

A Capillary Discharge for Determination of Plasmadiagnostically Relevant Atomic Quantities

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An improved capillary discharge technique renders possible the production of a plasma jet representing a radially symmetric LTE light source. It shows a special capability of producing plasmas of elements or compounds which exist in the solid state under normal conditions. This plasma source is also suited for the investigation of emission lines of ionised atoms. To demonstrate a possible application, relative transition probabilities of some prominent CuI lines in the visible are determined and compared with results of other authors.

1. Introduction

The determination of plasmaspectroscopically relevant atomic values frequently requires plasmas which fulfill certain conditions with respect to the plasma state. The establishment of larger sets of transition probabilities by measurements of line intensities for example makes the realisation of LTE conditions necessary. In many other cases (e.g. for the evaluation of line broadening parameters) LTE need not exist so strictly, but the plasma state should not be too far from it.

The stationary plasma sources used for these purposes (e.g. the Maecker type wallstabilised arc) show the disadvantage that many of the chemical elements normally existing in the liquid or solid state can hardly be introduced into the plasma if no suitable gaseous or volatile compounds are available. But even then problems usually arise: Disturbances of the spectra by too high concentrations of 'alien' elements are observed, or the burning time of the arc is too short for reproducible measurements, because chemical depositions block the gasflow channels. Furthermore, stationary plasma sources do not allow to investigate ionised atoms, with a few exceptions only.

High power pulse heated plasmas seem to solve most of these problems. In such cases higher tem-

peratures of the plasma can be achieved, which allow to evaporate considerable amounts of chemical elements from solid or liquid surfaces by the strong plasma radiation. In addition, those plasmas will meet LTE conditions more easily because of their higher electron densities.

To obtain simple geometric distributions of the plasmaparameters for side-on investigation a plasma column is to be produced which shows radial symmetry of these distributions, at least in one cross section.

Two plasma sources of this kind described in the past should be mentioned, because the source presented in this paper was developed taking into account similar considerations. In [1] a discharge through a lithium hydride capillary was produced and the plasma jet emerging from one end of it was observed side-on in order to measure LiI line widths.

In this way – in a first step – we tried to produce plasmas which contain elements of interest (Cu, Fe, Ni etc.) together with hydrogen (for the determination of electron density via H_{β}) and additional elements, which allow to measure the plasma temperature by the relative intensity method (e.g. Ba). All these elements should have proper concentrations in the plasma with respect to measurable line intensities. It turned out that this is realisable by coating the inner wall of a capillary with these elements in the form of suitable chemical compounds. Unfortunately, side-on investigations of the emerging jet at distances far enough from the end of the capillary (to guarantee sufficient low optical density) show turbulent plasma conditions out there.

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Another way to produce a suitable plasma column is described in [2]. A sliding discharge along the surface of a liquid jet evaporates chemical elements from this surface, which are solved in the liquid (e.g. water). At sufficiently low pressures of the surrounding gas a peripheral discharge of cylindrical symmetry can be observed. Sometimes problems arise, because the surface of the liquid jet must be very smooth for obtaining a satisfactory symmetry of the plasma column. A further restriction for this technique is given by the fact that a number of chemical elements cannot be prepared in this way in an appropriate concentration, because there exists a lack of chemical compounds having sufficient solubility in the liquid.

In this connection a result of similar experiments should also be mentioned: Peripheral discharges around thin metallic wires show excellent cylindrical symmetry, especially if the pressure of the surrounding gas is reduced [3]. The radiation of the plasma evaporates atoms from the surface of the wire in this case, too. But this attempt was not successful because a plasma column should be produced showing a large mixing zone of elements from the wire material together with atoms of the surrounding gas. The reason is, that the evaporating wire material shoves away the surrounding gas, yielding two – more or less – independent plasma regions with a very small mixing zone only [4]. (To be able to mix the metal atoms with those of chemical elements normally existing in the gaseous state is sometimes of interest, e.g. for the determination of the electron density from the line width of H_{β} [5].)

