GC Headspace Applications for VOC:

The Challenges of Obtaining Accurate Measurements with Decreasing VOC Levels

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Long ago, scientists stopped measuring the denier of hair with yard sticks and triple beam balances. Currently, the gas chromatograph (GC) analysis methods used, in the art, to measure volatile organic compounds (VOC) in colorants follow equally antiquated reasoning. Despite the interlaboratory precision that these methods may exhibit, they are frequently inaccurate due to a dependency upon the chemistry of coatings samples investigated. Nevertheless, numerous governing bodies—domestic and worldwide—attempt to regulate the amount of VOC in coatings dispersions without the presence of a truly accurate method. The global trend toward lower VOC in coatings markets, and the liability therein, are leading scientists to evaluate several methods for gas chromatography to accurately determine the VOC of coatings dispersions. In the United States, the Federal Trade Commission (FTC) is cracking down on false advertising as it relates to low- or no-VOC finished paints. Two top U.S. coatings companies faced charges from the FTC in October 2012 on misleading consumers that their paints were free of VOC.[1] Unfortunately, current methods for VOC analysis such as EPA 24, ISO 11890-2, ISO 17895, and ASTM D6886 are dependent upon sample, solvent, concentration, and GC column, each of which can contribute to inaccuracies.

The focus of this article is to demonstrate that gas chromatography mass spectroscopy headspace (GC-MS HS) analysis is preferable after quantitative screening methods have been applied. No current method is perfect for all requirements; therefore, verification methods for VOC results are reviewed and the degree of probable success evaluated.

INTRODUCTION

The simplest definition of volatile organic compounds (VOC) comes from Canada: "volatile organic compounds that participate in atmospheric photochemical reactions, excluding the following . . ." and a list of chemicals is presented.[2] The most complex definition(s) exist in the United States and there is insufficient room to present them fully within these pages. To get an idea of the complexity, imagine each county, state, and regional governing body having its own definitions, and that is a fair start. For example, the California South Coast Air Quality Management District applies this VOC definition in Rule 102 Definition Terms. "VOLATILE ORGANIC COMPOUND (VOC) is any volatile compound of carbon, excluding methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, and exempt compounds."[3]

The evolution of measuring VOC in coatings and colorants can trace its beginnings to the 1970s with the origins of the U.S. Environmental Protection Agency (EPA). Roy Ash, co-founder and president of the American company Litton Industries and director of the U.S. Office of Management and Budget, testified to Congress about the fragmented state of pollution control that "will seriously limit our solving the problem even as we expand our commitment to preserve and restore the quality of our environment."[4] The newly formed EPA raised concerns about the negative effect of organic compounds on the drinking water, soil, atmosphere, and ozone layer and began pressing industry to lower volatile emissions. The agency specifically stated that "the 1970s ab-

solutely must be the years when America pays its debt to the past by reclaiming the purity of its air, its waters, and our living environment."[4] In April of 1971, the EPA released standards for reduction of photochemical oxidants.[5]

In the early days, the EPA standard testing methods were neither accurate nor specific enough, relative to the U.S. regulations placed on product and manufacturers for requiring lower VOC content. Yet, pressure mounted for lower and lower VOC limits. The general concern of all global governing bodies, with respect to paints, involves minimization of volatiles from painted coatings into the environment.

As a side note, a pattern of lower limits becoming mandated prior to establishing accurate standardized testing methods repeats itself for all the governing bodies with respect to VOC limits. First, the regulatory bar is raised. Industry achieves the standard. They advertise lower-VOC products. Then, before the analytical chemist can catch his breath, an even lower VOC level is expected and mandated, and—all the while—laboratories try feverishly to verify accurate testing.

The Federal Trade Commission (FTC) released guidelines and an enforcement policy for manufacturers regarding advertising and labeling for the sale of no-VOC and low-VOC products. Essentially, the FTC states that a company cannot advertise a product as being "no VOC" unless a result of 0 g/L is obtained analytically. In addition, a company may not label or advertise "trace VOC" unless the VOC level is the same as background VOC levels.[6] Let us consider the impact of the FTC ruling. Should the colorant identified in the *Figure* 1 chromatogram be considered "no VOC"?

The answer depends on whether the background sample contains the same peaks and if the VOC peaks are exempt or nonexempt solvents. According to the FTC guidelines, if the peaks are not in the background and the solvents are nonexempt (meaning they do impact the ozone layer), then the colorant cannot be marketed as "no VOC" or "zero VOC."

