



Commentary/Commentaire

Commentary on the article *Potentialities of using liquefied gases as alternative solvents to substitute hexane for the extraction of aromas from fresh and dry natural products*, by Vincent Rapinel, Cyrille Santerre, Farnaz Hanaei, Justine Belay, Nadine Vallet, Njara Rakotomanomana, Alain Vallageas, and Farid Chemat, *C. R. Chimie* 21 (2018) 590–605



The article published in *C. R. Chimie* 21 (2018) 590–605, by V. Rapinel et al., entitled “Potentialities of using liquefied gases as alternative solvents to substitute hexane for the extraction of aromas from fresh and dry natural products”, calls for the following comments. 1. To intensify the appearance of novelty in the work that they report, the authors have omitted to cite a large number of published documents on the subject of extraction of aromatic or fragrant natural products with liquefied gases. Such documents include articles published in peer-reviewed scientific journals, professional publications, conference proceedings, and more importantly, published patent applications, whether subsequently granted or not.

In a nonexhaustive manner, one can cite some typical examples in chronological order:

- the patent GB 292983 filed in 1928 on the extraction of clove oil with liquid CO₂;
- the patent US2106200 filed in 1935 on the extraction with propane or butane of fragrant plant material, including lavender flowers;
- the article published in 1950 by Meunier in *Industrie de la Parfumerie*, describing the industrial extraction of fragrant flowers with butane;
- the patent US150050 filed in 1959 on the extraction of fragrant biomass with fluorohydrocarbon solvents;
- the patent FR1311766 filed in 1960 on the extraction of fragrant plant material with fluorinated liquefied gases;
- several articles by P. Wilde, including the one published in *Perfumer & Flavorist* in November 1994;
- the international patent application WO 98/45013 filed in 1997, claiming the use of mixtures of liquefied fluorinated gases for the extraction of odoriferous plant materials;
- the international patent application WO 00/64555 filed in 1999, on the extraction of fragrant natural raw

materials with various liquefied fluorinated gases, including R-245fa; and

- the patent GB2446596 filed in 2007, claiming the design of a portable device for the field extraction of fragrant plant material with liquefied fluorinated gases, and so forth.

2. The analytical technique used by the authors is doubly questionable because it deviates from good practice for the quantitative analysis of solvent extracts of fragrant natural products. The reason is that such products comprise a nonvolatile fraction, with constituents that are not eluted from a GC column under conventional conditions, and that the proportion of this fraction varies depending on the extraction solvent, which invalidates any comparison between different extracts, unless elementary precautions are taken. Concentrations measured by internal normalization (relative percentage) for GC-eluted constituents of the volatile fraction do not represent the reality for a given extract, and it is essential to operate by standardization, preferably internal. Moreover, and no less importantly, the use as a GC detector of the TIC of a GC–MS in electron-impact mode for the semi-quantification by internal normalization is notoriously inappropriate, due to the nonreproducibility of the response. It follows that all data shown in Table 4 are inaccurate.

The quality of this publication is therefore definitively jeopardized by the overestimation of the level of innovation, by the omission of existing work and patents on the subject, and by the lack of analytical rigor, invalidating the conclusions.

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