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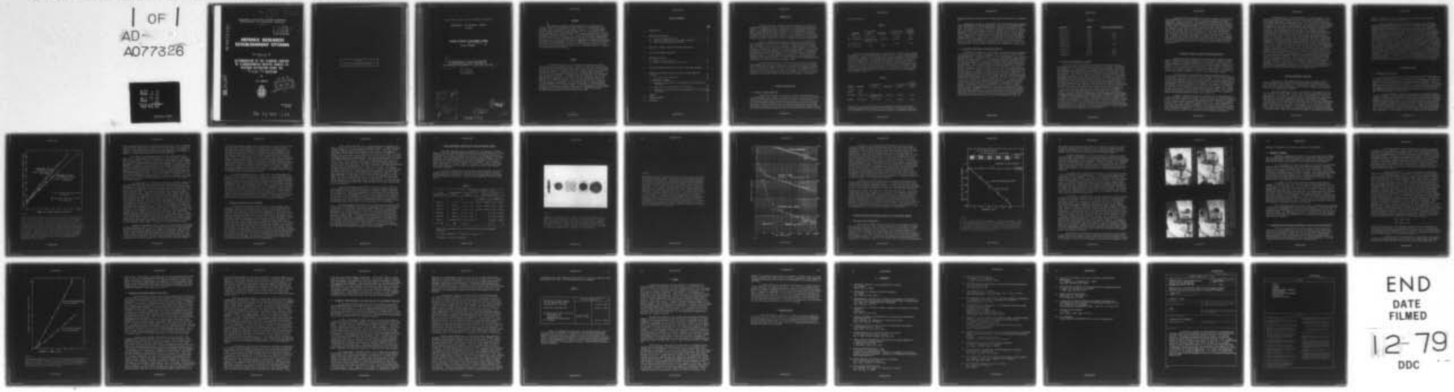

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DETERMINATION OF THE FLUORINE CONTENT OF FLUOROCHEMICAL-TREATED FABRICS BY NEUTRON ACTIVATION USING THE $^{19}F(n,2n)^{18}F$ REACTION

by

F.A. Johnson

OCTOBER 1979
OTTAWA

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ABSTRACT

An analytical procedure has been developed for determining the fluorine content of fluorochemical-treated fabrics by activation with fast neutrons, using Teflon film as the reference standard. The ultimate success of the technique depends on effective retention of the active recoil ^{18}F nuclei produced in the $^{19}F(n,2n)^{18}F$ reaction, which is accomplished by sealing all samples individually in Mylar film. It is demonstrated that recoil protons produced in the fabric substrate by the incident neutrons create a measurable amount of ^{18}F in the basic unfinished fabric through the $^{18}O(p,n)^{18}F$ reaction. The production of such excess ^{18}F tends to compensate for systematic deficiencies encountered in the measurement of the total ^{18}F activity of the finished fabric. It is shown that non-uniform activation of the irradiated samples due to the fall-off in neutron flux near the target could be overcome by use of a rotating and reciprocating sample holder.

RÉSUMÉ

Un procédé analytique a été développé pour déterminer, au moyen d'activation avec des neutrons rapides, la teneur en fluor des tissus traités avec des finis fluoro-chimiques, faisant usage d'une pellicule de Teflon comme l'étalon de référence. Le succès final de la technique dépend de la rétention efficace des noyaux ^{18}F radio-actifs de recul, produits dans la réaction $^{19}F(n,2n)^{18}F$, qu'on atteint en scellant tous les échantillons individuellement dans une pellicule de Mylar. On démontre que les protons de recul, qui sont produits dans le substrat du tissu par les neutrons incidents, créent une quantité de ^{18}F mesurable dans le tissu de bas non-apprêté par suite de la réaction $^{18}O(p,n)^{18}F$. La production d'un tel excès de ^{18}F tend à compenser les insuffisances systématiques qui se produisent dans la détermination de l'activité totale de ^{18}F du tissu apprêté. On démontre que l'activation non-uniforme des échantillons irradiés, par suite de l'abaissement du flux neutronique près de la cible, pourrait être surmontée par l'emploi d'une montre d'échantillon à mouvement de rotation et de va-et-vient.

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1. INTRODUCTION

Certain fluorocarbon compounds are used extensively as protective finishes for textiles in order to impart both oil- and water-repellent properties or to augment the overall effectiveness of conventional and less expensive hydrocarbon-based water repellents. A typical method of applying these finishes involves wetting the fabric with a solution of a fluorine-containing polymer in an organic solvent, or with a dispersion of the polymer in water, and then drying under controlled conditions so that the constituent fibres of the fabric become coated with a coherent film of the fluoropolymer.

Methods of measuring the fluorine content of such coated fabrics are of interest in order to ascertain whether manufacturing specifications have been adhered to, as well as to determine the durability of the finish under conditions of wear or after laundering. Chemical methods of fluorine analysis, as applied to coated fabrics, are generally hampered by the extreme resistance of most fluoropolymers to complete decomposition. In addition, such methods of analysis are destructive of the fabric and so do not permit continuing tests of the same sample to be carried out. Neutron activation analysis, however, is a non-destructive technique which can be adapted to analysis of the fluorine content of a fabric sample, and procedures employing this method of analysis have been developed at DREO.

The analytical procedures described in this report were developed using samples of a vat-dyed (colour OG 107) nylon/cotton twist fabric which had been treated with various commercially available fluorochemical finishes; this is a plain weave fabric with yarns consisting of an intimate blend of equal proportions of nylon and cotton, with a weight of 170 g/m^2 (5 oz/yd.^{2}). The amount of any fluorochemical applied was generally such that the fluorine content of the resulting finish was less than 1% by weight of the fabric.

2. GENERAL CONSIDERATIONS

2.1 Choice of Primary Reaction

Fluorine can be readily activated by neutron, charged-particle, or γ-ray bombardment, and a number of reactions can occur (1). With fast (14-MeV) neutrons three different nuclear reactions are possible, whereas thermal or slow neutrons produce only a single reaction product. In all cases the nuclei which are produced are radioactive, with characteristic half-lives, and emit distinctive γ-rays by means of which a particular nucleus may be identified. The possible reactions by which fluorine may be activated are listed in Table I, the first three reactions being due to fast neutrons, while the fourth is unique to thermal neutrons:

TABLE I

Reaction	γ rays emitted MeV	Half-life	Q of reaction, MeV	Reaction threshold MeV
i) $^{19}F(n,\alpha)^{16}N$	6.13, 7.12	7.4 s	-1.524	1.61
ii) $^{19}F(n,2n)^{18}F$	β^+ annihilation radiation, 0.511	109.9 min	-10.431	10.99
iii) $^{19}F(n,p)^{19}O$	0.2	29 s	-4.036	4.25
iv) $^{19}F(n,\gamma)^{20}F$	1.63	11 s		

All of the above primary neutron reactions have been used under various circumstances for the determination of fluorine (2-8). In the present application however, using only fast neutrons from a neutron generator, it was desired to avoid the complexity of a fast-transfer shuttle system such as would be required to transport the short-lived activated sample if either reactions i) or iii) had been chosen. In addition, the fact that the fluorine in this instance was intimately bonded to a fabric, which would also be activated, made it desirable to choose a fluorine reaction which would not be subject to interference by reactions produced in the H,C,N or O of the fabric. Possible fast-neutron-induced primary reactions resulting in activation of these elements are indicated in Table II.

TABLE II

Element	Reaction	γ rays emitted, MeV	Half-life	Q of reaction, MeV	Reaction threshold, MeV
Hydrogen	None				
Carbon	None				
Nitrogen	$^{14}N(n,2n)^{13}N$	β^+ annihilation radiation 0.511	9.96 min	-10.553	11.32
Oxygen	$^{16}O(n,p)^{16}N$	6.13, 7.12	7.4 s	-9.639	10.25

Thus, even if a fast-shuttle system were acceptable, the fact that oxygen yields the same activation product as does reaction i) of fluorine would rule out consideration of this particular reaction unless a differential technique involving additional activation with lower-energy neutrons were to be employed (3).

Reaction ii) in Table I was therefore the only reaction which could be considered suitable for the determination of fluorine in the present application. The half-life of ^{18}F is sufficiently long that interference by the other ^{19}F activation products, ^{16}N and ^{19}O, would not be a factor of concern, and interference by the 10-minute activity produced from the ^{14}N in the nylon component of the fabric could be avoided by waiting for the product isotope ^{13}N to decay until its contribution to the measured activity of the sample became insignificant. Thus by about 2-2½ hours after the end of the neutron irradiation the only significant activity remaining in the fabric should be due to ^{18}F, and a measurement of this activity can then be related to the fluorine content of the fabric by comparison with the specific activity of a suitably-chosen fluorine standard which had been irradiated at the same time.

2.2 Potential Interference by Secondary Reactions

Although the products of other primary reactions are thus not expected to interfere seriously with measurement of the ^{18}F activity, other possible interferences may be caused by secondary reactions initiated by the γ rays, charged particles, or neutrons produced by the various primary neutron-induced reactions discussed above (9, 10). In addition, especially energetic recoil protons can be generated in a hydrogen-containing organic material, such as the irradiated fabric, by scattering collisions of the primary neutrons with hydrogen atoms. Such knock-on protons could produce additional ^{13}N activity through $^{13}C(p,n)^{13}N$, $^{12}C(p,\gamma)^{13}N$ and $^{16}O(p,\alpha)^{13}N$ reactions in the fabric, and could introduce further interference in the form of a 20-minute positron activity due to ^{11}C through the reaction $^{14}N(p,\alpha)^{11}C$. More important in the present application, however, is the potential production of additional ^{18}F by such secondary reactions, initiated either by the recoil protons or by the α particles produced in the $^{19}F(n,\alpha)^{16}N$ primary reaction. Possible secondary reactions which could make such a contribution are $^{14}N(\alpha,\gamma)^{18}F$, $^{15}N(\alpha,n)^{18}F$, $^{17}O(p,\gamma)^{18}F$, $^{18}O(p,n)^{18}F$, $^{19}F(p,d)^{18}F$ and $^{19}F(p,pn)^{18}F$. It should be noted that the two reactions involving oxygen depend only on processes occuring in the basic fabric itself and are independent of the amount of fluorine present. Whether the ^{18}F activity produced by the $^{19}F(n,2n)^{18}F$ primary reaction in the fluoropolymer coating of the fabrics is significantly augmented by these secondary reactions will determine the practical utility of this analytical technique. It is to be noted that the two proton-induced reactions involving ^{19}F have relatively high thresholds and that the contribution due to the $^{17}O(p,\gamma)^{18}F$ reaction is expected to be negligible (11). The possible secondary reactions of concern are summarized in Table III.

