Absolute Vapor Pressure of Paints, Varnishes, Solvents

1. Introduction

Testing the absolute vapor pressure of paints, varnishes and solvents is required for a number of regulations, such as the ADR and the European REACH regulation ("Registration, Evaluation, Authorisation and Restriction of Chemicals"). Samples have to be classified and labelled correctly to comply with transport and environmental protection regulations, and material safety data sheets have to list the absolute vapor pressure.

In general, two temperatures are important for classification: The absolute vapor pressure at 20°C is required for material data sheets, and the absolute vapor pressure at 50°C must not exceed a certain pressure limit.

2. Test Standards

The **absolute vapor pressure** is defined as the vapor pressure of the **liquid, excluding** the vapor pressure of dissolved and fixed **gases** such as air. Some methods for testing the absolute vapor pressure are described here:

- **Static Vapor Pressure Method (REACH, Commission regulation EC No. 761/2009)**
  To measure the absolute vapor pressure according to the Static method, single- or multi-component samples have to be evacuated at a reduced temperature, to remove gases. For multi-component samples, the evacuation temperature has to be low enough so that the sample composition is not altered and the sample characteristics (e.g. the vapor pressure) are retained. After degassing, the sample is heated, vapors build and the absolute vapor pressure of the degassed sample is measured.

- **ASTM D2879 Isoteniscope method**
  The Isoteniscope method is based on the principle of the Static Method. This method is used for absolute vapor pressure determination of single component liquids and solids. To remove gases, careful boiling and degassing is required. According to REACH (Commission regulation EC No. 761/2009), this method is usually NOT SUITABLE for MULTI-component samples.

- **ASTM D6378 Grabner Triple Expansion Method**
  The Triple Expansion Method is based on the principle of the Static Method. The equilibrium vapor pressure of a liquid is measured in a closed system. The absolute vapor pressure is measured directly, following the principle of the ideal gas equation. Three total pressure values are determined. From these three total pressure values the partial pressure of the dissolved gas and the absolute vapor pressure of the liquid are calculated.

  The Triple Expansion Method has several advantages:
  - It can be used for single- and multi-component samples
  - Its does not require sample preparation, like boiling or evacuation prior to testing
  - The sample composition is not being altered
  - A test is performed fast and fully automatic
  - Automatic cleaning and rinsing is available
  - The absolute vapor pressure is measured directly, according to the latest vapor pressure standard ASTM D6378

3. Samples and Test Method

A number of UV-hardening brilliant, matt and base varnishes and a varnish thinner have been tested. All samples had a viscosity of less than 500 mPas, to allow automatic sample introduction via luer inlet.

All samples have been tested with the **MINIVAP VPXpert –L**, a vapor pressure for low vapor pressures, using **test method ASTM D6378, multipoint measurement.**

To prevent the varnishes from hardening in the luer inlet, the following procedure was used:

- **Prepare** a cup of proper **solvent**. The solvent has to be able to dissolve the varnish which is being tested.
- **Check** the luer inlet **for buckles.** If found, take a new luer inlet to allow proper filling and rinsing.
- Put the **luer** inlet directly **into** the varnish **sample container.**
- **Start** a **D6378 multipoint** measurement.
- When the sample has been taken in for measurement, **remove the luer** from the sample container and **place the open end into the solvent** cup to prevent hardening.
- **Clean/Rinse the analyzer diligently** after every measurement with the solvent from the cup. Closely monitor for residual-deposits in the luer inlet. If rinsing does not start, remove the luer inlet and clean the inlet from residuals.
  Change the luer inlet, if required.

4. Results

Results of the method ASTM D6378 for absolute vapour pressure (Pabs) are shown below. The **absolute vapor pressure Pabs** results from subtracting the partial pressure of dissolved air in the sample from the total vapour pressure of the liquid. This is done fully automatically in the analyzer.

Name	Sample Type	Method	Pabs @ 20°C [kPa]	[kPa]	Pabs @ 50°C [kPa]	[kPa]
4347	Brilliant varnish	D6378	0.43	Mean = 0.45	1.75	Mean = 1.86
4347	Brilliant varnish	D6378	0.48	Std = ±0.03	2.08	Std = ±0.19
4347	Brilliant varnish	D6378	0.44		1.76	
5414	Brilliant varnish	D6378	0.52	Mean = 0.52	2.16	Mean = 2.15
5414	Brilliant varnish	D6378	0.51	Std = ±0.01	2.15	Std = ±0.01
5414	Brilliant varnish	D6378	0.53		2.15	
5430	Matt varnish	D6378	2.82	Mean = 2.95	5.56	Mean = 5.82
5430	Matt varnish	D6378	3.29	Std = ±0.30	5.9	Std = ±0.23
5430	Matt varnish	D6378	2.73		5.99	
3378	Base varnish	D6378	0.43	Mean =0.41	1.41	Mean = 1.36
3378	Base varnish	D6378	0.34	Std = ±0.06	1.21	Std = ±0.13
3378	Base varnish	D6378	0.46		1.45	
5401	Thinner	D6378	1.91	Mean = 1.91	8.61	Mean = 8.61
5401	Thinner	D6378	1.91	Std = ±0.01	8.6	Std = ±0.01
5401	Thinner	D6378	1.92		8.62	

5. Conclusion

Measuring sticky and viscous paints and varnishes, with a very low vapor pressure, is a very challenging task for any laboratory. The **MINIVAP VPXpert –L** offers a very good solution to solve this task, because of the fast and automatic measurement procedure. Using a **Static Method to test single and multi-component substances,** the automatic instrument generates highly repeatable results and does not alter sample composition.

NOTE: Cleaning directly after each measurement with an adequate solvent is of critical importance, to prevent solidification of paints and varnishes inside the analyzer!