

Microwave-Assisted Extraction – A State-of-the-Art Overview of Varieties

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Abstract: The microwave-assisted extraction technique offers some advantages over conventional extraction methods. Applications include the extraction of high-value compounds from natural sources including nutraceutical and functional food ingredients, pharma actives from biomass, and phytonutrients. Compared to conventional solvent extraction methods, the microwave-assisted extraction (MAE) technique offers advantages such as improved stability of products and marker compounds, increased purity of crude extracts, the possibility to use less toxic solvents, reduced processing costs, reduced energy and solvent consumption, increased recovery and purity of marker compounds, and very rapid extraction rates.

Keywords: Extraction techniques · Food · Microwave-assisted extraction · Plant · Soxhlet extraction

Introduction

Extraction procedures aimed at the improvement of recovery from any kind of organisms, tissues or cell types can be found described in books, monographs, overviews and articles. After the first known studies by Chevreul on the dissolution of lipid materials in various solvents, Franz von Soxhlet described the first method based on an automatic solvent extraction (diethyl ether) for milk lipids ('Die gewichtsanalytische Bestimmung des Milchfettes' [1]). A further improvement was made by Bloor in 1914 when a mixture of ethanol/ether (3:1) was used for lipid extraction [2]. Despite the early use of chloroform in extracting lipids in 1931 the greatest improvement of the extraction of polar lipids from animal tissues was made by Folch in 1957 [3].

This procedure remains one of the best described and the most commonly used by all lipidologists. Some other procedures were proposed which also used solvent mixtures made of chloroform/methanol and ethanol/diethyl ether, respectively.

Microwaves were initially reported to accelerate rates of a large number of chemical reactions; the feasibility of microwaves to extract lipids from seeds, foods and soil was reported in 1986 [4]. The basis and applications of microwave-assisted extractions (Table 1) and comparisons with other recent extraction techniques will be described in this overview. The significant benefits in the pharmaceutical, nutraceutical, nutritional supplements, and agriculture-food industries will be discussed.

Background

The technical challenge in extracting substances for analysis from diverse, complex, and often inhomogeneous matrix materials is considerable. But the techniques employed, such as manual solvent extrac-

tion, are often underdeveloped, undercontrolled, and wasteful of analytical time and reagents. This leads to large uncertainties in analyte recovery. In other words: if the extraction fails, the whole analysis will certainly fail. It is not surprising, therefore, that publication rates now reflect an enormous interest in improved extraction techniques. This article will evaluate and validate various state-of-the-art instrumental extraction methods. Also data generated under the tightly controlled conditions needed to study the mechanisms of particular extraction processes will be presented together with proposals for improvement. Furthermore there is a drive to speed up the processing of extraction results, for instance with chemometric methods, to enable better automation with separation and measurement systems. Current extraction techniques include [5–7]:

- pressurised or accelerated solvent extraction (PSE or ASE)
- supercritical fluid extraction (SFE)
- flexible interfacing, *e.g.* accelerated solvent extraction – automated solid phase extraction (ASE-SPE)

Table 1. Application of microwave-assisted extractions

Food sector
Extraction of raw materials (flavours, fragrances, colourings, <i>etc.</i>)
Extraction of foodstuff (nutritional data, food safety, <i>etc.</i>)
Pharmaceutical, forensics, consumer products, <i>etc.</i>
Environmental sample preparation
Industrial quality control/product verification

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- techniques such as Soxhlet extraction and ultrasound extraction (sonication) and, here of special interest,
- microwave-assisted extraction (MAE) and its modifications such as
- the microwave assisted process (MAPTM), which is a high-speed method used to selectively extract target compounds from various raw materials [8–11].

The MAPTM process was developed, patented and licensed by Environment Canada. The technology uses a microwave applicator as the energy source during solvent extraction leading to benefits of microwave-assisted (solvent) extraction:

- *Speed*: Microwave extractions can be completed within minutes.
- *Simplicity*: Polar or non-polar solvents are used.
- *Consistency*: Precise, software-based control of all reaction parameters.
- *Effectiveness*: Microwave extraction produces higher analyte recoveries than older methods.
- *Economy*: Lower solvent usage reduces the costs of solvent purchase and disposal.

