



Determination of Volatile Organic Compounds Content Using Novel Ash and Total Solids Analysis for Chemical Agent Resistant Coating Systems

by Pauline Smith, William Lum, and Daniel Pope

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14. ABSTRACT Volatile organic compounds (VOCs) found in coatings are a major concern of the U.S. Army Research Laboratory, the Environmental Protection Agency (EPA), and local air quality boards. The current laboratory standards used to determine VOCs in Chemical Agent Resistant Coating and other military coating systems are EPA Method 24 or American Society for Testing and Materials ASTM D 3960. It has been reported that VOC measurements using this method produce errors that increase nearly exponentially at VOC concentrations <2.1 lb/gal (250 g/L). The solids or nonvolatile component of the coating takes 1.5 hr to measure by oven, and the ash takes multiple hours as described in ASTM D 3723. These values are necessary to validate VOCs; the primary goal is to minimize VOCs in all coatings. This report outlines experimentation to quantify actual VOC levels of formulated paints using both EPA Method 24 and a proposed alternative test method that utilizes a moisture analyzer. Analysis of the results verified comparable accuracy between the current process and the instrumental-based method, with the latter process producing a more rapid result.					
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1. Introduction

The U.S. Army Research Laboratory's (ARL's) Camouflage Coatings and Corrosion Team is responsible for developing and testing all Chemical Agent Resistant Coating (CARC) and other military coating systems. CARC originated from the need of military coatings to resist chemical warfare agents and to be easily decontaminated. CARC systems were implemented by the Army in 1983 for use on combat, combat support, tactical wheeled vehicles, aircraft, and ground equipment. In order to qualify as CARC, the coatings must adhere to strict parameters. Standards are enforced to optimize equipment that will enhance the warfighter's ability in the battlefield. Camouflage coatings are developed and formulated based upon a balance of three critical requirements: durability, environmental compliance, and survivability. New formulations must meet or exceed operational requirements and comply with air pollution regulations.

The Clean Air Act and other government regulations require reduced volatile organic compounds (VOCs) content. VOC is defined as any organic compound that participates in atmospheric photochemical reactions. Hazardous air pollutants (HAPs), both lead and hexavalent chromium (chromate), are also being reduced or eliminated from current formulations as a result of these regulations. Compliance with VOC regulations has resulted in the use of more VOC-exempt solvents and water-reducible coatings. Therefore, research is focused on continuing the growth of environmentally friendly coatings that are HAP-free with low VOC content.

In recent years, ARL has developed and revised the water-reducible, two-component polyurethane CARC topcoat MIL-DTL-64159 (1). This water-dispersible coating has reduced VOC content by 50% from the previous two-component system (MIL-C-46168 [2]) and eliminated HAP. The alternative, MIL-DTL-53039B (3), a solvent-borne aliphatic polyurethane, is also HAP-free with limited VOC content. These coatings are further designated as type I, containing silica-based flattening agents, or as type II, containing polymeric flattening agents.

To ensure that the military is receiving acceptable coatings, a qualified product list (QPL) was created, listing all of the vendors whose coatings have passed the specification requirements. Included are tests methods by Environmental Protection Agency (EPA) Federal Reference Method 24 (4) that are nearly analogous to the American Society for Testing and Materials (ASTM) to determine VOC. An important quality to be tested for both environmental and performance requirements is the total solids, i.e., the percent by weight of the nonvolatile component of the coating material that remains in the pan at the conclusion of the test. VOC content is calculated as a function of (1) the volume of coating minus water and any exempt solvents and (2) the volume of the coating's solids.

Currently, the standard test for determining VOC in paints and coatings is the EPA Method 24 and ASTM D 3960 (4). These methods are sometimes prone to errors of VOC levels below 2.1 lb/gal (250 g/L). Both EPA and ASTM methods require determination of the coating density (weight/gal) and total volatile content at a specified time and temperature, and also what the exempt solvents are. Total volatile content is calculated by determining the percent of weight lost at 110 ± 5 °C for 1 hr in a forced-air oven, per ASTM D 2369 (5). Water content may be determined by a Karl Fischer method (ASTM D 4017 [6]) or by gas chromatography (ASTM D 3792 [7]). The density of the coating is obtained using a pyrometer or a weight per gallon cup (according to ASTM D 1475 [8]). Exempt solvent content may be determined by a direct injection gas chromatography technique outlined in ASTM D 4457 (9).