The plasma source described below combines a capillary and a peripheral wire discharge. The wire is placed axially inside the bore of a capillary. The elements which should be introduced into the plasma can be inserted into the wire or into the inner wall of the capillary. If atoms of the wire material are not needed, a wire with small diameter is chosen

(20 μm and less). Its function then is just to start the ignition and to favour the establishment of a straight symmetric plasma column. It was found that using this device the radial symmetry of the emerging plasma is formed much better than by putting hollow electrodes directly on the ends of the capillary. The symmetry is in that way maintained even at those far distances where the column of the plasma jet has become optically thin (see also [6]).

2. Experimental

2.1. The Plasma Source

A schematic view of the plasma source is given in Figure 1, showing the relatively simple design. The wire is clamped between the two electrodes and axially led through the capillary bore. The emerging plasma jet is observed side-on at positions where the optical thickness of the layer becomes negligible but radial symmetry still exists. Therefore Abel inversion of the side-on emission data is possible out there.

As outer material of the capillary plexiglass was chosen. For the inner material (thickness about 3.5 mm) the use of paraffin or polyvinylalcohol was found to be favourable, in which the substances of plasmaspectroscopical interest are to be embedded. These substances should mainly be elements or compounds with poor conductivity such as oxides or hydroxides. For preparation a suspension of the powdered substances in molten high viscous paraffin was made. If well conducting substances are directly put into the paraffin matrix above a critical concentration (e.g. as powders), the discharge shifts into the wall material, so that the capillary wall normally gets damaged and only asymmetric plasma columns can be obtained. The whole device shown in Fig. 1 is mounted inside a discharge vessel that can be evacuated in order to be able to vary the surrounding gas and its pressure.

2.2. The Electrical Set Up

The energy was stored in a capacitor bank ($C = 20 \mu\text{F}$), which could be charged up to 30 kV (Figure 2). With a coil of variable inductivity the ringing period of the oscillating discharge could be varied from 20 μs to about 200 μs . For the investigations reported here the short circuit ringing period

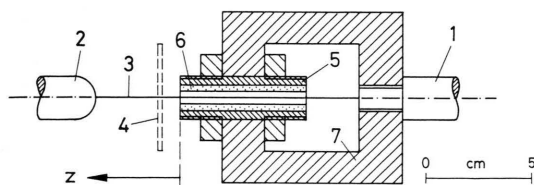


Fig. 1. The plasma source. 1 anode, 2 cathode, 3 ignition wire, 4 position of observation slit, 5 plexiglass, 6 inner capillary wall material, 7 insulating mounting device.

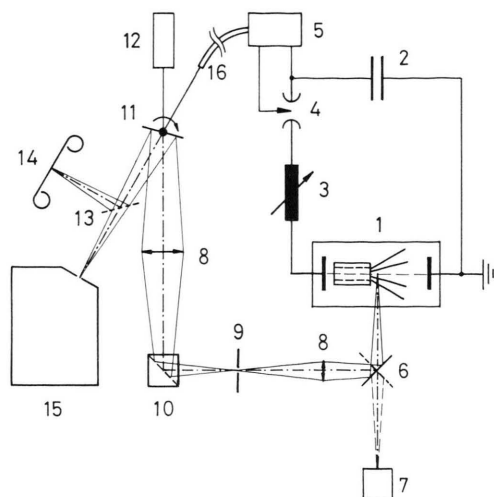


Fig. 2. Experimental set-up. 1 discharge vessel with plasma source, 2 capacitor bank, 3 coil of variable inductivity, 4 three-electrode spark gap, 5 trigger unit (including start-of-sequence synchroniser and thyatron stage), 6 turnable mirror, 7 radiation standard (carbon arc), 8 lens, 9 pre-slit (intermediate picture), 10 mirror system (to adjust spectrograph slit parallel or perpendicular to the discharge axis), 11 quartz frequency stabilised rotating mirror, 12 He-Ne-laser, 13 beam splitter, 14 streak camera, 15 spectrograph, 16 fibre optic.

was $180\ \mu\text{s}$ because the discharge parameters were found to be optimal at about this value. A low ringing frequency favours LTE conditions and makes it easier to achieve the necessary time resolution of the measuring system.