A comparison of MAPTM with some other extraction methods is shown in Tables 2 to 4.

The well known solid–liquid extraction (SLE) techniques are widely used for the early purification of natural products, from plant material and microorganisms. Classically, SLE can be divided into traditional and non-traditional methods. Traditional methods include Soxhlet extraction, maceration, percolation, turbo-extraction (high-speed mixing), and sonication. These techniques have been used for some decades; however, they are very often time-consuming and require relatively large quantities of (polluting) solvents. Supercritical fluid extraction (SFE), pressurised solvent extraction (PSE), and microwave-assisted extraction (MAE) are fast and efficient unconventional extraction methods developed for extracting analytes from solid matrices.

Microwave Heating

Microwaves are electromagnetic radiations with frequencies from 300 MHz to 300 GHz. In order to avoid interferences with official communications domestic and industrial or scientific microwave devices generally operate in Europe at 2.45 GHz. Owing to their electromagnetic nature, microwaves possess electric and magnetic fields which are perpendicular to each other. The electric field causes heating based on two simultaneous mechanisms: dipolar rotation and ionic conduction. Dipolar rotation is due to the alignment on the electric field of the molecules possessing a dipole moment (permanent or induced) in both the

Table 2. Comparison of microwave-assisted extraction with other methods [10]

	MAE	Soxhlet	UAE	SFE
Sample ^a [g]	0.5–1	5–10	5–30	1–10
Solvent	hexane/ethanol	^b	^b	CO ₂
Solvent [ml]	10–20	>300	300	5–25
Reactor [ml]	<100	500–1000	500	5–25
Temperature [°C]	40, 70, 100	b.p.	r.t.	50, 200
Time	minutes	hours	>30 min	<60 min
Press (bar)	1–5	ambient	ambient	>50

^adependent on the concentration and type of sample
^bdichloromethane, acetone, hexane, cyclohexane, toluene, etc.

Table 3. Technological MAP benefits ('Cost Savings' [10])

Parameter	'Hot Hexane'	MAP
Solvent to material ratio [hexane] ^a	5	5
Initial temperature [°C]	20	20
Final temperature (of mass to be heated)	100	100
Energy required [kJ per kg]	470	177
Relative MAP energy requirements		38%
Relative MAP solvent requirement		60%

^aa solvent reduction of 40% is also applicable to MAP (i.e. 3:1 ratio is sufficient)

Table 4. Economic MAP benefits ('more with less' [10])

Reduced operating costs:
– less solvent consumption (at least 50% reduction)
– less energy consumption (up to 90% reduction, depending on scale)
– reduced waste volume (about 60% reduction)
– reduced waste disposal costs (about 75% reduction)
– faster processes (from hours to minutes)
Increased profits by increased target yield and purity
Short 'pay-back' times and
Competitive advantages for commercial applications

solvent and the solid sample. This oscillation produces collisions with surrounding molecules and thus the liberation of thermal energy into the medium. With the a.m. frequency of 2.45 GHz this phenomenon occurs 4.9×10^9 times per second and the resulting heating is very fast. Indeed, the larger the dielectric constant of the solvent the more favourable the heating. Consequently, unlike classical conductive heating methods, microwaves heat the whole sample simultaneously. In the case of extraction, the advantages of microwave heating are the rapid disruption of weak hydrogen bonds promoted by the dipole rotation of the reacting molecules. Higher viscosity of the medium lowers usually this mechanism by affecting molecular rotation. In addition, the migration of dissolved ions increases solvent penetration into the matrix and thus

facilitates the solvation of the analyte. Ionic currents can be also induced in the solution by the electric field. As the medium resists these currents, frictions are possible and heat is liberated by the Joule effect. This phenomenon depends on the size and charge of the ions in solution.

