

Fig. 1. Relation between  $\beta$ -ray absorption and thickness of dust layer. Curve 1, filters labelled with thallium-204; curve 2, filters labelled with nickel-63

standards or by objective measurement as, for example, reflectance photometry<sup>4</sup>. Chemical reaction between suitably impregnated or wetted filters and aerosol droplets may also be employed with quantitative estimation of the resulting colour effects<sup>5</sup>.

It is known that various substances may be incorporated into the filter mass by adding suitable reagents to the stock solutions used for filter preparation<sup>6</sup>; thus it is possible to obtain filters containing chemical reagents in the form of very fine and homogeneous dispersion throughout the filter. Such reagents may react with aerosol droplets or with the surface layer of solid particles.

The application of radioactive thickness gauging for the estimation of deposit mass in filters has already been reported?. The present communication deals with the application of special features of membrane filters by converting the filters themselves into the radiation source used for thickness gauging, thereby eliminating the effect of filter thickness from measurement.

Although the incorporation of radioactive material into the filter mass is an evident procedure and will be reported in due course, initial work was performed by adsorbing radioactive nickel or thallium salts from solution upon the filter surface. The filters used had a mean pore size of  $2r = 0.9\mu$  and a thickness of 130µ. The diameters of the filter disks were 36 mm. Initial total filter activities were  $0 \cdot 1 - 0 \cdot 2$  µc. and  $1-5 \ \mu c.$  for thallium and nickel filters, respectively.

Filters of this kind were used for the estimation of the concentration of solid aerosols and industrial dust of constant composition. Prior to air filtration, initial filter activity was measured with a Geiger-Müller window counter (3.7 mgm./cm.2) (activity  $n_0$ ). Thereafter air was drawn through the filter, and as soon as a visible layer had formed on the filter, filtration was interrupted, residual activity measured and the mass of the deposit determined by weighing. This procedure was repeated several times and the expressions  $\log n_0/n_i$ , where  $n_i$  are the residual activities, calculated. These values were correlated with the amounts of deposit per unit filter area.

Fig. 1 illustrates a typical example with flue dust of mean particle size  $1.7\mu$ , the chief chemical components of which were alumina, ferric oxide, silica and traces of other components. Experiments summarized in Fig. 1 were performed with filters labelled with nickel and thallium.

Results indicate that the preparation of homogeneously labelled filters and measurement therewith are possible. Such filters may be used for the rapid assessment of air-borne material. The lower limit of sensitivity is at present found to be 1.6 mgm./cm.<sup>2</sup> and 6.0 mgm./cm.<sup>2</sup> for filters labelled with nickel and thallium, respectively. Because of their weak radiation and long half-lives, nickel filters seem to be the more suitable ones. With an effective filter area of 1 cm.<sup>2</sup>, absolute air volumes of 10-300 litres are sufficient to obtain deposits suitable for the assessment of high and medium dust concentrations.

It is evident that the present procedure provides mass-proportional values of dust concentration. More detailed investigation indicates that the sensitivity of measurement by the method outlined depends not only on the chemical composition of the assayed dust but also on its particle size distribution.

A more detailed account of this work will appear elsewhere.

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<sup>1</sup> Spurný, K., and Vondráček, V., Chem. listy, 50, 1331 (1956).

- <sup>2</sup> Kubie, G., Jech, C., and Spurný, K., Coll. Czechoslov. Chem. Comm. (in the press).
- Spurný, K., Prac. lékarství, 11, 197 (1959).
  Paulus, H. J., Talvitie, N. A., Fraser, D. A., and Keenan, R. G. Indust. Hyg. Quart., 18, 267 (1957).
- Lodge, J. P., and Tufts, B. J., Tellus, 7, 2 (1956).
- Spurný, K., Chem. listy (in the press).
- Stephan, D. G., Bohnslav, P. T., Herrick, R. A., Walsh, G. W., and Rose, jun., A. H., Amer. Indust. Hyg. Assoc. J., 19, 276 (1958).

# **RADIATION CHEMISTRY**

## **Changes in Conductivity of Pure Water** caused by X-Irradiation

Most of our present knowledge about the physicochemical processes occurring in the radiolysis of water has been obtained by purely chemical methods<sup>1</sup>. I have now tried to obtain some additional data by using a physical method. In the course of the primary and secondary processes which occur when water is irradiated with ionizing radiation, it is possible that charged particles will be formed which cause an increase in conductivity during irradiation. I therefore studied the variation with time of the conductivity of pure, non-degassed water when it was submitted to pulsed X-irradiation, in order to obtain information about the eventual concentration and life-time of such charged particles<sup>2</sup>.

In a preliminary investigation, water, prepared by distilling three times-twice in a quartz still-with access of air, was irradiated in a conductivity cell made of 'Plexiglas' and with silver electrodes, with X-ray pulses (60 kVp., average dose-rate about 5 kr./min.) obtained by a rotating sectored disk.

A d.c. voltage was applied to the cell through a resistor, so that a periodical change in conductivity synchronous with the X-ray pulses would give rise

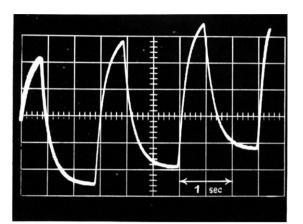


Fig. 1. Photograph of an oscilloscope picture showing the variation of conductance when water is irradiated with square wave X-ray pulses (light to dark period 1:2)

to an a.c. voltage with the same frequency. This voltage was measured by means of a synchronized amplifier. The synchronization was effected by interrupting the light beam falling on a photo-electric cell by the same sectored disk.

