

Sources of Error in VOC Determination via EPA Method 24

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Forty-five paint samples having volatile organic content (VOCs) ranging from 7 to 562 g/L were prepared and tested for VOC according to EPA Method 24. In addition, all individual raw materials utilized in preparing the paints were also tested for their VOCs. There were significant differences between claimed and measured VOCs for both raw materials and finished paints. The

measurement error for VOC of finished paints was eight percent. This error increased exponentially as the VOC declined below about 250 g/L, reaching about 200% at VOCs below 50 g/L. The range of error also increased exponentially below about 250 g/L, reaching 1000% below 50 g/L. The major sources of VOC error in all cases were in the water and nonvolatile determinations.

INTRODUCTION

Since the creation of EPA Method 24 in 1984,¹ the coatings industry has had a standard test by which to measure volatile organic content (VOC) in paint, as opposed to relying on calculated "theoretical" or "formulation" VOC. The test method to determine a paint's VOC has three component ASTM tests:

(1) Total volatile matter of paint is determined according to ASTM D 2369.² This method assumes that all volatile matter will leave the film after one hour at 110°C. There have been studies showing that certain coalescing solvents can be retained in the polymer phase under these conditions,^{3,4} thus decreasing the measured volatile matter content.

(2) Water content is determined either by gas chromatography (ASTM D 3792⁵) or the Karl Fischer method (ASTM D 4017⁶). With gas chromatography (GC), interferences in retention time from other volatile matter and water absorbed within the dilution solvent or internal standard can skew the results.⁷ With the Karl Fischer (KF) method, pH excesses and various side reactions can skew the results.⁸

(3) Paint density is determined according to ASTM D 1475.⁹ The most common problem with density measurements is with entrained air. This is commonly dealt with by some form of deairation, such as ultrasonic or vacuum treatment.

It is well known that VOC measurements carry a high degree of variability

or "error" due to the issues mentioned previously. In fact, it is possible to obtain VOC values that range from much higher than expected (according to the customer), to negative values with paints having very low nominal VOCs.¹ As of this writing, the only other significant work in systematically assessing the errors of EPA Method 24 was done by Jenkins et al.¹⁰ of the Los Angeles Society for Coatings Technology, which dealt largely with the determination of water. With this in mind, we designed a study to include all of the components of the VOC test, using some of the more typical types of paint samples that we have received for VOC analysis over the past year.

COMMERCIAL EXAMPLE

As an example of the issues involved, we measured the VOCs of two commercial paints purchased locally from major manufacturers. Each paint was tested on 10 successive work days by the same person. The first paint represented the difficult end of the spectrum: first line exterior latex flat that claimed a VOC of less than 100 g/L on the label. The second represented the easier end of the spectrum: exterior solvent-based alkyd (no VOC claim made). The average VOC for the exterior flat latex paint was 97 g/L, with a 25 g/L (26%) standard deviation and a range of 46 to 126 g/L (82%). The average VOC for the solvent-based paint was 325 g/L, with a standard deviation of 2.4 g/L (0.74%) and a range of 321 to 328 g/L (2.2%). This reinforces the point made by Brezinski¹ that the error in VOC measurements appears to be inversely proportional to the nominal VOC of the sample.

EXPERIMENTAL

Paint Samples

Our main study included 45 paints that were formulated and prepared in-house. They included two solvent-based paints (as reference/controls), four water reducible pigment dispersions, 18 water reducible paints, and 21 latex paints. Since the samples for the study were prepared in-house, the exact amount of each of the raw materials in each of the paints was known, and all of the raw materials could be individually analyzed.

The paints were formulated to yield a wide range of nominal VOC from very low (7 g/L) up to fairly high (562 g/L). The latex paints were made with an acrylic emulsion synthesized in-house that was not neutralized, so that we would have more accurate information about solids and water content. Both semigloss and flat paints were formulated ranging from no additional solvent or coalescent added, up to higher-than-normal levels of solvent and coalescent.

The water-reducible paints were made with two commercially available resins. One was a water-reducible alkyd that we formulated to contain minimal levels of solvent, up to higher-than-normal levels (both semigloss and flat samples). All of these samples were formulated to contain alcohols, since we thought that alcoholic solvents would pose the greatest problem with water concentration determination. The other resin used was a water-reducible epoxy-ester, formulated the same as with the water-reducible alkyd except that no alcoholic solvents were used. The pigment dispersion slurries used were the precursors to the previously mentioned water-reducible paints.

