METHOD 310

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS AND REACTIVE ORGANIC COMPOUNDS IN AEROSOL COATING PRODUCTS

(Including Appendices A and B)

Adopted: September 25, 1997
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Amended: [Date of Adoption]

DISCLAIMER: Mention of any trade name or commercial product in Method 310 does not constitute endorsement or recommendation of this product by the Air Resources Board.

NOTE: The regulatory amendments adopted in this rulemaking are shown in bold underline to indicate additions to the version of Method 310 as last amended on September 3, 1999.
METHOD 310

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS AND REACTIVE ORGANIC COMPOUNDS IN AEROSOL COATING PRODUCTS

1 APPLICABILITY

1.1 This method (Method 310) applies to the determination of the percent by weight of:

(1) volatile organic compounds (VOC) in consumer products, antiperspirant and deodorant products, and aerosol coatings products as those terms are defined in Title 17, California Code of Regulations (CCR), Division 3, Chapter 1, Subchapter 8.5 (Consumer Products), commencing with section 94500, and

(2) low vapor pressure-volatile organic compounds (LVP-VOC) as that term is defined in section 94508(a)(78), and

(3) the reactive organic compounds (ROC) contained in aerosol coating products, as that term is defined in Title 17, CCR, section 94521.

1.2 Method 310 determines the total volatile material in a product and the presence of any compounds prohibited by ARB regulations (“prohibited compounds”). Components of the product that do not meet the definition of a VOC or are exempted by ARB regulations for a specific product category (“exempt compounds”) are subtracted from the total volatile material to determine the final VOC content for the product. Method 310 is also used to determine the percent by weight of the ROCs contained in aerosol coating products, for the purpose of determining compliance with the Regulation for Reducing the Ozone Formed from Aerosol Coating Product Emissions, Title 17, CCR, sections 94520 to 94528 (the “Aerosol Coatings Regulation”).

1.3 Method 310 does not apply to the determination of the composition or concentration of fragrance components in products.

1.4 The term “Executive Officer” as used in this document means the Executive Officer of the Air Resources Board or his or her authorized representative.

2 TEST METHODS

Method 310 incorporates by reference the following American Society for Testing and Materials (ASTM), National Institute for Occupational Safety and Health
(NIOSH), and United States Environmental Protection Agency (US EPA) analytical test methods:


2.6 ASTM D 3074-94: Standard Test Methods for Pressure in Metal Aerosol Containers (November 15, 1994) with the modifications found in Appendix A to this Method 310.

2.7 ASTM D 3063-94: Standard Test Methods for Pressure in Glass Aerosol Bottles (November 15, 1994) with the modifications found in Appendix A to this Method 310.


2.10 Gas Chromatography/Mass Spectrometry for Volatile Organics (analysis of exempt and prohibited compounds in the product by headspace/gas chromatography/mass spectrometry).


2.18 ASTM D 2879-97: Standard Test Method for Vapor-Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope (April 10, 1997) with the modifications found in Appendix B to this Method 310.


3 CONSUMER PRODUCTS TESTING PROCEDURE

3.1 The testing begins when the Executive Officer selects a product for analysis by Method 310. The Executive Officer will maintain sample chain of custody throughout the selection and analytical process.
3.2 Initial Testing of Aerosol Products

If the sample is an aerosol product, the aerosol propellant is separated from the liquid portion of the product by using ASTM D 3074-94 (as modified in Appendix A for metal aerosol container) or ASTM D 3063-94 (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for exempt or prohibited compounds by using US EPA Reference Method 18. The remaining liquid portion of the product is then analyzed as specified in section 3.3.

3.3 Initial Testing of Non-Aerosol Products and the Liquid Portion of Aerosol Products

The liquid, solid, or gel product sample is analyzed to determine the total volatile material present in the sample and to determine the presence of any exempt or prohibited compounds. This analysis is conducted by performing the following tests:

3.3.1 Gravimetric analysis of samples to determine the weight percent of total volatile material, using US EPA Reference Methods 24/24A, ASTM D 2369-97.

