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HELPING CHEMISTS

APPLICATION REPORT

EX01 - CITRUS PEEL FLAVOR

Citrus peel Microwave Hydrodiffusion and Gravity (MHG)

Introduction

Citrus is the most abundant crop in the world, with about 64 million tons of orange and 13 million tons of lemon products produced during 2004. The amount of residue obtained from citrus fruits account for 50% of the original amount of whole fruit. Produced in tones per day, citrus by-products represent a problem for management, pollution, and environmental issues, due to microbial spoilage. Citrus peel of fruit processing which provides a great potential for further commercial use. During the process of juice extraction oil sacs break and release volatile oils which are in pockets localized in the external part of the mesocarpe of fruit (flavedo). These oils are used in food and pharmaceutical industries, but can also provide flavoring ingredients to drinks, ice creams and other food products. In addition, substantial quantity of these oils is also used in the preparation of toilet soaps, perfumes, cosmetics and other home care products. Virot, Tomao, Ginies, Visinoni, and Chemat (2008) reported that the d-limonene, major component of the oil extracted from citrus peels, could be used as green solvent instead of hazardous petroleum

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solvents for fats and oils determination. D-limonene is considered as a very versatile chemical which can be used in a wide variety of applications [1] [2].

[1] N. Sahraoui, M. Abert Vian, M. El Maataoui, C. Boutekedjiret, F. Chemat, Innovative Food Science and Emerging Technologies 2011, 12, 163-170.
[2] V. Virot, V. Tomao, C. Ginies, F. Visinoni, F. Chemat, Journal of Chromatography A 2008, 1196, 147-152.

Why to choose Microwave Flavor set-up?

The patented and revolutionary Microwave Hydrodiffusion and Gravity (MHG) system pays the way to new flavoring products which were impossible to be obtained with the ancient extraction concepts. Percolation, solvent extraction ecc… were inefficient and environmental-unfriendly methods of flavor extraction. MHG is going to improve the efficiency and the quality of flavoring products.

- New natural flavors
- Fast extraction
- No thermal degradation
- No solvent

Instrumentation and Principles of Operation

A very efficient extraction process can be achieved thanks to the selective heating of microwaves to materials through molecular interactions with the electromagnetic field via conversions of electromagnetic energy into thermal energy. The high quality fragrance were obtained through MHG techniques (see the "Microwave Extraction Techniques" section for theory and principle).

Results and experimental procedure

The MHG technique is suitable for both dry and fresh raw material, see the "Quick start guide" for a list of easy and sequential setting-up operations (*Table 1*).

Fresh Citrus peel (MHG)

Reactor	Weighted fresh raw material [g]*	Power [W]	Chiller		Total flavour extract [mL]	Volatile fraction [mL]	Total flavor extract yield [%]
			1kW	2.1kW			
Small	500	500	•		190	9.5	38
Medium	1580	1580		•	621	30	39.3
Large	3720	1800		•	1400	70.5	38.7

Dry Citrus peel (MHG)

Reactor	Weighted dry soaked material [g]*	Power [W]	Chiller		Total flavour extract [mL]	Volatile fraction [mL]	Total flavor extract yield [%]
			1 kW	2.1kW			
Small	500	500	•		150	6.2	30
Medium	1580	1580		•	540	24	34.2
Large	3720	1800		•	1330	59	35.8

*Time, Power
The extractions were carried out till complete recovery of the fragrance
≤ 1800 g: Power(W) = Weight(g) for 20 min.
> 1800g: Power = 1800W for 40min
Chiller settings:
≤ 900g, 1 kW Chiller
> 900g, 2.1 kW Chiller

Table 1

Important remarks

Please take into account that the interaction between microwaves and raw material is based on the water content. The optimized method (power and time) depends on the type of Citrus, mainly to the water content of Citrus itself. Please use the reported parameter as general application note to start to optimize your own method. Be careful, that using an excess power might cause burning of your sample.

Please take care to seal properly the glass reactor during the installation of the flavors set-up according to the manual, to avoid loss of vapor during extraction.

Conclusion

A newly and cleaner design process for extraction of flavors was developed in this study: MHG. This green process has been studied and tested using citrus peels. This new system was developed to date indicate that microwave extraction process of flavors offers important advantages over antiquated extraction techniques, namely, shorter extraction times, less energy consuming, lower costs as well as new flavoring products. The MHG system offers furthermore the possibility to work with scalar amounts of sample due to three different reactor vessels (small, medium, large), complying with a high range of extraction-scale needs.

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APPLICATION REPORT

EX02 - CITRUS PEEL FRAGRANCES

Citrus Peel Solvent-Free Microwave Extraction (SFME) and Microwave Hydrodistillation (MWHD)

Introduction

Citrus essential oils are the most widely used essential oils in the world. They are obtained as by-products of the citrus processing. They are used as aroma flavor in many food products, including alcoholic and non-alcoholic beverages, candy, gelatins. In pharmaceutical industries they are employed as flavoring agents to mask unpleasant tastes of drugs. In perfumery and cosmetic, they are used in many preparations. The traditional way to extract essential oils is by cold pressing the citrus peels. The oil is present in oil sacs or oil glands located at different depths in the peel and the cuticles of the fruit. Peel and cuticle oils are removed mechanically by cold pressing and since cold pressing yields a watery emulsion, this emulsion is then centrifuged to separate out the essential oil. Distillation is also used in some countries as an economical way to recover the oils. During distillation, the Citrus peels exposed to boiling water or steam, release their essential oils through evaporation. Researchers in many universities are working on novel techniques that could lead to compact, safe,

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efficient, energy saving, and sustainable extraction processes. Solvent-Free Microwave Extraction (SFME) as upcoming extraction techniques have been reported for the extraction of fragrances and flavors from citrus peel[3].

