or the *buffer addition technique* or a combination of both is used.

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

7. LASERS

In this section the laser will be considered as a *thermal source* and not as a primary source of highly monochromatic *coherent radiation*, although it may also be applied as such in analytical spectroscopy.

Radiation from a *laser source* is emitted with a very small *angle of divergence* (u). Its *radiant intensity*, i.e. its *radiant power per solid angle* can be very high. By focusing laser radiation with a *focusing lens* or a *focusing mirror* of focal length f onto a *target*, i.e. the surface of a sample, a high irradiance in a small *focal spot* is obtained. This is sufficient to cause vaporization and atomization of materials, irrespective of their physical properties, e.g. *boiling temperature*. The *laser vapour cloud* which is produced may contain enough neutral atoms in the ground state for atomic absorption analysis. If the laser-produced vapour cloud is sufficiently hot to radiate in the optical spectral region, it can be used directly as an excitation source for optical emission spectroscopy. Additional forms of excitation may be used to increase the spectral radiance of the vapour or to improve the analytical line-to-background intensity ratios.

7.1 Characterization of lasers

Basically, a laser consists of an *active medium* in which by *optical pumping* or *electrical excitation* (whichever is applicable) *population inversion* of energy levels and hence *stimulated emission of radiation* may be obtained. *Laser action* or *lasing* may either be continuous, i.e. *continuous wave* (cw-operated) or *discontinuous* in the form of a *laser pulse* or sequence of laser pulses.

Note a. When a single electrode is used, the source is also called a *one-electrode microwave plasma*.

In order to obtain sufficient optical amplification to cause oscillation in the direction of its axis, the active medium is placed in the *laser resonator*. This is essentially an interferometer consisting of the two *laser mirrors* (or similar optical devices) of *high reflectivity* and *low loss* (absorption). Of the various *mirror configurations*, the *parallel-parallel* is most generally used. A *semi-transparent mirror* permits the laser radiation to leave the resonator in the form of a *laser beam*.

Sources which *lase continuously* may be characterized by the *pumping or exciting energy* (or current strength), the *laser output power*, the wavelength and the angle of divergence (the transversal mode).

Pulsed laser sources may in addition, be characterized by the duration of the *pumping period*, the *laser output energy* and the number and *temporal spacing* of the laser output pulses. The individual pulses are characterized by the *pulse power*, the *pulse energy* and the *pulse duration*. The laser resonator can also be considered as a resonant cavity with, theoretically, an infinite number of possible *eigen-frequencies*, which are commonly described by their *modes*, i.e. *transversal* as well as *longitudinal*. By suppression of transversal modes by a *mode selector*, the laser beam angle of divergence can be decreased. Longitudinal mode selection is not effective in this kind of application.

7.2 Solid state lasers

The active medium is usually a rod 5 to 15 cm in length and 5 to 15 mm in diameter, consisting of a *host material* which is *doped* with a *laser-active substance*. Examples are *Nd-glass*, i.e. glass doped with neodymium; *Nd : YAG*, i.e. yttrium aluminium garnet doped with neodymium; or *ruby*, i.e. aluminium oxide doped with chromium. The active medium is placed in the *pumping cavity* where it is illuminated by the *pumping lamp*. The wavelength of the emitted radiation is either in the visible or near infra-red spectral region.

7.2.1 Continuous wave operation (cw-operation). Continuous wave operation is only feasible if the *pump power* required to exceed the *lasing threshold*, is low. This may be accomplished by optically pumping a Nd : YAG rod by means of a *tungsten-halogen lamp*. Power output is usually of the order of a few watts.

7.2.2 Free-running operation. Under *free-running operation* the laser output is characterized by the emission of a large number of *irregular and incoherent radiation pulses* called *laser spikes* or *spikes* of short duration, i.e. lasting less than a microsecond. Typical *spike power* is of the order of some kilowatts and the total duration of the laser action is of the order of some tenths of a millisecond.