TABLE III

Reaction	Q(MeV)	Reaction Threshold (MeV)
$^{12}C(p,\gamma)^{13}N$	1.944	
$^{13}C(p,n)^{13}N$	-3.003	3.24
$^{16}O(p,\alpha)^{13}N$	-5.218	5.55
$^{14}N(p,\alpha)^{11}C$	-2.920	3.13
$^{14}N(\alpha,\gamma)^{18}F$	4.416	
$^{15}N(\alpha,n)^{18}F$	-6.418	8.13
$^{17}O(p,\gamma)^{18}F$	5.609	
$^{18}O(p,n)^{18}F$	-2.438	2.57
$^{19}F(p,d)^{18}F$	-8.206	8.64
$^{19}F(p,pn)^{18}F$	-10.431	10.99

2.3 Basis of the Analytical Technique

Following the usual techniques which have been developed for the determination of other positron emitters produced by activation, measurement of the amount of ^{18}F will depend on detection of the 0.511-MeV γ rays which are produced as the emitted positrons (maximum energy 0.635 MeV) come to rest and annihilate with ordinary electrons in the material surrounding the activated sample. Since two such oppositely-directed γ rays are emitted in each annihilation process, both of these γ rays could be detected in a coincidence arrangement involving two scintillation detectors, or else only one of the two quanta could be detected by a single such detector. The coincidence technique ensures a very low background level, and is also especially useful in rejecting interactions of γ rays of other energies which might contribute in the region of the 0.511-MeV photopeak (as can occur in a NaI(Tℓ) scintillation detector where some of the pulses in the Compton distribution produced by γ rays of energy greater than 0.511 MeV cannot otherwise be distinguished from pulses in the photopeak produced by the interaction of 0.511-MeV γ rays). The much lower background level attainable with a coincidence arrangement generally permits a statistically better measurement of an activity to be made than is possible with a single detector. However a single detector is usually quite adequate when only a single activity is to be measured and provided the spectrum is not complex, but massive shielding is usually required to reduce the background to an acceptable level. Since any interference with the determination of ^{18}F can be effectively eliminated by delaying the start of counting until other positron activities, also produced in the coated fabric during activation, have decayed, the less complex system of a single scintillation detector could be employed in this application.

While short-lived activities will thus not seriously interfere with the determination of ^{18}F, the presence of activities longer-lived than ^{18}F could lead to analytical errors. Such activities could arise from unknown elements in compounds which had been absorbed from solutions used in the conventional textile finishing processes to which the fabric had been subjected or which were constituents of natural impurities in the cotton fibres. Since the presence of such long-lived activities could affect the apparent decay-rate of the component which is attributed to ^{18}F, and hence the measured activity at any particular time, determination of the actual decay-rate of this component could serve to establish the relative purity of the ^{18}F activity. A number of precise measurements of the half-life of ^{18}F are available, with which the decay-rate of the chosen fluorine standard should correspond and to which the decay-rate of the activated fabric can be compared; typical values for the half-life are 109.72 ± 0.12 min (13), and 109.72 - 109.73 ± 0.02 min (14).

3. ANALYSIS OF FABRIC FINISHES BY NEUTRON ACTIVATION

Neutron activation analysis has been adapted at a number of laboratories to routine analytical measurement of various textile additives or finishes. Thus silicon has been determined (15) by means of the $^{28}Si(n,p)^{28}Al$ reaction produced by 14-MeV neutrons, the silicon content being related to the activity of the 2.31-min ^{28}Al through detection of the 1.78-MeV γ ray which is emitted. The activation method in this case was demonstrated to be superior to the usual chemical technique of analysis, which was subject to uncontrolled silicon loss during incineration of the silicon-coated textile samples.

The determination of phosphorous in flame-retardant textiles (16) has also been carried out by means of activation analysis using 14-MeV neutrons, the analysis being based on the $^{31}P(n,\alpha)^{28}Al$ reaction. In this case the product of the nuclear reaction is the same as that produced by neutron irradiation of silicon, discussed above, and thus the presence of silicon can introduce serious interference. This interference can be corrected for, however, by estimating the silicon content on the basis of the activity of the 6.6 min ^{29}Al produced in the $^{29}Si(n,p)^{29}Al$ reaction through detection of the 1.28-MeV γ ray. Aluminum can also introduce a minor interference through the $^{27}Al(n,\gamma)^{28}Al$ reaction, but the contribution of this activity to the 1.78-MeV photopeak is negligible unless the aluminum/phosphorous weight ratio exceeds 5:1.

A number of different activation techniques for the determination of fluorine in fabrics have been reported. Thus the 110-min ^{18}F activity produced in the $^{19}F(n,2n)^{18}F$ reaction by 14-MeV neutrons has been employed in the analysis of the fluorine content of Quarpel-treated fabrics (17). Such fabrics exhibit superior water- and oil-repellent properties which are critically dependent on a fluorine-containing polymeric component of the finish. The analysis in this case, which was based on detection of the 0.511-MeV annihilation radiation with a NaI(Tℓ) detector, appeared to be limited to an accuracy of about 5%. However an inconsistency in some of the results which were obtained was apparent.

Another technique for the determination of fluorine based on the activities produced by reactor neutrons has been applied to analysis of anti-soil products deposited on fabrics (18), a typical such product being a perfluorohydrocarbon with the trade name Foboil. Two reactions were investigated. In the case of the $^{19}F(n,\gamma)^{20}F$ reaction the high resolution of a Ge(Li) detector in conjunction with a multi-channel analyzer was required to distinguish the 1.627-MeV γ ray emitted by the 11-sec ^{20}F from the 1.780-MeV γ ray of ^{28}Al. The latter γ ray was produced in the material of the pneumatic transport system which was required to deliver the sample from the irradiation position to the detector. The 1.635-MeV γ ray of ^{38}Cl, which could be produced by either the $^{37}Cl(n,\gamma)^{38}Cl$ or the $^{41}K(n,\alpha)^{38}Cl$ reaction, was also a possible source of interference. This isotope, however, has a half-life of 28 min and its activity was thus relatively constant during the short time required for counting the ^{20}F and for determining the background. Use of the $^{19}F(n,\alpha)^{16}N$ reaction, on the other hand, was considered to present a great advantage over the $^{19}F(n,\gamma)^{20}F$ reaction because the product isotope emits the most penetrating γ rays of any isotope, 6.130 and 7.112 MeV, with the result that the apparatus could be simplified and a NaI(Tℓ) detector and a single-channel analyzer with a window covering the range 4.5-8 MeV could be used. For this reaction the analysis cost was calculated to be about 50 times less than that entailed with the $^{19}F(n,\gamma)^{20}F$ reaction. Unfortunately the $^{16}O(n,p)^{16}N$ reaction interferes with the analysis, approximately 300 mg of oxygen producing the same amount of activity as 1 μg of fluorine. Thus for the case of a cloth made of flax which is impregnated with an anti-soil product, the large oxygen content of the flax results in about 65% of the ^{16}N activity being due to the oxygen in the flax. In order to make use of the $^{19}F(n,\alpha)^{16}N$ reaction the relative contribution of the oxygen reaction to the ^{16}N activity for a particular fabric must first be determined experimentally by using both fluorine reactions to measure the apparent fluorine content of the treated fabric.

4. INITIAL EXPERIMENTAL TECHNIQUE

Activation of the coated fabrics was carried out using 14.9-MeV neutrons produced by the DREO 150-keV Cockcroft-Walton neutron generator. A 5-Ci tritiated-titanium target (on 0.254-mm(10-mil) copper, 31.75 mm (1½")-diam., with a 25.4-mm (1-inch)-diam. active area) was employed and an output of $\sim 10^{10}$ n/sec was generally attained.

The fabric samples which were to be analyzed by activation were cut into 28.6-mm (1 1/8-inch) diam. circular discs which weighed about 100-110 mg each and were 0.23-0.36 mm (9-14 mils) thick. Varying numbers of these were sandwiched directly between two similar discs of 0.051-mm (2-mil) Teflon sheet which served as reference standards containing a known amount of fluorine (76%) and which were activated at the same time as the fabric and by essentially the same neutron flux. This sandwich of the materials to be activated was held rigidly between two discs of nylon or polystyrene 2.5-3.2 mm (3/32 - 1/8 inch) thick, which were bolted together. Either holder could be positioned directly on the water-cooled target cap of the neutron generator and was held in position by a strip of tape. With the nylon holder the plane of the sandwich was located about 6.4 mm (¼ inch) from the target itself, while with the polystyrene holder it was about 12.7 mm (½ inch) away.

After irradiation the fabric and Teflon samples were separated, placed in individual Mylar envelopes for ease of handling, and the activity of each was determined by means of a 7.6 cm × 7.6 cm (3" × 3") integrally-mounted NaI(Tℓ) scintillation detector and a single-channel analyzer set to cover the whole of the 0.511-MeV peak (from 0.45 to 0.56 MeV). The detector assembly was mounted vertically inside a Pb shield and the envelope containing the active sample was placed directly on the flat end of the housing containing the crystal and was covered with a 6.4-mm (¼-inch)-thick disc of Lucite of the same diameter as the crystal. The Lucite disc served to stop the backwardly-directed positrons and to permit them to annihilate in the near vicinity of the detector surface, thereby enhancing the observed counting rate by about 40%. The three samples were each counted in turn for periods of 10-15 minutes and the decay of each was generally followed for sufficiently long to establish the presence of the characteristic 110-minute half-life of ^{18}F and, in the case of the fabric, to confirm that any shorter-lived activity had disappeared and that no long-lived activity of significance was present. The fluorine content of the fabric sample was then determined in the usual manner on the basis of a comparison of its activity with that of the average specific activity of the two Teflon standards. In general at least 8-10 determinations of the fluorine content were carried out as the ^{18}F activity decayed through two half lives or more, one determination being based on each of the fabric counts obtained.

5. PRELIMINARY RESULTS

5.1 Effects of Recoil Nuclei

The first results, using the above technique, were inconsistent, as is apparent from inspection of the data presented in Figure 1. The points in this figure represent the amount of fluorine which was determined in different numbers of fabric discs which were activated and counted together. Results are given for two differently finished fabrics and for cases where two different sample holders were employed, one holder of nylon which was placed directly on the target cooling cap of the generator and the other of polystyrene, similar but somewhat less massive, which was held at a distance of 6.3 mm (¼ inch) away from the surface of the cooling cap.

