

Hatchard C G & Parker C A. A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer.

Proc. Roy. Soc. A 235:518-36, 1956.

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This paper presents the detailed results of the calibration, at a wide range of wavelengths and light intensities, of the chemical actinometer that was first described in an earlier paper.¹ The actinometer is now used as a standard for ultraviolet light measurement in many laboratories throughout the world. [The SCI® indicates that this paper has been cited in over 2,075 publications since 1956.]

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The basic idea behind this paper was described by me in an earlier paper.¹ At that time, 1950, there was an obvious need for an actinometer capable of measuring small doses of ultraviolet light of both long and short wavelength with simplicity and accuracy. I required such an actinometer both for laboratory work and for the determination of solar ultraviolet distribution in the field. The well-known actinometer based on uranyl oxalate was unsuitable for low light intensities owing to the difficulty of measuring accurately the small difference between two titrations. It was clear that actinometers in which the photolysis products are directly determined are intrinsically capable of greater sensitivity and versatility. The ultimate sensitivity depends upon the delicacy of the method for the determination of the photolysis products. For this method, absorption spectrophotometry (at that time a relatively new laboratory technique) was an obvious choice, but direct spectrophotometry, implying as it does a high absorption by the photolysis products, itself introduces the difficulty that the products act as inner filters and disturb the linearity of response of the actinometer.

These considerations prompted my investigation of systems in which the photolysis products absorb weakly, but in which they

can readily be transformed into strongly absorbing compounds by subsequent reaction with an appropriate reagent. The complex oxalate of ferric iron seemed a good candidate from the outset—it had been shown much earlier by Allmand and Webb² to photolyse with high quantum efficiency to give ferrous iron (as its oxalate), a product for which a sensitive colorimetric reagent (*o*-phenanthroline) was available.

However, there were two difficulties. First, in weakly alkaline solution, the ferrous oxalate precipitated. Allmand and Webb retained it in solution with an excess of oxalate, but this interfered with the reaction with *o*-phenanthroline. Second, in neutral or alkaline solution, the ferrous iron rapidly autoxidised, and air therefore had to be carefully excluded. This made the procedure extremely inconvenient. The breakthrough came when I discovered that in dilute acid, the trioxalato-ferric ion does not dissociate completely but forms the monoxalato-ferric ion, FeC_2O_4^+ . This was found to be highly photoactive. Furthermore, the ferrous ion produced by photolysis was stable in air and could be very easily determined at low concentration with *o*-phenanthroline.

The preliminary experiments reported in the 1953 paper thus demonstrated conclusively that the system was an almost ideal chemical actinometer for wavelengths between 250 and 500 nm. The actinometer was placed on a firm foundation by the calibration work done in collaboration with C.G. Hatchard and described in this highly cited paper. The reasons for its repeated citation are not far to seek. It gives precise values of quantum efficiency at a series of wavelengths between 254 and 579 nm. It demonstrates the constancy of quantum yield over a very wide range of intensities, including those from high-intensity flash lamps. Perhaps most important, it gives detailed instructions for using the actinometer, which have now become standard in many laboratories throughout the world.

1. Parker C A. A new sensitive chemical actinometer. I. Some trials with potassium ferrioxalate.

Proc. Roy. Soc. A 220:104-16, 1953. (Cited 485 times since 1955.)

2. Allmand A J & Webb W W. The photolysis of potassium ferrioxalate solutions. Part I. Experimental.

J. Chem. Soc. 1929:1518-31.