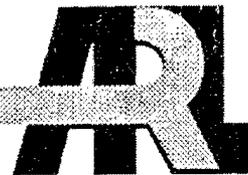


ARMY RESEARCH LABORATORY



Determining the Water Content of Coatings Utilizing Gas Chromatography

by Philip Patterson
and Pauline Smith

ARL-TN-172

November 2000

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Aberdeen Proving Ground, MD 21005-5069

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Determining the Water Content of Coatings Utilizing Gas Chromatography

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Abstract

The Coatings Team of the Polymers Research Branch has developed a method for the direct determination of water content in pigmented coating materials using gas chromatography. This report outlines the instrument parameters and the sampling procedures established to perform the determinations. A typical analysis is graphically presented with a brief explanation summarizing the tabulated results.

Acknowledgments

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1. Background

The Coatings Technology Team of the Polymers Research Branch, U.S. Army Research Laboratory (ARL) is responsible for the development and testing of environmentally compliant coatings to be applied on U.S. Army tactical equipment and vehicles. Due to ever-tightening air-pollution regulations, newly developed water dispersible coatings have been formulated to replace the existing solvent-based coatings that are typically higher in volatile organic content (VOC). The most recent example being a water-reducible, chemical-agent-resistant camouflage topcoat having a VOC of 1.8 g/liter.¹ In order to calculate the VOC content of these coatings, it is necessary to determine the amount of water present in the formulation. This is because water is considered a non-VOC compound and does not contribute to the final VOC value reported for the coating. The test method presented in this report provides a relatively simple and direct way to determine water content. The method uses the principles of gas chromatography (GC) to separate and quantitate the percentage of water in paint.

2. Approach

2.1 Instrumentation. Utilized in this study was a Hewlett-Packard (HP) 5890 Series II gas chromatograph equipped as follows.

- Column Size/Phase: 30 m × 0.53 mm × 3.0 μm/6%-cyanopropylphenyl-94% dimethyl polysiloxane (cross-linked).
- Oven: Programmable, set at 70 °C.
- Detector: Thermal conductivity, set at 225 °C.
- Carrier Gas: Helium, set at 7 ml/mn.

¹Escarsega, J. A., and J. L. Duncan. "A Water-Reducible Environmentally Compliant Chemical Agent Resistant Coating." ARL-TR-1089, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, May 1996.

- Injector: Split (20:1), set at 200 °C.
- Recorder: HP 1127 Chemstation with GC application software.
- Printer: HP Desk Jet 500.

2.2 Sample Preparation. Water standards and coating samples were prepared for the GC analysis by diluting preweighed representative portions with dimethylformamide (DMF). The coatings should be mixed well, with multicomponent paint systems admixed in the appropriate ratios before weighing. Isopropyl alcohol was added to each of the solutions for use as an internal standard. Aliquots of the mixtures were then injected directly into the GC using a microliter syringe. Further details regarding sample preparation are outlined in ASTM Method D3792.² The equations necessary to calculate the water concentrations of the coating samples are provided in the Appendix.

3. Results and Discussion

Five water-reducible polyurethane coatings were selected for an intralaboratory study. The formulation of each of the samples was different. The water content of the samples ranged from 37% to 47% by weight. Calibration runs were made using deionized water as the standard. Table 1 summarizes the results of the analyses. Each analyst made duplicate determinations with the averaged value reported as the final determinate.

