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Formaldehyde Release from Durable-Press Apparel Textiles Final Project Report to The U.S. Consumer Product Safety Commission

T. G. Matthews
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E. R. Merchant

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FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A05 Microfiche A01

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ORNL/TM-9790

FORMALDEHYDE RELEASE FROM DURABLE-PRESS APPAREL TEXTILES*

FINAL PROJECT REPORT
TO
THE U.S. CONSUMER PRODUCT SAFETY COMMISSION

T. G. Matthews, C. R. Daffron and E. R. Merchant

Date Published - October, 1985

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Oak Ridge, Tennessee 37830
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MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY

* Research sponsored by the U.S. Consumer Product Safety Commission under Interagency Agreement CPSC-IAG-82-1181 under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

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ACKNOWLEDGEMENT

Research sponsored by the U.S. Consumer Product Safety Commission under Interagency Agreement No. CPSC-IAG-82-1181 under contract DE-AC05-840R21400 with the Martin Marietta Energy Systems, Inc.

The authors express their gratitude to Dr. Bethlehem K. Andrews, U.S. Department of Agriculture (New Orleans) for her assistance in the performance of this study and review of this report.

FORMALDEHYDE RELEASE FROM DURABLE-PRESS APPAREL TEXTILES
FINAL PROJECT REPORT TO THE U.S. CONSUMER PRODUCT SAFETY COMMISSION

T. G. Matthews, C. R. Daffron and E. R. Merchant

SUMMARY

A survey of formaldehyde (CH_2O) release from durable-press apparel textiles has been performed to better characterize the CH_2O emission properties of fabrics marketed in the US. The potential for adverse dermal exposures to CH_2O from clothing in direct contact with skin (via perspiration) was investigated. A total of 180 fabrics among categories of (1) top-weight non-knits (for shirts and blouses), (2) bottom-weight (for pants), (3) cotton/cotton blend knits (for shirts and underwear) and (4) flatgoods (for sheets) were collected in January through June of 1984. Suppliers typically included three large domestic, four small domestic, and four foreign manufacturers.

The survey fabrics were analyzed using a simple aqueous extraction test that was modeled after the Japanese industrial standard test but modified to more closely simulate consumer use conditions. The ORNL extraction test incorporates (1) artificial perspiration solution for liquid extraction, (2) a pH=5 buffer, (3) a six hour extraction period at 35°C, and (4) a pararosaniline analysis procedure as a more sensitive back-up procedure to the commonly used Nash method. An intercomparison of the ORNL extraction, the Japanese standard and the American Association of Textile Chemists and Colorists (AATCC) sealed jar methods using 12 fabrics selected from the textile survey yielded an average emission ratio of 0.46 $\pm$ 0.16 for the ORNL/AATCC methods and 1.5 $\pm$ 0.5 for the ORNL/Japanese methods.

The average CH_2O releases from the survey fabrics, as measured with the ORNL extraction test, were 117 $\pm$ 140, 58 $\pm$ 72, 19 $\pm$ 17 and 31 $\pm$ 29 ug CH_2O/g fabric for top-weight, bottom-weight, knit and flatgood categories, respectively. Formaldehyde releases of <100 ug CH_2O/g fabric were measured from 86% of the survey fabrics. Estimates of the CH_2O releases under AATCC

test conditions were determined using the ORNL extraction data for the survey fabrics and the ORNL/AATCC intermethod comparison data. The results indicate potential two to threefold reductions in average CH_2O release between durable press textiles measured in the American Textile Manufacturers Institute survey of fabrics collected in 1982 and the ORNL survey of fabrics obtained in 1984.

An analysis of the variation among the CH_2O releases measured with the ORNL extraction test was performed for each of the four fabric categories from the textile survey. The results indicate coefficients of variation of typically 60 to 120% for inter-manufacturer variation, 30 to 60% for inter-fabric-sample variation, and 4 to 20% for combined intra-fabric-sample variation and measurement uncertainty. The length of storage period in sealed plastic bags also appeared to strongly affect the measured CH_2O releases in an unexpected manner. Three to fourfold increases in CH_2O release were observed with additional seven to nine weeks of storage in a laboratory environment between repeated testing using the ORNL extraction test.

The effect of repeated washing was studied on a total of eight fabric samples selected from all four fabric categories in the textile survey. The strongest emitting fabrics with initial emission levels of >125 ug CH_2O/g fabric exhibited a 74 $\pm$ 11% decline in CH_2O emission levels following the first washing, with an additional 13 $\pm$ 6% decline after the completion of six further washings. The weakest emitting fabrics with initial emission levels of <25 ug CH_2O/g fabric demonstrated both increases and decreases in CH_2O emission strength after washing but never exceeded 11 ug CH_2O/g fabric.

Two test methods were developed to estimate the aqueous CH_2O concentration in fabrics saturated with artificial perspiration solution. The ORNL extraction test was modified to reduce the extraction solution volume to that required to saturate the test fabric. A Skin Patch Test Simulator (SPATS) was developed to simulate the occluded application of perspiration-soaked fabric on skin in patch tests. The reduced solution volumes in comparison to the ORNL extraction test resulted in increased CH_2O concentrations (ug CH_2O/mL H_2O) but suppressed fabric emissions (ug CH_2O/g fabric). Approximately 90% of the survey fabrics are predicted to produce CH_2O concentrations <30 ug CH_2O/mL H_2O, the lowest reported concentration with

measured dermal response in sensitized individuals. With a single washing, all but one of the survey fabrics are predicted to be <30 ug CH_2O/mL H_2O. A 30 ug CH_2O/mL H_2O solution is approximately two orders of magnitude more dilute than the standard 1% formalin solutions used for patch testing.

INTRODUCTION

Formaldehyde release from durable-press apparel textiles is a potential health concern for a variety of irritative, allergenic and sensitization reactions on skin (Borzellica, 1980, Gibson, 1983). The widespread use of formaldehyde resins in 75 to 85% of apparel textiles in the U.S. textile industry to achieve durable-press characteristics also provides for broad public exposure (Batija, 1981). The transport of formaldehyde from the fabric to the skin has been found to be much stronger in direct liquid contact with the skin (e.g., through perspiration) than indirectly through an air layer (Hollies et al., 1982). A 65% transfer of ^{14}C labeled CH_2O to skin has been achieved with CH_2O solution occluded with a latex barrier over rabbit skin (Robbins et al., 1981). Much lower transfer rates (i.e., 0.09-2.61%, Hollies, 1982) were achieved with ^{14}C treated cloth patches, dependent on the type of cloth, CH_2O resin preparation, and the presence or absence of perspiration. The lower limits of CH_2O exposure with measured response on the skin of sensitized individuals is a subject of continued research. Jordan et al., (1979) report threshold concentrations as low as 30 ppm CH_2O (diluted from formalin) in occlusive and nonocclusive tests. Malbach reports (in Gibson, 1983) a threshold of no response of 80 ppm in nonocclusive tests. By comparison, the current industrial guidelines of Levi Strauss are 500 ppm (i.e., 500 ug CH_2O/g fabric) for unwashed fabrics as measured in the AATCC Sealed Jar test (Switzer, 1983). This guideline has been reduced from 2000 ppm over the past two decades. The American Textile Manufacturers Institute (ATMI) has performed two surveys of CH_2O release from apparel textiles in 1980 and 1983. ATMI analyzed test results taken in 1975, 1980 and 1982 that were voluntarily submitted from "main stream" industries (Poole, 1984). The sealed jar test of the American Association of Textile Chemists and Colorists (AATCC) "or equivalent" was used. Although the survey has ATMI-admitted "methodology limitations", a decline in "weighted average" CH_2O releases from 534 to 491 to

345 ug CH_2O/g fabric were determined for data from 1975, 1980 and 1982, respectively.

The test methods for CH_2O release from durable-press apparel textiles and the factors that affect CH_2O release have been extensively studied and reviewed (Vail et al., 1981, Switzer, 1983). The AATCC sealed jar test (AATCC-112, 1982) is most commonly used in the U.S. even though it was originally designed for worker protection in textile plants. The AATCC test measures the cumulative CH_2O emissions from a fabric sample to air inside a sealed mason jar over a 20 hour period at 49°C and near-100% relative humidity. The Japanese test is designed in part to simulate potential dermal exposures to CH_2O from fabrics. A fabric sample is extracted in H_2O for 30 minutes at 40°C. However, the lack of pH control and brief extraction period are potential concerns for simulation of normal consumer use conditions. The Italian test method, which is modeled after the Japanese test, incorporates control of pH at 6.0 (D'Angiuro, 1982). The Cold Sulfite Method for free CH_2O involves a brief seven minute extraction in sulfite-H_2O solution at low (i.e., 0-10°C) temperatures. The Shirley Institute Method uses a 20 minute extraction in H_2O at 25°C followed by digestion of residual resins in strong acid. Thus, there is a need to develop simple extraction tests that consider many of the important factors affecting CH_2O release from durable-press fabrics such as temperature, pH and extraction period, and are designed to more closely simulate consumer use conditions. Fabric washing is an additional factor that strongly influences CH_2O releases from durable-press textiles and potential CH_2O exposures to skin. Although strong decreases in CH_2O release have been observed after a few washings in moderate pH water (Reinhardt et al., 1981), the CH_2O release can persist at reduced levels for more than 25 washings (Harper et al., 1984).

To better quantify the CH_2O release from durable-press apparel textiles sold in the U.S., a study was initiated by the U.S. Consumer Product Safety Commission (CPSC) at Oak Ridge National Laboratory (ORNL). The study had five major components:

1. development of a simple extraction test for CH_2O release from durable-press apparel textiles that more closely simulates consumer use conditions than currently existent tests,

2. survey of CH_2O release from durable-press fabrics marketed in the U.S. by domestic and foreign manufacturers, including flatgood, bottom-weight, knit and top-weight categories using the ORNL extraction method,

3. evaluation of the effect of repeated washing on selected survey fabrics using the ORNL extraction method,

4. comparison of results from the new ORNL extraction method to that of the commonly used AATCC and Japanese tests, and

5. comparison of the CH_2O releases (ug CH_2O/g fabric) from the survey fabrics measured with simple extraction tests to aqueous CH_2O concentrations (ug CH_2O/mL H_2O) generated in perspiration-saturated fabrics under conditions simulating dermal exposure during skin patch tests.

ORNL EXTRACTION TEST DEVELOPMENT

A simple CH_2O extraction test has been developed to more closely simulate normal consumer use conditions and potential dermal exposures to CH_2O from durable-press apparel textiles than available industrial methods. The new extraction test is modeled after the Japanese Industrial standard test but incorporates several changes that are detailed in an experimental protocol given in Appendix I. Artificial perspiration solution, modeled after the perspiration solution used in the AATCC test for colorfastness of textiles (AATCC-15, 1979), is used for CH_2O t extraction of fabric samples. A sodium acetate-acetic acid buffer is used to maintain the pH 5 extraction solution in accordance with Mazur et al., (1979). It is recognized that the pH of human perspiration varies over a wide range (e.g., 4 to 7) and that this may have a significant impact on dermal exposure to CH_2O from apparel textiles (Behrendt et al., 1971, Hersmonn et al., 1955). An extraction temperature of 35°C was chosen as an approximate compromise between body temperature (i.e., 37°C) and the results of a limited sampling of clothing temperatures at each of three locations on four individuals (i.e., 34° ± 1°C). An extraction period of six hours was chosen to simulate consumer use within the limits of an eight hour extraction and analysis test. Ten gram fabric samples (in 100 mL extraction solution) were used instead of one gram samples to increase the sensitivity of the test and to reduce the impact of intra-sample variation in CH_2O emissions. No suppression in CH_2O emissions due to the increased sample size were

observed in tests of three knit fabrics using 1, 3, 7 and 10 gram samples in a 100 mL extraction volume. The pararosaniline (PA) colorimetric analysis was adopted as a more sensitive back-up method for the commonly used Nash procedure and used only when the fabric emissions were too weak to be quantified with the Nash method. A 12-fabric, intercomparison of extraction solutions analyzed with both the PA and Nash methods yielded nearly consistent results for most test fabrics. An average PA/NASH ratio of 1.14 $\pm$ 0.08 was determined for 10 of 12 fabric extracts (the 2.17 $\pm$ 0.04 ratio determined for the remaining two fabrics may have been due to experimental error). These results indicate that the PA method is unlikely to have a significant bias on the survey results in comparison to the Nash method.

SURVEY OF DURABLE-PRESS APPAREL TEXTILES

The survey of CH_2O release from durable-press apparel textiles marketed in the U.S. involved the sampling of 3 to 5 small domestic, 3 large domestic, and 3 to 5 foreign manufacturers in each of the following product categories: cotton and cotton blend knit (for shirts and underwear), top weight (non-knit for shirts and blouses), bottom weight (for pants) and flat goods (for sheets) (Little, 1983). The large domestic manufacturers were among the largest U.S. manufacturers. The selection of the small domestic manufacturers involved a somewhat arbitrary choice between numerous companies that were distinctly smaller than the large manufacturers. The foreign manufacturers were selected independent of sales volume to attempt to isolate fabrics produced and CH_2O treated outside of U.S.

The acquisition of survey fabrics came close to original CPSC goals for 50 fabric samples in each of the four product categories. The vast majority of manufacturers contributed the requested five samples to each product category in which they participated. A few manufacturers sent more than five samples. In such cases, a group of five samples were randomly selected for testing. Deficiencies in fabric acquisition were typically caused by difficulties in obtaining sufficient fabric samples from foreign manufactures. A total of 47 bottom-weight, 50 non-knit, 39 knit, and 44 flatgood samples were tested.