7.2.3 Q-switched operation. A shutter called a *Q-switch*, is inserted in the laser resonator to obstruct or impede the path of light during part of the pumping period. It may allow more energy to be stored in the active medium by population inversion. When the shutter opens sufficiently fast, the *Q* of the resonator and hence the *internal oscillation amplitude* rises rapidly, resulting in the emission of a short *single pulse*, also called *giant pulse*, of high power (typically of the order of several MW). Shutters which do not open fast enough may cause the emission of several spikes of *medium power* (100 kW). This action is called *semi-Q-switched*. *Q-switched operation* may be initiated several times during a pumping period. Many types of Q-switches are used, e.g. *saturable dye-switch* consisting of a *bleachable substance* which may be transparent or opaque to the laser radiation, depending on the degree of irradiance, *electro-optical shutters*, which make use of the *quadratic electro-optical effect* (*Kerr cell*) or of the *linear electro-optical effect* (*Pockels cell*), *mechanical shutters* such as a *rotating disc*, a *rotating mirror* or a *rotating prism*, *magneto-optical shutters*, which make use of the *Faraday effect* and *acousto-optical shutters*, which temporarily cause diffraction or refraction in the laser resonator. The latter type of Q-switch is capable of producing an *equidistant* series of spikes of medium power.

7.3 Other lasers

7.3.1 Liquid lasers. *Liquid lasers* having suitable host solutions doped with neodymium or dyes as the active medium, can give performances similar to solid state lasers. With *dye lasers* a wide variety of wavelengths is available.

7.3.2 Gas lasers. Electrically excited (i.e. low pressure electrical discharge) lasers can be operated in the various modes described previously. With some, a very high *laser output* can be obtained e.g. the CO₂ laser at a wavelength of 10.6 μm.

7.4 Vaporization and atomization

Vaporization takes place from an area of the sample on which the laser radiation is focused.

A *crater* is formed during evaporation characterized by the *crater diameter*, the *crater depth* and the *crater shape*. The crater diameter should not be confused with the *focal spot diameter* which may be larger or smaller than the crater diameter depending mainly on the

energy of laser output. The diameter of the focal spot also influences the crater diameter. The theoretical *ultimate focal spot diameter* is diffraction limited and, due to imperfections of the active medium, usually cannot be achieved (see Note a).

The vaporized material leaves the target in a vapour stream or jet forming the *laser plume* which may consist partly of free atoms. To prevent unwanted chemical reactions (e.g. oxidation) of the plume with the surrounding air, a sample chamber filled or flushed with a suitable inert gas is often used.

7.5 Lasers as atomizers for atomic absorption spectroscopy

Vaporized material which is sufficiently atomized can be utilized for atomic absorption measurements. Better analytical results can often be obtained by additional atomization of the material contained in the plume by means of a flame or a furnace.

7.6 Laser atomization and excitation for use in optical emission spectroscopy

Lasers of high power output, e.g. Q-switched lasers, may be capable of producing atomic vapour at such high temperatures that appreciable optical radiation is generated, thus acting as a *one-step excitation source* for OES. Due to the initial high pressure, the analysis lines may be broader and show more self-absorption than in other excitation sources such as arcs and sparks, thus restricting their useful analytical range.

7.7 Optical emission spectroscopy with laser atomization and additional excitation

The laser-produced plume can additionally be excited by a *supplementary source*. In this *two-step procedure*, the radiance of the analysis lines can be increased and the line-to-background intensity ratios can be improved.

7.7.1 Spark cross-excitation. If the laser plume is allowed to enter a spark gap across which a medium voltage spark discharge takes place, additional atomization and excitation are possible. This is called *spark cross-excitation*. The spectra produced in this way are essentially those of a medium voltage spark. Triggering of the *auxiliary discharge* may be effected by the laser plume itself or by external means.

7.7.2 Electrodeless excitation. Additional excitation by means of an electrodeless discharge results only in the production of a spectrum originating from the material of the laser-produced plume and of the surrounding atmosphere. Contamination from auxiliary electrodes can thus be avoided.

Additional excitation can take place in an inductively-coupled high frequency discharge (ICP) or in a microwave induced plasma (MIP).

7.8 Analytical applications

Because lasers are non-electric excitation sources, they can be applied to the analysis of a very large variety of electrically conducting as well as non-conducting substances.

Analyses may be improved upon by selecting a suitable gas atmosphere or by applying *time* and/or *space-resolving techniques*. Special sample preparation techniques may also be useful.

7.8.1 Local analysis with lasers. The possibility of vaporizing material from a pre-determined small area of a sample makes laser atomization suitable for *laser local analysis* (see Note b).