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VOC Testing

All of the VOC testing was conducted utilizing EPA Method 24,¹¹ and its three constituent ASTM methods, D 2369 "Test Method for Volatile Content of Coatings," D 1475 "Test Method for Density of Paint, Varnish, Lacquer, and Related Products," and either D 3792 "Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph," or D 4017 "Test Method for Water in Paints and Paint Materials by Karl Fischer method." Both of the methods for determining water in a paint were compared to a theoretical value as determined by each raw material's water concentration, as determined by KF method. This was done because it is generally accepted (and verified in this study) that KF method is the best method to determine water concentration, especially since most new methods involve a comparison to the Karl Fischer method. Therefore, it was believed that the best calculated VOC value for each sample will be obtained by using the water concentration for each raw material as determined by the Karl Fischer method.

With some exceptions that will be noted, the raw materials were analyzed using the same constituent methods as EPA Method 24 for % nonvolatiles, density, and water concentration. The Karl Fischer titration method was used to determine the water concentration in the raw materials. The density values for the solvents and powder materials were taken from literature values or from technical data sheets. All of the samples were analyzed for water content except for the powder materials, which were analyzed for solids content, and the % volatile was assumed to be water.

We made the following assumptions:

(1) All volatile material lost from powder (mostly pigments) raw materials was assumed to be absorbed by water. This assumption is based upon input from the various suppliers to this effect. Initial testing showed that the greatest loss of weight observed from a powder would translate to less than 0.1% difference in water concentration in any paint.

(2) All literature values for density of solvents and powder materials were considered accurate. This assumption is based upon test measurements that showed an average density difference of less than 0.01 lb/gal for solvents. We did not attempt to measure the density of powdered materials directly.

After we made all of the paints and analyzed all of the raw materials, we calculated theoretical density, % non-

volatile, and water concentration of each of the paint samples. The nonvolatile (NV) content of each paint was calculated by summing the solid weights of all the raw materials and dividing by the total weight used [equation (1)].

$$\% \text{ NV} = \left(\frac{\sum (\text{Solid weight of each raw material})}{\text{Total weight}} \right) \times 100 \quad (1)$$

The paint densities were calculated by summing the total weights used and dividing by the total volumes used [equation (2)].

$$\text{Density} = \frac{\sum (\text{Total weight of each raw material})}{\text{Total volume}} \quad (2)$$

The water concentration of each sample was calculated by summing the water content of each raw material, as well as the water added, and dividing

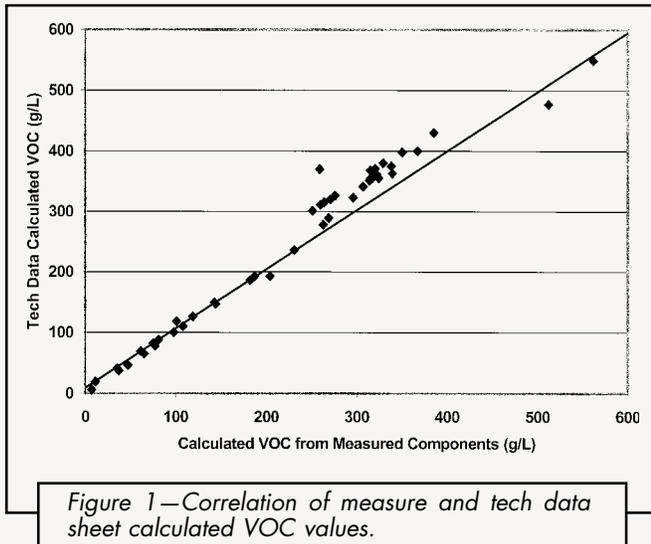
by the total weight of the sample [equation (3)].

$$\% \text{ Water} = \left(\frac{\sum \left(\frac{\text{Water in each raw material}}{\text{Total weight}} \right) + \frac{\text{Water added}}{\text{Total weight}}}{\text{Total weight}} \right) \times 100 \quad (3)$$

VOC values are typically reported in pounds or grams of total volatile organic material per dehydrated gallon or liter paint. Dehydrated paint is a regulatory concept created to prevent the simple dilution of paints with water to obtain compliance, and involves subtracting any water from component values before performing the VOC calculation. To obtain these numbers one must determine the density of the paint, the % volatile portion of the paint, and the water concentration, from which one can calculate VOC by using [equation (4)]:

Table 1—Calculated (from Measured vs. Claimed) VOC Values for All Samples

Sample Description	Analytically Derived Raw Material Values	Tech Data Sheet Raw Material Values
Flat Latex (FL)	7	6
Semigloss Latex (SGL)	11	19
SGL	35	41
FL	37	37
FL	47	46
SGL	61	69
FL	65	65
SGL	75	82
FL	77	78
SGL	81	88
FL	98	100
SGL	101	118
FL	108	110
SGL	119	126
SGL	143	149
FL	144	147
FL	182	186
SGL	187	193
FL	204	193
SGL	231	236
Water Reducible Dispersion (WRD)	251	301
Water Reducible Flat (WRF)	259	370
WRF	260	311
SGL	263	278
WRF	264	315
WRD	269	289
WRF	271	320
WRF	276	326
WRF	296	323
WRD	307	341
WRD	314	351
Water Reducible Semigloss (WRG)	315	355
WRG	315	368
WRG	317	355
WRG	320	371
WRG	322	361
WRF	324	355
WRG	329	380
WRG	338	375
WRF	339	363
WRG	350	398
WRG	367	400
WRG	385	430
Solvent Based Flat	512	477
Solvent Based High Gloss	562	549



$$\text{VOC} = \frac{(W_v - W_w)(D_c)}{100\% - (W_w)(D_c/D_w)} \quad (4)$$

where:

- W_w = wt% of water
- W_v = wt% of volatile
- D_c = Density of coating
- D_w = Density of water

RESULTS AND DISCUSSION

The following discussion will first cover the component tests, and then VOC as a composite result. For the balance of this paper, we use the term “measured” to refer to the direct measurement of finished paint VOCs or component VOCs; and the term “calculated” to refer to paint VOCs calculated from component VOCs, whether measured or taken from product literature (“claimed”).

Percentage differences are calculated using our best-case analytical values as the reference point. “Absolute” differences are the absolute values of the differences obtained. The use of absolute value is helpful in illustrating error levels, since they eliminate self-canceling tendencies with positive and negative differences.

Calculated Paint VOCs

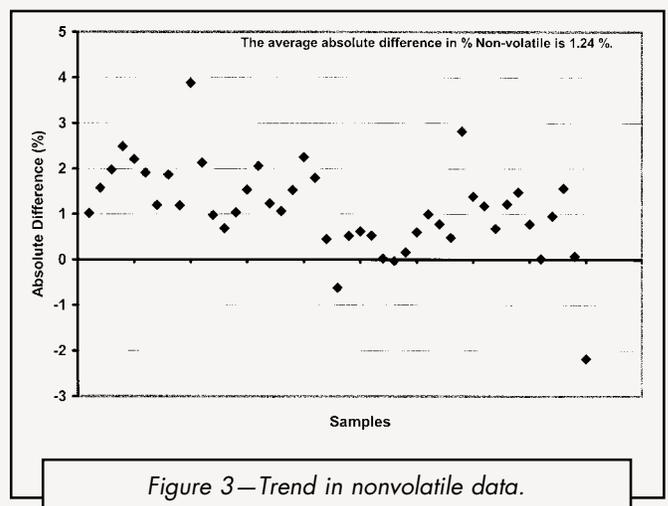
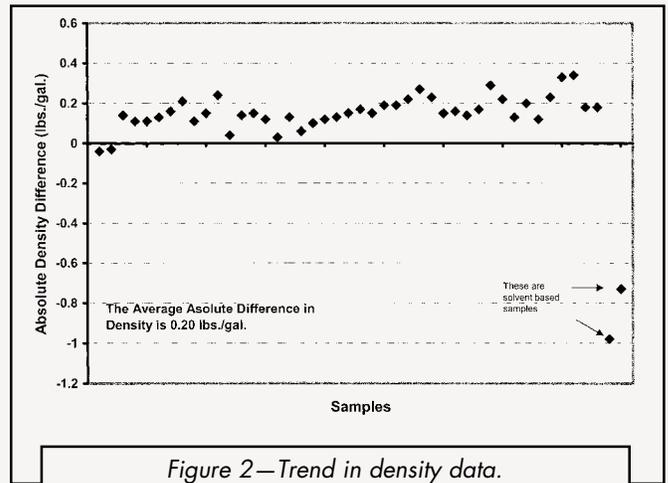
Table 1 contains a complete list of paints and their VOC values as calculated from measured physical constants for each raw material (“calculated/measured”) and as calculated from the claimed constants on each raw material technical data sheet (“calculated/claimed”). The table lists the paints in ascending order, according to the VOCs calculated from measured raw material VOCs. Figure 1 shows the correlation of the paint VOCs derived from measured values to that derived from claimed

component values. The diagonal line represents a hypothetically perfect agreement between claimed and measured VOCs.

The agreement appears to be quite good for samples below about 250 g/L, and for the two solventborne samples in the 500-600 g/L range. However, in the middle range, VOCs based on claimed constants are significantly higher than those based on measured constants, suggesting some sort of systematic bias for this group of samples. Further investigation showed that this group consisted of the water-reducible samples, and the source of deviation was from the difference between claimed and measured VOCs of the resin system components. This illustrates the importance of having verified component raw material VOCs if one wishes to rely on calculated VOCs for the paint, as paint manufacturers would like to do.

Density

Given the deviations noted previously, for the balance of our work, the only calculated values we use are those derived from measured component values. We found the measured paint densities to be 0.20 lb/gal on the average higher than the calculated ones. Figure 2 clearly shows a strong bias in the measurement of density towards the positive direction. The two samples with the very much lower densities than expected are the two solvent-based samples. Un-



fortunately, with only two solventborne samples, we cannot provide any meaningful explanation for this deviation.