The survey fabrics were acquired from industry during January to June, 1984. The storage periods prior to testing varied from 1-5, 2-7, 8-12, and 9-13 weeks for flatgood, knit, top-weight and bottom-weight product categories, respectively. The particularly long storage periods for the top-weight and bottom-weight categories resulted from both delays in sample acquisition and performance of laboratory tests.

All fabric samples were stored at room temperature, sealed inside two plastic bags (see Appendix I). Prior to testing, three specimens were then cut from each sample and allowed to condition in room air for 24 hours. Formaldehyde extraction was performed for six hours in artificial perspiration solution at pH 5 and 35°C. Each extraction solution was then filtered, and analyzed in duplicate with one of two colorimetric tests. The Nash procedure was used first for all fabrics. The extraction solutions for fabric specimens with absorbence values averaging <0.1 absorbence units were reanalyzed using the more sensitive pararosanaline method.

The average CH_2O release (ug CH_2O/g fabric) for each fabric specimen tested in the textile survey is listed in Tables 1 to 4 for top-weight, bottom-weight, knits and flatgood product categories, respectively. Included in these tables are (1) the manufacturer classifications of domestic-small (DS), domestic-large (DL), and foreign (F) companies, and (2) an assignment of manufacturer and sample number. The CH_2O release data for the survey fabrics are summarized in Table 5. The CH_2O release (i.e., ug CH_2O/g fabric) of the individual fabric specimens are averaged by manufacturer classification in each product category. The ranking between product categories from strongest to weakest emitters is top-weight, bottom-weight, flatgoods, and knits with average CH_2O releases of 117, 58, 31, and 19 ug CH_2O/g fabric, respectively. No consistent ranking between manufacturer classifications is observed in all product categories. The domestic-large and domestic-small classifications have strongly overlapping distributions of CH_2O release levels. Among the bottom-weight, knit and flatgoods, the average CH_2O releases for the foreign manufacturers are a factor of two to ten lower than corresponding levels for the domestic manufacturers. A further breakdown of the survey results by the percentage of fabric test specimens with CH_2O releases less than selected values is given in Table 6. For example, 86% of the fabrics had CH_2O releases

less than approximately 100 ug CH_2O/g fabric. Ninety and 95% of the test specimens had CH_2O releases of less than approximately 150 and 250 ug CH_2O/g fabric, respectively.

An analysis of variance among the CH_2O releases measured for the test fabrics has been performed. Intra-sample (i.e., inter-specimen), inter-sample and inter-manufacturer variation are compared within each of the four fabric categories. Intra-sample and inter-sample variation are estimated using a one-way analysis of variance statistical technique (see Appendix II for detailed treatment). The estimate of intra-sample variation is an inseparable combination of measurement uncertainty due to the test method and intra-sample variation in CH_2O release strength. The estimate of inter-sample variation is due only to variation in CH_2O release strength between fabric samples acquired from the same manufacturer (in a given product category). The inter-manufacturer variation is estimated by the coefficient of variation between the average results for each manufacturer in a given product category.

The results of the analysis of variance among the CH_2O release data are presented in Tables 7-10 for fabric categories top-weight, bottom-weight, knits, and flatgoods, respectively. The coefficients of variation (CV) for intra-sample, inter-sample, and combined intra-sample plus inter-sample variation are given for individual manufacturers and summarized by manufacturer classification. The inter-manufacturer coefficients of variation are presented by manufacturer classification. The manufacturers are grouped simply according to domestic and foreign manufacturers instead of DS, DL and F classifications because of the strong overlap in CH_2O release data among small and large domestic firms in most fabric categories. Statistical data are presented in Tables 7-10.

The largest source of variability among the CH_2O releases from the survey fabrics as determined from the analysis of variance is inter-manufacturer variation. The CV values range from about 50% to 140% and are generally about twofold larger than the CV for combined intra-sample and inter-sample variation. Large inter-sample variation is also observed in all four product categories. The CV values span from typically 30% to 70%. The intra-sample CV values, which include uncertainty due to the test method and site-to-site

variation in fabric CH_2O release, are typically less than 10% for all but the flatgoods data set. Increased measurement uncertainty is expected in this data set because some of the fabric samples were tested during different time periods; a single specimen and then duplicate specimens were tested a week apart. A one-way analysis of variance of the flatgoods data set with the single specimen data removed resulted in a reduction in the average CV for intra-sample variation from 20% to 12%, but only a small change in inter-sample CV from 33% to 30%. This result is consistent with increased measurement uncertainty for specimens from a given sample that are tested over a one week period instead of the normal protocol where all three specimens are tested on the same day. The average CV of 12% for the flatgoods in comparison to 4%, 4% and 9% for top-weight, bottom-weight and knit fabrics may also indicate greater site-to-site variation in the application of CH_2O resins to the flatgood materials. Overall the combined intra-sample variation in CH_2O releases and uncertainty due to the test method are very small in comparison to inter-sample and inter-manufacturer variability.

EFFECTS OF REPEATED WASHING

Repeated washing has been shown to strongly reduce CH_2O release provided that the water is of moderate pH (e.g., pH 4-9, Jaco et al., 1982, Reinhardt et al., 1981). The survey of durable-press apparel textiles provided a spectrum of fabric types and emission strengths to test the effectiveness of common laundering for reducing CH_2O releases. A selection of eight fabrics, two each from the bottom-weight, top-weight, knit and non-knit categories were tested, including two foreign and six domestic samples. The initial range of CH_2O releases varied from 0.6 to 178 ug CH_2O/g fabric as measured by the ORNL extraction test (see Table 11). The procedure for washing was modeled after AATCC Test Method 124-1982 for repeated launderings. A General Electric automatic washer, AATCC Standard Detergent 124 and General Electric automatic dryer were used. The dry weight of the test fabrics was approximately 2.6 kg. The temperature and pH of the wash water were 43 $\pm$ 2°C and 6.5 $\pm$ 0.5, respectively. The temperature of the dryer was approximately 38°C. All test fabrics were laundered a total of seven times. The ORNL extraction test was performed before washing and after 1, 2, 3, 5 and 7 washings. Fabric

quantities limited testing to three specimens of each fabric sample prior to the first washing and typically two specimens after subsequent launderings.

The results of the repeated washing experiment showed very different behavior for relatively strong and weak emitting fabrics. Fabrics with initial CH_2O releases of >125 ug CH_2O/g fabric (i.e., Sample Nos. 2,6,7,8) showed a strong decline after the first washing, followed by continued but slower declines with subsequent washing (see Table 11 and Figure 1). An average 74 $\pm$ 11 percent decline was observed after one wash. A further decline of 13 $\pm$ 6 percent (from the initial CH_2O releases) was observed after the next six washings. The relatively weak emitting fabrics with initial CH_2O releases of 0.6 - 25 ug CH_2O/g fabric (i.e., Sample Nos. 1,3,4,5) demonstrated both increases and decreases in CH_2O release with washing (see Table 11 and Figure 2). However, none of the relatively weak emitting fabrics ever exceeded approximately 11 ug CH_2O/g fabric with washing. It is interesting to note that the weakest emitters, fabrics number 5 and 1, showed the largest increases in CH_2O releases after two washings. All of this data exceeds the limit of quantitation for the PA analysis (i.e., approximately 0.25 ug CH_2O/mL H_2O).

INTERMETHOD COMPARISON OF ORNL, AATCC, AND JAPANESE EXTRACTION TESTS

A intermethod comparison was performed between the commonly used AATCC and Japanese tests and the ORNL extraction method. A total of 12 fabrics were selected from the four fabric categories, emphasizing the cotton and cotton blend knit fabrics because of their relatively high CH_2O releases (see Table 12). Products from all three manufacturer classifications (i.e., DS, DL, F) were included. Three specimens were tested from each fabric sample for all test methods. The average CH_2O releases for the fabric samples spanned from 26 to 1764 ug CH_2O as measured by the ORNL extraction test. The correlation between the three different methods are summarized as the average ratios of the test results between two test methods. Intermethod, linear regression analyses are not used because of the strong bias that fabric number 10 exerts over such a calculation. The average ratio of the ORNL/AATCC, ORNL/Japanese

and Japanese/AATCC tests are 0.46 ± 0.05* (i.e., CV=35%), 1.49 ± 0.14* (i.e., CV=33%), and 0.36 ± 0.07* (i.e., CV=69%), respectively. The results of the ORNL test are approximately twofold lower than the AATCC test and 50% higher than the Japanese test. The CV values indicate that the results of the ORNL test are more comparable to both the AATCC and Japanese tests than an analogous comparison between the results of the AATCC and Japanese tests.

The results of the intermethod comparison between the ORNL and AATCC extraction tests can be used to qualitatively compare the results of the surveys taken by ORNL and ATMI of CH_2O release from durable-press apparel textiles. The average CH_2O releases predicted for the AATCC test from the results of the ORNL extraction test are 280 ± 40*, 140 ± 20*, 46 ± 7*, and 75 ± 10* ug CH_2O/g fabric for all top-weight, bottom-weight, knit, and flatgood fabrics, respectively. If the comparison is limited to domestic fabrics from the ORNL survey, the predicted results for the AATCC test are generally somewhat higher. Formaldehyde releases of 280 ± 40*, 190 ± 30*, 53 ± 7*, and 110 ± 13* ug CH_2O/g fabric are predicted for AATCC tests of the top-weight, bottom-weight, knit, and flatgood fabrics, respectively. The mean values predicted from the ORNL survey are all lower than the mean result of 345 ug CH_2O/g fabric from the ATMI survey for 1982. More quantitative comparisons are difficult because of (1) intersurvey variation in fabric storage, conditioning and testing procedures, and (2) the absence of any breakdown of the ATMI results by product category. However, the ORNL results for fabrics obtained in 1984 indicate substantial reductions in CH_2O releases from those reported by ATMI for fabrics obtained in 1982.

A comparison of the ORNL test results for fabrics tested in the survey and intermethod comparison studies show substantial changes in CH_2O release (see Table 13). Ten of 12 fabrics demonstrated 1.4- to 5.2-fold increases in CH_2O releases; one fabric was unchanged and another decreased 1.6 fold. These fluctuations cannot be definitively explained but may be the result of the sometimes lengthy storage periods between the survey and intermethod comparison studies. Significant increases in CH_2O releases have been previously observed over three month storage periods (Jaco, 1982). Consistent

* Standard errors of the mean are reported.

with this result, the test fabrics with the greatest additional storage periods between the survey and intermethod comparison studies typically show the largest increases in CH_2O releases. For example, three of four fabrics with $\geq$ 31 weeks additional storage (i.e., fabrics number 1, 3, 5) increased approximately three to fourfold. Seven of the remaining eight fabrics with four to seven weeks additional storage either increased by approximately twofold or less, remained constant or declined in emissions. Nevertheless, the length of the storage period in double sealed plastic bags under laboratory environmental conditions appears to be a strong contributor to variance among the test results.

RELATION BETWEEN FABRIC CH_2O RELEASE AND AQUEOUS CH_2O CONCENTRATION IN PERSPIRATION-SATURATED FABRICS

Two methods have been used to relate the CH_2O release from durable-press apparel textiles as measured in simple extraction tests to the potential CH_2O concentrations in aqueous solutions that could be exposed to skin from perspiration-wet textiles. The first method, called a Wring test, is modeled after the ORNL extraction test. It is designed to minimize the volume of artificial perspiration solution used in the ORNL extraction test to more closely simulate the volume of perspiration solution encountered on textiles worn by individuals. Fabric samples are saturated with artificial perspiration solution and conditioned for 6 hours at 35°C; the exposure period and temperature are chosen in accordance with the protocol for the ORNL extraction test. An aliquot of the CH_2O-containing perspiration solution is then removed from the fabric (by compressing the specimen inside a syringe) and analyzed using colorimetric methods (see Appendix III for details). The results of the Wring test (see Table 15) show comparable precision to that of the ORNL extraction test. The CV for intra-sample variation, which includes the uncertainty of the test method, varys from 2 to 19% with an average CV of 8%.

A second method, called the Skin Patch Test Simulator (SPATS), has been developed to simulate the application of wetted, CH_2O-containing fabrics on skin in patch tests. To simulate skin exposure, fabric specimens are

saturated with artificial perspiration solution and occluded in direct liquid contact with a semi-permeable membrane in a 35°C oven. In contrast to skin, which readily sorbs CH_2O in surface layers due to its large water content, the membrane readily transports CH_2O to an aqueous reagents stream beneath the membrane that is subsequently analyzed for the concentration of CH_2O.

The SPATS consists of a flat aluminum plate with four channels covered by a 0.02 mm thick, semi-permeable, dimethylsilicone membrane (Bulletin General Electric Co., 1968) that is adhered to the aluminum surface (see Figure 1, Appendix 4 for exploded view). Mixed aqueous reagent of mercuric chloride and sodium sulfite for a CEA Instruments Model 555 Analyzer are flowed through four channels beneath the membrane using an eight channel peristaltic pump, four channels each for supply and drainage of the SPATS. Fabric specimens are saturated with artificial perspiration solution, incubated for three hours in a closed jar at 35°C, and then sealed in liquid contact with the membrane for testing. A portion of the CH_2O released from the test fabric is transported through the membrane to the aqueous reagent solution, which flows to the CEA instrument for measurement (Matthews, 1982). The CH_2O response of the SPATS is calibrated daily with a weakly-emitting fabric specimen saturated with dilute formalin solution. Results for a CH_2O-emitting fabric specimen from typically the same day of testing are then normalized to the response of the SPATS to the fabric exposed to standardized CH_2O solution.

$$[CH_2O]\ (ug/mL)_{\text{Test Fabric}} = \frac{\text{CEA Response for Test Fabric (mv)}}{\text{CEA Response for Std Fabric (mv)}} \cdot [CH_2O]\ (ug/mL)_{\text{Std Fabric}} \quad (1)$$

A summary of the experimental data and calculated results for the SPATS testing is given in Table 14. The daily SPATS calibration factors are determined as the quotient of the CEA response in millivolts divided by the concentration (ug CH_2O/mL H_2O) of the stock solution applied to a weakly-emitting (i.e., blank) test fabric. The estimate of CH_2O concentration generated in the artificial perspiration solution saturated on a test fabric during a SPATS test is determined using Equation 1. Although there is

inadequate data to conclusively evaluate the precision of the SPATS test, the duplicate results for Fabric 10 indicate good precision (i.e., ± 14%) in the SPATS testing.

