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BOILING TEMPERATURES AND ENTHALPY CHANGES OF ESSENTIAL OILS
Using capillary glass sample holder

J. S. Chaar, V. E. Mouchreck-Filho, Susete T. Breviglieri, É. T. G. Cavalheiro and G. O. Chierice*

Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, CxP. 780, São Carlos/SP 13560-970, Brazil

Abstract

A capillary long neck glass sample holder is proposed for the determination of boiling temperatures of essential oils containing a majority component. Essential oils from *Aniba dukei K.* and *Pimenta dioica L.* containing linalool and eugenol, respectively, as major constituents were used after optimization of parameters such as scan rate, sample mass and starting temperature. Best performance in the determination of boiling temperatures was obtained with the proposed sample holder in comparison with commercial aluminum pans. Good agreement was obtained for the boiling temperature and enthalpy for the essential oil samples with the linalool and eugenol standards.

Keywords: boiling temperatures, differential scanning calorimetry, essential oils, sample holder

Introduction

Essential oils represent a very important economic class of natural products since they are often applied in cosmetic and food industry as flavoring agents [1–3] and pharmaceutical products as analgesic, bactericide, sedative, expectorant, etc. [3–5]. Some of the most important characteristics are their nice and intense smell [6] and their oily appearance that give them the nomination as ‘oils’.

Usually essential oils are complex mixtures of lipophilic and volatile substances that are liquid at room temperature. However there are examples in which a single component is the major constituent as vanilin in vanilla oil [6, 7]. Linalool and eugenol are the major constituents of the essential oils from Brazilian trees *Aniba dukei Kostermans* (pau-rosa from Amazon) and *Pimenta dioica Lindl*, respectively. Linalool is widely used in preparation of perfumes and popularly employed in the treatment of rheumatic diseases, while eugenol is a well-known antiseptic. Their chemical structures are represented in Fig. 1.

* Author for correspondence: E-mail: cavalheiro@iqsc.sc.usp.br

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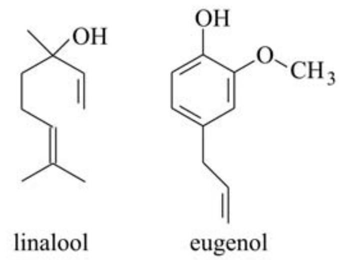

Fig. 1 Chemical structures of the linalool and eugenol

The characterization of essential oils involves a series of physical parameters including melting and boiling temperatures and others. The determination of such parameters is not always easy and depends on the technique employed, and temperature ranges are often used to express such physical constants instead of a unique temperature.

This work describes the use of the differential scanning calorimetry (DSC) technique in which a glass sample holder with a capillary long neck is used in order to determine boiling temperatures of major components of essential oils from *Aniba dukei K.* and *Pimenta dioica L.* The optimized conditions were applied in the determination of the boiling temperatures of commercial essential oils and methyl and acetyl derivatives. The use of the proposed sample holder led to well defined curves which allow the boiling temperature determination that presents the advantages of a DSC procedure such as speed and accuracy.

Experimental

Reagents

Standard linalool and eugenol 99% (Diesberg Óleos Essenciais LTDA., Barra Bonita, Brazil) were used as received. Essential oils from *Aniba dukei K.* and *Pimenta dioica L.* were extracted from dry leaves and small branches by hydrodistillation in a Clevenger extractor [8–10] and dried with anhydrous Na_2SO_4.

Methyl derivatives from the oil of *Pimenta dioica L*. were prepared, purified and characterized as described elsewhere [11, 12].

Gas chromatography

Gas chromatograms of the oils and standards were recorded in an HP 5890 Series II gas chromatograph (HP, USA) equipped with a split-splitless injector and a FID detector, a cross-linked polyethyleneglycol LM 100 HMW column (LM, Brazil) and hydrogen was used as carrier gas (40 mL min^{-1}). Samples were diluted in pure ethanol before injection.