When calculating paint density, most formulators sum the weights and divide by the sum of the volumes, as we did to obtain our theoretical density values. By determining the density in this manner, the formulator is making an assumption that all of the volumes are additive, at least to a first approximation. Given that 41 of 45 cases provide higher than expected densities, perhaps this assumption should be revisited in the future in more detail to determine its relative contribution to the observed bias.

Nonvolatile Content

We found the measured nonvolatile content to be, on the average, 1.24% higher than the calculated values. Figure 3 shows a strong bias in the measurement of nonvolatile contents in the positive direction.

When calculating the nonvolatile content of a coating, most formulators sum

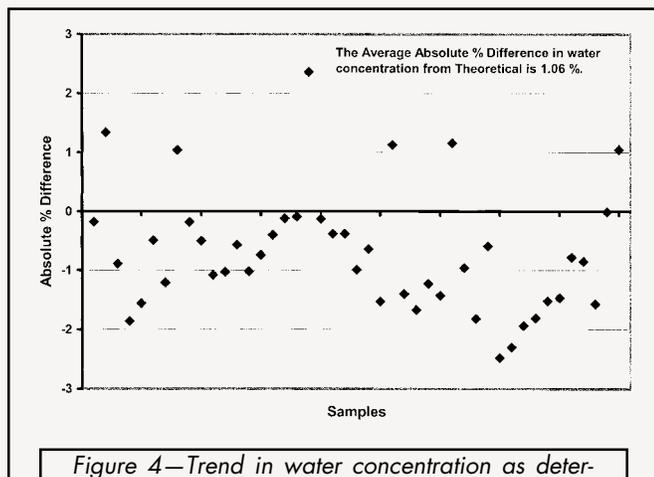


Figure 4—Trend in water concentration as determined by the Karl Fischer Method.

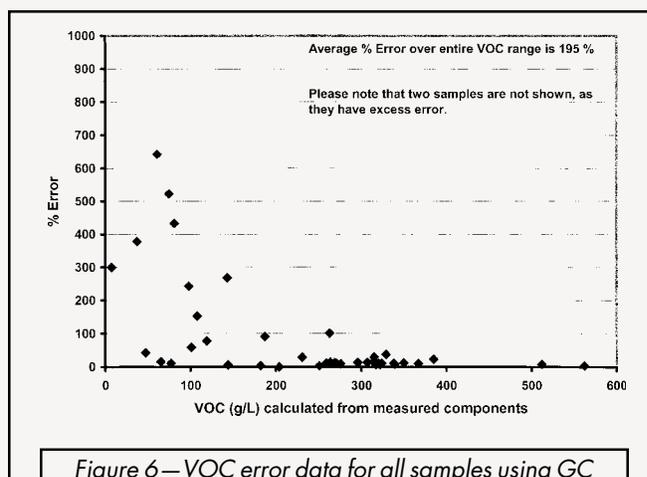


Figure 6—VOC error data for all samples using GC water data.

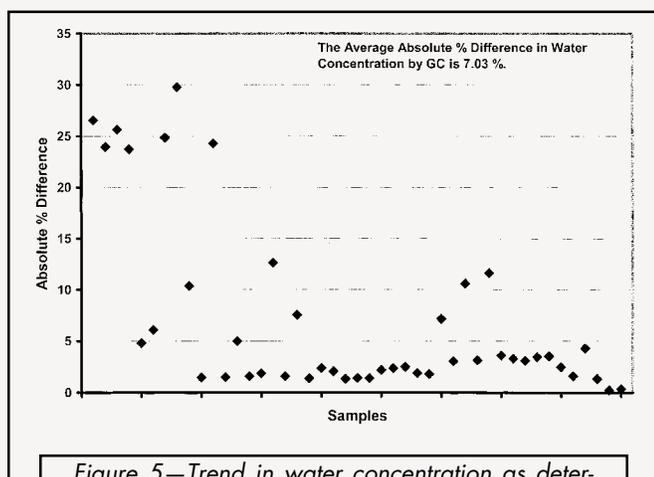


Figure 5—Trend in water concentration as determined by Gas Chromatography.

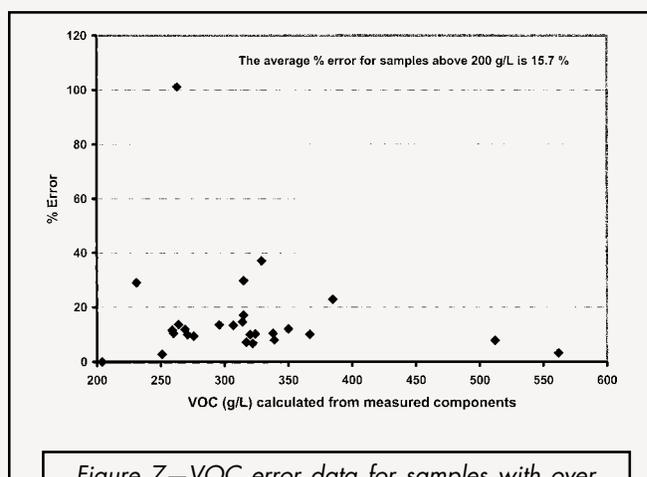


Figure 7—VOC error data for samples with over 200 g/L VOC using GC water data.

