

MICROWAVE PHOTOCHEMISTRY: PREPARATION OF THE ELECTRODELESS DISCHARGE LAMPS AND THEIR PHOTOCHEMICAL APPLICATIONS

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ABSTRACT

The electrodeless discharge lamps (EDLs) consists of a glass tube (quartz or Pyrex) filled under a reduced pressure with argon and an excitable substance (Hg, HgI₂, Cd, I₂, 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 apparatus for easy preparation of EDLs will be described in detail. The spectral measurements for prepared EDLs are accomplished in a modified MW oven described by us.

KEYWORDS: microwave photochemistry; electrodeless discharge lamps; UV/VIS

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. Several original papers [2-4] describing a photochemical reactor consisting of mercury-EDL placed directly into a reaction mixture in modified microwave oven have been published in the past nine 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 [5].

The EDLs have been used in various applications as light sources and also in scientific devices for atomic spectrometry [6]. 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 [7] 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 we describe the easy preparation of EDLs for photochemical applications using our original equipment.

EXPERIMENTAL

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, 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, Czech Republic), the Hg manometer (2) with movable scale (0-200 mm Hg, Anschütz-type; Kavalier, Sázava, Czech Republic), the tilting-type McLeod pressure gauge (3) with Hg (MSP Prague, Czech Republic), the EDL

blank (4) tubing (Pyrex or quartz; Kavalier, Sázava, Czech Republic), the modified microwave oven (5) with hole in the top according to [3], 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).

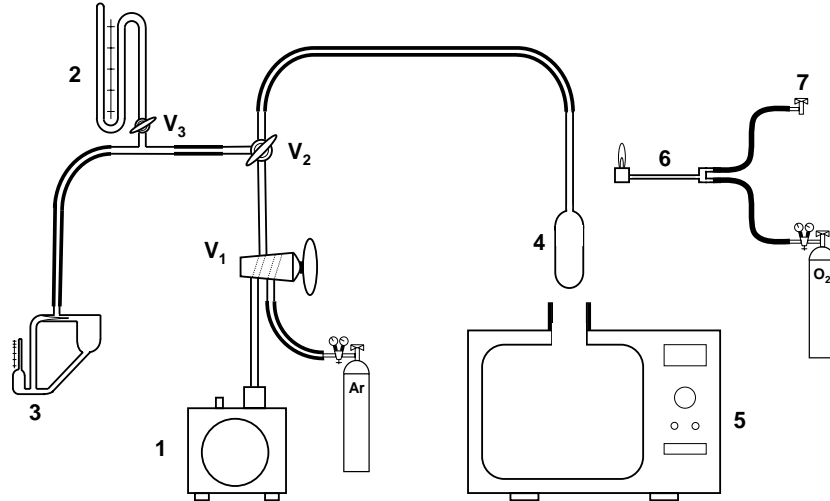


Fig. 1. The vacuum system for preparation of EDLs: (1) rotary vacuum pump; (2) Hg manometer; (3) tilting-type McLeod pressure gauge; (4) EDL blank; (5) modified microwave oven [3]; (6) glass-working burner; (7) natural gas. V_1 - V_3 are stopcocks.

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) (1-10 mg) was placed to the EDL blank (4) (Fig. 1), the system was flushed with argon and then pumped down. When the Hg 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). 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.

A typical experimental system for testing of the lamp performance consisted of a round-bottom flask (250 mL) containing *n*-heptane (bp 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.



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

Spectral distribution of the lamps was examined by us [8,9] 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, HgI₂, Cd, P) and continuous (I, KI, Se, S) emission spectra [9] were then observed between 250-650 nm.

DISCUSSION

The general method of preparation of EDL for analytical applications is very simple and makes it possible to produce the lamp in the laboratory. A search of the literature gives many detailed procedures for EDL preparation [7]. 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 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 [7] 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 compromise 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 [7]. The pure metal can only be used when sufficient vapor pressure (0.133 kPa) can be obtained and is restricted to the more volatile elements such as Cd, Hg, S, Se and Zn, although the EDLs have been prepared with slightly less volatile metals such as Cs, I, Mg, Na, K, Rb, Sn, Pb, As, Sb, Bi, In, Te and Tl.

In general, the pressure of argon as the filling gas was recommended to hold between 0.27-2.66 kPa (2-20 Torr) for satisfactory results. The effect of pressure on the EDL performance [8, 9] is associated with the lamp and filling gas temperature.

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, HgI₂, Cd, I₂, KI, P, Se and S-EDLs were accomplished in a modified MW oven described by us [8, 9]. The EDL characteristics (filling material, Pyrex and quartz, temperature effect, MW output power) were measured and discussed.

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