A summary of the results for the Wring and SPATS tests plus comparison results for the ORNL extraction tests are presented in Table 15. Both the Wring and SPATS tests were performed using fabric specimens cut from the same 12 fabrics used in the intermethod comparison of the AATCC, Japanese and ORNL extraction methods (see previous section). The results are presented in two sets of units to facilitate a variety of intermethod comparisons. The units ug CH_2O/g fabric are presented for comparisons between the results of simple extraction tests such as the ORNL extraction and Wring tests. These units are most commonly used for industrial tests such as the AATCC and Japanese tests. The units ug CH_2O/mL H_2O are primarily used to estimate the CH_2O concentration in the artificial perspiration solution saturated on test fabrics. In the case of the Wring and SPATS tests this is used to compare potential skin exposure to CH_2O from perspiration-wetted fabrics and dilute formalin solutions used in patch tests and other dermatological studies of CH_2O.

A comparison of the ORNL extraction and Wring tests show that the CH_2O concentrations (ug CH_2O/mL H_2O) were consistently higher with the reduced liquid volume in the Wring test, but that the CH_2O releases (ug CH_2O/g fabric) were consistently lower in the Wring test than in the extraction test. This indicates some suppression of the CH_2O releases from the test fabrics with the increased CH_2O concentration resulting from the smaller volumes of perspiration solution used in the Wring test. The Wring test averaged 2.7 ± 0.8* fold higher in CH_2O concentration in the artificial perspiration solution than the ORNL extraction test. In contrast the Wring test averaged 4.1 ± 2.7* fold lower in CH_2O release (ug CH_2O/g fabric) than the ORNL extraction test results. The intermethod comparison between the ORNL extraction and Wring tests can be used to predict the CH_2O concentrations measured by the Wring test for all test fabrics from the textile survey that were analyzed using the ORNL extraction test.

* Standard errors of the mean are reported

$$\text{Wring Test (ug } CH_2O/mL\ H_2O) = \text{ORNL Extraction Test (ug } CH_2O/g\ fab) \cdot \frac{10g\ fab}{100\ mls} \cdot 2.7 \pm 0.8^{*} \quad (2)$$

The predicted average CH_2O concentrations for Wring test measurements of all top-weight, bottom-weight, knit and flatgood fabrics from the textile survey (based on ORNL extraction test results taken during the survey) are 32 ± 4*, 16 ± 2*, 5 ± 1* and 8 ± 1* ug CH_2O/ mL H_2O, respectively. The predicted maximum CH_2O concentrations for Wring tests of the strongest emitting fabrics (based on ORNL extraction test results taken during the survey) in each of the above fabric categories are 940 ± 85*, 76 ± 7*, 17 ± 2*, and 33 ± 3* ug CH_2O/mL H_2O, respectively.

The results of an intermethod comparison between the SPATS and ORNL extraction tests are similar to the results of an intermethod comparison of the Wring and ORNL extraction tests. The results of the SPATS tests of five fabrics averaged 2.6 ± 0.7* fold higher than the ORNL extraction test in CH_2O concentration units of ug CH_2O/mL H_2O. Analogous to Equation 2, the intermethod comparison between the ORNL extraction and SPATS tests can also be used to predict the CH_2O concentrations measured by the SPATS test for all test fabrics from the textile survey.

$$\text{SPATS Test (ug } CH_2O/mL\ H_2O) = \text{ORNL Extraction Test (ug } CH_2O/g\ fab) \cdot \frac{10g\ fab}{100\ mls} \cdot 2.6 \pm 0.7^{*} \quad (3)$$

The results predicted for the SPATS tests are slightly lower (i.e., 2.7/2.6 = 0.96 fold) than those for the Wring test, but indistinguishable within the uncertainties of the intermethod comparisons.

The results of the textile survey of 180 fabric samples using the ORNL extraction test and the intermethod comparisons between the ORNL extraction test and the SPATS and Wring tests indicate that only one fabric is predicted to exceed 100 ug CH_2O/mL H_2O in artificial perspiration solution when saturated with the perspiration solution. Twenty-two fabrics, approximately 12% of the survey data, are predicted to exceed 30 ug CH_2O/mL H_2O, the lowest

* Standard errors of the mean are reported

reported concentration with measured dermal response in sensitized individuals. However, the results of the repeated washing experiments indicate that only one fabric is predicted to exceed 30 ug CH_2O/mL H_2O after a single laundering. A 30 ug CH_2O/mL H_2O solution is about 120-fold more dilute than the 1% formalin solution commonly used in skin patch testing (North American Contact Dermatitus, 1982).

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Table 1: Results of apparel textile survey for top-weight non-knits (for shirts and blouses) taken using the ORNL extraction test

Obs	Fabric	Manufacturer No.	Manufacturer Class.	Sample	Extraction Soln ($ugCH_2O/gFab$) Spec. 1	Spec. 2	Spec. 3
1	0043	1	DL	1	39.3	37.1	38.0
2	0044	1	DL	2	79.7	78.6	80.6
3	0045	1	DL	3	221.4	226.4	227.7
4	0046	1	DL	4	43.3	44.6	44.7
5	0047	1	DL	5	49.5	49.2	50.6
6	0975	2	DL	1	56.0	56.2	54.2
7	0976	2	DL	2	50.2	52.1	48.9
8	0977	2	DL	3	59.1	60.6	60.8
9	0978	2	DL	4	41.6	41.9	43.8
10	0979	2	DL	5	44.1	46.9	45.7
11	1491	3	DL	1	42.4	42.1	42.7
12	1492	3	DL	2	116.2	119.1	110.0
13	1493	3	DL	3	150.3	144.5	144.6
14	1494	3	DL	4	90.7	87.0	88.2
15	1495	3	DL	5	38.1	40.2	40.8
16	2444	4*	DS	1	45.1	44.4	45.5
17	2445	4*	DS	2	158.9	161.8	159.6
18	2446	4*	DS	3	31.8	31.8	31.6
19	2447	4*	DS	4	43.8	44.7	45.9
20	2448	4*	DS	5	62.4	63.4	64.4
21	2449	4*	F	1	144.8	152.5	145.7
22	2450	4*	F	2	154.1	149.2	151.9
23	2451	4*	F	3	218.4	226.8	211.0
24	2452	4*	F	4	192.7	185.7	191.3
25	2453	4*	F	5	244.9	256.9	323.1
26	2461	5*	F	1	51.0	50.4	56.6
27	2462	5*	F	2	99.5	102.1	102.1
28	2463	5*	F	3	55.8	52.4	56.1
29	2464	5*	F	4	20.9	20.2	21.8
30	2465	5*	F	5	37.9	36.5	34.9
31	2466	5*	DS	1	2.4	2.3	2.6
32	2467	5*	DS	2	257.3	259.2	253.7
33	2468	5*	DS	3	286.8	285.8	285.5
34	2469	5*	DS	4	836.8	940.2	915.4
35	2470	5*	DS	5	281.4	286.4	284.3
36	3803	6	DS	1	34.7	32.5	33.5
37	3804	6	DS	2	87.5	84.9	87.7
38	3805	6	DS	3	67.1	65.8	64.5
39	3806	6	DS	4	48.6	47.2	47.7
40	3807	6	DS	5	22.5	22.5	22.6

* Fabric specimens were obtained from both foreign and domestic manufacturing plants of the same textile company.

Table 1: Results of apparel textile survey for top-weight non-knits (for shirts and blouses) continued

Obs	Fabric	Manufacturer No.	Manufacturer Class.	Sample	Extraction Soln ($ugCH_2O/gFab$) Spec. 1	Spec. 2	Spec. 3
41	3808	7	DS	1	57.7	55.2	65.3
42	3809	7	DS	2	57.5	57.5	59.9
43	3810	7	DS	3	75.4	71.8	73.5
44	3811	7	DS	4	71.8	76.3	73.3
45	3812	7	DS	5	38.5	39.8	39.8
46	8224	8	DS	1	141.9	140.7	143.9
47	8225	8	DS	2	285.6	295.8	301.7
48	8226	8	DS	3	57.0	57.3	60.1
49	8227	8	DS	4	49.0	47.7	47.7
50	8228	8	DS	5	302.3	289.3	291.6

Table 2: Results of apparel textile survey for bottom-weight (for pants) taken using the ORNL extraction test

Obs	Fabric	Manufacturer No.	Manufacturer Class.	Sample	Extract Soln ($ugCH_2O/gFab$) Spec. 1	Spec. 2	Spec. 3
1	0032	1	DS	1	16.3	16.5	16.5
2	0033	1	DS	2	11.9	11.7	11.2
3	0034	1	DS	3	23.2	22.9	23.9
4	0035	1	DS	4	6.5	6.3	6.0
5	0036	1	DS	5	10.9	10.8	10.5
6	0737	2	DS	1	247.2	237.1	226.6
7	0738	2	DS	2	95.6	92.9	94.0
8	0739	2	DS	3	240.9	232.2	234.7
9	0740	2	DS	4	274.2	273.9	279.2
10	0861	2	DS	5	272.6	276.1	279.9
11	0826	3	DL	1	149.9	148.0	151.8
12	0827	3	DL	2	21.6	20.6	21.7
13	0828	3	DL	3	67.6	70.0	67.5
14	0829	3	DL	4	92.0	87.2	88.4
15	0830	3	DL	5	110.8	104.9	107.0
16	0831	4	DL	1	106.6	107.3	103.6
17	0833	4	DL	2	91.4	91.8	93.7
18	0834	4	DL	3	83.9	85.6	82.4
19	0835	4	DL	4	10.5	7.0	9.8
20	0970	5	DL	1	16.3	16.5	16.5
21	0971	5	DL	2	30.4	29.4	28.4
22	0972	5	DL	3	22.3	22.4	21.4
23	0973	5	DL	4	21.9	21.3	21.1
24	0974	5	DL	5	38.4	37.6	37.8
25	2486	6	DS	1	18.1	18.8	19.5
26	2490	6	DS	2	75.9	80.3	80.5
27	2491	6	DS	3	47.5	45.1	47.2
28	2492	6	DS	4	56.2	54.4	54.3
29	2493	6	DS	5	46.1	45.6	46.5
30	3191-5	7	DS	1	53.4	52.8	53.3
31	3191-6	7	DS	2	20.3	20.0	20.2
32	3191-7	7	DS	3	149.7	157.7	152.8
33	3191-8	7	DS	4	74.8	74.4	77.3
34	3191-9	7	DS	5	11.2	11.0	11.4
35	3192	8	F	1	3.3	2.7	2.9
36	3194	9	F	1	56.3	58.8	55.2
37	3195-3	10	F	1	7.6	7.6	7.8
38	3971	11	F	1	5.7	5.9	5.9
39	3972	11	F	2	4.8	4.3	5.1
40	3973	11	F	3	12.6	10.5	10.4
41	3974	11	F	4	4.2	4.4	4.0
42	3975	11	F	5	1.2	1.4	2.3
43	8195	12	F	1	3.8	3.6	4.1
44	8196	12	F	2	4.6	4.8	4.8
45	8197	12	F	3	4.1	3.9	4.4
46	8198	12	F	4	10.4	11.1	11.2
47	8199	12	F	5	19.7	19.9	20.0

Table 3: Results of apparel textile survey for cotton and cotton blend knits (for shirts and underwear) taken using the ORNL extraction test

Obs	Fabric	Manufacturer No.	Manufacturer Class.	Sample	Extraction Soln ($ugCH_2O/gFab$) Spec. 1	Spec. 2	Spec. 3
1	0467	1	DL	1	2.3	1.9	2.0
2	0468	1	DL	2	14.0	14.4	16.4
3	0469	1	DL	3	3.6	3.3	3.2
4	0470	1	DL	4	3.8	4.1	4.6
5	0471	1	DL	5	15.6	16.5	15.8
6	1481	2	DS	1	7.3	7.2	7.3
7	1482	2	DS	2	6.9	6.9	6.6
8	1483	2	DS	3	3.7	3.4	3.6
9	1484	2	DS	4	5.9	5.3	5.5
10	1485	2	DS	5	4.9	4.3	4.9
11	2561	3	F	1	27.7	23.0	25.3
12	2562	3	F	2	7.0	8.0	7.9
13	2563	3	F	3	6.1	6.4	6.3
14	2564	3	F	4	13.8	12.6	14.3
15	2565	3	F	5	8.3	8.9	9.8
16	2566	4	F	1	2.7	2.8	2.7
17	2568	4	F	2	3.9	3.2	3.3
18	2569	5	F	1	35.9	35.5	34.6
19	2570	5	F	2	2.8	2.8	3.1
20	2571	5	F	3	5.1	5.1	4.4
21	3193	5	F	4	6.9	7.0	7.4
22	31911	6	DS	1	4.1	4.0	9.4
23	31912	6	DS	2	5.0	4.4	4.8
24	31913	6	DS	3	3.0	3.3	2.7
25	31914	6	DS	4	6.5	3.2	2.8
26	6887	7	DL	1	24.2	23.5	23.6
27	6888	7	DL	2	25.1	23.5	25.1
28	6889	7	DL	3	24.7	26.4	23.2
29	6890	7	DL	4	28.1	28.9	28.9
30	6891	7	DL	5	24.6	26.1	26.5
31	8543	8	DS	1	36.8	36.8	35.4
32	8544	8	DS	2	52.3	52.8	53.4
33	8545	8	DS	3	40.2	41.1	39.1
34	8546	8	DS	4	51.5	51.2	51.1
35	8547	8	DS	5	38.5	39.7	38.7
36	9895	9	DL	1	64.1	63.4	62.9
37	9896	9	DL	2	41.0	41.0	40.7
38	9897	9	DL	3	48.2	49.2	52.1
39	9898	9	DL	4	41.5	39.6	40.6

