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Determination of the Chemical Composition of Volatile Oils of Plants Using Superheated Water Extraction with Comprehensive Gas Chromatography-Time-of-Flight Mass Spectrometry

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1. Introduction

Plants or plant extracts can be used in traditional medical remedies. Plants have evolved the ability to synthesize chemical compounds that help them defend against attack from a wide variety of predators such as insects, fungi and herbivorous mammals. By chance, some of these compounds, whilst being toxic to plant predators, turn out to have beneficial effects when used to treat human diseases. Herbal medicines do not differ greatly from conventional drugs in terms of how they work. Many of the herbs and spices used by humans to season food yield useful medicinal compounds. They are of great economic importance which is not only related to their use as a spice or herbal tea. In fact, many of the medicinal plants are used traditionally in many other ways as their essential oils have antimicrobial, antifungal and antioxidant activity. Volatile oils of plants, also known as essential oils, often contain a mixture of flavour, fragrant and medicinal compounds. They contain complex mixtures including monoterpenes, sesquiterpenes and their oxygenated derivatives such as aliphatic aldehydes, alcohols and esters (Simandi et al., 1998; Vokou et al, 1998; Ozel et al., 2003; Ozel et al., 2006; Ozel & Kutlular, 2011).

Analysis of plants normally involves a sample preparation stage such as extraction or distillation followed by analysis with gas chromatography or liquid chromatography. The common methods used currently for the isolation of essential oils from natural products are steam distillation and solvent extraction (Ozel & Kaymaz, 2004). Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated compounds through thermal or hydrolytic effects, and toxic solvent residue in the extract may be encountered with these extraction methods. Recently, more efficient extraction methods, such as supercritical fluid extraction (SFE) (Simandi et al., 1998) and accelerated solvent extraction (ASE) (Schafer, 1998) have been used for the isolation of organic compounds from various plants. Subcritical or superheated water extraction (SWE) is non-toxic, readily available, cheap, safe, non-flammable and is a recyclable option.

SWE was found to give recoveries comparable to those of steam distillation and Soxhlet extraction of essential oils from two *Origanum onites* samples (Kutlular & Ozel, 2009). The kinetics of SWE under optimum working conditions mean that the extraction is mostly completed in 15 minutes (Ozel et al., 2003). Soxhlet extraction is time-consuming and labour-intensive. Steam distillation is cheap but has no selectivity and is also time-consuming. SFE is a complicated system and often problems occur during extraction. ASE is quick but uses toxic organic solvents. In contrast, SWE is cheap, relatively fast and environmentally sound as solvents do not have to be used. It is also selective in that the operator is able to extract various polar and non-polar organic compounds by choice by varying the temperature as long as the water is kept in a liquid state using minor adjustments in pressure.

Plant volatile oils normally contain a complex mixture of organic compounds. They are largely composed of a range of saturated or partly unsaturated cyclic and linear molecules of relatively low molecular mass and within this range a variety of hydrocarbons and oxygenated compounds occur. Conventional one dimensional gas chromatography generally does not provide sufficient separation for complex mixtures. Since essential oils contain numerous components, it is possible that some components can obscure the analytes of interest. Two-dimensional gas chromatography is known as comprehensive gas chromatography (GCxGC). GCxGC is a fully multi-dimensional technique achieving a much increased peak capacity in limited analysis time. GCxGC has been shown to be an extremely powerful technique for the analysis of essential oils. High acquisition rates of time of flight-mass spectrometry (TOF-MS) offer a superior separation power. The coupling of GCxGC to TOF-MS is very effective (Marriott et al., 2000; Ozel et al., 2004)

2. Extraction of plant volatiles using superheated water

SWE is a technique based on the use of water as an extractant, at temperatures between 100 and 374 °C and at a pressure high enough to maintain the liquid state. Lab-scale SWE can be performed using 1-5 g of air-dried solid samples, a 5-20 mL stainless steel extraction cell, 0.5-5.0 mL min⁻¹ flow rate, temperatures of 100-175 °C, a pressure of 15-60 bar and 15-60 min of extraction time. A typical SWE system is shown in Figure 1. Previous workers (Ayala & Luque de Castro, 2001; Ozel et al., 2003; Ozel & Kaymaz, 2004) reported that SWE of essential oils is a powerful alternative, because it enables a rapid extraction and the use of low working temperatures. This avoids the loss and degradation of volatile and thermo labile compounds. Additional positive aspects of the use of SWE are its simplicity, low cost, and favourable environmental impact. Soxhlet extraction is time consuming (6-24 h) and uses a large amount of environmentally-unfriendly organic solvents (Ozel & Kaymaz, 2004). Steam distillation is also time-consuming, taking 6-24 hours.

