

VOC Testing Comparison: EPA Method 24 Versus the Cal Poly Pomona Method

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A new method for water determination of latex paints that gives reliable and precise results is presented. This method agrees with the results obtained using the traditional Karl Fischer titrations of EPA Method 24; therefore eliminating the need for Karl Fischer titrations. Equipment needs are minimal and the procedure is performed quickly and conveniently. Hopefully, in the future EPA Method 24 will not be the only method accepted by regulatory agencies. Until that time, however, this new method will be useful for quality control and assurance, in-house regulatory compliance monitoring, and research and development purposes.

In recent years the paint and coatings industry has come under pressure to develop new products and formulations that reduce environmental hazards. Much of the focus on achieving this goal has been on the development of waterborne products containing reduced levels of volatile organic compounds (VOCs). Both federal and local regulatory agencies have exerted pressure to develop low or zero VOC products. This regulatory push is illustrated, for example, in *Chemical and Engineering News*.¹ There was some early reluctance to move away from familiar solvent-based formulations which had proven to be effective. As much as 20 years ago, initial laboratory studies addressed the development of new waterborne products.² All areas of product development have come under scrutiny in the effort to reduce VOC levels, while retaining application and performance characteristics. Dougherty and Medina reported in the *European Coatings Journal*³ on new surfactant technology for waterborne systems. These surfactants display desirably low intrinsic VOC contents of about 1.5% as measured by the EPA Method 24.⁴ Howard and Manock have presented a discussion of polyurethane dispersions and high-solids waterborne systems which have zero VOC content.⁴ The issue of rheology modifiers for low

VOC bake coatings to help overcome the problem of increased sag encountered at elevated cure temperatures has been addressed.⁵ These examples point to the level of activity within the industry to comply with ever more restrictive regulatory requirements.

Government agencies are constantly monitoring products to insure adherence to regulations. A major part of the monitoring process as carried out by agencies is the measurement of the water content of paints. The methods used to certify compliance demand that paints be analyzed for water content. EPA Method 24⁶ and ASTM Practice D 3960⁷ are the basis of the determinations as carried out by regulatory agencies. Integral to these procedures is the method developed by Karl Fischer⁸ to measure water content in liquids and solids. An accurate determination of the water content is critical since this value enters into the equation used by EPA Method 24 to calculate the VOC content. The equation used to make this calculation is presented as equation (1) here.

$$C = \frac{[W \times D]}{[100\% - V]} \quad (1)$$

C = VOC content in pounds per gallon less water

W = weight percent organic volatile compounds

D = paint density in pounds per gallon

V = volume percent water in paint

Our work focused on the determination of the volume percent water, V,

found in equation (1). The goal was to develop a method to measure the water percentage by a method other than Karl Fischer (KF) titrations, due to the health risks associated with the use of typical KF reagent.⁹ Even though modern imidazole modified KF reagents have been developed,¹⁰ we felt that elimination of the need to do titrations would be worthwhile. The direct KF titration of typical waterborne paints presents practical problems not found in the analysis of other materials. The KF titration is carried out in a water-free medium. When a waterborne paint is introduced, the paint often forms large droplets from which the water must then be extracted into the KF solvent for reaction with the KF reagent to occur. This extraction process is not instantaneous, even if turbo mixers are used, and not every laboratory has turbo mixers available. The formation of droplets in the absence of turbo mixers can lead to end-points being difficult to achieve and thus potentially not as precise as might be desired. Analysis of raw paints also brings with it the issue of the effect of the many components of paint. The presence of these materials can lead to unwanted complications varying from the bothersome fouling of equipment, especially electrodes, to actual chemical interference. In particular the presence of amines, including ammonia, can present significant problems. One particularly vexing feature of amines is their ability to raise the pH of the medium. It is known that the optimum pH range for

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Table 1—Refractive Index Calibration Curve Experimental Data

Wt. Water, g	Wt. MPA, g	Wt.% Water	Refractive Index
0	4.2396	0	1.4029
4.8794	0	100	1.3337
2.8513	1.8130	61.13	1.3740
1.1609	1.9583	37.22	1.3910
0.7433	3.7192	16.66	1.4002
2.3029	0.9033	71.83	1.3643
4.0253	0.7538	84.23	1.3494
0.3474	3.8395	8.297	1.4021
2.9834	2.3678	55.75	1.3793
0.6890	0.5167	57.14	1.3761

KF titrations is approximately 5 to 7.¹¹ Clearly it would be a tremendous advantage to have a method available that could be performed easily and rapidly in-house. Even if the method yielded results which had some amount of error, a benefit could be realized through the savings of time and money especially in the R & D of new product lines and the routine quality control and assurance of established product lines.

