# Extraction and Identification of Natural Fragrances

**KEYWORDS:** Solvent Extraction / Citrus essential oils (CEOs) / Liquid–Liquid equilibrium (LLE)/ Aroma-active compounds

**The aroma profile of crude Citrus sinensis essential oil (EO) and its phases from the fractionation process by solvent extraction were evaluated. Ethanol with (30 and 40)%w/w water were prepared as solvents, and different mass ratios between EO and the solvent were used to reach the liquid–liquid equilibrium (LLE). The concentration of the components in the vapour phase above the liquid mixtures (crude EO and LLE phases) was experimentally assessed by headspace analysis. The solvent extraction was an efficient technique to yield extract phases with aroma resembling the crude orange EO, which may be incorporated into aqueous products, such as perfumes and beverages.**

**The air diffusion of aroma-active compounds found in crude CEOs, orange and acid lime, and their extract phases obtained by liquid–liquid extraction using hydroalcoholic solvents were thus evaluated. Experimental assays were conducted in a diffusion tube, where lower odor intensities were related to longer distances from the liquid mixture. Terpenes were mainly responsible for crude CEOs and orange extract phase aroma due to their high concentration in the vapor phase, while citral exhibited higher odor intensity in a region close to the acid lime extract phase.**

## Introduction OR Objectives

*Citrus sinensis* (L.) Osbeck (orange) is the most cultivated citrus species in the world, representing almost 25% of the global flavour market, and being one of the most used flavours in beverages. Citrus essential oils (CEOs) are important raw materials present in the formulation of perfumes, foods, beverages, soft drinks, cosmetics and pharmaceuticals. Thus, the aroma profile of each LLE phase (raffinate and extract) of the systems composed of crude orange EO and solvent (ethanol and water mixtures) was investigated and compared to the original orange EO aroma. In order to achieve this aim, systems containing different ratios of EO and solvent (EO/S = 4/1, 1/1 and 1/2), and two different concentrations of water in the solvent (30 and 40)%w/w were prepared.

Furthemore, the volatile fraction of CEOs is mainly composed of terpenes (~0.95 mass fraction), which have been reported as unstable components, easily degraded when exposed to the air, light, or heat, generating compounds with unpleasant odor that will compromise the final aroma and commercial value of the CEOs. The air diffusion of aroma-active components of extract phases obtained from the fractionation of CEOs was thus evaluated. Extract phases from C. sinensis and C. latifolia EOs, obtained by solvent extraction with hydroalcoholic solvents, were studied simulating an alcoholic beverage with high ethanol content (over 0.4 mass fraction). The propagation of the volatiles from crude C. sinensis and C. latifolia EOs was also studied for comparison purposes. The experimental diffusion profiles were evaluated over time and distance from the liquid mixture in a diffusion tube at 298.2 K.

## Current Development

Concerning the liquid mixtures, chemical analysis revealed monoterpenes as the major group of components present in the crude orange EO and raffinate phases, whereas the extract phases were abundant in solvent (ethanol and water). In terms of odour intensity, results indicated that α-pinene and limonene dominated the aroma of the crude EO and that ethanol, α-pinene, and limonene dominated the odour of the LLE phases. The headspace analysis highlighted α-pinene > limonene > octanal > linalool > citronellal > nonanal as the components most responsible for the typical orange EO aroma, which was also confirmed by the sensory analysis using a model orange EO mixture.

Based on the present study it is possible to infer that the solvent extraction technique using ethanol/water mixtures applied to the fractionation of crude orange EO led to extract phases with typical orange EO. Furthermore, the majority of the panelists demonstrated preference for the extract phase, in terms of aroma qualities. Finally, this study highlights that the extract phase using EO/S = 1/1 and ethanol with 40 (%w/w) water was the best candidate in terms of sensory quality and lesser use of solvent to be incorporated in liquid products, such as perfumes and beverages (Fig.1).