Table 4: Results of apparel textile survey for flatgoods (for sheets) taken using the ORNL extraction test*

Obs	Fabric	Manufacturer No.	Manufacturer Class.	Sample	Extraction Soln ($ugCH_2O/gFab$) Spec. 1	Spec. 2	Spec. 3
1	0672	1	F	1	.	1.9	1.7
	0672	1	F	1	0.9	.	.
2	0757	1	F	2	.	1.8	1.5
	0757	1	F	2	1.4	.	.
3	0758	1	F	3	.	1.6	1.3
	0758	1	F	3	1.1	.	.
4	0759	1	F	4	.	1.3	1.2
	0759	1	F	4	0.9	.	.
5	0760	1	F	5	.	1.7	1.5
	0760	1	F	5	1.0	.	.
6	0743	2	DL	1	11.2	11.6	11.2
7	0744	2	DL	2	20.0	18.0	19.3
8	0745	2	DL	3	13.3	13.1	12.0
9	0746	2	DL	4	20.5	21.1	21.8
10	0747	2	DL	5	32.1	36.2	39.6
11	0822	3	DS	1	17.8	17.1	23.5
12	0823	3	DS	2	14.1	.	.
	0823	3	DS	2	.	25.3	33.4
13	0824	3	DS	3	55.7	.	.
	0824	3	DS	3	.	72.1	89.4
14	0825	3	DS	4	14.7	.	.
	0825	3	DS	4	.	42.2	36.0
15	0863	4	DS	1	59.8	56.1	56.7
16	0864	4	DS	2	42.5	54.3	59.4
17	0865	4	DS	3	58.2	54.3	62.1
18	0866	4	DS	4	75.2	67.7	89.3
19	0867	4	DS	5	41.2	40.7	51.6
20	1486	5	DL	1	56.2	64.0	84.5
21	1487	5	DL	2	60.9	84.2	94.1
22	1488	5	DL	3	30.4	49.6	47.7
23	1489	5	DL	4	78.7	70.4	98.7
24	1490	5	DL	5	94.3	90.5	122.3
25	1496	6	DL	1	12.8	.	.
	1496	6	DL	1	.	14.5	14.7
26	1497	6	DL	2	40.3	.	.
	1497	6	DL	2	.	50.5	49.4
27	1498	6	DL	3	23.2	.	.
	1498	6	DL	3	.	30.7	32.5
28	1499	6	DL	4	19.6	.	.
	1499	6	DL	4	.	20.8	21.8

* For some fabrics, a single specimen and then two specimens were tested about one week apart instead of the normal protocol of testing all three specimens of a given fabric sample at the same time.

Table 4: Results of apparel textile survey for flatgoods (for sheets) continued*

Obs	Fabric	Manufacturer No.	Manufacturer Class.	Sample	Extraction Soln ($ugCH_2O/gFab$) Spec. 1	Spec. 2	Spec. 3
29	1500	6	DL	5	26.8	.	.
	1500	6	DL	5	.	25.6	26.0
30	2421	7	F	1	.	3.0	4.6
	2421	7	F	1	1.5	.	.
31	2422	7	F	2	.	2.3	2.9
	2422	7	F	2	1.4	.	.
32	2423	7	F	3	.	4.6	4.4
	2423	7	F	3	1.5	.	.
33	2424	7	F	4	.	4.0	2.1
	2424	7	F	4	1.2	.	.
34	2427	7	F	5	.	5.6	5.2
	2427	7	F	5	4.2	.	.
35	3177	8	F	1	6.4	7.3	8.9
36	3178	8	F	2	4.8	5.0	5.5
37	3179	8	F	3	4.5	4.8	5.5
38	3180	8	F	4	5.2	5.6	5.1
39	4001	8	F	5	6.5	7.2	7.0
40	3234	9	DS	1	15.1	.	.
	3234	9	DS	1	.	14.4	14.7
41	3235	9	DS	2	88.7	.	.
	3235	9	DS	2	.	86.6	75.5
42	3236	9	DS	3	70.5	.	.
	3236	9	DS	3	.	49.3	52.7
43	3237	9	DS	4	62.7	.	.
	3237	9	DS	4	.	46.2	46.0
44	3238	9	DS	5	71.9	.	.
	3238	9	DS	5	.	44.4	51.3

* For some fabrics, a single specimen and then two specimens were tested about one week apart instead of the normal protocol to test all three specimens of a given fabric sample at the same time.

Table 5: Summary of apparel textile survey results taken using the ORNL extraction test

Fabric Category	Manufacturer Classification	Results (ug CH_2O/g fabric) Average	Std.Dev.	Std.Err.	Range
Top-Weight	Domestic-Large	75	51	8	37 - 228
	Domestic-Small	139	183	21	2 - 940
	Foreign	125	83	15	20 - 323
	(All Samples)	117	140	11	2 - 940
Bottom-Weight	Domestic-Large	61	43	7	7 - 152
	Domestic-Small	87	92	12	6 - 280
	Foreign	10	14	2	1 - 59
	(All Samples)	58	72	6	1 - 280
Cotton and Cotton Blend Knit	Domestic-Large	25	18	3	2 - 64
	Domestic-Small	19	19	3	3 - 53
	Foreign	11	10	2	3 - 36
	(All Samples)	19	17	2	2 - 64
Flatgoods	Domestic-Large	41	29	4	11 - 122
	Domestic-Small	50	22	3	14 - 89
	Foreign	4	2	0.3	1 - 9
	(All Samples)	31	29	3	1 - 122
All Fabrics	Domestic-Large	51	42	3	2 - 228
	Domestic-Small	85	126	9	2 - 940
	Foreign	32	61	5	1 - 323
	(All Samples)	59	92	4	1 - 940

Table 6: Frequency distribution of CH_2O releases from test fabrics expressed as the cumulative percentage of test results that are less than given values of CH_2O release (ug/g fabric).

CH_2O releases for selected cumulative percentage values		Cumulative percentage values for selected CH_2O releases	
Cumulative Percentage	CH_2O Release (ug/g fabric)	CH_2O Release (ug/g fabric)	Cumulative Percentage
0	0	0	0
10	3.6	10	25.9
25	8.3	25	43.1
50	36.5	50	63.7
75	64.1	75	78.5
80	78.7	100	86.1
85	93.7	150	90.4
90	149.2	200	92.8
95	244.9	300	98.9
99	295.8	500	99.4
99.5	323.1	1000	100
100	940.2		

Table 7: Results of the analysis of variance among CH_2O release data of top-weight non-knits (for shirts and blouses)

Manufact.	Class.	Mean Squares Model	Mean Squares Error[a]	Mean CH_2O Release Rate (ug/g fabric)	No. Test Samples	Coefficient of Variation (%) Intra Sample[b]	Coefficient of Variation (%) Inter Sample[c]	Coefficient of Variation (%) Combined[d]	Coefficient of Variation (%) Inter Manufact.[e]
1	DL	18562.3	2.89	87.4	5	2	90	83	-
2	DL	155.3	1.61	50.8	5	3	14	13	-
3	DL	6415.2	7.66	86.5	5	3	53	50	-
4	DS	8160.8	0.94	69.0	5	1	76	70	-
4	F	8312.7	374.71	196.6	5	10	26	26	-
5	F	328167.8	585.74	345.3	5	7	96	89	-
5	DS	2722.5	4.21	53.2	5	4	57	53	-
6	DS	1963.1	1.17	51.3	5	2	50	46	-
7	DS	599.7	7.73	60.9	5	5	23	22	-
8	DS	44287.5	24.11	167.4	5	3	73	67	-
Average Domestic				114.8		3	59	55	87
Range Domestic				51 - 345		1 - 7	14 - 96	13 - 89	-
Average Foreign				124.9		7	42	40	81
Range Foreign				53 - 197		4 - 10	26 - 57	26 - 53	-
Average for all top-weight				116.8		4	56	52	81
Range for all top-weight				51 - 345		1 - 10	14 - 96	13 - 89	-

a See Equations 4, 5, in Appendix II.
b See Equation 6 in Appendix II.
c See Equation 3 in Appendix II.
d Combined intra-sample and inter-sample variation, see Equation 7 in the Appendix II.
e Coefficient of variation between manufacturer-average CH_2O release levels.

Table 8: Results of the analysis of variance among CH_2O release data of bottom-weight (for pants)

Manufact.	Class.	Mean Squares Model	Mean Squares Error [a]	Mean CH_2O Release Rate (ug/g fabric)	No. Test Samples	Coefficient of Variation (%) Intra Sample [b]	Inter Sample [c]	Combined [d]	Inter Manufact. [e]
1	DS	126.55	0.103	13.7	5	2	48	44	-
2	DS	16928.80	30.04	223.8	5	2	34	31	-
3	DL	6785.68	4.23	87.3	5	2	55	51	-
4	DL	5653.84	2.84	72.8	4	4	60	54	-
5	DL	210.41	0.333	25.4	5	2	33	31	-
6	DS	1392.00	2.06	49.1	5	3	44	41	-
7	DS	9706.91	3.78	62.7	5	3	91	84	-
8	F	-	0.093	2.97	1	10	-	-	-
9	F	-	3.40	56.8	1	3	-	-	-
10	F	-	0.013	7.67	1	2	-	-	-
11	F	37.09	0.421	5.51	5	12	63	60	-
12	F	142.36	0.071	8.69	5	3	79	73	-
Average Domestic				76.4		3	52	48	92
Range Domestic				14 - 224		2 - 4	33 - 91	31 - 84	-
Average Foreign				16.3		6	71	67	139
Range Foreign				3 - 57		2 - 12	63 - 79	60 - 73	-
Average for all bottom-weight				51.4		4	56	52	120
Range for all bottom-weight				3 - 224		2 - 12	33 - 91	31 - 84	-

a See Equations 4, 5 in Appendix II.
b See Equation 6 in Appendix II.
c See Equation 3 in Appendix II.
d Combined intra-sample and inter-sample variation, see Equation 7 in Appendix II.
e Coefficient of variation between manufacturer-average CH_2O release levels.

Table 9: Results of the analysis of variance among CH_2O release data of cotton and cotton blend knits for shirts and underwear)

Manufact.	Class.	Mean Squares Model	Mean Squares Error [a]	Mean CH_2O Release Rate (ug/g fabric)	No. Test Samples	Coefficient of Variation (%) Intra Sample [b]	Inter Sample [c]	Combined [d]	Inter Manufact. [e]
1	DL	137.14	0.425	8.1	5	8	83	78	-
2	DS	6.87	0.054	5.6	5	4	27	25	-
3	F	180.39	1.437	12.4	5	10	62	59	-
4	F	0.81	0.073	3.1	2	9	16	15	-
5	F	700.94	0.177	12.6	4	3	121	110	-
6	DS	4.18	3.463	4.4	4	42	11	43	-
7	DL	10.71	0.955	25.5	5	4	7	8	-
8	DS	172.39	0.483	43.9	5	2	17	16	-
9	DL	346.33	1.350	48.7	4	2	22	20	-
Average Domestic				40.3		10	28	32	88
Range Domestic				4 - 49		2 -42	7 - 83	8 - 78	-
Average Foreign				9.4		7	66	61	58
Range Foreign				3 - 13		3 - 10	16 - 121	15 - 110	-
Average for all knits				18.3		9	41	42	95
Range for all knits				3 - 49		2 - 42	7 - 121	8 - 110	-

a See Equations 4, 5 in Appendix II.
b See Equation 6 in Appendix II.
c See Equation 3 in Appendix II.
d Combined intra-sample and inter-sample variation, see Equation 7 in Appendix II.
e Coefficient of variation between manufacturer-average CH_2O release levels.

Table 10: Results of the analysis of variation among CH_2O release data of flatgoods (for sheets)

Manufact.	Class.	Mean Squares Model	Mean Squares Error [a]	Mean CH_2O Release Rate (ug/g fabric)	No. Test Samples	Coefficient of Variation (%) Intra Sample [b]	Inter Sample [c]	Combined [d]	Inter Manufact. [e]
1	F	0.084	0.112	1.4	5	24	0	23	-
2	DL	287.97	3.22	20.1	5	9	48	46	-
3	DS	1758.91	149.58	36.8	4	33	63	66	-
4	DS	445.54	50.49	57.9	5	12	20	22	-
5	DL	1445.07	225.87	75.1	5	20	27	32	-
6	DL	450.96	11.67	27.3	5	13	44	43	-
7	F	3.71	1.71	3.2	5	41	26	47	-
8	F	4.19	0.439	6.0	5	11	19	21	-
9	DS	1822.86	95.33	52.7	5	19	46	46	-
Average Domestic				45.0		18	41	43	46
Range Domestic				20 - 75		9 - 33	20 - 63	22 - 66	-
Average Foreign				3.5		25	15	30	65
Range Foreign				1 - 6		11 - 41	0 - 26	21 - 47	-
Average for all flatgoods				31.2		20	33	38	85
Range for all flatgoods				1 - 75		9 - 41	0 - 63	21 - 66	-

a See Equations 4, 5 in Appendix II.
b See Equation 6 in Appendix II.
c See Equation 3 in Appendix II.
d Combined intra-sample and inter-sample variation, see Equation 7 in Appendix II.
e Coefficient of variation between manufacturer-average CH_2O release levels.