Prof. Max Wills and his research group at California Polytechnic State University, San Luis Obispo, in association with the Technical Committee of the Los Angeles Society for Coatings Technology, has described a new method which overcomes many of the problems associated with the traditional KF titration.¹² They have described their method as the "Cal Poly Method." For clarity we will refer to their method as the "SLO Method" to distinguish it from work carried out at California State Polytechnic University, Pomona. We will refer to our work as the "Pomona Method."

The starting point for the work described here as the Pomona Method has its roots in the SLO Method. The SLO Method is based on an azeotropic extraction of water from paint samples using 1-methoxy-2-propanol (MPA). For a full description of the particulars of this method the reader is referred elsewhere.¹² Briefly, the SLO Method employs MPA to azeotropically extract water from the paint sample. The resultant mixture of water and MPA is then titrated with KF reagent in the traditional manner. The SLO method gives results which agree with those obtained via the EPA Method 24. The goal of the Pomona Method was to eliminate the need for KF titrations. A way to characterize the water content of the MPA/water mixture of the SLO Method was needed.

Our attention was eventually drawn to the use of refractive index measurement as a means to achieve our goal. The refractive index of liquid mixtures is often used to determine their

composition through the use of calibration curves.¹³ We describe below the procedure and results of our work on several commercial paints using refractive index measurements on MPA/water mixtures. Work is also being conducted on a variation based on the use of isopropyl alcohol (IPA), rather than MPA, to extract water from paint. Work is continuing on the IPA extraction technique but initial results appear to be promising. The use of IPA as an extraction solvent promises to show utility for analyzing paints which contain IPA as part of their formulation.

PROCEDURE

The actual laboratory procedures may be divided conveniently into several distinct parts as follows:

1. Calibration curve preparation
2. Azeotropic extraction
3. Sample size determination
4. Water content evaluation
 - a. Karl Fischer titration
 - b. Refractive index determination

Each of these four parts will be discussed separately. All of the glassware used was carefully cleaned. The major concern was to exclude all water. Our practice was to thoroughly clean all glassware according to standard laboratory procedure. After cleaning and rinsing with distilled water, a final rinse with acetone was followed by at least one hour in a 110°C drying oven. The glassware was routinely left in the drying oven until immediately before use. If storage is necessary, it is best to do so in an efficient dessicator if possible.

Preparation of Standard Calibration Curve

Ten mixtures of MPA and water were prepared by carefully weighing to the fourth decimal appropriate amounts of the MPA and water into

separate containers having securely sealable tops. Five milliliter capacity glass vials with plastic stoppers are convenient. The series of mixtures prepared must cover the entire concentration range from pure water to pure MPA. A total mass of 2.0000 grams is convenient. For example, one solution may be prepared by placing 0.1000 grams of water and 1.9000 grams of MPA into a vial. This mixture will be 5.000% by weight water. In a similar fashion, additional mixtures were prepared to uniformly cover the entire concentration range. Once all mixtures were prepared the refractive index of each one was carefully measured. The refractive index of the pure water and the pure MPA used to make these mixtures was also measured. These data were then plotted with the weight percent water on the y-axis and the refractive index value on the x-axis. All refractive index measurements were made on azeotropic distillates at the same temperature used to construct the calibration curve, namely, 21°C plus or minus one degree. In this way no problems associated with temperature variations were encountered. It is best to use a computer and appropriate software to fit the data with a least squares linear regression line or some other similar statistical program.

