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FEASIBILITY STUDY TO DETERMINE THE FLUORINE CONTENT IN QUARPEL-TREATED FABRICS BY ANALYSIS WITH A 14 MeV NEUTRON ACTIVATION SOURCE

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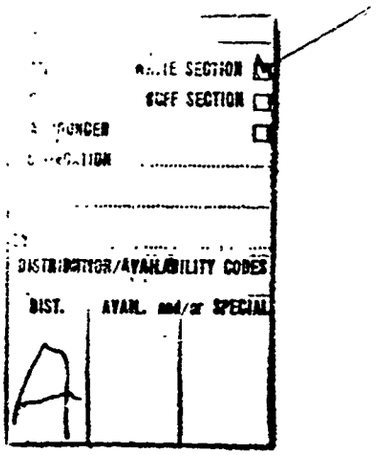

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13 ABSTRACT

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Clothing and Personal Life Support Equipment Laboratory
U. S. ARMY NATICK LABORATORIES
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FOREWORD

This project is a joint effort conducted under the Production Engineering Program, "New Applications for Quarpel." Quarpel-treated fabrics were prepared at the U. S. Army Natick Laboratories prior to analysis for fluorine content using a 14 MeV neutron accelerator at the Army Materials and Mechanics Research Center, Watertown, Mass. The co-authors of this report, Mrs. Hubertina D. Hogan and Mr. Gil Dias of NLABS, performed the laboratory work with the guidance and assistance of Mr. Forrest Burns, the principal author and member of Watertown's Materials Science Division.

The authors wish to acknowledge the cooperation of Dr. Richard N. Macnair, Textile Research and Engineering Division, NLABS, in the preparation of this report.

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ABSTRACT

A study was initiated on an Army-developed water-and oil-repellent fabric known as "Quarpel" containing a fluorochemical component critical to the performance of the finished fabric. To analyze for fluorine content, Quarpel-treated fabrics were subjected to neutron activation. This technique of exposing a fabric to neutrons from a 14 MeV accelerator has not been previously reported. Fluorine content of the treated fabric thus can be measured before and after laundering or dry cleaning and correlated with other physical tests to indicate the durability of the fabric treatment.

INTRODUCTION

In 1960, personnel of the U. S. Army Natick Laboratories developed a durable water and oil resistant treatment for textiles to provide better environmental protection for the soldier [1]. This treatment, called Quarpel, is a combination of a quaternary pyridinium salt and a fluorine containing polymer applied in a single bath system. Comparative data showed the superior performance of textiles treated with Quarpel as compared with the standard water repellent finishes then in use. Several variants combining different quaternary compounds and fluorine-containing polymers have since been explored and approved as Quarpel type systems meeting the essential requirements established for the Quarpel label.

A series of tests were devised to evaluate the effectiveness of these various Quarpel treatments. These tests include spray rating, Suter Hydrostatic, dynamic absorption, rain-room simulated rainfall at an intensity of 1"/hour and oil contact angle ratings before and after laundering of the treated textile.

While these tests provide quite complete information on the durability and effectiveness of the Quarpel treatment, a need has been felt for a sensitive analytical method that can reveal the fluorine and nitrogen concentrations on fabrics that have undergone various degradative tests. A non-destructive test technique is preferred since it would permit continued monitorship of a given specimen through a whole sequence of processes and still allow other non-destructive analytical procedures to be made after each process. Chemical analysis and physical test data could thus be compared effectively on the same specimen. This, of course, is not possible with currently used wet chemical analysis techniques.

As a result of discussion with scientists at the U. S. Army Materials and Mechanics Research Center, the use of neutron activation analysis was selected since there are no obvious interfering nuclear reactions (Table I), and a system especially designed to analyze inhomogeneous samples such as Quarpel treated fabrics was available. [2] Fluorine analysis was set as the primary goal since a large amount of nitrogen was already present in some of the fabrics to be analyzed. This was the basis for the cooperative effort, the results of which are reported herein.