CURRENT METHODS FOR MEASURING VOC

How should the analytical chemist measure the amount of VOC that would come off of a coating once applied to a substrate?

Currently, there are several methods (under EPA and ASTM administration) to measure volatile organic components in colorants. In 1993, the Environmental Protection Agency presented EPA 24 for the "Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids, and Weight Solids of Surface Coatings." EPA Method 24 is the most common method for determining VOC content in coatings.[7] EPA 24 measures VOC content indirectly by incorporating gravimetric analysis (ASTM 2369-81, 87, 90, 92, 93, or 95), percent water analysis (ASTM 3792-79 or 91 or ASTM 4017-81, 90, or 96a), density (ASTM D1475-60, 80, or 90), and gas chromatography for dichloromethane and trichloroethane (ASTM D5403-93).

Unfortunately, Method 24 does not provide good precision with waterborne coatings nor does it perform well with coatings that contain low VOC. When performing multiple methods to achieve a final result, the measurement percentage errors accumulate.[9]

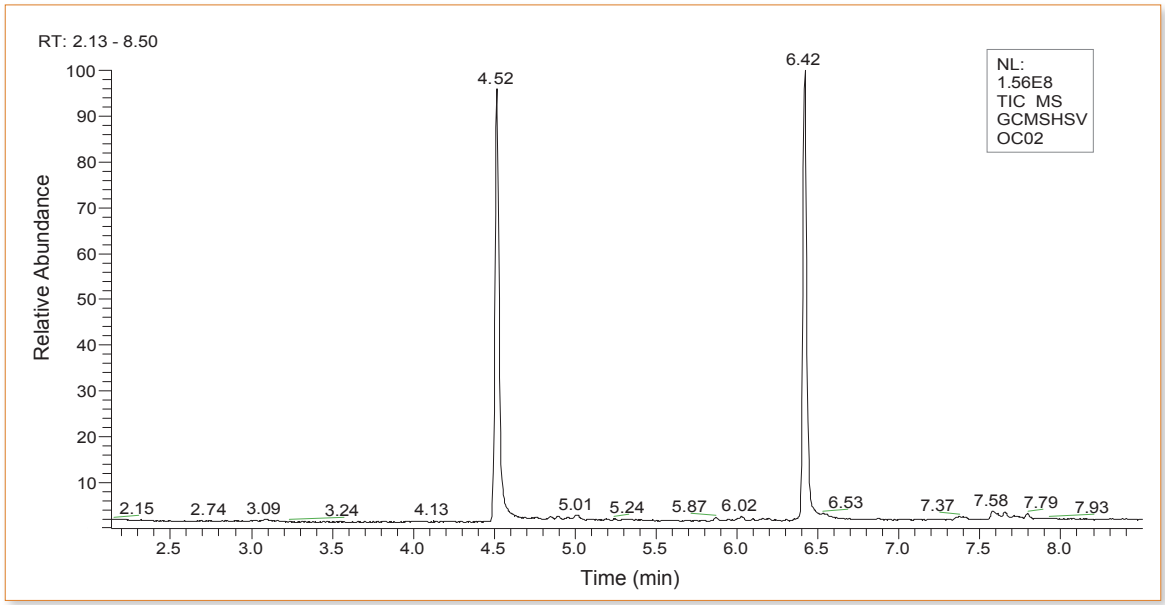

Figure 1—Chromatogram of a "zero-VOC" colorant.

Among the more precise methods is ISO 11890-2:2006. This is a method developed in the year 2000 by the International Standards Organization (ISO) and is the responsibility of the European Committee for Standardization (CEN). This method measures VOC content within the range of 15% (150000 ppm) to 0.1% (1000 ppm) by mass. The standard "Paints and varnishes—Determination of volatile organic compound (VOC) content—Part 2: Gas-chromatographic method" measures VOC content in coatings with direct injection gas chromatography and a flame ionization detector (FID). The samples are prepared by dilution with tetrahydrofuran (THF) or methanol. Quantification is performed against an internal standard, isobutanol, and a 250°C marker of tetradecane or diethyl adipate. One of the challenges with this method is that it requires a priori knowledge of the sample. Coating samples containing less than 1000 ppm in the coating or samples with greater than 15% VOC may provide erroneous results. The CEN recommends ISO 11890-1 for VOC content in coatings where the expected amount is larger than 15%. This is a simpler method that involves oven determination of volatiles. Also, the range is too large to be accurate for a peak area comparison by one internal standard. Slight error in measuring peak areas could drastically affect the accuracy of VOC in the lower end of the method range as well as the upper end. Finally, the flame ionization detector identifies peaks, but does not provide identification of volatiles. This method is not suitable for coatings with exempt solvents because it does not identify the volatiles in the coating. One must match known standard peaks in the standard addition samples to peaks within the chromatogram of the coating without the standard additions to indirectly identify the volatile.