In lab-scale SWE, separation of the compounds from the aqueous extract obtained is the critical stage. A liquid-liquid extraction technique often causes emulsion and breaking this can be very difficult. It has been found that solid phase extraction is a better technique for the removal of compounds from the aqueous environment of SWE when compared with liquid-liquid extraction (Rovio et al., 1999; Ozel et al., 2003). Headspace solid phase microextraction with GC-MS may be another alternative (Deng et al., 2005).

The optimal subcritical water extraction conditions can be decided upon by using various pressures, times, water flow rates and temperatures. Perez-Serrafilla et al. (2008) performed

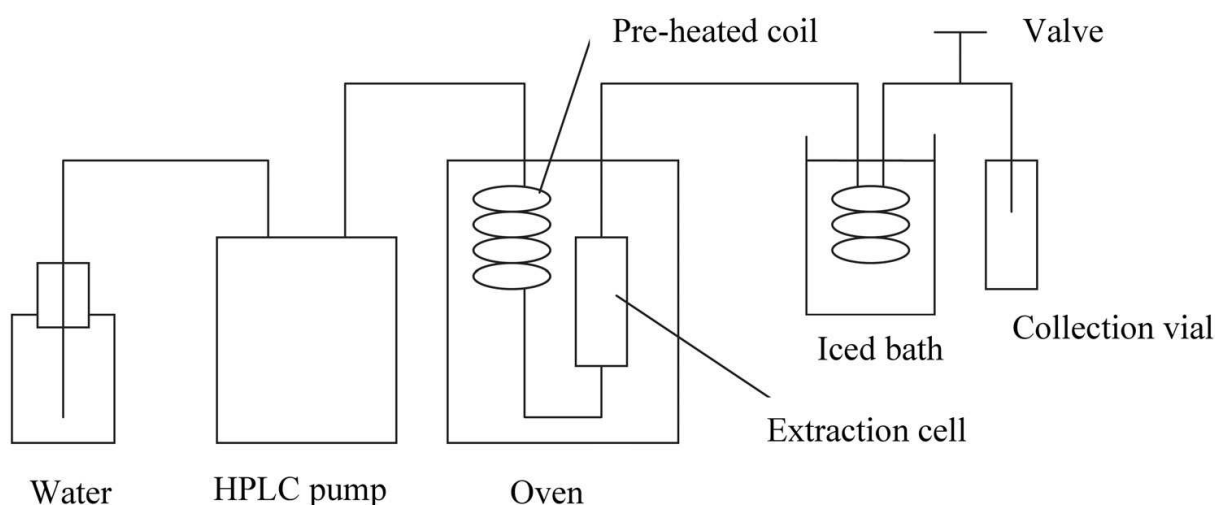


Fig. 1. Schematic representation of basic SWE apparatus

selective extraction of fatty acids and phenols using static and dynamic SWE. Selective extraction is also possible for target compounds using different conditions. The yields of essential oils of *Thymbra spicata* for a 30 minute extraction at a flow rate of 2 mL.min⁻¹ and 60 bar, and at four different temperatures (100, 125, 150 and 175°C) were carried out (Ozel et al., 2003). The yield increased with temperatures up to 150°C. A further increase to 175°C resulted in a small decrease in the yield.

The pressures of 20, 60 and 90 bar (Ozel et al., 2003) and 20, 50 and 80 bar (Deng et al., 2005) have been observed to cause no significant difference in the amounts of extracted oils from *Thymbra spicata* and *Fructus amomi*. Enough pressure should be preserved to keep the water in a liquid state. Optimization of SWE conditions has been studied (Ayala & Luque de Castro, 2001; Ozel et al., 2003; Ozel & Kaymaz, 2004; Deng et al., 2005). Ayala & Luque de Castro (2001) discovered that a temperature of 125 °C, 2MPa pressure and a 1 mL.min⁻¹ flow rate is optimum for SWE of essential oils. Conditions for SWE of *Origanum onites*, *Thymbra spicata* and *Fructus amomi* were optimal at a temperature of 150 °C, a pressure of 20-60 bar, a flow rate of 2 mL.min⁻¹ and 30 minutes of extraction time (Ozel & Kaymaz, 2004; Ozel et al., 2003; Deng et al., 2005). In SWE of marjoram by Jimenez-Carmona et al. (1999), of clove by Rovio et al. (1999) and of fennel by Gamiz-Gracia and Luque de Castro (2000), the yield reached its maximum at 150°C over a temperature range of 50-175°C.

