Hyphenated thermoanalytical methods for characterization of essential oil microparticles

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INTRODUCTION

Essential oils (EO) contains contain high amount of volatile and/or thermosensitive compounds. EO can undergo irreversible changes in their physicochemical properties when exposed to contact with other materials or external agents without adequate protection. Microencapsulation is a technology that can be applied to transform EOs into more stable materials (lower volatility and less susceptibility to oxidation) providing easy handling (solid form), longer shelf life, and in some cases solving bioavailability problems. Spray drying (SD) is commonly used for microencapsulation. Product properties depend on microencapsulation composition and drying conditions (Fernandes 2008). Physical properties commonly used in characterization of EO microparticles include particle size and shape, density, porosity, EO composition and load, etc.

Thermal analytical methods associated with scanning electronic microscopy (SEM), X-ray diffraction and spectroscopic methods are powerful techniques to characterize SD products. Conventional thermal analytical methods includes the thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). However more robust information can be obtained by using simultaneous techniques (e.g. TGA-DTA) and/or combined with techniques capable to generate qualitative and quantitative information, such as the evolved gas detection (EGD), and evolved gas analysis (EGA). The use of hyphenated techniques, such as TG combined with mass spectroscopy (TG-MS) and thermogravimetry–Fourier transformed infrared spectroscopy (TG-FTIR), proved to be highly sensible and reliable (Novak 2006, Fernandes 2009).
The aim of this work was to characterize SD microparticles of *Lippia sidoides* essential oil based on different maltodextrin:gum arabic (MD:AG) ratios, by conventional and hyphenated thermal analytical techniques (TG, EGD, TG-MS). SD Microparticles were also characterized by determination of process yield, EO load, moisture content (Xp) and particle size (dp). *Lippia sidoides* is an aromatic herb from Northeast of Brazil, whose EO has properties comparable of thyme oil (one of top ten essential oils in food and pharmaceutical applications).

MATERIALS AND METHODS

Lippia sidoides EO was purchased from Pronat (Fortaleza-CE-Brazil). Thymol (99.99%), used as chemical marker, were supplied from VETEC (Brazil). Maltodextrin DE 10 and GA were supplied by Corn products - Brazil, and Colloides Naturales - Brazil, respectively. The organic chemicals used in the analysis were of analytical grade.

Microencapsulation was carried out in a Lab-Plant SD-05 spray dryer (drying temperature of 160 °C, atomizer pressure of 5.0 bar, gas flow rate of 60 m^3/h, feed composition flow rate of 4.0 g/min, and feed composition temperature of 50 °C). MD:AG (4:1; 3:2; 2:3; 0:1, m/m) were used as carrier. Feed was prepared by blending and rehydrating the carriers in warm distilled water at 50°C for 2 hours, followed by cooling to room temperature. EO:carrier ratio was 1:4, and solids content of feed composition set at 50%. Product were characterized by moisture content (Sartorius MA 35 moisture analyzer), size (laser light scattering in a Beckman Coulter LS 13 320), total EO load (hydrodistillation using a Clevenger apparatus), GC-MS analysis of total oil retained and entrapped thymol within the microparticles (SHIMADZU® GCMS-QP 2010 gas chromatograph coupled with mass spectrometer, equipped with auto sampler mod. AOC-20I SHIMADZU and DB-5 capillary column - 30 x 0.25 mm; 0.25 µ film thickness). Thermal analysis: TG measurements were carried out using a TA 2960 STD equipment (TA Instruments Co, Newcastle, Delaware, USA). Evolved gas detection (EGD) experiments were carried out in a DuPont 916 (Carle 3000) equipment with a built-in hydrogen-air flame ionisation detector. TG-MS analysis was carried out in a Balzers Thermostar GSD 300T quadrupole mass spectrometer (Lichtenstein) operating from 1 to 300 specific mass/charge range, connected to the outlet of the TG furnace through a heated silica capillary transfer tube. Experimental runs were carried out according to Fernandes (2009).

RESULTS AND DISCUSSION

Moisture content, mean diameter, process yield, and EO load of SD microparticles are shown in Table 1.

Table 1 - Properties of SD microparticles.

FEED	SD microparticles			
MD:AG (m/m)	Xp (%, d.b.)	dp (µm)	Yield (%)	EO Load (%)
4:1	4.28 ± 0.10	14.82	31 ± 3.0	43.9
3:2	4.23 ± 0.15	11.28	40 ±1.8	52.3
2:3	4.56 ± 0.15	15.87	38 ± 2.1	56.1
0:1	4.82 ± 0.11	13.81	63 ± 2.9	63.6

Moisture content of the SD microparticles produced from different MD:AG ratios were almost similar, ranging from 4.23 to 4.82 % (d.b). In the same way, mean particle diameter were similar and independent of encapsulating composition. EO retention increased with the MD:AG ratio, as expected due to emulsifying properties of the Arabic gum. Process yield was higher when high proportion of Arabic gum was used. GC analysis showed effectiveness of the mixtures maltodextrin/Arabic gum for thymol retention, which ranged from 72 % to 81 % in the SD microparticles.