Table 1 shows a set of experimental data used to construct the calibration curve shown in Figure 1. The data from Table 1 may also be fitted using the equation for a straight line rather than the quadratic equation which appears in Figure 1. The result is shown in Figure 2. Notice in Figure 2 the R² value of 0.940, while quite high, is not as high as the value of 0.987 shown in Figure 1. This indicates that the equation of Figure 1 should generate a more precise value for the weight percent of water in a mixture based on an experimentally measured refractive index. All of the results presented here are based on the use of the quadratic equation. In every case of the determination of a water percentage the measured refractive index value was substituted into the appropriate equation and the water percentage was calculated. In no case was the water percentage evaluated by visual interpolation from either of the curves.

Azeotropic Extraction Procedure

About 30 g of the paint sample was weighted to four decimal places and placed into a 250 ml round bottom one necked flask, which was fitted with a standard taper joint of 19/22 or 14/20 size containing a Teflon[®]-coated stir

bar. About 100 ml of dry MPA which had been dried over a molecular sieve was added. The refractive index of the MPA should be measured before use to insure the purity. A reflux condenser was fitted to the round bottom flask. No packing material was used in the reflux condenser nor was water cooling used. At the top of the reflux condenser a three-way adapter was positioned to permit a thermometer to be inserted to monitor the vapor temperature. A condenser was attached to the horizontal arm of the three-way adapter. This condenser should have an adapter which permits it to be attached via a ground glass vacuum adapter to a 100 ml volumetric flask. In the absence of the vacuum adapter, there should be a suitable extension to the exit of the condenser to permit it to extend several centimeters into the volumetric flask. It is important to weigh the volumetric flask, including its stopper, on an analytical balance and record the weight. Once the apparatus containing the paint sample was assembled, it was fitted with a heating mantle and cooling water flow started in the condenser which empties into the volumetric flask. At this time the magnetic stirrer was started and adjusted to provide a reasonable amount of circulation without excessive splashing. The

distillate was then collected in the volumetric flask while carefully monitoring the distilling temperature. In order to avoid collecting any methanol which might be present, collection of the distillate did not begin until the temperature reached 70°C. A distilling temperature in the neighborhood of 115°C is a good indication that all of the water has been removed from the paint since MPA boils at 115°C and water boils at 100°C. At this point the cooling water flow was stopped. An additional 10 ml or so of distillate was collected after turning off the cooling water in order to flush out any water which might remain within the apparatus. The distilling process typically required from 20 to 40 min depending on the particular apparatus used. Once the distillate had been collected, its refractive index was measured immediately before moisture could be absorbed. The total weight of the distillate was also measured and recorded.

Sample Size Determination

The quadratic equation shown in Figure 1 was used throughout. It is wise to insure that the measured parameter, the refractive index, displays maximum sensitivity to the water concen-

tration while minimizing relative errors. An examination of Figure 1 shows that the approximate region from 15 to 50% water by weight corresponds to the range of maximum sensitivity. It is, therefore, desirable to arrange to have sufficient water in the original paint sample in order that the ultimate distillate falls in this range of refractive index; namely, from a refractive index of 1.3670 to 1.4000. For the typical waterborne latex paint whose water content is approximately 50%, the 30 g sample size specified is appropriate. If, however, the paint is significantly different, it may be necessary to scale the initial sample up or down as needed. For example, suppose an initial 30 g sample of paint generates a measured refractive index of 1.3500 which corresponds to a water concentration of about 85% by weight according to Figure 2. A reasonable refractive index to target might be 1.3800 which is about in the middle of the range corresponding to a distillate water concentration of about 45%. A simple ratio may be used to determine amount of paint to use to achieve this refractive index as shown in equation (2).

$$m = [45\%/85\%] [30g] = 16 g \quad (2)$$

m = desired paint sample size in grams.