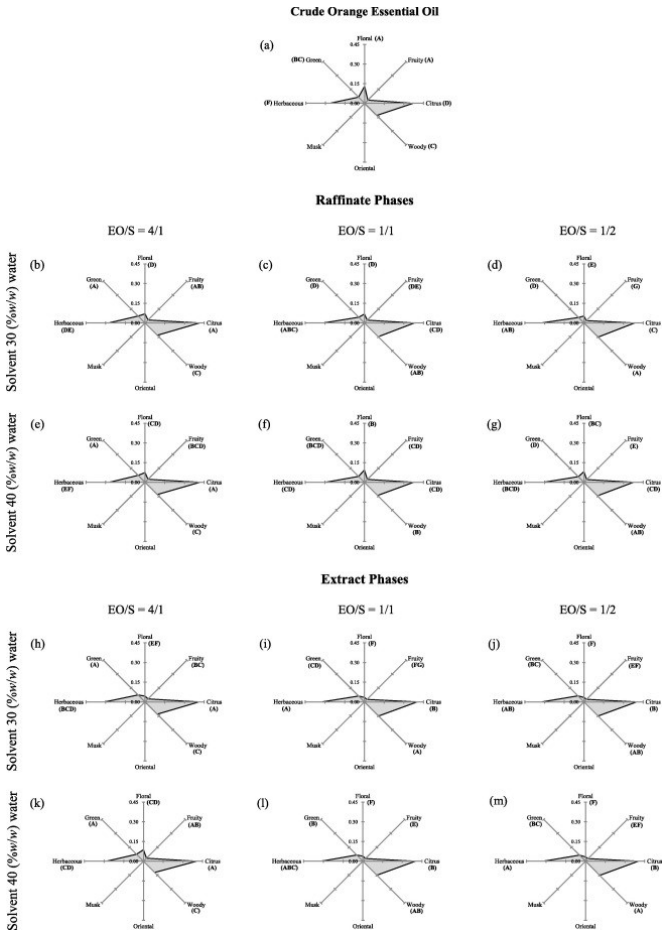


Fig 1. Perfumery Radars: (a) crude orange essential oil; LLE phases: (b) to (g), raffinate phases; (h) to (m), extract phases. Water in the solvent: (b) to (d) and (h) to (j), 30 (%w/w); (e) to (g), and (k) to (m), 40 (%w/w). Essential oil to solvent mass ratio (EO/S): (b), (e), (h), and (k), 4/1; (c), (f), (i), and (l), 1/1; (d), (g), (j), and (m), 1/2. Olfactory families followed by the same letter do not show significant differences by Duncan's test ($P \leq 0.05$).

Regarding the air diffusion studies, the odor intensity of the components decreases as the distance from the liquid source increases. In practical terms, when a bottle containing the crude orange EO is opened, limonene and α-pinene will dominate the aroma up to 7 h and up to 1.13 m from the liquid source. In the case of the crude acid lime EO, it will smell like α-pinene; however, an a larger distance from the liquid, its odor intensity will be very low. The aroma of the extract phases is less intense in comparison with that of the crude CEOs. Ethanol did not present strong odor intensity, mainly at a distance close to the liquid mixture, which is interesting in the case of alcoholic beverages or perfumes. Limonene and α-pinene were mainly responsible for the aroma of the extract phases despite their low compositions in the liquid mixtures. In the case of the acid lime extract, at a distance close to the liquid mixture, citral dominated the odor space up to 7 h, indicating a strong lemon/lime typical odor.

**Future Perspectives**

The extraction and identification of high-value aromatic components with pleasant fragrance properties suggest that essential oils are an exploitable source of relevant compounds which may be incorporated into different products.

**Related Sustainable Development Goals**

**Outputs**

**PhD Theses**

[1] Daniel Gonçalves, Fracionamento de óleos essenciais cítricos utilizando etanol com diferentes níveis de hidratação como solventes: Equilíbrio de fases, propriedades físicas e extração em equipamento contínuo, FZEA, USP, Brasil, PDEQB, FEUP, 2017

**Selected Publications**

[1] H. Noureddine, I. P. Fernandes, S. A. Heleno, P. Costa, Z. Boucherit-Otmani, K. Boucherit, A. E. Rodrigues, I. C.F.R. Ferreira and M. F. Barreiro, Molecules 23, 1571 (2018)

[2] H. Noureddine, S.A. Heleno, P. Costa, I.P. Fernandes, R.C. Calhelha, B. Kebir, A.E. Rodrigues, I. Ferreira, M. F. Barreiro, INDCROP 119, 249-254 (2018)

[3] D. Gonçalves, C. Rodrigues, P. Costa and A. E. Rodrigues, Journal of Chemical Thermodynamics 116, 166-175 (2018)

[4] D. Gonçalves, P. Costa, C. Bejar, A. Bocquet, C. Rodrigues and A.E. Rodrigues, Ind Eng Chem Res 57(16) 5670-5679 (2018)

**Team**

**Alírio E. Rodrigues** Professor; **Patrícia Costa,** Researcher; **Daniel Gonçalves,** PhD student

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