For each different finish, and depending on the particular sample holder, the amount of fluorine which was determined in each analysis increased reasonably linearly with the number of fabric discs which had been irradiated together, as indicated in Figure 1 by the straight lines which have been drawn through the appropriate points. In no case, however, do any of the straight lines extrapolate through the origin, all having a positive intercept on the ordinate axis equivalent to approximately 1 mg ^{19}F. This fact suggests that more ^{18}F was consistently being detected than could reasonably be accounted for on the basis of the fluorine in the fabric alone. It will also be noted that, while more ^{18}F was detected in the two finishes when the polystyrene

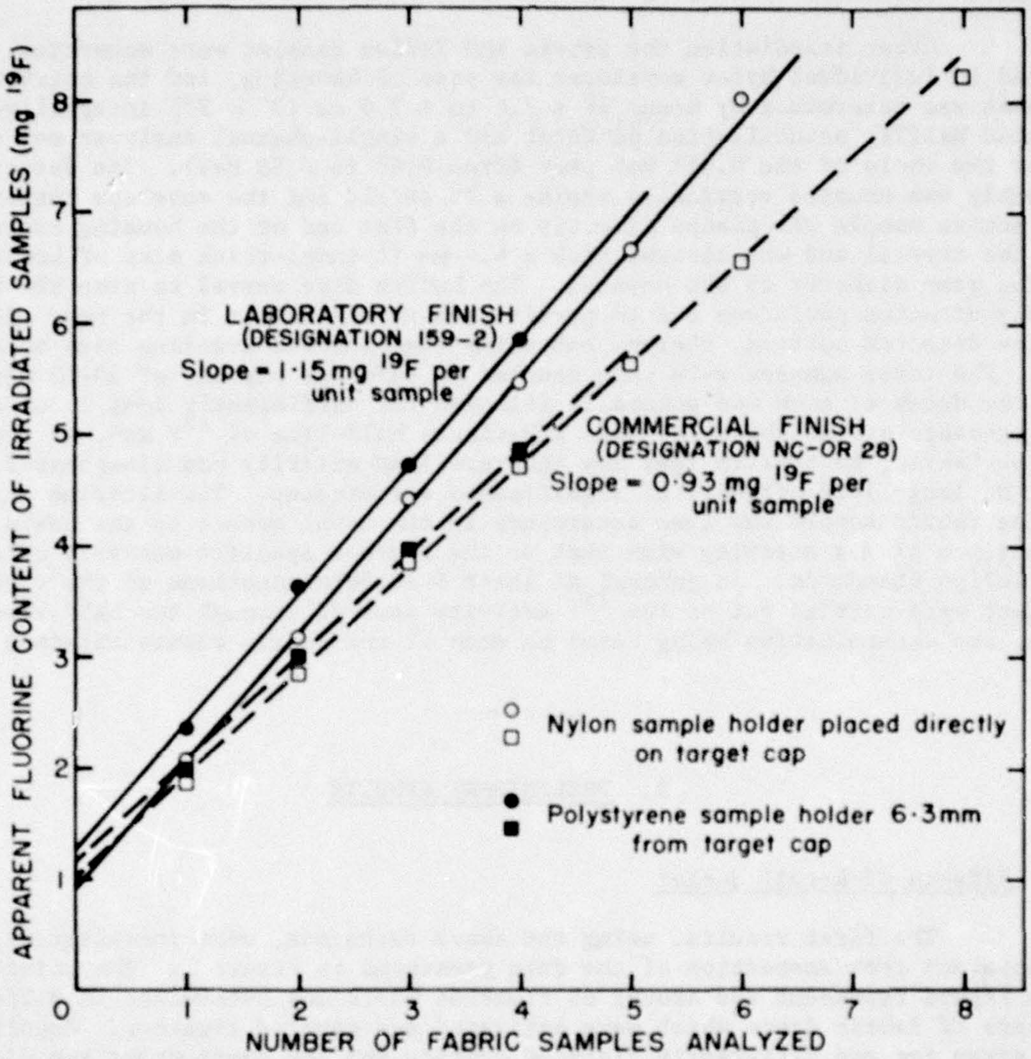


Figure 1

Typical preliminary results of analyses of fabric samples which had been treated with different formulations containing the same fluorochemical finish (FC-232(Scotchgard), manufactured by 3M Company), one treatment having been carried out in a commercial mill and the other at DREO. The straight lines have been drawn by eye to give the best apparent fit to the various sets of points. The actual fluorine content of these fabrics, as determined using the final analytical technique which was developed (Sec. 6), was 1.157±0.010 (159-2) and 0.899±0.008 (NC-OR 28) mg ^{19}*F per unit sample. Considering the uncertainties to which the preliminary technique was subject (see text) and the errors involved in determining the activity of multiple samples (Sec. 7.3), it is probable that the linearity evident in the figure is fortuitous and resulted from a combination of many factors.*

holder was employed than was the case with the nylon holder, the two separate lines which have been drawn for each finished fabric appear to be essentially parallel. This suggests that, depending on the sample holder, the amount of excess ^{18}F which was detected was about the same regardless of the number of samples of a particular finished fabric which was analyzed.

The origin of this apparent excess ^{18}F was attributed to recoil nuclei (19). Thus, because of the kinematics of the $^{19}F(n,2n)^{18}F$ reaction, some of the activated ^{18}F nuclei in the Teflon standard nearest to the target had sufficient kinetic energy (2.03 MeV at 0°) to break their chemical bonds and escape in the forward direction and become embedded in the fabric, thereby adding to its activity. This supposition was confirmed by irradiating one of the Teflon standards sandwiched between two thin sheets of polyethylene; substantial ^{18}F activity was evident on that sheet of polyethylene which intercepted the forward recoils from the Teflon, but none could be detected on the polyethylene nearest the target. Such observations were consistent with the fact that the kinematics of the reaction do not permit ^{18}F nuclei to be projected into the backward hemisphere when the reaction is initiated by 14.9-MeV neutrons, the recoil nuclei being confined to a cone of 47.3° half angle in the forward direction.

The larger amount of ^{18}F which was detected in the fabric samples in all those cases where the polystyrene holder had been employed can also be accounted for on the basis of the recoil nuclei. With this particular holder the plane of the sandwich of the Teflon standards and fabric discs was 6.4 mm (¼ inch) further away from the plane of the target than was the case when the nylon holder was used. Thus, while the neutron flux through the sandwich would have been slightly smaller, proportionately fewer neutrons would have been incident on the components of the sandwich at large angles ($\rightarrow 90^\circ$), with the result that the number of recoil nuclei capable of escaping from the front Teflon standard into the fabric would appear to be enhanced relative to the total activity produced. The fact that this enhancement was slightly less for the commercially applied finish than for the finish applied in the laboratory could possibly be accounted for by the fact that the commercial formulation contained a non-fluorinated resin as a binder, and the presence of this binder could affect the chemical mechanism by which the recoil nuclei were caught and retained. Thus, assuming that the amount of excess ^{18}F which was detected was the same for each analysis involving a particular fabric and a particular sample holder, the common slope of the pair of straight lines drawn in Figure 1 for each finished fabric should give a measure of the actual fluorine content of the fabric alone. However, because of the possibility of a similar loss of recoil nuclei from the fabric finish itself and also from the Teflon standard farthest from the target, determination of the fluorine content of the fabric by this technique would appear to be subject to considerable uncertainty.

A number of experiments were carried out in which either polyethylene or Mylar films were used to catch the recoils from one of the Teflon standards, and it was found that the amount of ^{18}F activity retained on these films did not bear a particularly constant relationship to the activity induced in the Teflon. Thus, using the polystyrene sample holder, between 1.36% and 1.56% of the activity of the Teflon was found on the polyethylene films, and from 1.66% to 1.87% on the Mylar. With the nylon holder only 1.09% of the activity was apparent on the polyethylene film. Since the Teflon standards weighed

∿ 66 mg, these figures implied that the equivalent of 0.55 mg to about 1 mg of fluorine could be transferred to such catcher foils by means of recoils. Since the fabric discs which were to be analyzed were each expected to contain less than 2 mg of fluorine, it is apparent, for the arrangement which has been described, that ^{18}F recoils from the front Teflon standard would contribute a substantial error to any individual determination of the fluorine content of a fabric sample, as is very evident in the results plotted in Figure 1. While the amount of recoil activity retained by either polyethylene or Mylar appeared to be variable, it was found, as already indicated, that the activity retained by a particular finished fabric under similar conditions seemed to be relatively constant, considering the potential for uncertainty in the determination of the total fluorine content of the fabric. Again, it can only be suggested that the different nature of the chemical structures of polyethylene, Mylar and the coated fabric affects the manner in which the recoil fluorine nuclei are caught and retained.

In other experiments with the catcher foils it was determined that the recoil ^{18}F nuclei were stopped by a 0.012-mm (0.5-mil) polyethylene film, since no activity could be detected on a second such film placed immediately behind the first. Thus it appeared that the recoils from the Teflon standards could be effectively contained if these standards were each sealed in 0.5-mil polyethylene film. On the assumption that recoil ^{18}F nuclei would similarly be emitted in the forward direction from the fluoropolymer coating of a coated fabric, all of the fabric discs which were to be irradiated at one time were also collectively sealed in polyethylene. Since the recoil nuclei produced in a thin film can only escape from a surface layer which is thinner than the range of these nuclei in that film, the proportionate loss of ^{18}F activity from the thin fluoropolymer coating of the fabric could be expected to be much greater than from the 2-mil-thick Teflon standards. Thus retention of the recoils from the coated fabrics was deemed to be especially important.

5.2 Effects of Diffusion of Active Nuclei

Irradiation of the Teflon standards and the fabric samples, each individually sealed in polyethylene film, appeared to produce somewhat more consistent values for the fluorine content of a particular fabric, but discrepancies still remained. Thus repeated determination of the fluorine content of a given fabric sample did not always agree even to within two or three times the standard deviations which were to be expected on the basis of the counting statistics, and a plot of fluorine content versus the number of fabric discs which had been irradiated still indicated a positive, though much reduced, intercept on the ordinate axis. Of particular significance was the observation that a weighted least-squares analysis of the decay of the activity of the 2-mil-thick Teflon standards in different time intervals over a period of more than three half-lives indicated an initial decay more rapid (by more than 3 minutes in some cases) than the 110-minute half-life expected, the half-life gradually approaching more closely to the accepted value as time progressed. For the case of a 1-mil-thick Teflon sample, also sealed in polyethylene, the initial decay rate was even more rapid, an apparent half-life of the order of 105 minutes being observed. The cause of this abnormally rapid decay rate of the activated Teflon samples was attributed to physical loss of some of the fluorine activity during the course of the measurements.