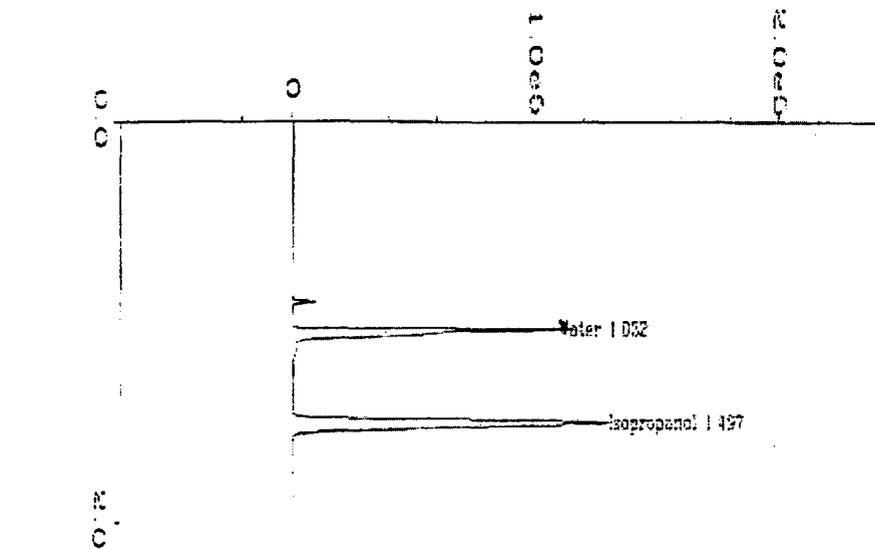
As shown in Table 1, the analysts' results agree reasonably well with each other and are also close to the theoretical values reported for each coating product. The calibration runs also agreed well between analysts, with averaged results within 1% of each other.

A chromatogram and area integration report of a coating analysis is shown in Figure 1.

²American Society for Testing and Materials. "Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph." ASTM D3792, May 1997.

Table 1. Water Content (% by Weight)

Sample No.	Theoretical Value	Analyst No. 1 Result	Analyst No. 2 Result
1	47.4	46.8	48.8
2	44.5	42.1	42.9
3	40.6	39.8	39.4
4	44.8	43.8	43.0
5	37.5	39.0	38.2



Area Percent Report

```

Data File Name   : C:\HPCHEM\1\DATA\TEST\SIG10037.D
Operator        : Smith
Instrument       : ANALYZER1
Sample Name     : tar, ipa dmf
Run Time Bar Code :
Acquired on    : 26 Oct 99 12:44 PM
Report Created on : 26 Oct 99 12:46 PM
Sample Info    : 70 deg oven
Page Number    :
Vial Number    :
Injection Number :
Sequence Line  :
Instrument Method :
Analysis Method :
  
```

Sig. 1 in C:\HPCHEM\1\DATA\TEST\SIG10037.D

PK#	Ret Time	Area	Height	Type	Width
1	1.032	204315	110671	HB S	0.029
2	1.497	342277	129339	PB T	0.044

Total area = 546592

Figure 1. Typical Sample Chromatogram.

The solvent peak, DMF, is not shown. However, it should be noted that DMF is a late-eluting compound, having a retention time of about 5 min. Therefore, time must be allotted for its elution before the next sample is introduced.

4. Conclusion

Gas chromatography utilizing a cross-linked megabore (30 m × 0.53 mm) column has been successfully used for the direct determination of a coating's water content. Analysis time is short, generally requiring no longer than 5 min per sample. The established working range for the procedure was approximately 35–50% water by weight of the whole paint. However, it is believed that higher or lower percentages of water could also be determined using this method. It is important to use anhydrous-grade chemical when preparing the samples, since any addition of extraneous water will bias the final determinations.

Appendix:
Water Content Calculations

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Calculate the water content of each sample using the following equations.

$$\% \text{Water} = \frac{W_{\text{H}_2\text{O}} \times W_{\text{IPA}} \times 100}{A_{\text{IPA}} \times W_{\text{C}} \times R}, \quad (\text{A-1})$$

where

$A_{\text{H}_2\text{O}}$ = integrated area of water peak,

W_{IPA} = weight of isopropyl alcohol added,

A_{IPA} = integrated area of the isopropyl alcohol peak,

W_{C} = weight of coating, and

R = detector response factor from the standard (de-ionized water) analysis, calculated as follows.

$$R = \frac{W_{\text{IPA}} \times A_{\text{STD}}}{W_{\text{STD}} \times A_{\text{IPA}}}, \quad (\text{A-2})$$

where

A_{STD} = integrated area of water peak, and

W_{STD} = weight of de-ionized water standard.

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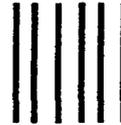
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