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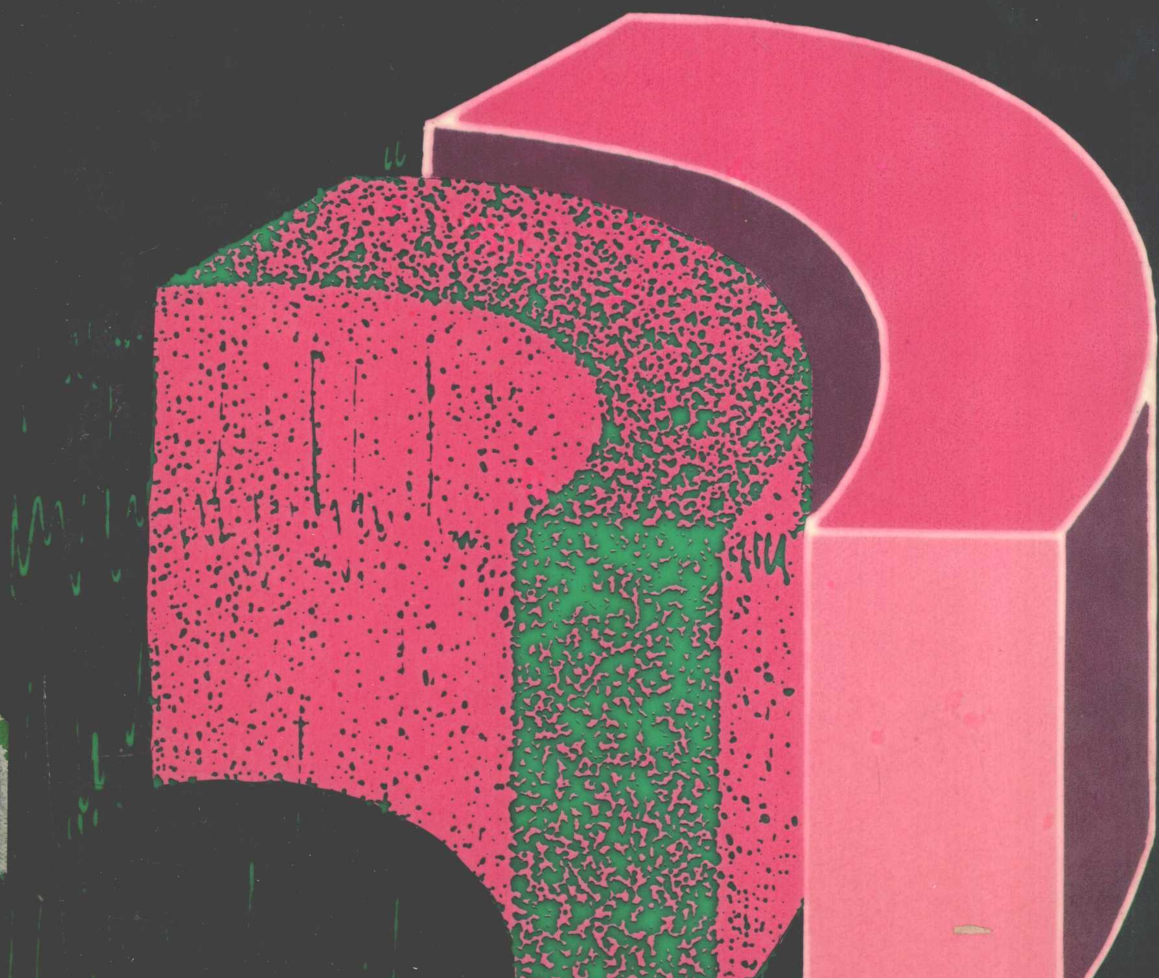
IMPROVED HOLLOW CATHODE LAMPS FOR ATOMIC SPECTROSCOPY

editor
SERGIO CAROLI



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IMPROVED HOLLOW CATHODE LAMPS FOR ATOMIC SPECTROSCOPY

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Foreword

Although the basic properties of hollow-cathode discharges have been known for about seventy years and a number of applications have been reported in the course of time, their use as spectroscopic radiation and excitation sources has been rather limited. Their use as primary sources for atomic-absorption and atomic-fluorescence spectroscopy is well known. The high efficiency of excitation, low background intensity and the narrow line-width of the spectral lines are promising properties for their application as excitation sources in atomic-emission spectroscopy, but they have never gained a popularity similar to that of arc and condensed-spark discharges, irrespective of the fact that, under favourable circumstances they are particularly well suited for trace analysis, analysis of small samples, determination of gases, and efficient excitation of elemental lines of high excitation potential.