Such a loss of activity over a prolonged time period suggested that some of the active ^{18}F nuclei could be escaping by means of a gaseous diffusion process through the thin polyethylene film (20,21,22,23). Since the variety of gaseous compounds which can be formed by recoil nuclei will depend to a great extent on the chemical environment in which they are produced (24), it is unlikely that the gaseous products produced in Teflon would be exactly the same as those produced in the coated fabrics. Thus for this reason, and also because of possible variations in the thickness of the polyethylene films, it is probable that the rate of loss of activity by diffusion would be different in the two cases. Also, because the thickness of the fluorochemical coating of a fabric is much less than that of the Teflon standards, (finished and unfinished fabrics cannot be distinguished by the naked eye) the loss of activity by diffusion would be much more serious in the case of a fabric. For example, the greater apparent loss of activity observed for a sealed 1-mil Teflon sample as compared with that for a 2-mil sample can be attributed to the fact that, while the relative total activities would have differed by a factor of two, a comparable number of free recoil nuclei would have been produced in the two cases. Thus for the same absolute loss of activity by diffusion the thinner sample would appear to decay more quickly, as was observed. It can be concluded, therefore, that measurement of the relative activity of a fabric sample and the Teflon standards under such conditions would not provide the basis for an accurate analysis.

Since it was obviously imperative to retain the recoil ^{18}F nuclei, it was evident that the samples still had to be sealed in some material, but one through which the active nuclei would not so readily diffuse. Polyester film is known to be relatively impermeable to common gases (25) and finds use as a barrier film. The permeability of this film to such gases is typically of the order of 100 times smaller than that of polyethylene, a fact which indicated that a film of this material might be more effective in containing the recoil nuclei. On this premise all samples were then re-sealed in 1.5-mil polyethylene-coated Mylar film (0.75 mil polyethylene + 0.75 mil Mylar).

The effectiveness of the Mylar film in reducing the diffusion of the active nuclei to negligible proportions was immediately evident in an analysis of the decay of the activity of the sealed Teflon standards. No significant difference in the decay rate could be discerned, within the probable error dictated by the counting statistics, over a period covering more than three half-lives, and the measured half-life was in satisfactory accord with the generally accepted value. In addition, measurements of the fluorine content of a typical coated fabric now appeared to be independent of the number of fabric discs on which the determination was based, in spite of the fact that the specific activities of the two Teflon standards could differ by 11% (for the case of three fabric discs interposed) as a result of the neutron flux gradient through the sample. Thus it could be concluded that the basis for a satisfactory analytical technique had been established.

6. FINAL EXPERIMENTAL TECHNIQUE AND TYPICAL ANALYTICAL RESULTS

The final technique which was developed for the analysis of coated fabrics by neutron activation depends critically on effective retention of those active recoil ^{18}F nuclei, produced in the ^{19}F(n,2n)^{18}F reaction, which have sufficient kinetic energy to escape from either the fabric samples or the Teflon standards. As has been demonstrated, loss of these nuclei by migration or diffusion can be avoided by sealing all the samples individually in thin Mylar film before they are sandwiched together to be activated. Figure 2 shows the sealed componenets of a typical sandwich and details of the polystyrene sample holder which was employed to position the sandwich in front of the target of the neutron generator.

In order to evaluate fully the neutron-activation method, the results obtained using this technique were compared with those obtained by standard chemical methods for a selection of fabrics which had been treated with different fluorochemical finishes (26). The results are summarized in the following table:

TABLE IV

Fabric Identification	Fluorochemical Finish	% Fluorine by Weight of Fabric		
		Chemical	Neutron Activation	
			1 disc	3 discs
NC-OR-28	FC-232[a]	0.83 ± 0.03	0.826 ± 0.008	0.830 ± 0.006
NC-OR-35	FC-232	0.71 ± 0.03	0.694 ± 0.007	0.693 ± 0.006
NC-OR-34	Zepel B[b]	0.46 ± 0.02	0.508 ± 0.005	0.502 ± 0.005
NC-OR-36	Zepel B	0.40 ± 0.02		0.420 ± 0.005
CF-C-889	Zepel B	0.43 ± 0.02		0.434 ± 0.008
NC-OR 13	Tinotop T-10[c]	0.24 ± 0.02		0.242 ± 0.004
X77-402A	None	0.02*		0.0[+]

*Within the experimental error associated with the chemical analysis technique.

[+] No distinct evidence of ^{18}F half-life. See Sec. 7.4.

[a] 3M Company, [b] Du Pont, [c] Ciba-Geigy.

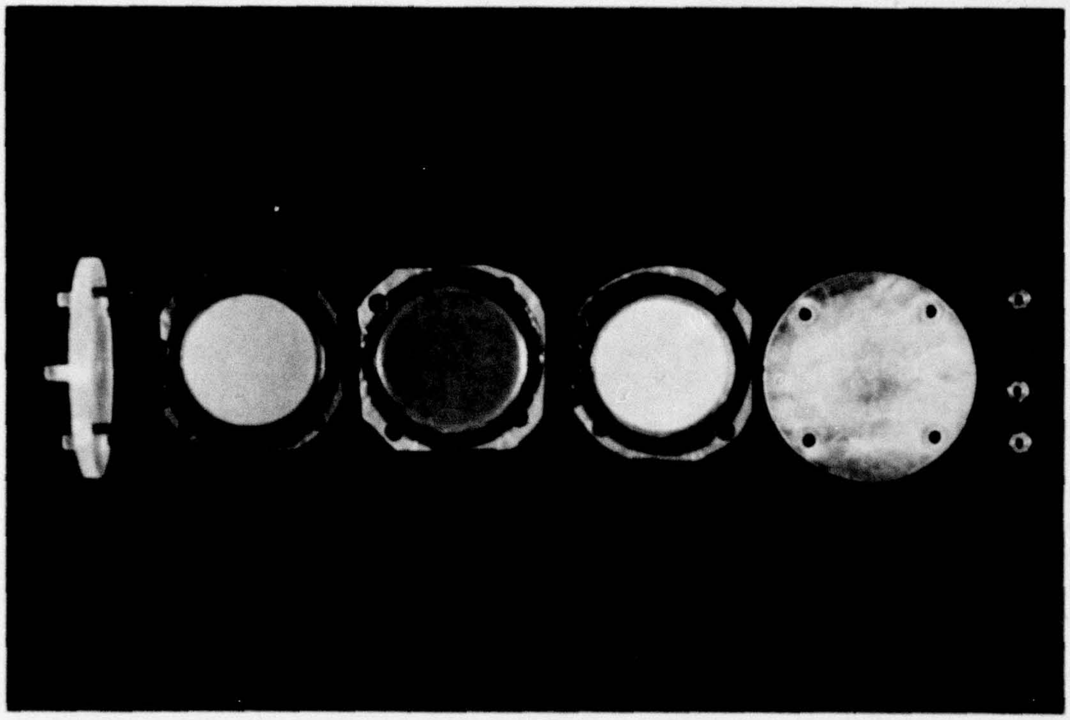


Figure 2

Components of the polystyrene sample holder and the elements of the sandwich. From left to right: base of holder which sits on the target cap of the neutron generator; front Teflon standard sealed in Mylar; fabric sample sealed in Mylar; rear Teflon standard sealed in Mylar; rear plate of holder; nuts to fit bolts protruding from base of holder in order to hold the sandwich together. The indentations in the Mylar of the Teflon standards are for purposes of identification.

Figure 3

Typical decay curves (background subtracted) obtained for an activated fluorochemical-treated fabric and the two Teflon standards which were irradiated at the same time. Also shown is the decay curve obtained for a sample of the basic unfinished fabric which had been irradiated in approximately the same flux as had the finished fabric and for the same time. In each case the measured activity was that obtained for three discs of the fabric. For the basic fabric the main activities observed were 9.96-min ^{13}N produced mainly by the $^{14}N(n,2n)^{13}N$ primary reaction in the nylon component and 110-min ^{18}F produced mainly by the $^{18}O(p,n)^{18}F$ secondary reaction initiated by recoil protons (see Sec. 7. 5). The amount of the latter activity corresponded to an apparent fluorine content of $\sim 0.004\%$ for the unfinished fabric. Further resolution of the decay curve of the unfinished fabric indicated a small contribution by a 20-min activity which was attributed to ^{11}C produced in the $^{14}N(p,a)^{11}C$ reaction by recoil protons; activation of a pure nylon film suggested that the initial contribution of the ^{11}C activity was $\sim 5\%$ of the initial ^{13}N activity.