The thermal effect is almost instantaneous at the molecular level. This effect, however, is limited to a small area near the surface of the dielectric material because microwaves have a low penetration depth and are completely absorbed at the boundary. In large particles and agglomerates of small particles, this may lead to inhomogeneous distribution of heat. The heating of the rest of the material results from passive distribution of the heat along the temperature gradient from the outer areas to the centre by conduction. It may be possible

to adjust the wavelength of the microwave radiation so that the energy at the source itself is high and the depth of penetration is enhanced. Usually in a microwave-absorbing medium the power of the microwave radiation is almost exponentially reduced over distance.

The effect of microwave energy is strongly dependent on the physicochemical properties both of the solvent (Table 5) and the solid matrix. Solvents generally used cover a wide range of polarities, *e.g.* from hexane to water. Most of the time, the chosen solvent possesses a high dielectric constant and strongly absorbs microwave energy; however, the extracting selectivity and the ability of the medium to interact with microwaves can be arranged by using tested mixtures of solvents. In some cases, the matrix itself interacts with microwaves while the surrounding solvent possesses a low dielectric constant and thus remains cold. This last phenomenon presents some obvious advantages in the case of thermosensitive compounds and has been successfully used for the extraction of essential oils. Indeed, microwaves interact selectively with the polar ingredients present in glands, trichomes or vascular tissues. Localised heating (hot spots) leads to expansion and rupture of cell walls and is followed by the liberation of essential oils into the used solvent(s). This operation can also be obtained when a dry sample has been re-hydrated before extraction. In fact, moisture content is essential in MAE because water locally superheats and promotes analytes to be liberated into the surrounding solvents. In addition, control of the water content of the matrix allows more reproducible results.

Microwave-assisted extraction is a method for very rapid and efficient heating of solvent(s) under microwave influence and two very different reactor types. By usage of closed reactors the extraction is performed at higher temperatures. The consequence is that the rate of extraction is dramatically enhanced. The extraction is possible in a

- microwave-absorbing solvent
- mixture of solvents with different absorption properties or
- solvent with small microwave absorption in combination with various heating tools (*e.g.* WelfonTM, carbonyl iron materials or ionic liquids) (Table 6).

Manufacturers and Instrumentation

From all the manufacturers of microwave setups, CEM (www.cem.com) and Milestone (or MLS) [12] (www.milestone.com) and www.mls-mikrowellen.de, see also www.biotage.com and www.anton-paar.com) are the best-placed ones on the market. Two different reactor approaches are com-

Table 5. Dielectric constants and dipole moment values of common used extraction solvents

Solvent	Dielectric constant [20 °C]	Dipole moment [25 °C, Debye]
Acetone	20.7	2.69
Dichloromethane	8.9	1.14
Ethanol	24.3	1.69
Hexane	1.89	<0.1
Methanol	32.6	2.87
Toluene	2.4	0.36
Water	78.5	1.87

Table 6. Microwave activity of possible extraction solvents

Inefficient	Average	Good
Tetrachloromethane	Acetone	Dichlorobenzene
Benzene	Ethylacetate	1-Butanol
n-Hexane	Acetonitril	Methanol
Toluene	Chloroform	2-Propanol
Dichloromethane	Water	Ethanol
Tetrahydrofurane	DMF	Ethylene glycol

mercially available [13]. The most common procedure involves the extraction in a closed vessel under controlled temperature and pressure, whilst the contrary approach uses an open extracting vessel under atmospheric pressure. It must be strongly stressed that using a domestic microwave oven for laboratory purposes should not be considered [14]. Application of microwave energy to highly flammable organic solvents can cause serious hazards. Furthermore, reproducibility may be poor with a domestic oven because of the lack of homogeneity of the microwave field. It is hereby seriously recommended that only equipment approved for MAE should be used [14].

