MILESTONE
HELPING CHEMISTS

MICROWAVE EXTRACTION OF CITRUS ESSENTIAL OIL

Solvent-free microwave extraction (SFME) has been tested as new and green alternative technique for the extraction of essential oil from various citrus peels. In this study, microwave was compared to the two most popular conventional extraction techniques for citrus peels, hydrodistillation and cold pressing. Milestone's ETHOS X family shows to be the fastest and the most efficient extraction technique, maximizing the quality of the organoleptic profile of the final oil.

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 byproducts represent a problem for management, pollution, and environmental issues, due to microbial spoilage.

During the process of juice extraction, oil sacs break and release volatile oils, which are in pockets located 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 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 (N. Sahraoui, 2011) (M. Virot, 2008). This application report describes how the Milestone ETHOS X family can help citrus processors to take advantage of the unique microwave selective heating mechanism for a fast and efficient solvent-free extraction of the complete essential oil profile.

| EXPERIMENTAL

INSTRUMENT

- ETHOS X Microwave Green Extraction of Natural Products
- Stainless-steel fragrances kit set up
- Fragrances extraction vessel 2 L
- Chiller 1 kW

ETHOS X 2.0 and ETHOS XL defer from the ETHOS X only for their production capacity. These two systems are based on the same technology and designed for enhanced production capacity.

SAMPLE AND REAGENTS

- Citrus samples: Eureka (*Citrus limon* L.), Villa França (*Citrus limon* L.), Lime (*Citrus aurantifolia*), Marsh Seedless (*Citrus paradisi* L.)
- Distilled water

PROCEDURE

Citrus fruits were peeled to separate the external part of the lemon, giving a yield of 20% (w/w) of the peel with respect to the whole fruit. 500g of fresh peels were employed in all extractions.

SOLVENT-FREE MICROWAVE EXTRACTION (SFME):

500g of fresh peels of each plant species was weighed and placed in a separate mixing container. 250 mL of distilled water was added and the material was soaked and mixed for 5 minutes to ensure complete rehydration. The wet material was then transferred inside the 2 L glass extraction vessel. Once closed, the reactor was placed inside the ETHOS X cavity and the stainless steel distillation module was assembled. The sample was heated at 1200 W for 5 min and for further 30 min at 500W. After 5 min, the aromatic essential oil fraction started to be collected in the graduated burette, above the water layer. The extraction was completed after 35 min when the terpenes were completely extracted. At the end of the extraction, the essential oil fraction was collected from the glass distillation module, frozen for 30 min to remove extra water and then stored in a refrigerator at 4°C.

CONVENTIONAL HYDRODISTILLATION (HD)

HD was carried out with a conventional Clevenger-type apparatus starting from 500 g of fresh citrus peels with 3 L of water for 3 h until no more essential oil was obtained (Nabil Bousbia a, 2009).

COLD PRESSING (CP)

For CP, essential oil was collected from 1 kg of whole lemon fruit using an automated cold pressing machine. The epidermis and oil glands were lacerated by a needle, creating areas of compression in the peel, surrounded by areas of lower pressure, across which the oil flowed to the exterior. The oil is carried down to a decantation vessel in a stream of water, the emulsion being collected and then separated by centrifugation (Nabil Bousbia a, 2009).

The essential oil fraction and relative quantification was performed by gas chromatography coupled to mass spectrometry (GC-MS) and the relative percentage of the components was calculated from GC-FID peak areas. Most constituents were tentatively by comparison of their mass spectral fragmentation patterns with those stored in the MS database (National Institute of Standards and Technology and Wiley libraries) and with mass spectra literature data (l'Europe, 1996).
The organoleptic properties of essential oils extracted by SFME, HD and CP have been done according to sensory evaluation conducted by twelve trained panelists who were graduate students and staff members in the laboratory of the University of Avignon. Randomly coded samples were individually served to panelists (Nabil Bousbia a, 2009).

RESULTS AND DISCUSSION

Table 1: SFME, HD and CP results

	EXTRACTION TECHNIQUE		
PARAMETERS	SFME	HD	CP
Time	35 min	180 min	60 min
Extraction Yield	1.0±0.1%	1.1± 0.1%	0.2± 0.1%
Sensory evaluation	Fresh, light, flora woody, sweet	Fresh, pungent with boiled odor	Fresh, light, flora woody, sweet

As shown in table 1, SFME allows an essential oil recovery of 1.0 ± 0.1% in yield (w/w) compared to 1.1 ± 0.1% (w/w) of Conventional Hydrodistillation and 0.2 ± 0.1% (w/w) of the Cold Pressing. Total extraction time are 35 minutes for SFME, 180 minutes for HD and 1 hour for CP (Nabil Bousbia a, 2009). The essential oils of lime peels extracted either by MHG, HD or CP are rather similar in their composition and contains the same dominant components (Table 2). The same number of volatile secondary metabolites is found in the essential oil isolated by MHG, HD or CP, with relatively similar percentages.

