Journal of Photochemistry and Photobiology A: Chemistry 179 (2006) 229–233

# Microwave photochemistry IV: Preparation of the electrodeless discharge lamps for photochemical applications

Vladimír Církva*, Leona Vlková, Stanislav Relich, Milan Hájek

*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Praha 6, Czech Republic*

Received 3 June 2005; received in revised form 12 August 2005; accepted 14 August 2005
Available online 17 October 2005

**Abstract**

The electrodeless discharge lamps (EDLs) have been found to be suitable sources of UV/vis light for photochemical reactions. The EDL usually consists of a glass tube (quartz or Pyrex) filled under a reduced pressure with argon and an excitable substance (e.g. Hg, $HgI_2$, Cd, $I_2$, KI, P, Se, S), and generates UV/vis radiation when placed into the microwave field. The utilization of other filling material than mercury is practical and environmentally safe in the EDL performance. The original equipment for easy preparation of EDLs has been described in detail.

*Keywords:* Microwave photochemistry; Electrodeless discharge lamp; UV/vis source

## 1. Introduction

The field of microwave photochemistry [1] is frequently, but not irreplaceably, focused to the electrodeless discharge lamps (EDLs), which generates UV/vis radiation when placed into the microwave field. The lamp is excited at frequency 2.45 GHz owing to the ready commercial availability of the suitable microwave generators (magnetrons).

Several original papers [2–9] describing a photochemical reactor consisting of mercury-EDL placed directly into a reaction mixture in modified microwave oven have been published in the past 9 years. There was a great interest in EDLs as primary light sources of narrow spectral lines covering the spectrum from the vacuum UV to the infrared region [10,11].

The EDLs have been used in various applications as light sources and also in scientific devices for atomic spectrometry [12]. Since they are used above all as the low-pressure lamps, such discharges provide a relatively high intensity of resonance radiation frequencies of the substance being excited. The spectral bands are narrowed and therefore some photochemical applications are limited.

Various papers [13–16] are available describing the general procedure required to produce the EDLs. However, for the sake of conciseness, many minor details are often omitted which are critical in producing a lamp that will function properly. The investigator who wants to prepare an EDL is faced with a very large amount of information dispersed in literature. Therefore, in present study, we describe the easy preparation of EDLs for photochemical applications using our original equipment.

## 2. Experimental section

### 2.1. Equipment

Electrodeless discharge lamps (EDLs) were made (vide infra) of 12 mm quartz (4 ml) or 20 mm Pyrex (9 ml) envelope tubing (of approximately 1 mm thick glass) of the ca. 40 mm length, containing the corresponding filling material (Table 1), and sealed under 0.7 kPa argon atmosphere.

The typical experimental vacuum system for preparation of EDLs (Fig. 1 ) is consisting of a rotary oil vacuum pump (1) (single-stage, limiting total pressure 10 Pa, type model VR 1.5–12; Lavat, Chotutice, Czech Republic), the mercury manometer (2) with movable scale (0–200 mmHg, Anschütz-type; Kavalier, Sázava, Czech Republic), the tilting-

* Corresponding author. Tel.: +42 220390292; fax: +42 220920661.
*E-mail address:* cirkva@icpf.cas.cz (V. Církva).

doi:10.1016/j.jphotochem.2005.08.020

Table 1
The filling and envelope material characteristics of the EDLs[a]

| Filling material | Amount (mg) | Envelope material[b] |
|---|---|---|
| Hg | 10 | Q |
| Hg | 10 | P |
| $HgI_2$ | 5 | P |
| Cd | 5 | Q |
| Cd | 5 | P |
| $I_2$ | Vapor | Q |
| $I_2$ | Vapor | P |
| KI | 4 | P |
| P | 1 | P |
| P | 10 | P |
| Se | 2 | P |
| S | 1 | P |
| S | 6 | P |
| S | 12 | P |

[a] The pressure of argon was 0.7 kPa (5 Torr).
[b] P: Pyrex, Q: quartz.

type McLeod pressure gauge (3) with mercury (0.01–10 mmHg, MSP Prague, Czech Republic), the EDL blank (4) tubing (Pyrex, quartz; Kavalier, Sázava, Czech Republic), the modified microwave oven (5) with hole in the top according to [4], the glass-working burner (6) (type model R-1; Kavalier, Sázava, Czech Republic). $V_1$ is three-way double oblique bore stopcock, $V_2$ is three-way T-bore stopcock and $V_3$ is straight way stopcock (all stopcocks from Kavalier, Sázava, Czech Republic) greased with high vacuum silicone lubricant (Dow Corning Co., Midland, USA). The system units are connected each other by the silicon rubber hose (5/15 mm).

