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Lightsources: ionization and excitation of atoms

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Different types of light sources for the production of emission spectra as well as background continua for absorption spectroscopy are reviewed. The mechanisms for ionization and excitation, which depend to a large extent on the type of source, are discussed. Advantages and disadvantages of these light sources are compared.

1. Introduction

The purpose of this paper is to review different types of lightsources for spectroscopic purposes. The use of lasers will only be included as a high power source of light, and not as a source of coherent radiation. Lightsources for emission spectroscopy fall broadly into six classes:

- flames,
- electrodeless discharges,
- arcs,
- hollow cathode discharges, continuous and pulsed,
- sparks,
- laser produced plasmas.

As sources of a background continuum for absorption spectroscopy we can distinguish:

- capillary discharges,
- BRV source,
- laser produced plasmas,
- synchrotron radiation.

These lists should not be considered exhaustive. Other devices have been designed or applied as lightsources, but have, in general, never found widespread application.

2. Flame

Flames are being used as an absorption medium in analytical atomic absorption spectroscopy. These devices allow a carefully controlled introduction of materials in atomized form for quantitative determination of trace elements. They play nowadays an important role in analytical emission spectroscopy.

3. Electrodelless discharge

This lightsource consists, in its most common form, of a small quartz tube, usually containing a rare gas at low pressure and a small amount of the element to be studied. This tube is placed in a microwave cavity. Excitation produces the first and second spectrum of the element in question besides, of course, the spectrum of the rare gas. It is a fairly common source for production of a thorium-reference spectrum in the visible and ultraviolet region.

There are also variants developed for use in the vacuum ultraviolet [1], where an open connection between the excited plasma and the spectrograph is needed and a continuous gas flow is necessary. Often the tube passes in the latter case through the walls of the microwave cavity, while in the former the much smaller and sealed-off tube is wholly contained inside the cavity and light is emitted through a small hole in the cavity wall.

In using an electrodeless discharge lamp one has to be aware of anomalous spatial intensity distributions in the bulb, which can be very different for different lamps as well as for different elements between the buffer gas and the metal, or even for different lines originating from the same element and ionization state (see Fig. 1).

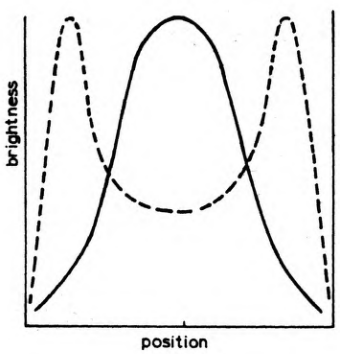

Fig. 1. Intensity distribution in an electrodeless discharge. Solid line – buffer gas, dashed line – metal

Especially an intensity distribution with more than one maximum can cause systematic errors in wavelength calculations due to abnormal illumination of the dispersive element in the spectrograph.

4. Electric arc

This is maybe the most classical light source for spectroscopic purposes after the sun and the flame. In this discussion it is the first example of an electrical discharge used as a lightsource. Many very common and also modern devices depend on this mechanism. They range from street lighting and illumination systems for IC-production to spectral lamps and gas lasers. As mentioned before I will not treat lasers in detail.

We will, at this point, mention a few important facts about gas discharges. In

general, we can distinguish different regions in a gaseous (glow) discharge (see Fig. 2): the Crookes dark space, the negative glow, the Faraday dark space and the positive column, each with its characteristic properties.

In the Crookes dark space there is a high net positive space charge and nearly the whole voltage drop in the discharge occurs in this area. The electric field falls linearly

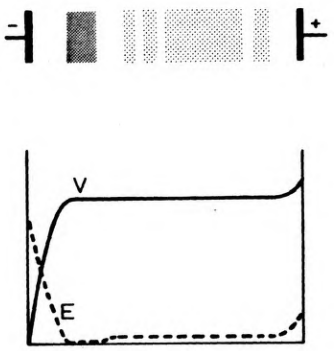

Fig. 2. Glow discharge. The dark grey areas are the negative glow, the light grey — the positive column. The blank areas are the dark spaces. The second figure shows that the negative glow is fieldfree, and the positive column — nearly. In the hollow cathode (lower picture) the cathode dark space is much smaller and the electric field is limited to this part

from the cathode till the edge of the negative glow and there is a highly directed movement of the electrons away from the cathode.

In the negative glow the electric field is very low. We have here a plasma consisting of both ions and electrons at high density. Electrons are injected in this region with an energy approximately equal to the cathode fall and they are in part slowed down by collisions to a thermal energy distribution. The light emitted originates from both ions and neutral atoms (resonance lines!).

In the Faraday dark space the field rises slightly higher again, while in the positive column the field remains constant, which means that also here we have a natural plasma as in the negative glow. In this case, however, at relatively low temperature. We see spectral lines originating from states of very low energy.

The length of the Crookes dark space and of the negative glow depends strongly on the voltage across the discharge and the gas pressure. The remaining space in the discharge is occupied by the Faraday dark space and the positive column. These can have very small dimensions.