Limonene, a monoterpene hydrocarbon, is the main abundant component in the essential oil extracted from lime with equivalent relative amounts for both extraction methods: 70.9%, 71.22% and 71.86%, respectively for MHG, HD and CP. Geranial, an oxygenated monoterpene, is present at 1.37%, 0.85%, and 1.82%, respectively for MHG, HD and CP. These results proved the ability of ETHOS X to provide a superior terpene profile protecting the valuable volatile molecules from the oxidation process (Nabil Bousbia a, 2009).

For SFME and CP, the extracted essential oils have the same scent of terpenes hydrocarbons with fresh, light, flora woody and sweet citrusy odour. For HD, the essential oil has an odour of terpenes hydrocarbons fresh, pungent but different from fresh fruit and with a persistent boiled odour. SFME method offers the possibility for a better reproduction of natural aroma of the fruit essential oil comparable to CP but more than the hydro-distilled essential oil. SFME could be a good alternative for the isolation of essential oils from citrus fruits (Nabil Bousbia a, 2009).

Table 2: GC-MS results for SFME, HD, and CP on different citrus plant species

N°	COMPOUNDS	Eureka			Villa França			Lime			Marsh Seedless		
		SFME	HD	CP	SFME	HD	CP	SFME	HD	CP	SFME	HD	CP
	Monoterpenes	**92.10**	**92.76**	**93.73**	**89.68**	**88.39**	**93.60**	**88.70**	**92.50**	**95.80**	**97.93**	**97.03**	**97.27**
1	Pinene<Alpha->	1.60	1.75	1.62	1.53	1.18	1.02	1.86	1.94	1.62	0.41	0.45	0.27
2	Pinene<Beta->	10.20	15.35	14.00	6.99	7.08	9.24	11.60	13.09	14.00	-	-	-
3	Myrcene<Beta->	1.57	1.33	1.42	1.51	1.52	1.55	1.40	1.46	1.42	1.73	1.81	1.55
4	Carene<Delta-3->	0.11	0.20	0.15	0.16	0.15	0.15	-	-	-	-	-	-
5	Limonene	69.65	65.25	68.81	70.92	71.22	71.86	60.56	63.44	68.81	95.05	94.21	94.54
6	Terpinene<Gamma->	8.25	8.08	7.04	7.70	6.58	8.90	11.91	11.17	8.90	0.01	0.03	0.01
	Oxygenated Monoterpenes	**3.01**	**3.89**	**2.65**	**3.72**	**3.75**	**3.65**	**5.11**	**4.91**	**3.71**	**0.45**	**0.51**	**0.36**
7	Linalool	0.20	0.18	0.10	0.20	0.35	0.22	0.25	0.36	0.22	0.17	0.18	0.07
8	Citronellal	0.1	0.05	0.08	0.09	0.06	0.07	0.05	0.05	0.08	0.05	0.02	0.03

9	Terpin-4-ol	0.08	0.42	0.03	0.09	0.37	0.02	0.08	0.19	0.03	0.02	0.09	0.02
10	Terpineol<Alpha->	0.21	0.56	0.22	0.29	0.53	0.23	0.38	0.37	0.23	0.06	0.08	0.05
11	Nerol	0.26	0.49	-	0.30	0.44	0.09	0.20	0.13	0.09	-	-	-
12	Neral	0.76	0.68	0.77	0.94	0.53	1.06	1.66	1.55	1.06	0.04	0.03	-
13	Geraniol	0.24	0.60	-	0.32	0.56	0.07	0.12	0.07	0.07	0.02	0.02	-
14	Geranial	1.08	0.89	1.30	1.37	0.85	1.82	2.23	2.05	1.82	0.03	0.04	0.04
15	**Sesquiterpenes**	**0.85**	**1.06**	**1.65**	**0.99**	**0.85**	**0.88**	**2.12**	**3.56**	**1.92**	**1.98**	**0.49**	**0.50**
16	Elemene<Beta->	-	-	-	-	-	-	-	-	-	0.06	0.04	0.08
17	Caryophellene <E->	0.13	0.18	0.24	0.17	0.16	0.35	0.56	0.31	0.35	0.17	0.20	0.72
18	Bergamotene< Alpha-Trans->	0.03	0.04	0.06	0.03	0.05	0.09	0.13	0.06	0.09	0.04	0.04	0.17
19	Farnesene<(E)-Beta->	0.01	0.02	0.02	-	0.01	0.02	0.03	0.06	0.02	-	-	0.03
20	Germacrene D	-	-	-	-	-	-	0.05	-	-	-	-	-
21	Valencene	-	0.04	-	0.01	0.07	0.11	-	-	-	-	-	-
22	Bisabolene<(Z)-Alpha->	0.02	0.03	0.05	0.03	0.02	0.07	0.10	0.05	0.07	-	-	-
23	Bisabolene(Beta-)	0.38	0.44	0.75	0.43	0.31	0.87	1.51	0.81	0.87	-	-	-
24	**Oxygenated Sesquiterpenes**	**0.02**	**0.03**	**0.03**	**0.1**	**0.24**	**0.04**	**0.02**	**0.02**	**0.03**	**0.10**	**0.16**	**0.26**
25	Elemol	-	-	-	-	-	-	-	-	-	0.01	0.01	0.04
26	Nerolidol<E->	-	-	-	-	-	-	-	-	-	0.01	0.01	0.02
27	Bisabolol<Alpha->	0.01	0.03	0.03	0.09	0.15	0.04	0.02	0.02	0.03	-	-	-
28	Nootkatone	-	-	-	-	-	-	-	-	-	0.07	0.13	0.15
29	**Other oxygenated compounds**	**0.95**	**0.86**	**0.65**	**0.75**	**0.71**	**0.69**	**1.19**	**0.82**	**0.59**	**0.52**	**0.74**	**0.38**
30	**Nonanal<N->**	0.08	0.09	0.06	0.10	0.02	0.08	-	-	-	0.04	0.04	-
31	**Citronellyl Acetate**	0.02	0.03	0.04	0.02	0.02	0.04	0.04	0.02	0.04	0.01	0.01	0.05
32	**Neryl Acetate**	0.30	0.26	0.19	0.34	0.36	0.32	0.87	0.60	0.19	0.01	0.01	0.05