The ever increasing need for more powerful analytical methods, especially in the field of simultaneous multielement trace determinations, has brought about a significant revival of interest in the use of such discharges. This has been further enhanced by the recognition that customary excitation sources, in which local thermal equilibrium prevails, cannot be further developed to such a degree as sources not in thermal equilibrium. If, in the latter case, means can be found to increase the power of detection for many kinds of application in the analysis of metals, non-metals and liquids, by an order of magnitude, much simpler analytical procedures can be developed, in which, for example, pre-enrichment can be avoided. If, at the same time, the precision and accuracy can be kept at a high level, as with some of the low-pressure discharges, it will be all the better. An answer to these requirements may be in many cases hollow-cathode discharges in their present, most modern form. It is indeed amazing, how much progress has recently been made by using pulse techniques, additional excitation with the help of electric and magnetic d.c. and RF fields, combination with thermal vaporization etc.

Therefore, a critical and comprehensive review of the current state of development, offered by experts in their respective fields and well chosen and matched by the editor of this book, is most welcome and deserves urgent attention by everybody concerned with improving old techniques and developing new methods in any branch of optical analytical spectroscopy. The editor has aimed at and succeeded in providing a wealth of information relevant to many kinds of application. The literature cited in the various articles is extracted from many sources which otherwise would be difficult to trace. It should be particularly helpful to those who might wish (and who should be encouraged) to enter this field by joining the research work in progress elsewhere.

I am sure that the book will serve its purpose well, and stimulate not only further work on hollow-cathode discharges, but perhaps also on plane-cathode discharges which in many aspects are quite similar, but in other aspects different, regarding the field of optimum application.

I congratulate the authors and editor for the result of their combined efforts and sincerely hope that excitation sources of such power, versatility and promise should definitely be made available to the general analytical problic by some enterprising instrument-making firms.

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Preface

Most of the popularity gained by the hollow-cathode discharge stems from its utilization in atomic-absorption spectrometry, the discovery and exceptional development of which was greatly influenced by the availability of this source of sharp and stable spectral lines. On the other hand, the remarkable properties of the hollow-cathode discharge have not yet been fully exploited. Discovered by Paschen at the beginning of this century, it is obviously far from being the latest novelty in the spectroscopist's shop. It is only over the last two decades, however, that it has really come of age, thus significantly contributing to the renaissance of emission spectroscopy.

Besides its innovative applications in fields such as laser technology and mass spectrometry, from a purely analytical point of view the hollow-cathode discharge could be used as a radiation source in atomic-emission spectroscopy, with direct profit from its characteristics, to a much wider extent than is actually the case. Its properties in fact make the hollow cathode something unique, equally suitable for the determination of trace, minor and major elements in a variety of matrices such as metals and alloys, electrically non-conducting powders, gaseous mixtures, and residues from evaporation of solutions.

Recently, renewed interest in this type of low-pressure discharge has prompted further research, particularly in order to increase the intensity of spectra emitted by the hollow cathode, since these are generally less intense than those obtainable with other more conventional sources.

This multi-authored book, written by well-known specialists, attempts to give a comprehensive account of the progress made so far in developing new versions of the hollow-cathode lamp to promote enhancement of radiation output. Such points as coupling with a magnetic field, superposition of microwave irradiation, separation of atomization and excitation processes in the so-called furnace atomic non-thermal excitation spectrometry system, boost by means of an auxiliary discharge, modifications in the hollow-cathode geometry (essentially by modifying its bottom or by reducing its diameter so as to operate in a microcavity), as well as variations in the operative mode of the lamp through a burst of radiofrequency energy or by application of a pulsed current, are thoroughly discussed and considered for their analytical potential in both emission and atomic-absorption spectroscopy.

The editor hopes that this book will not only outline the state-of-the-art in this field, but also mark future trends in stimulating fashion.

Finally, the editor wishes to acknowledge the professional assistance of Alessandro Alimonti, Oriano Falasca, Francesco Petrucci, Oreste Senofonte and Nicola Violante, whose co-operation and efforts greatly facilitated the compilation of this book. Gratitude is also expressed for Giovanni Briancesco's skilful technical assistance in the preparation of a large part of the drawings and schemes.