5. DC hollow cathode discharge

This is one of the most interesting and versatile spectroscopical lightsources. It has found a wide-spread use in analytical atomic absorption spectroscopy (AAS), [2],

and is also used in the construction of metal vapour lasers. In atomic emission spectroscopy its most important features are its brightness and the sharpness of the spectral lines produced. The latter is one of the reasons for its application in hyperfine structure measurements.

Although the hollow cathode discharge (HCD) has been used for more than half of a century since PASCHEN [3] in 1916 described it for the first time (see Fig. 3), its

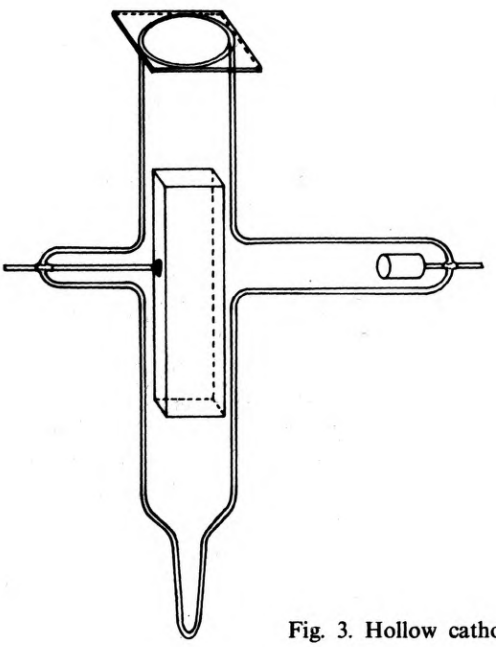

Fig. 3. Hollow cathode design of Paschen (after [3])

characteristics are not completaly understood yet. We will briefly review the following properties of the HCD:

- discharge characteristics: current distribution, voltage current characteristics, pressure dependencies,
- electron energies and densities,
- atom and ion densities and energy distributions,
- ionization,
- sputtering,
- geometrical properties,
- excitation,
- spectral line intensities and intensity distributions.

The transition from a plane cathode geometry to a hollow one has a pronounced effect on the discharge: at a particular pressure the negative glow is contained wholly in the hollow and fills it completely. The intensity of the spectral lines increases appreciably and at the same time they become sharper. The former can be explained from the fact that we have an enclosed discharge, which means that we make very efficient use of the available electrons for ionization and exciation. The latter is due

to the fact that we have a natural plasma enclosed in a conducting box. Furthermore, we have also a high "photon efficiency", which means that the chance that photons escape through the opening of the hollow cathode is small and they are mostly absorbed by either the plasma or the cathode wall, in which case their energy, to a large extent, is used for excitation, ionization and/or even sputtering. Two important geometrical parameters, influencing the behaviour of the discharge, are the areas of the cathode wall and the opening in the cathode.

A characteristic difference between the HCD and a discharge between plane electrodes is, that in a HCD the dark space is only a few free pathlengths long. If the buffer gas pressure is too low the dark space becomes too large and the negative glow is pushed out of the hollow. If the pressure becomes too high the electrons can not reach the opposite dark space, where they normally would be reflected by the electric field. In both cases the hollow cathode effect will disappear. In the dark space, near the cathode, positive ions will feel the full potential and will impinge on the cathode with maximum energy. As a result of this impact they will sputter electrons and atoms from the cathode material. Atoms and electrons will move to the glow region and recombination between ions and electrons will occur there, giving rise to emission of spectral lines. The life time of ions in the glow can be rather long. In a normal glow discharge the current density distribution which gives the lowest energy will be selected. This depends on the processes of electron production, ionization, recombination and diffusion. The outcome will be that the used cathode area will be optimized. An increase or decrease of the current through the discharge will increase or decrease the area used. If we increase the current beyond the point where the whole cathode area is used, we will get an abnormal glow discharge. Here, the voltage drop across the discharge will increase, because optimization of the used cathode area is no longer possible. One of the results will be an increase in ionization.

If we consider the atomic properties of the HCD we can be guided by two principles. The first is the similarity principle which states that the voltage across the discharge is a function of pd, the product of the pressure and the distance between the electrodes, while j/p^2 is constant when the potential is constant, j being the current density. The second is the economy principle: the dark space is just large enough to generate enough ions, photons or metastables to produce one new electron for each one that leaves it [4].

The electron energy distribution in a HCD is far from Maxwellian. There is a large fraction of slow electrons, but the distribution peaks again for fast electrons (see Fig. 4), [5]. The latter peak increases with current and decreases with pressure. The spatial electron distribution (see Fig. 5) is measured under different circumstances [6], and fairly well known. In the negative glow the order of magnitude of the electron densities is about 10^{13} electrons/cm^3, in the positive column it is roughly one fifth of this value.

The ion densities are related to the electron densities – in the negative glow we have a natural plasma – but with increasing current or pressure the maximum of the density moves outward so we get an annular distribution.