TABLE I

Possible Nuclear Reactions Induced in Quarpel Treated Fabrics by 14 MeV Neutrons

Major Elements Present	Natural Isotope	14 MeV Neutron Reactions	Half-Life
Nitrogen	N-14	$N^{14}(n,2n)N^{13}$	10 min.
	N-15		
Carbon	C-12	none	--
	C-13	none	--
Hydrogen	H-1	none	--
	H-2	none	--
Fluorine	F-19	$F^{19}(n,2n)F^{18}$	109.5 min.
		$F^{19}(n,p)O^{19}$	29 sec.
Oxygen	O-16	$O^{16}(n,p)N^{16}$	6.1 sec.

TECHNIQUE

The technique of performing an activation analysis is based on the equation:

$$A = \sigma \phi N(1 - e^{-\lambda t})$$

where

A = number of counts produced by neutron bombardment

σ = nuclear cross section of the reaction in barns

ϕ = neutron flux in neutrons/cm^2/sec.

N = number of atoms of the isotope involved in the nuclear reaction

$(1 - e^{-\lambda t})$ = saturation factor based on the half-life of the isotope being produced

λ = product decay constant

t = irradiation time (sec)

Actually, by irradiating a standard of known elemental concentration in conjunction with an unknown, σ, ϕ and $(1 - e^{-\lambda t})$ can be cancelled out by saying that the number of counts produced are directly proportional to the molar isotopic concentration of the sample as follows:

$$\frac{Ax}{A_2} = \frac{Wx}{W_2}$$

where

$$W = \frac{\text{\# of atoms X \% isotopic abundance}}{\text{Molecular wt. x } 6.023 \times 10^{23} \text{ atoms}}$$

When this equation is modified to apply to this study it becomes:

$$\frac{\%F \text{ of Standard X wt. of Standard}}{\text{Counts on Standard}} = \frac{\%F \text{ of Sample X wt. of Sample}}{\text{Counts on Sample}}$$

or:

$$\%F \text{ of Sample} = \frac{\%F \text{ of Standard X wt. of Standard}}{\text{Counts on Standard}} \times \frac{\text{Counts on Sample}}{\text{wt. of Sample}}$$

EXPERIMENTAL

Apparatus.

The 14 MeV neutron source used in this work was a Kaman Nuclear A-700 Sealed tube unit with an output of approximately 6×10^{10} neutrons/second. The complex irradiation system has been described in detail elsewhere[2/], but the accelerator is shown in Figure 1, with the sample irradiation holders in position. These holders are fabricated from polyethylene and have a diameter of 0.35-inches and a length of 1.6-inches (Figure 2). Subsequent to irradiation the samples were taken from the irradiation holders and placed in special counting holders (Figure 3), measuring 1-inch x 7/8-inch x 9/16-inch. The amount of activation was determined by placing the held sample on a 3-inch X 3-inch NaI(Tl) well-crystal* with a Nuclear Data 130A Multichannel Analyzer.

* Thallium-activated sodium iodide crystal.

