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The use of thermal analysis to study the change in air-freshner gels

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Abstract

Water-based air-freshener gels are replacing traditional organic solvent-based gels, making them environment-friendly. A water-based gel was prepared in this study. The gel contains perfume ingredients and water that vaporizes over a period of time. In order to characterize the rate of fragrance dissipation, thermal analysis was used. The loss of functional characteristic was studied using an accelerated program employing thermogravimetry and derivative thermogravimetry. The DTG plot showed the disappearance of the perfume ingredient as the gel was heated. Water-based gels were prepared in this way and characterized.

Keywords: Air freshner; Thermogravimetry; Gel

1. Introduction

The analysis of perfumes was formerly restricted to skilled olfactory perception for acceptance followed by aging the perfume and subjecting it to another olfactory examination to test its stability and study its rate of evaporation. Lately, with the advent of modern instrumentation, several analytical tools have been efficiently utilized by perfumers to study various characteristics of a fragrance [1,2]. A modified gas chromatograph attached to a computer database, aptly called 'the nose' can actually distinguish between different fragrance notes, render advice on and provide a basis for altering a fragrance [3]. Gas chromatograph and mass spectrometry (GC-MS) are vital to the analysis of the various components in a fragrance, facilitating an exact match or duplication of the fragrance [4]. IR and UV spectroscopy, refractive index measurements and NMR spectroscopy [5] have also been used as analytical tools in perfumery, though to a lesser extent. However, there is no effective analytical tool currently being used to study the aging and evaporation of a perfume/fragrance composition. In an earlier study, we have demonstrated that the rate of evaporation of perfumes can be studied using a thermal balance [6]. The thermal analysis was conducted using a thermogravimetry (TG) unit in which the amount of substance lost is recorded as a function of time or temperature [7]. The temperature is scanned at a rate of a few degrees per minute while weight loss is being monitored continuously. This thermogram obtained can then provide a quantitative picture of the weight changes occurring in the sample being analyzed. From this data, a quantitative estimation of the weight changes occurring in the sample being heated can be determined. Thus, TG was used for an accelerated aging study to determine the evaporation of the material. In the previous study, the rate of evaporation of a liquid ingredient used in formulation of fragrances was calculated from a simple DTG plot.

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The investigation indicated that TG can be used at different heating rates, thereby providing a standard analysis tool on the basis of which various ingredients in a perfume were studied making the task highly reproducible and expeditious. However, the study did not indicate whether the results would hold true for a gel system.

A new challenge to perfumers and chemists alike is the formulation of volatile organic content (VOC) compliant gels. Under current EPA laws, it is mandatory to the use only 3% VOCs in air-freshener gels. Thus, many chemists and perfumers have resorted to using water-based gels. The study of evaporation profiles from this type of gel can be lengthy and frustrating, particularly if the gel under examination does not provide the desired results. In this study, we subjected a water-based air-freshener gel containing a fragrance material to thermal analysis and present the results obtained.

2. Experimental

The TG experiments were conducted, using a simultaneous TG-DTA unit from TA instruments, model # 2960. The atmosphere around the samples was maintained constant using a gas flow rate of 100 ml min^{-1}. Platinum crucibles were used to hold the samples, with an empty crucible being used as reference. The VOC compliant water-based gel was prepared using modified cellulose as the gelling agent. The following general formula was used to prepare the 'Cherry Fragrance' gel: water 70–77.5%; carboxymethyl cellulose 2.3%; hydroxyethyl cellulose 0.2–