The circuit could be triggered by a three electrode spark gap. The moment of triggering depends on the proper position of the quartz frequency stabilised rotating mirror (operation range: 11.1 Hz to 66.6 Hz) and could be varied in the following way: An auxiliary small mirror, mounted on the same axis as the main mirror but – according to the desired delay time – more or less twisted against the main mirror, reflected a He-Ne-laser ray on a fibre optic input which led to a photodiode. With a start-of-sequence synchronizer and stepwise amplification of the signal a thyatron stage could be triggered, the output pulse of which (spike about 15 kV) then was led to the three-electrode spark gap of the main circuit. The precise adjustment of the trigger moment could be achieved by an electronic delay. Current measurements were performed using an induction coil with subsequent RC integration.

2.3. The Optical Arrangement

The applied technique (Fig. 2) allows to obtain both an instantaneous spectrum and a streak photograph from a single discharge (see also [3]). The pre-slit at the position of the intermediate picture of the plasma column (slit orientation perpendicular to the discharge axis, see Figure 1) selects a certain layer of the plasma column perpendicular to its axis, the time dependent radiation of which now can be recorded on a film (see streak image in Fig. 3 as an example). Instantaneous spectra are obtained for the time interval when the moving image of the pre-slit hits the entrance slit of the spectrograph.

If, on the other hand, only the change of the integral radiation along the axis of the plasma is to be detected, the pre-slit is adjusted parallel to the plasma column. With help of the mirror system (10) in Fig. 2 it was possible to turn the image of this slit by 90° , so that its orientation becomes now parallel to the spectrograph slit.

The spectrograph is a Steinheil Spectrovar equipped for the visible range with a 1200 grooves/mm grating, yielding a reciprocal linear dispersion of about $12\ \text{\AA}/\text{mm}$. As radiation standard a carbon arc was operated according to the suggestions of [7]. All spectra were recorded photographically on Ilford HP5 flat film. Photographs of different phases of the discharge could be taken using a Kerr cell shutter (see Fig. 4, the exposure time being about 30 ns). Photographs of the discharge are shown in Figures 3 and 4.

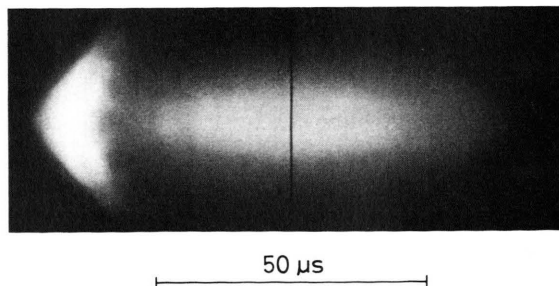


Fig. 3. Example of a side-on streak photograph of a capillary discharge with 16 kV charging voltage, taken at an observation slit distance $z = 5\ \text{mm}$ from the capillary end. Inner diameter of the capillary 5 mm, pressure of surrounding air 0.5 bars.

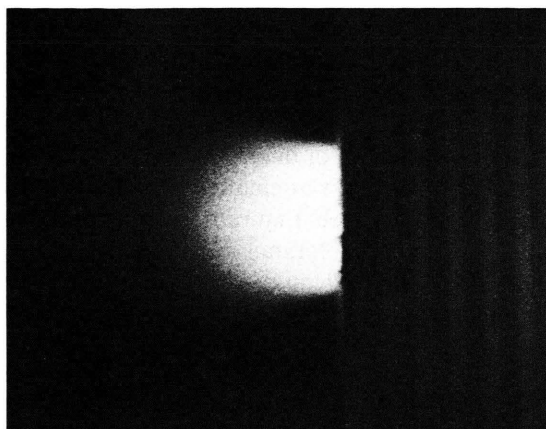


Fig. 4. Kerr-cell photograph of the capillary discharge with 20 kV charging voltage, taken 45 μ s after ignition.