Superheated water for the extraction of plant volatiles is a powerful technique because it enables a rapid extraction. The solubility of organic compounds in superheated water is high for two reasons. Firstly, solubility increases with increasing temperatures and secondly, water becomes less polar as the temperature rises. Other advantages of the use of SWE are its simplicity, low cost, speed and the fact it is considered more environmentally friendly. With solvent extraction, steam distillation and water extraction, the loss of some volatile compounds, long extraction times and the toxic solvent residue may be considered a disadvantage. The temperature is a very important parameter in superheated water extraction. In the extraction of eugenol and eugenyl acetate from cloves using superheated water, the workers found that the extraction kinetics were very fast at high temperatures (250°C and 300°C), giving a 100% recovery after 15 min, compared to extraction at 125°C,

where the same recovery took 80 min to achieve (Rovio et al., 1999). Conversely, at high temperatures essential oils may be destroyed (Ozel et al., 2003). Kinetic studies were carried out under optimum conditions for SWE (Ozel et al., 2003). Figure 2 shows the kinetics of the 5 main compounds in the SWE extract of *Thymbra spicata* (Ozel et al., 2003). Although the extraction was completed in 20 minutes, the time for the SWE was selected to be 30 minutes to make sure all the essential oils had been extracted (Ayala & Luque de Castro, 2001; Ozel et al., 2003; Ozel & Kaymaz, 2004).