As small crater dimensions are of primary importance for obtaining high spatial resolution on the sample, the laser output energy has to be small. This makes additional excitation almost obligatory.

7.8.2 Microanalysis with lasers. *Microanalysis* is possible if a *microsample* can first be concentrated into a small volume and positioned onto a suitable *support* in such a way that a *local analysis* can be carried out. Additional excitation is also necessary.

7.8.3 Macroanalysis with lasers. *Homogeneous samples* of almost any kind can be analysed by laser atomization. Rather high energy and high power single laser-shot operation should be used. This leads to the vaporization of sufficiently representative amounts of sample

Note a. Typical angles of practical divergence range from 2 to 4 mrad, typical focal lengths are $5 < f < 50$ mm, resulting in a minimum focal spot diameter of about 20 μm under typical operating conditions.

Note b. The use of the term *laser microprobe analysis* is discouraged.

material. Alternatively, scanning a part of the sample area by using a number of laser shots of lower energy and power may form the basis of *scanning laser analysis*. High precision may be obtained by the *super-position* of a sufficiently large number of *laser shots*. Direct excitation is sufficient for the determination of the major constituents, but additional excitation is preferable for the determination of trace elements.

8. LOW PRESSURE ELECTRICAL DISCHARGES (LPED) (see Note a)

Low pressure electrical discharge sources (see Note b) are radiation sources in which radiation is produced by electrical discharges in gases at low pressures, i.e. pressures from 10^{-2} to 10^3 Pa (see Note c). Atoms or molecules of the samples to be analysed are present or are introduced into the discharge. Usually one of the *noble gases* such as argon or neon is used, but mixtures of these gases and/or small quantities of *diatomic* or *polyatomic gases* may also *sustain a discharge*. Such a gas is called the carrier gas (see Note d).

Generally the sample is introduced by making it form a part of the cathode and, as a result of *ionic bombardment* and *atomic bombardment* of its surface, material is removed by the process of *cathodic sputtering* and/or thermal evaporation. This material enters the plasma and atoms are excited to produce characteristic radiation. If the sample is already in a *gaseous form*, it may be introduced into the discharge separately or mixed with the carrier gas.

8.1 Terms relating to the processes

The processes of LPED are explained in terms of a classical discharge chamber of *cylindrical shape* in which two plane electrodes of conductive materials are separated by a distance l (see Fig. 8.1). The pressure, voltage and current are three controllable and variable parameters which may be interdependent (*pressure-voltage-current relationship*).

The vessel may be sealed or it may be *flushed* (pumped) continuously (see Note e).

If the vessel is evacuated to high vacuum, the carrier gas allowed to fill it to a pre-determined low pressure and a voltage applied to the electrodes from a dc source, a current will flow. This current will initially be very small, but once the voltage reaches the breakdown voltage U_{br} , a higher current will flow between the anode and cathode, depending on the characteristics of the external circuit.

Simultaneously with the flow of current a *glow discharge* with specific characteristics will develop between the electrodes.

8.1.1 Radiation. The *spatial distribution of radiation* moving axially from the cathode towards the anode, has specific *luminosity* characteristics.

At the cathode a narrow dark space (*Aston Dark space*) (see Note f) is seen. A slightly *luminous layer* then occurs. This is called the *cathode glow*. Then a non-luminous volume known as the *cathode dark space* (or *Crookes (Hittonf) dark space*) is seen, which has a sharp distinction with the highly luminous *negative glow*. The negative glow tails off into the *Faraday dark space*, followed by another luminous region. This luminous region, called the *positive column*, may have several alternating or moving dark and luminous regions. Should the positive column have structure, these luminous and dark regions are called *striations*. Near the anode another dark space occurs (the *anode dark space*). The anode itself is usually covered with a slightly luminous sheath called the *anode glow*.

Note a. The term low pressure gas discharge (LPGD) is commonly used, but is not recommended because it could mean the discharge of a gas instead of an electrical discharge in a gas.

Note b. Source is the preferred term when a low pressure electrical discharge is used as the sampling source. The term *lamp* usually indicates a primary source that generally is permanently sealed, e.g. hollow cathode lamps for atomic absorption spectroscopy (see Terms, units and symbols for the description of processes common to all radiation sources and Part III, Section 3.2).