the solid material weights and divide by the total formulation weight, as we did. However we obtained measured values that were typically higher than expected. This could have a number of possible explanations. First, the paint could skin over while drying and entrap a small amount of volatile matter under or in the film. In previous studies¹² it has been shown that 0.2% of the water in a sample remained even after heating *in vacuo* for eight hours at 100°C. According to Hoy,³ some coalescents exist in the polymer phase of the paint system and therefore will act more like a plasticizer and may not leave the film at an appreciable rate. There is also the fact that some volatile components used will simply not come out of the sample at the temperature/time that is specified in EPA Method 24.⁴

Water Content

The water content of the paint samples was analyzed according to both of the EPA Method 24 accepted water

content methods. We will discuss them individually, as the Karl Fischer method proved to be much more reliable than the gas chromatography (GC) method.

KARL FISHER METHOD: The samples, as shown in Figure 4, were shown to have an absolute real difference in measured water content of 1.06% from the calculated value. Five samples had values higher than the calculated value; the remaining 40 samples had 0.81% less water than expected. Figure 4 also shows a bias in the negative direction for water content as determined by the KF.

The Karl Fischer titration is still one of the best methods available to determine water concentration, but it is not without drawbacks. For example, if the pH is too low (below 4)⁸ the titration reaction becomes sluggish and can yield higher than expected values. If the pH is too high (above 7) the titration reaction does not proceed.⁸ Certain metal oxides, such as zinc oxide,¹² interfere with the reaction. The presence of aldehydes and ketones can give erroneous results, as

they can react with most titration reagents and consume water, thus giving lower than expected results. Methanol has been shown to be the best overall solvent to use with the Karl Fischer titration; however, it may not be an adequate solvent for every particular coating, or even for a particular component of a coating. Even with the use of a homogenizer, which has been shown to greatly improve results with paints, there still exists the possibility that some of the water may become entrapped within methanol insoluble polymer droplets. With so many components in paints it is hard to judge for sure whether or not a particular component will interact with another component in such a way as to cause an interference with the overall titration reaction.

GAS CHROMATOGRAPHY METHOD: Figure 5 shows the overall trend for water content with respect to data recovered by gas chromatography. The value obtained by GC was less than the calculated value by an average of 7.03%. In

addition, 11 samples were found to contain over 10% less than the calculated value. Of the remaining 34 samples the average value was still found to be 2.71% less than the expected value. *Figure 5* shows convincingly the very strong bias in the negative direction of the water concentration as determined by GC. Thus, the KF method with an absolute difference of 1.06% is far more accurate than the best-case samples done by the GC method. It is important to note that all of the samples at the left of the graph with the greatest difference in water concentration are all semigloss latex paints.

The GC method relies on the peak area of the water in comparison to the peak area of an internal standard. Some problems with this method could be the change in retention of the peaks, which could alter the peak areas over time as solids become entrapped within the column packing material. Certain samples may entrap water within a particular matrix, whether pigment or polymer, and not be dissolved in the dimethyl formamide (DMF), and thus not be de-