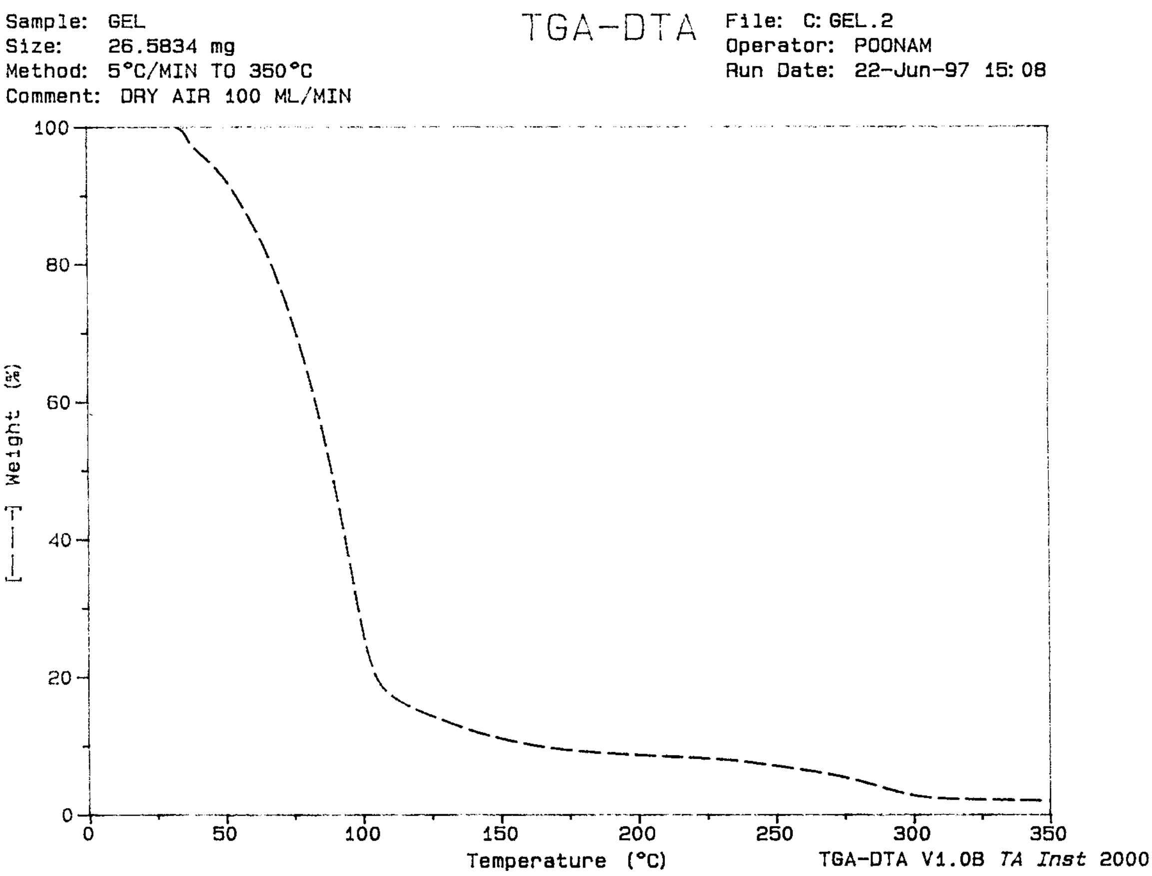

Fig. 1. TG Plot of cherry gel in an atmosphere of flowing dry air.