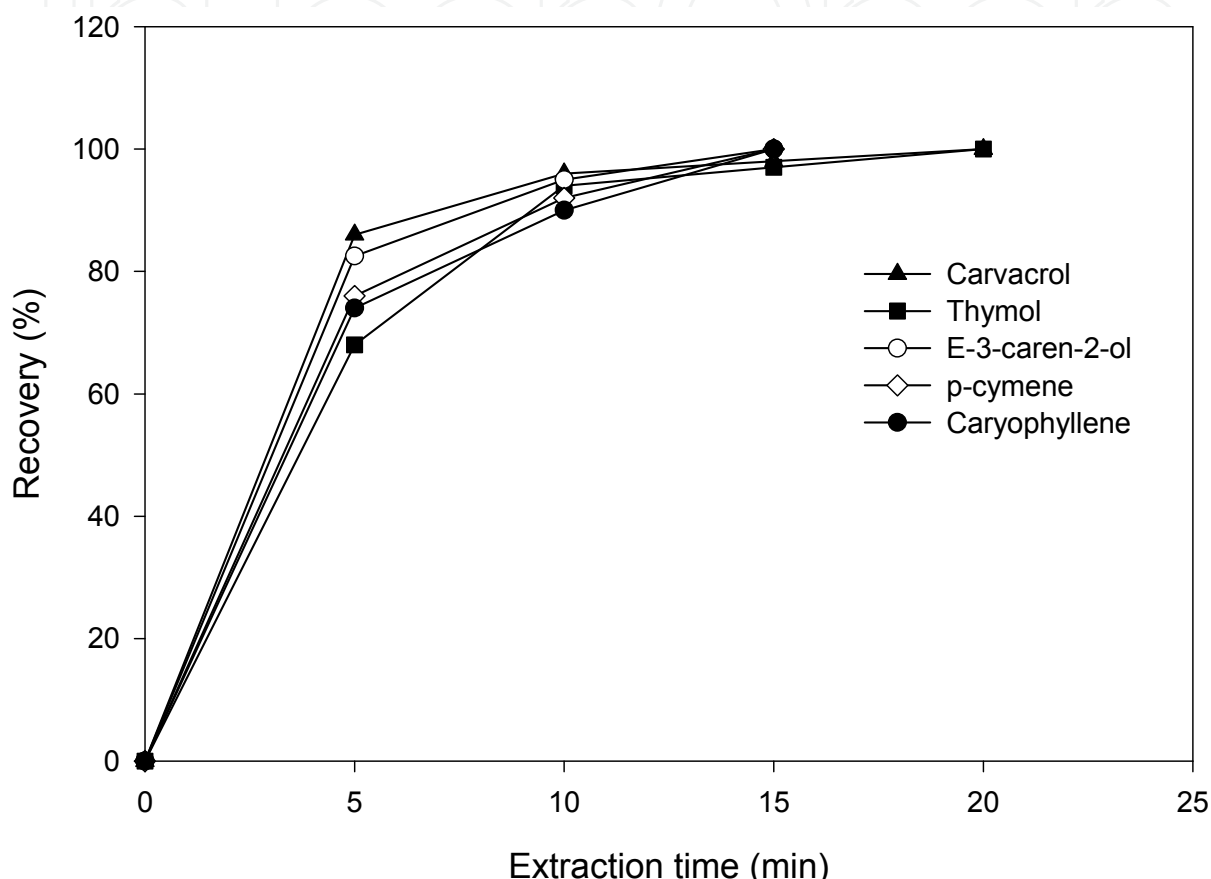


Fig. 2. Effect of extraction time on the extraction efficiency of some compounds of essential oils of *Thymbra spicata* using subcritical water extraction at a temperature of 150°C and a flow rate of 2 ml min⁻¹ (Ozel et al., 2003).

There is a growing interest in natural foods, because of the increased demand for non-synthetic natural antioxidants. Some species of *salvia* are used as medicinal and aromatic plants. *Salvia* is used in food, cosmetics, perfumes and pharmaceutical products (Schwarz & Ternes, 1992). Different functional groups and/or chemicals such as flavonoids, vitamins, antioxidants and antimicrobials, can be extracted selectively using SWE (Rodriguez-Meizoso et al., 2006; Hartonen et al., 2007; Mendiola et al., 2007). Extraction of essential oils of *Salvia fruticosa* using superheated water has been studied using samples collected from Denizli, Fethiye, Korkuteli and Gundogmus (Turkey). The amounts and compositions of recovered essential oils can be influenced by different collection locations. In Table 1, it can be seen that there is a slight difference in the amounts and compositions of essential oils according to location, especially in the case of the *Salvia fruticosa* sample from Korkuteli (Ozel & Kutlular, 2011).

Compound	RI	%			
		Denizli	Fethiye	Korkuteli	Gundogmus
Essential oil content	-	1.86	0.97	1.78	1.53
α -Pinene	939	2.18	1.16	8.65	4.21
Camphene	953	2.57	3.61	0.66	2.35
Sabinene	972	- ^e	-	0.29	-
β -pinene	976	1.11	2.18	13.39	1.08
Octenol	982	0.07	0.18	-	0.22
Myrcene	992	0.27	0.12	-	0.27
α -Phellandrene	1006	-	-	0.29	-
3-Carene	1009	-	-	1.33	-
1,8-Cineole	1030	37.25	33.85	16.64	42.72
Limonene	1033	-	-	0.25	-
γ -Terpinene	1074	-	-	0.59	-
Terpinolene	1088	-	-	0.62	-
Linalool	1098	-	0.58	5.85	-
α -Thujone	1101	4.76	7.06	2.76	3.10
β -Thujone	1113	9.02	3.87	-	1.52
Fenchyl alcohol	1130	-	-	0.46	-
Camphor	1139	17.91	22.12	3.96	28.27
Borneol	1162	4.79	6.45	0.84	1.99
Pinocarveol	1169	0.06	-	1.90	-
Terpinen-4-ol	1179	1.62	-	1.63	-
α -Terpineol	1194	0.77	3.27	9.16	4.03
Dihydrocarvone	1195	-	0.32	-	-
Bornyl acetate	1238	0.12	-	-	0.73
Cinnamaldehyde	1240	0.05	0.09	0.26	-
Carvone	1254	0.16	-	0.17	-
Thymol	1290	2.97	2.96	6.24	0.47
Eugenol	1364	0.13	3.97	3.21	0.12
Caryophyllene	1426	9.69	3.13	16.81	3.78
Butylated	1516	0.10	-	0.11	-
Hydroxytoluene					
Eicosane	2000	0.08	-	-	-
Unknown		4.32	5.08	3.93	5.14
Total compounds		21	17	24	15

RI, Retention index

Table 1. Percentage compositions of essential oils of *Salvia fruticosa* isolated using the SWE technique (Ozel & Kutlular, 2011).

