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# Comparison of Gravimetric and Gas Chromatographic Methods for Assessing Performance of Textile Materials Against Liquid Pesticide Penetration

**Anugrah Shaw**
**Ruchika Abbi**

Department of Human Ecology, University of Maryland Eastern Shore, Princess Anne, MD, USA

*Penetration of liquid pesticides through textile materials is a criterion for determining the performance of protective clothing used by pesticide handlers. The pipette method is frequently used to apply liquid pesticides onto textile materials to measure penetration. Typically, analytical techniques such as gas chromatography (GC) are used to measure percentage penetration. These techniques are labor intensive and costly. A simpler gravimetric method was developed, and tests were conducted to compare the gravimetric and GC methods of analysis. Three types of pesticide formulations and 4 fabrics were used for the study. Diluted pesticide formulations were pipetted onto the test specimens and percentage penetration was measured using the 2 methods. For homogeneous formulation, the results of the 2 methods were fairly comparable. However, due to the filtering action of the textile materials, there were differences in the percentage penetration between the 2 methods for formulations that were not homogeneous.*

protective clothing PPE pesticides gravimetric method gas chromatograph

## 1. INTRODUCTION

Personal protective equipment worn by pesticide users can be broadly divided into four categories—whole body, hand, face, and foot protection. Materials used for body protection range from air-permeable woven fabrics to plastic-coated or rubberized materials. The degree of penetration of liquid pesticides through textile materials is one of the criteria for determining the performance of these materials. National and international standards that are commonly referred to as gutter, pipette, and atomizer tests are used to quantify penetration of the pesticide through the materials [1]. The pipette and atomizer methods require chemical analysis of the active ingredient present in the pesticide formulation [2, 3]. Gas chromatograph (GC) and high performance liquid chromatography (HPLC) are commonly used for chemical analysis of active ingredients. Chemical analysis is active ingredient specific and requires sophisticated equipment and a high level of expertise to obtain accurate results. In addition, it is expensive and very time consuming. The gutter test uses a gravimetric method of analysis to measure penetration of liquids [4]. Recently, the gravimetric method of analysis developed for the pipette method has been

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Correspondence and requests for offprints should be sent to Anugrah Shaw, Department of Human Ecology, University of Maryland Eastern Shore, Princess Anne, MD, USA. E-mail: <ashaw@umes.edu>.

approved as part of the ISO 22608:2002 standard [5]. The gravimetric method is much simpler and less expensive, but in some cases may not give accurate results as the weight and not the active ingredient in the test liquid is used to measure penetration. This study was conducted to compare the gravimetric and GC methods for measuring pesticide penetration through textile materials using the pipette method.

## 2. MATERIALS AND METHODS

Typically, pesticide formulations include inert ingredients that have been added to produce formulations that are stable, safe, and practical to apply. Formulations that are applied as liquid spray are commonly available as emulsifiable concentrates (EC); liquid concentrates (SL); suspension concentrates (SC), which are also called flowable (F); wettable powders (WP); and water dispersible granules (WDG). The type of formulation is dependent, among other factors, on the solubility and particle size of the active ingredient. Preliminary studies conducted at the University of Maryland Eastern Shore indicated that formulation type was a major factor in the penetration of pesticides through the materials. For this study, formulations were selected from the EC, SC and WDG categories. For the purpose of this study the WP and WDG categories were combined, as both of them are suspensions with relatively large particle size. SL was not included due to limitations in analyzing the active ingredient. Information on pesticide formulations is provided in Table 1. The surface tension and dynamic viscosity of the formulations were measured in the laboratory. Distilled water was used to dilute the formulations to a concentration of 5% active ingredient.

Five woven fabrics with varying fabric characteristics were selected for the study. Fabric 1 was a lightweight fabric commonly used for shirts. All other fabrics were heavier weight fabrics commonly used to construct pants and/or coveralls. Fabric 3 had a residual finish and Fabric 5 a water-repellent finish. Physical properties of the fabrics are given in Table 2.