Closed Vessel Systems

Closed systems are generally advised for digestions, acid mineralisations or for extractions under drastic conditions, since the solvents may be heated to about 100 °C above their atmospheric boiling points. Both extraction speed and efficiency are increased in this procedure. Hazards occasioned by heating highly flammable solvents are overcome by the use of newer security techniques such as high-capacity exhaust fans, solvent vapour detectors or pressure-burst safety membranes placed on each vessel. In order to overcome the inhomogeneity of the field, the vessels are placed on a rotating carousel. The solvents can be varied, and the pressure in the vessels essentially depends on the volume and

boiling point of the solvents used (Table 2). The extraction temperature can be set at an assumed or fixed value by adjusting the microwave power. Typically, the vessels are made of Teflon. In closed vessel systems, the maximal power delivered is about 600–1000 W, but the chosen power has to be set correctly to avoid excessive temperature ‘crashes’ leading to possible solute degradation and overpressure problems. The vessel must be cooled to room temperature before opening: this is especially important in the presence of volatiles which can partition into the head-space: this step can considerably increase the overall extraction time. Furthermore, an additional filtration or centrifugation step is often necessary in order to remove the solid residue. Closed vessels are used for the microwave-driven extraction of pyrimidine glycosides, gossypol, alkaloids, terpenes, essential oils, carotenoids, steroids, taxanes [15–38].

Open Cells

These cells are glass or quartz vessels topped by a vapour condenser. The system works at atmospheric pressure, and the maximum temperature is determined by the boiling point of the solvent used. The solvent is heated and refluxed through the sample, and in this case the microwave irradiation is focused on the sample in the vessel which allows homogeneous and very efficient heating. The sample to be extracted can be placed into a Soxhlet-type cellulose

cartridge in order to avoid filtration steps, or may be directly dipped into the solvent. Compared to closed vessel extractions, open vessels offer increased safety in sample handling and they allow, if necessary, larger samples to be extracted. Open vessels have found application for the MAE (for example) of alkaloids and steroids.

Modification of MAE

The purpose of this paper is also to mention various methods based on microwave-assisted extraction [7][16][21–23][28][32][33][36][37][39]. Focused microwave-assisted Soxhlet extraction (FMASE), based on Soxhlet extraction but assisted by focused microwaves, has shown surprising results in both environmental and food analysis compared to conventional extraction methods [23][26]. FMASE retains the advantages of conventional Soxhlet extraction while overcoming restrictions such as the long extraction time and non-quantitative extraction of strongly retained analytes due to the easier cleavage of analyte-matrix bonds by interactions with focused microwave energy (up to 300 W maximum power).

Conventional extractions of plant material often involve, for example, steam distillation or various solid-liquid extraction procedures relying on organic solvents. However, solvent extractions may leave prohibited residues in food. An additional disadvantage in using organic solvents is the chemical transformations that the components of the extract may undergo during the elimination of the solvent residue.

The use of microwave energy in sample treatment has attracted growing interest in the past few years. In recent years, numerous applications have been reported on the use of microwaves for assisting extraction from plant materials but only a few papers exist on the distillation of volatile components. The microwave-assisted hydrodistillation (MWHD) is a new technique for the production of essential oils [17][40]. The essential oils of selected plants are normally obtained by hydrodistillation (HD) or steam distillation, cf. [27][34][37]. MWHD appears to be an effective method for the production of essential oils in a short time. Solvent-free microwave-extraction (SFME), a combination of microwave-heating and dry distillation, is also a new green technique developed in recent years. Conventional SFME performed at atmospheric conditions without adding any solvent or water provided a new idea in the extraction of volatile compounds from fresh plant materials or prior moistened dried materials, and it made the whole process simpler, faster and more economic. Because there is water within the moist plant materials, essential oil can be evaporated

by heating *in-situ* water that can absorb microwaves. But fresh plant materials are not easy to preserve. Many species and herbs are dried before being preserved and used. Therefore, the plant material is usually not fresh but dried. There is no water or other components to absorb microwave energy and heat the materials. Therefore, essential oils in dried plant material cannot be evaporated simply by *in-situ* water by conventional SFME [17]. Although essential oils can be extracted by SFME by moistening the dried plant materials prior to extraction, the pretreatment makes the whole process complex and time-consuming. To simplify the process of pretreatment, adding some microwave-absorption solid medium to the sample can be an innovative way in SFME of essential oils from the dried plant materials. The types of material must have good microwave absorption capacity and good chemical stability. Carbonyl iron powders (CIP) are among the possible conventional magnetic absorption materials that have good microwave absorption capacity. By absorbing microwave energy, the calcination speed of CIP as a microwave absorption solid medium in SFME is justifiably believed to be a sustainable way to make the process simpler, faster and more economic.