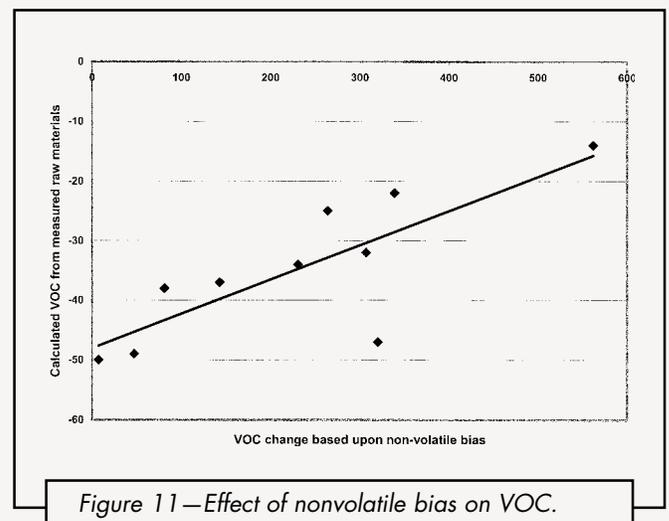
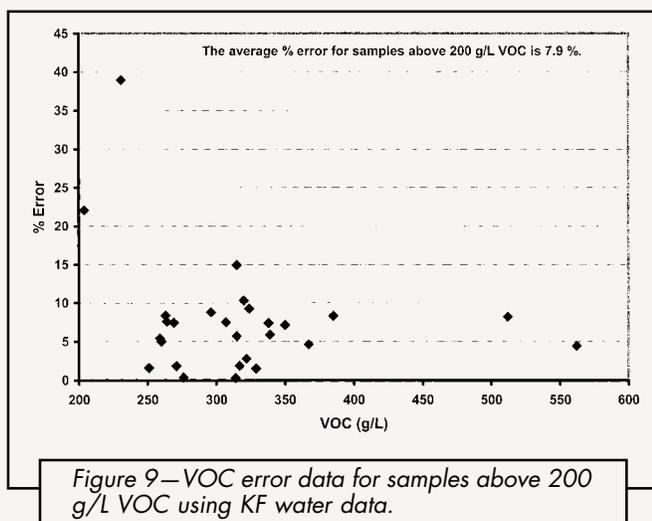
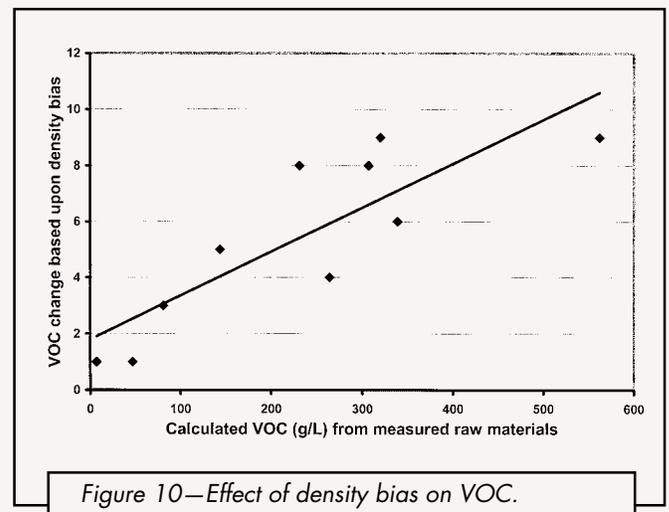
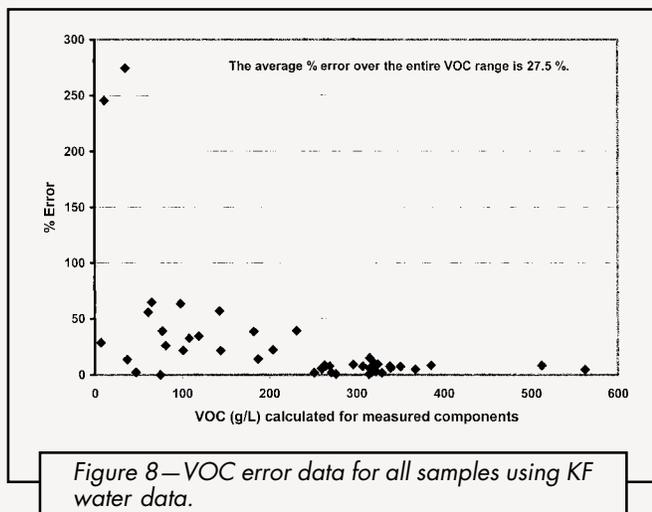
tected. Since the method requires the calculation of a response factor, the magnitude of error is now squared since the response factor has to be calculated and then used to calculate the water concentration. It is not surprising that the KF method, in most instances, is the method of choice in determining water concentration within a sample.

Volatile Organic Content

In the original project design we formulated some of the paints with varying solvents and levels of solvent. Analysis of the results did not show any pattern of VOC error as a function of the solvents that were used in the study, including alcohols. Since the water concentration error is the greatest using the data obtained by the GC method, we will discuss its impact on the VOC numbers first.

We used the measured values for nonvolatile content, density, and water (by GC) to determine the VOC value for each sample, and then compared those

values to the calculated values and determined that there existed an average of almost 192% error (using calculated as the true value) in all samples. The % error decreases to nearly 16% when looking at samples with calculated VOCs above 200 g/L. When only using the data for the 18 samples with calculated VOCs below 200% the error is nearly 75% and using the 11 samples with a calculated VOC of less than 100g/L the average error increases to above 685%. It is important to note that of the 45 samples studied two were found to have errors in excess of 1000%, and eight more were found to have errors over 100%. In essence, over 20% of the samples investigated were shown to have over 100% error, while only one of these samples had a calculated VOC above 200 g/L. *Figure 6* shows the overall trend in VOC error for samples over the entire VOC range (7 g/L to 562 g/L), while *Figure 7* shows the much-reduced error in VOC for the range above 200 g/L. Note that a sample having almost 4000% error was left off of *Figure 6*



