

## Short Communication

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### Use of the potassium ferrioxalate actinometer below 254 nm

ERNESTO FERNÁNDEZ<sup>†</sup>, JUAN M. FIGUERA and AURORA TOBAR

*Instituto de Química Física Rocasolano, C.S.I.C., Serrano 119, Madrid-6 (Spain)*

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The wavelength range 220 - 254 nm is readily accessible and of great interest for photochemical studies. However, no high sensitivity actinometer (uranyl oxalate may be used at 208 nm with low sensitivity [1]) is available to cover this spectral region.

Ferrioxalate [2 - 6] has been successfully used [7 - 19] but its use is restricted to wavelengths not less than 254 nm because quantum yield data are not available below this wavelength. This communication is intended to fill the gap.

The ferrioxalate actinometer presents an intrinsic problem below 254 nm: the absorption of light by the photolysis products [3].

The ratios of the extinction coefficients of the actinometer to its products are 0.05 (230 nm) and 0.38 (200 nm). We therefore used the actinometer in this region and maintained the  $[\text{Fe}^{2+}]$  formed below 4%, so that even in the most unfavourable case (*i.e.* at 222 nm) in which the extinction coefficient ratio is 0.09, the light absorbed by the products at the end of irradiation was only 2% of the total.

The general actinometric procedure was followed but the orthophenanthroline solutions were not older than five weeks, as recommended by Bowman and Demas [11]. The order of addition of reagents did not influence the results.

Each of the 220, 230, 238 - 240 and 248 nm emission bands of a medium pressure mercury arc (550 W Hanovia 679A36) was selected using a Bausch and Lomb monochromator (grating of 1200 lines  $\text{nm}^{-1}$  blazed at 210 nm). The light output of the system was checked at each wavelength with a 0.5 m Jarrell Ash monochromator (maximum resolution 0.02 nm) and the detector described below. The ratio of the light intensity at a given wavelength relative to that at 254 nm was measured with an EMI 9783B photomultiplier (Farnell Model EHT-1 power supply) whose quantum efficiency in the range 220 - 300 nm only varied from 21.8 to 22.2% [12]. This change in sensitivity was taken into account.

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<sup>†</sup>Permanent address: Universidad de Chile, Valparaiso, Chile.

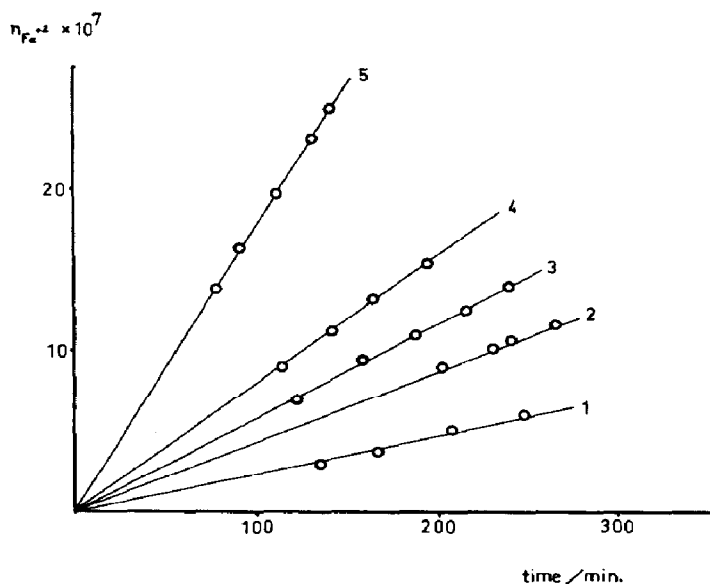


Fig. 1. The actinometry : number of moles of  $Fe^{2+}$  formed as a function of irradiation time. The straight lines are the least squares fits to the experimental points at the following wavelengths: 1,  $\lambda = 222$  nm; 2,  $\lambda = 230$  nm; 3,  $\lambda = 238 - 240$  nm; 4,  $\lambda = 248$  nm; 5,  $\lambda = 254$  nm.

TABLE 1

Quantum yield for the potassium ferrioxalate actinometer between 222 and 254 nm

Wavelength (nm)	$\frac{Fe^{2+}(\lambda)^a}{Fe^{2+}(254)}$	$\frac{I(254)^b}{I(\lambda)}$	$\Phi(Fe^{2+}, \lambda)^c$
248	0.433	2.45	1.35
238 - 240	0.330	1.65	0.68
230	0.240	2.27	0.67
222	0.144	2.80	0.50

<sup>a</sup> Ratio of the  $Fe^{2+}$  rate of formation at  $\lambda$  and at 254 nm.

<sup>b</sup> Ratio of the incident light intensities at the indicated wavelengths measured with an EMI 9783B photomultiplier.

<sup>c</sup> Mean values of three determinations; maxima standard deviation less than 6%.

Actinometries were carried out by comparing the rate of  $Fe^{2+}$  formation at the wavelengths given with that obtained at 254 nm (Fig. 1). The light ratios were measured at the same time.

Possible lamp decay or instability was not observed but in any case the actinometry at 254 nm was performed separately for each wavelength and the total determination of each quantum yield was repeated three times, alternating the experimental order of the operations.

The quantum yields  $\Phi(\lambda)$  for  $\text{Fe}^{2+}$  presented in Table 1 were obtained using the expression

$$\Phi(\lambda) = \frac{\text{Fe}^{2+}(\lambda)}{\text{Fe}^{2+}(254)} \frac{I(254)}{I(\lambda)} \Phi(254)$$

where  $I(254)/I(\lambda)$  is the light intensity ratio measured with the photomultiplier and  $\text{Fe}^{2+}(\lambda)/\text{Fe}^{2+}(254)$  is the ratio of the  $\text{Fe}^{2+}$  formation rate at  $\lambda$  and 254 nm.

The validity of our results was checked by recalculation, using the same method, of some values of Hatchard and Parker [7] reported for the 300 - 313 nm range. The discrepancies were well within 5%.

Moreover, the quantum yield of diazoisopentane decomposition at 230 nm determined in our laboratory using the actinometer values reported here was in agreement with expectations [13].

## References

- 1 G. S. Forbes and L. J. Heidt, *J. Am. Chem. Soc.*, **56** (1934) 2363.
- 2 A. J. Almand and W. W. Webb, *J. Chem. Soc.*, (1929) 1518.  
R. Livingston, *J. Phys. Chem.*, **44** (1940) 601.
- 3 C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220** (1953) 104.
- 4 C. A. Parker, *Trans. Faraday Soc.*, **50** (1954) 1213.
- 5 K. Yamashita and H. Imai, *Bull. Chem. Soc. Jpn*, **41** (1968) 1339.
- 6 G. D. Cooper and B. A. De Graff, *J. Phys. Chem.*, **75** (1971) 2897.
- 7 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235** (1956) 518.
- 8 G. B. Porter, J. G. W. Doering and S. Karanka, *J. Am. Chem. Soc.*, **84** (1962) 4027.
- 9 J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40** (1964) 519.
- 10 J. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59** (1955) 783.
- 11 W. D. Bowman and J. N. Demas, *J. Phys. Chem.*, **80** (1976) 2434.
- 12 EMI photomultiplier specifications.
- 13 M. J. Avila, J. M. Figuera, V. Menéndez and J. M. Pérez, *J. Chem. Soc. Faraday Trans. I*, **72** (1976) 422.