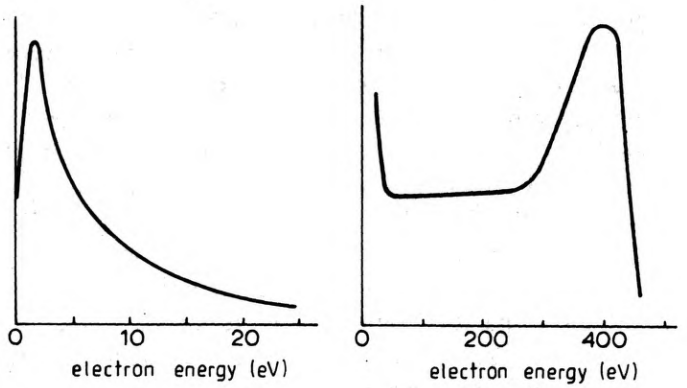

Fig. 4. Electron energy distribution in a HCD (after [5])

In atomic emission spectroscopy the intensity distribution is very important. It influences the amount of light we can usefully collect into our spectrograph – an annular distribution, which can appear, can cause problems – but it can also provide information about excitation or ionization. We see also that with increasing current or pressure the maximum intensity shifts outwards. Here, we encounter several

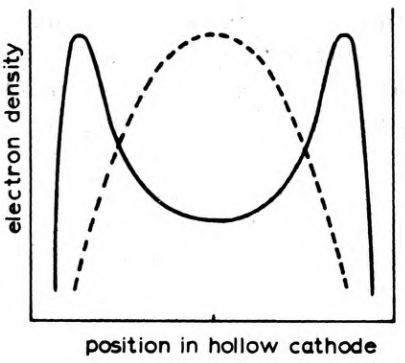

Fig. 5. Radial electron density distributions in a HCD (after [6]). Solid line – at 0.7 Torr, dashed line – at 0.2 Torr

pitfalls in the interpretation of spectroscopic data. One neglects ofter the geometry effects or integrates them, in fact, in a rather undefined way. Or, one measures the light from the negative glow through the positive column, which itself emits and absorbs light, but mainly of neutrals. This can lead to large errors, especially if one uses a short hollow cathode, while the distance to the anode is large and the positive column is long. Furthermore it is very difficult to extract information about the ion/atom ratio from emission spectroscopy, excitation processes influence the populations of levels in different ionization stages differently. And the density of atoms of the buffergas in the groundstate can not be easily measured using absorption spectroscopy, because the resonance lines of the rare gases are far down in the VUV.

The following processes play an important role in ionization:

– collisions with fast electrons,
– Penning ionization and related processes,
– recombination (which has a negative effect).

When ionization by electron impact is a one step process then the intensity of the spectral lines involved is proportional to the discharge current, while if two step processes dominate, e.g., using metastable buffergas atoms as intermediate, the intensity changes proportionally to i^2. In practice one finds values between 1 and 2 for the exponent [12].

Excitation is caused by:

– electron impact,
– charge exchange,
– recombination.

In general, the excitation is from the ground state of ion or atom. The dependence of spectral line intensities on electron collisions shows a behaviour corresponding to that for ionization.

Atoms of the cathode material enter the discharge through a mechanism called sputtering. This is no thermal effect, evaporation does not contribute to this process. There is, however, a temperature effect. The free path length in the discharge depends on the temperature and this affects the size of the cathode dark space. Atoms of the cathode wall are released as the result of impact of ions and atoms, mainly accelerated while traversing the dark space. There is a threshold voltage for this process, which for instance is the reason that Al is not sputtered in a normal glow discharge. The increasing of the current to change the discharge for an abnormal one can increase the voltage to a value, where Al is also sputtered. The mass ratio of buffergas as well as metal atoms and the structure of the cathode surface also influence the sputtering rate. A rough surface is better than a smooth one. A pressure dependence of the sputtering rate, however, seems not to exist. Both atoms and ions can be released mainly in their ground states. Measurements have shown that the sputtering rate varies as $i^{2.5}$, as does the absorption rate. A somewhat unusual way of using a hollow cathode discharge is, as a source of atoms rather than photons, to provide a medium for absorption spectroscopy. Special types of hollow cathodes have been constructed with a small hole in the bottom, where the atoms produced are ejected in a plume of rather high density through a small hole [7].

Several authors have tried to calculate density distributions for neutrals and ions [8], [9]. The procedure used is briefly as follows: one sets up diffusion and rate equations for the processes involved, and source functions for the species to be studied. Boundary conditions are established at the wall of the hollow cathode, and then one has to solve the equations. Usually, this is done for a cathode configuration, consisting of two infinite plane and parallel plates as cathode, contrary to the more usual experimental setup which consists of a cylindrical hollow cathode. The experimental results are in general agreement with these calculations, but nobody has ever observed the spatial distributions of the buffergas atoms in the ground states due to the fact that the resonance lines of the rare gases are in the VUV wavelength range, which makes the required absorption measurements difficult.