Sergio Caroli

1

Analytical potential of the microwave-coupled hollow-cathode discharge

S. Caroli, A. Alimonti and F. Petrucci

1.1 MICROWAVE-INDUCED PLASMAS

1.1.1 Introduction

There has been considerable renewed interest over the past few years in low-pressure microwave-supported (MW) discharges as a means for generating plasmas, which in turn are capable of exciting chemical species introduced into them. Not only atomic-absorption and fluorescence spectrometry (AAS and AAF, respectively), the analytical potentials of which were appreciably expanded by the availability of electrodeless discharge lamps, but also atomic-emission spectroscopy (AES) have taken advantage of the many attractive features shown by plasmas for elemental analysis. This is extensively documented in numerous scientific papers (see for instance an excellent review by Zander and Hieftje [1]).

The gases most often used for sutaining the plasma are He and Ar, which provide a medium energetic enough for the excitation of almost every element in the periodic table, including the halogens and many other non-metals that are difficult to determine. The higher ionization potential and energy of metastable helium species result in detection limits better than those obtained with argon, though the higher atomic weight of argon greatly simplifies the problem of nebulization of liquids. The relatively high degree of excitation peculiar to MW plasmas, the sharpness of the emitted spectral lines, together with reduced background emission, as well as the relatively low installation and running costs of MW generators (powers of 200 W are seldom exceeded and noble gas consumption is as a rule less than 1 litre/min), constitute important properties, the exploitation of which is still far from complete.

On the other hand, sample introduction procedures are not yet entirely satisfactory, the plasmas are not very stable to liquid aerosols or sample injection, and the atomization step also remains a critical point simply as a consequence of the low power available. Matrix interferences are often severe and further limit the wider applicability of the MW discharge radiation source in AES. Notwithstanding, the significant advances reported in the recent past (see e.g. [2] and [3]), show that the limitations may be circumvented, at least to some extent, for example by combination of the MW radiation source with other excitation devices less prone to the disadvantages listed above. In this respect the MW-coupled hollow-cathode discharge (MW-HCD) is of promise for various analytical purposes. This will be demonstrated in more detail after some general considerations on the mechanism of MW plasma breakdown and stabilization.

1.1.2 Microwave plasma formation

The application of an electric field at a frequency of 10–2500 MHz to a noble gas, ordinarily contained in a closed tube, generates a plasma with characteristics that may vary considerably with the experimental conditions. The MW frequency most commonly adopted is 2450 MHz, because several power generators commercially available as medical diathermy units operate at this frequency, in accordance with international regulations. The ultimate consequence of energy transfer from the applied electric field to the electrons in the plasma is excitation and ionization of the gas atoms through their collisions.

The breakdown and stabilization of the MW plasma are conditioned by an appropriate choice of noble gas pressure (p), and the maximum amplitude (E_o) and frequency (ω) of the electric field. At constant E_o and ω, the number of collisions undergone by an electron increases with p until the gas particle density becomes too high to allow the attainment of sufficient electron momentum for the ionization of an atom. Ignition of the plasma, on the other hand, takes place at too low values of p since adequate power (P) cannot be transferred from the field. For one electron the power absorbed from the field is given by Eq. (1.1) [4]:

$$P = \frac{e^2 E_o^2}{2m(f^2 + \omega^2)} \tag{1.1}$$

where e is the charge and m the mass of the electron, and f the frequency of collision.

The ionization of the gas atoms through collisions with electrons continues until a dynamic equilibrium state is reached; this is characterized by the partition of the energy supplied by the MW field, between electrons and ions. Balance between the energy supplied to the plasma and that dissipated from it through, for example, inelastic collisions and impacts on the tube walls, is essential for obtaining a steady-state plasma.

The pressure of the supporting gas determines whether the plasma is in local thermodynamic equilibrium (LTE) or not. It can be assumed in fact that plasmas at atmospheric pressure are in LTE as a consequence of the high particle density.

In this instance both the Boltzmann equation describing the population of a given atomic level and the Saha equation accounting for the ionization equilibrium are valid, and the thermodynamic temperature is therefore sufficient to characterize the plasma. There is no need to examine in detail the processes occurring at microscopic level, to exploit them analytically. A much more complex situation arises when the gas pressure is decreased to some hundred Pa or even less. Reduction of the particle density changes the overall character of the deactivation mechanism of excited states from collisional to radiational. As a consequence of the smaller number of collisions per unit time a significant portion of the energy transmitted to the plasma is converted into electron motion and excitation of electronic states. If the plasma is assumed to be optically thin, as is often the case, energy is lost mainly by emission of photons. This means that the plasma can no longer be described as being in LTE and the interpretation of the microscopic processes resulting in excitation requires the determination of quantities such as spectroscopic temperature, electron temperature and concentration, and concentration of metastable noble gas species [5].

