# Method 310 - Appendix B

## 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:

$$P_{model} = P_{vapor} + P_{fixed\_gas}$$

$$P_{model} = B0*10^{(B1/(T+B2))} + B3*T$$

where T is the absolute temperature (K) and B0, B1, B2 and B3 are coefficients to be determined via a nonlinear regression which minimizes the sum of squares $\sum (P_{meas}-P_{model})^2$ for all experimental data points. The vapor pressure at 20º C is then calculated as:

$$P_{vapor}(293.15\ K) = B0*10^{(B1/(293.15+B2))}$$

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° 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.** $-235 \leq B2 \leq 0$**. Positive values of B2 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 B2 for many pure compounds. For hydrocarbons in the LVP-VOC range,** $B2 \geq -100$ **provides reasonable agreement between measured and literature vapor pressures.**

**d. The fixed gas coefficient, B3, should normally be** $\geq 0$**.**

# Isoteniscope Vapor Pressure Measurement Apparatus