Another European method practiced to measure VOC content is ISO 17895:2005-06, "Determination of the Volatile Organic Compound Content of Low-VOC Emulsion Paints (In-Can VOC)." This method was approved in 2005 and superseded DIN 55649:2001-03. It measures VOC content from 0.1% (1000 ppm) to 0.01% (100 ppm) by mass. This method is a headspace gas chromatography method. The samples are prepared by 50% dilution with citrate buffer and measured against a standard addition calibration curve ranging from 100 ppm to 1000 ppm of a known solvent mix. A 15 mg sample of the buffer/coating mix is added to the bottom of a headspace vial. The method allows for the buffer/coating mixture to be heated to 150°C in a septum-sealed vial and, when fully evaporated, the vapor phase is transferred to a nonpolar capillary column. The peak areas of all the components with retention times less than that of tetradecane or diethyl adipate are integrated to determine the amount of VOC content. Issues with this method revolve around the low weights that technicians must add to the headspace vials. The low mass allows for a higher percentage of relative error with each handling of the samples for the numerous trials. Slight differences in peak area integration lead to large differences in VOC content. Also, this method requires a large amount of consumables as well as time. Each sample with standard addition curve is run in triplicate and requires 20 headspace vials.

ASTM D6886-12 is currently being used by many U.S. companies to determine VOC content in many different types of coatings. ASTM International initially released this method in 2003 and reapproved it in 2009, with the recent modification made in 2012. This method is intended primarily for waterborne coatings with VOC content between 0.005% and 5%, but the method states it has been used successfully with higher percentages. The method may also be used to measure exempt solvents, as in D6133 and D6438. Samples are diluted in THF or methanol for direct injection onto the column, but the description of the method also allows for solid phase microextraction (SPME) to detect levels below 0.05%. Using SPME, samples are not diluted with solvent and headspace is collected. Calculation of volatile content in ASTM D6886-12 is based on integration of peak areas compared to an internal standard. This method, however, requires a priori knowledge of the sample in order to obtain accurate results and has percentage error results over 15% based upon the coating type.[8] The method recommends the use of the mass spectrometer for proper

Table 1—ISO 11890-2 and ISO 17895 Results

ISO 11890-2				2nd Lab VOC
Sample	**mg/kg**	**g/L**	**VOC wt%**	**wt% Results**
Red Colorant	914.5775	1.32065	0.09%	0.10%
Orange Colorant	919.4116	1.200752	0.09%	0.10%
Violet Colorant	1456.344	1.740331	0.15%	0.16%
Green Colorant	1668.262	2.627512	0.17%	0.34%
Black Colorant	988.8448	1.465468	0.10%	0.11%

ISO 17895				2nd Lab VOC
Sample	**mg/kg**	**g/L**	**VOC wt%**	**wt% Results**
Red Colorant	956.723	1.3815	0.10%	0.12%
Orange Colorant	511.8525	0.6685	0.05%	0.05%
Violet Colorant	not run	not run	not run	0.81%
Green Colorant	3331.563	5.2472	0.33%	0.49%
Black Colorant	930.929	1.3796	0.09%	0.09%

identification of samples, as well as knowing the response factor of each solvent in the specific GC system. The method contains response factors for several solvents, but they pertain to the ASTM laboratory's GC system and may not correlate to the GC systems in other labs. When using any solvent as a dilution, e.g., methanol or THF, it is not possible to predict the effects on the complex matrices of paint coatings.

None of the methods mentioned thus far are uniformly ideal for all coatings on the market today. As one can readily observe, it is difficult to collect and measure the volatiles from a controlled sample. Let us go one step further and envision the VOCs emanating over time from the side of a building or a classroom wall, as an example. There are emission method standards involving small sections of painted substrates in an oven attached to a GC for concentration analysis. These VOC emission GC methods are currently being assessed in Europe and have their own measurement inaccuracies. So far, the focus is on VOC analysis of the paint dispersion with the assumption that all of the volatiles in the can make it to the coating on the wall and then eventually volatilize from the coating. This assumption is debated among the paint manufacturers, coating societies, and governing bodies.