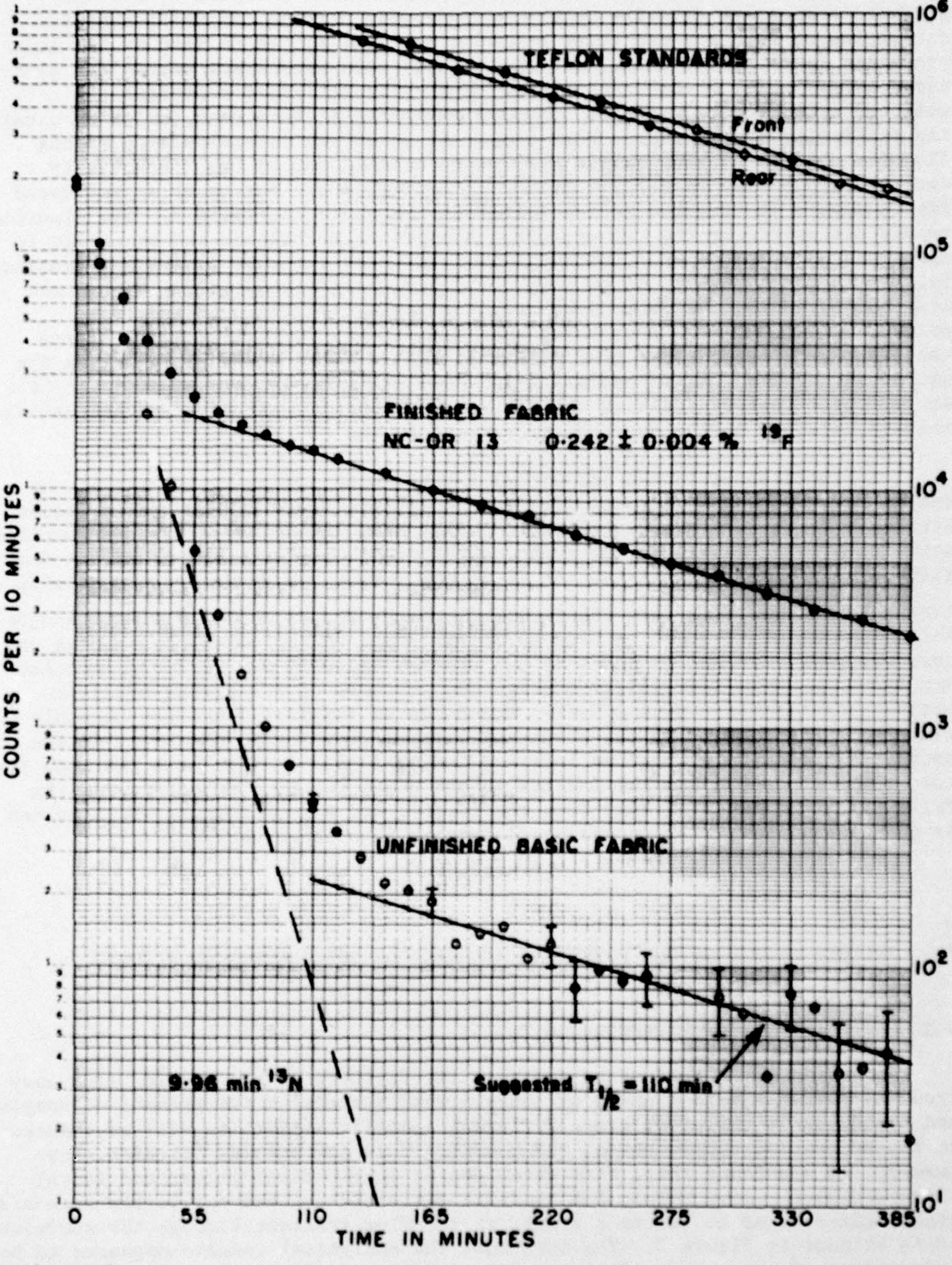

TEFLON STANDARDS
Front
Rear
FINISHED FABRIC
NC-OR 13 0·242 ± 0·004 % ^{19}F
UNFINISHED BASIC FABRIC
9·96 min ^{13}N
Suggested $T_{1/2}$ = 110 min
COUNTS PER 10 MINUTES
TIME IN MINUTES
0
55
110
165
220
275
330
385
10^6
10^5
10^4
10^3
10^2
10^1

Figure 3

For some of the finished fabrics which were analyzed by neutron activation separate fluorine determinations were carried out using samples consisting of both one and three sealed discs and, as can be seen by the data presented in the above table, the two results were consistent within the estimated errors. The quoted activation results in all cases represent the weighted mean and the weighted standard deviation of this mean (based on counting statistics alone) of, in most cases, at least ten determinations of the fluorine content of each sample which were carried out as the ^{18}F activity decayed through two half-lives or more. Typical decay curves of an activated fabric sample and the two Teflon standards are shown in Figure 3. The fluorine values determined by the two different analytical techniques are generally in agreement with one another, although in some cases there is an evident tendency for the chemical results to be somewhat lower than those obtained by neutron activation. While such a tendency was not unexpected (26), it should be pointed out that the samples which were analyzed by the two techniques were not identical, being taken from different areas of the fabric roll. Thus the uniformity of the fluorochemical finish over the area of the fabric would be an important factor affecting the detailed agreement to be expected between the results obtained by the two analytical methods.

Confidence in the analytical results obtained by activation of the coated fabrics was provided by irradiation of five individually-sealed Teflon standards which were all sandwiched together. In this case, while the specific activity of each sample decreased according to its distance away from the target, reflecting the fall-off in neutron flux, the rate of decrease was essentially constant with distance (see Figure 4). Thus the actual activity of any single Teflon sample or group of samples in the interior of the sandwich could be accurately predicted on the basis of the average activity of the two particular samples which were immediately contiguous. Because of the higher specific activity attainable with the Teflon standards as compared with that possible with the finished fabrics for comparable irradiation times, the error in the estimate of the activity of an interior Teflon sample in this case was much less than the 1-2% quoted for the fabrics in the above table. The effects of the fall-off in neutron flux away from the target, and a technique by which it can be compensated for, will be discussed further in a later section.

7. FACTORS AFFECTING THE POTENTIAL ACCURACY OF THE ANALYTICAL RESULTS

7.1 Non-uniform Flux Distribution

In neutron activation analysis the fall-off in the neutron flux away from the target can be a cause of concern when a sandwich arrangement of sample and standards is employed, since different specific activities will be induced in the successive components of the sandwich. In the present instance, for example, it was found that, with three sealed fabric discs interposed (total thickness 31.5 - 39.0 mils), the specific activities of the two Teflon standards could differ by up to 11% as a result of the flux gradient through the sandwich, as is evident in Figure 3. The fact that the analytical results appeared to be independent of the number (from 1 to 3) of fabric discs on which the determinations

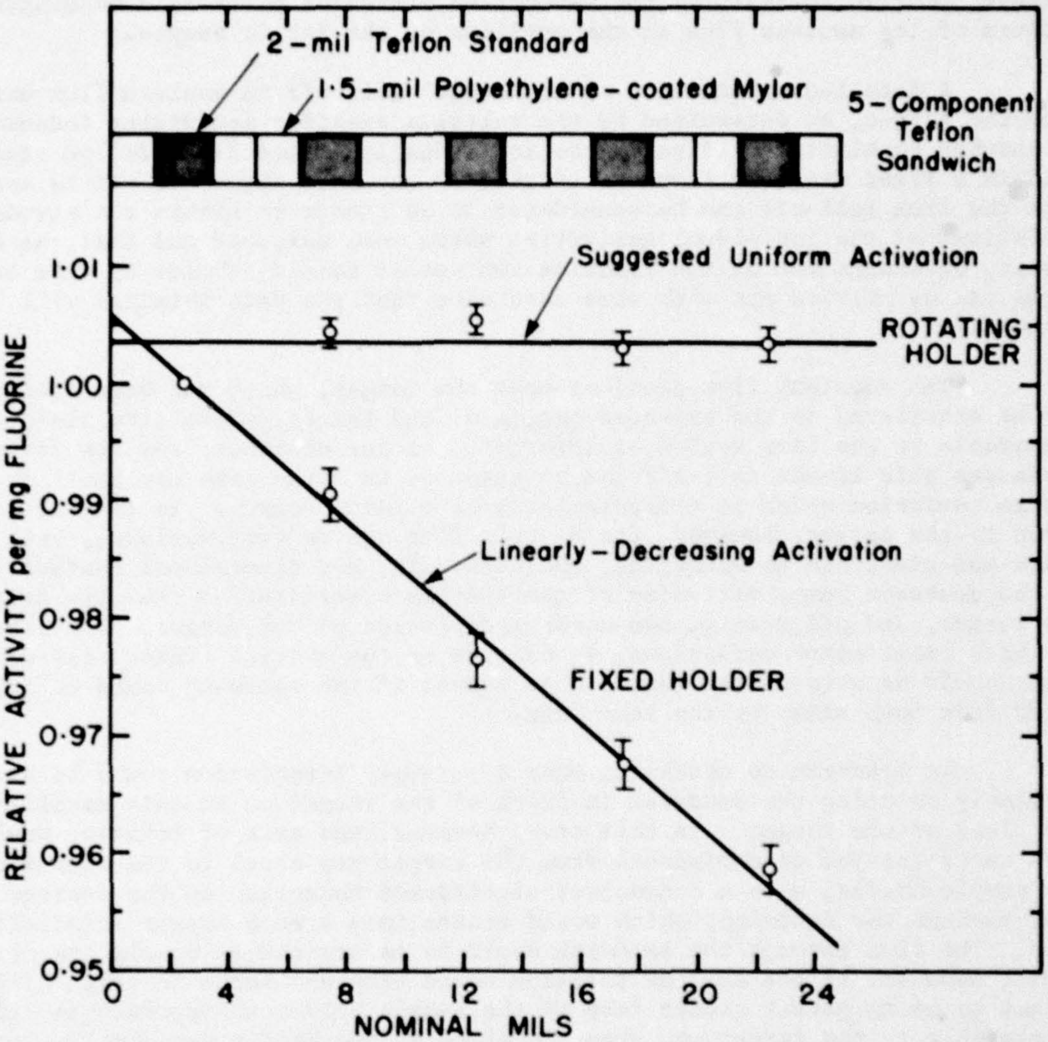


Figure 4

Relative specific activities induced in a sandwich consisting of five of the individually-sealed 2-mil Teflon standards for the cases where i) the sandwich was held rigidly at a fixed distance from and parallel to the plane of the target, and ii) the plane of the sandwich was rotated about an axis paralled to the plane of the target by means of a rotating and reciprocating sample holder.

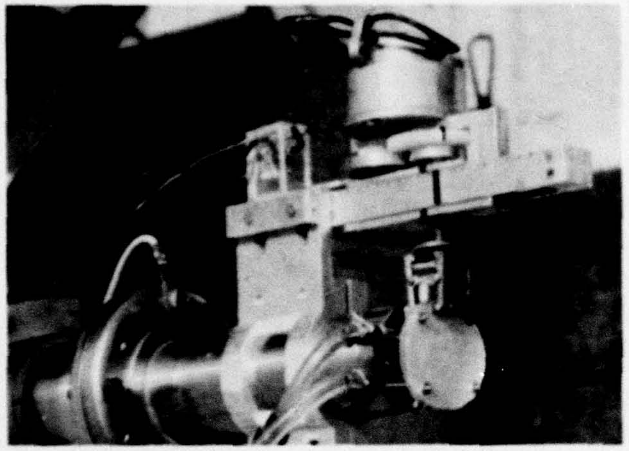
were based implied that the flux gradient was essentially constant at least across the thickness of the sandwich. Thus it could be concluded that the average specific activity of the two Teflon standards provided a meaningful measure of the neutron flux at the position of the fabric sample.

A detailed examination of the actual fall-off in neutron flux away from the target, as determined by the relative specific activities induced in a sandwich consisting of five of the individually-sealed 2-mil Teflon standards, held in a fixed distance from the target, is shown in Figure 4. It is apparent that the flux fall-off can be considered to be linear to within the standard deviations of the individual activities which were measured and that, as a result, determination of the fluorine content of coated fabrics by this technique can be carried out with some assurance that the data obtained will be realistic.