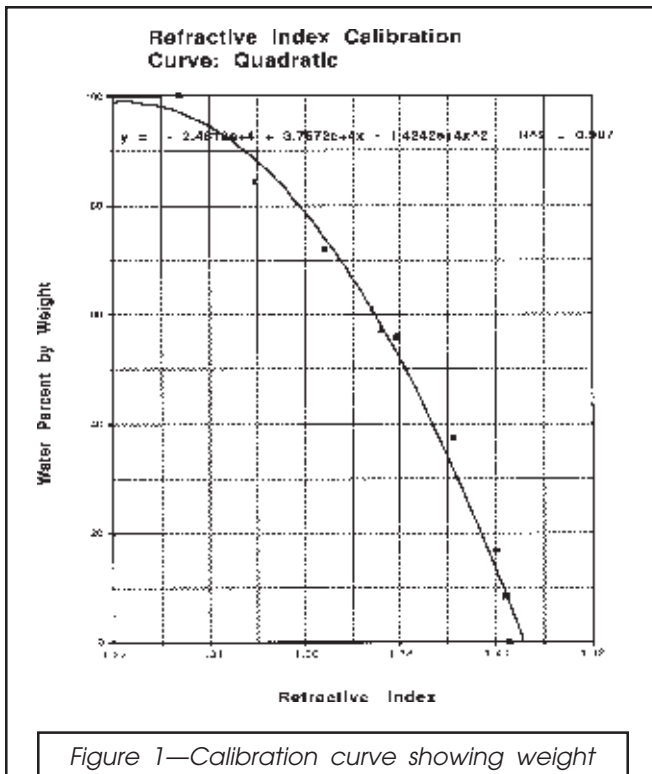


Figure 1—Calibration curve showing weight percent water in MPA/water mixtures as a function of refractive index. Data fitted with quadratic equation.
Legend—Refractive index calibration curve: quadratic.

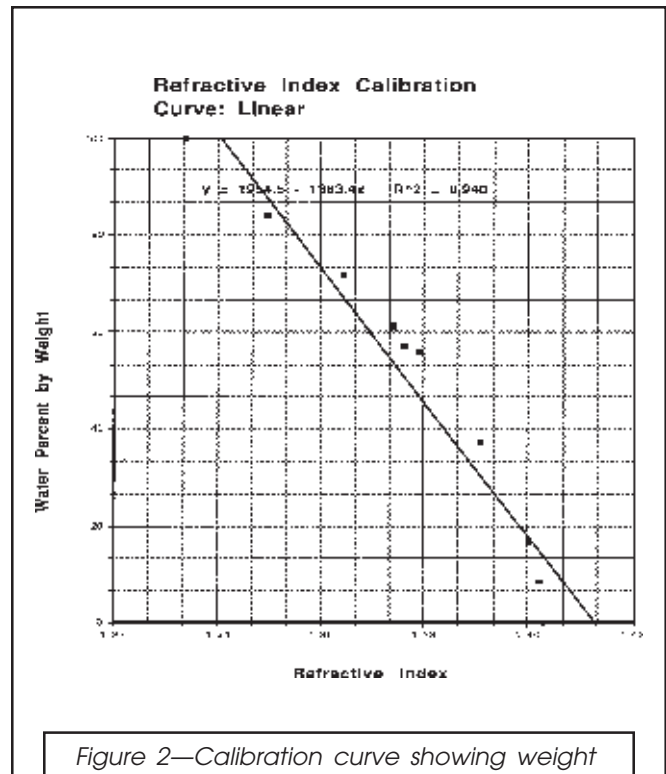


Figure 2—Calibration curve showing weight percent water in MPA/water mixtures as a function of refractive index. Data fitted with a straight line equation.
Legend—Refractive index calibration curve: linear.

Water Content Evaluation

The following calculations illustrate the process of taking an experimentally measured refractive index value and calculating from it the actual VOC content of an original paint sample. One calculation is based on the use of the linear equation of *Figure 2* and one calculation is based on the quadratic equation in *Figure 1*. It is interesting to note the comparison of the two results. Based on such a comparison, it is obvious that the linear equation is quite good and should suffice for all but the most exacting of circumstances. Nevertheless, all of the results presented in this paper have been obtained using the quadratic equation. The experimental data from an actual determination are shown in the following. The paint density and percent by weight total solids were obtained by customary standard methods which are straightforward and need no further comment here.

