Determining Volatile Organic Compounds by Differential Scanning Calorimetry

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ABSTRACT

Differential scanning calorimetry (DSC) may be used to qualitatively determine Volatile Organic Compounds (VOC) through the determination of their boiling temperature.

INTRODUCTION

Volatile Organic Compounds (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 (1, 2). In another move, countries of the European market have agreed to reduce and stabilize VOC emissions to 70 % of the 1991 values (3). And 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 chemicals and solvent cleaning processes.

VOCs 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, and the latter under reduced pressures.

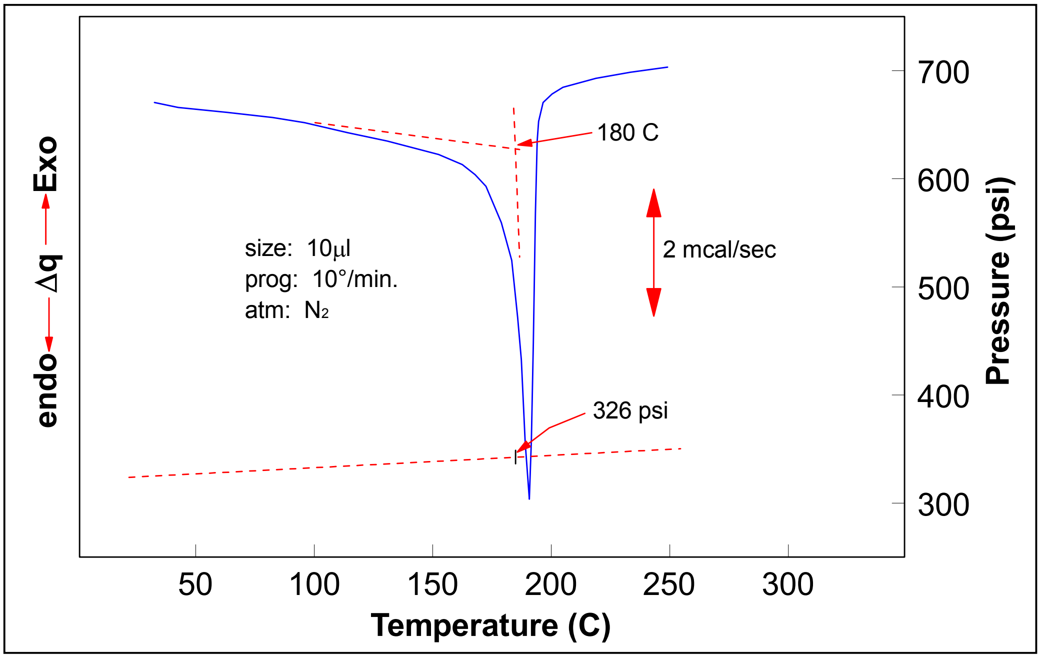
Nielson and coworkers (5) have observed that:

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

Nielson's guidelines may be used to screen candidate materials so that a detailed vapor pressure determination need be performed only on those materials with boiling temperatures between 170 and 260 °C. Vapor pressure may be determined through the

ASTM International standard E1782 (6) and a Pressure DSC cell operating under vacuum.

Figure 1 - Boiling Temperature Determination



* pressure is in units of psig. SI units are the kPa gauge pressure. 1kPa = 0.145 psia.

The determination of boiling temperature requires special experimental conditions. The accurate determination of phase change transition temperatures requires 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.

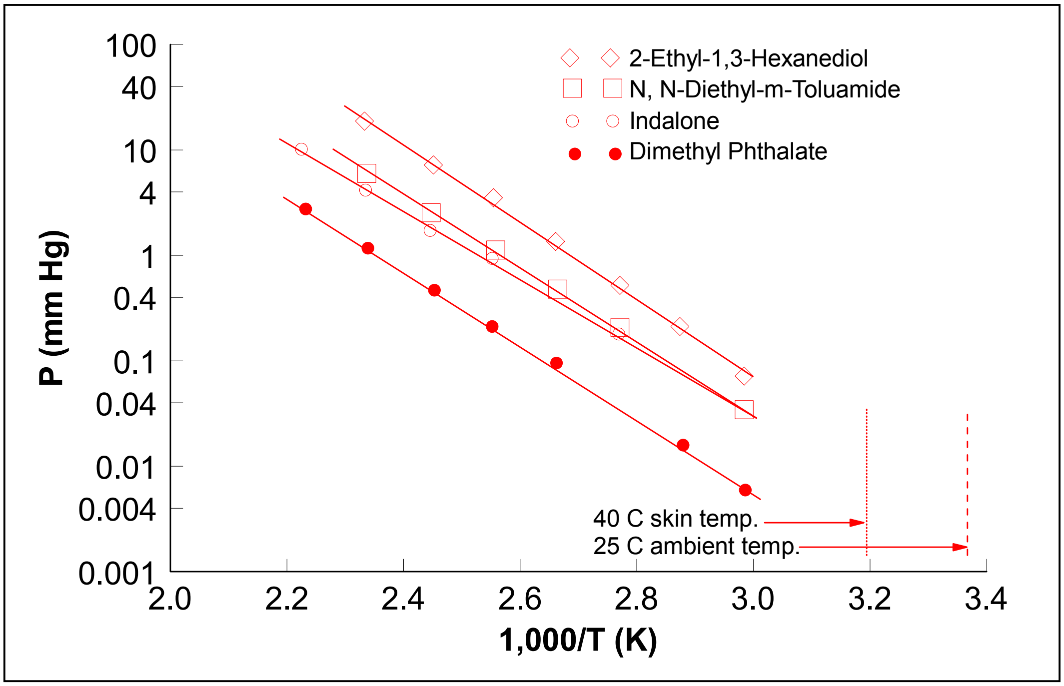
To overcome this difficulty, boiling temperature determinations are carried out in hermetically sealed sample pans where vapor may be retained in the headspace over the liquid phase. Constant pressure is maintained through the use of a small molecular leak hole (often called a “pin hole” even though they are not made with a pin) 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 (7).

EXPERIMENTAL

Ten µL of the test specimen are sealed in an aluminum 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 (see 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 Nielson’s criteria to determine if the candidate material needs more detailed vapor pressure determination work.

This same process may be used under vacuum conditions (using a PDSC cell) to obtain boiling temperatures as a function of reduced pressure. Plotting natural logarithm of the pressure versus the reciprocal of absolute boiling temperature produces a (nearly) straight-line plot (see Figure 2). This presentation may be fit to the Antoine equation (6) using multiple linear regressions 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.

Figure 2 - Vapor Pressure Determination



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KEYWORDS

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