Thermal analysis: TG analysis of EO shows a unique weight loss between 50 to 120 °C, corresponding to EO evaporation. Microparticles showed similar behavior between room temperature and 105°C, attributed evaporation of water and of volatiles. Increase in Arabic gum from 20% to 100% in the carrier mixture improved thermal stability of the product, since the decomposition temperature changed from 178°C to 212°C. EGD curves of SD microparticles as a function of MD:AG ratio are presented in Figure 1.

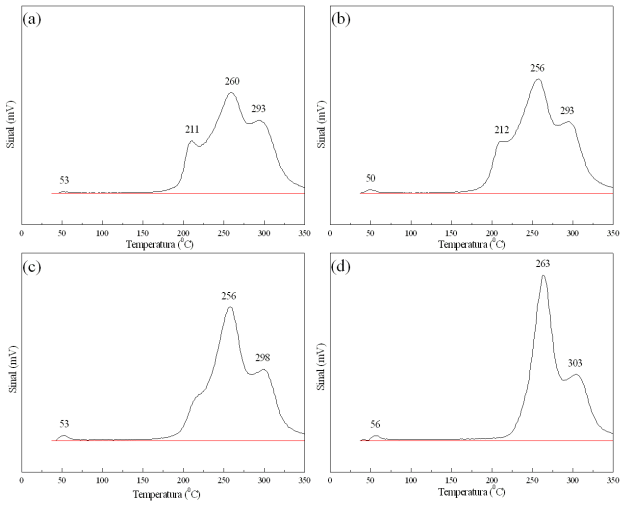

Figure 1. EGD graphs of SD microparticles for MD:AG ratios of: (a) 4:1; (b) 3:2; (c) 2:3; (d) 0:1.

Small amounts of EO adsorbed on particles surface were released at temperatures lower than 100 °C. Samples 1.a to 1.d show peaks at 210, 250 and 290 °C. Peak at 210 °C tends to vanish conversely with MD:AG ratio, indicating its probable association with MD degradation. EGD graphs show that release of organic compounds starts around 170-175 °C for samples with 20 and 40 % of AG, being dislocated to right at higher AG concentrations. TG-MS permits to follow precisely the EO release from SD microparticles through monitoring characteristics fragments, at mass to charge (m/z) of 91, 135, and 150. Multiple Ion Detection (MID) graphs shown in Figure 2 do not show significant evaporation of volatiles below 105 °C, with a steady increase beyond. Significant volatile release begins around 205 °C for samples 2.a to 2.c, evidencing the start of carriers degradation. Typical fragment signals intensify, generating peaks from 230-235 °C and 275-280 °C. TG, EGD and TG-MS results showed close agreement. For AG microparticles (sample 2.d), volatile release begins only at 235 °C; and at 270 °C it is observed an intense peak, linked to the encapsulated EO. Therefore, the carrier system affects not only the product thermal stability, but also the release pattern, which was more gradual for microparticles containing high MD:AG ratio.

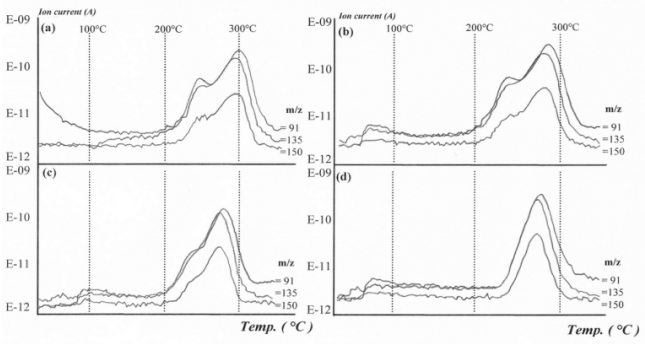

Figure 2. MID graphs of SD microparticles for MD:AG ratios of: (a) 4:1; (b) 3:2; (c) 2:3; (d) 0:1.

CONCLUSION

EO load in product increased conversely with MD:AG ratio. Conventional and hyphenated thermoanalytic techniques (TG, EGD, and TG-MS) are powerful tools to evaluate carriers performance and release patterns of spray dried EOs microparticles. Increasing AG in the encapsulating mixture improves product thermal stability, and changes the EO release patterns.

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ACKNOWLEDGMENTS

FAPESP for financial aid (Grant 2008/03588-0) and to CNPq for the fellowship to the second author.