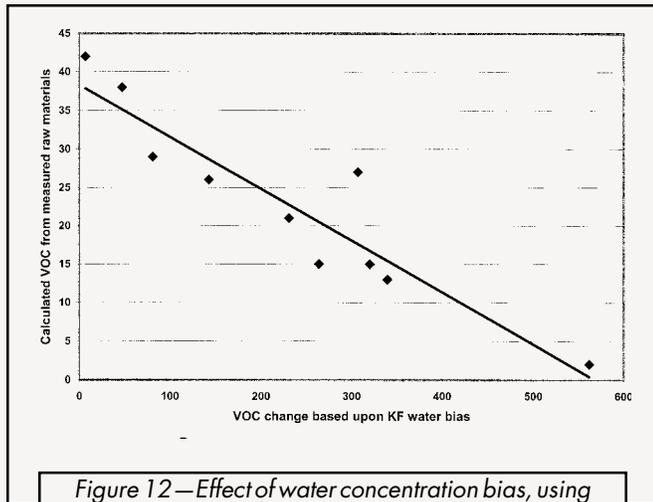


Figure 12—Effect of water concentration bias, using KF water data, on VOC.

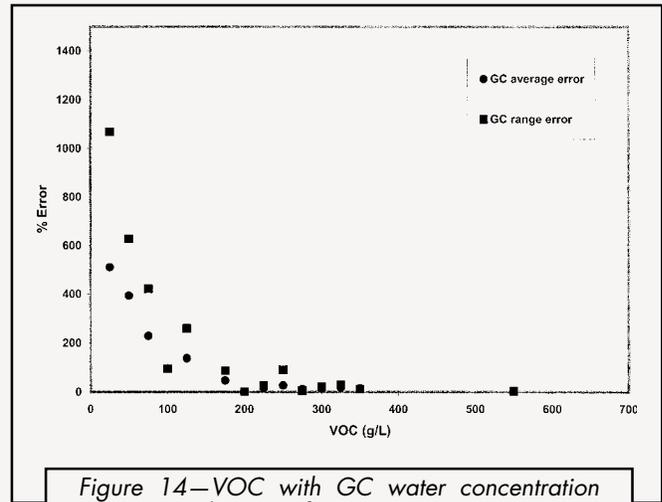


Figure 14—VOC with GC water concentration average and range of error.

so that a continuity in scale could be maintained with Figure 8.

The KF method produced similar graphs for the entire range of VOC and the range above 200 g/L (refer to Figures 8 and 9, respectively). The main difference between the graphs is the magnitude of the error. For the entire range using the KF water data, the VOC error was determined to be 21.64%, while above 200 g/L it was improved to 7.86%. While the error increased up to 42.3% for samples below 200 g/L VOC, it increased to 52.3% for samples below 100 g/L. The maximum error in VOC obtained using KF water data was nearly 275%, with 20 samples having error above 10%. The errors obtained in VOC values using the KF water data are much improved over the error obtained using the GC water data, however, the error is still significant enough to call into question the validity of the VOC values determined by EPA Method 24, especially for samples con-

taining less than 200 g/L. With this information in mind, henceforth when we refer to water concentration data we will be using the KF water concentration data.

Impact of Errors in Density, Nonvolatile, and Water on Paint VOC

We then set out to determine the effects of the differences in values measured versus the calculated values for density, nonvolatile and water on the overall VOC of the coating. We constructed graphs (see Figures 10-12) to show how the difference between each of the three measured values will each individually change the VOC value. This was accomplished by using the calculated values and determining the VOC value. We then substituted for one of the calculated values (either density, nonvolatile, or water) with the measured average absolute difference. For

example, with respect to density, we calculated the VOC value using all of the calculated values; we then recalculated substituting for the measured average absolute difference density value. This was done to 10 samples ranging from low to high VOC, to illustrate what effect the difference in density measured versus calculated has upon the VOC value. Notice in Figure 10 that the VOC change increases as the calculated VOC of the sample increases. Following the same procedure for the nonvolatile we obtain Figure 11 that shows a dramatic increase, over 40 g/L, in VOC using the average difference value as the VOC approaches zero. A similar graph (Figure 12) is made by substituting the calculated water concentration with the measured value. A similar graph (not shown) could be constructed using the GC water data, except that it would be almost seven times higher in VOC change.

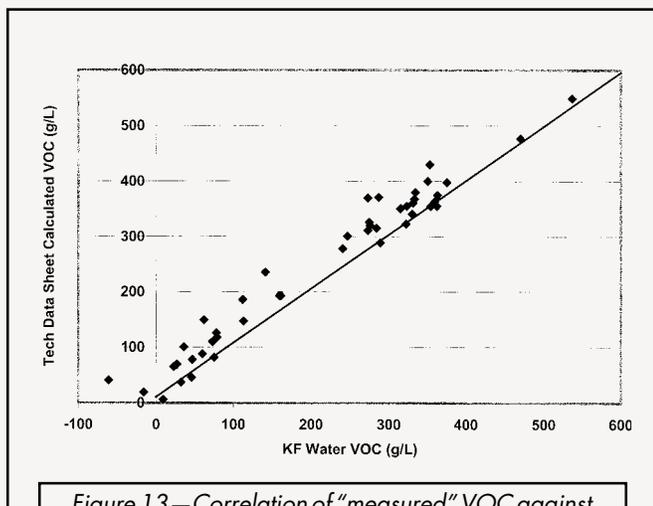


Figure 13—Correlation of "measured" VOC against tech data calculated VOC.