Sample collection times also change the volatile profile of plant materials (Kutlular & Ozel, 2009). *Origanum onites* is a perennial species with woody stems. It is encountered in the Southern Greek mainland, the islands and the western and southern coastal areas of Turkey (Vokou et al., 1998). The essential oils of *Origanum* species have been proven to have

Compound	RI	%		
		15 June, 2006	25 June, 2006	05 July, 2006
3-Thujene	938	0.01	0.03	0.02
α -Pinene	939	0.02	0.04	0.06
Camphene	953	0.01	0.01	0.02
Benzaldehyde	960	0.02	0.02	0.02
β -pinene	981	0.05	0.13	0.93
Myrcene	992	-	0.08	0.06
3-Octanol	1004	0.02	-	-
α -Phellandrene	1006	0.01	0.02	-
p-Cymene	1027	0.88	0.92	0.61
Eucalyptol	1030	0.03	0.20	0.05
Limonene	1033	0.02	0.05	0.03
Ocimene	1052	-	0.01	0.02
Acetophenone	1068	-	-	0.02
γ -Terpinene	1074	-	-	0.01
Terpinolene	1088	0.23	0.52	0.38
Undecane	1100	0.02	0.01	0.03
Linalool	1100	0.14	4.44	5.14
2-Decen-1-ol	1110	0.17	0.32	0.19
α -Campholenal	1125	0.01	0.01	0.02
Camphor	1139	0.01	0.04	0.01
cis-Verbenol	1140	-	-	0.01
Borneol	1162	0.34	0.41	0.79
Pinocarveol	1169	0.01	0.03	0.03
Terpinen-4-ol	1179	0.47	0.75	0.86
cis-Linalool oxide	1186	0.01	0.09	0.20
α -Terpineol	1195	0.19	0.39	0.56
Carveol	1197	0.03	0.03	0.14
Dihydrocarvone	1202	0.04	0.08	0.01
Nerol	1233	0.01	0.04	0.12
Carvone	1254	0.10	0.15	0.12
Thymol	1290	0.18	0.41	1.45
Carvacrol	1295	92.66	86.71	84.33
Eugenol	1364	-	0.19	-
Eicosane	2000	0.02	-	0.01
Unknown		4.29	3.89	3.73

RI, Retention indice

Table 2. Percentage compositions of volatile components of *Origanum onites* leaves collected on various dates, isolated using the SWE technique (Kutlular & Ozel, 2009).

antibacterial, antifungal and antioxidant activities (Kutlular & Ozel, 2009). *Origanum* is accepted as a volatile yielding plant, its essential oils consist mainly of carvacrol and thymol type compounds which are well known phenolic antioxidants. Extraction of *Origanum onites* leaves collected on three different dates (15 June; 25 June; 5 July, 2006) using superheated water was performed (Kutlular & Ozel, 2009). The results are shown in Table 2. Carvacrol was found as the main compound. The total amount of essential oil increased with later collection dates in contrast to the amount of carvacrol which actually decreased with the date. Since carvacrol is one of the most valuable compounds, a compromise must be struck between the desired to obtain the greatest quantity of oil possible whilst at the same time obtaining the highest possible percentage of carvacrol. As a result, the date of sample collection is a very important parameter for the quantity and value of the essential oil of plant materials.

3. Analysis of plant volatiles using gas chromatography

Gas chromatography can be applied to the analysis of volatile and semi-volatile organic compounds, containing boiling points from near zero to over 400°C (Bartle & Myers, 2002). Plant volatiles such as essential oils, are often highly complex mixtures. Good separation methods are necessary to analyse these molecules. Hyphenation of different techniques is currently the preferred method for analysing these volatile essential oils (Welthagen et al., 2007). In general, the coupling of a GC separation step with a mass spectrometric detector is the most common set-up. For complex mixtures like essential oil, however, selectivity and separation capability of the GC-MS is not sufficient. Multidimensional GC separation with selective MS detection (such as TOF-MS) can improve separation and identification of complex plant volatiles (Welthagen et al., 2007). Small, highly polar molecules (such as amino acids and sugars) cannot be analysed using GC technology. A possible solution is the use of chemical derivatization methods where the polar groups of the target molecules are converted into less polar molecules.

