

Headspace enrichment of bergamot and mandarin juices by means of Monolithic Material Sorptive Extraction (MMSE)

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INTRODUCTION

Mandarin and bergamot fruits and their by-products represent a valuable raw material for food, cosmetic and pharmaceutical industry. In particular, there is much interest toward the volatiles present in these matrices, which are naturally mixed in a so peculiar way that makes their artificial reconstitution very challenging. In order to investigate the headspace released by such matrices, many techniques have been utilized in the last decades (solvent extraction, purge & trap, SDE, SPME, SBSE, etc.). Techniques such as SPME or SBSE, although become very common, present some disadvantages mainly due to their small surface areas and low trapping capacity. In many cases, the recovery rate is very low and the time required for reaching equilibration state is quite long, with a consequent loss of efficiency. In the present study, samples of lab-extracted mandarin and bergamot juices have been subjected to headspace extraction by means of a novel sample preparation technique, namely Monolithic Material Sorptive Extraction (MMSE). This technique exploits the highly adsorptive capability of monolithic material which presents mesopores and through-pores in a silica frame, with an extra adsorbent constituted by activated carbon and terminal octadecyl chains (see figure 1). A parallel extraction on the same samples was carried out by means of SPME and the results compared with those obtained by MMSE.

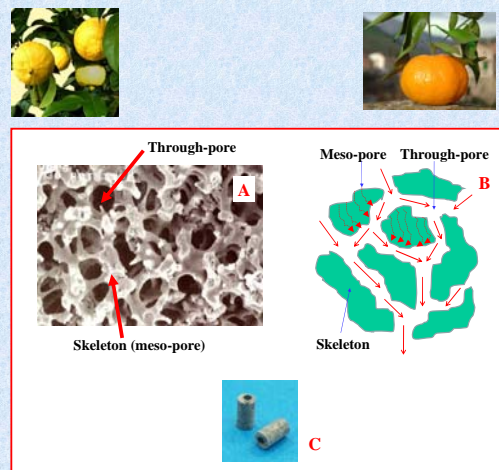


Figure 1 – A: image of the internal structure of the monotrap; B: scheme of the adsorption mechanism; C: a rod-type MMSE system

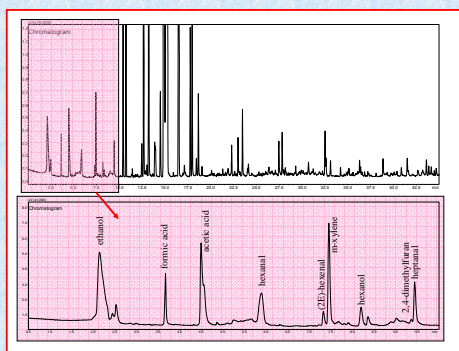


Figure 2 – GC-FID chromatogram of the headspace of mandarin juice extracted with monotrap and injected by thermal desorption

EXPERIMENTAL

Samples: Mandarin juice was obtained by hand squeezing fruits purchased from local stores. Bergamot juice was obtained by hand squeezing fruits harvested in Calabria and kindly provided by Simone Gatto company (Messina). Fresh samples were immediately subjected to extraction, when possible, otherwise they were sealed and kept at -18°C until extraction.

Headspace extraction: For MMSE extraction, a rod-type RCC 18 monotrap (GL Sciences, Japan) (monolith of Octadecyl silica plus active carbon) was used. For SPME extraction a Car/PDMS fiber (Supelco, USA) was used. Aliquots of 10 mL of juice were added with 1.0 g of NaCl, agitated and extracted for 30 min at 60°C .