If only it were as simple as measuring the paint, coating, or film. There is more. Some base paint systems experience interactions that negatively skew the results. For example, several colorants, mixed with THF, during dilution, form gelled material and the mixture cannot be tested. Other colorants interact with methanol, creating more volatiles than originally present in the dispersion. Another example of the complexity of these methods is the comparison of ISO 11890-2 and ISO 17895. One might think that these two methods complement each other due to the range of percentage VOC. ISO 11890-2 measures VOC content from 15% to 0.1%, while ISO 17895 measures VOC content from 0.1% to 0.01%. Testing results in *Table* 1 attest to the contrary.

Some of the colorant results (red, orange, and black) possess comparable results between methods. However, the violet and the green results are incongruous. The results of ISO-17895 for the violet are five times higher than the results of ISO 11890-2.

Running these methods concurrently with a sample leads to more confusion than accurate results. For example, the direct injection method of ISO 11890-2, after dilution with THF, may lead to a VOC content result of 0.16%, as in the violet colorant. This result is within the range for this test method, but at the low end. However, to assure continuity, the analyst also runs ISO 17895. The result of analysis using headspace ISO 17895 on the same sample, now diluted with citrate buffer, is 0.81%. Which answer is correct? Is either one correct?

Sample Using 11890-2	mg/kg	g/L	VOC wt%
Yellow Oxide Formula A	50611.29	93.75	5.06
Yellow Oxide Formula B	253.11	0.47	0.03
Yellow Oxide Formula C	1313.00	2.46	0.13

Table 2—ISO 11890-2 Results on Different Formulations

Yellow Oxide	Average VOC Results		
Sample	mg/kg	g/L	VOC wt%
Formula A	5548	10.38	0.55%
Formula B	92.9	17	0.01%
Formula C	2469	4.57	0.25%

Table 3—ISO 11890-2 Wax Column Results on Three Formulations

Samples in *Table* 2 were run using the ISO 11890-2 method without a priori knowledge of the samples.

The tabular results seemed reasonable until the analyst presented them back to the formulator and learnt that Formula A has 24% volatile glycols. Had she known the approximate volatiles of each sample, she would have known the proper method for VOC. Formula A should have undergone method ISO 11890-1 because it contained volatiles over 15%. The analyst had used THF as the solvent with these samples instead of methanol; had she known the samples were waterborne, she would have chosen the appropriate solvent and an appropriate column. What effect does the column have on results? The sample results from *Table* 2 were obtained using a PDMS column. The results in *Table* 3 were obtained using a wax column.

As can be seen, the wax column was less effective in picking up glycols in Formula A and obtained nearly double the VOC in Formula C. The type of column does affect the results of VOC. It's more than likely that the solvent, THF, which was used as the dilution solvent for this method, affected the results on the different types of columns.

Of all the methods mentioned, the headspace analyses possess the greatest promise and logically are the most relevant with respect to the overall goal of measuring the amount of volatiles that could potentially leave a coating and have a negative effect on the environment. With that in mind, headspace makes the most sense. If the chemist could minimize the sample preparation (e.g., dilution with solvent and/or buffer), that would reduce the intricacies of otherwise complicated matrices, and create a more ideal result.