Table 11: Results of repeated washing experiment taken using the ORNL extraction test

Fabric Number	Fabric Category	Manufacturer No.	Manufacturer Class.	Wash Number	CH_2O Release ug/g fabric	Normalized CH_2O Release
1	Flatgood	1	F	0	0.6	1.00
				1	9.6	16.81
				2	9.4	16.61
				3	5.3	9.36
				5	2.3	4.19
				7	1.9	3.32
2	Flatgood	3	DS	0	176.6	1.00
				1	49.4	0.28
				2	40.4	0.23
				3	41.5	0.24
				5	33.6	0.19
				7	27.4	0.16
3	Bottom-Weight	4	DL	0	25.0	1.00
				1	9.0	0.36
				2	10.3	0.41
				3	11.3	0.46
				5	10.4	0.42
				7	7.0	0.28
4	Top-Weight Weight	5	F	0	10.1	1.00
				1	10.7	1.07
				2	9.2	0.93
				3	6.9	0.67
				5	6.4	0.62
				7	5.0	0.49
5	Bottom-Weight	6	DS	0	3.4	1.00
				1	8.8	2.63
				2	10.8	3.21
				3	6.5	1.94
				5	3.5	1.05
				7	3.1	0.92
6	Top-Weight	8	DS	0	178.1	1.00
				1	70.3	0.39
				2	49.8	0.28
				3	47.3	0.26
				5	36.8	0.20
				7	32.3	0.18

Table 11: Results of repeated washing experiment (continued)

Fabric Number	Fabric Category	Manufacturer No.	Manufacturer Class.	Wash Number	CH_2O Release ug/g fabric	Normalized CH_2O Release
7	Knit	8	DS	0	135.5	1.00
				1	32.1	0.24
				2	24.4	0.18
				3	24.0	0.18
				5	9.3	0.07
				7	14.7	0.10
8	Bottom-Weight	8	DS	0	157.1	1.00
				1	21.4	0.13
				2	17.2	0.11
				3	15.3	0.10
				5	12.6	0.08
				7	10.0	0.06

Table 12: Results of intermethod comparison of ORNL, AATCC and Japanese Methods

Fabric Number	Fabric Category	Manufacturer No.	Manufacturer Class.	Extraction Test Results (ug CH_2O/g fabric) Japanese	AATCC	ORNL
1	Knit	8	DS	192.2	468.0	209.0
				173.2	515.0	220.9
				195.1	518.0	223.3
	(Average)			189 ± 14	500 ± 28	218 ± 8
2	Bottom-Weight	7	DS	158.3	604.0	279.2
				157.3	713.5	270.6
				161.0	692.0	284.4
	(Average)			159 ± 2	670 ± 58	278 ± 7
3	Flatgood	9	DS	120.7	219.6	162.4
				114.6	206.5	164.5
				118.4	209.3	163.1
	(Average)			118 ± 3	212 ± 7	163 ± 1
4	Knit	3	F	42.3	34.9	23.4
				45.7	51.3	27.7
				44.0	38.0	27.5
	(Average)			44 ± 2	41 ± 9	26 ± 2
5	Flatgood	2	DL	65.4	172.4	74.5
				74.4	163.0	72.9
				73.8	172.0	69.7
	(Average)			71 ± 5	169 ± 5	72 ± 2
6	Bottom-Weight	6	DS	49.3	150.6	70.8
				55.9	150.8	64.5
				60.3	159.0	65.8
	(Average)			54 ± 12	154 ± 5	67 ± 3
7	Top-Weight	5	F	50.0	342.3	88.0
				55.5	347.5	87.2
				60.7	324.7	87.3
	(Average)			55 ± 5	338 ± 11	88 ± 1
8	Top-Weight	4	F	115.0	703.0	207.1
				100.9	685.5	203.3
				111.8	651.5	213.8
	(Average)			114 ± 4	680 ± 26	208 ± 5
9	Top-Weight	3	DL	94.9	279.8	152.6
				92.9	249.6	158.8
				101.7	273.3	159.1
	(Average)			96 ± 5	268 ± 16	157 ± 4

Table 12: Results of intermethod comparison of ORNL, AATCC and Japanese Methods (continued)

Fabric Number	Fabric Category	Manufacturer No.	Manufacturer Class.	Extraction Test Results ($\mu g\ CH_2O/g$ fabric) Japanese	AATCC	ORNL
10	Top-Weight	5	DS	666.5	2694.0	1746.0
				736.6	2892.0	1700.0
				736.0	2897.0	1846.0
	(Average)			713 ± 40	2828 ± 116	1764 ± 75
11	Top-Weight	4	F	139.5	767.0	212.3
				150.0	713.0	215.8
				150.7	821.0	221.1
	(Average)			147 ± 6	767 ± 54	216 ± 4
12	Top-Weight	5	DS	105.3	557.0	173.5
				104.7	585.0	188.0
				101.9	497.6	187.0
	(Average)			104 ± 2	546 ± 45	183 ± 8

Table 13: Comparison of ORNL extraction test results taken during the textile survey and intermethod comparison studies

Fabric[a] Number	Fabric Category	ORNL Test Results (ug/g) Survey	Intermethod	Delay Between Tests (weeks)	Intermethod Survey
1	Knit	53 ± 0.6	218 ± 8	31	4.1
2	Bottom-Weight	53 ± 4.0	278 ± 7	4	5.2
3	Flatgood	58 ± 11	163 ± 1	39	2.8
4	Knit	14 ± 0.9	26 ± 2	31	1.9
5	Flatgood	19 ± 1.0	72 ± 2	31	3.8
6	Bottom-Weight	46 ± 0.4	67 ± 3	4	1.4
7	Top-Weight	36 ± 1.5	88 ± 1	6	2.4
8	Top-Weight	152 ± 2.4	208 ± 5	6	1.4
9	Top-Weight	89 ± 1.9	157 ± 4	6	1.8
10	Top-Weight	897 ± 54	1764 ± 75	7	2.0
11	Top-Weight	219 ± 7.9	216 ± 4	7	1.0
12	Top-Weight	284 ± 2.5	183 ± 8	6	0.6

[a] Fabric number determined from intermethod comparison, Table 12.

Table 14: Summary of results for SPATS testing

Fabric Number	Fabric Category	SPATS Calibration [CH_2O][a] (ug/mL)	SPATS Calibration CEA(mv)	SPATS Calibration Calibration Factor(mv·mL/ug)	Fabric Testing CEA(mv)	Fabric Testing [CH_2O][b] (ug/mL)
1	Knit	75 ± 5	38 ± 6	0.51 ± 0.08	25 ± 3	49 ± 10
2	Bottom-Weight	150 ± 10	51 ± 12	0.34 ± 0.08	30 ± 8	89 ± 31
5	Flatgood	300 ± 20	179 ± 12	0.60 ± 0.04	16 ± 3	26 ± 5
9	Top-Weight	300 ± 20	179 ± 12	0.60 ± 0.04	21 ± 5	36 ± 8
10	Top-Weight	500 ± 33	261 ± 20	0.52 ± 0.04	161 ± 11	310 ± 32
10	Top-Weight	500 ± 33	287 ± 14	0.57 ± 0.03	172 ± 16	301 ± 32

[a] CH_2O concentration in reference solution used to soak fabric specimens for calibration of SPATS response.

[b] CH_2O concentration calculated using Equation 1 that is generated by a test fabric in aqueous solution above the SPATS membrane.

Table 15: Comparison of results from the ORNL extraction, Wring and SPATS tests for fabrics examined in the intermethod comparison of extraction tests

Fabric Number	Fabric Category	ORNL Test-CH_2O Release ($ugCH_2O/gfab$)	ORNL Test-CH_2O Release ($ugCH_2O/mLH_2O$)	Wring Test-CH_2O Release ($ugCH_2O/gfab$)	Wring Test-CH_2O Release ($ugCH_2O/mLH_2O$)	Spats Test [a] ($ugCH_2O/mLH_2O$)
1	Knit	209.0	20.4	154.0	61.3	49 ± 10
		220.9	22.1	156.7	56.8	
		223.3	22.3	139.4	55.5	
(Average)		218 ± 8	22 ± 1	150 ± 9	58 ± 3	
2	Bottom-Weight	279.2	27.7	168.1	119.5	89 ± 31
		270.6	30.3	157.7	106.8	
		284.4	28.3	169.2	110.7	
(Average)		278 ± 7	29 ± 1	165 ± 6	112 ± 6	
3	Flatgood	162.4	16.5	107.8	47.9	-
		164.5	16.3	114.1	52.0	
		163.1	16.5	102.0	44.5	
(Average)		163 ± 1	16.4 ± 0.1	108 ± 6	48 ± 4	
4	Knit	23.4	2.4	13.9	5.4	-
		27.7	2.8	14.2	5.5	
		27.5	2.8	15.5	5.6	
(Average)		26 ± 2	2.6 ± 0.3	14 ± 1	5.5 ± 0.1	
5	Flatgood	74.5	7.6	32.4	29.4	26 ± 5
		72.9	7.4	34.6	29.6	
		69.7	7.0	31.3	26.8	
(Average)		72 ± 2	7.3 ± 0.3	33 ± 2	29 ± 2	
6	Bottom-Weight	70.8	6.9	32.7	17.0	-
		64.5	6.5	31.2	17.9	
		65.8	6.5	30.5	16.6	
(Average)		67 ± 3	6.6 ± 0.2	32 ± 1	17.2 ± 0.7	

[a] Response of SPATS to test fabric ($ugCH_2O/mLH_2O$) determined from a daily calibration with with a standard fabric specimen saturated with a dilute formalin solution made with an artificial perspiration solution.

Table 15: Comparison of results from the ORNL extraction, Wring and SPATS tests (continued)

Fabric Number	Fabric Category	ORNL Test- CH_2O Release ($ugCH_2O/gfab$)	ORNL Test- CH_2O Release ($ugCH_2O/mLH_2O$)	Wring Test-CH_2O Release ($ugCH_2O/gfab$)	Wring Test-CH_2O Release ($ugCH_2O/mLH_2O$)	SPATS Test [a] ($ugCH_2O/mLH_2O$)
7	Top-Weight	88.0	8.9	17.8	8.7	-
		87.2	8.8	11.9	10.1	
		87.3	8.8	-	-	
(Average)		87.5 ± 0.4	8.8 ± 0.1	15 ± 4	9 ± 1	
8	Top-Weight	207.1	20.4	27.4	38.2	-
		203.3	20.7	42.0	56.1	
		213.8	21.4	34.8	47.5	
(Average)		208 ± 5	20.8 ± 0.5	35 ± 7	47 ± 9	
9	Top-Weight	152.6	15.2	36.4	46.9	38 ± 8
		158.8	15.7	34.4	46.7	
		159.1	15.9	22.1	40.0	
(Average)		157 ± 4	15.6 ± 0.4	31 ± 8	44 ± 4	
10	Top-Weight	1746.0	171.2	114.4	677.7	310 ± 32
		1700.0	172.5	146.8	639.1	301 ± 28
		1846.0	182.0	272.7	485.3	
(Average)		1764 ± 75	175 ± 5	178 ± 84	600 ± 100	306 ± 43
11	Top-Weight	212.3	21.3	31.8	55.4	-
		215.8	21.5	43.2	49.2	
		221.1	21.9	41.6	51.4	
(Average)		216 ± 4	21.6 ± 0.3	39 ± 6	52 ± 3	
12	Top-Weight	173.5	17.6	36.5	50.9	-
		188.0	19.1	-	-	
		187.0	18.4	23.7	48.7	
(Average)		183 ± 8	18.4 ± 0.8	30 ± 9	50 ± 2	

a Response of SPATS to test fabric ($ugCH_2O/mLH_2O$) determined from a daily calibration with with a standard fabric specimen saturated with a dilute formalin solution made with an artificial perspiration solution.