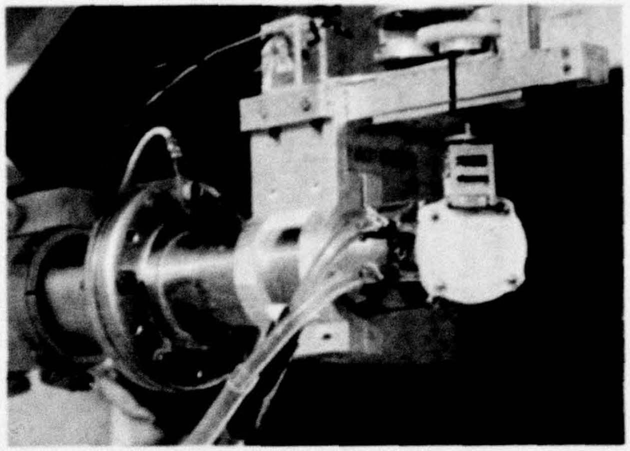
The constant flux gradient near the target, which has been discussed, can be attributed to the extended nature of the target, whose dimensions are comparable to the flux region of interest. As the distance from the target increases this linear fall-off can be expected to merge into the usual inverse-square variation which is characteristic of a point source. In the region close to the target, however, the neutron flux can be very variable, both in space and time, due to wandering, non-uniformity and dimensional instability of the deuteron beam, variation of the tritium concentration over the area of the target, and progressive non-uniform depletion of the target. The effects of these local space variations, as well as of the overall linear fall-off in flux, could be compensated for to some extent if the sandwich could be irradiated from both sides by the same flux.

An approach to obtaining such a uniform irradiation could be attained by simply rotating the sandwich in front of the target on an axis parallel to the plane of the target. In this case, however, the axis of rotation would have to be located at a distance from the target cap equal to the radius of the sample holder, with a consequent significant reduction in the average flux through the sandwich, which would necessitate a much longer irradiation time. The flux through the sandwich could be maintained at nearly its original level, however, if the axis of rotation moved back and forth in front of the target so as to permit either face of the sample holder to approach as closely as possible to the target cap when the plane of the holder was parallel to the plane of the target; the axis would then move away from the target to permit the holder to rotate in order to present its other face to the target. Such a rotating and reciprocating device to provide the required motion of the sample holder was designed and built and is shown in Figure 5. The period of the cycle was 2 seconds and the motion was continuous; an obvious refinement would be to permit a dwell time for the sample at its two positions of closest approach to the target. Using this device, the results of activating the same five Teflon standards as had been activated previously are also shown in Figure 4, and the near-uniformity of the relative specific activities of the components of the sandwich is apparent.

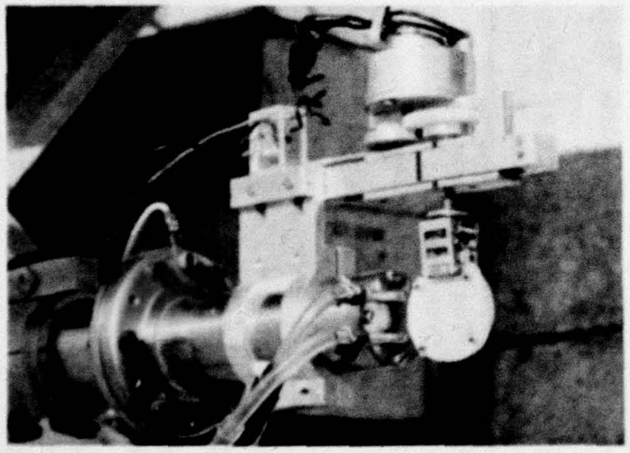
While rotation of the sample holder was not employed in development of the technique for analysis of fabric samples by neutron activation, it is evident that its use for this purpose would remove much of the potential source of uncertainty or error which is inherent in any method which depends on inter-



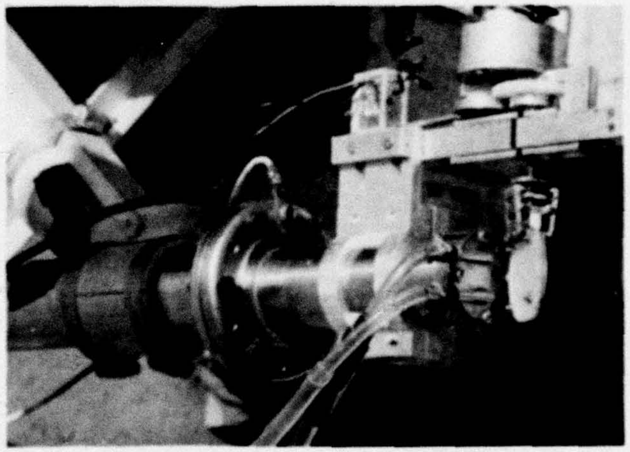
1. *Sample parallel to plane of target.*



2. *Rotation axis has moved away from target as sample rotates. (clockwise from above)*



3. *Rotation axis at maximum distance from target, sample at 90° to plane of target.*



4. *Rotation axis moves closer to target as sample continues rotation to present its opposite side to the target.*

Figure 5: Rotating and reciprocating sample holder fastened to target end of drift tube of neutron generator. Note relative positions of black marking strips on support arm and sliding plates above sample holder.

polation of the neutron flux over the thickness of the sandwich.

7.2 Weighing of Samples

The Teflon standards and the fabric discs which were to be activated were all weighed on a Sartorious microbalance before being sealed in the polyethylene-coated Mylar. The microbalance was situated in a controlled atmosphere and all samples were allowed to equilibriate before being weighed.

It is recognized (27) that microweighing can contribute an appreciable source of error to any analysis where a mass must be determined. Absolute errors of up to 10 μg can usually arise from the non-linearity of the optical scale and uncertainty in its calibration, and errors of at least 20 μg can be attributed to combinations of the reference weights. While the absolute weights of the Teflon and fabric samples were not required in the present instance, it was hoped that the relative masses could be determined consistently. Thus special efforts were made to ascertain the reproducibility with which the apparent weight of a given sample could be determined.

Of a number of 2-mil Teflon standards (64-68 mg) which were reweighed at different times over a period of many months, the greatest discrepancy which was observed was 40 μg, representing a difference of about 0.06%. Other samples of 1-mil Teflon (31-36 mg) were also weighed repeatedly, and the maximum difference observed in this case was 54 μg or 0.15%. In the case of the fabrics, individual discs were weighed and the summed weights were compared with those actually obtained when these were grouped into pairs or triples. For three such discs, of total weight ∿ 340 mg, discrepancies of 20-200 μg were noted, the maximum difference amounting to 0.06%. At times some difficulty was experienced in obtaining stable values for the weights of the fabric discs, and this was attributed to gain or loss of moisture even after sufficient time had been allowed for apparently adequate equilibriation.

While a detailed study of potential errors in weighing was not attempted, a satisfactory weighing procedure was finally evolved(28). It was concluded that it would not be unreasonable to assign an average uncertainty of 0.1% to the weighing process. The magnitude of this error is thus much less than that which could be attained from the counting statistics characteristic of the analytical technique, particularly with reference to the activities of the fabric samples which could be produced.

7.3 Systematic Errors Related to Measurement of the Activity of the Fabric

It is to be expected that a fluorine analysis which is based on measuring the total activity of a stack of two, three, or more fabric discs should give a consistently lower value for the percentage fluorine content than that derived using a single disc, both because of the progressively greater distance of each disc from the detector surface and also because of γ-ray absorption in the underlying discs. A quantitative measure of the magnitude of this effect was obtained in the following manner.

One of the sealed Teflon standards was activated and the pure ^{18}F decay was then followed for a period of more than four hours by sequential counting of the activity of the standard alone, and of this standard with two, four, and six unsealed fabric discs placed between it and the detector surface. The best estimate of the decay curve appropriate to each of the four cases was determined by means of a weighted least-squares logarithmic fit to the series of counts which were obtained in each case. On the basis of these fitted curves the quantitative effect of the interposed fabric discs on the apparent activity of the Teflon standard could be determined. A similar series of measurements were carried out for one, three, and five interposed fabric discs. The percentage reduction in counting rate which was observed for all these cases is plotted in Figure 6.

Using the factors R_1, R_2, --R_N, which express the fractional reduction in counting rate which was observed for the case of various numbers, 1, 2, ----N, of interposed fabric discs, it is possible to estimate the reduction in counting rate which might be expected when a given number of equally-activated fabric discs are counted together. Thus, for the case of a single disc of total activity A, it can be assumed that the measured activity will be $\frac{1}{2} R_1 A$ less than the true activity. This is based on the simple assumption that the average reduction in counting rate for the case of activity uniformly dispersed through the fabric disc will be one half that which would be the case if the activity were concentrated on that surface of the disc remote from the detector, as had been the case in the experiments with the activated Teflon standards, discussed above. Alternatively, the total activity of the single fabric disc could be considered to be concentrated equally on its two surfaces; in this case the activity $\frac{1}{2} A$ on the side nearest the detector would be counted without any absorption by the fabric, while the counting rate of the activity on the side away from the detector would be reduced by the amount $R_1 \frac{1}{2} A$, the factor R_1 incorporating the effects of both distance and absorption. This viewpoint is useful in considering the counting rates to be expected with multiple fabric discs. Thus, for the case of two discs, that part of the counting rate due to the disc nearest the detector would be reduced by $\frac{1}{2} R_1 A$, the same as for the single disc already discussed; for the second disc, with activity $\frac{1}{2} A$ considered to be on each surface, the counting rate due to the activity on its bottom surface (adjacent to the first disc) will be reduced by $R_1 \frac{1}{2} A$ because of absorption in the first disc, and that due to the activity on its top surface by $R_2 \frac{1}{2} A$ because of absorption by both discs. Thus the total reduction in counting rate to be expected for the two discs would be:

$$\tfrac{1}{2}R_1A + \tfrac{1}{2}R_1A + \tfrac{1}{2}R_2A$$

$$= \; 2A \times \tfrac{1}{4}(2R_1 + R_2)$$

Since the total activity of the two discs together is 2A, the fractional reduction in counting rate to be expected will be $\frac{1}{4}(2R_1 + R_2)$. Similarly, for three discs, the fractional reduction will be $\frac{1}{6}\,(2R_1 + 2R_2 + R_3)$. The reduction in counting rate to be expected for various numbers of equally-activated fabric discs, counted together, is also plotted in Figure 6.