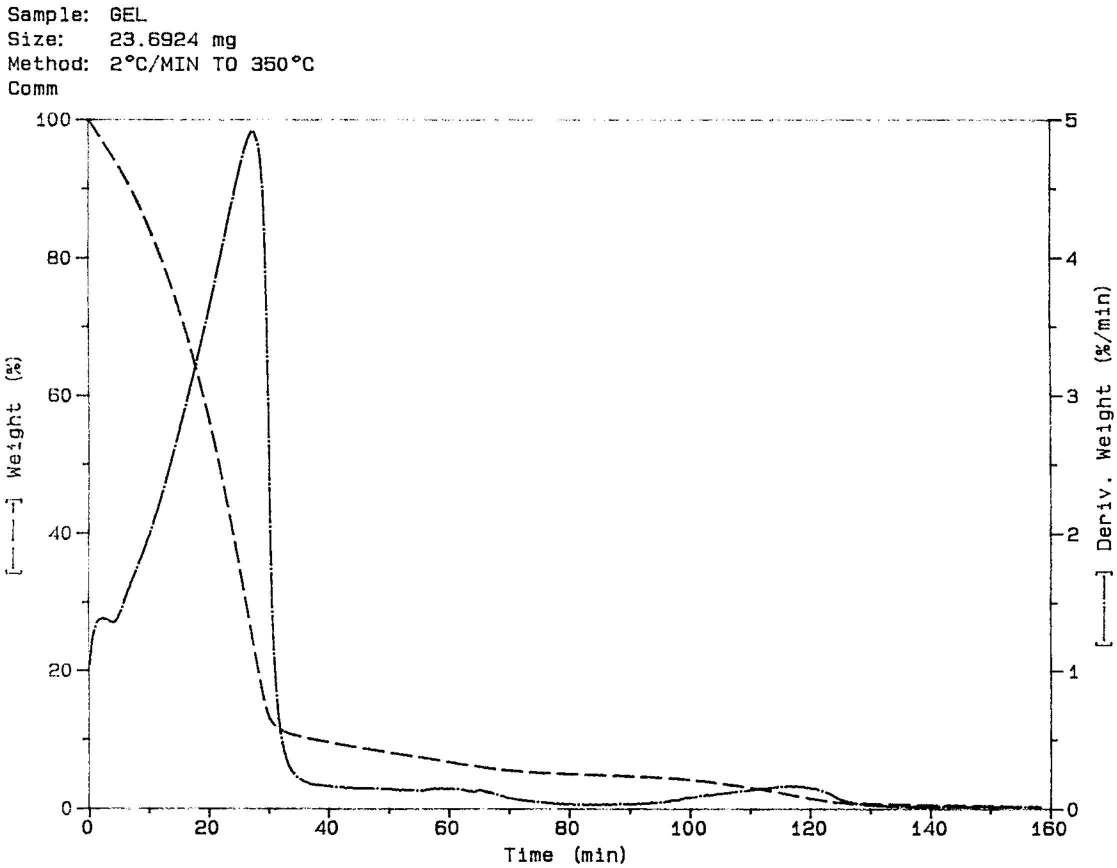

Fig. 2. TG DTG plot of cherry gel in an atmosphere of flowing dry air.

0.5%; sodium benzoate 0.2%; aluminum salt 0.1–0.3%; emulsifier combination 4–6% (polyethoxylated nonyl phenol or polyethoxylated alkyl esters or a combination of the two); fixative 4–6% (glycerol, propylene glycol or alkyl ethers of glycerol and propylene glycol), cherry fragrance 12% (combination of esters, aldehydes and ketones, 25% of which are VOCs). The gel was prepared in accordance with the technical bulletin of The Aqualon Company; bulletin # VC-522.

3. Results and discussion

Three evaporation profiles of the gel used in this study were generated using a TG unit by heating the gel at a rate of 2, 4 and 5°C min^{-1} (e.g., see Fig. 1 at a heating rate of 5°C min^{-1}). This plot shows that the maximum weight loss occurs between 45° and 105°C. The coefficient of evaporation was calculated using a derivative plot of percent weight against time (DTG) as seen in Fig. 2 from the data points between 45° and 105°C. Any point on this plot is proportional to the percent weight lost per unit area and this will hold while zero-order conditions prevail. The conditions for zero order break down, once there is very little material left. [8]. The coefficient of evaporation k, obtained from any point on the DTG plot, is then used to construct an Arrhenius plot of the following form:

$$\ln k(T) = \ln A - E_{\text{act}}/RT \qquad (1)$$

where k is the coefficient of evaporation (as read from the DTG plot), A the Arrhenius parameter and E_{act} the activation energy.