- weight of original raw paint sample = 30.8404 grams
- weight of azeotrope collected = 61.5677 grams
- refractive index value measured = 1.3974
- raw paint density = 11.91 lbs/gal (1.406 g/ml; "weight per gal cup determination")
- weight percent total solids = 51.42% (weight loss upon oven drying)

Using the linear equation the calculation proceeds as follows:

- wt% water in azeotrope = $1954.5 - 1383.4 [1.3974] = 21.34\%$
- weight water in raw paint = $[61.5677 \text{ g azeotrope}] [0.2134] = 13.14 \text{ g water total}$
- wt% water in raw paint = $[13.14 \text{ g water}] / [30.8404 \text{ g paint}] \times 100\% = 42.60\%$

Using the quadratic equation the calculation proceeds as follows:

- wt% water in azeotrope = $-24812 + 37672[1.3974] - 14242[1.3974]^2 = 20.12\%$
- weight water in raw paint = $[61.5677$

- g azeotrope] $[0.2012] = 12.39 \text{ g water total}$
- wt. % water in raw paint = $[12.39 \text{ g water}] / [30.8404 \text{ g paint}] \times 100\% = 40.17\%$

We now have all of the information to use in equation (1) in order to evaluate the VOC content of this paint. Equation (1) is shown again here for reference.

$$C = \frac{[W \times D]}{[100\% - V]}$$

Before doing the calculation, however, it is necessary to convert the weight percent water of the raw paint into (1) volume percent water, V. To do this requires knowledge of the total volume of the water and the raw paint sample.

- volume of water = $[12.39 \text{ g water}] / [1.000 \text{ g/ml}] = 12.39 \text{ ml water}$
- volume raw paint = $[30.8404 \text{ g paint}] / [1.406 \text{ g/ml}] = 21.93 \text{ ml paint}$
- V = $[12.39 \text{ ml}] / [21.93 \text{ ml}] \times 100\% = 56.50 \text{ volume percent water}$

Equation (1) also requires the weight percent volatile organic compounds, W, which is easily calculated as

$$W = 100\% - 40.17\% \text{ water} - 51.42\% \text{ solids} = 8.41\% \text{ volatile organic}$$

Using these data in equation (1) gives the following

$$C = \frac{[8.41 \times 11.91 \text{ lb/gal}]}{[100\% - 56.50\%]} = 2.30 \text{ lb/gal VOC less water}$$

$$C = 276 \text{ g/lit VOC less water}$$

RESULTS

The sample calculations have been carried out to evaluate the actual VOC content in order to illustrate the entire process. The main point of discussion in this paper, however, is the development of a method to measure the water content of paint. The role played by the water content in calculating the VOC content is clear from these sample calculations. Therefore, the results of

applying the Cal Poly, Pomona refractive index method of water determination may simply be reported here as the appropriate water by weight percentages. These results

are presented in *Table 2* for three commercial paints. Each paint listed in was also analyzed by the KF titration method. The results of the KF titrations are included in *Table 2* for comparison.

DISCUSSION

The information presented in *Table 2* is convincing evidence of the utility of using refractive index measurements to determine the water content of the latex paints tested. In this study all samples were analyzed by both the traditional KF method and the refractive index method. In this way the KF data serves as a standard for determining the accuracy of the refractive index method. When the standard deviations of the various measurements are taken into account, the values obtained using refractive index measurements agree with those obtained using the traditional KF titration method which is integral to the EPA Method 24. For example, consider paint 1 in *Table 2*. The refractive index method gives a water percentage, using the quadratic equation calibration, in the range of 44.94 to 49.20%. Using the linear equation calibration the water percentage falls in the range of 47.68 to 50.26%. These two ranges overlap one another suggesting that there is no significant difference between the two variations of the refractive index method. The KF titration method gives a range of 49.83 to 54.49% for the water content in paint 1. The KF titration method and the refractive index method using the quadratic calibration equation generate overlapping results. The linear calibration curve of the refractive index method produces results which do not overlap the ranges of either the KF method or those obtained using the quadratic calibration curve of the refractive index method. This is not unanticipated as was pointed out in the Procedure Section.