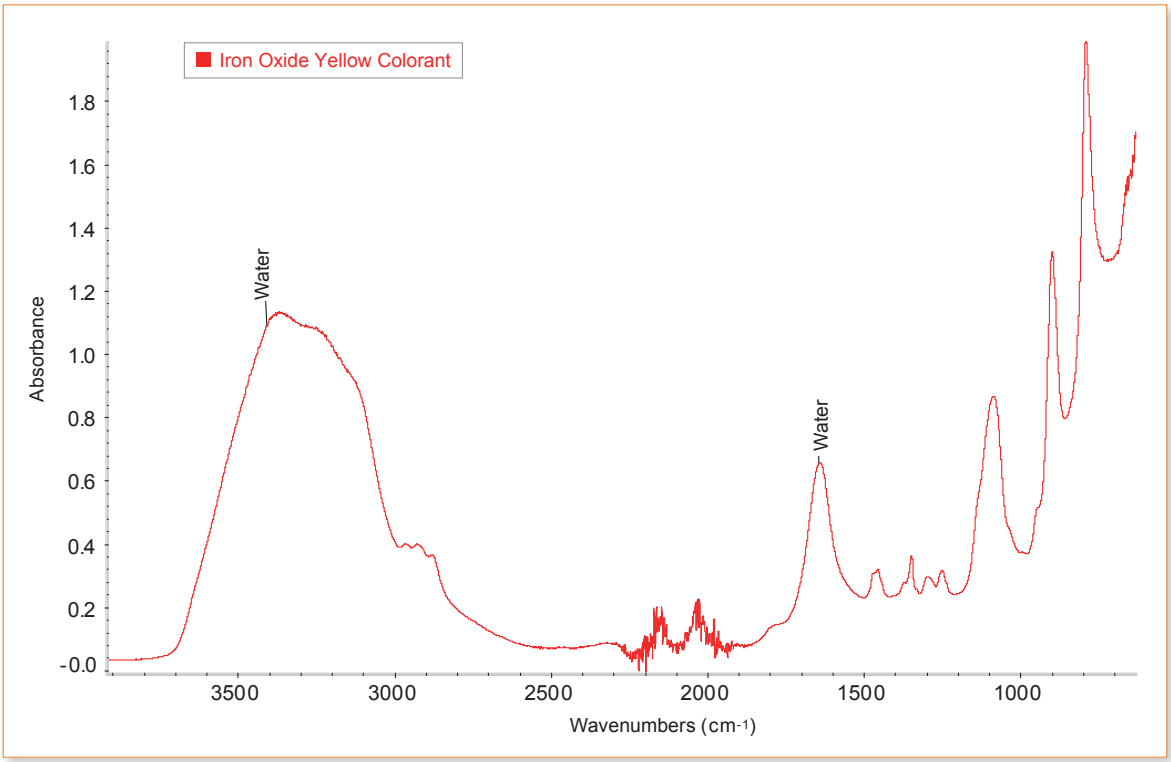

Figure 2—FTIR of waterborne colorant Formula B.

Table 4—Thermogravimetric Analysis Results

Yellow Oxide Sample	Volatiles RT-100°C with Isotherm	Volatiles 100–250°C	Volatiles 250°C Isotherm	Volatiles 250–600°C	Residual Solids
Formula A	33.25%	4.25%	6.60%	4.90%	51.00%
Formula B	27.50%	0.71%	5.18%	11.86%	54.75%
Formula C	20.23%	1.14%	10.74%	16.46%	51.43%

To that end, the D6886-12 modification for non-solvent dilution headspace with or without solid phase microextraction (SPME) is the best option for VOC content below 5%. This method selection requires a priori information on the sample before headspace GC analysis.

ANALYSIS OF UNKNOWN COATINGS SAMPLES FOR VOC CONTENT

The following method allows for testing of unknown coatings samples to determine VOC content. Initially, samples undergo Fourier transform infrared spectroscopy (FTIR) analysis for determination of coatings type and possible solvent types. Begin by determining if the sample is waterborne, 100% solids, or solventborne by FTIR. If it is waterborne, develop a technique such as 9-ATR FTIR for glycol identification via evaporation of water.

After the FTIR determination, the next step of sample preparation involves thermogravimetric analysis (TGA). TGA measures weight loss through volatilization of a sample after heating on a balance in an oven under nitrogen gas. Determination of the amount of volatiles at a 100°C isothermal period and then at a 250°C isothermal period is an important step in determining the appropriate GC headspace method.

Karl Fischer titration moisture analysis is required to measure the amount of water in the coatings sample. The amount of water subtracted from the volatiles in the TGA results approximates the relative amount of organic volatiles in the coatings sample. This result is used to determine the appropriate GC headspace method.

The final step is GC-MS headspace analysis on the sample. This is a deviation from ASTM D6886-12 and ISO 17895. The method calls for 15 mg

of neat sample (no dilution with solvent) weighed into a headspace vial and incubated to 150°C for 4 min. The headspace is then injected onto the column for separation and analysis by the mass spectrometer. The standard addition model follows the ISO 17895 method but without dilution of citrate buffer.

Example of Analysis of Unknown Coating for VOC Content

The following example depicts the test method. Yellow oxides of Formulas A, B, and C were tested using the above method. Results of FTIR indicate that all samples contain water. As shown in *Figure* 2, the peaks for water are easily discernible.