### 2.2. Chemicals

Mercury (99.9999%, electronic grade), mercury(II) iodide (99.999%, powder), cadmium (99.9+%, foil), iodine (99.999%, beads), potassium iodide (99.998%, beads), red phosphorus (99.99+%, powder), selenium (99.999%, powder), sulfur (99.998%, powder) (all from Sigma–Aldrich) were used as received. Argon (4.8 grade) was purchased from Linde Technoplyn (Czech Republic).

### 2.3. Preparation of EDLs

A pattern of the vacuum system for preparation of EDLs is shown in Fig. 1. In order to obtain high quality lamps the EDL blank should be cleaned in water–soap mixture, then washed with distilled water, aqueous 10% hydrofluoric acid, ethanol and dried in a clean oven.

The corresponding amount of the EDL filling material (e.g. Hg, $HgI_2$, Cd, $I_2$, KI, P, Se or S) (Table 1) was placed to the EDL blank (4) (Fig. 1), the system was flushed with argon and then pumped down. When the mercury manometer (2) and tilting-type McLeod pressure gauge (3) indicated that the pressure has reached 13.3 Pa (0.1 Torr), the ice-water bath was put around the EDL blank (4) to reduce the loss of the mercury. Then stopcock $V_1$ was turned off and the system was again flushed with argon (this operation was repeated 10 times). Finally, when the McLeod pressure gauge (3) indicated 0.7 kPa (5 Torr) of argon, the stopcocks $V_1$–$V_3$ were closed. The EDL blank (4) was removed from ice-water bath, inserted to the microwave oven (5) and excited (ignited) by using a microwave field (2.45 GHz) [14]. The extent and color of the discharge plasma indicated the efficiency of the cleaning process. Water vapor and oxygen were the two major impurities that they quenched the plasma. The milky white plasma indicated extensive water vapor still on the walls of the lamp. This scrubbing procedure was repeated with fresh samples of argon until the light blue plasma was not observed. Finally, the EDL blank was sealed applying a narrow flame (natural gas-oxygen) glass-working burner (6), the lamp was pulled off and the end was rounded.

### 2.4. Testing of the EDL performance

A typical experimental system for testing of the lamp performance consisted of a round-bottom flask (500 mL) containing

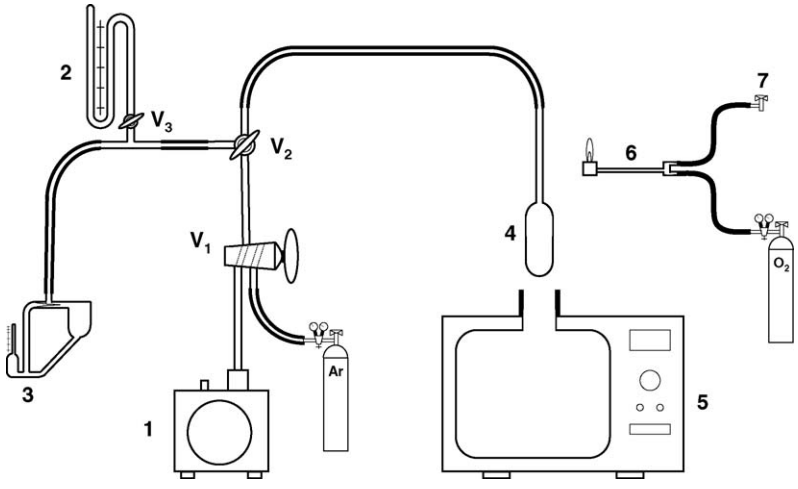


Fig. 1. The vacuum system for preparation of EDLs: (1) rotary vacuum pump; (2) mercury manometer; (3) tilting-type McLeod pressure gauge; (4) EDL blank; (5) modified microwave oven [4]; (6) glass-working burner; (7) natural gas. $V_1$–$V_3$ are stopcocks.