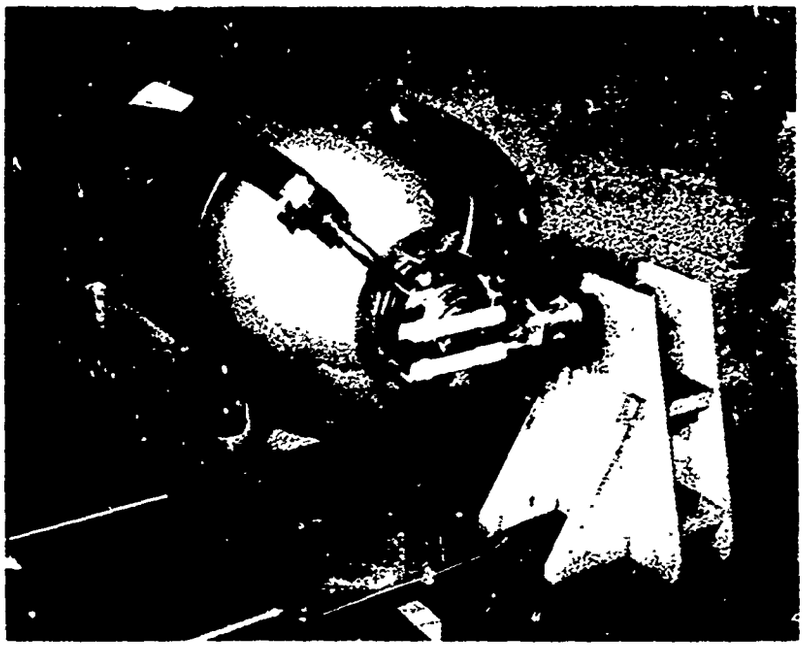

Figure 1 - Neutron Activation Accelerator with Sample Irradiation Holders in Position

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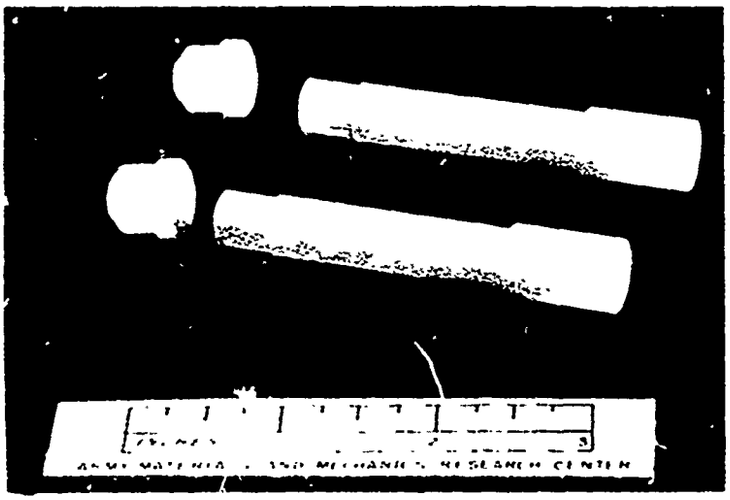

Figure 2 - Sample Irradiation Holders

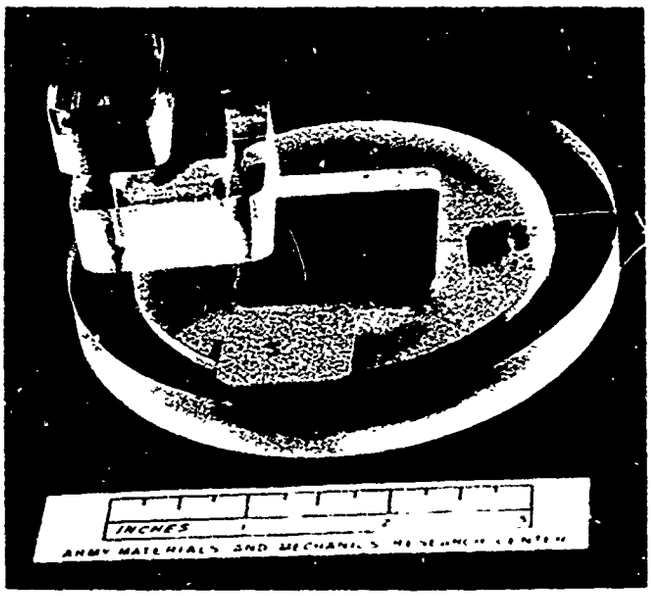

Figure 3 - Sample Holders for Counting Irradiated Samples

Procedure

Samples of the fabric and teflon tape were cut 1-inch x 7/8-inch so that identical geometric shapes were obtained, placed collectively in the irradiation holders, and irradiated simultaneously for a total of 6 minutes. The fabric sample and the teflon standard were then placed in individual counting holders and the amount of irradiation in each determined over a 4 minute period on the NaI(Tl) crystal. The fluorine in the sample was then calculated according to the modified equation given in the Technique Section. The theoretical fluorine content of the teflon tape was used as its actual fluorine content.

RESULTS

Evaluation of Untreated Fabric

Initially untreated fabric samples were irradiated to determine if there were any interfering radioactive nuclides present. The spectra from these samples showed only a positron emitter of 10 minute half-life (Figure 4), indicating the presence of nitrogen, an element known to be in fabrics either as a component thereof (nylon), or in applied treatments (dyestuffs, urea, quaternary nitrogen salts).

