Analysis of Ultra-thin Fluorine-containing Layers on Polyethylene by $^{19}F(p,\alpha\gamma)$ Spectrometry

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Summary The $^{19}F(p,\alpha\gamma)^{16}O$ nuclear resonant reaction has been used for accurate measurement of fluorine depth and spatial concentration distributions on surface fluorinated polyethylene.

THE $^{19}F(p,\alpha\gamma)^{16}O$ nuclear resonant reaction has often been used for analytical purposes,[1–3] especially for depth profiling.[4,5] It is possible to determine non-destructively very low fluorine concentrations[6] ($<5 \times 10^{-4}\,\mu g\,cm^{-2}$), to analyse very small areas[7] ($<4\,\mu m$ diameter), and, by combination of depth profiling and scanning over the sample surface, to construct three-dimensional concentration profiles. The technique is not normally applied to plastics because of the difficulty of measuring the incident beam current on the insulating surface and the probability of radiolytic damage. We have successfully applied the technique to the measurement of the spatial distribution and depth profile of the fluorine concentration on the surface of fluorinated polyethylene. The technique is readily applicable to layers of other elements on other materials including teeth.

High-density polyethylene sheets (British Petroleum) were exposed in a cell containing either purified fluorine or commercial cylinder fluorine. These methods[8] are referred to as 'slow' and 'fast', respectively. Exposure times ranged from minutes to several days, and coherent fluorine-containing coatings might have been expected. The sheets were bombarded with mono-energetic protons from a 3 MV Dynamitron accelerator with energies in the region of the large resonance at 872 keV in the $^{19}F(p,\alpha\gamma)^{16}O$ reaction[9] and the 6–7 MeV γ-rays from the reaction were detected in a 7·6 cm × 7·6 cm NaI(Tl) crystal. As the protons pass into the surface of the plastic they lose energy and the yield of γ-rays for any given incident beam energy is related to the concentration of fluorine at a depth at which the proton energy is reduced to the reaction resonance energy. As the natural width of the resonance is 4·7 keV the depth resolution achievable is limited to approximately 0·15 μm. The polyethylene samples were coated with a thin conducting layer (*ca.* 0·01 μm) of Specpure gold in order to aid beam charge collection and heat dissipation.

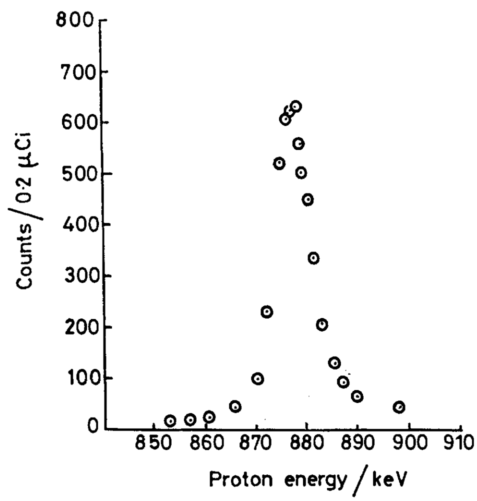

FIGURE 1. Yield curve of 1-min fast-fluorinated polyethylene sample at 872 keV resonance.

The yield of γ-rays was measured as a function of increasing proton energy covering the whole range of resonant response and a typical resonance curve is shown in Figure 1. Such curves can be analysed to give absolute fluorine concentrations by comparison with standard fluorine layers produced by vacuum evaporation of LiF on to tantalum backings. A typical depth profile is shown in Figure 2. Surface homogeneity was also measured by repeating measurements on 1 mm diameter areas across the sample and the results for several different samples are shown in Figure 3.

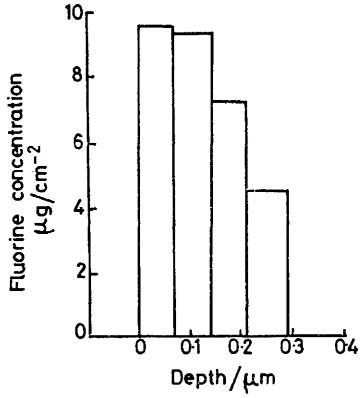

FIGURE 2. Fluorine concentration depth profiles of 1-min fast-fluorinated polyethylene.

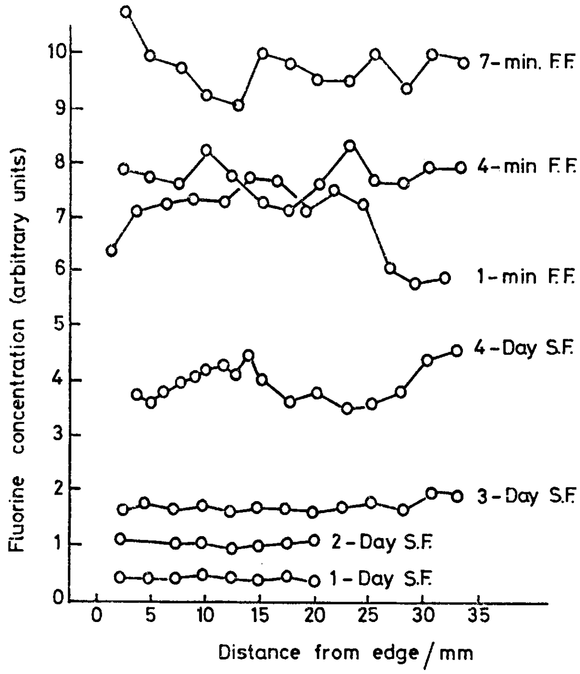

FIGURE 3. Uniformity of surface fluorine concentration of several surface-fluorinated polyethylene strips; S.F. = slow fluorination, F.F. = fast fluorination.

The nuclear technique has been found much more valuable than chemical methods of analysis in several aspects, such as the ability to handle very small sample size, the speed and ease of measuring surface uniformity, its ability to measure depth profiles, and its relatively non-destructive nature allowing repeat measurements.

By interpretation of E.S.C.A. data it is possible[10,11] to deduce information about fluorine depth concentration profiles in similar layers on polyethylene. The complementary nature of these techniques must be emphasised; much thicker fluorine layers may be examined by the $^{19}F(p,\alpha\gamma)$ technique which also gives results directly by simple comparison with a standard.

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