**TABLE 1. Physio-Chemical Properties of Pesticides**

| Formulation Code | Pesticide Name | Formulation Type | Active Ingredient | Conc. | Viscosity (mPa s) | Surface Tension (dynes/cm) |
|---|---|---|---|---|---|---|
| Formulation I | Atrazine 90 | WDG | Atrazine | 5% a.i. | 1.33 | 35.64 |
| Formulation II | Aatrex 4L | SC | Atrazine | 5% a.i. | 3.23 | 28.59 |
| Formulation III | Prowl 3.3 | EC | Pendimethalin | 5% a.i. | 1.83 | 31.50 |

*Notes.* WDG— water dispersible granules, SC—suspension concentrates, EC—emulsifiable concentrates, Conc.—concentration.

**TABLE 2. Physical Characteristics of Fabrics**

| Fabric Code | Fiber Content | Fabric Weight ($g/m^2$) | Fabric Construction | Yarn Count (yarns/cm) |
|---|---|---|---|---|
| 1 | Cotton | 126 | Plain | 58 × 30 |
| 2 | Polyester | 202 | Twill | 26 × 22 |
| 3 | Cotton/Polyester | 245 | Twill | 40 × 25 |
| 4 | Cotton | 268 | Twill | 44 × 20 |
| 5 | Cotton | 211 | Twill | 35 × 23 |