Note c. See Section 2.3.3, footnote.

Note d. Carrier gas is preferred to *fill gas* or *discharge gas*. The carrier gas is the main gas responsible for the conductance of the electrical current.

Note e. Continuously flushed systems, also known as *dynamic* or *pumped systems*, occur in those sources where the carrier gas is being replaced continuously and the flow controlled either by means of a *needle valve* or a *gas-restricting orifice*.

Note f. In all electrical terminology the dark spaces were named after early pioneers in research on electrical discharges.

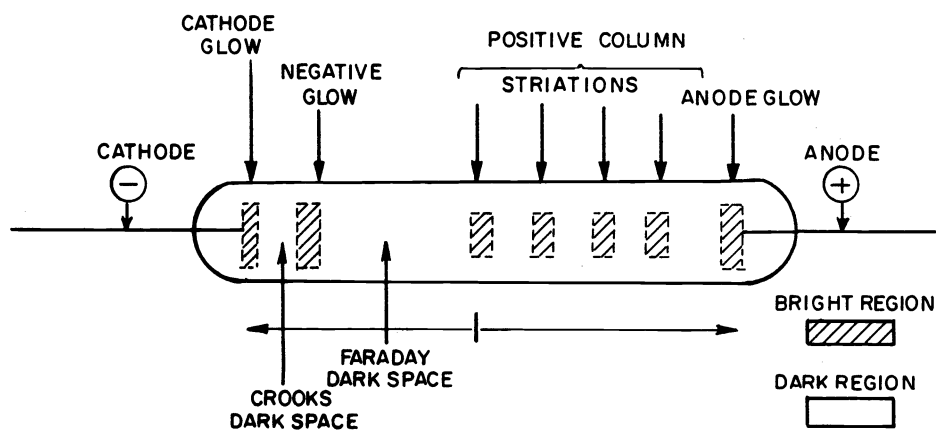


FIG. 8.1 : SCHEMATIC DIAGRAM OF A LOW PRESSURE ELECTRICAL DISCHARGE BETWEEN PLANE ELECTRODES

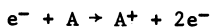
If the distance l , is changed while maintaining constant pressure and voltage, the axial lengths of the zones from the cathode to the positive column remain unaltered. The length of the positive column will change however.

If the anode is brought so close to the cathode that it enters the negative glow, the positive column may disappear completely, but all other parameters of the discharge remain almost the same.

The dimensions of the *negative zones* are dependent on the pressure, on the shape and area of the cathode and on the current.

Radiation processes in the chamber depend on the interaction of electrons with atoms and ions of the carrier gases or *analyte atoms* and *analyte ions*.

8.1.2 The discharge. At a voltage less than the breakdown voltage *residual ionization*, which is present in any gas (see Note a), results in a dark (non-luminous) *discharge*. At the breakdown voltage electrons are released from the cathode at their *ejection energy* (~ 1 eV). Due to this low energy these electrons are unable to transfer their energy on collision to the excitation of atoms (Aston dark space). As they are accelerated through the *cathode fall region*, the region of high *voltage gradient*, they gain enough energy to excite atoms by collision. This results in the luminous cathode glow. Other electrons acquire energies in excess of the excitation energy and are rapidly accelerated into the cathode (Crookes) dark space. Here they collide with neutral atoms of the carrier gas causing ionization.



Electron multiplication occurs, but the electron population consists of two distinct groups - *fast* and *slow electrons*. Fast electrons are those initiated at or near the cathode and slow electrons are those created by ionization processes.

Note a. This ionization may be caused by *interatomic collisions* or by *charged particles* due to the presence of *cosmic radiation*.

Slow electrons are only partially accelerated by the cathode fall potential and have a current-energy distribution sufficient to cause excitation of gas atoms in the highly luminous negative glow.

Fast electrons finally impart their energy through collisions of the first kind to cause ionization. Due to the *weak potential gradient* in the positive column they are then unable to achieve significant energy.

Partial acceleration and loss of energy through excitation, which may take place repeatedly, cause the striations in the positive column.

A *Penning gas mixture* consists of a rare gas containing impurity atoms possibly at very low concentrations. The impurity atoms have an ionization potential V_{ion} which is lower or equal to the metastable potential (V_{meta}) of the parent noble gas.