3.3.2 Determination of sample water content. For determination of water content either ASTM D 4017-96a, or ASTM D 3792-91 may be used, or results from both procedures may be averaged and that value reported.

3.3.3 Determination of ammonium content using ASTM D 1426-93 or US EPA Method 300.7.

3.3.4 Determination of ketones and alcohol content using NIOSH Method 1400.


3.3.6 If LVP-VOC status is claimed or the analysis indicates the presence of an LVP-VOC component and the percent VOC is not in compliance, the Executive Officer will request formulation data as specified in Section 3.5.2.

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1 Alternate test methods may be used, as provided in section 7.0
3.4 Prohibited Compounds

If the sample is found to contain compounds prohibited by ARB regulations (i.e., ozone-depleting compounds) at concentrations equal to or exceeding 0.1 percent by weight, the Executive Officer will reanalyze the sample for confirmation.

3.5 Initial Determination of VOC Content

The Executive Officer will determine the VOC content pursuant to sections 3.2 and 3.3. Only those components with concentrations equal to or greater than 0.1 percent by weight will be reported.

3.5.1 Using the appropriate formula specified in section 4.0, the Executive Officer will make an initial determination of whether the product meets the applicable VOC standards specified in ARB regulations. If initial results show that the product does not meet the applicable VOC standards, the Executive Officer may perform additional testing to confirm the initial results.

3.5.2 If the results obtained under section 3.5.1 show that the product does not meet the applicable VOC standards, the Executive Officer will request the product manufacturer or responsible party to supply product formulation data. The manufacturer or responsible party shall supply the requested information. Information submitted to the ARB Executive Officer may be claimed as confidential; such information will be handled in accordance with the confidentiality procedures specified in Title 17, California Code of Regulations, sections 91000 to 91022.

3.5.3 If the information supplied by the manufacturer or responsible party shows that the product does not meet the applicable VOC standards, then the Executive Officer will take appropriate enforcement action.

3.5.4 If the manufacturer or responsible party fails to provide formulation data as specified in section 3.5.2, the initial determination of VOC content under this section 3.5 shall determine if the product is in compliance with the applicable VOC standards. This determination may be used to establish a violation of ARB regulations.

3.6 Determination of the LVP-VOC status of compounds and mixtures. This section does not apply to antiperspirants and deodorants or aerosol coatings products because there is no LVP-VOC exemption for these products.
3.6.1 Formulation data. If the vapor pressure is unknown, the following ASTM methods may be used to determine the LVP-VOC status of compounds and mixtures: ASTM D 86-96 (April 10, 1996), ASTM D 850-93 (April 15, 1993), ASTM D 1078-97 (July 10, 1997), ASTM D 2879-97 (April 10, 1997), as modified in Appendix B to this Method 310, ASTM D 2887-97 (April 10, 1997) and ASTM E 1719-97 (March 10, 1997).

3.6.2 LVP-VOC status of “compounds” or “mixtures.” The Executive Officer will test a sample of the LVP-VOC used in the product formulation to determine the boiling point for a compound or for a mixture. If the boiling point exceeds 216°C, the compound or mixture is an LVP-VOC. If the boiling point is less than 216°C, then the weight percent of the mixture which boils above 216°C is an LVP-VOC. The Executive Officer will use the nearest 5 percent distillation cut that is greater than 216°C as determined under 3.6.1 to determine the percentage of the mixture qualifying as an LVP-VOC.

3.6.3 Reference method for identification of LVP-VOC compounds and mixtures. If a product does not qualify as an LVP-VOC under 3.6.2, the Executive Officer will test a sample of the compound or mixture used in a product's formulation utilizing one or both of the following: ASTM D 2879-97, as modified in Appendix B to this Method 310, and ASTM E 1719-97, to determine if the compound or mixture meets the requirements of Title 17, CCR, section 94508(a)(78)(A).