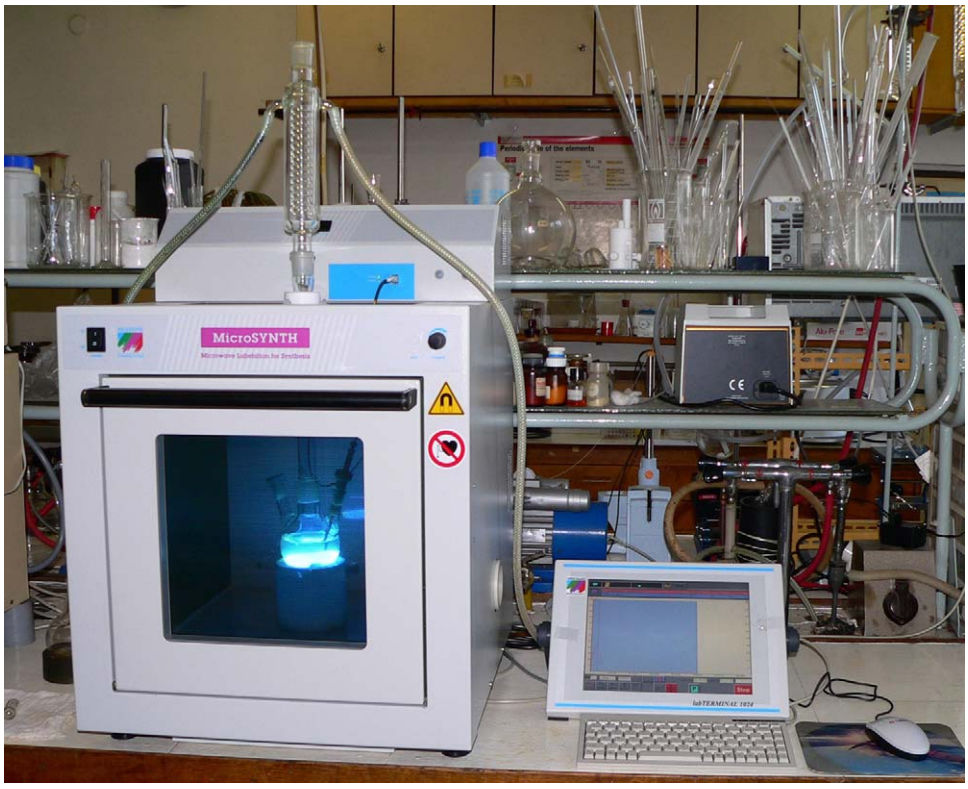


Fig. 2. Testing of the EDLs performance on Milestone's MicroSYNTH Labstation.

*n*-heptane (200 mL, b.p. 98 °C), equipped with a magnetic stirrer, a fiber-optic temperature probe with thermowell, Dimroth condenser, and placed to a MW oven (Fig. 2 ). Once the lamp is started (1000 W of MW output power), it produces except UV/vis light also the heat, and therefore the *n*-heptane is warmed up. The EDL was conditioning for 10 min until no lamp blinking occurred.

### 2.5. Spectral distribution of the EDLs

Spectral distribution of the lamps was examined by us [17,18] using AVS-S2000 spectrometer with AvaSoft software package and USB2000 spectrometer with a fiber-optic probe and operating software package OOIrrad-C (Ocean Optics). The line (Hg, $HgI_2$, Cd, P) and continuous (I, KI, Se, S) emission spectra [18] were then observed between 250 and 650 nm.

## 3. Results and discussion

The general method of preparation of EDL for analytical applications is very simple [19] and makes it possible to produce the lamp in the laboratory. A search of the literature gives many detailed procedures for EDL preparation [16]. However, in practice it is very difficult to reproduce these methods to develop the EDLs which have the same properties as those described in the literature.

The preparation of EDLs for photochemical applications is performed according to Fig. 1. The vacuum system is described in Section 2.3. Some selected variables are optimized, i.e. the envelope material (quartz, Pyrex), lamp dimensions and the amount and chemical form of the filling material. These preparation parameters of EDLs are important for the investigation of EDL performance.