Figure 4 - Gamma Ray Spectra Showing the 0.511 MeV Positron Annihilation Peak

Determination of Positron Emitters in Quarpel Treated Fabric

Samples of Quarpel treated fabric were then irradiated and the gamma ray spectra obtained showed only a 0.511 MeV peak on the Nuclear Data 130A Multichannel Analyzer. This indicated only positron emitters to be present. Further study of the exponential decay curve (Figure 5) yielded a composite of two components having half-lives of 10 minutes and 109 minutes; nitrogen ^{13} and fluorine ^{18} respectively. Since fluorine was the primary interest, the nitrogen ^{13} was allowed to decay out; a period of 2 hours was found to be adequate.

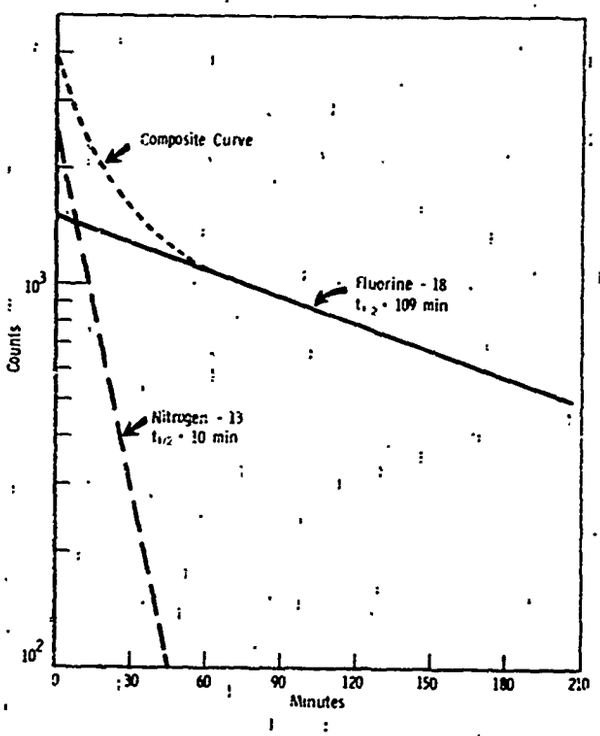

Figure 5 - Exponential Decay Curve Showing Two Different Positron Emitters with Half-lives of 10 and 109 Minutes

Evaluation of Treated, Laundered, Extracted and Weathered Fabrics

Polyester/cotton poplin, 5.7 oz/yd^2, Cadet Grey 345 fabric was treated in a finishing plant under controlled conditions with two of the accepted fluorine-containing polymers (Product A and Product B). Samples of these fabrics were used to determine:

A. Reproducibility of the fluorine analysis. The sample used for this was treated with Product B and the results obtained are listed in Table II.

B. Comparison of the change in fluorine content of treated fabric containing Products A and B, initially and after laundering and chloroform extraction, (Table III).

C. The fluorine content of fabric treated with 19.0% and 22.8% fluorochemical B, (Table IV).

D. The fluorine content of fabric treated with fluorochemical A, initially and after laundering and weathering (Table V).

Determination of the Homogeneity of Fluorine-containing Polymer in Commercially Treated Fabrics.

Four different fabrics were drawn from the Defense Personnel Support Center: (1) 9 oz/yd^2 Nyco-sateen; (2) 5.5 oz/yd^2 cotton oxford; (3) 5.5 oz/yd^2 cotton warp-nylon fill oxford; and (4) 5.7 oz/yd^2 cotton/polyester poplin. These materials had been procured by the Army as Quarpel treated fabrics but no further knowledge was received as to their history. The homogeneity was studied by following the fluorine concentration along the width (fill direction) on the first two fabrics and along the length of the last two fabrics (warp direction). The results are shown in Table VI.