3.7 Final Determination of VOC Content

If a product's compliance status is not satisfactorily resolved under sections 3.5 and 3.6, the Executive Officer will conduct further analyses and testing as necessary to verify the formulation data.

3.7.1 If the accuracy of the supplied formulation data is verified and the product sample is determined to meet the applicable VOC standards, then no enforcement action for violation of the VOC standards will be taken.

3.7.2 If the Executive Officer is unable to verify the accuracy of the supplied formulation data, then the Executive Officer will request the product manufacturer or responsible party to supply information to explain the discrepancy.

3.7.3 If there exists a discrepancy that cannot be resolved between the results of Method 310 and the supplied formulation data, then the results of Method 310 shall take precedence over the supplied formulation data. The results of Method 310 shall then determine if the product is in compliance with the applicable VOC standards, and may be used to establish a violation of ARB regulations.
4 CALCULATION OF VOC CONTENT

This section specifies the procedure for calculating and determining the final VOC content of a product, which is reported as a single percent by weight of VOC.

4.1 Aerosol Products

For aerosol products, the percent VOC content shall be calculated using the following equation:

\[
\text{PERCENT VOC} = \frac{\text{WL} \times (\text{TV} \times \text{A} \times \text{H} \times \text{EL}) + \text{WP} \times \text{EP}}{\text{WL} + \text{WP}} \times 100\%
\]

Where:

- WL = weight (gm) of liquid product excluding container and packaging
- TV = weight fraction of non-propellant total volatile material (US EPA Reference Methods 24/24A, ASTM D 2369-97)
- A = weight fraction of ammonia (as NH₄) in liquid (ASTM D 1426-93) or US EPA Method 300.7
- H = weight fraction of water in liquid (ASTM D 3792-91 or ASTM D 4017-96a)
- WP = weight (gm) of propellant (ASTM D 3074-94 [as modified and include ASTM D 3064-89] or ASTM D 3063-94 [as modified and include ASTM D 3064-89])

\(^2\)Alternate test methods, as provided in 6.0, or appropriate approved methods from section 2.0 may be used.
4.2 Non-Aerosol Products

For non-aerosol products, the percent VOC content shall be calculated using the following equation:

\[
\text{PERCENT VOC} = \frac{\text{TV} - \text{A} - \text{H} - \text{EL}}{\text{TV}} \times 100\%
\]

5 TESTING TO DETERMINE REACTIVE ORGANIC COMPOUNDS IN AEROSOL COATING PRODUCTS

This section specifies the procedure for determining the percent by weight of the reactive organic compounds contained in aerosol coating products, for the purpose of determining compliance with the Aerosol Coatings Regulation.

5.1 The testing begins when the Executive Officer selects a product for analysis. The Executive Officer will maintain sample chain of custody throughout the selection and analytical process. When a product is selected for testing, the Executive Officer will request the product manufacturer or responsible party to supply the product formulation data specified in Title 17, CCR, section 94526(b)(2). The manufacturer or responsible party shall supply the requested information within 10 working days. Information submitted to the Executive Officer may be claimed as confidential; such information will be handled in accordance with the confidentiality procedures specified in sections 91000 to 91022, Title 17, CCR.

5.2 Initial Testing of the Propellant Portion of Aerosol Coating Products

The aerosol propellant is separated from the non-propellant portion of the product by using ASTM D 3074-94 (as modified in Appendix A for metal aerosol container) or ASTM D 3063-94 (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for reactive organic compounds and other compounds by using US EPA Reference Method 18. The remaining non-propellant portion of the product is then analyzed as specified in section 5.3.
5.3 Initial Testing of the Non-Propellant Portion of Aerosol Coating Products

The non-propellant portion of the product sample is analyzed to determine the reactive organic compounds in the sample, including the presence of any prohibited compounds. This analysis is conducted by performing the following tests:

5.3.1 Gravimetric analysis of samples to determine the weight percent of total volatile material, using US EPA Reference Methods 24/24A, ASTM D 2369-97.