There is strong experimental evidence that, under such conditions, two distinct groups of electrons exist [5-7] – one with low density and high energy and the other with high density and low energy. Whereas the electron temperature is essentially determined by the first group, the second group is considerably more abundant, constituting the major part of the overall electron concentration. The fraction of high-velocity electrons responsible for the ionization process is, however, large enough to counterbalance the loss of ions caused by recombination and ambipolar diffusion to the walls. The electron temperature required to sustain the plasma is, as a consequence, directly related to the ionization potential of the noble gas employed to generate the plasma. For argon and helium the electron temperatures span the ranges of 26000-53000 and 50000-130000 K, respectively, depending on the operating pressure and the applied power [5,8,9].

1.2 METHOD FUNDAMENTALS

1.2.1 Characteristics and drawbacks of the hollow-cathode discharge

Among sputtering sources, the HCD has gained wide popularity not only because of its fundamental role in AAS, but also as a powerful excitation device directly applicable to AES. From this point of view it is particularly worth mentioning the stability and reproducibility of the emitted spectra, the lines of which are notably sharp and narrow, as well as the low effects of matrix composition, the limited spectral interferences, and reduced background intensity [10,11]. The versatility of the HCD for analytical purposes makes it equally suitable for the determination of trace, minor and major elements in dry residues from solution [12,13], metal alloys [14], electrically non-conducting powders [15] and gaseous mixtures [16]. The pretreatment of samples that is almost always necessary and the inadequacy of HCD in the direct analysis of liquids (injection into the discharge zone perturbs plasma stability) to a certain extent limit a more generalized use of this source. Furthermore, in spite of the prolonged residence time of analyte atoms (depending on the particular cathode configuration) and the absence of LTE (which enhances the signal-to-background ratio by two or three orders of magnitude with respect to sources in LTE [17]), the absolute emission intensity as well as the detection power of the HCD cannot be considered entirely adequate for trace analysis. In order to maintain its advantages, this discharge must be operated at relatively low direct currents. An excessive increase in current would lead to broadening (by self-absorption) and even self-reversal of the atomic resonance lines.

1.2.2 Main physical processes in the hollow-cathode discharge

It can be stated that HCD and MW plasmas share some important features, thus justifying the assumption that their superposition could lead to a sort of mutual reinforcement. The question is whether this can occur without compromising any of their more attractive properties. Both discharges are characterized by a marked insensitivity of the spectroscopic temperature to working conditions and, just as in the MW plasma, at least two groups of electrons with very different energies and densities can be identified in the HCD. A unique feature of the HCD, however, is the effect of the cathode geometry, in that a fraction of the electrons released from the cavity surface and accelerated across the dark space can undergo a limited number of collisions with plasma particles, reverse direction and repeatedly cross the glow region. This possibility of making multiple passages greatly increases the ion- and photon-producing effectiveness of these electrons, with energies up to a few tens of eV, which form part of the non-Maxwellian energy distribution [11,18]. The presence of a group of very fast electrons which make very few or no collisions is also predicted and agrees with the high discharge currents found in an HCD.

Figure 1.1 illustrates schematically the zones formed within the cathode cavity when the discharge is operated.

The atomization and excitation mechanism characteristic of the HCD can be broken into the following main steps: ionization of the carrier gas under the influence of the applied electric field; impact of the ions thus generated, as well as of metastable and neutral species, on the sample, where they partly dissipate their kinetic energy by extracting atoms or clusters of atoms from its surface; and transport into the plasma with subsequent excitation. The amount of sputtered material Q has been found [19] to obey Eq. (1.2):

$$Q = \frac{CL^2 t}{hFp} \tag{1.2}$$

where L is the applied power, t the sputtering time, h the depth of the cavity, F the frontal surface area of the cathode, p the gas pressure, and C a constant depending only on the carrier gas and the nature of the cathode material. The role of the photons originating in the dark space or in the glow region in the generation of electrons is still open to debate. The nature and extent of the phenomena occurring in the HCD plasma depend strongly on the working parameters and also on the type of rare gas used to sustain the discharge. It can