[3] N. Bousbia, M. Abert Vian, M. Ferhat, B. Meklati, F. Chemat, Journal of Food Engineering 2009, 90, 409-413.

Why to choose Microwave Fragrances set-up?

The standard method is the Clavenger method, which was published for the first time in 1928. According to that method, the essential oil from cistrus peel can be extracted by hydrodistillation or steam distillation. These techniques take several hours of heating which may cause degradation of thermolabile compounds present in the starting plant material and therefore odor deterioration. The patented and innovative Microwave Hydrodistillation (MWHD) and Solvent-free Microwave Extraction (SFME) techniques allow the production of essential oils with higher quality.

- High quality frangrances
- No thermal degradation
- Fast extraction
- High purity, no artifacts

Instrumentation and Principles of Operation

A very efficient extraction process can be achieved thanks to the selective heating of microwaves to materials through molecular interactions with the electromagnetic field via conversions of electromagnetic energy into thermal energy. The high quality fragrance were obtained through the SFME or MWHD techniques (see the "Microwave Extraction Techniques" section for theory and principle).

Results and experimental procedure

The SFME and the MWHD techniques are respectively suitable for fresh and dry raw materials. See the "Quick start guide" for a list of easy and sequential setting-up operations (*Table 2*).

Fresh Citrus peel, SFME						
Reactor	Weighted fresh raw material [g]*	Power [W]	Chiller		Volatile fraction [mL]	Yield [%]
			1kW	2.1kW		
Small	500	500	•		4.9	1.0
Medium	1580	1580		•	16	1.0
Large	3720	1800		•	48.4	1.3

Dry Citrus peel, MWHD						
Reactor	Weighted dry soaked material [g]*	Power [W]	Chiller		Volatile fraction [mL]	Yield [%]
			1 kW	2.1kW		
Small	500	500	•		2.8	0.56
Medium	1580	1580		•	9	0.57
Large	3720	1800		•	22.7	0.61

*Time, Power
The extractions were carried out till complete recovery of the fragrance
≤ 1800 g: Power(W) = Weight(g).
> 1800g: Power = 1800W
Chiller settings:
≤ 900g, 1 kW Chiller
> 900g, 2.1 kW Chiller

Table 2

Important remarks

The system is developed with an automatic recirculation of the distilled water. This allows to manage extraction power and time to match your own specific requirements. Please take care to seal properly the glass reactor during the installation of the fragrances set-up according to the manual, to avoid loss of vapor during extraction.

Conclusion

In this study, we propose state-of-the-art processes for extraction of essential oils from Citrus peel through SFME and MWHD. It is the unique modern concept of the antiquated Clavenger method, highly accelerating the isolation process, without causing changes in the volatile oil composition. The efficiency of the new techniques SFME and MWHD are considerably higher than the conventional procedure, if we take into account short distillation times required, cost and energy used and cleanliness of the process. An added-value feature is the possibility to work with scalar amounts of sample due to three different reactor vessels (small, medium, large), complying with a high range of extraction-scale needs.

No.	Compounds[a]	R.I.[b]	R.I.[c]	SFME
	Monoterpenes			**92.76**
1	Pinene<Alpha->	926	1023	1.75
2	Pinene<Beta->	974	1109	15.35
3	Myrcene<Beta->	988	1165	1.33
4	Carene<Delta-3-> 1101	1101	1290	0.20
5	Limonene	1030	1206	65.25
6	Terpinene<Gamma->	1103	1285	8.08
	Oxygenated Monoterpenes			**92.76**
7	Linalool	1125	1538	0.18
8	Citron ellal	1167	1478	0.05
9	Terpin-4-ol	1191	1590	0.42
10	Terpineol<Alpha->	1203	1677	0.56
11	Nerol	1237	1781	0.49
12	Neral	1268	1670	0.68
13	Geraniol	1271	1828	0.60
14	Geranial	1284	1714	0.89
	Sesquiterpenes			**1.06**
15	Elemene<Beta->	1373	1583	-
16	Caryophellene<E->	1391	1594	0.18
17	Bergamotene<Alpha-Trans->	1437	1577	0.28
18	Humulene<Alpha->	1450	1657	0.04
19	Farnesene<(E)-Beta->	1453	1650	0.02
20	Germacrene D	1477	1696	-
21	Valencene	1488	1705	0.04
22	Bisabolene<(Z)-Alpha->	1498	1761	0.03
23	Bisabolene(Beta-)	1508	1718	0.44

Table 3. Chemical compositions of essential oils from citrus peel obtained by SFME

No.	Compounds[a]	R.I.[b]	R.I.[c]	SFME
	Oxygenated Sesquiterpenes			**0.03**
24	Elemol	1540	1381	-
25	Nerolidol<E->	1555	2026	-
25	Bisabolol<Alpha->	1684	2212	0.03
27	Nootkatone	1799	2250	-
	Other oxygenated compounds			**0.86**
28	Nonanal<N->	1126	1400	0.06
29	Citronellyl Acetate	1342	1645	0.04
30	Neryl Acetate	1351	1706	0.19
	Extraction time (min)			180
	Yield (%)			0.8
	Total oxygenated compunds (%)			4.78
	Total non oxygenated compounds (%)			93.82

[a] Essential oil compounds sorted by chemical families and percentages calculated by GC-FID on non-polar HP5MS™ capillary column.
[b] Retention indices calculated on non-polar HP5MS™ capillary column.
[c] Retention indices calculated on polar Carbowax™-PEG capillary column.

Table 3 (continued).