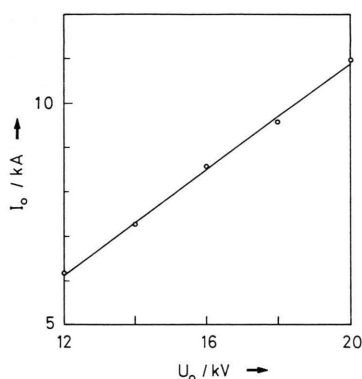


Fig. 5. First current maximum I_0 as a function of charging voltage U_0 .

3. Results

Only a part of the results obtained will be given here, which may demonstrate the typical properties of this source.

3.1. Characteristic Parameters of the Discharge

In these investigations the charging voltage of the capacitor bank was varied within 10 kV to 20 kV in steps of 2 kV. The dependence of the first current maximum on the charging voltage is plotted in Figure 5. The electrodes were short circuited by a 12 cm long and 20 μ m thick copper wire for ignition; the dimensions of the capillaries were: length 60 mm, inner diameter 5 mm, outer diameter 20 mm. Paraffin as matrix material for the inner wall has several advantages; two of them should be empha-

sized: The high resistivity against shock-wave-damage because of its plasticity, and the fact that paraffin is a compound which contains hydrogen which can serve as a calibration substance for the determination of the electron density e.g. via the profile of H_β [5].

In order to be able to evaluate the temperature, barium oxide powder was carefully mixed into the paraffin (3.8 weight% BaO) before forming the capillary. The intensity ratio of the lines BaII 452.493 nm and BaII 585.368 nm with upper level energies of 5.24 eV and 2.72 eV, respectively, served as the necessary 'thermometer'. The corresponding transition probabilities were taken from [8]. Later on also copper oxide powder was added to the paraffin (3.8 weight% BaO, 57.7% Cu₂O, 38.5% paraffin), in order to determine copper line widths and transitions probabilities (see chapter below). Based on these the temperatures were then obtained normally by measuring intensities of CuI lines, e.g. 427.513 nm and 578.213 nm, having upper levels of 7.74 eV and 3.79 eV, respectively, a difference also large enough to apply the relative intensity method for the temperature determination.

Temperature values obtained at the first current maximum are plotted in Figure 6. They show that the temperature decrease along the axis of the jet is relatively small within the observed interval. The difference of about 6% between the slopes of temperature for 12 kV and 18 kV charging voltage is lying within the limits of uncertainty of the temperature determination.

A characteristic plot of radial profiles of temperatures and electron densities – evaluated after Abel inversion of the side on data – is given in Fig. 7, indicating a nearly trapezoidal distributions of these plasma parameters. For a charging voltage of 16 kV the optimal spatial region of proper intensity of H_β was found to cover a range from $z = 5$ to 8 mm (z being the distance from the end of the capillary). Within that region the electron density n_e could now be determined using the tables of [5], so that C_4 constants for Stark broadening of several CuI lines could be evaluated, which will be reported in a separate paper [9].

At larger distances from the capillary end the intensity of H_β becomes too small, whereas CuI lines were found to be still observable. For this reason the electron density determination at larger distances was carried out using the broadening con-

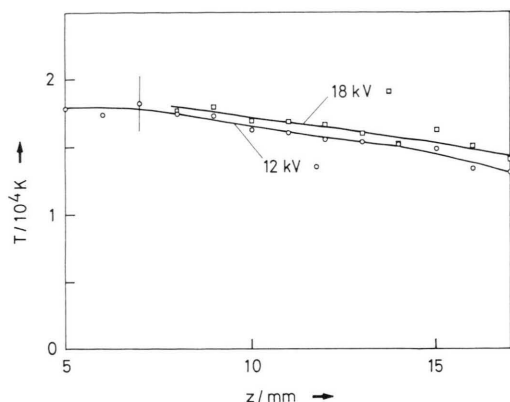


Fig. 6. Axis temperature at different distances from the capillary end for 12 kV and 18 kV discharges. Pressure and inner diameter of capillary are the same as for Figure 3.