As mentioned before, the geometry of the HCD has an important effect on the characteristics of the discharge. The area of the cathode determines in conjunction with the current the type of electrical discharge. But also, the distribution of the metal atoms is clearly affected by geometrical parameters such as bore diameter and length, and the relative area of the opening. Very little systematic reserch has been done up to now to study these effects.

Different designs of hollow cathodes have been used. An example is given in Fig. 6. Liquid nitrogen cooled HCDs are used to minimize linewidths and lineshifts. In our laboratory we often use a very simple design, based on standard vacuum connections, which simplifies dismantling and replacement [10], (Fig. 7). Also

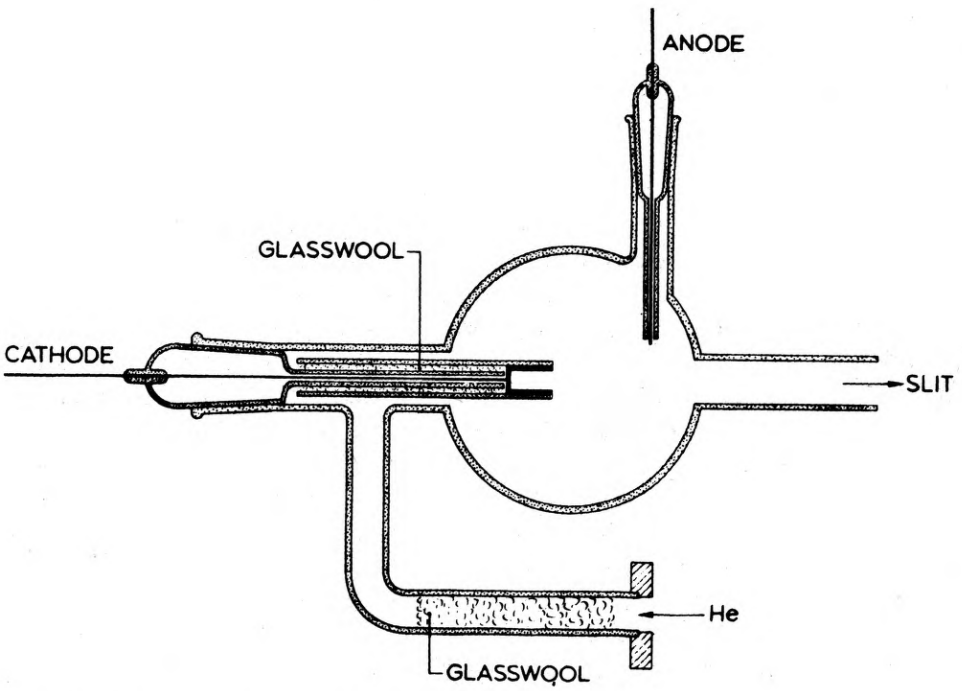

Fig. 6. Hollow cathode for pulsed discharges (after [13])

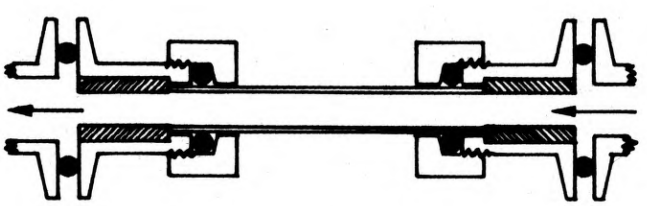

Fig. 7. Hollow cathode (after [10]). The anode and cathode are inserts (hatched), isolated by the glass tube between them. As anode is usually used Al, the cathode is of the metal under study. The standard vacuum connections make connections to a vacuum spectrograph and changes in the setup easily. A flow of the buffergas prevents accumulation of contaminations

combination of a HCD with a microwave discharge has been studied. Different designs are used, too, in metal vapour lasers, including hollow anode cathodes were a cage-like structure is placed inside the cathode as an anode [11]. Good reviews of hollow cathode discharges are given by PILLOW [12] and in paper [2].

6. Pulsed hollow cathode discharge

In a DC hollow cathode the current is limited to a few amperes and is usually below 1 A. This implies that only the first and second spectrum are excited, and sometimes a few lines of the third. To produce spectral lines of higher ionization stages one has to use much larger currents – of the order of hundreds or even thousands of Amperes – which for practical reasons is possible only in a pulsed mode. If we try to do this with a DC discharge, this leads, in general, to destruction of the source because the excess energy will damage the source. Only a very small fraction of the total energy supplied is used to produce photons and almost all the energy is dissipated as heat. A pulsed discharge has the advantage of releasing a large amount of energy in a short time, which can lead to a high ionization stage, while at the same time a low duty cycle prevents overheating. This source has been applied succesfully to excite spectra as highly ionized as Ta V [13]. In the afterglow, electron capture becomes an important process, and successively lower ionization stages are seen. To control the ionization stage as well as possible, one should keep the current constant during a time long compared with the atomic processes. In this way, selection of the desired degree of ionization is possible. This is especially necessary if one wants to study the pulse HCD. A damped discharge, combined with time integrated registration, can easily lead to results which are too complicated to be useful. Self absorption can be important especially for resonant lines. The pulse length should also be sufficient for the metal atoms and ions to diffuse through the cathode space. Experiments have shown [14] that it takes 50–75 μs for metal atoms to reach the centre of a 4 mm bore. A combination of a DC and a pulsed discharge seems to influence the excitation of the ionization stage studied [10], [15], both with high (> 100 A) and low (< 10 A) current in the pulse. Electron and ion densities are about 10^{15} particles/cm^{-3} in a pulsed HCD.