Results of TGA testing in *Table* 4 reveal the approximate amount of volatiles in each sample at 100°C with isotherm and 250°C with isotherm.

Results of Karl Fischer titration analysis in *Table* 5 indicate that all three products are formulated with significant amounts of water. When comparing the TGA results with the Karl Fischer titration results in *Table* 6, one obtains an approximation of the VOCs in the colorant formulas.

Given the approximate VOC results from the TGA and FTIR, Formulas B and C are eligible for ISO 11890-2 testing. The results of this testing are tabulated in *Table* 7. The VOC content for Formula A is too high for ISO 11890-2 testing.

Results of ISO 11890-2 indicate that the samples are eligible for ISO 17895 testing. *Table* 8 contains the ISO 17895 results.

Each test in the method is predicated on the results of the previous test, except the FTIR test. The results of the solvent/dilution free method, GC-MS HS, are displayed in *Table* 9.

Results of *Table* 9 show that GC-MS HS could not detect all of the 24% volatile glycol mix in Formula A. That result would indicate an approximate maximum 5% VOC for this method. Results also show a reduction in VOC for Formula B and an increase in VOC for Formula C.

A second analysis of this method, shown in *Table* 10, incorporated an entire colorant line of 12 different colors compared to ASTM D6886-12 using the same column and mass spectrometer.

The GC-MS HS method measured lower VOC in 10 of 12 samples except for the organic yellow and the organic red. *Figure* 3 illustrates the differences in the measurement results.

It is possible that the solvent use in ASTM D6886 suppresses VOC in some samples and creates more VOC in others.

Another example of ASTM D6886-12 exhibiting higher VOC results than GC-MS HS includes three competitive samples from European suppliers,

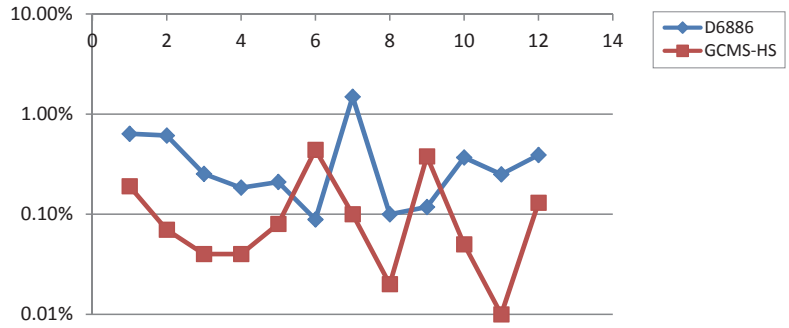

Figure 3—D6886 vs GC-MS HS VOC.

Table 5—KF Titration Results

Yellow Oxide	Average
Sample	% Water
Formula A	10.76%
Formula B	25.77%
Formula C	17.40%

Table 6—Approximate VOCs after TGA and KF Titration Analyses

Yellow Oxide	Volatiles	Average	Approx.
Sample	<250°C	% Water	VOC
Formula A	37.50%	10.76%	26%
Formula B	28.21%	25.77%	2%
Formula C	21.37%	17.40%	4%

Table 7—ISO 11890-2 Results on Formulas B and C

Yellow Oxide	Average VOC Results		
Sample	mg/kg	g/L	VOC wt%
Formula B	253	0.47	0.03%
Formula C	1313	2.46	0.13%

Table 8—ISO 17895 Results

Yellow Oxide	Average VOC Results		
Sample	mg/kg	g/L	VOC wt%
Formula B	588.2	1.10	0.06%
Formula C	913.4	1.71	0.09%

Table 9—GC-MS HS Method Results

Yellow Oxide	Average VOC Results		
Sample	mg/kg	g/L	VOC wt%
Formula A	69961	130.83	7.00%
Formula B	77.9	0.15	0.0078%
Formula C	1909.9	3.57	0.1910%