In [16] essential oils from dried *C. cyminum L* and *Z. bungeanum Maxim* were obtained using an improved SFME method by adding microwave absorption solid medium (CIP) without any pretreatment. The improved SFME is highly attractive for extraction of essential oils compared to conventional SFME, MAHD and HD.

The following list contains examples for the hot extraction filtration (HEF) method, developed by MLS GmbH (Table 7):

- piperidine (1-piperoyl piperidine) from black or white pepper
- hesperidine from orange peels
- trimyristine from nutmeg, transesterification of triglycerides
- betulinic acid from bark of *platanus acerifolia*.

This demonstrates the high development application level of the HEF technique, which is also suitable for use in teaching and training courses (www.ituc.uni-jena.de and www.oc-praktikum.de) [41]. Furthermore new equipment for the extraction of plants, manufactured by MLS GmbH

should be mentioned. High-value compounds can be extracted by simultaneous influence of CO₂-SFE and microwaves in the presence of moisture (www.uni-leipzig.de/~Inc) [42].

Applications

In the last years there has been a growing interest in natural foods, with increased demand for nonsynthetic, natural antioxidants. The use of synthetic antioxidants in the food industry is severely restricted by law as to both application and level of use. The usage of MAE and modification is a powerful technique to overcome this legislative barrier.

Sample preparation is the crucial first step in the analysis of herbs. In recent years there has been strong increasing interest worldwide in the use of alternative or herbal medicine for the prevention and treatment of various illnesses. Currently, however, quality-related problems (lack of consistency, safety, and efficiency) seem to be overshadowing the potential genuine health benefits of various herbal products. Thus, the development of innovative sample-preparation techniques with significant benefits over conventional methods, for the extraction and analysis of medicinal plants would be of benefit to consumers in Europe and overseas. Recent developments and applications of modern sample-preparation techniques for the extraction, clean-up, and concentration of analytes from medicinal plants or herbal materials are reviewed [18][38][39][43–45].

Commonly studied for optimisation of the MAE process are the effects of solvent or solvent composition, solvent volume, extraction temperature, and matrix characteristics (effect of sample granulometry, effect of 'on-line' filtration of sample, and effect of sample moisture). The assessment of these parameters seems to be most important for plant materials.

Recently, kinetics during the microwave extraction was studied as a function of power and time. Based on the obtained results and conclusions the understanding of both effects on the MAE extraction of plant materials with medicinal significance, *i.e.* leaves from rosemary and peppermint, could be extended. The results indicated

Table 7. Characteristics of the system Hot Extraction Filtration 270 [41] (see also www.ituc.uni-jena.de and www.oc-praktikum.de)

Maximal content of extraction material about 15–20 g per single reactor
Maximal content of solvent about 120 ml per single reactor
Up to six reactors per rotor
Maximal temperature about 200 °C and
Maximal pressure about 15 bar.

particularly that for a sample matrix such as a plant, which usually contains water as a component with dielectric loss, the use of pure, microwave-transparent solvents such as hexane could result in the rapid extraction of essential oil components. This is probably because of the direct interaction of microwaves with the free water molecules present in the glands and vascular systems, which results in the subsequent rupture of the plant tissue and the release of the essential oil into the organic solvent (hexane). More effective microwave heating of this particular system (hexane and leaves) could therefore be achieved by increasing the weight of leaves relative to the volume of hexane. For a system involving the usage of an organic solvent which absorbs microwaves more strongly (ethanol and leaves), more effective heating of sample mixture could be achieved by increasing the microwave power output, because in this system ethanol (rather than water in the leaves) absorbs the bulk of the microwave energy. Recent applications of the common MAE to the extraction of medicinal plants include the leaching of:

- alpha-hedrin and hederasaponin from *Hedera helix* leaves,
- saponin and saponin from *Paris polyphylla*,
- salsdroside and tyrosol from *Rhodiola sachalinensis*,
- essential oils from the leaves of *Lippoa sidoides*,
- lupin alkaloid (sparteine) from seeds and
- taxanes from *Taxus* biomass.

