

Fig. 3. Fluorescence spectra at 78°K. *a*, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{MnO}_4^{2-}$. *b*, $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{MnO}_4^{2-}$. *c*, $\text{Ca}_5(\text{PO}_4)_3(\text{Cl},\text{F}):\text{MnO}_4^{2-}$. *d*, Blue apatite from Hugo mine in Keystone, South Dakota.

proximately $5 \times 10^{19} \text{ cm}^{-3}$. By chemical analysis the total manganese present is about $6 \times 10^{20} \text{ cm}^{-3}$. The difference between these two amounts probably represents the amount of Mn^{2+} present in the mineral either incorporated in the apatite or in precipitated phases. Natural blue apatite can be bleached by heating in air for a few minutes at about 600°C. The resulting material has a slightly pink body color. Under 2537 Å ultraviolet excitation it has the luminescence of Mn^{2+} , and shows a peak at 5700 Å, which is characteristic of synthetic apatites used in the manufacture of fluorescent lamps.

It is interesting that the synthetic apatites containing MnO_4^{2-} are not bleached by heating at 600°C as is the natural crystal. However, after

irradiation of these crystals with $2 \times 10^7 \text{ r}$ of 1 mev electrons, heating at 600°C does result in an appreciable amount of bleaching of the MnO_4^{2-} absorption as well as of the color centers formed on irradiation. The radiation dosage to which the synthetic samples were subjected is typical of that received on the surface of the earth in about 2×10^8 years as the result of natural radioactivity (7). We conclude that the thermal bleaching of both the natural apatite and our synthetic crystals requires the presence of other defects. The presence of the blue color in natural crystals requires that either the crystals grew at temperatures much less than 600°C or that those other defects were formed after the crystals cooled below 600°C (8).

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Photochemical Production of the Solvated Electron in Ethanol

Abstract. Flash photolysis of several inorganic anions in ethanol gives an absorption spectrum attributed to the solvated electron.

The production of the hydrated electron by flash photolysis of inorganic salts in aqueous solution has been reported recently (1, 2). Comparable results have been obtained in ethanolic solution, giving spectra in good agreement with those obtained by pulse radiolysis (3).

Figure 1 shows the transient spectra that we obtained by flash photolysis of 0.0001M potassium iodide in air-free ethanol. We used the experimental method that was described previously

(2), except that the spectra were taken with Kodak types 103-F and I-N spectroscopic plates and the data reported here are corrected for the spectral sensitivities of the emulsion. The broad, red band of short lifetime is assigned to the solvated electron. The absorption of longer duration is due to the diiodide ion, which was identified in aqueous solution by Grossweiner and Matheson (4) and in ethanolic solution by Edgcombe and Norrish (5). A weak solvated electron spectrum was also

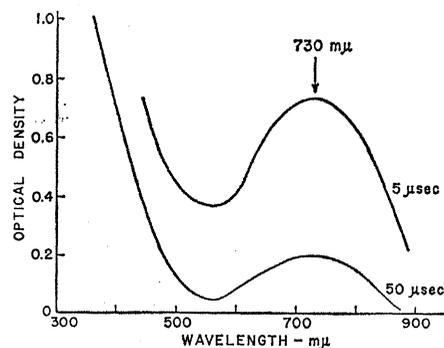


Fig. 1. Transient spectra obtained by flash photolysis of an air-free solution of 0.0001M potassium iodide in ethanol. The band below 500 mμ is due to the di-iodide ion; the shorter-lived red absorption band is attributed to the solvated electron.

obtained from 0.01M potassium bromide in ethanol, but pure ethanol gave a negative result. A strong solvated electron spectrum was obtained by flash photolysis of 0.10M potassium hydroxide in ethanol. The associated longer-lived radical spectrum has a maximum at 380 mμ and has not been identified.

Although the phenol derivatives give strong hydrated electron spectra (2), this is not the case for *p*-cresol in ethanol. Negative results were obtained from 0.001M *p*-cresol and from 0.001M *p*-cresol containing 0.005M potassium hydroxide; for the latter case the 280 mμ band of *p*-cresol was shifted to 299 mμ, indicating that dissociation of the hydroxyl group was almost complete. The strong absorption of the *p*-methyl phenoxyl radical was observed in both cases, showing that the light intensity was adequate for photolysis. The different behavior of the aromatic anion in water and in ethanol remains to be explained (6).

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