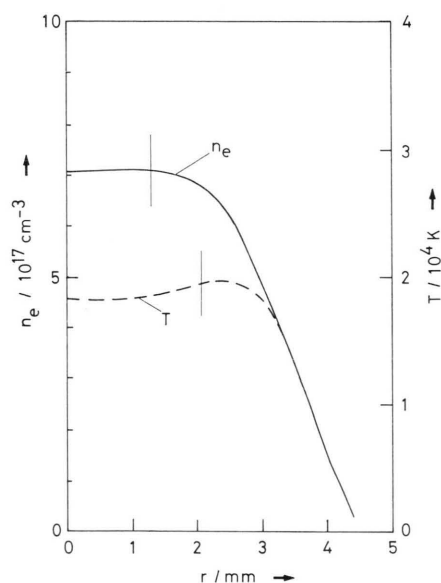


Fig. 7. Example for radial profiles of temperature T and electron density n_e , evaluated from side-on emission spectrum. Experimental parameters: Charging voltage 16 kV; length of capillary 60 mm; inner diameter 5 mm; inner wall material: 3.8 weight% BaO + 57.7% Cu₂O + 38.5% paraffin; pressure 0.5 bars (air); distance between observation slit and capillary end $z = 5$ mm.

stant $C_4 = 4.05 \cdot 10^{-15} \text{ s}^{-1} \text{ cm}^4$ of the CuI line 427.513 nm, the profile of which was subject to a deconvolution procedure in order to eliminate the profile of the apparatus. In Fig. 8 the evaluated electron densities (at the first current maximum) along the axis of the plasma column are compared with respect to a variation of the charging voltage U_0 .

3.2. Relative Transition Probabilities of CuI Lines

For an application of this modified capillary discharge method an evaluation of transition probabilities of some prominent CuI lines for the visible spectral range was performed. Copper lines are frequently observed in industrial plasmas and would be – in principle – well suited for a temperature determination by the relative line intensity method because of the sufficient differences of their upper energy levels. In a previous paper [10] a set of relative gf values for CuI lines, predominantly for the uv range, was reported by combining results of hook and emission measurements. For the visible range relatively large discrepancies among the data of different authors are still existing in some cases, therefore any newly measured values seem to be desirable.

The relative transition probabilities of the CuI lines were obtained by measuring the intensity ratios of their emission lines. The temperatures were obtained by measuring intensities of BaII lines as described in the preceding chapter.

The check-up regarding the optical depths of the layer was carried out by comparing the theoretical black body radiation according to the temperature with the peak intensity of the measured line profile. Only data from lines with peak intensities of less than 10% of the corresponding Kirchhoff Planck function were considered for further data reduction.

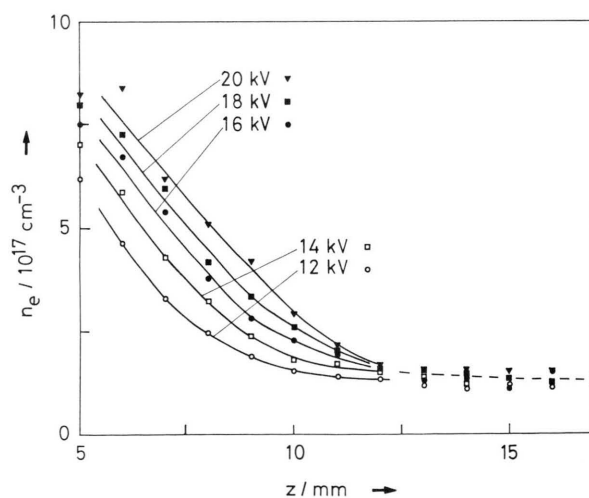


Fig. 8. Electron density n_e versus axis position z of the emerging plasma jet for different charging voltages. Pressure and inner diameter of capillary are the same as for Figure 3.

