

DETERMINING VOLATILE ORGANIC CARBON BY DIFFERENTIAL SCANNING CALORIMETRY

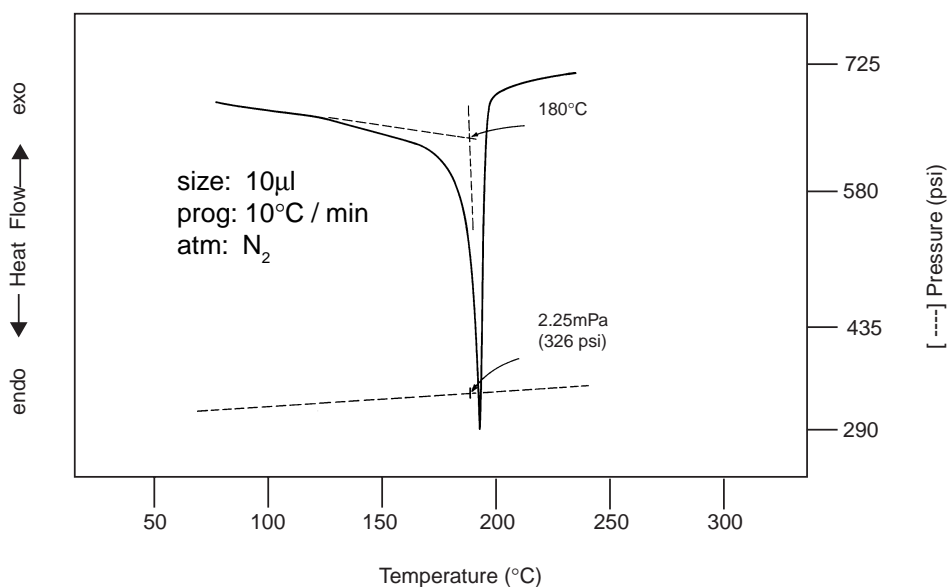
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Volatile Organic Carbons (VOCs) are known to have serious environmental effects. Because of these deleterious effects, large scale attempts are being made to measure, reduce and regulate VOC use and emission. The California EPA, for example, requires characterization of the total volatility of pesticides based upon a TGA loss-on-drying test method [1, 2]. In another move, countries of the European market have reached a protocol agreement to reduce and stabilize VOC emissions by the year 2000 to 70% of the 1991 values [3]. And recently the Swiss Federal Government has imposed a tax on the amount of VOC [4]. Such regulatory agreements require qualitative and quantitative tools to assess what is a VOC and how much is present in a given formulation. Chief targets for VOC action include the paints and coatings industries, agricultural pesticides and solvent cleaning processes.

VOC's are defined as those organic materials having a vapor pressure greater than 10 Pa at 20 °C or having corresponding volatility at other operating temperatures associated with industrial processes [3].

Differential scanning calorimetry (DSC) is a useful tool for screening for potential VOC candidates as well as the actual determination of vapor pressure of suspect materials. Both of these measurements are based on the determination of the boiling (or sublimation) temperature; the former under atmospheric conditions, the latter under reduced pressures.

Figure 1



Nielson and co-workers [5] have observed that:

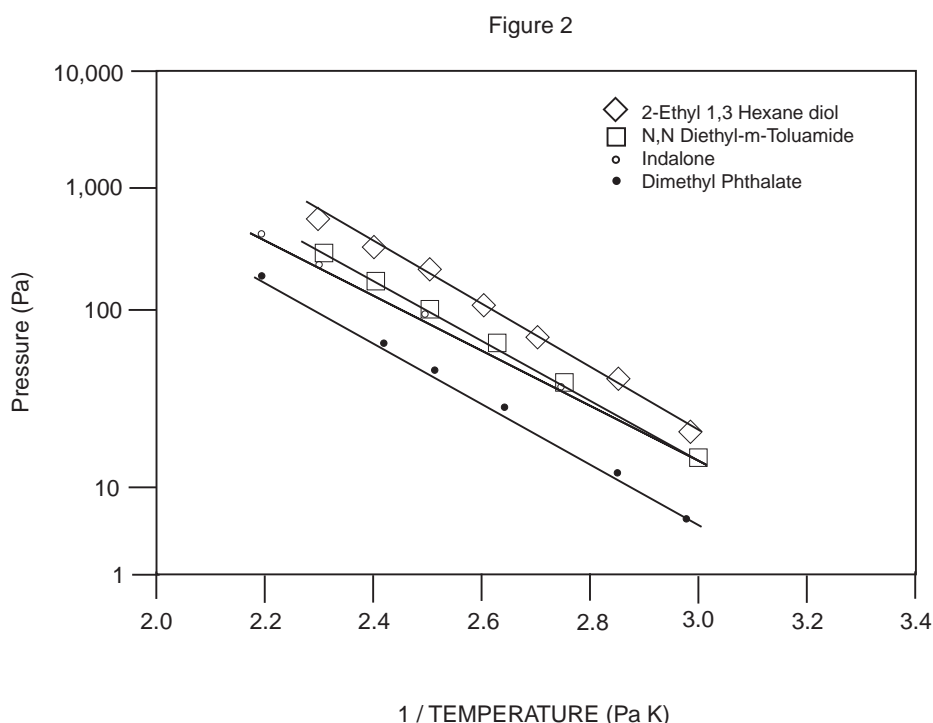
- All organic solvents with boiling temperatures below 170 °C are classified as VOCs, and
- No organics solvents with boiling temperatures greater than 260 °C are VOCs.

Nelsen's guidelines may be used to screen candidate materials so that a detailed vapor pressure determination need be performed only those materials with boiling points between 170 and 260 °C. Vapor pressure determination may be determined through the use of ASTM standard E 1782 [6] and a Pressure Differential Scanning Calorimeter operating under vacuum.

The determination of boiling temperature requires special experimental conditions. The accurate determination of phase change transition temperatures required equilibrium between the two phases. This is easily achieved with the solid-to-liquid transition of the melting process. It is more difficult with the liquid-to-vapor transition as the vapor phase may be easily removed from the transition region causing the transition temperature to appear at a lower temperature than that of the liquid-vapor equilibrium.

To overcome this difficulty, boiling temperature determinations are carried out in hermetically seal sample pans where vapor is be retained in the head space over the liquid phase. Constant pressure is maintained through the use of a small molecular leak (often called a "pin hole") in the hermetic pan lid (P/N 900860-901). The size of the "pin hole" is critical. If the hole is too large, the test specimen may be completely volatilized before the boiling temperature is reached. If the hole is too small, the pressure may build up during the boiling process moving the boiling temperature to a higher value than the equilibrium value. Extensive studies have shown that holes 75 μm in diameter are optimum for this determination.

Ten μL of the test specimen is sealed in an aluminum hermetic pan with a laser drilled 75 μm hole in the lid. The test specimen is heated at 10°C/min through the boiling temperature region. The extrapolated onset temperature of the boiling endotherm is used to identify the boiling temperature (Figure 1). Typical precision for boiling temperature determinations is ±4°C. [6]. The determination of boiling temperature under atmospheric pressure conditions may be compared to Nelsen's criteria to determine if the candidate material needs more detailed vapor pressure determination work.



This same process may be used under vacuum conditions to obtain the boiling temperature as a function of reduced pressure using the Pressure DSC cell. Plotting natural logarithm of the pressure versus the reciprocal of absolute boiling temperature produces a (nearly) straight line plot (Figure 2). This presentation may be fit to the Antoine equation [2] using multiple linear regression or to the Clausius-Clapyron equation using a best fit straight line. The resultant equation (or line) may be used to determine the anticipated vapor pressure at 20 °C = 293.15 K. If this value is greater than 10 Pa, the material is classified as a VOC.

References

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- [3] Proposal for a Council Directive on Limitation of Emissions of Volatile Organic Compounds Due to the Use of Organic Solvents in Certain Industrial activities, COM (96) 538 final Office Journal, 99 pp 32-50 (1997).
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- [5] Nielsen, C.; Hogh, B.; Wallston, E., Surf Coat. Int., 80 (10) 467-472 (1997).

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