5.3.2 Determination of sample water content. For determination of water content either ASTM D 4017-96a, or ASTM D 3792-91 may be used, or results from both procedures may be averaged and that value reported.

5.3.3 Determination of ammonium content using ASTM D 1426-93 or US EPA Method 300.7.

5.3.4 Determination of ketones and alcohol content using NIOSH Method 1400.


5.4 Prohibited Compounds

If the sample is found to contain compounds prohibited by the Aerosol Coatings Regulation (e.g., ozone-depleting compounds) at concentrations equal to or exceeding 0.1 percent by weight, the Executive Officer will reanalyze the sample for confirmation.

5.5 Initial Determination and Verification of Reactive Organic Compound Content

The Executive Officer will determine the reactive organic compound content by verifying formulation data pursuant to sections 5.2 and 5.3. Only those components with concentrations equal to or greater than 0.1 percent by weight will be reported.

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Alternate test methods may be used, as provided in section 7.0.
5.5.1 Based on manufacturers formulation data and the analysis conducted under section 5, the Executive Officer will make an initial determination of whether the product meets the applicable requirements specified in the Aerosol Coatings Regulation. If initial results show that the product does not meet the applicable requirements, the Executive Officer may perform additional testing to confirm the initial results.

5.6 Final Determination of Reactive Organic Compound Content

If a product’s status is not satisfactorily resolved under section 5.1 - 5.5, the Executive Officer may conduct additional analyses and testing as necessary to verify the formulation data.

5.6.1 If the Executive Officer is unable to verify the accuracy of the supplied formulation data, then the Executive Officer will request the product manufacturer or responsible party to supply additional information to explain the discrepancy.

5.6.2 If the additional information supplied by the manufacturer or responsible party shows that the product does not meet the applicable requirements, then the Executive Officer will take appropriate enforcement action.

5.6.3 If the manufacturer or responsible party fails to provide additional information as specified in section 5.6.1, the initial determination of reactive organic compound content under section 5.1 – 5.5 shall determine if the product is in compliance with the applicable reactive organic compound limits. This determination may be used to establish a violation of the Aerosol Coatings Regulation.

5.6.4 If there exists a discrepancy that cannot be resolved between the results of Method 310 and the formulation data or additional information supplied by the manufacturer or responsible party, then the results of Method 310 shall take precedence over the supplied formulation data or additional information. The results of Method 310 shall then determine if the product is in compliance with the applicable requirements, and may be used to establish a violation of the Aerosol Coatings Regulation.

6 METHOD PRECISION AND ACCURACY

6.1 The precision of Method 310 for determining VOC content was evaluated using seven representative products with known volatile organic compound (VOC) contents ranging from 6.2 to 81.2 percent VOC by weight. Each sample was divided into six portions, and each portion was separately analyzed to determine the VOC content. Based on the results of this analysis, the 95 percent confidence interval for Method 310 is 3.0 percent by weight (Wt/Wt%).
6.2 For determining the percent by weight of the individual ingredients in aerosol coating products, the precision and accuracy of the determination for each ingredient is governed by the precision and accuracy of the test method used to ascertain the percent by weight of each ingredient.

7 ALTERNATE TEST METHODS

Alternative test methods which are shown to accurately determine the concentration of VOCs or constituent components in antiperspirant/deodorants, consumer products, or aerosol coating products (or their emissions) may be used upon written approval of the Executive Officer.
Method 310 - Appendix A

PROPELLANT COLLECTION PROCEDURES

1 APPLICATION

The procedure applies to modify ASTM D 3074-94 and D 3063-94 to allow collection of the propellant for analysis and density measurement for metal aerosol containers and glass aerosol containers, respectively. These modified procedures also retain the aerosol standard terminology listed in ASTM D 3064-89. The aerosol product container is pierced and the propellant is bled into an evacuated manifold. After the manifold reaches atmospheric pressure, approximately 1 liter of the propellant is collected in a clean, evacuated Tedlar bag. For density measurement the propellant is collected into an evacuated 250 mL glass dilution bulb that has been weighed to the nearest 0.1 mg. After filling, the dilution bulb is re-weighed to determine the density of the propellant. Alternately, density may be determined using a Density/Specific Gravity Meter. The Tedlar bag with the propellant aliquot is taken to the laboratory for analysis.