Table 10—VOC Measurement Comparison of D6886-12 and GC-MS HS

Colorant	D6886-12 (MS)			GC-MS HS VOC		
Sample	mg/kg	g/L	VOC wt%	mg/kg	g/L	VOC wt%
Black	2346.8	2.8	0.24%	1896.1	2.22	0.19%
Yellow Oxide	6132.5	11.83	0.61%	728.2	1.4	0.07%
Green	2528.3	3.29	0.25%	378.3	0.49	0.04%
Blue	1840.2	2.26	0.18%	444.8	0.55	0.04%
Red Oxide	2098.2	2.65	0.21%	825.2	1.82	0.08%
Yellow	885.6	1.17	0.09%	4417.1	5.81	0.44%
Violet	14887.8	18.61	1.49%	1041.1	1.03	0.10%
Raw Umber	997.6	1.26	0.10%	243.5	0.31	0.02%
Red	1180.1	1.49	0.12%	3784.2	4.78	0.38%
Quindo Violet	3687.1	4.72	0.37%	477.5	0.61	0.05%
Titanium Dioxide	2477.5	5.03	0.25%	56.1	0.11	0.01%
Medium Yellow	3860.5	4.67	0.39%	1276.7	1.54	0.13%

which claim to have low or no VOC. In this case, the three samples underwent three different methods to determine VOC—ISO 17895, ASTM D6886-12, and GC-MS HS—shown in *Table* 11.

ASTM D6886-12 results show dramatic increases in VOC from the other two methods by 5000-7000%! The perplexed analyst wonders, "Which numbers are accurate?" It appears as though the methanol used in ASTM D6886-12 creates volatiles that were not present previously or lowers the volatility of otherwise nonvolatile ingredients. FTIR, MS, and TGA results reveal that the HEEU in the colorants interacts with the methanol and volatilizes at a much lower temperature than 400°C.

In general, architectural coatings formulations have complex matrices and interactions with dilution solvents that are nearly impossible to predict. The regulations requiring lower VOC take more and more ingredients out of formulators' hands. These lower-VOC regulations lead to even higher complexity formulations with newer types of ingredients and different chemistries than have been historically used. All of these factors increase the likelihood of solvent dilution–coatings interactions that affect the VOC testing results. Using a method without a solvent dilution makes the most sense and mimics field applications closer than direct injection of a THF, methanol, or buffer solution.

The GC-MS HS method eliminates the variables of coatings–solvent interactions because of the minimal sample preparation that could result in variation. The greatest variation occurs in the standard addition sample preparation. That variation is measured with a coefficient of determination, R^2, plot shown in *Figure* 4. The plot of the sample points in the standard addition should be linear with this method. The higher the R^2 value from the data points, the greater the linearity and the greater the confidence in the method.

Ideally, each standard point should be in contact with the solid trend-line. The slope is critical in calculation of the weight percent of VOC. A slight error in slope affects the value of x when y equals 0 in the equation of the line, $y = mx + b$. *Figure* 5 illustrates a poor mix of the solvent standard blend with the architectural colorant in some of the addition samples (1000 ppm and 1400 ppm).

When a poor correlation occurs, sample standard addition preparation of the colorants and standards begins again. An analyst quickly learns the importance of proper shaking. When the method does not involve a dilution, the standard addition solvents are more difficult to incorporate into the samples. Assurance of homogeneity is a known variable, which contains observable effects, R^2. The coefficient of determination is a measure of the method accuracy.

CONCLUSIONS

The GC-MS HS method is believed to be preferable to the other methods mentioned here due to its lower inherent variability and its adaptability to future regulations for lower-VOC requirements. This method was developed for use in measuring VOC (<5% by weight) in architectural waterborne coatings for the purpose of obtaining consistent results without the use of dilution solvents. This method is not a perfect one, but it reduces the pitfalls of the

Table 11—Comparative VOC Methods for Three Colorants Within the Same Line

Colorant	ASTM D6886-12			ISO 17895			GC-MS HS VOC		
Sample	mg/kg	g/L	VOC wt%	mg/kg	g/L	VOC wt%	mg/kg	g/L	VOC wt%
Yellow Oxide	25548	34.69	2.55%	102	0.14	0.01%	339	0.46	0.03%
Red Oxide	31838	59.15	3.18%	293	0.54	0.03%	624	1.16	0.06%
Titanium Dioxide	28176	43.57	2.82%	153	0.31	0.02%	496	0.99	0.05%

