high temperature symmetry have taken place. The unit cells of the high temperature modifications are all assumed to be face-centered cubic. The lattice parameters are given in Table 2.

A preliminary study of the second modification of $K_3AlF_6$ (143°C–327°C) indicates that the structure is still tetragonal.

*Experimental.* The compounds were prepared by fusing aluminium fluoride and the respective alkali fluoride in a mole proportion 1:3. The aluminium fluoride was prepared by vacuum sublimation of anhydrous $AlF_3$ (A. D. Mackay, Inc., U.S.A.). The method has been described in detail by Rolin.[5] The other chemicals used were commercially available reagent grade potassium fluoride (Baker & Adamson, U.S.A.), rubidium fluoride (Light Laboratories LTD, England) and cesium fluoride (The British Drug Houses LTD, England). The chemicals were carefully dried in a vacuum furnace at 400–500°C before use.

The DTA cooling curves were recorded by a Speedomax G X–Y recorder and by use of a D. C. Microvolt Amplifier (range 50–2000 microvolt, Leeds and Northrup, U.S.A.). The low temperature X-ray investigations were carried out with a Nonius type Guinier camera using Cu$K\alpha$ radiation, $\lambda(K\alpha_1) = 1.5405$ Å. At higher temperatures the samples were investigated by a conventional parafocusing X-ray diffraction technique using the same Cu$K\alpha$ radiation. The intensity was recorded with a Geiger counter connected to a Philips PW 1051 recorder (Philips, Eindhoven, Holland). The temperature in the furnace was held constant within ±5°C by a temperature controller (Siemens, Germany) connected with a Pt/Pt 10 Rh thermocouple. Purified nitrogen ($N_2$ 99.99 %, Norsk Hydro, Norway) was led through the furnace.

The density measurements were carried out at 25°C by a vacuum pycnometric method using Shell Odourless Kerosene as a displacement liquid.

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# Tritiated Naphthalene as a Chemical Dosimeter for Low Radiation Doses

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The most commonly used chemical system for the determination of radiation doses is the $Fe^{2+}/Fe^{3+}$-dosimeter, generally referred to as the Fricke dosimeter, which has been studied by a large number of investigators.[1-3] In spite of its many advantages, this system has a serious drawback, namely its insensitivity, which makes it useful only down to about 1000 R.

Rudstam and Svedberg [4] have tried to improve the Fricke dosimeter by the use of $^{59}Fe$, but the internal dose from the isotope seems to limit the usefulness of this system. Another attempt at increasing the sensitivity of this dosimeter involves the addition of organic compounds.[5,6] However, the systems thus produced, are like other systems utilizing chain reactions, *e.g.* those including chlorinated hydrocarbons,[7] sensitive to impurities and strongly dependent on dose rate and temperature.

Other attempts to solve the problem have been the aqueous benzene dosimeter described by Klein [8] and the benzoic dosimeter described by Moroson and Laughlin.[9] Both methods are claimed to be usable for doses down to the region of 10–20 R.

In our search for a more sensitive and reproducible dosimeter, capable of measuring doses over a wide range, we have tested different lipophilic substances yielding more hydrophilic products on irradiation and thereby enabling a separation. In order to extend the dose range to doses

lower than those measurable by chemical analysis, we used isotope-labelled compounds. The most suitable substances found so far are benzene and naphthalene. Preliminary results from these investigations have been reported earlier.[10]

*The naphthalene dosimeter.* It was found that commercially available benzene and naphthalene had to be purified if doses below about 10 rad were to be made measurable. In this respect, naphthalene is far easier to handle than benzene owing to its sublimation ability and therefore naphthalene was selected for the present investigation.

*Experimental procedure.* Naphthalene-1-T (Radiochemical Centre, Amersham) was purified in two steps: (1) shaking of a two-phase system of petrol ether and aqueous sodium hydroxide to which were added labelled naphthalene and small amounts of inactive α-and β-naphthol. Non-labelled naphthalene was added at this stage if a lowering of the specific activity was desired; (2) evaporation of the petrol ether phase followed by sublimation of the residual naphthalene. Yields of purified naphthalene were usually 90–95 %. The naphthalene was dissolved in triple-distilled water at 20°C (magnetic stirring for 6–12 h) and stored at 5°C.

It was found that, compared to the original procedure,[10] the separation of the naphthalene from the radiation produced compounds could be considerably simplified by evaporation (70°C) of the irradiated water solutions on metal dishes designed for proportional counters. The evaporated naphthalene is collected in a cool trap. The reaction products, which are more or less polar substances such as naphthols and carboxylic acids, become firmly bound to the metal surface in this process, and can be removed only by ignition. However, due to the autoxidation of naphthalene, this method results in increased control values. This can be prevented by the addition of an antioxidant before the evaporation, or by a single benzene extraction of the excess naphthalene from an ammoniacal water phase, which is then evaporated.