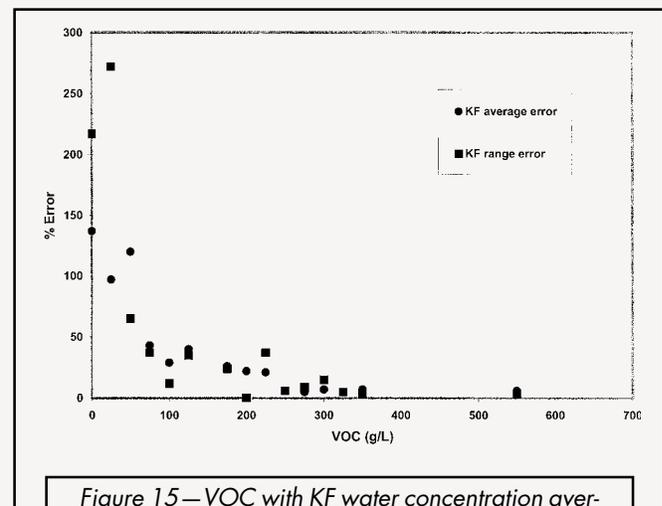


Figure 15—VOC with KF water concentration average and range of error.

Average Error

Next we constructed a correlation graph (Figure 13) of the VOC values as calculated from the raw material tech data sheets versus the measured VOC values, using the best case KF determined water values. It is apparent that there exists a strong bias in the negative direction for VOC values as obtained according to EPA Method 24, using the KF water determination, with respect to what a formulator would predict.

Using the KF data we found that for VOCs above 250 g/L the average error was eight percent, while below 250 g/L the average error increased exponentially as the VOC decreased, reaching approximately 35% at 100 g/L, approximately 50% at 50 g/L, and approximately 150% at 10 g/L.

Range of Error

However, the range of error diverged even more as the VOC decreased, reaching over 250% below 50 g/L. Figure 15 shows the average and range of error for the measured VOC with water concentration determined by KF. Figure 14 illustrates the same point using measured VOC with water concentration determined by GC. The main difference is the magnitude, where the KF average error for any range maxed out at approximately 275%, GC reached over 2100% average error under 25 g/L, and the average range topped out at almost 3700% under 25 g/L. It is important to note that the GC graphs were scaled down to 1500% so that the overall trend would be clearly visible. The VOC increment used in Figures 14 and 15 is approximately 25 g/L.

Accumulated Error

When comparing claimed and measured VOC values, the first level of error comes from the claims simply being incorrect. Incorrect values can come from the use of typical or average values in technical product literature, and from overstating VOCs or understating solids just to be on the safe side of regulatory requirements.

A second level of error is encountered when calculating an overall VOC based on component VOC values. The error of each component measurement accumulates in the overall calculation as the sum of the variances of each component measurement. However, sample calculations show that the contribution from this source is far less than one percent of the total paint VOC value.

Regulatory Implications

While technical personnel in the industry may well understand the issues presented in the current study, others may not. In particular, the authors can foresee a situation where well-intentioned environmental activists may purchase paint from retail outlets, submit them to a laboratory for VOC testing, and then draw conclusions regarding a given manufacturer's degree of compliance with existing VOC regulations. As can be seen from the present study, the validity of such conclusions from single determinations can be highly suspect.

Furthermore, as commercial paints are formulated at progressively lower VOCs the magnitude of the errors in determining VOC becomes so great that the authors must question the validity of using EPA Method 24 for VOCs much below about 250 g/L. The authors suggest that any future discussion on a regulatory level of the issue of VOC should include a proper consideration of the errors involved in making VOC determinations, and how those errors will be dealt with from a regulatory point of view.

CONCLUSIONS

In the present study, EPA Method 24 under the best conditions yielded results with an average error of 8%. Below about 250 g/L, the measurement error in VOC determinations increases exponentially as nominal VOC declines. If regulatory implications are considered, the range of this error can be of equal importance to the average error. Raw material physical properties should always be verified experimentally if used in calculating the VOC of a formulated product such as paint. Further study with other systems (e.g., epoxies, urethanes, alkyds, etc.) would be appropriate to determine the generality of these findings.

Regulatory agencies should consider the issue of error in any future considerations of VOC, and should include means for dealing with that error in any future regulatory actions.

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