DSC measurements

All the DSC curves were recorded in a DSC-910 modulus (DuPont) coupled to a TA 2000 Thermal Analyser (TA Instruments). The best parameters for the determinations were achieved optimizing the sample mass (5–18 mg), heating rate (5–20°C min^{-1}),

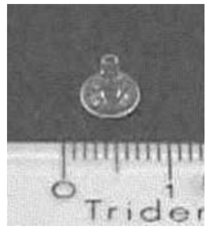

Fig. 2 Photography of the glass sample holder proposed in the present work. Reference scale in cm

starting temperature (5–20°C) and the sample holder geometry. All the measurements were performed under dynamic nitrogen atmosphere with a gas flow of 50 mL min^{-1}.

In such studies open and covered (with a central hole) commercial aluminum and a 20 μL homemade capillary long neck glass sample holders have been used.

All the temperatures and enthalpy changes were determined in relation to the melting of In metal (99.99%). The uncertainties refer to the standard deviation of a set of five In runs. All the boiling temperatures were determined by the onset value obtained by a linear baseline between the final and initial temperatures for the endothermic boiling peak.

Several glass sample holders were prepared and grouped as pairs by their mass similarity. An empty one was used as reference and another was filled with the desired amount of essential oil with the help of a 1.0 mL syringe. The photography of the glass sample holder is shown in Fig. 2. Their average masses were 55±1 mg, the capillary neck is 2 mm longer with internal diameter around 1.5 mm and were prepared in the glass shop of the Universidade Federal de São Carlos (São Carlos/SP, Brazil).

Results and discussion

In Fig. 3 the gas chromatograms for the essential oil obtained for the *Aniba dukei K.* and the linalool standard used in the present work are presented. From this figure is possible to observe that although there are some minor peaks in the oil chromatogram the content of linalool is much higher than the other substances and it is the major constituent of the essential oil (90% *m*/*m*). Similar results were obtained for eugenol in the *Pimenta dioica L.* essential oil.

Using the glass sample holder with linalool standard

The sample holder geometry plays an important role in the shape of the DSC curve, and is considered one of the parameters that can influence a DSC curve profile [13]. The use of the commercial aluminum sample holders in comparison with the glass sample holder is presented in Fig. 4, for linalool standard as probe with sample mass around 15 mg, heating rate of 10°C min^{-1} under nitrogen flowing at 50 mL min^{-1}.

As can be observed in this figure not only the shape but the number of peaks is changed by the different geometry of the sample holder. The proposed glass sample holder presents the best results with a sharp well-defined peak that allows a more accurate boiling temperature determination.

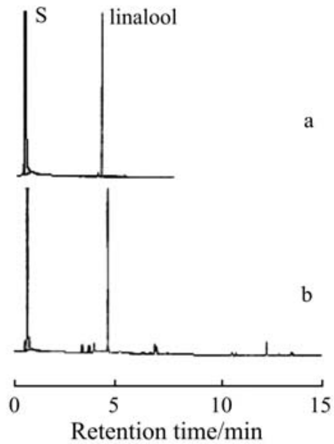

Fig. 3 Gas chromatograms of the a – linalool standard and b – the essential oil obtained from *Aniba dukei K*. under the same conditions. The peaks relative to the solvent (*S*=ethanol) and linalool are marked in the top

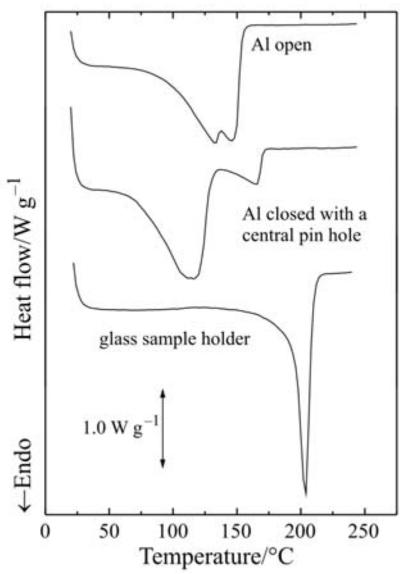

Fig. 4 DSC curves obtained using commercial and the glass sample holders for linalool standard samples. Sample mass 15 mg, heating rate 10°C min^{-1}, nitrogen flow 50 mL min^{-1}