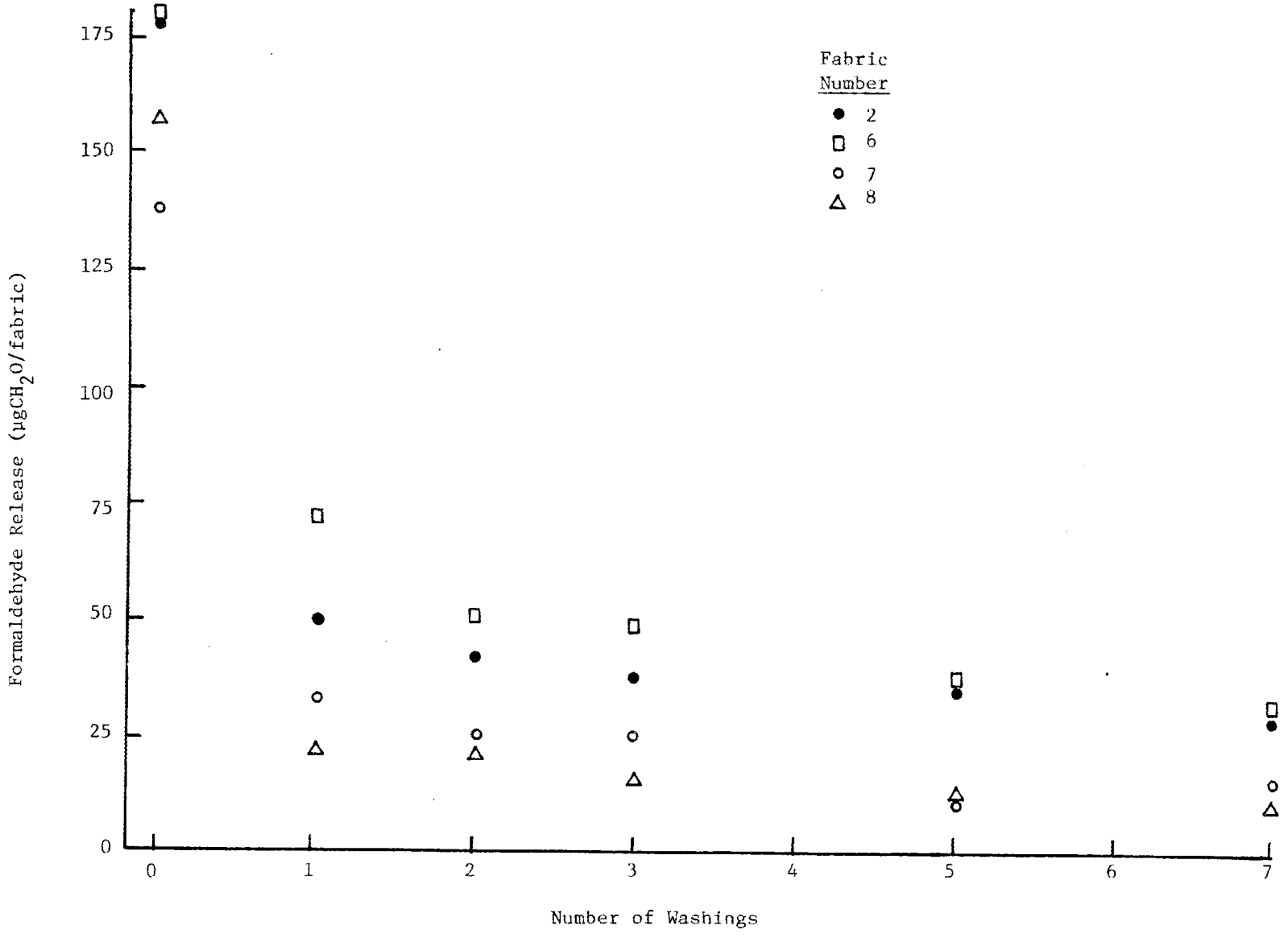

Figure 1: Decline in Formaldehyde Release from Relatively Strong Emitting Fabrics with Washing.

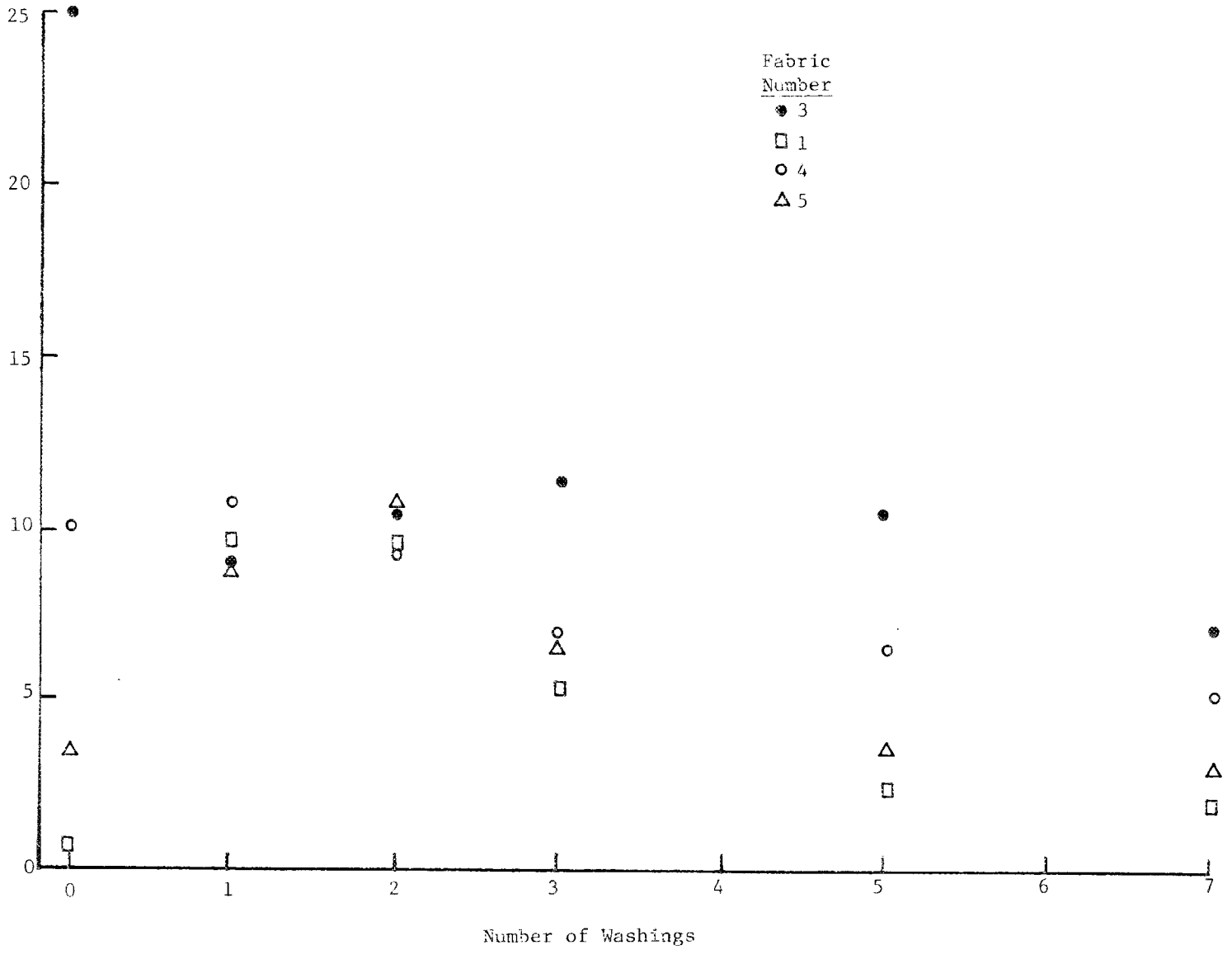

Figure 2: Variation in Formaldehyde Release from Relatively Weak Emitting Fabrics with Washing.

APPENDIX I: Formaldehyde Extraction from Textiles: ORNL Protocol II (5/85)

1. Scope

There is a need to improve extraction methods for formaldehyde (CH_2O) release from durable press apparel textiles to more closely simulate dermal CH_2O exposure under normal consumer use conditions. Current extraction test methodologies measure CH_2O release under widely varying environmental conditions, some of which are inconsistent with consumer use. The Japanese method (1) is the only one specifically designed to approximate dermal exposure under consumer use conditions. A new procedure is described here that builds upon the Japanese test in an attempt to measure CH_2O released from apparel textiles under conditions more closely related to consumer use. The results from this new procedure will be compared with those from the Japanese test and the AATCC Sealed Jar test (2) which is widely used in the United States. However, the ORNL protocol is not intended to replace or modify contemporary quality control methods for CH_2O release from textiles.

The primary modifications to the Japanese test that are incorporated in the ORNL extraction procedure are (1) use of perspiration chemicals in the extraction solution, (2) use of a pH=5 buffer in the extraction solution, (3) an extraction temperature of 35°C, (4) an extraction period of six hours, (5) use of pararosaniline colorimetric analysis as a more sensitive back-up method for the Nash procedure, and (6) use of 10 g fabric samples in a 100 mL extraction solution.

The chemical composition of the artificial perspiration solution is modeled after the perspiration solution used in the AATCC test for colorfastness of textiles (3). A sodium acetate-acetic acid buffer is added to maintain the pH of the perspiration extraction solution at 5.0 in accordance with Mazur et al (4). It is recognized that the pH of human perspiration varies over a wide range (i.e., 4 to 7) and that this may have a significant impact on dermal exposure to CH_2O from apparel textiles (5,6). An extraction temperature of 35°C was chosen as an approximate compromise between body temperature (i.e., 37°C) and the results of a limited sampling of

clothing temperatures on three locations of four individuals (i.e., 34 $\pm 1°C$). An extraction period of six hours is designed to simulate consumer use within the limits of an eight hour extraction and analysis test.

The pararosaniline (PA) colorimetric analysis provides a four-fold increase in sensitivity over the Nash method, which has a limit of quantitation of about 1 ug (ug = microgram) CH_2O/mL H_2O. The PA method also provides a second colorimetric procedure with a different absorption spectrum (i.e., 570 nm maximum versus 412 nm for the Nash reagent) that is useful for testing fabrics that release colored dye which can optically affect the CH_2O test result. Ten gram fabric specimens are used to increase the sensitivity of the extraction test and reduce the impact of intra-sample variation in CH_2O emission strength.

2. Analytical Apparatus and Materials

2.1 Absorption spectrometer, Spectronic 20, or equivalent.

2.2 Oven, Precision Scientific, Model 28, or equivalent.

2.3 Pipettes, 5 mL and 1 mL volumetric with adjustable capacity.

2.4 Disposable pipette tips.

2.5 Test tubes, 1.2 x 10.3 cm, with screw caps.

2.6 Paper cutter, blade length 15 in.

2.7 Funnels, glass 12 cm diameter x 8.5 cm long.

2.8 Whatman #1 filter paper, 15.0 cm diameter.

2.9 Brown reagent bottle, 500 mL.

2.10 Ball regular quart Mason jars with bands and dome lids.

2.11 Erlenmeyer flasks, 250 mL.

2.12 Sealable plastic bags.

2.13 Volumetric flasks; 2 L, 500 mL, 100 mL.

2.14 Graduated cylinder, 100 mL.

2.15 Timer, 0 to 60 minute.

2.16 pH meter, Corning 610A or equivalent.

3. Chemical Reagents

3.1 Artificial Perspiration Preparation

3.1.1 To a 2.0 L volumetric flask partially filled with distilled-deionized water, add the following chemicals: 20.0 g NaCl, 2.0 g Na_2HPO_4 (anhydrous), 0.50 g histidine HCl:H_2O, 2.46 g CH_3COONa. Shake until solids are dissolved.

3.1.2 Add 1.43 mL 85% lactic acid and 0.58 mL glacial acetic acid. Fill to mark with distilled-deionized water.

3.1.3 Check pH. Adjust with CH_3COONa or CH_3COOH if necessary to achieve a pH of 5.0.

3.2 Nash Reagent Preparation

3.2.1 Add to a 500 m volumetric flask 75.0 g ammonium acetate, 1.5 mL glacial acetic acid, and 1.0 mL acetylacetone. Fill to mark with distilled-deionized water.

3.2.2 Transfer solution to a ground glass stoppered brown reagent bottle for storage. Shelf life of this reagent is approximately 7 weeks (2).

3.3 Formaldehyde Stock Solution Preparation

3.3.1 Pipette 5.00 mL of formalin solution [37% by weight formaldehyde (Mallinckrodt)] into a 500 mL volumetric flask and fill to mark with artificial perspiration. (Be sure all residual formalin solution has been rinsed from the pipette tip into the 100 mL flask).

3.3.2 Heat solution to approximately 30°C and cool to room temperature to completely dissolve the formalin.

3.3.3 Standardize this approximately 4000 ug/mL CH_2O solution using the procedure given in Appendix A.

3.3.4 Calculate the volume required for the preparation of 2.0 L ug/mL CH_2O (for use with PA method) using the following equation:

x mL = (2000 mL) (1 ug/mL)/standardized [CH_2O] (ug/mL)

3.3.5 Pipette x (as calculated in 3.3.4) mL of standardized solution into a 2.0 L volumetric flask and fill to mark with artificial perspiration solution. This completes the preparation of the 1 ug/mL CH_2O stock solution for use with the PA method. Store in refrigerator. Discard when 75% depleted.

3.3.6 Calculate the volume required for the preparation of 2.0 L of 4ug/mL CH_2O (for use with Nash method) using the following equation:

x' mL = (2000 mL) (4 ug/mL)/standardized [CH_2O] (ug/mL)

3.3.7 Pipette x' (as calculated in 3.3.6) mL of standardized CH_2O solution into a 2.0 L volumetric flask and fill to mark with artificial perspiration solution. This completes the

preparation of the 4 ug/mL CH_2O stock solution for use with the Nash method. Store in refrigerator. Discard when 75% depleted.

3.4 Pararosaniline is obtained from CEA Instruments, Inc., 15 Charles Street, Westwood, NJ 07675. To a 50 mL aliquot of PA stock, add 6.2 mL of 4M HCl. After 24 hours, add 21.2 mL of distilled-deionized water to obtain the final pararosaniline reagent.

3.5 Sodium Sulfite, 0.10% solution, is made by dissolving 0.10 g anhydrous sodium sulfite in 100 mL distilled-deionized water.

4. Fabric Preparation

4.1 Samples of fabric are stored at room temperature (23 ± 1°C), sealed inside two plastic bags.

4.2 Three 10.0 ± .2 g specimens are cut from random positions of each sample. The length and width are measured (±0.6 cm) to determine the area of each rectangular specimen.

4.3 The specimens are removed from the plastic bags and allowed to condition in room air (23 ± 1°C) 24 hours prior to testing.

4.4 If necessary, each fabric specimen is cut into small pieces (e.g., less than 25 cm^2) just prior to liquid extraction to insure that all pieces will remain submerged in the extraction solution during the extraction period.