On the basis of the above analysis, and as evident from Figure 6, a fluorine determination based on the activity of a single fabric disc can be expected to be less than ½% too low, and that based on three discs will be

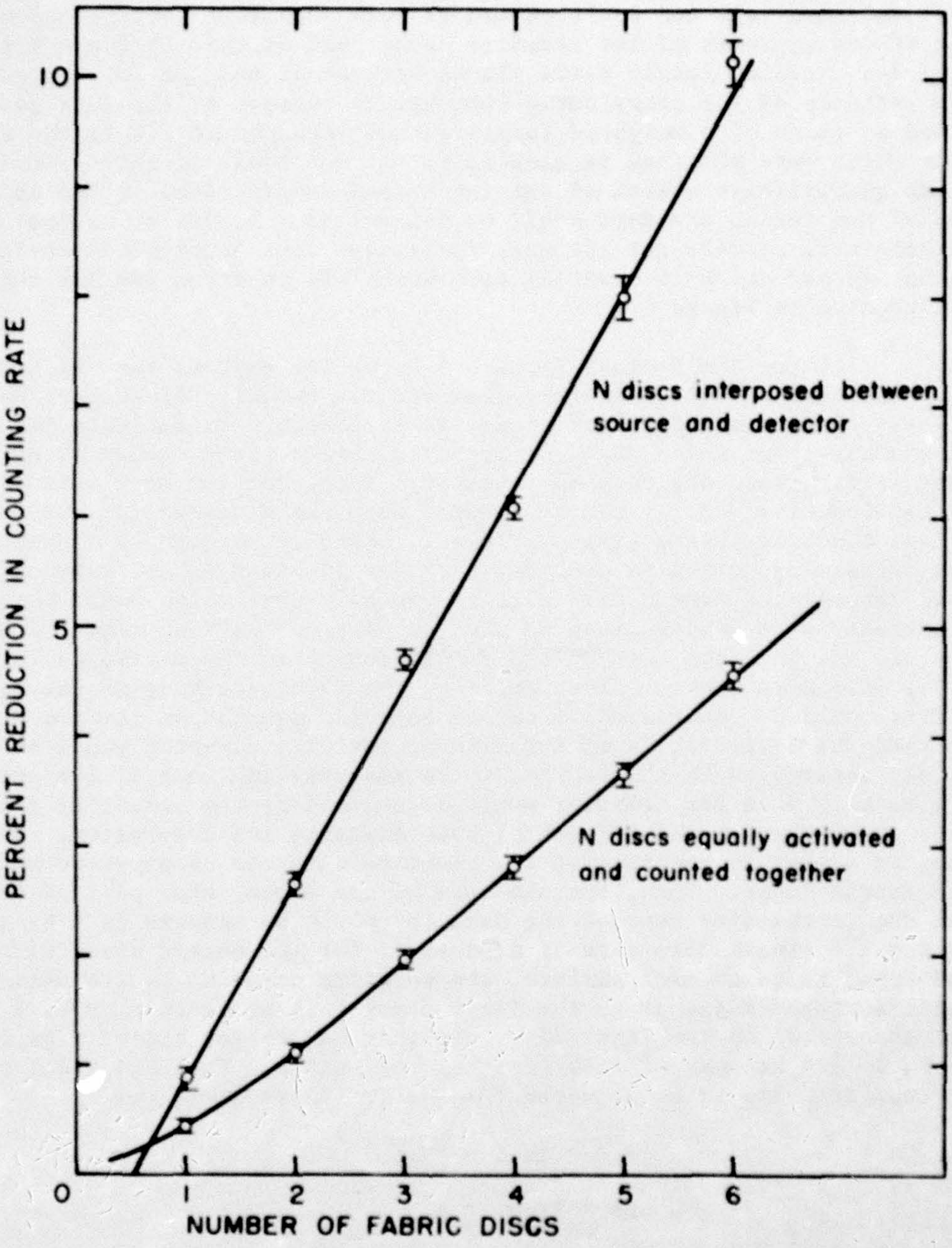


Figure 6

The percentage reduction in counting rate produced by various numbers of fabric discs interposed between a sealed activated Teflon standard and the detector surface. This data permits calculation of the reduction in counting rate which is to be expected when a given number of equally-activated fabric discs are counted together.

about 2% low. Since similar, though much smaller, self-absorption effects will occur in the 2-mil activated Teflon standards, such systematic errors in the analytical results can be expected to be somewhat less than the figures quoted above. In any event, these figures are comparable to the uncertainties attributable to the counting statistics which could usually be attained, the latter being limited by the activity which could be induced in the coated fabrics in reasonable irradiation times (less than 1 hour).

7.4 Long-lived Activities Produced in the Fabric

In the analytical technique which has been developed for the analysis of coated fabrics, the short-lived activities (mainly ^{13}N) produced in the fabric are allowed to decay and then, after about 2½ hours, the activity remaining is followed for 3 to 4 hours, during which time the fluorine content is determined. The decay of the activity is monitored during this period in order to confirm that the decay rate, as determined from a least-squares logarithmic fit (assuming a single linear component), corresponds with that to be expected for ^{18}F. The degree to which the decay rate of the activated fabric was found to conform to that of ^{18}F can best be summarized by the value of the weighted mean half-life which was calculated from the half-lives actually determined in nine separate analyses of fabrics which had been treated with different fluorochemical finished (including all those coated fabrics listed in Table IV); the analyses were based on the activation of 1,2, or 3 of the fabric discs, and from 9 to 15 determinations of the fabric activity (10-minute counts) were made in each analysis as this activity decayed. The weighted mean half-life of the fabric activity, and the weighted standard deviation of this mean, was 109.83 ± 0.84 min. For the case of the various pairs of Teflon standards which were employed in these different analyses, the weighted mean half-lives were 110.01 ± 0.22 min and 109.88 ± 0.18 min for the front and rear standards respectively. Thus, over the time periods during which the fluorine analyses were usually carried out, the fabric activity appeared to decay with a half-life which could be attributed solely to ^{18}F to within the statistics of the counting process.

In spite of the apparent compatibility of the decay rate of the activated coated fabrics with that of a pure ^{18}F activity, however, it was evident that a long-lived activity was also present. This was observed when the decay of some of the fabric samples was followed for 20 hours or more. Thus, about 12 hours after the first fluorine determination had been made, at which point the decay curve fitted to the activity measured during the 3-4 hours that the fluorine determinations were carried out had decayed through nearly 7 half-lives to 1%, the net activity (background subtracted) which was measured was approximately 0 - 35% greater, depending on the particular coated fabric, than that suggested by extrapolation of the fitted decay curve. Since this net activity (in the case of 3 fabric discs) was typically of the same order as the normal background, the error in the estimate of the magnitude of the excess activity could be very large. Continued observation of the decay of the net activity, however, indicated the definite presence of a long-lived component with a half-life certainly greater than 10 hours but, because of the low counting rate available, a more precise value or an attempt at identification was not possible. It was estimated, however, that any such long-lived activity would contribute less than 0.5% to the measured activity, attributed to ^{18}F, during the period when the fluorine determinations were normally carried out.

Since the relative amount of the long-lived activity appeared to depend on the particular coated fabric which was being analyzed, it is evident that a precise analysis of the fluorine content of any coated fabric should include a determination of the potential contribution of any such long-lived component. In this context it should be noted that no significant amount of any long-lived activity (>10 hours) could be detected in samples of the basic fabric prior to finishing. Since these samples were irradiated and counted under identical conditions to those which obtained for the coated fabrics, it must be concluded that the source of the long-lived component found in the activated coated fabrics had probably been introduced during the fluorochemical finishing process itself.

While the definite presence of a long-lived activity in some of the fluorochemical-treated fabrics could be detected, the possibility of a suggested identification on the basis of half-life was precluded by the very low activity which remained after the contribution of the ^{18}F activity had become insignificant. More distinct evidence of a similar long-lived activity, however, was found in other fabric samples which had been treated with a water-repellent finish which did not contain fluorine. Thus the activity of fabric X77-402A, which had been analyzed for fluorine and the negative result reported in Table IV, was followed for more than 24 hours. After about 7 hours the decay curve appeared to consist of a single component which, on the basis of a least-squares fit to the activity measured over the next 17½ hours, had a half-life of 12.3 ± 0.9 hours. Extrapolation of this component and subtraction from the activity measured in the first 7 hours permitted a component to be resolved which decayed with a half-life of 35-40 min as measured over a 3½ hour period, as well as a component of shorter half-life which was attributed to the 10-min ^{13}N. Such components (12.3 h and 35-40 min), if present in a fluorochemical-treated fabric, together would have contributed about 10% to the total activity measured during the period when the fluorine determinations were usually carried out (assuming a comparable irradiation time and a 0.24% fluorine content, such as in NC-OR 13 (Table IV)), and the longer-lived component itself would have constituted more than 60% of the measured activity at the point where the fluorine activity had decayed to 1%. At later times, however, after the fluorine contribution had become negligible, it was apparent that the magnitude of the activity of the long-lived component found in the fluorochemical-treated fabrics was ∿ 10% of the long-lived component found in the water-repellent fabric.

In the absence of more detailed information concerning the composition of the dyes and other finishes with which the fabrics which were analyzed had been treated, and without further experimental work which would go beyond the original intent of the investigation, definite identification of the long-lived activity found in the water-repellent fabric X77-402A cannot be provided. On the basis of the measured 12.3 ± 0.9-hour half-life, however, it could be suggested that this activity was due to the positron emitter $^{64}Cu(T_{\frac{1}{2}}\ 12.7\ h)$, which would have been produced by either of the reactions $^{64}Zn(n,p)^{64}Cu$ or $^{65}Cu(n,2n)^{64}Cu$. That the former reaction was more likely, however, is suggested by the presence of the 35-40 min activity which was also found in the same fabric; this activity could be attributed to the positron emitter ^{63}Zn ($T_{\frac{1}{2}}$ 38 min) produced in the reaction $^{64}Zn(n,2n)^{63}Zn$. The possible presence of zinc in the fabric X77-402A could be related to the dye which had been used; this was a white fabric (colour Sugar White No. 2584) and ZnO is known to be used as the white pigment in some dyes. On the other hand it is also known that metal salts of organic fatty acids, such as zinc octoate or similar salts of aluminum, are employed as catalysts during the treatment of textiles with various water repellents. That the latter source of zinc was more probable was suggested when a similar blue-dyed water-proofed fabric X77-402H (colour French Navy No. 2670) was activated. The activity of this fabric was followed for only 6½ hours and thus the half-life of any long-lived component was not established; however an examination of the first 2 hours of the decay curve, and subtraction of the estimated contribution of 10-min ^{13}N, clearly suggested a component with a half-life of 35-40 min which was similar to the component revealed when the X77-402A decay curve was analyzed in the same manner.