Analysis: GC-FID analyses were carried out by means of a GC-2010 (Shimadzu) equipped with a 30 m x 0.25 mm I.D. x 0.25 μm d_f SLB-5MS column (Supelco); oven temperature program: 40°C to 250°C at $3^{\circ}\text{C}/\text{min}$, held 5 min; injection mode: split, with a split ratio of 20:1; injector and FID temperature: 250°C and 280°C ; a cryotrap (SGE, Australia) was mounted at the column head, and pressurized (90 bar) CO_2 was used as cooling gas. Carrier gas: helium, at 30.0 cm/s and a pressure of 97.4 KPa. Data processed by GCsolution software (Shimadzu). GC/MS analyses were carried out with a GCMS-QP2010 system (Shimadzu) with the following parameters: injection temp: 270°C ; inj. mode: splitless, sampling time 1.0 min, split ratio of 50:1; carrier: He, pressure 33.7 KPa; linear velocity: 32.4 cm/s; ion source temperature set at 200°C ; interface temperature at 250°C ; scan interval: 0.25 s; mass range: 40-400 m/z. Data handling was performed by the software GCMSsolution ver.2.5 (Shimadzu). The same cryotrap used in the GC-FID analysis was utilized in the GC-MS system. For peak assignment, the FFNSC 1.3 library (Chromaleont, Messina) has been used.

RESULTS AND DISCUSSION

The GC profiles of the headspace of mandarin and bergamot juices are shown in figures 2 and 3, respectively. A series of low boiling compounds has been detected, as can be seen in the two pink expansions relative to the first parts of the chromatograms. For both the matrices under investigation, the GC profile, approximately after 10 minutes, was more or less comparable with those of mandarin and bergamot essential oils, being characterized by terpenes and their oxygenated derivatives. These data are in good agreement with literature [1]. As previously mentioned, samples were subjected to SPME extraction as well. For some classes of compounds, recovery rates were definitely higher when MMSE was applied, demonstrating that the monolithic structure with meso-pores and through-pores acts as a larger surface of adsorption. In particular, MMSE resulted to be more suitable for the low-boiling compounds, as shown in figure 4, rather than SPME. In fact, as can be seen in figure 5, MMSE extracted an amount of monoterpenes and alcohols 4.6 and 4.5 times more than SPME. On the other hand, SPME showed to be more efficient toward aldehydes, esters and sesquiterpenes, whose recovery was twice higher than MMSE. The MMSE conditions are the result of a method development which involved different types of Mono Trap (rod-type, disk-type, with and without active carbon); different times of extraction (from 15 minutes up to 3 hours); different temperatures of extraction (from ambient up to 60°C). Final conditions were chosen based on a compromise between analysis time and recovery rate. Each sample was run in triplicate; repeatability was evaluated in terms of RSD, that fell in the range of 3.6 – 9.6%. In conclusion, compared to SPME, MMSE had better sensitivity toward the low boiling compounds because of higher recovery. Furthermore, it resulted to be a useful tool for investigating the chemical constituents responsible for the first perception of freshly squeezed juice aroma.

REFERENCE

[1] Moshonas M.G., Shaw P.E. Quantitative determination of 46 volatile constituents in fresh, unpasteurized orange juices using dynamic headspace gas chromatography. *J. Agric. Food Chem.*, 1994, 42, 1525-1528

ACKNOWLEDGEMENTS

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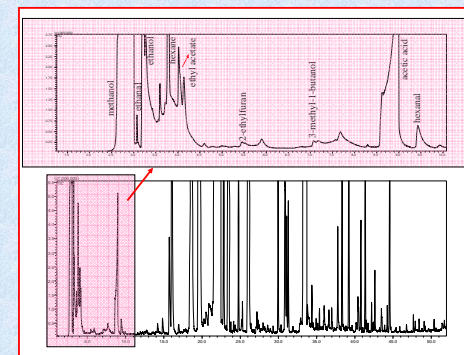


Figure 3 – GC-MS chromatogram of the headspace of bergamot juice extracted with monotrap and injected by thermal desorption

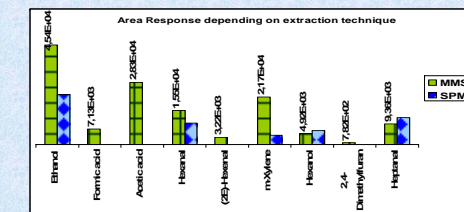


Figure 4 – Comparison of the extraction efficiencies of MMSE and SPME relative to the most volatile analytes

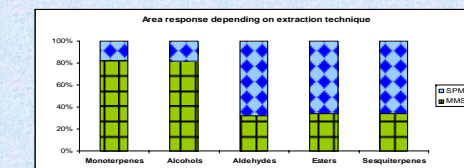


Figure 5 – Comparison of the extraction efficiencies of MMSE and SPME relative to the other classes of compounds