Conclusion

The use of microwave-assisted extraction as a counterpart to diffusion leads to very fast extraction rates and greater solvent flexibility. Some variables, including the microwave power and energy density, can be tuned to deliver desired product attributes and optimise process economics. The common proof-of-concept has been established for a wide spectrum of actives and biomass substrates with very large associated markets. The process can be optimised for commercial reasons and excellent extracts are produced from widely varying substrates. Practical examples include antioxidants from fresh and/or dried herbs, carotenoids from single cells and plant sources, taxanes from *taxus* biomass, essential fatty acids from microalgae and oilseeds, phytosterols from medicinal plants, polyphenols from green tea, flavour constituents from vanilla and black pepper, essential oils from various sources, and many more.

In summary, the microwave method is reproducible, easy to run, allows simultaneous analysis of many samples, and offers an

excellent alternative to methods that utilize gram amounts of material, *i.e.* steam distillation and solvent extraction. Researchers engaged in evaluating the role of essential oils in plant–insect interactions, terpenoid differences in individual plants, and biogeographical studies of essential oils, could profit greatly from using this modified method.

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- [1] F. von Soxhlet, *Polytechnisches J. (Dingler's)* **1879**, 232, 461.
- [2] W.R. Bloor, *J. Biol. Chem.* **1914**, 17, 377.
- [3] J. Folch, M. Lees, G.H. Sloane Stanley, *J. Biol. Chem.* **1957**, 226, 497.
- [4] K. Ganzler, A. Salgo, K. Valko, *J. Chromatogr.* **1986**, 371, 299.
- [5] C. Turner, in 'Modern Extraction Techniques', Ed. C. Turner, ACS Symp. Series 926, Washington (DC), **2006**, 3.
- [6] 'Modern Extraction Techniques', Ed. C. Turner, ACS Symp. Series 926, Washington, **2006**.
- [7] C. Sparr Eskilson, E. Björklund, *J. Chromat. A* **2000**, 902, 227.
- [8] J.R.J. Paré, M. Sigomin, J. Lapointe, US Pat. 5 002 784, **1990**.
- [9] J.R.J. Paré, J.M.R. Belanger, S.S. Stafford, *TRAC Trends Anal. Chem.* **1994**, 13, 176.
- [10] E. Norrena, D.E. Thornton, J.R.J. Paré, J.M.R. Belanger, Proceed. Green Chemistry Meeting, Washington, **2000**.
- [11] V.A. Yaylayan, J.R.J. Paré, G. Matni, J.M.R. Belanger, *Nat. Prod. Lett.* **2001**, 15, 187.
- [12] G. Kopp, W. Lautenschläger, *LaborPraxis* **1996**, 11, 82.
- [13] B. Kaufmann, P. Christen, *Phytochem. Anal.* **2002**, 13, 105.
- [14] M. Nüchter, B. Ondruschka, D. Weiss, R. Beckert, W. Bonrath, A. Gum, *Chem. Eng. Tech.* **2005**, 28, 871.
- [15] P. Seifert, C. Bertram, D. Chollet, *SOFW J.* **2000**, 126, 3.
- [16] Z. Wang, L. Ding, T. Li *et al.*, *J. Chromatogr.* **2006**, 1102, 11.
- [17] M.E. Lucchesi, F. Chemat, J. Smadja, *J. Chromatogr.* **2004**, 1043, 323.