### 3.1. The preparation parameters of EDLs

The envelope material must be impermeable to gases, an electrical insulator, and chemically resistant to the filling compounds at the temperature of operation. High quality quartz is the most widely used lamp envelope material that has many excellent properties: low thermal expansion, excellent elasticity, temperature shock resistance, low electric conductivity, and above all the good optical and microwave transmissions. In preparation of the EDLs, the Pyrex is also used as envelope material. It has advantage of absorbing most of the UV radiation below 290 nm, however, the borosilicate glass is softening at higher working temperature and the envelope implosion can follow.

Diameter and length of the lamp are mainly dependent on the cavity used and the volatility of the material introduced. Early work [20] on the influence of lamp diameter on intensity showed that the best signals were obtained with diameters in the 8–20 mm range. Intensity dropped dramatically when diameters of 20 mm were exceeded. When the lamp was too long, the plasma did not fill the EDL completely and this resulted in extra fluctuations of the lamp intensity. In practice, the lamps of 8–20 mm diameter, 30–45 mm in bulb length, and 1 mm thickness are generally used and widely accepted as a com-

promise between high intensity and acceptable lifetime and stability.

The amount of filling material (in mg) depends on the compound and the operating conditions. The substance must have sufficient volatility and should not react with glass. The decrease of the signal with increase of material in the EDL is attributed to the increasing pressure, giving self-reversal and line-broadening.

The chemical forms of the material that have been used in EDL preparation are the pure element, metal halide, or other metal compounds [15,16]. The pure metal can only be used when sufficient vapor pressure (0.133 kPa) [15] can be obtained and is restricted to the more volatiles such as Cd, Hg, S, Se and Zn, although the EDLs have been prepared with slightly less volatile elements such as Cs, I, Mg, Na, K, Rb, Sn, Pb, As, Sb, Bi, In, Te and Tl [21].

In general, the pressure of argon as the filling gas was recommended to hold between 0.27 and 2.66 kPa (2–20 Torr) for the best compromise between maximum lamp intensity and long life [15]. The effect of pressure on the EDL performance [17,18] is closely associated with the lamp and filling gas temperature.

The MW energy is used for the excitation of EDLs, the frequency is 2450 MHz and the maximum power varies from 30 to 1000 W. For the coupling of the MW energy to the EDLs, cavities (Broida-type, Evenson-type) and antennas (Raytheon) have been used [15]. However, optimum conditions ascertained for operation of a lamp in one type of MW cavity will by no means be optimal for operation in another one. Therefore, the results obtained in the MW oven do not have to be same as for other tested cavities.

In plasma system, the photons emitted from radiative excited states are absorbed by ground state atoms. These emission and absorption processes may be repeated many times until the photon finally reaches a wall and escapes the EDL. This phenomenon is called the *radiation trapping* effect [22] and it can change the spectrum of emitted light. In 1–10 Torr pressure regime (a large collision frequency), the dominant energy loss mechanism of electrons is inelastic collision with neutral gas. As for the radiative state, *resonance collision broadening* is the dominant mechanism of the radiation.

### 3.2. Spectral characteristics of EDLs

Testing of the EDL performance was carried out in order to prepare the lamps for spectral measurements. For the mutual EDLs comparison we measured their temperature profiles during 5 min (Fig. 3) using EasyWAVE software (Milestone). It was observed that EDL-S (1 mg) is faster warmed up than EDL-Hg (10 mg, Pyrex), apparently for the higher operating pressure inside of EDL-S envelope (lower volatility of sulfur).

Spectral characteristics of EDLs are of general interest for microwave photochemical research. Knowledge of spectral characteristics of EDL is clearly essential for planning the photochemical experiments. The right choice of the preparation and operation parameters can provide a desired UV/vis radiation.

The spectral measurements for prepared Hg, $HgI_2$, Cd, $I_2$, KI, P, Se and S-EDLs were accomplished in a modified MW oven described by us [17,18]. The EDL characteristics (filling material, Pyrex and quartz, temperature effect, MW output power) were measured and discussed.