Using the glass container the effect of other parameters in the boiling temperature of linalool standard have been evaluated. Using sample mass around 5 mg the peak is broad and the boiling temperature much lower than those observed for the other masses. For masses of 10 mg and higher the shape and the boiling temperature do not change markedly. The results obtained for the influence of sample mass are presented in Fig. 5.

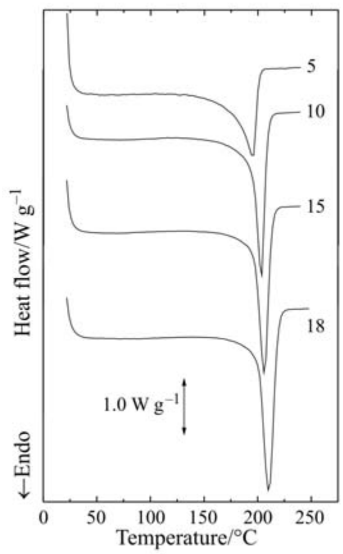

Fig. 5 DSC curves obtained at different sample mass (5.0–18 mg) using the capillary glass sample holder and the linalool standard as probe. Heating rate 10°C min^{-1}, nitrogen flow 50 mL min^{-1}

According to these results a sample mass at 15 mg was fixed in further experiments. Running the DSC curve at different scan rates at the glass sample holder, no significant changes in the shape of the boiling peaks were observed. As expected only the initial temperature and peak height changed. These results are presented in Fig. 6.

Due to the better resolution and sharpness the scan rate of 10°C min^{-1} was chosen as the optimum scan rate.

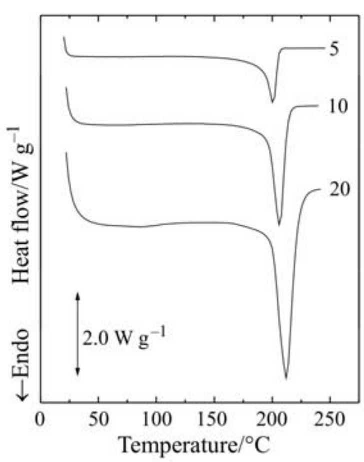

Fig. 6 DSC curves obtained at different scan rates (5.0–20°C min^{-1}) in the capillary glass sample holder using the linalool standard as probe. Sample mass 15 mg, nitrogen flow 50 mL min^{-1}

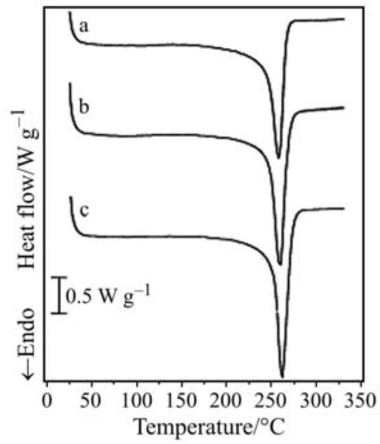

Fig. 7 DSC curves obtained in the capillary glass sample holder using the essential from a – leaves, b – fruits of *Pimenta dioica L.* and c – eugenol standard. Sample mass 15 mg, scan rate 10°C min^{-1}, nitrogen flow 50 mL min^{-1}

The last parameter investigated for the linalool standard was the initial heating temperature. In this experiment no change was observed in the boiling peak starting the run at 0, 5, 10 or 20°C.