5. Formaldehyde Extraction

5.1 Fill each Mason jar with 100 mL of pH=5 artificial perspiration. Place jars in oven for 12 hours befpre use to ensure a 35°C extraction solution. Additional jars filled with 100 mL pH=5 artificial perspiration, that are to be used for blanks, should also be placed in the oven at this time.

5.2 Put each fabric specimen in a separate jar and shake until the specimen is completely wet.

5.3 Return jars to 35°C oven for 6 hours.

5.4 Filter each solution (including blanks) into separate 250 mL Erlenmeyer flasks.

6. Analytical Methods

6.1 Nash Method

6.1.1 Use separate pipette tips for each solution listed in 6.1.2 - 6.1.5.

6.1.2 Pipette two 2.0 mL aliquots of each filtrate solution (including blanks) into separate test tubes. (Dilutions of the filtrate solution must be performed at this time if the final absorbance of the colorimetrically developed solution will exceed approximately 0.8 absorbance units. This is the practical limit of most single beam absorption spectrometers).

6.1.3 Pipette three 2.0 mL aliquots of the formaldehyde stock solution (3.3.7), warmed to room temperature, into separate test tubes.

6.1.4 Pipette 2.0 mL Nash reagent (3.2) into each test tube. (Be careful not to contaminate the pipette tip with the solutions in each test tube). Cap tubes and shake. Incubate for 30 minutes in a 40°C water bath.

6.1.5 Zero the spectrometer at 412 nm using distilled-deionized water.

6.1.6 Dry all tubes approximately five minutes before recording the absorbance of each tube. Periodically check the zero reading of the spectrometer. Rotate each tube in the spectrometer to insure that an abnormally high or low value is not recorded.

6.1.7 Any test solution that gives absorbance readings less than 0.1 units should be analyzed a second time using the more sensitive pararosaniline method.

6.2 Pararosaniline Method

6.2.1 Use separate pipette tips for each solution listed in 6.2.2 - 6.2.6.

6.2.2 Pipette two 3.0 mL aliquots of each filtrate solution into separate test tubes. (Again, dilutions must be performed at this time for reasons described in 6.1.2).

6.2.3 Pipette three 3.0 mL aliquots of distilled-deionized water into separate test tubes.

6.2.4 Pipette three 3.0 mL aliquots of the formaldehyde stock solution (3.3.5), warmed to room temperature, into separate test tubes.

6.2.5 Pipette 0.30 mL pararosaniline reagent (3.4) into each test tube. Cap tubes and shake. Incubate tubes for 10 minutes.

6.2.6 Pipette 0.30 mL of sodium sulfite reagent (3.5) into each test tube. Cap tubes and shake. Incubate tubes for 55 minutes in the dark by covering with a dark cloth.

6.2.7 Zero the spectrometer at 570 nm using distilled-deionized water.

6.2.8 Record the absorbance of each tube, periodically checking the zero reading of the spectrometer. Rotate each test tube in the spectrometer to insure that an abnormally high or low value is not recorded. The residence time for each test tube inside the spectrophotometer should be less than 30 seconds. Perform all absorbance readings within a 10 to 15 minutes period.

7. Calculations

7.1 Formaldehyde concentration in the extraction Solutions

$$[CH_2O]\ (ug/mL) = \frac{\overline{DF}\ (\overline{EXP} - \overline{H_2OB})}{(\overline{ST} - \overline{H_2OB})/X}$$

where:

$\overline{DF}$ = dilution factor. For undiluted solutions $\overline{DF} = 1$. For solutions diluted to 50% of their original concentration, $\overline{DF}$ =.ps 10 2.

$\overline{EXP}$ = mean absorbance for the colorimetrically developed extraction solutions.

$\overline{H_2OB}$ = mean absorbance of the colorimetrically developed water blank solutions.

$\overline{ST}$ = mean absorbance of the colorimetrically developed formaldehyde stock solution.

X = 1 when the PA method is used (i.e., CH_2O stock concentration is 1 ug CH_2O/mL) and 4 when Nash method is used (i.e., CH_2O stock concentration is 4 ug CH_2O/mL).

7.2 Formaldehyde Release per 1.0 g fabric

$$\frac{[CH_2O]\ (ug/mL) \times 100\ mL}{mass\ fabric\ (g)} = ugCH_2O/g$$

7.3 Formaldehyde release per 1.0 cm^2 fabric

$$\frac{[CH_2O]\ (ug/mL) \times 100\ mL}{area\ fabric\ (cm^2)} = ug\ CH_2O/cm^2$$

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APPENDIX A: Standardization of Approximate 4 mg CH_2O/mL H_2O Solutions to Indirectly Calibrate All More Dilute CH_2O Stock Solutions

Preparation of an approximately 4 mg CH_2O/mL H_2O Stock Solution:

1. Pipettete 5.00 mL volumetric flask and fill to mark with distilled-deionized water. (Be sure all residual formalin solution has been rinsed from the pipette tip into the 500 mL flask).

2. Warm solution to approximately 30°C and cool to room temperature to completely dissolve formalin.

pH Titration using Thymolphthalein Indicator:

1. Pipette 12.5 mL 1.0 M sodium sulfite solution into a 250 mL Erlenmeyer flask.

2. Add three drops of indicator solution (0.1% Thymolphthalein in ethanol). The solution should be a pale blue color. 0.1 N HCl is added dropwise until the solution is colorless (usually two to five drops of HCl are required).

3. From a pipette, add 25 mL of an approximately 4 mg CH_2O/mL H_2O solution.

4. Titrate to a 'colorless' (faint blue haze) end point with 0.100 N HCl. The 'colorless' end point should persist for three minutes.

5. Perform three titrations and take the mean value. Replicates should be within $\pm 0.3\%$.

6. Measured CH_2O concentration in mg CH_2O/mL H_2O in the approximate 4 mg CH_2O/mL H_2O solution is given by:

$$CH_2O(\text{mg/mL}) = \frac{\text{HCl titrant (mL)} \times (0.1 \text{ mmole HCl/mL}) \times 30.03 \text{ mg } CH_2O/\text{mmole}}{25 \text{ mL}}$$

APPENDIX II: One-Way Analysis of Variance for the Survey of Durable-Press Apparel Textiles.

A goal in the survey of CH_2O releases from durable-press apparel textiles is to examine sources of variation in the measured CH_2O emission rates among the test fabrics and to separate the variability of the test method from these results. To quantitate intra-fabric-sample (i.e., inter-specimen) and inter-fabric-sample variability of the CH_2O release data, a one-way analysis of variance (Snedecor et al., 1973) has been performed on all of the top-weight, bottom-weight, flatgood and knit data sets. The statistical model assumed for each collection of fabric samples obtained from a given manufacturer in a given fabric category is

$$CH_2O_{ij} = \mu + \beta_i + \varepsilon_{ij} \tag{2}$$

where CH_2O_{ij} is the CH_2O release of the jth specimen cut from the ith fabric sample; μ is the population mean for all of the test specimens of a given manufacturer and fabric category; β_i is the between-fabric-sample variation in CH_2O emission rate, which is assumed to be random with variance σ^2_{inter}; and ε_{ij} is the combined within-fabric-sample variation and measurement error with variance σ^2_{intra}. An estimate of the inter-sample variance (i.e., σ^2_{inter}) is calculated as

$$\sigma^2_{inter} = (\text{Model Mean Square} - \text{Error Mean Square})/n \tag{3}$$

where n is the number of specimens (i.e., 3) cut from each fabric sample. The Model Mean Squares and Error Mean Squares are defined as

$$\text{Model Mean Squares} = [\sum_{i=1}^{a} (\sum_{j=1}^{n} CH_2O_{ij})^2/3 - (\sum_{i=1}^{a}\sum_{j=1}^{n} CH_2O_{ij})^2/(a \cdot n)]/(n-1) \tag{4}$$

and

$$\text{Error Mean Squares} = [\sum_{i=1}^{a}\sum_{j=1}^{n} CH_2O_{ij}{}^2 - \sum_{i=1}^{a}(\sum_{i=1}^{n} CH_2O_{ij})^2/3]/(a\cdot n-a) \quad (5)$$

where a is the number of fabric samples from a given manufacturer and fabric category. Note that σ^2_{inter} is the minimum variance that can be achieved assuming an ideal analytical method that measures the CH_2O release of the entire fabric sample, accounting for all intra-sample variation in emission strength (i.e., $\sigma^2_{inter} = 0$). This is the best estimate of strict inter-fabric variance among fabric samples obtained from a given manufacturer and fabric category. The intra-sample variance is estimated as

$$\sigma^2_{intra} = \text{Error Mean Square} \quad (6)$$

This is a combination of the measurement error of the analytical method for a fabric with spatially and temporally invariant emission strength and the intra-sample variance based upon the sampling characteristics (i.e., area of fabric specimen test specimen) of the ORNL extraction test. The model for combined inter-fabric and intra-fabric variance is

$$\sigma^2_{combined} = \sigma^2_{intra} + \sigma^2_{inter} \cdot (a\cdot n-n)/(a\cdot n-1) \quad (7)$$

Equation 7 has been previously derived (Matthews, CPSC XII). However, calculated $\sigma^2_{combined}$ values represent expected values based on the measured CH_2O releases for each manufacturer and fabric category rather than a true population parameter.

The results of the one-way analysis of variance for all of the survey fabrics are listed in Tables 7-10. The results for each estimated component of variance are reported as coefficients of variation (CV), expressed as a percentage of the mean CH_2O emission rate ($\overline{CH_2O}$).

$$CV(\%) = 100 \cdot \sigma/\overline{CH_2O} \quad (6)$$

Appendix III: Modifications in the ORNL Extraction Test (i.e., Appendix I) for Performance of the Wring Test.

A modification of the ORNL extraction test called the ring test has been developed to more closely simulate the amount of water (i.e., artificial perspiration) in perspiration saturated fabrics. The specific modifications to the experimental protocol for the ORNL extraction test that are required for the ring test are listed below.

4. Fabric Preparation

4.1 Same

4.2 Three specimens are cut from random positions of each fabric sample. The weight of the specimen is adjusted to acieve a minimum of 3 mL of extraction solution. Specimen weights of 7 to 16 g are typically used.

4.3 Same

4.4 Delete

5. Formaldehyde Extraction

5.1 Dip each fabric specimen into pH=5 artificial perspiation solution at 35°C to ensure that the fabric is saturated with liquid.

5.2 Allow each fabric to drip until there is $\leq$ 1 drop of liquid per second.

5.3 Place each specimen into an empty mason jar, seal, and incubate in a 35° oven for 6 hours.

5.4 Remove most of the extraction solution from the fabric specimen using a plastic syringe to squeeze the fabric. If necessary, add sufficient artificial perspiration solution to achieve 10 mLs total volume. Perform all such volume analyses gravimetrically noting the additional dilution factor in subsequent calculations (i.e., Section 7.)

5.5 Centrifuge the rinse solutions

Appendix IV: Skin Patch Test Simulator: Construction and Experimental Procedures

1. Introduction

A Skin Patch Test Simulator (SPATS) has been developed to simulate the application of wet, formaldehyde (CH_2O) resin-containing fabric on skin. The fabric is sealed in liquid contact with a semipermeable membrane thats readily transports CH_2O to a stream of aqueous reagents that is flowed through the SPATS and subsequently analyzed with a CEA Instruments Model 555 Analyzer. All SPATS testing is performed at 35°C inside an environmental chamber to simulate dermal exposure conditions. The SPATS is used to directly compare the CH_2O concentration generated at the surface of the semipermeable membrane by (1) weakly-emitting fabric specimens saturated with dilute formalin solution and (2) CH_2O resin-containing fabrics saturated in artificial perspiration solution. The estimated CH_2O concentrations generated by the test fabrics are then compared against the CH_2O concentrations of solutions applied to skin in common skin patch tests and other dermatological testing.

The general procedure for SPATS testing consists of a single calibration and measurement series for each day of testing. To calibrate the CH_2O response of the SPATS, a weakly emitting fabric is saturated with a CH_2O stock solution prior to SPATS testing. Stock solutions of 75, 150, 300 and 500 ug CH_2O/mL H_2O were used in the ORNL study to evaluate the CH_2O response of the SPATS over the range of the stronger emitting fabrics used for intermethod comparison testing (see Table 14). Although the response of the SPATS was found to be generally linear with CH_2O concentration, the day-to-day variation in the response of the SPATS required that the instrument be calibrated at a time close to the measurement period for a test fabric. Often, a CH_2O stock solution was chosen to approximate the CH_2O concentration generated by the fabric selected for SPATS testing as measured with the Wring test. Each test fabric was saturated in artificial perspiration solution and incubated for three hours at 35°C prior to SPATS testing. Each SPATS test then consisted of (1) a blank test using a perspiration-saturated fabric specimen with negligable CH_2O content, (2) evaluation of a CH_2O-containing fabric specimen

and (3) a repeat blank test.

The successful operation of the SPATS is experimentally very difficult to perform. It is anticipated that individuals wishing to repeat the SPATS studies performed at ORNL will need to have detailed discussions with the authors.

2. Apparatus and Materials

2.1 SPATS (see Section 4 for fabrication).

2.2 Eight channel peristaltic pump, Autoanalyzer Model 1 (or equivalent), Technicon Corp. with 0.025 In I.D. tubing to deliver approximately 0.25 mL/min per channel.