Recently, an alternative test method using an automated thermal moisture analyzer based on the rapid loss-on-drying technology has provided a simple and cost-effective alternative for testing nonvolatile content in coatings. Rapid loss-on-drying technology has many advantages over traditional methods, making it an ideal choice for companies who want to efficiently produce quality products while minimizing energy and time expenditures typically associated with the traditional testing methods.

2. Technical Approach

Many within the coatings industry have anticipated a rapid ASTM method that would allow quick and uncomplicated tests for nonvolatile content in their raw materials, in-process materials, or finished products. This test method would be used to quickly determine the weight-percent of nonvolatile (solids) content via instrumental loss in weight technology. This rapid method has been used for water-reducible and solvent-based finished products. To determine the validity and optimal test conditions for these materials, a calibrated forced draft oven was employed and the materials were tested in accordance with ASTM D 2369 (5).

3. Experimental Procedure

The tests were conducted with a Computrac MAX5000L moisture analyzer, manufactured by Arizona Instruments LLC, Tempe, AZ. The machine was operated in accordance with ASTM D 7232 (10). This test method is intended to be used as a rapid quality control, acceptance, and validation test. Prior to testing, the appropriate settings must be selected to achieve proper coating results. Solvent-borne systems must be tested at a temperature of 150 °C with an end rate of 0.100 %/min. For waterborne systems, the appropriate temperature is 135 °C with an end

rate of 0.100 %/min. A clean, flat sample pan covered by a piece of glass filter paper with the rough side up is placed in the moisture analyzer. The analyzer will prompt for the lid to be closed. The analyzer is allowed to equilibrate at the desired temperature. The internal scale on the analyzer tares and prepares for the sample to be placed on the glass filter paper. The sample must be prepared as discussed in ASTM D 3925 (11). The specimen is placed on the sample pan in a spiral pattern. To produce a viable reading, the analyzer will require between 1.5 and 2.5 oz of material. Once the proper amount of sample is placed onto the pan, the analyzer will prompt for the lid to be closed. After the lid is closed, it reads the exact weight of the sample and begins the process. The testing should take ~10 min. At the end of the test, the moisture analyzer displays the total solids expressed as a percent. After 5 min, the Computrac MAX5000L will heat up to 450 °C and measure ash content in the sample. The ash measurement duration is ~10 min. Upon completion, the moisture analyzer will display total ash expressed as a percent.

The conventional testing is generally done in a forced-dry oven. The model used was a model 31619 from Thelco. It was operated in accordance with ASTM D 2369 (5). The specification required that the oven must be preheated to 100 ± 5 °C for ~30 min. An aluminum foil dish is prepared with a glass filter paper and weighed using a Mettler AE100 scale. This weight must be recorded. While the dish is still on the scale, the scale must be tared and the specimen must be swirled onto the glass filter paper. Reference is made in accordance with ASTM D 2369 (5) for proper specimen weights depending on expected volatile values. All samples are to be properly collected using ASTM D 3925 (11). As part of ASTM D 2369 (5), three samples of each coating must be analyzed to determine an average. This average comprises the results. After the samples have been prepared, they are placed into the preheated oven for 60 min. At the conclusion of 60 min, the samples are immediately removed from the oven and weighed. Any delay in removing samples from the oven may cause a discrepancy in the results. Once the samples are weighed, the findings must be inputted into the formula detailed in ASTM D 2369 (5) to calculate the percent volatile. An average value of the samples is taken as the result for the samples.

The ash testing also requires 1 hr in a forced-dry oven. The temperature and preparation of the forced-dry oven is the same as the solids testing illustrated in ASTM D 2369 (5) except for the sample size. For ash testing as described in ASTM D 3723 (12), one will need 1.5 g of the coating. In addition, this test method requires the use of 2 mL of water meeting the purity standard outlined in ASTM 1193 (13). Following another hour in the forced-dry oven, the sample is transferred to a muffle furnace set to 450 ± 25 °C. The sample will remain in the muffle furnace for 1 hr. Once completed, the sample is removed and weighed. Using the formula detailed in ASTM D 3723 (12), the ash content is determined.

4. Experimental Data

Twelve coatings were tested in accordance to EPA Method 24 to analyze total solids. The theoretical solids were calculated based upon the information provided by the vendor on the statement of composition (SOC) form. All samples were run three times to produce the oven and instruments results. The average values are listed in table 1. Selected samples were run multiple times to validate results.

Table 1. Comparison of total solids results for the oven and Computrac.