Table 1. Transition probabilities for some CuI lines. The relative scale of this work is normalised to the absolute A_{ki} – value of CuI 510.554 nm of [11] and [12].

| λ (nm) | Energies (eV) | A_{ki} (10^7 s^{-1}) | | |
|----------------|---------------|------------------------------------|------|------|
| | | this work | [11] | [12] |
| 427.513 | 4.84–7.74 | $3.1 \pm 35\%$ | 3.45 | 3.18 |
| 437.820 | 4.97–7.80 | $2.1 \pm 35\%$ | — | 1.32 |
| 458.695 | 5.10–7.80 | $3.4 \pm 35\%$ | 3.20 | 2.57 |
| 465.113 | 5.07–7.74 | $4.4 \pm 35\%$ | 3.80 | 4.20 |
| 510.554 | 1.39–3.82 | 0.2 — | 0.20 | 0.20 |
| 529.252 | 5.39–7.74 | $2.9 \pm 35\%$ | 1.09 | 1.09 |
| 578.213 | 1.64–3.79 | $0.17 \pm 12\%$ | 0.17 | 0.19 |

The values obtained are listed in Table 1 and compared with those discussed in the review articles [11] and [12]. The relative scale of transition probabilities is normalised to the absolute value of CuI 510.554 nm for an easier comparison with those of other authors.

It should be mentioned that CuII lines were also observed in the visible range of our spectra. In order to obtain a larger set of data step by step, the capillary discharge technique described here was applied in combination with the so-called axial discharge of copper wires, a special discharge type of an exploding wire yielding a pure copper plasma [3, 13]. In that case the overlapping of the line profiles to be measured, especially by lines of other elements (e.g. Ba lines), could be reduced. The results for CuII will be reported in a separate paper [14].

4. Discussion

The light source described here gives the possibility of recording emission spectra of a plasma jet emerging from one end of a capillary discharge in regions with negligible self absorption by simply choosing positions of the observation slit at larger distances from the capillary end. This is possible because of the good symmetry of the emerging plasma over a relatively large region. For $z \geq 5$ mm the pressure in the plasma has decreased so much that most emission lines are showing self absorption of less than 10% of the Kirchhoff-Planck function.

For $z \geq 13$ mm the electron density (see Fig. 8) becomes nearly constant, which might be explained by a finished expansion process of the plasma. As the electron densities are still greater than 10^{17} cm^{-3} there and the ringing period (180 μs) is relatively long, LTE conditions seem to be guaranteed within the spatial interval for $z \leq 13$ mm.

The region $z < 5$ mm shows only restricted capability for emission spectroscopy because of the occurrence of the molecular SWAN-bands (C_2 -molecule) in absorption. They stem from the paraffin and can partly overlap the spectra to be investigated. On substituting paraffin by other substances it was found that polyvinylalcohol avoids those SWAN-bands completely.

The seeding of the paraffin with the substances of interest is rather simple, however attention must be paid in order to achieve homogeneous mixtures. In such cases the reproducibility of the spectra from shot to shot is very good.

Finally a few comments on some limits of our set up should be made. The radiation of the standard carbon arc in the blue spectral region was on the limit of being recorded because the restriction of comparable exposure times in order to avoid the Schwarzschild effect had to be considered. The exposure time for the instantaneous spectra was strictly adjusted not to exceed 4.5 μs , which is exactly 10% of the current raise time.

On one hand the electron density determination via H_β is simplified by its large half width. On the other hand there exists an increased possibility of overlapping with other spectral lines. For that reason frequently the red wing of H_β could not be taken into account. The deconvolution procedure in the case of the n_e -determination by the copper line CuI 427.513 nm enlarges the uncertainty of n_e , particularly for small half widths. Together with the requirement of Abel inversion of the side-on data this leads to relatively large errors, especially for the transition probabilities. However, as the interest of this investigation was rather focused on a demonstration of the properties and quality of this light source, the procedure mentioned above seemed to be acceptable.

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