7.5 Systematic Errors Related to the Production of ^{18}F by Secondary Reactions

It has been pointed out previously that recoil protons, produced in any hydrogenous material by incident neutrons, can initiate reactions which lead to the production of ^{18}F. Thus the secondary reactions $^{17}O(p,\gamma)^{18}F$ and $^{18}O(p,n)^{18}F$ can be expected to occur in oxygen-containing organic materials such as the nylon and cotton (cellulose) components of the base fabric. Other contributions to the ^{18}F activity could also be produced through the $^{14}N(\alpha,\gamma)^{18}F$ and $^{15}N(\alpha,n)^{18}F$ tertiary reactions in the nylon, the α-particles being produced in the $^{16}O(p,\alpha)^{13}N$ and $^{14}N(p,\alpha)^{11}C$ secondary reactions.

In order to determine the amount of any ^{18}F activity which might be produced by the above reactions, samples consisting of three discs of the basic fabric as obtained prior to finishing were irradiated and counted in the usual manner. The decay curve which was obtained is shown in Figure 3. The main activity observed was that of 10-min ^{13}N in an amount comparable to that found in the coated fabrics, as expected. After about 2½ hours, when the initial activity had decayed by a factor of 1000 to give a net activity of the same order as that of the natural background, the activity which remained appeared to represent a single component which decayed at a rate consistent with a half-life of 110 min, as observed over the following 5 hours. On the basis that this activity was due to ^{18}F which had been produced by secondary reactions in the basic fabric, and in the Mylar in which the fabric had been sealed, a comparison with the activity induced in the two Teflon standards which had been irradiated at the same time indicated an apparent fluorine content of ∿ 0.004% for the untreated fabric. Continued observation of the net activity of the fabric did not yield statistically significant data on which the presence or absence of an additional activity of long half-life could be based.

As a consequence of the above result, it is evident that the percentage fluorine content which is determined by activation of any fluorochemical-treated fabric will include the detectable contribution of ^{18}F which is produced in the basic fabric itself. Thus in the case of the fabric NC-OR 13, referred to in Table IV, whose fluorine content was measured to be 0.242 ± 0.004% on the basis of the activity produced in three discs of the fabric, the fluorine content attributable to the fluorochemical finish alone should perhaps more correctly have been quoted as 0.238 ± 0.004%, the secondary contribution being of the same magnitude as the nearly 2% statistical uncertainty in the measurement itself. However, this secondary ^{18}F contribution would be practically entirely compensated for by the similar ∿2% deficiency to be expected in the measurement of the total activity of the three fabric discs (see Fig. 6), and thus the originally quoted fluorine content of 0.242 ± 0.004% need not be corrected in this case. For fabrics with a significantly greater fluorine content the constant secondary ^{18}F contribution would generally be more than compensated for by the systematic error associated with measurement of the activity of the fabric, with the result that the net effect of this latter source of error would become of less overall significance in relation to the magnitude of the statistical uncertainty inherent in measurement of the total activity.

Other possible secondary reactions which could contribute excess ^{18}F activity require the presence of fluorine itself. Thus the ^{19}F(p,d)^{18}F and ^{19}F(p,pn)^{18}F reactions could be produced in the fluorochemical coating of the fabric by knock-on protons from the hydrogenous basic fabric, or by protons emitted in the ^{19}F(n,p)^{19}O reaction, and the ^{14}N(α,γ)^{18}F and ^{15}N(α,n)^{18}F reactions could also be produced in the fabric substrate by the α particles emitted in the ^{19}F(n,α)^{16}N primary reaction in the coating. Since the energy of the α particles from the latter reaction ranges from 12.7 MeV at 0° to 7.7 MeV at 180°, it was not possible to investigate separately the production of ^{18}F by direct bombardment of the untreated fabric, or a nitrogen-containing plastic, with α particles of this energy using the DREO 3-MeV Van de Graaff accelerator. Similarly, energetic protons in the range emitted in the ^{19}F(n,p)^{19}O reaction, 10.75 - 8.34 MeV, or compatible with the spectrum of the recoil protons, 14-0 MeV, were not available for separate bombardment of a coated fabric or a fluorinated hydrocarbon. Thus a different approach to assessing whether measurable amounts of ^{18}F could be produced by such secondary reactions was required. It should be noted, however, that production of excess ^{18}F, due specifically to reactions with fluorine initiated by protons emitted in the ^{19}F(n,p)^{19}O reaction, would occur in both the fluorochemical coating and in the Teflon standards. Since the relative amount of ^{18}F so produced would depend on the fluorine content in the two cases, any excess amount of ^{18}F in the coated fabric, produced in this manner, would not be detected by a comparison of the specific activities.

From the above discussion it is therefore apparent that, because of secondary reactions which could occur only as a result of the intimate contact between the fluorochemical coating and the fabric, the amount of ^{18}F produced in a coated fabric might be greater than that which would be produced in the isolated coating alone. On this basis a model of a coated fabric was devised which simulated the essential features of a typical coated fabric in such a manner that the conditions for the production of excess ^{18}F would be similar to those in the coated fabric itself, and in which the component which simulated the coating could also be examined in isolation. The simulated or mock fabric consisted of a disc of Teflon, 0.025-mm (1-mil) thick, sandwiched directly between two similar discs of pure nylon film, each 0.76-0.102 mm (3-4 mils) thick, the total weight being 131.963 mg. Thus, with this configuration, the α particles actually produced by the ^{19}F(n,α)^{16}N reaction in the Teflon could interact with the nitrogen in the nylon in an environment similar to that found in a coated fabric, and also the knock-on protons from the nylon could similarly interact with the fluorine in the Teflon. The simulated fabric sample, sealed in Mylar in the usual manner, was sandwiched between two sealed Teflon standards, and the amount of fluorine was determined on the basis of the amount of ^{18}F produced by activation. The fluorine content determined in this manner was then compared with that which had been determined by a previous separate activation of the

1-mil Teflon disc alone, similarly sealed in Mylar, in which the same two Teflon standards had been used. The following results were obtained:

TABLE V

	Fluorine Content mg ^{19}F	
Theoretical fluorine content of 1-mil Teflon disc, based on total weight of 32.448 mg.		24.660 ± 0.025
Teflon disc activated alone		24.676 ± 0.068
Simulated coated fabric activated		
Determination #1	24.649 ± 0.073	
Determination #2	24.785 ± 0.068	
Weighted mean and weighted S.D. of mean.		24.721 ± 0.068

Thus it is apparent that the actual known fluorine content of the mock fabric was not obviously incremented by contributions from secondary reactions involving fluorine to a degree which could be ascertained with respect to the relatively large amount of fluorine already present, or which could be identified within the statistical uncertainty attached to the measurements. These measurements do, however, provide a practical demonstration of the basic feasibility of determining fluorine in a coated fabric by means of neutron activation.

8. SUMMARY

An analytical technique has been developed for determining the fluorine content of fluorochemical-treated fabrics by neutron activation using the $^{19}F(n,2n)^{18}F$ reaction. The fabric samples which are to be activated are cut into circular discs and sandwiched between two similar discs of Teflon which serve as reference standards. The sandwich of the materials to be activated is then held rigidly in a sample holder which is positioned on the target cap of the neutron generator. After activation the relative activities of the individual components of the sandwich are determined using a NaI(Tℓ) detector. The success of the technique depends critically on effective retention of those active recoil ^{18}F nuclei, produced during activation, which have sufficient kinetic energy to escape from either the fabric samples or the Teflon standards. Loss of these nuclei by migration or diffusion can be avoided by sealing all samples and standards individually in thin Mylar film before they are sandwiched together to be activated. It is probable that the loss of active nuclei was mainly responsible for the inconsistency in some of the data which was noted in previous work (17) which employed the same nuclear reaction and a similar technique.

The potential accuracy of the results obtained can be affected by a number of factors, although the overall uncertainty is dominated by the magnitude of the counting statistics which can usually be obtained, these being determined by the amount of ^{18}F activity which can be induced in the coated fabric in a reasonable irradiation time. The factor which is of main concern is the fall-off in neutron flux away from the target, which results in different specific activities being produced in the successive components of the sandwich. It was determined, however, that the flux gradient was essentially constant across the thickness of a sandwich composed of at least three fabric discs and that the activities of the Teflon standards could therefore provide a meaningful measure of the neutron flux at the position of the fabric sample. This potential for uncertainty can be effectively overcome by imparting a rotary motion to the sample holder so that the sandwich is irradiated equally from both sides by the same flux to give a nearly uniform activation throughout.

Other factors of less serious concern relate to systematic errors encountered in measurement of the actual activity of the irradiated fabric samples, and to the presence of ^{18}F activity in the activated fabric which is unrelated to the amount of fluorine in the coating itself. Thus the measurement of the total activity of two or three equally activated fabric discs can be expected to lead to a lower apparent fluorine content than that derived from the activity of a single disc, both because of the progressively greater distance of each disc from the detector surface and because of γ-ray absorption in underlying discs. Separate measurements of the reduction in counting rate caused by various numbers of fabric discs interposed between a source and the detector enable appropriate correction factors to be derived. The use of such correction factors is obviated to some extent, however, particularly for the case of fabrics with a small percentage of fluorochemical finish, by the presence of excess ^{18}F activity which is produced in the basic fabric itself by knock-on protons, mainly through the $^{18}O(p,n)^{18}F$ reaction. The excess ^{18}F so produced is equivalent to an apparent fluorine content of 0.004% for the untreated basic fabric, and this tends to compensate to some degree the systematic deficiencies which arise in the measurement of the total activity of the fabric.

A final factor which can affect the accuracy of a fluorine analysis is the presence of any long-lived activity. Such an activity can arise from elements contained in compounds employed in various of the finishing processes and is thus probably independent of the actual fluorine content of the finished fabric. However the magnitude of this contribution should be determined if a precise analysis is to be made. For the case of the particular coated fabrics which were analyzed in the course of this investigation it was estimated that any such long-lived activity would contribute less than 0.5% to the measured activity which was attributed to ^{18}F, and would thus generally tend to be masked by the 1-2% counting statistics which could be attained.

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An analytical procedure has been developed for determining the fluorine content of fluorochemical-treated fabrics by activation with fast neutrons, using Teflon film as the reference standard. The ultimate success of the technique depends on effective retention of the active recoil ^{18}F nuclei produced in the $^{19}F(n,2n)^{18}F$ reaction, which is accomplished by sealing all samples individually in Mylar film. It is demonstrated that recoil protons produced in the fabric substrate by the incident neutrons create a measurable amount of ^{18}F in the basic unfinished fabric through the $^{18}O(p,n)^{18}F$ reaction. The production of such excess ^{18}F tends to compensate for systematic deficiencies encountered in measurement of the total ^{18}F-activity of the finished fabric. It is shown that non-uniform activation of the irradiated samples due to the fall-off in neutron flux near the target could be overcome by the use of a rotating and reciprocating sample holder.

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