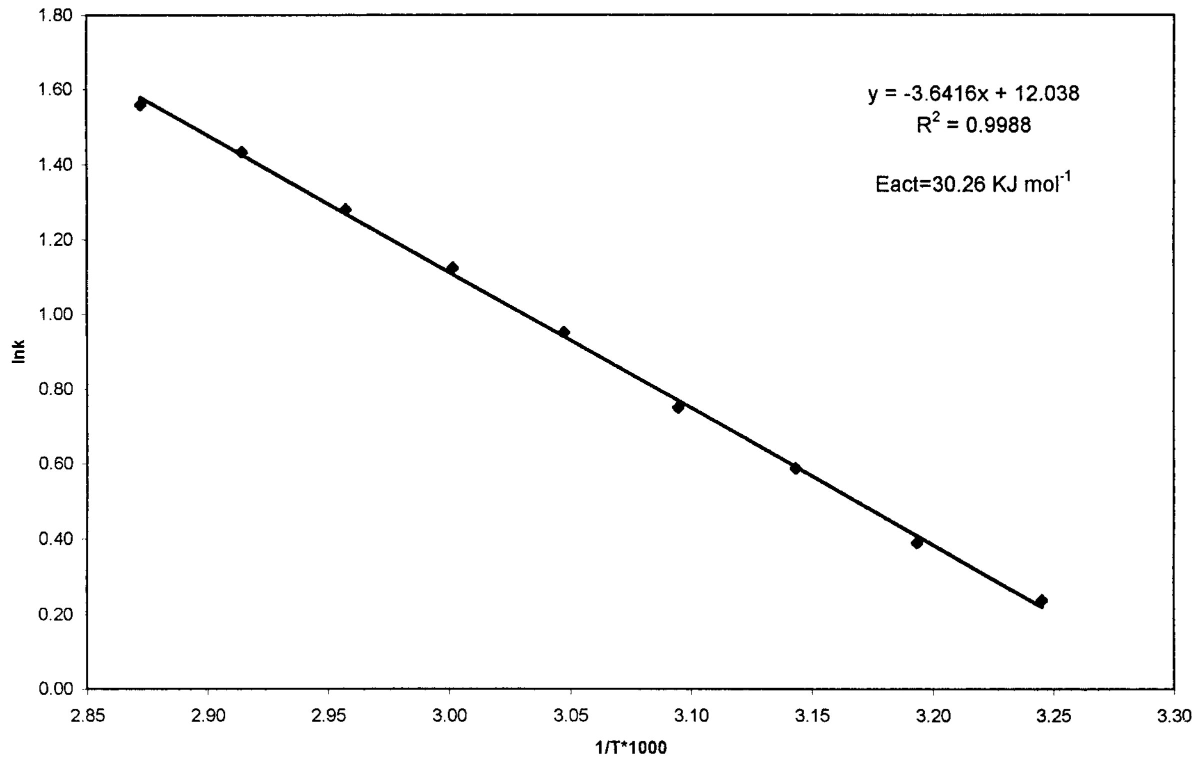

Fig. 3. A typical Arrhenius plot constructed from the DTG values obtained at a heating rate of 2°C min^{-1}.

A typical Arrhenius plot constructed in this way is shown in Fig. 3, and from this the values of A and E_{act} can be calculated. The slope obtained at each heating rate gives the value for E_{act}. The intercept corresponds to the value of A. As can be seen from the plot, a value of E_{act}=30.2 KJ mol^{-1} was obtained using the three different heating rates employed.

Rigid cellulose-based gels allow liquid trapped within the framework of the gel to evaporate from the surface interstices until the gel shrinks and then collapses. From the information provided about the approximate percent of the various ingredients in the gel, it is clear that the gel loses weight by releasing its fragrance constituents and water in an azeotropic manner. This evaporation occurs only on the exposed (top) surface of the gel and, thus, the weight loss between 45° and 105°C is a zero-order reaction. When 85–87% mass loss is recorded, corresponding to the loss of water and perfume, the zero-order evaporation profile breaks down and a complex evaporation pattern along with degradation of the cellulosic material starts. The individual evaporation of some of the fixatives and emulsifiers/surfactants is also discernible by the two broad DTG peaks seen at 150° and 270°C.

4. Conclusions

The rate of evaporation of liquid material from an air-freshener gel matrix through its surface was calculated using thermal analysis. This was done by simply reading off any point on the DTG plot and the Arrhenius plot was constructed from that value, providing a simple tool for the convenient and easy investigation of perfumery ingredients, making the task reproducible and expeditious. This investigation indicated that TG can be used at different heating rates, thus providing a standard analysis equipment on the basis of which various ingredients in a perfume can be studied.

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