TABLE II

Reproducibility of Fluorine Analyses

% Fluorine	Variation
0.64	+0.02
0.59	-0.03
0.62	0.00
0.62	0.00

TABLE III

Percent Fluorine Content of Quarpel Treated Fabric Samples Containing Two Different Fluorochemicals

Fluorochemical	Initial	Laundered	$CHCl_3$ Extracted
A	0.72	0.68	0.44
B	0.70	0.75	0.63

TABLE IV

Fluorine Content of Fabric Treated with Two Concentrations of Fluorochemical B

	19.0% Fluorochemical B	22.8% Fluorochemical B
	0.64%	0.70%
	0.59%	0.73%
	0.62%	0.69%
Avg.	0.62%	Avg. 0.71%

TABLE V

Fluorine Content of Fabric Treated with Fluorochemical A, Initially and After Laundering and Weatherin_

Initial	Laundered	Exposure (Days)		
		18	42	60
0.61%	0.56%	0.63%	0.53%	0.65%

TABLE VI

Fluorine Content * of Commercially Treated Quarpel Fabrics

Fill Direction	Left End %	Center %	Right End %
Nyco/sateen, 9 oz/yd^2	0.41	0.55	0.42
Cotton-oxford, 5.5 oz/yd^2	0.78	0.65	0.55
Warp Direction			
Cotton Warp-Nylon Fill oxford, 5.5 oz/yd^2	0.67	0.54	0.52
Cotton/Polyester poplin 5.7 oz/yd^2	0.41	0.56	0.58

* Measurements made at a minimum of 18 inches apart and at least 3 inches from the selvage.

DISCUSSION

Neutron activation analysis as applied to Quarpel treated fabrics is a new analytical tool. It is a fast, non-destructive method for determining the fluorine content of such fabrics. Results obtained on the AMMRC unique nuclear irradiation transfer apparatus are highly reproducible (Table II). Two of the presently accepted fluorine-containing polymers were used in the Quarpel formulations and compared (Table III). Equal fluorine concentrations were found on both treated samples before and after laundering. However, the sample containing Product A showed greater loss of fluorine when extracted with chloroform than did the Product B sample. Interpretation of this phenomenon can not be made at this time.

This new analytical tool can be used to determine the relative add-on of the polymers used in the Quarpel formulations (Table IV). A slight increase in the percent of Product B in the pad application bath (from 19.0 to 22.8%) produced a 0.09% numerical increase in the percent fluorine content of the treated fabric.

Fluorocarbon loss in laundered and weathered fabrics can be determined by the limited data in Table V. Thus, laundering appears to reduce fluorine content somewhat while weathering causes very little loss on an overall basis.

The inconsistency in the weathering data (Table V) may have been due to inhomogeneity in the sample treatment. Experience has taught that commercially prepared Quarpel treated fabrics had a non-homogeneous finish. However, in general, those fabrics procured under government contracts were able to meet the specification requirements for physical water and oil repellency tests because of the wide tolerance range indicated. Analysis of four stock fabrics drawn from the Defense Personnel Support Center substantiated this hard-earned experience (Table VI) indicating significant non-homogeneity. By effective use of neutron activation analysis these Laboratories will be able to correlate maximum and minimum fluorine contents with relative performance of Quarpel treated fabrics. With such correlations more exact specifications than now possible should be attainable for monitoring procurements, thus assuring the best environmental protection for the soldier that is possible.

CONCLUSIONS

Neutron activation analysis is an effective means of determining fluorine content of Quarpel treated textiles. It is non-destructive and allows correlation of physical test evaluation data with quantitative fluorine data on identical samples. In addition, the decay curve produced (Figure 5) could be resolved with the aid of a least squares computer program allowing the Army to monitor both the fluorochemical and the nitrogen contents of Quarpel treated fabrics and compare them with performance requirements.

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1. "Quarpel Water and Oil Resistant Treatment for Textiles," Textile Series Report No. 111, Headquarters, Quartermaster Research and Engineering Command, Natick, Mass., 1960.

2. Priest, H. F., F. C. Burns, and G. L. Priest, "An Irradiation Transfer and Counting System for Neutron Activation Analysis of Short-lived Components in In-homogeneous Samples," TR 70-21, Army Materials and Mechanics Research Center, Watertown, Mass., 1970.