7. Sparks

The pulsed hollow cathode was the first example of a pulsed light source. Different types of sparks are also used for the production of spectra of ions and, in fact, sparks are one of the oldest and most common pulsed light sources. The fact that the spectrum of the ion is called spark spectrum illustrates this. In its simplest form a spark discharge is simply made by discharging a capacitor across a gap between two electrodes. The oldest type is the spark at atmospheric pressure [16]. When a sufficiently high voltage is applied to the spark gap – at first an electron avalanche is obtained. This starts the formation of streamers from the electrode surface followed

by the formation of a discharge channel. Then, the energy stored in the capacitor is transferred to the spark gap. The whole process is a kind of explosion, and ionization is to a large extent caused by a shockwave. Electron capture causes decreasing stages of ionization to appear successively in time (see Fig. 8).

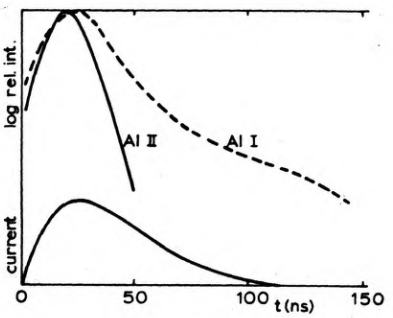

Fig. 8. Time dependence of intensity of atomic and ionic lines in a spark (after [16])

8. Sliding spark

An atmospheric spark is nowadays not often used as a spectroscopic lightsource. More convenient sources have been developed. Most of them are derivatives of the open spark (which will be described in more detail later), where a high voltage is applied to a high vacuum gap between two electrodes. A very common source, nowadays, to produce emission spectra of multiply ionized atoms is – besides the pulsed hollow cathode discharge – the so-called sliding spark [17]. In this source, the spark discharge slides or creeps along the surface of an insulator between the two electrodes. In this way, the breakdown voltage is much lower than with an open spark in high vacuum due to the fact that previous discharges have left some sputtered material on the surface of the insulator, which evaporates when the voltage is applied. The plasma formed in this way is sufficient to allow a spark discharge to start in the free space between the electrodes. BOCKASTEN [18] improved this source by using a cylindrical insulator where the discharge is kept enclosed inside the cylinder (see Fig. 9). A small hole in the wall allows light from the spark to be

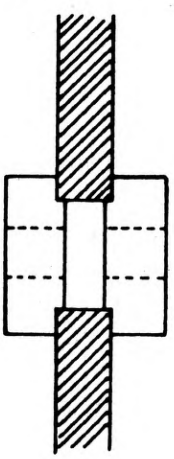

Fig. 9. Sliding spark. The discharges take place between the two electrodes (hatched), inside the insulator

registrated with a spectrograph. This source allows a higher ionization stage than the pulsed hollow cathode (up to ten times ionized as compared to four times ionized with the PHC), and also allows access to wavelengths below 500 Å where even the most transparant buffergas (helium) starts to absorb light, but the lines are not so sharp as in the hollow cathode discharge.

9. Triggered sparks

Another way of operating a spark at a moderately low voltage, typically a few kV compared with the 60 kV which is necessary in an average high voltage high vacuum spark, is to provide a starting mechanism by a low power discharge which produces some ions and electrons in the spark gap, or to inject in some other way sufficient particles in the gap to start the discharge. Several types have been developed in the past, each with its own particular advantages and disadvantages.

A very common one is a design where one of the electrodes is replaced by a sliding spark as depicted in Fig. 10. The sliding spark produces enough ions and

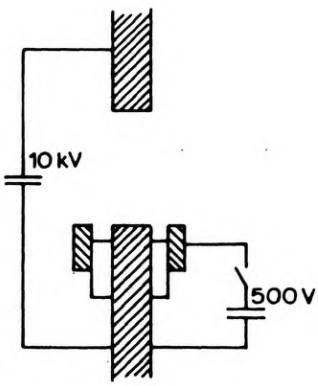

Fig. 10. Three-electrode spark triggered by a sliding spark

electrons to trigger the main discharge. This is used at a higher voltage (10–20 kV) than the sliding spark and allows higher ionization stages. A variation on this three electrode discharge is the use of a very low power, high voltage discharge between one of the main electrodes, and an auxiliary electrode. A car ignition coil can provide this trigger spark. In our laboratory we have tried a design (see Fig. 11) where a nearly enclosed sliding spark is used as a "plasma gun" to inject a plasma between the main electrodes, without any galvanic connection between the two discharge circuits. Both the spactrum of the metal of the main electrodes and of the metal of the sliding spark can be studied. The latter allows us to produce a spectrum of an element which has a relatively low melting point and which would be completaly evaporated after a few sparks in the main discharge. In this case we choose Al for the main electrodes, which produces a very well known and not dense spectrum. Electron and ion densities can vary several ordes of magnitude around 10^{20} cm^{-3}.