In GC-MS, ions are produced by electron or chemical ionisation. But, the ions are now sorted according to molecular weight (or mass to charge, m/z ratio) by one of a range of analysers: magnetic sector quadrupole, ion trap or time of flight (Bartle & Myers, 2002). Mass spectrum is related to the molecular weight and fragmentation of the analyte, allows identification through comparison with a library. The advantages of TOF-MS lie in the possibilities for accurate mass measurement and rapid rates of accumulation of spectra (up to 500 Hz), which allow GC peaks as narrow as 12ms to be identified (Bartle & Myers, 2002).

Injection of the sample into the column head is usually carried out using a syringe and a hypodermic needle. In order to be able to detect lower concentrations, a large volume injection technique has been developed allowing a sample size of 20-100 μL , rather than the formerly standard 1-2 μL (Bartle & Myers, 2002). Low levels of volatile compounds in plant materials may be analyzed by headspace, dynamic stripping or purge-and-trap sampling (Bartle & Myers, 2002). Direct thermal desorption (DTD) at one or more temperatures followed by pyrolysis can yield important information. Selection of temperatures is a very important parameter. The lowest temperature possible should be selected in order that the native volatile compounds can be determined without generating new compounds (Koning et al., 2008). This is illustrated by the study of essential oils of *Pistacia vera* (Ozel et al., 2004). A number of species can be seen to appear only at the higher temperatures of 200 and

250 °C, and these are known not to be components of essential oil of *Pistacia vera*, but are the browning reaction products (e.g. furfural, 2-furanmethanol, acetylfuran, 2-furanone, 2,4-dimethyl-furan, furfuryl acetate and furfuryl alcohol). Most of these components are low in concentration at 200 °C, however show a significant increase at 250 °C. The browning reaction products may be produced either by caramelization or by Maillard reactions during the higher temperatures of 200 and 250 °C.

The one dimensional GC technique cannot always provide sufficient separation of all components of plant volatiles. In order to enhance peak capacity, multidimensional gas chromatography can be used. Marriott & Shellie (2002) define multidimensional analysis in chromatography as 'any technique that combines two or more distinct separation/analysis steps'. The first dimensional separation is based on separation by boiling point in a non-polar column. The second dimensional separation is based on separation by polarity using a polar column. The inclusion of this makes this overall a two dimensional chromatogram.

Today, there are two kinds of two dimensional GC: heart-cutting and comprehensive two-dimensional gas chromatography (GCxGC). In the heart-cutting technique, one or more unresolved fractions from the first column are transferred to a second column having a different polarity where the separation of the compounds will be achieved. In general, the first column is non-polar with a length of 30 to 60 m, whilst the second is 30 m long with a higher polarity. The heart-cut can be directly transferred to the second column or it can be trapped on a cryogenic device and transferred later. With comprehensive GC (GCxGC), the entire sample, not only fractions, are separated on two different columns. The columns are shorter, typically 15 to 60 m (100% polydimethylsiloxane or 5% diphenyl 95% polydimethylsiloxane stationary phase) for the first and only 1 to 2 m (50% diphenyl 50% polydimethylsiloxane or polyethylene glycol) for the second column. The short length of the second column enables very fast separations whilst collecting the fractions from the first column. The most important component of the system is the 'modulator', which will accumulate the fractions coming from the first column on a short segment of column, and then release it quickly into the second one. There are different kinds of modulators but in general the mechanisms involve alternate cryofocussing and thermal desorption of the trapped analytes. GCxGC has advantages over the heart-cutting technique (Marriott et al., 2000; Marriott & Shellie, 2002).

GC-on-a-chip is receiving more attention now especially from field workers. There is interest in the development of a microfabricated gas chromatography system suitable for the separation of volatile organic compounds and compatible with use as a portable measurement device. A planar 2-dimensional GC chip with fully circular channel profiles has been microfabricated from glass using acid-etching techniques. Coupling of the directly heated column to a low cost, low-power photoionization detector showed reasonable separation of gasoline vapour. Comprehensive separation has given some promising results from the separation of ppm gas mixtures of a set of volatile organic compounds when coupled with commercial GC detectors (Halliday et al., 2010)

GCxGC typically generates peak capacity of the order of several thousand, making it highly appropriate technology for the separation and analysis of complex samples such as essential oil. Plant essential oil is used in numerous traditional medicines. Essential oil is usually rich in monoterpenes, sesquiterpenes and oxygenated derivatives. One dimensional GC lacks the

resolving power to provide adequate separation of the complex mixture of essential oil. GCxGC has an estimated separation increase of about ten times over one dimensional GC. Another advantage of GCxGC, regarding the second dimension retention times of the compounds, is demonstrated by the lines on the chromatogram indicating groups such as hydrocarbons, alcohols, aldehydes etc. (Schnelle-Kreis et al., 2005). Due to the very fast separations, GCxGC also needs very fast detection systems such as TOF-MS.