The *Penning effect* in a Penning gas mixture is the ionization by *charge transfer (charge exchange)* during collision between a metastable atom and a neutral atom which decreases the average energy to form an ion pair, e.g. $Cu + Ar_{meta} = Cu^+ + Ar + e^-$. In a glow discharge this results in an increase of the *ionization coefficient (Townsend first coefficient)*, a decrease in breakdown potential and a lowering of the cathode fall potential.

The *magnetic Penning effect* describes the increase of the *ionization probability* of a gas in a low pressure electrical discharge resulting from the helical (spiral) movement of electrons in a magnetic field placed normal to the anode-cathode electrical field.

8.1.3 Cathodic sputtering. Ions from the Crookes (Hittorf) dark space are accelerated towards the cathode. Most of the positive ions impinge upon the cathode and by *momentum transfer* impart their energy in a succession of *binary collisions* to atoms in a surface layer of the cathodic material. Other ions in their movement towards the cathode become neutralized, either by *free electrons* (see Note a) in the *space charge* near the cathode or by charge transfer with other atoms, but still maintain their momentum towards the cathode. A large portion of these atoms will impart their energy to the cathode. Some ions enter the *crystal lattice* by a process called *channelling*. In this way they penetrate relatively deeply into the *solid state crystal lattice*, releasing their energies within the crystal. Part of the energy released below the surface is transported to the topmost monolayer by way of *collisional chains* and gives rise to the ejection of atoms from the sites where the collision chains terminate. Ejected atoms include atoms of gases absorbed onto the surface of the cathode.

The process is called cathodic sputtering and is a non-thermal process in the sense that no statistical energy distribution exists in the crystal as a whole. The sputtered atoms may be in several stages of excitation and ionization. Further excitation by collisional processes and ionization by the Penning effect may take place.

The *sputtering yield* S_{sp} is the number of sputtered atoms released per incident ion. The *sputtering rate* q_{sp} is the amount of material sputtered per unit time.

8.1.4 Clean up. *Clean up* is a process caused by sputtering, *trapping* (or adsorbing) metallic atoms, gas atoms or molecules on the walls of the vessel or anode. This has the effect of reducing the gas pressure in sealed lamps, and may be useful for cleaning up or *gettering* unwanted gases.

8.2 Types of glow discharges

If the discharge vessel shown in Fig. 8.1 and referred to in this section is kept at a constant pressure of about 100 Pa and the applied voltage increased while the current is measured, the voltage-current relationship enables discharges with *specific discharge characteristics* to be identified, viz.

8.2.1 Normal glow discharge. The *normal glow discharge* is characterized by a constant burning voltage U_b for a range of current from $\sim 10^{-5}$ - $\sim 10^{-2}$ A. The current density (j) at any point at the cathode remains constant, but the cathode area is not fully covered by the glow (see Note b). As the current increases, more of the cathode becomes covered by the glow.

8.2.2 Abnormal glow discharge. After the negative glow fully covers the cathode area, a further increase of current results in a rise in the burning voltage and thus in the current density. This is an abnormal glow discharge. The voltage and current rise almost linearly

Note a. The process of deionization is also described as *electron capture*. Atoms created in this way carry no charge and are thus unaffected by space charges.

Note b. The onset of the normal discharge is highly dependent on the shape, the size and the material of the electrodes, the carrier gas and the impurity gases and to a lesser extent, on the shape of the containing vessel.

for a current change of $\sim 5 \times 10^{-3} - \sim 5 \times 10^{-1}$ A. After this current is reached the ion bombardment on the cathode is so energetic that thermal effects cause the discharge to change to an electric arc (see Section 3).

An *abnormal glow discharge* also results when the area of the cathode in the original normal discharge is reduced. This is called a *restricted glow discharge* or a *restricted abnormal glow discharge* (see Note a). This occurs for example when an *annular anode* which restricts the cathode area is placed within the cathode fall region of the discharge. *Differential pumping* of the gap to a higher vacuum than the discharge region, enlarges the cathode fall in that region.

8.2.3 Spray discharge. The *spray discharge* develops when a very thin insulator or *semi-conducting surface*, (e.g. an oxide layer) covers the cathode surface. A discharge without a dark space develops. The cathode fall is lower and a much higher voltage is required to sustain the discharge.