Another type of lightsource which shows some resemblance to this design is the gas-injection source [19]. We developed it in our laboratory to produce spectra of

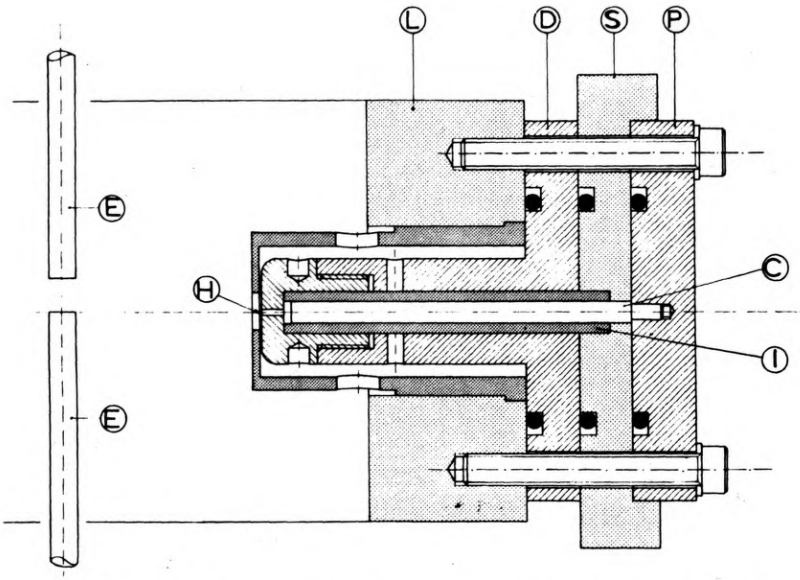

Fig. 11. "Plasma fun" for triggering a high vacuum spark. E – electrodes high vacuum spark, H – hole for ejecting plasma, L – wall of light sources chamber, D – outer electrode of sliding spark, C – inner electrode, I – insulator, S – insulator separating the electrodes, P – base plate for mounting the inner electrode

multiply ionized rare gas atoms (see Fig. 12). In this source a small amount of the rare gas under study is injected through a bore in one of the electrodes, to provide, at the same time, the gas in the discharge and to trigger the spark. This overcomes the problem that it is not possible to contain a rare gas in one of the electrodes. This

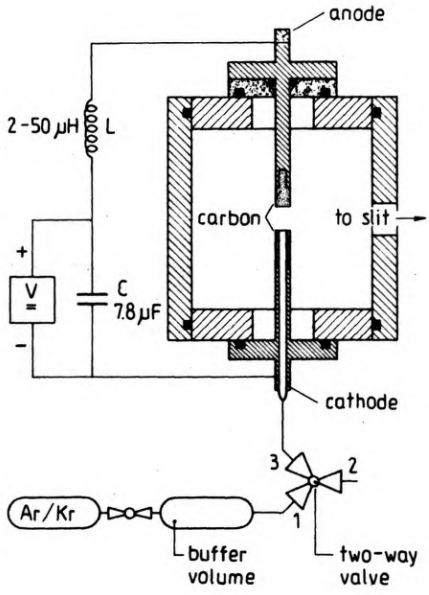

Fig. 12. Gas injection source (after [19])

source is also much simpler and easier to handle than the theta-pinch, which often was used for this purpose. In the latter design a very high pulsed magnetic field along a capillary filled with the rare gas at low pressure is used to compress and ionize the gas.

Another possibility is to focus a high power laser onto one of the electrodes to evaporate some of the metal to ignite the discharge. A laser-produced plasma as a lightsource in its own right will be treated later.

10. Open spark

For higher ionization stages than a few times ionized, one has to use a spark in high vacuum. This device has been studied in great detali by MANDELSTAM and coworkers [20]. To ignite a spark in a vacuum below 10^{-4} mbar a voltage of about 60 kV is necessary.

As in the case of the atmospheric spark, the mechanism of spark-channel formation is an explosion. This leads to the production of very highly ionized atoms [21] and the high vacuum high voltage source is very often applied to the analysis of the fifteenth to twentyfifth spectrum.

A cylindrical shockwave is formed, which at the same time causes the ionization and excitation, and moves the ionization zone outwards. Fast non-equilibrium electrons play no important role in these processes. The discharge channel remains small due to the short pulse length. The density is low, ion and electron density are about 10^{-17} per cm^{-3}. The electron, excitation and ionization temperature is about 40000 K. The conditions are close enough to local thermal equilibrium to allow the application of Saha's law [20] to describe the ionization degree. The stationary state for excitation is reached is about 10^{-10} s, while for ionization the time scale is about 10^{-7} s. The potential across the discharge channel drops after breakdown rapidly to about 100 V, so the high voltage is not a necessary condition for the spark discharge but only for the ignition. During the expansion of the spark channel the excitation energy as well as line broadening and lineshift decrease continuously.

