Optica Applicata, Vol. XI, No. 4, 1981

Application of an electrodeless discharge mercury lamp in the photochemical flow reactor*

MARIAN ELBANOWSKI

Institute of Chemistry, Adam Mickiewicz University, Poznań, Poland.

EDMUND LISICKI

Institute of Physics, Nicolaus Copernicus University, Toruń, Poland.

DANUTA SŁAWIŃSKA, JANUSZ SŁAWIŃSKI, LESZEK CIEŚLA

Institute of Physics and Chemistry, Agriculture Academy of Poznań, Poland.

The energetic and spectral characteristics of an electrodeless discharge, RF-powered (140 MHz), home-made mercury lamp used in the photochemical flow reactors are given. The parameters optimizing those reactors are discussed.

In the investigations of photochemical reactions as well as photoinduced chemiluminescence (*CL*), the choice of a radiation source with proper intensity (I_{ir}), energy ($h\nu$), and spectral width ($\Delta\lambda$) is very important. Mercury lamps are suitable sources of the radiation which evoke photolysis, generation of radicals and initiate the energy transfer processes in the investigated systems.

Until now only a few types of statical and hydrodynamical reactor systems with the mercury light sources have been described [1, 2]. Unfortunately, account has not be taken of some important experimental factors that influence the proper course of photochemical reactions or initiate the chemiluminescence [1].

In this paper the energetic and spectral characteristics of an electrodeless discharge low-pressure mercury lamp and parameters optimizing the photochemical flow reactors are given. These reactors can be used for photochemical purposes as well as for the excitation of the chemiluminescence in solutions containing, for instance, aminoacids and proteins.

The electrodeless discharge lamp powered by a high frequency electromagnetic field (140 MHz) was constructed in the Institute of Physics, of the University of Toruń. The use of the lamp is characterized by: i) very long working time of the lamp, ii) small thermal effect, iii) constant I_{ir} output.

The energetic and spectral characteristics of the mercury lamp are given in table.

The intensity of UV radiation emitted by the lamp was estimated by using a chemical actinometer (uranyl oxalate) [3].

---

* This work was carried out under the Research Project R III. 13.1.2.

The spectral characteristics of the Hg-lamp include a relative spectral distribution of its energy estimated by the spectrographic method, using a Zeiss (GDR) grating spectrograph, type PGS-2, and spectrographic plates of the 200–500 nm sensitivity range, produced by ORWO (GDR).

The scheme of the apparatus containing the electrodeless mercury lamp and its coupling to a pump and the detecting-analyzing system is shown in fig. 1.

The following factors are very important for the optimization of a photochemical flow-system inducing *CL*:

1. Dead-time (t_d) elapsing from the moment when the irradiated liquid medium left the light-field in the reactor (lamp) to the moment of its entry into the cuvette *k*, i.e., the

Table. Energetic and spectral characteristics of the electrodeless RF-powered mercury lamp used in a photochemical flow reactor

Power consumption [W]	Intensity of radiation [hν/min/cm³]	Emission lines [nm]	Blackening intensity
40	$4.0 \cdot 10^{17}$	253.7	[100.0]
		265	3.1
		275	0.9
		280	0.8
		289	1.4
		297	2.4
		302	2.4
		312/313	39.3
		334	1.4
		366	48.3

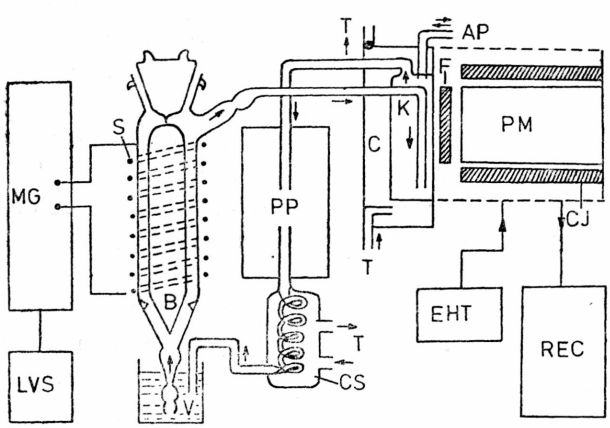

Fig. 1. Block diagram of the system for the excitation and measurement of photochemiluminescence containing a mercury electrodeless lamp:

MG – RF-wave generator, *B* – quartz mercury lamp, *S* – Cu-spiral wire, *V* – auxiliary vessel with a tested solution and thermostatic coil, *LVS* – low-voltage power supply, *PP* – peristaltic pump type 372-1 Unipan, *C* – light-tight cover, *K* – cuvette, *AP* – auxiliary pipe, *T* – cooling water (thermostat), *F* – filter, *CJ* – cooling jacket, *PM* – photomultiplier EMI 9558 QB cooled with a solid CO_2, *EHT* – high voltage unit, *REC* – recorder, *CS* – cooling spiral

measurement of *CL* intensity:

$$t_d = V_d/W,$$

where V_d — the volume of liquid present in the pipe joining the reactor with the cuvette k,
W — the output (expense) of liquid, i.e., the flow-rate ($dm^3\ s^{-1}$).

The dosage system should ensure the lowest possible value of t_d because of the exponential character of *CL* intensity decay. Our apparatus gave the minimal value $t_d = 0.1$ s for the maximum flow rate $W = 0.9\ dm^3 \cdot s^3$ (using the improved peristaltic pump, type 372-1, Unipan).