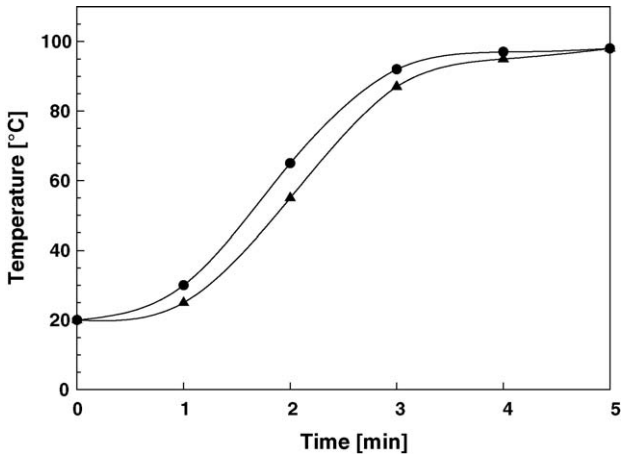


Fig. 3. Temperature profiles of the radiating EDL-S (1 mg) (●) and EDL-Hg (10 mg, Pyrex) (▲) in heptane at 1000 W MW output power.

## Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/02/0879) and the project AS CR No. K4040110. We are grateful to Milestone s.r.l. (Italy) for technical support.

## References

[1] P. Klán, V. Církva, Microwave photochemistry, in: A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley/VCH, Weinheim, 2002, p. 463.
[2] V. Církva, M. Hájek, Proceedings of the International Conference of Microwave and High Frequency Heating, Fermo, Italy, 1997, p. 153.
[3] V. Církva, M. Hájek, J. Photochem. Photobiol. A: Chem. 123 (1999) 21.
[4] P. Klán, M. Hájek, V. Církva, J. Photochem. Photobiol. A: Chem. 140 (2001) 185.
[5] P. Klán, J. Literák, S. Relich, J. Photochem. Photobiol. A 143 (2001) 49.
[6] J.L. Moruzzi, PCT Int. Appl. WO 0109924 (2001).
[7] J. Literák, P. Klán, D. Heger, A. Loupy, J. Photochem. Photobiol. A 154 (2003) 155.
[8] V. Církva, J. Kurfürstová, J. Karban, M. Hájek, J. Photochem. Photobiol. A 168 (2004) 197.
[9] S. Horikoshi, F. Hojo, H. Hidaka, N. Serpone, Environ. Sci. Technol. 38 (2004) 2198.
[10] P. Warneck, Appl. Opt. 1 (1962) 721.
[11] D.O. Wharmby, Proc. IEEE A 140 (1993) 465.
[12] A. Ganeev, Z. Gavare, V.I. Khutorshikov, S.V. Khutorshikov, G. Revalde, A. Skudra, G.M. Smirnova, N.R. Stankov, Spectrochim. Acta B 58 (2003) 879.
[13] M. Zelikoff, P.H. Wyckoff, L.M. Aschenbrand, R.S. Loomis, J. Opt. Soc. Am. 42 (1952) 818.
[14] W.S. Gleason, R. Pertel, Rev. Sci. Instrum. 42 (1971) 1638.
[15] J.P.S. Haarsma, G.J. De Jong, J. Agterdenbos, Spectrochim. Acta B 29 (1974) 1.
[16] J. Sneddon, R.F. Browner, P.N. Keliher, J.D. Winefordner, D.J. Butcher, R.G. Michel, Prog. Anal. Spectrosc. 12 (1989) 369.

[17] P. Müller, P. Klán, V. Církva, J. Photochem. Photobiol. A: Chem. 158 (2003) 1.
[18] P. Müller, P. Klán, V. Církva, J. Photochem. Photobiol. A: Chem. 171 (2005) 51.
[19] M.D. Seltzer, R.G. Michel, Anal. Chem. 55 (1983) 1817.
[20] J.M. Mansfield, M.P. Bratzel, H.O. Norgordon, D.O. Knapp, K.E. Zacha, J.D. Winefordner, Spectrochim. Acta B 23 (1968) 389.
[21] R.M. Dagnall, M.D. Silvester, T.S. West, Spectrochim. Acta B 28 (1973) 51.
[22] H.J. Lee, J.P. Verboncoeur, J. Appl. Phys. 90 (2001) 4957.