11. Pulse forming networks

If one wants to control the discharge conditions one has to keep in mind that most of the atomic processes relevant for us take place at a time scale of about 10^{-7} s[20].

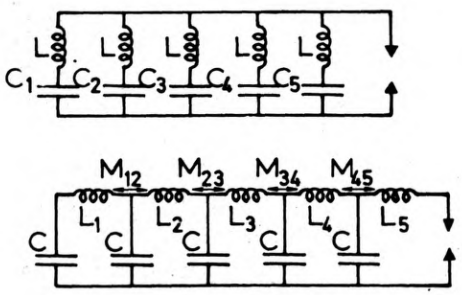

Fig. 13. Two types of pulse forming networks (after [13])

Diffusion of sputtered material in a HCD can take several tens of microseconds [14]. This means that it is useful to have a stable discharge during a time of 10 μs or longer. In this way, one is as close to LTE as possible. This can be achieved by a circuit as depicted in Fig. 13. With such a device the current is constant within 5% during more than 90% of the pulse time. Of course, more strict requirements are possible but require much more effort.

12. Laser produced plasmas

If the beam of a high power pulsed laser is focussed onto a surface a high density high temperature plasma is formed [22]. The shockwave induced by the primary plasma, produced by the laser pulse, plays an important role in forming the luminous secondary plasma. The emitted radiation originates from highly ionized atoms. Different regions of the plasma give rise to different ionization stages. Ionization stages of, e.g., Fe XX and higher are realized. This gives rise to spectra in the XUV (below 500 Å) and the high temperature and high velocity of the expanding plasma are causes of linebroadening which could present problems for high accuracy wavelength determinations. Typical lasers used for these experiments are a Nd-glass laser with a pulse energy of 30 J in a time of about 30 ns. Also ruby lasers (typically emitting 1–10 J) and Nd:YAG lasers (0.1–1 J) are used for this purpose. The latter offers a higher repetition frequency, but a lower pulse energy than the former. Frequency doubling allows a more efficient use of the energy of a Nd:YAG laser than it is possible with a laser in the red. The electron and ion densities are of the order of 10^{21}, resp. 10^{20} cm^{-3}.

13. Continuum sources

A very different group of lightsources are those which are used to produce a continuum to serve as a background for absorption spectroscopy. The most common sources of this type are:

- halogen filament lamp (for use in the visible region),
- deuterium lamp (for the UV),
- capillary discharges,
- BRV (Ballofet, Romand, Vodar) source,
- laser produced plasmas,
- synchrotron radiation.

The first two are normal, commercially available lamps, not much more complicated to use than an ordinary light bulb, and will not be discussed here.

In a capillary discharge a current density of the order of 30000 A/cm^2 is used in hydrogen or a noble gas at low pressure. The capillary has a diameter of a few millimeters. The spectrum covers only a limited range (see Figs. 14 and 15), which can be both useful – prevention of overlap of orders in a grating spectrograph – or

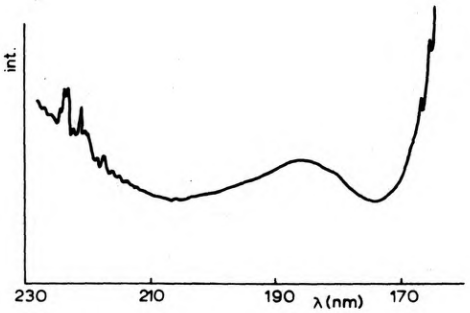

Fig. 14. H_2 continuum

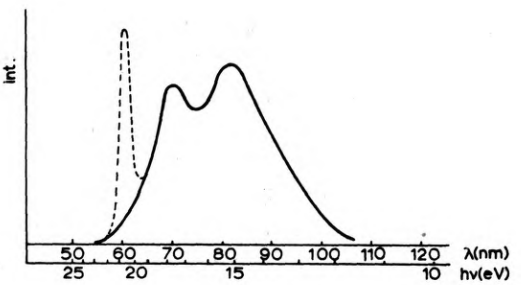

Fig. 15. He continuum

cause problems. The spectrum originates from transitions between a bound excited molecular state and a lower repulsive state.

The BRV [23] source produces a spectrum which closely resembles a black body radiator of typically about 20000 K. This spectrum extends from a few Å until the visible. It is a high voltage triggered spark between a uranium (or another heavy element) anode and a cathode which incorporates a sliding spark as trigger. Typical discharge parameters are 20 kV and 55 kA. The discharge current has to rise to its maximum value in a time much shorter than 1 μs. A typical capacitor used has a value of 0.5 μF and a self-inductance of less than 0.08 μH. The main drawback of this source is that it has to operate at high vacuum (10^{-5} mbar), which can limit the pulse frequency, for the plasma should be pumped away in time, and in the XUV this necessitates a complicated differential pumping system because windows can not be used.