Application of the optimized conditions to real samples

The optimized conditions: heating rate 10°C min^{-1}, sample mass 15 mg, initial temperature 20°C, and the capillary long neck glass sample holder, were selected on the basis of giving shorter analysis time and well defined boiling peaks. Such conditions have been used to measure the boiling temperatures of some standards, with boiling temperature described in [14] as being 198 and 255°C for linalool and eugenol respectively and essential oils samples obtained in our laboratory. The results are summarized in Table 1.

Table 1 Results of the determination of boiling temperatures and the corresponding enthalpy values for standards and essential oil samples, obtained under the optimized conditions and using the proposed capillary long neck glass sample holder[a]

Sample		Boiling temperature/°C	Enthalpy/J g^{-1}
Pimenta dioica L.	oil/leaves	243±1	260±2
	eugenol standard	248±1 (255)[b]	262±2
	methyled oil/leaves	253±1	240±2
	methyleugenol standard	252±1	240±2
Aniba dukei K.	oil/leaves	195±1	172±1
	linalool standard	198±1 (198)[b]	194±1

[a]uncertainties based on five successive runs of In metal (99.99%): ±2% for enthalpy and ±0.03% in temperature
[b]in brackets data from [14]

The data presented in Table 1 showed good agreement in temperatures and energies of boiling temperatures for the samples analyzed when compared with the standards. Minor differences, mainly in the enthalpy determined can be attributed to the presence of other components in the essential oil.

Conclusions

From the results obtained in this work it is possible to conclude that the use of the proposed sample holder can be a useful tool in the determination of boiling temperature of essential oils containing a major constituent as those from *Pimenta dioica L*. and *Aniba dukei K*. This statement is based on the good agreement in the results obtained in samples and standards.

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References

1 Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 16, 1981, p. 307.
2 A. F. Costa, Farmacognosia, 5th Ed., Kaloust-Gulbenkian, Lisboa 1994.
3 C. Robles and S. Garzino, Phytochemistry, 48 (1998) 1343.
4 H. Kollmannsberger and S. Nitz, Chem. Microbiol. Tech. Lebensmittel, (1993) 116.
5 A. A. Craveiro, A. G. Fernandes, C. H. S. Andrade, F. J. A. Matos, M. I. L. Machado and J. W. Alencar, Óleos Essenciais de Plantas do Nordeste, EUFC, Fortaleza 1981.
6 G. M. London, Organic Chemistry, Addison-Wesley, Des Moines 1984, p. 1107.
7 H. G. Richey Jr., Fundamentals of Organic Chemistry, Prentice-Hall, Englewood Cliffs 1983, p. 268.
8 J. F. Clevenger, Am. Perfumer Essent. Oil Rev., (1928) 467.
9 J. S. Chaar, D. D. Silva, A. P. Inocentini, V. E. Mouchrek-Filho, M. S. Galhiane and G. O. Chierice, Proceedings of the II - IUPAC Intl. Conf. Biodiversity, Belo Horizonte 1999, PN-042.
10 V. E. Mouchrek-Filho, C. M. S. Melo and G. O. Chierice, Proceedings of the VII - Latin American Conference on Chromatography and Related Techniques, Águas de S. Pedro 1998, p. 108.
11 J. S. Chaar, D. D. Silva, M. S. Galhiane, V. E. Mouchrek-Filho and G. O. Chierice, Proceedings of the VIII - Latin American Conference on Chromatography and Related Techniques, Buenos Aires 2000.
12 V. E. Mouchrek-Filho, Thesis, Universidade de São Paulo, 2000.
13 W. W. M. Wendlandt, Thermal Analysis, in Chemical Analysis, P. J. Elving and J. D. Winefordner (Eds), Vol. 19, 3rd Ed., John Wiley, New York 1986.
14 The Merk Index, S. Budavari (Ed.), 12th Ed., Merk and Co., Whitehouse Station, 1996.