A typical DTD with GCxGC-TOF-MS separation / total ion chromatogram (TIC) of *Rosa damascena* is shown in Figure 3. The chromatographic peak data consists of first dimension retention times, second dimension retention times and peak area (TIC). 54 compounds can be identified from this chromatogram. The first dimension separation axis extends to 2900 s and the second dimension axis ends at 6 s. The TIC is created as a reconstructed chromatogram from the peaks detected by an automatic peak detection algorithm. The peak finding routine, based on deconvolution techniques, detected several hundred peaks and a mass spectrometry library search resulted in the majority of them being assigned a library match. (Ozel et al., 2006)

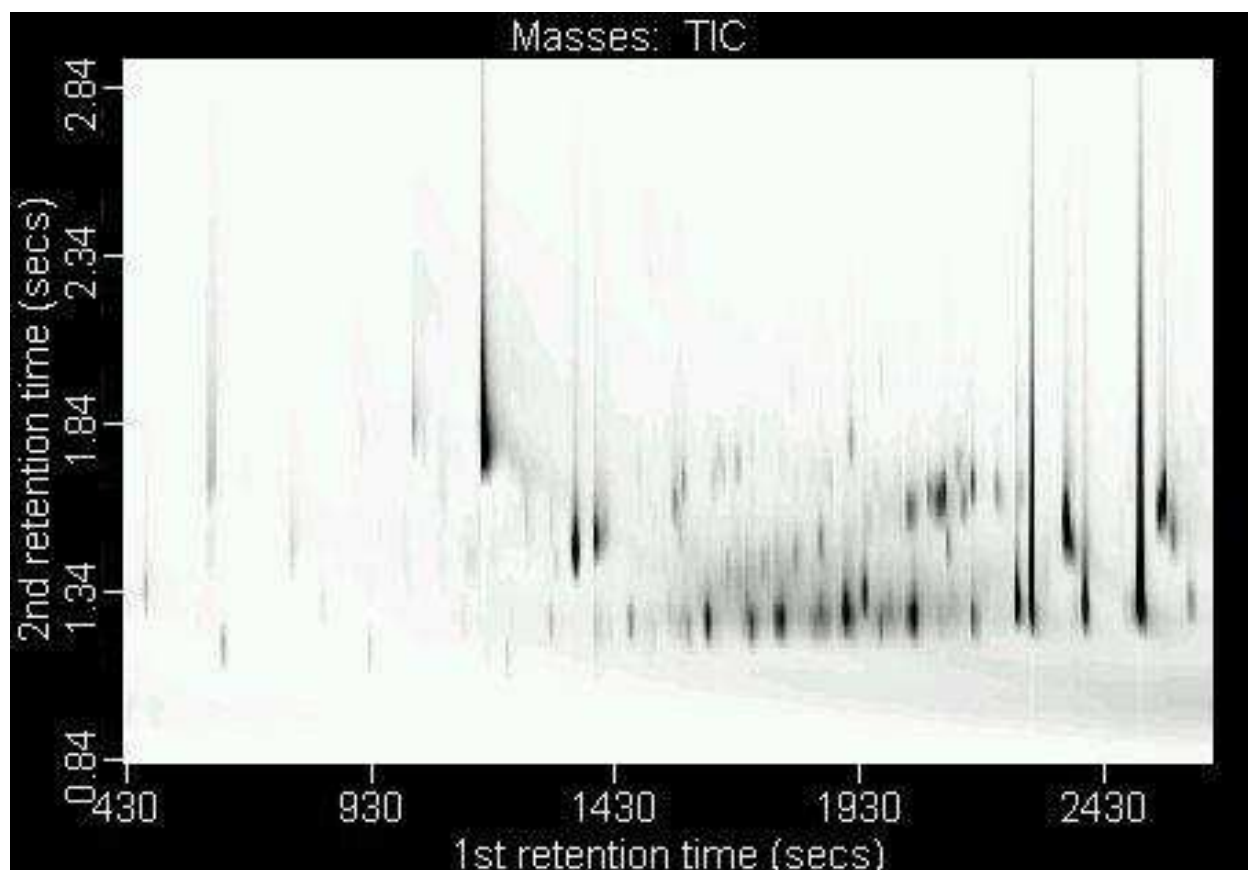


Fig. 3. GCxGC-TOF-MS total ion current (TIC) plot of *Rosa damascena* Mill. volatile18 components at 150°C using the DTD technique (Ozel et al., 2006).

Ozel et al., (2006) studied the volatile profile of *Rosa damascena* using various techniques, namely DTD, SWE and water distillation. DTD volatiles showed a greater total number of different components than either of the other two methods. The numbers of volatile components identified with a percentage higher than 0.05%, were 54, 37, and 34 for the

DTD, SWE and WD techniques respectively. DTD, unlike the other two methods, does not require any sample preparation beforehand, thus making it faster. In the above study, DTD was also shown to be quantitative. Commercial producers of essential oils could therefore use the DTD technique to select which batches of leaves or flowers would produce the highest quality oil, as they would be able to see quickly if their desired components and in what amounts were present. It was concluded that DTD is a promising method for qualitative and quantitative analysis of volatiles which can yield a highly accurate and comprehensive chromatographic profile with a low contamination risk, without the need for costly and time consuming sample preparation techniques.

4. Conclusion

The main aim of this chapter is to highlight the extraction of various plants using highly effective, quick, environmentally-friendly superheated water followed by analysis using the high-resolution separation technique of GCxGC-TOF-MS. It has been discussed in many earlier studies that SWE is a very promising alternative to traditional extraction techniques (Simandi et al., 1998; Vokou et al., 1998; Ozel et al., 2003; Ozel et al., 2006; Ozel & Kutlular, 2011). Water / steam distillation and solvent extraction are widely used techniques in the essential oil industry. Solvent extraction is time-consuming and toxic. Steam distillation is cheap although time consuming and with no selectivity. In contrast, SWE is cheap, selective, fast and environmentally friendly. Lab-scale SWE can extract only a small quantity of essential oil during