2 LIMITATIONS

Nitrogen analysis: Nitrogen may be used as a component of the propellant system. Ambient air is 78 percent nitrogen and may be present as a contaminant in the system prior to sample collection. This is eliminated by completely evacuating the propellant collection system and sweeping out any connecting lines to the Tedlar bag with product before starting sample collection. This procedure will eliminate or reduce nitrogen contamination to less than 0.1% by weight of the sample and the analysis of the propellant gas will be unaffected.

3 APPARATUS AND MATERIALS

3.1 Propellant Collection System: See Figure 1. The system was built from 1/4" stainless steel and Teflon tubing. The vacuum pump is of bellows diaphragm design.

3.2 Tedlar Bags, 1 liter, equipped with slip valve and septum

3.3 Density Measurement

3.3.1 250 mL gas dilution bulb, or

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The metal piercing adapter is available from Mid-West Screw Products, Inc., 3523 North Kenton Ave., Chicago, IL 60641. Interim Part Number: 8013A-3/4 Longer SS. The gasket is available from Alltech Associate 2051 Waukegan road, Deerfield, IL 60015, part number 80-16. The glass aerosol adapter is available from Modern Machine Ship, Inc. P.O. Box 826, 123 N. Hazel Street, Danville, IL 61832.
3.3.2 Density/Specific gravity meter meeting the following minimum specifications:

3.3.2(a) Measurement Method: Natural Oscillation Type

3.3.2(b) Range: 0 - 3 g/cm$^3$

3.3.2(c) Measurement Temperature Range: 4 °C ~ 70 °C.

3.3.2(d) Temperature Accuracy: +/- 0.02 °C (10 °C ~ 30 °C) and +/-0.05 °C (4 °C ~ 70 °C).

3.3.2(e) Temperature Control Accuracy: +/- 0.01 °C.

3.3.2(f) Measurement Time: 1- 4 minutes.

3.4 Gas tight syringe, 100 µl

3.5 Balance, capable of accurately weighing to 0.1 mg

3.6 Can Piercing Platform. See Figure 2 (metal cans) and Figure 3 (glass containers).

3.7 Platform Shaker, equivalent to Thermolyne M49125

4 PROCEDURE

4.1 Propellant Collection for Metal Aerosol Containers

4.1.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).

4.1.2 Remove the valve actuator on the aerosol can and weigh can to the nearest 0.01 g. Invert the can into cork holding ring on the piercing apparatus, center and snug against the gasket. (Figure 2)

4.1.3 Connect Tedlar bag to output 2, evacuate bag and seal. Connect 250 mL glass dilution bulb to output 1, evacuate bulb and seal.

4.1.4 Slowly raise the hydraulic jack until the can is pierced. Record the pressure of the can.

4.1.5 Vent the can until the pressure is at about 25 psi. Collect the propellant in the Tedlar bag.

4.1.6 After the propellant is collected, close and remove the Tedlar bag and vent the remainder of the propellant.
4.1.7 Weigh the evacuated 250 mL bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the Tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.

4.1.8 After the flow ceases from the can, it is removed from the assembly and allowed to vent overnight. The can may be placed on a platform shaker to vent the remainder of the propellant.

4.1.9 Reweigh can to the nearest 0.01 gm and record weight loss (total gms propellant). The can may now be opened for analysis of the liquid product.

4.2 Propellant Collection for Glass Aerosol Containers

4.2.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).