2. The ratios of the "active" volume (V_{ir}) to cuvette volume (V_k), and to the total "dead" volume (V_d) (the volume of joining pipes). V_{ir} corresponds to the volume of a medium in the reactor. To obtain the maximum value of *CL* intensity the following condition must be fulfilled:

$$V_{ir} \geqslant 5(V_k + V_d).$$

3. The time for which the medium stays in the measuring cuvette (k):

$$t_k = X\frac{V_k}{W},$$

where X — the geometrical factor depending on the space of a cuvette and the location of input and output liquids.

Because of the exponential character of the decay of *CL* intensity, t_k should take the minimal value that requires the minimization of V_k and maximization of W values. The decrease of the V_k value diminishes the signal-to-noise ratio of the system which records the photoinduced chemiluminescence.

4. The value of the ratio τ^*/t_d, where τ^* is a mean lifetime of the electronic excited states production of photoproduct molecules (reciprocal to the mean rate constant of the light-producing reactions). For $\tau^* \geqslant t_d$, the value of V_d only slightly influences the *CL* intensity, whereas for $\tau^* < t_d$, the value of V_d should be minimized. These relationships have been checked by using N,N'-dimethyl-9,9'-biacridyl nitrate (lucygenine) and DL-tryptophane as compounds which are substrates of slow and fast reactions producing emitters (τ^*), respectively.

The above discussion leads to the conclusion that the optimization of the system is a complex problem and usually requires a reasonable compromise among factors 1–4.

Next, the part of radiation coming onto the photomultiplier (*PM*) photocathode from a uniformly luminescent, homogeneous, transparent medium of a cylindrical shape (cuvette k, fig. 2) has been estimated. The following formula was used [4]:

$$dI = \frac{I_0\,dv}{4\pi}\int_0^{\Theta_{max}} \sin\Theta d\Theta \int_0^{2\pi} d\varphi = \frac{I_0\,dv}{2}(1-\cos\Theta_{max}),$$

where I and I_0 are the respective light intensities passing through the cuvette k and generated in 1 cm^3 of a medium, and φ is a radial coordinate of dv projection. Since the cuvette of the dimensions $r = 2$ cm, and $z = 1$ cm is aluminized (reflection coefficient $\simeq 0.9$)

about 65% of the light generated in the medium is let through the front of the cuvette. Assuming that from each point of the cuvette front the light comes out isotropically at the acceptance angle 2π, a photocatode of the radius $R' = 2$ cm, placed at the distance $l = 2$ cm from the cuvette front, will receive about 25% of the total light passing throught the cuvette.

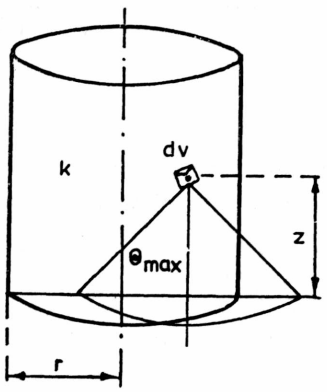

Fig. 2. The scheme of a luminous medium in a cylindrical cuvette k and parameters of its measurements. Explanations in the text

The coefficient of light transfer K between the cuvette k and the photocathode face may be roughly estimated as:

$$K = \frac{1}{2\pi} \int_0^{\arctan \frac{R'}{l}} \sin\Theta d\Theta \int_0^{2\pi} d\varphi.$$

Under the given geometrical conditions about 30% of the radiation generated in the medium reaches the photocathode. Finally, the quantum yield of the photocathode (S-20), equal to about 20% at $\lambda = 440$ nm, lets out 4% of the total radiation transformed into photoelectrons recorded with $\simeq 90\%$ efficiency in the electronic system.

These data allow to estimate the efficiency of the detection system

$$\eta = \frac{n_c}{n_{h\nu}},$$

and the photochemical yield of *CL*:

$$\Phi_{PCL} = n_{h\nu}/n_a,$$

where n_c, $n_{h\nu}$ and n_a are the respective numbers of counts, photons emitted from the cuvette k, and of UV photons absorbed by the medium in the reactor. The values of $n_{h\nu}$ and η may also be calculated using the low-level *CL* standard reaction with luminol [5].

The geometrical parameters of the electrodeless Hg-lamp and its power supply system are being modified in order to increase the I_{ir} value, and to decrease the size of the Hg-lamp and the dead-time (t_d).

Results of photochemical investigations performed with the help of the described electrodeless mercury lamp are published elsewhere [6].

References

[1] SAPEZHINSKII I. I., *Biolyuminescenciya*, Vol. XVI, Trudy Moskovskogo Obshchestva Ispytatelnei Prirody, Moskva 1966.
[2] SCHMIDT H., STAUFF J., Studia Biophys. (GDR) **3** (1967), 81.
[3] CALVERT J. G., PITTS J. N., JR., *Photochemistry*, Wiley and Sons, New York 1966.
[4] MARGULIS G. F., *Sverkhslabye svecheniya v biologicheskikh sistemakh*, Vol. XXXIX, Trudy Moskovskogo Obeshchestva Ispytatelnei Prirody, Moskva 1972.
[5] LEE J., SELIGER H. H., Photochem. Photobiol. **4** (1965), 1015.
[6] SŁAWIŃSKI J., et all., Photochem. Photobiol. **32** (1980), 253.

Received December 18, 1980

Применение безэлектродной ртутной лампы в фотохимическом проточном реакторе

Представлены энергетическая и спектральная характеристики безэлектродной ртутной лампы, возбуждаемой высокочастотным разрядом (140 МГц), польского производства, применяемой в фотохимических проточных реакторах. Обсуждены параметры этих реакторов.