Thus three alternative procedures giving about the same yields are described. 2 ml samples of aqueous naphthalene are utilized in these processes. (*a*) 1 ml 0.5 M NaOH solution is first added to the sample, after which 5 ml benzene is introduced. The mixture is shaken vigorously in a glass-stoppered tube for 2 min. This step is repeated three times, the benzene phase being discarded on each occasion. After this extraction process, the water phase is acidified by the addition of 1 ml concentrated hydrochloric acid, and the undissociated acids of the hydrophilic reaction products from the irradiation can now be extracted by repeated shaking with benzene (3 × 2 ml). (*b*) 0.1 ml of an antioxidant solution (0.2 ml antioxidant per ml) is added to the aqueous naphthalene and the sample evaporated on a metal dish. Pyrogallol and hydroquinone as antioxidants have been found to lower the control values. The autoxidation of these substances yields small amounts of hydrogen peroxide which may oxidize the naphthalene and therefore the control values can be further reduced by the addition of small amounts of catalase to break down the $H_2O_2$. (*c*) 1 ml concentrated ammonia solution and 0.5 ml benzene are added to the irradiated naphthalene solution. After 2 min of vigorous shaking the benzene phase (containing at least 95 % of the naphthalene) is withdrawn, 1 ml benzene is added cautiously through a pipette, care being taken not to mix the phases, and after immediate removal of the benzene, the water phase (or a certain part of it) is evaporated on stainless steel dishes.

The benzene extract prepared according to method (*a*) is most conveniently measured in a liquid scintillation counter. The evaporation of the water solutions from (*b*) and (*c*), and the benzene extract from (*a*) results in "infinitely" thin samples, which can be measured in a windowless proportional counter without loss of counting efficiency due to self absorption.

Irradiations were carried out either in a large $^{60}$Co-source, type Picker Hot Pot, equipped with an additional Pb-shield inside the irradiation chamber and giving a dose rate of about 50 000 R per hour, or at different distances from a small $^{60}$Co-source giving 1.6 Rhm. The Fricke dosimeter was used for determinations of absolute dose rates and an ionization chamber for relative measurements.

*Results and discussion.* The yield of hydrophilic compounds produced by irradiation of a naphthalene-water solution was studied as a function of the naphthalene concentration in the range 0.01–0.16 mmole/l (Fig. 1). For further experiments a concentration of 0.065 mM was selected. This concentration yielded the lowest control value, while still being in the range where the yield is independent of the concentration of naphthalene.

The production of hydrophilic substances, expressed as counts per minute, as a function of the radiation dose is represented in Fig. 2; separation according

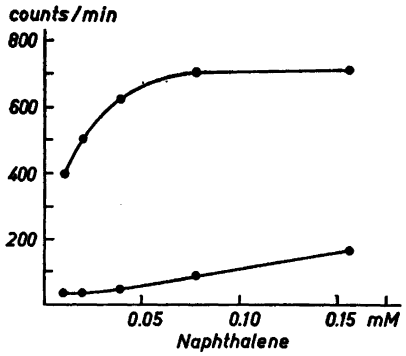


*Fig. 1.* Production of hydrophilic substances at a constant dose (50 rad) as a function of the naphthalene concentration.

to method (*c*). Each sample was measured with a "counting error" of 1 %. Mean values of two determinations give a standard deviation of 13 %, with no difference in the error between the low and high dose parts of the curve. The main errors are obviously introduced during the chemical procedures (extraction, evaporation) which means that the reproducibility can be improved by refining the method and/or increasing the number of samples for each dose.

The naphthalene dosimeter was originally only designed to measure the lowest possible doses without considering the upper limits. Further experiments have proved that a 0.065 mM solution gives a linear dose response curve up to at least 3000 rad. The upper limit is set by the concentration ratio of the radiation produced compounds and the naphthalene in the solution. At 3000 rad about 15 % of the naphthalene is destroyed and this means that the radiation products begin to compete with the naphthalene as radical scavengers. An increase of the naphthalene concentration will consequently increase the linearity towards higher doses, but also reduce the reliability of the dosimeter in the lowest dose range.

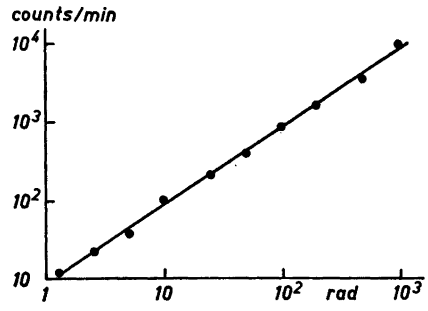


*Fig. 2.* Production of hydrophilic substances as a function of the dose.

As no determinations of G-values in the naphthalene system have yet been performed (loss of $^3H$ from the 1-position has to be considered), a reference standard must be used for absolute dose measurements. The overlap of the dose regions of the naphthalene dosimeter and the Fricke dosimeter facilitates the use of the latter as a standard.

In the investigation described, naphthalene of a specific activity of 17 c/mole was used. Thus, with a concentration of 0.065 mM, an internal dose of 0.3 rad per day is obtained. The chemical change caused by this dose is equal to about 6 % of the zero value for a freshly prepared solution.

The naphthalene dosimeter described above is characterized by (*a*) a linear dose response between 1 and 3000 rad (0.065 mM solution), (*b*) independence of dose rate within a wide range (investigated between 3 and 50 000 R/h, (*c*) a storage life of at least 14 days with retained capacity to measure doses down to 1 rad.

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