4.2.2 Connect Tedlar bag to output 2, evacuate bag and seal. Connect 250 mL glass dilution bulb to output 1, evacuate bulb and seal.

4.2.3 The gauge assembly is prepressurized in order to minimize product expulsion and system contamination.

4.2.4 Remove actuator from valve of the aerosol glass container, and weigh container to the nearest 0.01 gm.

4.2.5 With container in an inverted position place the valve onto the tapered adaptor. Bring the top plate down to the flat of the container and tighten the nuts. A cork ring may be required to stabilize the container.

4.2.6 Record pressure of container and vent until the pressure is approximately one-half of recorded pressure. Collect propellant sample into the Tedlar bag.

4.2.7 After the propellant is collected, close and remove the Tedlar bag and vent the remainder of the propellant.

4.2.8 Weigh the evacuated 250 mL bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the Tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.

4.2.9 Continue to vent container on the platform assembly overnight.

4.2.10 Remove container from platform and loosen valve assembly, do not remove valve assembly at this time.

4.2.11 Place container on a platform shaker to vent the remainder of the propellant.
4.2.12 Reweigh container and valve assembly to the nearest 0.01 gm and record weight loss (total gms propellant). The container may now be opened for analysis of the liquid product.
FIGURE 2

6" X 6" X 3/16" Steel Jack Plate
Center Holes 5/8" from edge
Drill 4 perimeter holes to allow for a 1/2" bushing that works with the smooth portion of the 1/2" rod.
Tack weld the lift portion of the hydraulic jack to the center of the plate (and while jack is fully extended as to not damage it).

6" X 6" X 1/2" Aluminum Piercing Plate
Center holes 5/8" from edge
Drill 4 perimeter holes with 3/16" bit
Drill center holes with 7/16" bit
Tap center using 1/2 X 20 NF tap.
Sample piercer is included to ensure drill bit and tap size as center hole is crucial to apparatus.

6" X 6" X 3/4" Aluminum Base Plate
Center holes 5/8" from edge
Drill 4 perimeter holes with 23/32" bit
Tap 4 perimeter holes with 1/2 X 13

1/4" Piercer
Pressure Gasket
45° Taper

1/2" Nut
1/2" Washer

Manual Hydraulic Jack (2 Ton)

1/2" Steel Retaining Rod
MODIFICATIONS to ASTM D-2879-97 (April 10, 1997)

This procedure modifies ASTM D-2879-97 (April 10, 1997) as follows:

1. Modifications to the isoteniscope apparatus include:
   a. capacitance manometers and digital readout
   b. manifold system made of stainless steel and modified in design
   c. Ultra-torr fittings and Ultra-torr flex-lines
   d. ballast on the vacuum side of the isoteniscope manifold as depicted in ASTM D 2879-97 schematics, has been removed.
   e. stainless steel liquid nitrogen trap (Cold Trap)
   f. stainless steel high vacuum valves
   g. recirculating cooling system (required for extremely low pressure work only)
   h. diffusion pump (required for extremely low pressure work only)
   i. hot ion cathode vacuum gauges (required for extremely low pressure work only)

2. A purge and degassing procedure consisting of lower pressures and a liquid nitrogen bath replaces the step of lightly boiling the sample as outlined in ASTM D 2879-97.