the plant extraction process. In addition, it is necessary to use a solvent during liquid-liquid extraction or SPE before GC analysis. However, realistically, in a big SWE extraction unit solvent will not be needed as the oil will float on the water making collection easy. With increasing interest in avoiding organic solvents in the extraction of volatile organic compounds from plant samples, SWE has been shown to be a feasible alternative for use in industrial essential oil production.

Using the DTD technique, the volatile components of plant materials can be analysed with no extraction process or sample preparation. On an industrial scale, water distillation and occasionally SWE would still be the main methods used in actual extraction of essential oil but DTD could be used to check which components are being missed out in this process very quickly and easily without the need for time consuming, expensive sample preparation. It could also be used to check samples of batches of plant materials from different regions, times of collection or different parts of the plant for their desirable or undesirable components without first having to go through the expensive, time consuming extraction techniques. DTD can also be used quantitatively to determine the amounts in which essential oils are present in samples. Thus DTD could help a producer decide upon which batch to use.

TOF-MS can operate at acquisition frequencies of more than 100 spectra per second. This provides the capability to deconvolute mass chromatograms for compounds with retention times that differ by more than about 120 ms. Combining DTD with GCxGC-TOF-MS enables a rapid study of the characteristic classes of compounds emitted when solid plant materials are treated at different temperatures during preparation. The major advantages of the GCxGC technique are improved peak resolution and enhanced sensitivity over one dimensional GC. The coupling of TOF-MS with GCxGC greatly enhances the information that can be drawn from analysis of complex plant volatile mixtures.

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The aim of this book is to describe the fundamental aspects and details of certain gas chromatography applications in Plant Science, Wine technology, Toxicology and the other specific disciplines that are currently being researched. The very best gas chromatography experts have been chosen as authors in each area. The individual chapter has been written to be self-contained so that readers may peruse particular topics but can pursue the other chapters in the each section to gain more insight about different gas chromatography applications in the same research field. This book will surely be useful to gas chromatography users who are desirous of perfecting themselves in one of the important branch of analytical chemistry.

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