QPL	Total Solids		Instrument (%)	Spec	Test Procedure
	Standard Oven (%)	Theoretical (%)			
Q1698	72.90	73.08	73.28	11195G/II	Solvent borne
Q1711	65.40	56.96	61.06	53039B/II	Solvent borne
Q1764	48.00	48.72	49.24	64159/II	Waterborne
Q1734	41.90	42.74	40.99	64159/II	Waterborne
—	41.90	42.74	41.14	—	Waterborne
—	41.90	42.74	41.49	—	Waterborne
07 E 01	61.50	62.10	61.63	53030B	Solvent borne
Q1722	73.20	74.13	71.82	11195G/II	Solvent borne
Q1699	72.90	73.06	73.20	11195G/II	Solvent borne
Q1705	44.08	39.39	47.47	64159/II	Waterborne
Q1783	—	76.50	75.61	11195G/II	Solvent borne
F93H00505	48.30	—	47.19	64159/II	Waterborne
—	48.30	—	47.06	—	Waterborne
WU2K-725	—	47.40	41.14	64159/II	Waterborne
—	—	47.40	40.63	—	Waterborne
—	—	47.40	40.59	—	Waterborne
Q1782	—	53.90	50.59	64159/II	Waterborne
—	—	53.90	50.78	—	Waterborne

Twelve coatings were tested in accordance with EPA Method 24 to analyze total pigment. The theoretical pigments were calculated based on the formulations and also on information provided by the vendor on the SOC form. All samples were evaluated three times to obtain the ASTM and instruments results. The average values are listed in table 2. Selected samples were run multiple times to validate results.

Table 2. Comparison of ash results for the oven and Computrac.

QPL	Ash (% Pigment)			Spec
	ASTM (%)	Theoretical (%)	Instrument (%)	
Q1698	65.40	47.50	43.21	11195G/II
Q1699	66.80	48.08	45.25	11195G/II
Q1722	47.30	47.96	34.77	11195G/II
Q1734	13.46	22.91	12.93	64159/II
—	13.46	22.91	13.12	—
—	13.46	22.91	12.99	—
Q1783	—	52.44	49.68	11195G/II
WU2K-725	—	28.00	14.43	64159/II
—	—	28.00	13.87	—
—	—	28.00	13.46	—
Q1711	—	33.07	17.01	53039B/II
—	—	33.07	17.15	—
Q1764	—	28.76	23.49	64159/II
07/E01	—	35.20	31.54	53030B
—	—	35.20	36.89	—
—	—	35.20	36.99	—
Q1782	—	37.50	25.94	64159/II
—	—	37.50	26.12	—
Q1705	—	15.99	18.98	64159/II

5. Results and Discussion

The analytical data demonstrates no significant differences between the forced-dry oven and moisture analyzer test methods. Analysis of the data provided in the prior table figures reveals strong reproducibility in data. The consistency in the data sets illustrates with high confidence that either test method could be used to determine total solids. With this numerical value, the VOC can also be calculated using the equation in ASTM Standard Practice D 3960 (4).

The greatest advantage of using the ASTM D 7232 (10) test method is to save time and resources. Rapid determination and user-friendly instrumentation with the menu-driven operations facilitated rapid completion of testing. Under this improved method, a multitude of QPL samples can be validated in a short time with ease. The VOC content is now determined very quickly and checked for compliance with the requirement from its appropriate CARC specification.

Cost is another significant factor. Although both methods are comparable in results, the labor cost is less through man-hours saved via use of the moisture analyzer method. It is no longer as labor intensive. Moisture, total solids, and ash or dry weight results are obtained in a single run, making it a most efficient run. Through this method, increased productivity has been realized. More samples may be analyzed in a given time than the oven system. The purchase of a moisture analyzer will save significant labor hours in the future, increase laboratory efficiency through increased sample throughput, and provide a rapid return on investment.

The moisture analyzer also reduces the human error in results through reduction in human measurements and handling. Because the scale is incorporated into the machine, it is able to collect and compute all the data that would be done by hand when using ASTM D 2369 (5). The moisture analyzer eliminates human calculations and check points where the data can become corrupted and lead to incorrect findings. Using a moisture analyzer therefore increases accuracy.

New technologies are driving the analytical world of test methods. The improvements behind the moisture analyzer have relegated forced-dry oven testing to a backup or verification role to the preferred moisture-based method. It is now possible to validate VOC content in a shorter amount of time without sacrificing accuracy. Using the moisture analyzer has made this kind of rapid analysis possible.

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