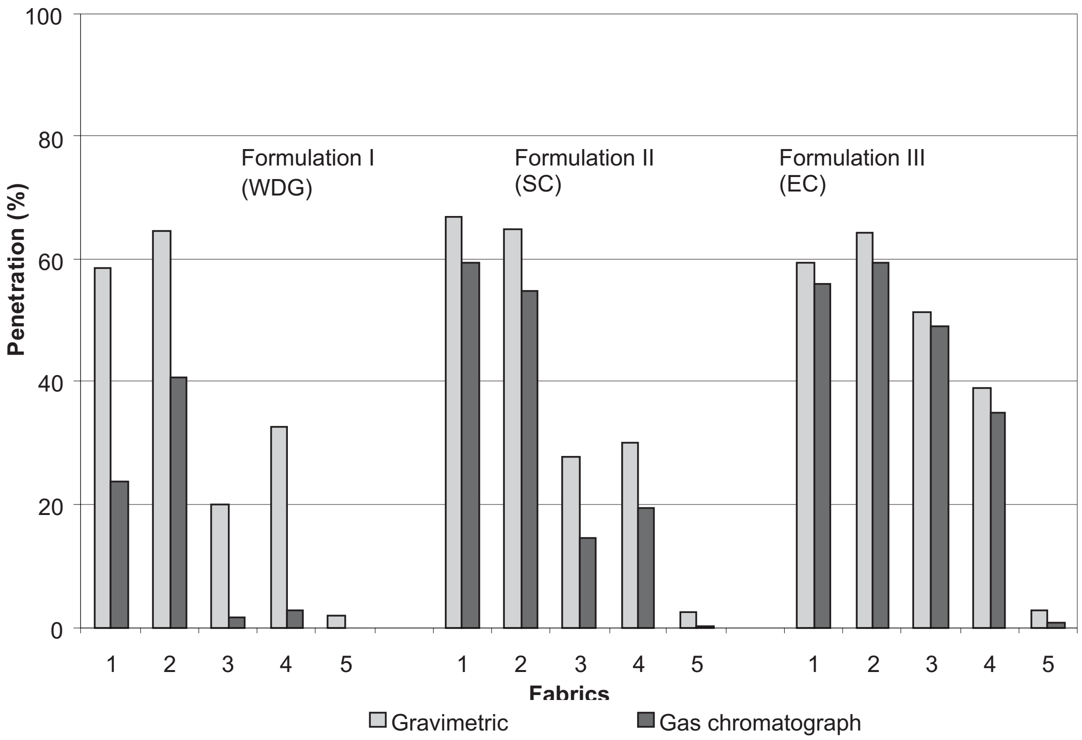


**Figure 1. Pipette test apparatus.**

The pipette method (Figure 1) was used to measure percentage penetration through 8 × 8 cm fabric specimens. The modified ISO/DIS 22608:2002 draft, recently approved as the ISO 22608 standard [5], was used to measure percentage penetration for each fabric specimen using the gravimetric and GC methods of analysis. The top layer, fabric specimen, and the collector layer were weighed prior to conducting the experiment. The test assembly was prepared by placing the fabric specimen and the collector layer between the base and the cover plate of the specimen holder. A fixed-volume pipettor was used to apply 0.2 ml of the pesticide formulation to the center of the fabric specimen. A 10 × 10 cm transparency film was placed to cover the cover plate to reduce evaporation. After 10 min, the top layer, used to measure repellency, was placed between the fabric specimen and the cover plate and then removed after two additional minutes. The three layers were separated and re-weighed. The data were used to calculate percentage penetration and mass balance (an indictor for percentage loss due to evaporation) for the gravimetric method. For each test specimen, the mass balance was within the range (95–105%) specified in the test method. In order to compare percentage penetration using the gravimetric and GC methods of analysis for the same test specimens, each layer was extracted twice in 50 ml of acetone in an orbital shaker for 30 min at 200 rotations per minute. The two aliquots were combined and analyzed using a gas chromatograph with an N/P detector (Agilent Technology, formerly Hewlett Packard, USA). The data was used to calculate percentage penetration for the GC method.

Means and standard deviations were calculated for each fabric-formulation-method combination. In addition, one-way Analysis of Variance (ANOVA) and Tukey's test were conducted to determine the significant differences between the two test methods for each of the fabric-formulation combination. Percentage penetration was used as the response variable at the 95% confidence level.

## 3. RESULTS AND DISCUSSIONS

Mean and standard deviation of percentage penetration of the pesticide formulations through the five fabrics was calculated (Table 3). To illustrate the difference between the two methods of analysis, the mean values of percentage penetration are presented graphically in Figure 2. Analysis of Variance results and variance components are reported in Tables 4a, 4b, 5a and 5b. Results of Tukey's pair-wise comparisons test are given in Table 6.

**TABLE 3. Mean and Standard Deviation of Percentage Penetration of Formulations Through Fabrics Using Gravimetric and Gas Chromatography (GC) Methods of Analysis**

| | | Gravimetric | | GC | |
|---|---|---|---|---|---|
| Formulation | Fabric Code | *M* (%) | *SD* | *M* (%) | *SD* |
| Formulation I (WDG) | 1 | 58.4 | 6.6 | 23.8 | 1.3 |
| | 2 | 64.7 | 3.1 | 40.7 | 3.8 |
| | 3 | 20.1 | 6.5 | 1.7 | 1.4 |
| | 4 | 32.5 | 8.1 | 2.9 | 0.6 |
| | 5 | 2.0 | 1.3 | <0.1 | 0.0 |
| Formulation II (SC) | 1 | 66.8 | 2.5 | 59.2 | 4.4 |
| | 2 | 64.8 | 1.3 | 54.7 | 0.8 |
| | 3 | 27.7 | 5.1 | 14.5 | 6.0 |
| | 4 | 30.2 | 0.4 | 19.5 | 0.5 |
| | 5 | 2.4 | 0.4 | 0.2 | 0.1 |
| Formulation III (EC) | 1 | 59.3 | 2.8 | 55.8 | 4.6 |
| | 2 | 64.2 | 3.0 | 59.4 | 5.5 |
| | 3 | 51.2 | 1.0 | 49.2 | 3.2 |
| | 4 | 39.1 | 1.1 | 34.9 | 2.4 |
| | 5 | 2.8 | 0.6 | 0.6 | 0.4 |

*Notes.* WDG— water dispersible granules, SC—suspension concentrates, EC—emulsifiable concentrates.

**TABLE 4a. Analysis of Variance for Gravimetric Method**

| Source | *DF* | *SS* | *MS* | *F* Ratio | Prob. > *F* |
|---|---|---|---|---|---|
| Formulation | 2 | 465.7031 | 232.852 | 1.3598 | .310 |
| Fabric | 4 | 23057.04 | 5764.26 | 33.6626 | .000 |
| Formulation * Fabric | 8 | 1369.892 | 171.237 | 11.9054 | .000 |
| Within | 30 | 431.4943 | 14.3831 | | |
| Total | 44 | 25324.13 | 575.548 | | |

*Notes*. Prob.—probability.