- [18] J. Hao, W. Han, S. Huang, B. Xue, X. Deng, *Sep. Purif. Tech.* **2002**, 28, 191.
- [19] S. Gao, W. Han, X. Deng, *Flavor Fragr. J.* **2004**, 19, 244.
- [20] X. Pan, G. Niu, H. Liu, *J. Chromatogr.* **2001**, 922, 371.
- [21] Q. Wang, S. Ma, B. Fu, F.S.C. Lee, X. Wang, *Biochem. Eng. J.* **2004**, 21, 285.
- [22] Z. Kerem, H. German-Shashoua, O. Yarden, *J. Sci. Food Agric.* **2004**, 85, 406.
- [23] S. Morales-Munoz, J.L. Luque-Garcia, M.J. Ramos, M.J. Martinez-Bueno, M.D. Luque de Castro, *Chromat.* **2005**, 62, 69.
- [24] G. Raman, V.G. Gaikar, *Ind. Eng. Chem. Res.* **2002**, 41, 2521.
- [25] G. Raman, V.G. Gaikar, *Ind. Eng. Chem. Res.* **2002**, 41, 2966.
- [26] A. Ortiz Moreno, L. Dorantes, J. Galindez, R.I. Guzman, *J. Agric. Food Chem.* **2003**, 31, 2216.
- [27] J. Huang, Z. Zhang, *Anal. Sci.* **2004**, 20, 395.
- [28] A. Brachet, P. Christen, J.-L. Veuthey, *Phytochem. Anal.* **2002**, 13, 162.
- [29] A. Assenov, E. Leventieva, I. Tsibranska, *Hung. J. Ind. Chem.* **2000**, 28, 241.
- [30] A.I. Carrapasio, C. Garcia, *Lipids* **2000**, 35, 1167.
- [31] G.A. Csiktusnadi Kiss, E. Forgacs, T. Cserhati, T. Mota, H. Morais, A. Ramos, *J. Chromatogr.* **2000**, 889, 41.
- [32] M. Lo Prestin, S. Ragusa, A. Trozzi, *et al.*, *J. Sep. Sci.* **2005**, 28, 273.
- [33] E. Anklam, H. Berg, L. Mathiasson, M. Sharman, F. Ulberth, *Food Add. Contam.* **1998**, 15, 729.
- [34] N.E. Gomez, L. Witte, *J. Chem. Ecol.* **2001**, 27, 2351.
- [35] R.G. Diagne, G.D. Foster, S.U. Khan, *J. Agric. Food Chem.* **2002**, 50, 3204.
- [36] N. Asfaw, P. Licence, A.A. Novitskii, M. Poliakov, *Green Chem.* **2005**, 7, 352.
- [37] M. Kosar, Z. Tunalier, T. Ozek, M. Kürkcüoğlu, K. Hüsni Can Baser, *Z. Naturforsch.* **2004**, 60C, 501.
- [38] A.C. Kimbaris, N.G. Siatis, D.J. Daferera, P.A. Tarantilis, C.S. Pappas, M.G. Polissiou, *Ultrasonics Sonochem.* **2006**, 13, 54.
- [39] X. Pan, G. Niu, H. Liu, *Biochem. Engin. J.* **2003**, 12, 71.
- [40] F. Chemat, M.E. Lucchesi, J. Smadja, L. Favretto, G. Colnaghi, F. Visinoni, *Anal. Chim.* **2006**, 555, 137.
- [41] a) M. Nüchter, B. Ondruschka, B. Fischer, A. Tied, W. Lautenschläger, Proceed. Symp. and Workshop 'Plant extracts and Processes', Frankfurt/Main, **2003**; b) M. Nüchter, B. Ondruschka, B. Fischer, W. Lautenschläger, Proceed. Ampere 2003, Loughborough, **2003**; c) M. Nüchter, B. Ondruschka, B. Fischer, A. Tied, W. Lautenschläger, *Chem. Ing. Tech.* **2005**, 77, 171; d) M. Nüchter, B. Ondruschka, C. Hofmann, R. Zuhse, Proceed. Narotech, Erfurt, **2005**; e) C. Hofmann, Diploma Thesis, Jena, **2005**.
- [42] a) H. Sonnenschein, I. Germanus, P. Harting, *Chem. Ing. Tech.* **2002**, 74, 270; b) R. Staudt, Proceed. Innovationsforum, Zittau, **2004**.
- [43] T. Track, *CIT plus* **2005**, 3, 4.
- [44] C.W. Huie, *Anal. Bioanal. Chem.* **2002**, 373, 23.
- [45] P. Christen, J.-L. Veuthey, *Curr. Med. Chem.* **2001**, 8, 1827.