8.3 Terms and description of sources

8.3.1 Arc lamps. Certain spectral radiation sources in sealed vessels operate as arcs at low pressures. They are known as *arc lamps*. These arcs are sustained mainly as a result of *thermal processes* and are characterized by a cathode fall potential, much lower than a glow discharge, a thinner cathode glow region and high current densities. The spectrum emitted is due to the discharge gas and the cathode material. Atomic line spectra are dominated by transitions of the lower energy levels of neutral atoms.

Low pressure arc lamps ($10^2 - 10^5$ Pa) may have supplementary heating of the electrodes (see Note b) to *strike (initiate)* the arc and constricting devices to increase the *positive column current density* (j_a), resulting in increased *spectral radiance*.

Low pressure arcs usually require voltages between 300 and 600 V to strike, but the operating voltage falls once the arc is initiated.

Metal vapour arcs (metal vapour arc lamps) usually contain metals with low melting points and low ionization potentials. These include the alkali metals, some alkaline earths and metals such as mercury and cadmium. Mercury, having a high vapour pressure does not usually require supplementary heating of electrodes.

Radiation comes mainly from the arc column and the electrodes may be *screened off* by means of *shields*. The intensity of radiation may also be enhanced by restricting or confining the discharge.

High pressure arc lamps (>100 kPa) give broadened spectral lines, but have high intensities and heavy continuous backgrounds. Low pressure arc lamps give lower intensities, but have *narrower spectral lines*.

Metal vapour lamps usually operate on alternating current so that anode and cathode construction can be identical. Argon and neon are the most commonly used carrier gases.

Arc lamps are used as primary spectral radiation sources, e.g. for atomic absorption spectroscopy, calibration of spectrometers and spectrographs and for lighting purposes.

8.3.2 Geissler lamps. *Geissler lamps* are glow-discharge sources operating in the normal mode. They have a *capillary tube* between the annular anode and cathode to constrict the discharge of the positive column. These sources are either continually flushed or sealed. The excitation mechanisms of Geissler sources involve atoms being excited in the positive column. Constriction results in the availability of fast electrons to cause ionization of the carrier gas.

The main usage of these sources is for gas analysis. Impurity gases are *bled* into the vacuum system. Spectra are viewed *end-on* through the annular anode. Molecular spectra may also be measured if the capillary tube between the electrodes is not too narrow (see 8.2.2, footnote).

Note a. The restricted (abnormal) discharge should not be confused with the *constricted glow discharge*. In the constricted discharge the radius of the vessel between the anode and cathode is reduced to the order of one free *ionic path length*. Fast electrons from the cathode reach the anode and produce X-rays which together with fast positive ions release secondary electrons from the cathode.

Note b. Supplementary electrodes are often coated with a material or mixtures of materials having low *work function* (e.g. *tri-oxide* layers) to reduce the voltage at which the arc will strike.

8.3.3 Hollow cathode sources. The *hollow cathode source* (hollow cathode lamp (HCL) has a cylindrically shaped cathode, one end of which may be closed (see Note a).

The hollow cathode discharge may operate as an abnormal or a normal discharge, depending on the dimensions of the cathode, the carrier gas and the cathode material. More complex ion, electron and photon processes take place in the discharge than in a plane cathode glow discharge (see Section 8.3.4). This gives rise to profuse cathodic sputtering and high spectral line intensities. When used as sampling sources they are usually continually flushed to remove impurity gases generated from the sample in the cathode.

There are several theories to describe the sputtering and excitation processes in the hollow cathode discharge. The most generally accepted is that based on the *parallel plate cathode*.

In the *cold hollow cathode* source the cathode may be cooled externally (e.g. by air, water or liquid nitrogen).

The result is that thermal effects on the cathode surface are kept to a minimum even at high current densities. Most material is removed from the cathode by cathodic sputtering. High intensities and narrow spectral lines are obtained.

Hot hollow cathode sources are designed to enable the temperature of the cathode to rise appreciably and to cause material to be vaporized by thermal heating and sputtering. The temperature may be so high that the material in or on the cathode is liquid or molten. This material may be a sample introduced into the cathode.