**TABLE 4b. Variance Components for Gravimetric Method**

| Component | Variance Component | % of Total | Sqrt (Variance Component) |
|---|---|---|---|
| Formulation | 4.10767 | 0.6 | 2.027 |
| Fabric | 621.44703 | 89.8 | 24.929 |
| Formulation * Fabric | 52.28447 | 7.6 | 7.231 |
| Within | 14.38314 | 2.1 | 3.793 |
| Total | 692.22231 | 100.0 | 26.310 |

*Notes*. Sqrt—square root.

**TABLE 5a. Analysis of Variance for Gas Chromatography (GC) Method**

| Source | *DF* | *SS* | *MS* | *F* Ratio | Prob. > *F* |
|---|---|---|---|---|---|
| Formulation | 2 | 5212.013 | 2606.01 | 7.4042 | .01514 |
| Fabric | 4 | 15976.2 | 3994.05 | 11.3478 | .00222 |
| Formulation * Fabric | 8 | 2815.725 | 351.966 | 36.9083 | .00000 |
| Within | 30 | 286.0867 | 9.53622 | | |
| Total | 44 | 24290.03 | 552.046 | | |

Notes. Prob.—probability.

**Table 5b. Variance Components for Gas Chromatography (GC) Method**

| Component | Variance Component | % of Total | Sqrt (Variance Component) |
|---|---|---|---|
| Formulation | 150.26940 | 22.1 | 12.258 |
| Fabric | 404.67617 | 59.6 | 20.117 |
| Formulation*Fabric | 114.14315 | 16.8 | 10.684 |
| Within | 9.53622 | 1.4 | 3.088 |
| Total | 678.62495 | 100.0 | 26.050 |

*Notes*. Sqrt—square root.

**TABLE 6. Tukey's Pair-Wise Comparisons of Gravimetric and Gas Chromatography (GC) Methods of Analysis**

| Formulation | Fabric Code | Difference of Means | *SE* of Difference | *T*-Value | Adjusted *p*-Value |
|---|---|---|---|---|---|
| Atrazine 90, WDG | 1 | 34.640 | 3.3400 | 1.0370 | 0.0000 |
| | 2 | 24.050 | 2.7020 | 8.9010 | 0.0000 |
| | 3 | 18.490 | 3.6160 | 5.1120 | 0.0027 |
| | 4 | 29.590 | 2.8280 | 10.4300 | 0.0000 |
| | 5 | 1.950 | 0.5270 | 3.6970 | 0.0283 |
| Aatrex 4L, SC | 1 | 7.580 | 3.3400 | 2.2710 | 0.2766 |
| | 2 | 10.140 | 2.7020 | 3.7510 | 0.0258 |
| | 3 | 13.200 | 3.6160 | 3.6500 | 0.0306 |
| | 4 | 10.700 | 2.8280 | 3.7700 | 0.0250 |
| | 5 | 1.947 | 0.5265 | 3.6970 | 0.0109 |
| Prowl 3.3, EC | 1 | 3.560 | 3.3400 | 1.0650 | 0.8860 |
| | 2 | 4.810 | 2.7020 | 1.7810 | 0.5105 |
| | 3 | 2.060 | 3.6160 | 0.5705 | 0.9912 |
| | 4 | 4.210 | 2.8380 | 1.4820 | 0.6808 |
| | 5 | 2.170 | 0.5265 | 4.1220 | 0.0138 |

*Notes.* WDG— water dispersible granules, SC—suspension concentrates, EC—emulsifiable concentrates.

## 3.1. Gravimetric Analysis

Data obtained using the gravimetric method of analysis measured the liquid that penetrated though the materials. As seen in Figure 1, characteristics that affect the liquid holding capacity of materials play an important role in percentage penetration data using gravimetric methods. Regardless of the formulation, the

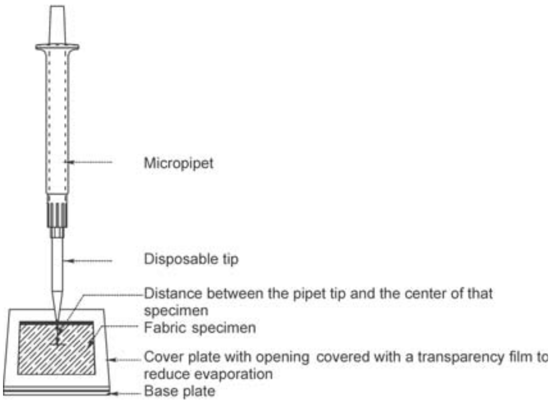


**Figure 2. Percentage penetration using the gravimetric and Gas Chromatography (GC) methods for analysis.**
*Notes.* WDG—water dispersible granules, SC—suspension concentrates, EC—emulsifiable concentrates.