2.3 Constant temperature chamber to house SPATS, peristaltic pump and CEA Instrument reagent resevoirs at 35°C.

2.4 CEA Instruments Model 555 Analyzer equipped for formaldehyde monitoring.

3. Chemical Reagents

3.1 Artificial perspiration (see Appendix I, Section 3.1 for preparation).

3.2 Mercuric chloride for CEA instrument(1).

3.3 Sodium sulfite for CEA instrument(1).

3.4 Pararosaniline (PA) for CEA instrument(1).

3.5 Formaldehyde Stock Solution.

Aqueous CH_2O solutions are used to saturate weakly-emitting fabric specimens for calibration of the SPATS response to wet CH_2O-containing fabrics. All CH_2O solutions were diluted from a 4 mg CH_2O/mL H_2O stock solution that was prepared and standardized according to procedures given in Appendix I, Section 3.3.

3.5.1 Calculate the volume (X mL) of approximate 4 mg CH_2O/mL H_2O stock required for the preparation of 100 mL of Y ug CH_2O/mL H_2O solution for SPATS testing using the following equation:

$$X \text{ mL} = (100 \text{ mL})(Y \text{ ug } CH_2O/\text{mL } H_2O)/[CH_2O]_{Stock}(\text{ug } CH_2O/\text{mL } H_2O)$$

3.5.2 Pipet X mL of standardized stock solution into a 100 mL volumetric flask and fill to mark with distilled-deionized H_2O. Store in refrigerator.

4. Fabrication of SPATS

4.1 Mechanical Construction

A blow-up view of the SPATS is given in Figure 1. The base of the SPATS is machined from a block of aluminum measuring 9.25 In wide x 7.0 In long x 0.75 In thick. Four parallel troughs measuring 5 In long, 0.63 In wide and 0.06 In deep) are machined in the center of the aluminum block, spaced 0.25 In apart. Both ends of each trough are tapered from a 0.63 In width to a 0.13 In width over a length of 0.25 In. Half-cylindrical slots for 0.13 In O.D. tubes are machined in the aluminum block from the 0.13 In ends of each trough to the edge of the block. The 0.13 In diameter tubes carry reagent for the CEA instrument into and out of the troughs. The troughs are painted with three coats (allowed to dry two hours between coats) of Scotch Grip Plastic Adhesive (3M Co., St. Paul, MN) to prevent reaction between the the aluminum block and the $HgCl_2$ reagent for the CEA Instrument. The attachment of the 0.13 In tubes and semipermeable membrane to the Aluminum base are desribed in Section 4.2. The plexiglass cover for the SPATS measures 9.25 In wide x 7 In long x 0.75 In thick. The cover has half-cylindrical slots for 0.13 In O.D. tubes to accomodate the input and output tubes for each trough cut into the the aluminum base of the SPATS. A rectangular portion of the plexiglass cover centered over the four troughs and measuring 4.25 x 4.0 In is conveniently removable using an attached handle to allow placement of fabric specimens over the semipermeable membrane of the SPATS. Two 0.03 In thick neoprene rubber gaskets are used to seal the plexiglass cover to the aluminum base of the

SPATS (with adhered membrane). The bottom gasket measures 9.25 In wide and 7.0 In long with a 4.25 x 4.0 In rectangular hole positioned identically with the hole in the plexiglass cover of the SPATS. The second gasket is shaped in a loop that follows the outer perimeter of the troughs in the base of the SPATS and is uniformly 0.5 In wide. The plexiglass cover and gaskets are clamped to the aluminum base with 8, 6-32 machine screws, two in each corner.

4.2 Semipermeable Membrane and Reagent Supply Tubes

The eight reagent supply and drain tubes shown in Figure 1 are attached to the aluminum base of the SPATS prior to attaching the semipermeable membrane. The 2 In long by 0.13 In O.D. stainless steel tubes that supply and drain the CEA reagents from the troughs of the SPATS are glued into the slots of the aluminum base with Scotch Grip Plastic Adhesive. To adhere the membrane, one coat of Silicone Form-a-Gasket (Permatex, Locktite Corp.) is spread in a continuous layer over uncut surfaces of the aluminum base both between the troughs and in a strip approximately 0.75 In wide around the perimeter of the troughs. The first coat of adhesive is allowed to set about 24 hours before a second coat is applied. While the second coat of the Form-a-Gasket is still tacky, place a sheet of dimethyl silicone membrane [2] on top of the glue and press until the membrane is uniformly adhered across the base of the SPATS. Unattached membrane material is removed with a scapel. The SPATS is allowed to set 24 hours prior to testing.

5. Preparation of Fabric Specimens

5.1 Fabric Specimens with Unknown CH_2O Content

5.1.1 Store fabrics in sealed double plastic bags prior to testing. Cut a fabric specimen measuring 4.25 x 4.0 In.

5.1.2 Immerse fabric specimen in artificial perspiration solution warmed to 35°C to wet fabric.

5.1.3 Remove fabric specimen from the perspiration solution, allow to drip momentarily, and seal inside a 125 mL Erlenmeyer flask at 35°C. Incubate 3 hours at 35°C prior to testing in SPATS.

5.2 Fabric Specimens for Blank Response Testing of SPATS

Select a fabric specimen with negligible CH_2O content (i.e., <2 ug CH_2O/g fabric) and extract in distilled H_2O at 35°C at all times when not in use. Remove specimen from water and allow to drip momentarily prior to SPATS testing.

5.3 Fabric Specimens for Calibration of SPATS Response

Saturate fabric specimen (cut from same fabric sample for blank testing) in CH_2O solution at 35°C. Remove wet specimen and allow to drip momentarily prior to SPATS testing.

6. Operation of CEA Instruments Model 555 Analyzer

6.1 See Reference 1 for directions concerning cleaning, chemical reagents, start up and shutdown procedures.

6.2 Modifications to the CEA instrument involve the input of the $HgCl_2$ and Na_2SO_3 reagents. These reagents are mixed in small quantities at room temperature and pumped to the input of the SPATS inside the 35°C test chamber. The mixed reagent stream from the drain of the SPATS is then pumped to the input of the CEA Instrument outside of the chamber. The PA reagent enters the CEA Instrument from inside the chamber without interacting with the SPATS. Other modifications to the CEA given in Reference 1 are not necessary.

7. Operation of the SPATS

7.1 Place SPATS, peristaltic pump and PA reagent for the CEA Instruments Model 555 Analyzer inside a 35°C chamber.

7.2 Connect each input (i.e., supply) tube from the SPATS to separate channels of the peristaltic pump to supply the mixed $HgCl_2$-$NaSO_3$ reagent solution (stored in small quantities outside of the 35°C chamber)to the SPATS. Allow the SPATS troughs to fill with reagent solution.

7.3 Connect the drain tubes of the SPATS to separate channels of the peristaltic pump to remove CH_2O-exposed reagent solution from the SPATS. The effluent from the four drain channels of the peristaltic pump are flowed into a glass cell where the two, pumped supply tubes for the $HgCl_2$ and $NaSO_3$ reagents to the CEA Instrument are connected. The glass cell is designed to drain excess reagent from the SPATS that is not pumped to the CEA Instrument.

7.4 Placed wetted blank fabric onto the SPATS membrane and smooth with fingers to ensure good contact between the fabric and the membrane. Seal fabric against membrane by installing the removable top of the SPATS.

7.5 Collect baseline data for the blank fabric specimen for one hour. Remove blank fabric and dry the membrane with a tissue.

7.6 Place a (1) blank fabric specimen that has been saturated in CH_2O solution or (2) perspiration wetted test fabric onto the SPATS membrane and smooth with fingers to ensure good contact between the fabric and membrane. Put removable top into place.

7.7 Collect data for the CH_2O containing fabric specimen for one hour.

7.8 Remove CH_2O-containing fabric specimen from the SPATS. Remove screws and plexiglass cover to the SPATS. Rinse the membrane well with distilled-deionized water. Dry the membrane with a tissue.

7.9 Replace the plexiglass cover of the SPATS. Repeat steps 7.4, 7.5.

7.10 Cleaning the SPATS

7.10.1 Remove the input and output tubes from the SPATS.

7.10.2 Pour reagents remaining in the channels into a waste bottle.

7.10.3 Rinse SPATS channels by repeated injection of distilled-deionized water with a syringe

7.10.4 Rinse the membrane with distilled-deionized water.

8. Formaldehyde Data Acquisition and Concentration Calculations

8.1 A microprocessor data acquisition system was used. The output voltage of the CEA Instrument was sampled 50 times/minute. A voltage average and standard deviation was calculated after each consecutive 100 data points and stored for analysis.

8.2 SPATS Calibration

8.2.1 Identify CEA data belonging to (1) the first and second baseline with the blank fabric and (2)the fabric saturated in CH_2O solution. The response time of the SPATS-CEA test system following a change in fabric specimen was typically about 25-35 minutes. This time delay was used to empirically identify the plateau in the data for each baseline and peak condition.

8.2.2 The CH_2O calibration of the SPATS in units of millivolts of CEA response per ug CH_2O/mL H_2O in the CH_2O stock solution used to soak the fabric specimen is calculated using the following equation.

$$\text{SPATS Cal.} \left\{\frac{\text{mv}}{\text{ug/ml}}\right\} = \frac{\overline{\text{Test Fab. (mv)}} - [\overline{\text{Baseline1 (mv)}} - \overline{\text{Baseline2 (mv)}}]/2}{\text{Stock } [CH_2O] \text{ (ug/mL)}}$$

8.3 Measurement of Test Fabrics

8.3.1 Identify CEA data belonging to (1) the first and second baseline with the blank fabric and (2) the test fabric containing CH_2O resins. The approximate 25-35 minute response time of the SPATS-CEA test system following a change in fabric specimen was used to empirically identify the plateau in the data for each baseline and peak condition.

8.3.2 The estimated CH_2O concentration generated by the test fabric was calculated using the following expression.

$$[CH_2O]\ (ug/mL) = \frac{\overline{\text{Test fabric (mv)}} - [\overline{\text{Baseline1 (mv)}} - \overline{\text{Baseline2 (mv)}}/2}{\text{SPATS Calibration } \{mv/(ug/mL)\}}$$

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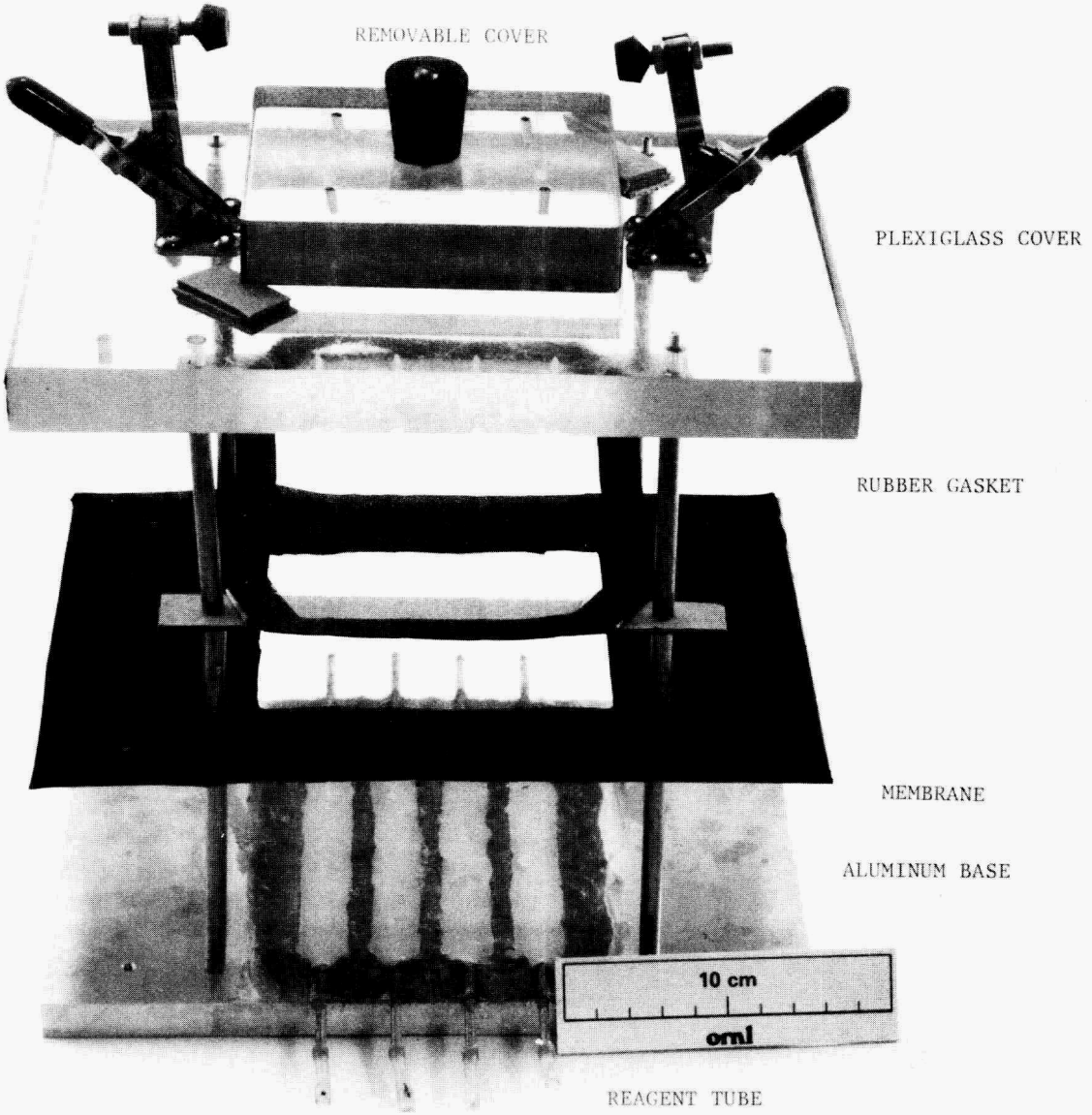

Figure 1: Blow-Up View of Skin Patch Test Simulator.

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