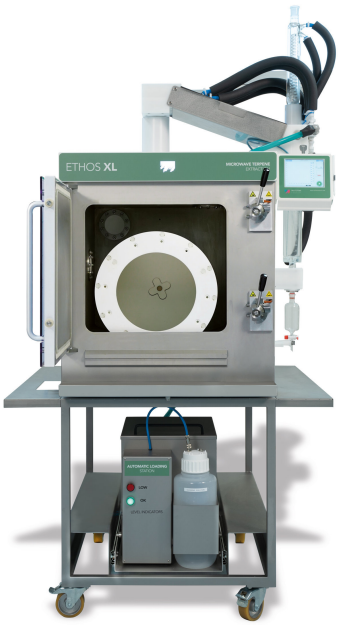
CONCLUSIONS

The data shown in this work demonstrates that solvent-free microwave extraction is able to maximize the extraction of essential oils from Citrus peels within 35 minutes total extraction time, showing to be the most efficient and rapid process on the market, compared to conventional extraction techniques. The fast-processing times and its ability to work with fresh material produces a superior organoleptic profile that is unmatched by conventional extraction techniques. Milestone's ETHOS X family has proven to be a unique and beneficial solution for Citrus peels essential oil producers, allowing them to obtain scents with unmatched quality in very short runs.

APPLICATION REPORT
ETHOS X | CITRUS PEELS

Based on the same technology and approach Milestone has developed the ETHOS X 2.0 and the ETHOS XL dedicated to more intense processes. The ETHOS X 2.0 is available with a 15 L reactor and a simplified handling, to ensure fast and easy craft production capacity.

The ETHOS XL has been built for medium-large size producers. It has a rotating drum with a total capacity of 45 L, high power to ensure fast processes and a semiautomated workflow to streamline the production.



REFERENCES

l'Europe, C. d. (1996). Pharmacopée Européenne 1. Sainte Ruffine: Maisonneuve S.A. Editions.

M. Virot, V. T. (2008, July 4). Microwave-integrated extraction of total fats and oils. Journal of Chromatography , pp. 147-152.

N. Sahraoui, M. A. (2011). Valorization of citrus by-products using Microwave Steam Distillation (MSD). Innovative Food Science and Emerging Technologies, 12, pp. 163-170.

Nabil Bousbia a, b. M. (2009). A new process for extraction of essential oil from Citrus peels: Microwave. Journal of Food Engineering, pp. 409–413.

https://www.milestonesrl.com/products/microwave-extraction/ethos-x-for-natural-products

ABOUT MILESTONE

At Milestone we help chemists by providing the most innovative technology for metals analysis, direct mercury analysis and the application of microwave technology to extraction, ashing and synthesis. Since 1988 Milestone has helped chemists in their work to enhance food, pharmaceutical and consumer product safety, and to improve our world by controlling pollutants in the environment.

MILESTONE
HELPING CHEMISTS

MILESTONE Srl - Via Fatebenefratelli, 1/5 - 24010 Sorisole (BG) - Italy
Tel: +39 035 573857 - Fax: +39 035 575498
www.milestonesrl.com - email: analytical@milestonesrl.com