A more detailed comparison of the refractive index method and the KF method based on the information in *Table 2* is useful. For each paint the KF method gives a value which is higher than both variations of the refractive index method. There are several ways to interpret this observation. Within plus or minus one standard deviation unit, the quadratic equation calibration method and the KF method produce results which are in agreement. Therefore, statistically the KF method and the refractive index method using the quadratic calibration curve are indistinguishable. Alternatively, since the KF method gives results uniformly higher than either of the refractive

Table 2—Results of Water Determinations Using Cal Poly, Pomona Refractive Index Method with Comparison to Karl Fischer Titration Method

Calibration Equation	Paint 1	Paint 2	Paint 3
Linear (<i>Figure 2</i>)	48.97%	41.22%	49.40%
Standard deviation	1.29%	1.88%	2.13%
Quadratic (<i>Figure 1</i>)	47.07%	38.70%	46.73%
Standard deviation	2.13%	2.87%	3.03%
KF titration	52.16%	45.52%	52.26%
Standard deviation	2.33%	1.94%	2.90%

index method variations it might be argued that the refractive index methods are not influenced by the presence of compounds in the paint other than water. The presence of such compounds, which can react with the KF reagent, may lead to higher values for the water content as measured by Karl Fisher titrations. This problem might be avoided by the refractive index method since only water is quantitatively removed by distillation leaving interfering compounds behind. Continued work to determine whether the apparent differences between the two methods are real or simply statistical artifacts, as well as an attempt to assess the influences of impurities which may be present in raw materials is underway.

Table 3 contains the results of experiments that attempt to determine the influence of impurities in propylene glycol used to prepare three different paints. Each of the paints was formulated identically except for the total water percentage. The as-prepared water percentages are indicated in Table 3. The propylene glycol used contained an unknown impurity which imparted a distinct yellow color to the propylene glycol. The azeotropic extractions were also found to have a distinct yellow color, indicating that the impurity was co-distilled with the MPA and water. As can be seen in Table 3, the water determination shows unacceptably large variation when the refractive index method is used. In the presence of this impurity, even the KF method shows untypically large variation in the water percentages. Regardless of whether the refractive index method or the KF method was used, the result was seriously high compared to the actual as prepared water percentage. The inference is that the impurity is showing up as water independent of the analysis method. Since the nature of the impurity in the commercially obtained propylene glycol was unknown nothing definitive can be concluded based on this set of experiments other than that the purity of raw materials is important. Work is progressing to identify methods to accommodate the problems associated with these impurities.

SUMMARY

This new method to determine the VOC content of latex paints is based on a solvent extraction of water from the paint using 1-methoxy-2-propanol (MPA) in an azeotropic distillation.

Table 3—Influence of Propylene Glycol Impurities on Water Percentage Determination

Method		Paint I	Paint II	Paint III
Refractive index (linear curve)	exp 1	51.71	49.42	48.70
	exp 2	63.67	56.41	50.73
Refractive index (quadratic curve)	exp 1	42.52	41.21	42.94
	exp 2	60.75	52.52	45.70
Karl Fischer	exp 1	56.79	54.93	50.66
	exp 2	60.91	55.77	50.99
Actual water percentage		60.00	50.00	40.00

This azeotropic extraction method provides several advantages compared to the traditional ASTM Method D 4017, which is a Karl Fischer titration based technique. In this new method, the water content is determined through the use of refractive index measurements and the use of a calibration curve. Typically only one to two hours is required to complete an individual determination. When combined with the measurement of percent solids, it is possible to determine the VOC content of latex paints.

This new method was used to analyze several actual paints and the results of the water determination were compared to the values obtained using the accepted KF method. In each case the two methods generated results which agree to within experimental error. This new refractive index method appears to have several advantages over other methods available. A significant advantage is the elimination of the use of the KF reagent which is a costly and hazardous substance requiring proper disposal procedures. This method requires only a relatively common and affordable Abbe refractometer as opposed to the expensive Karl Fischer titrators and chromatography equipment needed for other methods. Using this new refractive index method it is possible to quickly perform analyses that are particularly useful for purposes of quality control and assurance, compliance monitoring, and research and development activities.

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