Sealed hollow cathode lamps are used as primary sources for atomic absorption spectroscopy, because of their relatively intense radiation, narrow spectral lines and stable emission (when operated from current-stabilized supplies).

High intensity hollow cathodes (also called high brightness (see Note b)) are made by shielding the cathode lip or reducing its diameter and thus increasing the current and ion densities. This partly inhibits the emission of sputtered material and may result in a higher atomic line intensity per unit current.

With *boosted hollow cathodes* it is possible to increase the intensity of the *primary discharge* by introducing a *secondary discharge* via one or two *supplementary electrodes*. The electrodes may be placed so that the *supplementary discharge* (mainly its positive column) runs across the front of the cathode or through an open-ended cathode. The supplementary electrodes are made from or are coated with material having a low work function, so as to enable the supplementary discharge to be of lower voltage than the primary (glow) discharge. They may also be resistively heated. Supplementary discharges are generally aimed at enhancing the resonance spectral lines to higher intensities with reduced self-absorption effects.

Intensity modulated hollow cathode lamps are widely used in atomic absorption and atomic fluorescence spectroscopy.

Hollow cathode sources are used as sampling sources for the emission analysis of small quantities of materials or where material should not be lost, e.g. precious metals (gold) or radioactive materials. Elements with high excitation potentials may be excited in a hollow cathode discharge to give stable and narrow line spectra.

They have been used as high resolution sources, e.g. for *isotopic analysis*, vacuum ultraviolet studies, gas analysis and the analysis of non-metals. They are also well suited as sample sources for gas analysis.

8.3.4 Plane cathode glow-discharge sources. *Plane cathode glow-discharge sources* (see Note c) operate under abnormal glow-discharge conditions. The sample, which must have a plane surface, is made the cathode of the discharge. Restriction of the area to be sputtered can be achieved by several means, e.g. by using an annular anode (see Section 8.2.2) which faces the sample surface with such a small gap (100 - 200 μm), that no *short circuit discharge* can occur. Another device for restricting the discharge is a *restrictor plate* made from an insulating material and placed close to the cathode. With the first system, two vacuum pumps are used. One is a differential pump to evacuate the *gap (anode-gap)* and the other is used to evacuate the chamber and maintain the discharge pressure while the lamp is continually being flushed with fresh carrier gas. A single pump may also be used.

Note a. In a normal hollow cathode the ratio of length to diameter is >1 . *Open-ended hollow cathodes* have both ends open.

Note b. High brightness or hi-brightness are not recommended.

Note c. The Grimm glow-discharge source is an example of this type of source.

The discharge is essentially abnormal and voltages of up to 2 kV may be used. The gas flow flushes away *residual* or absorbed gases released from the cathode. The high operating voltages enable profuse sputtering to take place, even from poorly conductive materials.

Two of the three parameters, current, voltage and pressure generally are variable, while the third is kept constant.

Sputtering takes place in much the same way as in any glow discharge, except that the abnormal conditions allow higher voltages resulting in much more energetic sputtering and excitation. The flow of gas across the sample surface is radially away from the surface so that atomic species including gas released from the sample are swept away. This results in an *optically thin plasma* with little self-absorption of lines.

It is possible to introduce supplementary electrodes to cause a secondary discharge and by so doing, to enhance the sample spectra. This discharge may be modulated and, by using a *tuned amplifier measuring system*, only the enhanced radiation is measured. This lamp is called a *boosted output glow-discharge source*.

Glow discharges may be operated under the influence of an external magnetic field. Such *magnetic field glow-discharge* sources have either a permanent magnet or an electromagnet placed in such a way that ions and electrons are influenced by the magnetic field to achieve enhanced intensities and more profuse sputtering.

If in such a discharge source one or more supplementary electrodes are introduced to modify the discharge it is called a *boosted magnetic field glow discharge source*.

8.4 Analytical procedures

Low pressure electrical discharge sources are used for many different types of analysis, particularly metals. Because the discharge takes place in closed vessels, they are also well suited for the analysis of radioactive material.

The plane cathode glow-discharge source is well suited for the analysis of metals. It may also be used for the analysis of non-conducting powders by mixing them with conducting powders such as copper and silver and pressing a solid pellet from the mixture.

Solutions are generally not analysed directly by low pressure electrical discharge sources.

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