3. Purge and Degassing Cycle
   a. With the U-tube connected, the system is evacuated to approximately 1.0 mm Hg. This readily removes most of the higher volatility gases from the sample.
   b. The stainless steel, liquid nitrogen cold trap is filled. The manifold is now brought to approximately 300 mm Hg with the purified nitrogen, regulated through the needle valve.
   c. The isoteniscope tube is carefully placed into a Dewar of liquid nitrogen. The ½ atmosphere pressure of nitrogen prevents the sample from splashing while being frozen. After the sample freezes, the system is evacuated to 0.05 mm Hg.
   d. The U-tube is removed from the Dewar, secured and allowed to warm to room temperature. The U-tube bulb head should be angled so the dissolved gases will be readily evacuated as the frozen sample starts to melt. When gases build up, it may be necessary to tilt the U-tube to release the gases.
   e. Repeat the freeze and degas process once, reducing pressure each time to less than 0.05 mm Hg. After the sample has returned to room temperature, close valve #3. There should be minimal dissolved gases left once the frozen sample starts to melt. Tilt the tube to release any gas pockets (if necessary). Do not
push nitrogen into the evacuated space between the sample in the arm and the sample in the reservoir. At this point, if the sample is properly degassed, a “natural break” should form in the sample. This creates a vapor space as the liquid level in the bulb leg of the manometer falls to a quasi-equilibrium position, usually with the fluid level higher in the long manometer leg. If there is no pendulum effect, and the liquid level in the long leg of the manometer is significantly higher than the level in the short leg (> 2 mm), degassing is probably incomplete, and the degassing procedure should be repeated.

4. Data Evaluation

The regression based on the plot of Log P vs. 1/T as outlined in ASTM D 2879-97 has been removed and replaced with a nonlinear regression to generate the coefficients for an Antoine equation. The data analysis procedure assumes that the measured pressure is the sum of the compound’s vapor pressure and a residual fixed gas pressure. The vapor pressure’s dependence on absolute temperature is represented by an Antoine expression, and the fixed gas as pressure is directly proportional to absolute temperature as outlined in ASTM 2879. This leads to the model equations:

\[ P_{\text{model}} = P_{\text{vapor}} + P_{\text{fixed gas}} \]

\[ P_{\text{model}} = B_0 \times 10^{\frac{B_1}{(T+B_2)}} + B_3 \times T \]

where \( T \) is the absolute temperature (K) and \( B_0, B_1, B_2 \) and \( B_3 \) are coefficients to be determined via a nonlinear regression which minimizes the sum of squares \( (P_{\text{meas}}-P_{\text{model}})^2 \) for all experimental data points. The vapor pressure at 20\(^\circ\) C is then calculated as:

\[ P_{\text{vapor}}(293.15 \text{ K}) = B_0 \times 10^{\frac{B_1}{(T+B_2)}} \]

With a set of pressure vs temperature measurements, the nonlinear regression can be performed using a statistical software packages. The following constraints are imposed to obtain meaningful Antoine equation coefficients for low vapor pressure samples:

a. Pressures shall be measured at temperatures ranging from room temperature to about 180\(^\circ\) C. Narrower ranges will not provide sufficient information to determine the Antoine curvature, i.e., B2 coefficient. Wider ranges can lead to experimental difficulties maintaining the vapor space in the isoteniscope. A minimum of 12 points is necessary to provide ample degrees of freedom for the calculations.
b. Initial pressures at room temperature shall be less than 1 mm Hg. Higher values are indicative of significant levels of dissolved fixed gases. These will vaporize during the course of the experiment as temperature is increased and invalidate the model's assumption for the fixed gas contribution.

c. \(-235 \leq B_2 \leq 0\). Positive values of \(B_2\) imply that the heat of vaporization of the substance increases with increasing temperature. Thermodynamic data for many compounds suggests this is unrealistic. Large negative values can lead to unrealistically low vapor pressure values coupled with excessive fixed gas contributions. The -235(K) bound is chosen to be consistent with literature values of \(B_2\) for many pure compounds. For hydrocarbons in the LVP-VOC range, \(B_2 \geq -100\) provides reasonable agreement between measured and literature vapor pressures.

d. The fixed gas coefficient, \(B_3\), should normally be \(\geq 0\).
Isoteniscope Vapor Pressure Measurement Apparatus

Diagram of apparatus components:
- Pressure Transducer
- Ballast
- Heating Chamber / U-Tube
- Needle Valve
- Nitrogen Gas
- Cold Trap
- Diffusion Pump
- Vacuum Pump

Diagram shows the connections and flow of the apparatus.