amount of liquid that penetrated through the 100% polyester fabric (Fabric 2) was about the same when gravimetric analysis was used to measure percentage penetration. This is because the liquid holding capacity of the hydrophobic polyester fabric was low, and thus over 60% of the liquid filtered through the fabric. Penetration of the liquid through light-weight cotton (Fabric 1) was also very high as the liquid holding capacity of the cotton fabric seemed to have been reached. Fabrics 3 and 4, heavier weight cotton/polyester and cotton fabrics had much lower penetration. Fabric 5 had a water-repellant finish and liquid penetration was very low.

### 3.2. GC Analysis

Data obtained using GC analysis measured the active ingredient that penetrated through the materials. In general, Formulation III (EC) had the highest percentage penetration and Formulation I (WDG) the lowest. This may be due to the particle size of the active ingredients in the various formulations. As the particle size of the active ingredient in WDG formulations was comparatively large, the particles were trapped in the fabrics that acted like sieves. Due to the filtering action of the fabrics, the percentage penetration of WDG was comparatively lower. The extent to which the particles were trapped was dependent on the fabric characteristics. Mean percentage penetration through the heavier weight cotton/polyester and cotton fabrics was lower than 3% when the GC method was used to calculate pesticide penetration. The active ingredient particles in SC formulations were smaller than in WDG and thus a higher amount penetrated through Fabrics 1 and 2.

### 3.3. Comparison of Gravimetric and GC Analysis

Analysis of Variance results show a significant bias between the test methods. The gravimetric method is, on average, 11 percentage points higher than the GC method. The measurement standard deviation (based on triplicate determinations) is 3.8 for the gravimetric method and 3.1 for the GC method (Tables 4 and 5). For both test methods, the variability between replicates is small compared to the differences due to fabrics and formulations. The total standard deviation (this included all values for the respective methods) was 26.3 for the gravimetric method and 26.0 for the GC method. Although the total standard deviation values for the two methods were very similar, the gravimetric method showed 8% of its total variance associated with formulation differences, while the GC method showed 39% of its total variance associated with formulation differences (sum of variance due to formulation and formulation-fabric interactions for both the methods). The aforementioned values indicate that the gravimetric method may be better at determining differences between fabrics, whereas the GC method may be more sensitive to differences in penetration due to formulations.

Tukey's multiple comparisons procedure indicated significant differences between the two test methods for all of the Formulation I-fabric combinations (Table 6). The difference between the means ranged from 34.64 to 18.49 for Fabrics 1 through 4. The difference in means was small (1.95) for the fabric with water-repellant finish (Fabric 5), due to overall lower penetration through all test specimens. For Formulation I (WDG), the gravimetric method grossly overestimates percentage penetration through fabrics that have no water-repellent finish.

For Formulation II (SC), there was no significant difference between the means of the gravimetric and the GC method for Fabric1, which was a lightweight fabric. All other combinations for Formulation II showed significant differences between two methods. For Fabrics 1–4, the difference in means for Formulation II (SC) was lower than those for Formulation I (WDG). For the water-repellent fabric (Fabric 5), the difference of means was similar for Formulations I and II. For Formulation III (EC), there were no significant differences between the percentage penetration means for all fabrics except Fabric 5. For Fabric 5, the percentage penetration was 2.8 and 0.6% respectively for the gravimetric and the GC methods of analysis. Although the values are statistically different, the actual difference between the means is only 2.2%, with the gravimetric method being the higher of the two values.

The study indicates that the method used to measure percentage penetration should be carefully selected. For formulations with larger particles of the active ingredient, like Formulation I (WDG), the gravimetric method of analysis may grossly overestimate the amount of pesticide that penetrates through some fabrics. The gravimetric method may be suitable for formulations with a very small particle size, like Formulation III (EC). Additional research on particle size is needed to assist in the development of a criterion for selection of method for analysis.

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