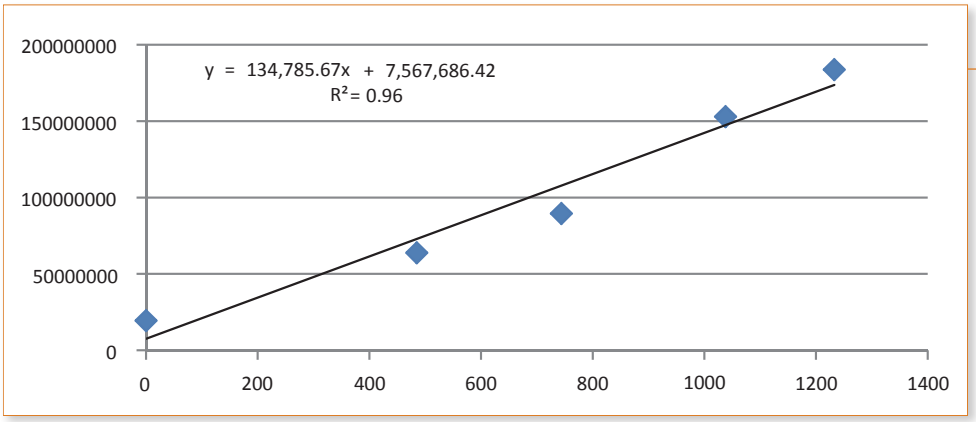

Figure 4—Peak area vs ppm, standard addition chart with good R^2.

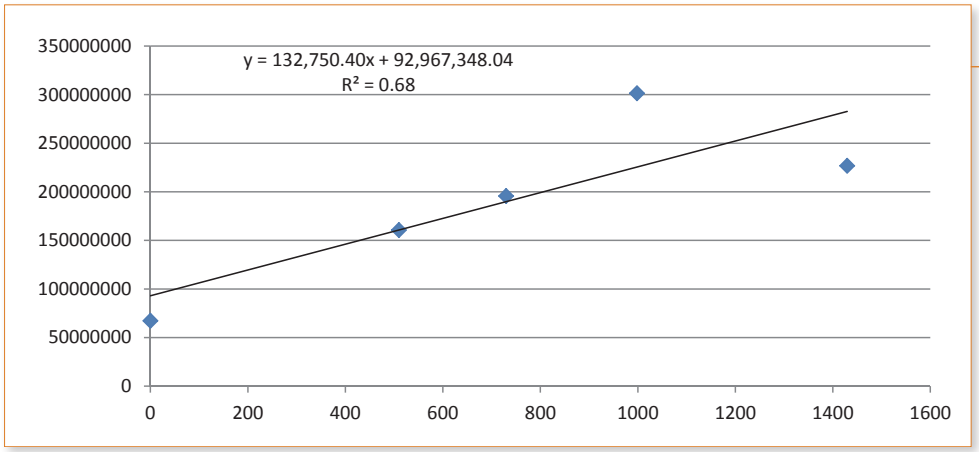

Figure 5—Peak area vs ppm, standard addition chart with poor R^2.

other methods in a step-wise reduction of handling errors and solvent–sample interactions. It reduces the amount of consumables, solvents, and solvent waste. More work in this area is necessary from the skilled chemist to determine method error, reproducibility, applicability to other coatings, and interlaboratory correlation of results.

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References

1. Paint and Coatings Industry News, "FTC Hits Paint Makers on Green Claims," *J. Arch. Coat.*, Durability and Design News, October 26, 2012; http://www.durabilityanddesign.com/news/?fuseaction=view&id=8614.
2. Environment Canada, Definition of VOC; http://www.ec.gc.ca/inrp-npri/default. asp?lang=En&n=EF5C823B-1.
3. South Coast Air Quality Management District, Definition of Terms, SCAQMD Rule 102, March 2013; http://www.aqmd.gov/rules/reg/reg01/r102.pdf.
4. Environmental Protection Agency (Content Source); Cutler J. Cleveland (Topic Editor) "Origins of the Environmental Protection Agency," In: *Encyclopedia of Earth*, Cleveland, C.J. (Ed.) [First published in the *Encyclopedia of Earth*, November 17, 2009; Last revised November 17, 2009; Retrieved March 7, 2013]; http://www.eoearth.org/article/Origins_of_the_Environmental_Protection_Agency.
5. Environmental Protection Agency, Press release, "EPA Sets National Air Quality Standards," April 1971.
6. Federal Trade Commission, "Enforcement Policy Statement Regarding VOC-Free Claims for Architectural Coatings," p 1-2, 2012.
7. Brickweg, L., Guillermo, A., Jones, D., and Wills, M., "Comprehensive VOC Analysis Method for Architectural Coatings,"*Technology Today*, p 2 (2007).
8. Jones, D. and Wills, M., "Development of an Improved VOC Analysis for Architectural Coatings," California Air Resources Board Report and California EPA, July 31, 2006.

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