Also laser produced plasmas can produce a continuum [24]. The power density has to be high enough (0.1–10 J) and a rare earth (samarium is a good choice) is used as a target for the wavelength range of 50–200 nm (Fig. 16), while below 50 nm other metals like W and Mo are used, although the spectrum in the latter case is not so clean.

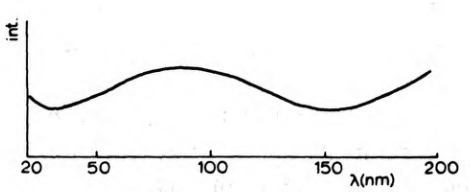

Fig. 16. Continuum of Sm in a laser produced plasma (after [24])

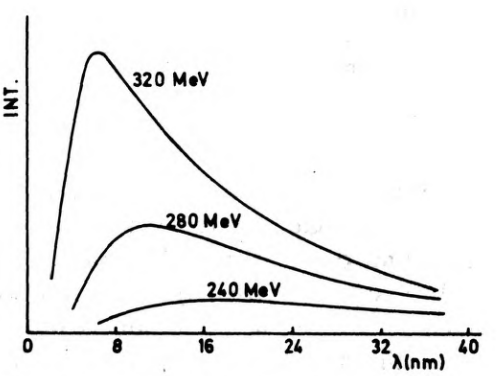

Fig. 17. Synchrotron radiation continuum (after [25])

At wavelengths below 20 nm the spectrum originates from eight to fifteen times ionized atoms with many broadened spectral lines, while above 50 nm recombination processes and brehmstrahlung are important mechanisms [24].

Synchrotron radiation has been used for absorption experiments for the last twenty years. CODLING [25] has given an excellent review of its possibilities and I will not dwell here upon the theory of these devices. The spectrum is intense and clean, and extends over a large wavelength range (see Fig. 17). Synchrotrons, howeve r, are very expensive devices, which cannot be moved, and only recently high resolution spectrometers, which are necessary to detect narrow absorption features, are being build at those sites.

Table 1 summarizes the most important characteristics of some continuum sources.

Table 1. Comparison of continuum sources

Synchrotron radiation	1000–1 nm	intensed, polarized, collimated, pulsed, expensive, immovable
BRV source	500–2 nm	pulsed, high vacuum required
Capillary discharge	limited range	pulsed, gas filled, range depends on the gas used
Laser produced plasma	200–4 nm	pulsed, any environment

14. Concluding remarks

We have seen that different mechanisms play a role in the ionization and excitation processes in lightsources for spectroscopic purposes. They are summarized in Table 2.

Table 2. Mechanisms for ionization and excitation processes

Ionization	Excitation
1. Collisions with electrons (one and two step processes)	1. Electron impact (one and two step processes)
2. Penning ionization	2. Charge exchange
3. Shock waves	3. Photon absorption
4. Photon absorption	4. Atomic collisions
	5. Recombinations

In the arc, ionization is mainly the result of electron collisions, Penning ionization, excitation of electron impact, charge exchange, and atomic collisions, depending on density and pressure.

In microwave discharges, where also interaction with and at the wall has to be taken into account, excitation is due to electron impact and atomic collisions.

In the DC hollow cathode discharge the same mechanisms as in the arc dominate, while ionization can also be caused by photon absorption. Atomic collisions are in this case somewhat less important, recombinations have however a

large influence. In the spark the situation is very different: ionization is due to a shockwave, and excitation is due to recombination. Atomic collisions can be neglected.

Electron, ion, and current densities, as well as the temperature can differ by many orders of magnitude, as can be seen in Table 3.

Table 3. Electron and ion-densities and temperatures

Source	Electron density [particles per cm^{-3}]	Ion density [particles per cm^{-3}]	Current density [A/cm^2]	Temperature [K]
Arc	10^{16}	10^{16}	10^3	10000
Spark	10^{17}	10^{17}	10^5	40000
DC HCD	10^{13}	10^{13}	10^{-3}	6000
Pulsed HCD	10^{15}	10^{15}	10^3	20000
LIVS*	10^{23}	10^{22}	10^9	20000
BRV	10^{20}	10^{19}	10^8	40000
LPP**	10^{21}	10^{20}		100000

* Low Inductance Vacuum Spark
** Laser Produced Plasma

For some sources a very complete description is known of the relevant physical processes (e.g., the spark discharge); other sources are not completely understood yet, although they sometimes are the object of many studies, and much knowledge has been collected (e.g., about the hollow cathode discharge). Further research is necessary to reveal more of the physics of these devices.

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Источники света: ионизация и возбуждение атомов

Совершен обзор разных типов источников света для образования спектров испускания и сплошного фона для абсорбционной спектроскопии. Продискутирован механизм ионизации и возбуждения, который в значительной степени зависит от типа источника. Сравнены положительные и отрицательные черты этих источников.