The experiment showed that there was in fact a periodical change in conductivity, the amplitude of which was inversely proportional to pulse frequency in the range from 10 to 3,000 c.p.s. covered in this investigation. It could therefore be concluded that during irradiation ions were formed with a life-time greater than 0.1 sec.

Based on these results, I constructed an apparatus with which I could display on an oscilloscope screen the variation with time of the conductivity of water irradiated with slow X-ray pulses (0.2-20)c.p.s.).

The water used in this experiment was pre-distilled first from alkaline permanganate and then from acid dichromate solution before being further purified in the quartz still, in order to be certain that no organic impurities were present. Between the two quartz distillation stages the vapour was heated to about 800° C. The conductivity cell, this time made of quartz and with platinum electrodes, was con-

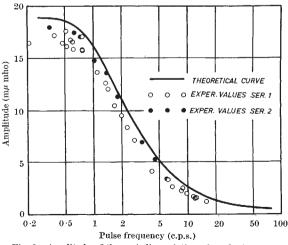


Fig. 2. Amplitude of the periodic variation of conductance as a function of pulse frequency. The theoretical curve is calculated from the experimentally obtained dose-rate dependence and life-time. Maximum dose-rate, 11-9 krads/min.

nected to an a.c. bridge operating at 2 kc.p.s. The diagonal voltage, which was proportional to the variation of conductance, was amplified, rectified, and fed to a d.c.-oscilloscope ('Tektronix').

Fig. 1 shows a photograph of the oscilloscope picture showing the variation of conductance caused by irradiation with square wave-pulses (light to dark period = 1:2). In Fig. 2 the amplitude of the periodical conductance changes is plotted against pulse frequency. Two effects seem to be superimposed : (1) A reversible increase in conductivity during irradiation which returns to zero after the end of irradiation; (2) an irreversible rise in conductivity which starts practically instantaneously with irradiation and continues until the end of irradiation.

An analysis of the variation of conductivity as a function of pulse-frequency and dose-rate leads to the conclusion that the reversible effect may be due to the formation of ions the concentration of which varies according to the differential equation :

$$\frac{\mathrm{d}[X]}{\mathrm{d}t} = G_x \frac{\delta}{N_a} - k'[X][S] - 2k[X]^2$$

where [X] is the concentration of the ions in question, [S] that of a scavenger substance with which these ions can react monomolecularly,  $N_a$  the Avogadro number,  $\delta$  the dose-rate, k and k' reaction constants, and  $G_x$  the yield of the ions formed.

A comparison of the properties of the observed ions with radiation-chemical data from the literature suggests that the ion X may be identical with the radical-ion  $\cdot O_2$ , that is, the anion of the radical  $HO_2$  (ref. 3). If this is assumed and if the radical  $HO_2$  is completely dissociated at the pH of the water investigated  $(5\cdot5)$ :  $G_x = 4\cdot3$  radicals/ 100 eV., k' [S] = 2.9 sec.<sup>-1</sup>, and  $k = 1.45 \times 10^7$ litres/mole × sec. The radical-ion  $\cdot O_2^{-1}$  is, according to Haïssinsky<sup>4</sup>, formed directly by the reaction of H-radicals with the dissolved oxygen :

$$\mathrm{H} \cdot + \mathrm{O}_{2} \rightarrow \mathrm{H}^{+} + \mathrm{O}_{2}^{-}$$

A more detailed discussion of a chemical reaction mechanism suggested leads to the equation :  $G_x = G_{\rm H} + G_{\rm OH} + G_{\rm HO_2} - 0.4 = 4.6$  radicals/100 eV. (with radical yields according to Allen and Schwarz<sup>5</sup>). Dainton and Rowbottom<sup>6</sup> have determined the recombination constant of the radical HO2. as  $3\,\times\,10^6$ litres/mole  $\times$  sec. The difference between this value and mine (for  $\cdot O_2^{-}$ ) might be explained by a difference in pH.

The irreversible effect observed in my experiment is probably due to the formation of percarbonic acid from the carbon dioxide dissolved in the water?. According to my experiment the yield of this reaction would be  $G(H_2CO_4) = 0.2$  molecule/100 eV. The term 0.4 in the equation for  $G_x$  mentioned above is twice this value.

A full account of this investigation will be published elsewhere.

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- <sup>1</sup> Dainton, F. S., Brit. J. Radiol., 31, 645 (1958).
- <sup>2</sup> Lotz, A. P., and Schmidt, K., Strahlentherapie, 110, 223 (1959).
- <sup>3</sup> Weiss, J., Trans. Farad. Soc., 31, 668 (1935).
- <sup>4</sup> Haïssinsky, M., J. chim. phys., 53, 542 (1956).
- <sup>3</sup> Allen, A. O., and Schwarz, H. A., Proc. Internat. Conf. Geneva (1958). <sup>6</sup> Dainton, F. S., and Rowbottom, J., Trans. Farad. Soc., 49, 1160 (1953).
- <sup>7</sup> Günther, P., and Holzapfel, L., Z. Phys. Chem., 49, 303 (1941).