Headspace Gas Chromatography as a Green Analytical Technique

*by Fernando Sotoca Usina, Christof Stönner and Miguel de la Guardia**
Analytical Chemistry Department, Universityof Valencia, C/ Dr. Moliner 50, 46100 Burjassot, Valencia, Spain.
**Corresponding author: miguel.delaguardia@uv.es*
Tel: +34 96 354 48 38 Fax: +34 96 354 48 45

Headspace-Gas Chromatography (HS-GC) has been evaluated as a green alternative for the elimination, or at least the large reduction, of solvents in analytical determinations. The direct use of HS-GC and the pre-concentration of analytes in the HS vial offer fast, safe, sensitive and selective methods for the quantitative determination of volatile and semi volatile analytes in many types of samples and based on these approaches, green analytical determinations are available for environmental, clinical and food applications.

Introduction

Gas chromatography (GC) provides a useful analytical tool for the determination of a large number of organic molecules. The development of new powerful detectors, together with the research on new columns and stationary phases have contributed to improving the utility and the performance of this analytical technique. In particular the determination of volatile and semivolatile compounds, which can be determined directly in many cases, without the need for derivatisation reactions, has resulted in an increase in laboratory productivity and a reduction in the use of reagents and their collateral environmental effects [1].

The introduction of samples to chromatographic columns can be done either directly or indirectly [2]. In this paper we will focus on direct methods of sample introduction for gas chromatography analysis. The advantages of this approach are the omission of sample preparation steps, and as a consequence reduces the amount of deleterious solvent consumption. In addition to the introduction of liquid samples, in the case of gas chromatography, the use of thermally aided injection, where the sample is heated and the vapour injected onto the column, must be considered as a solvent free alternative which can improve safety and reduce analysis times (see Figure 1).

Direct injection of the samples onto the column is the oldest approach in GC sample introduction. The advantages are its simplicity, reliability, ease of operation and throughput. Using this method the sample must be dissolved in a high boiling solvent and an aliquot is then transferred into a GC vial of an autosampler or directly injected onto the column.

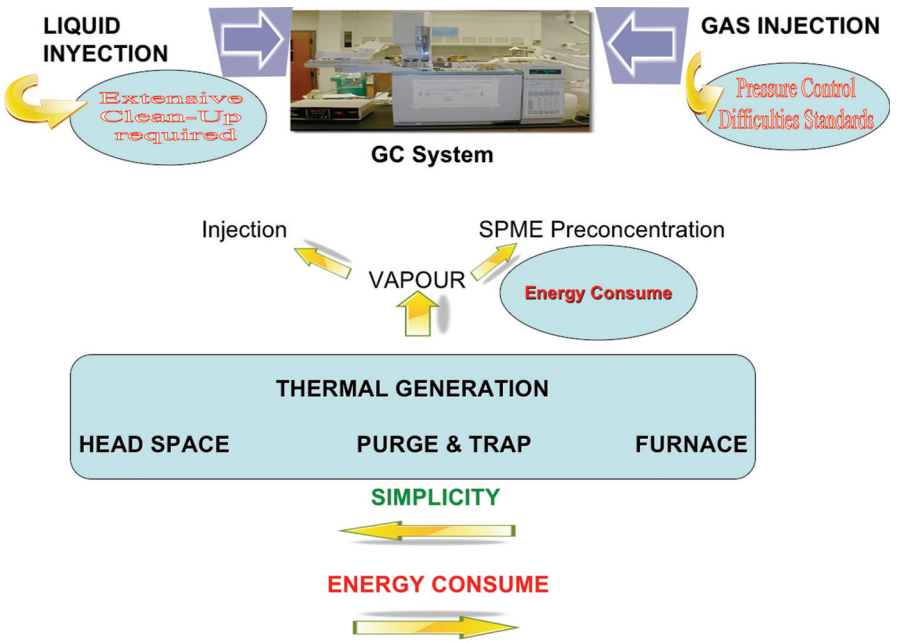

Figure 1: Sample introduction methods in GC

The main challenges associated with this approach are the contamination of the injector and the column due to the injection of the sample matrix together with the organic injection solvent. The other environmental disadvantages of this approach are associated with the dilution of samples involved with this strategy - due to additional extensive sample cleanup, which consumes significant volumes of solvents, labour and energy. Further disadvantages with this approach are the low sensitivity obtained in many cases due to the dilution of the sample [3].

Compared with direct liquid injection, the introduction of gaseous samples inside the GC can avoid the dilution factor but is a relatively restricted technique which creates many challenges associated with the preparation of standards and a need for precise control of flow and leaks. Therefore, the use of headspace, both in the static and dynamic mode, and pyrolysis are the best alternatives.

In static headspace analysis the vapour phase, in equilibrium with the sample, is injected onto the GC column. To quantify the amount of volatile compounds in the liquid or solid sample the equilibrium state between the sample phase and the vapour

phase has to be reached. The obvious way to enhance the sensitivity of the method is to increase the vapour pressure of the analytes. Some traditional techniques have been established like heating, 'salting-out' or adjusting pH to achieve this, but also novel approaches like the use of a trap for pre-concentration or the introduction of ionic liquids as solvents are available [4]. Moreover, the process can be automated and possesses a broad range of applicability for the determination of volatile organic compounds (VOCs) in food and beverages as well as in environmental samples. However, it sometimes lacks sensitivity and only volatile and semi-volatile compounds can be determined [5].

Dynamic headspace often refers to the purge-and-trap technique. Here an inert gas flows over the surface of the sample carrying the volatile and semivolatile analytes from the sample matrix to a sorbent trap. The compounds present in the gas phase are collected by a cooled absorbent and are finally desorbed by heating onto the GC column. In comparison to the static HS technique, the sensitivity can be enhanced by the purge step and the following pre-concentration on the trap. Hence, it is possible to determine concentrations of volatile organic compounds in samples with an unfavourable partition constant. However, this approach does require a more complicated sampling device than that used in the static mode. The main disadvantages of the HS approach are

- environmental contamination
- breakthrough-related problems
- lower precision values compared to static HS results [5].

In the context of green analytical methods, this strategy is not as beneficial as static HS due to the high consumption of gas and energy consumption due to the temperature treatment of the trap (both cooling and heating).

Furnace pyrolytic injection allows the determination of non-volatile compounds, by heating the sample in an oven up to 600°C. Thus, large molecules such as polymers or plant fibres can be pyrolised and swept into the vapour phase. The extreme thermal treatment of the sample causes molecular bonds to be cleaved, releasing small-volatile compounds onto the GC column. According to the obtained fragments and the possible decomposition mechanisms, it is possible to reconstruct the structure of the original molecule. Additionally, small molecules like

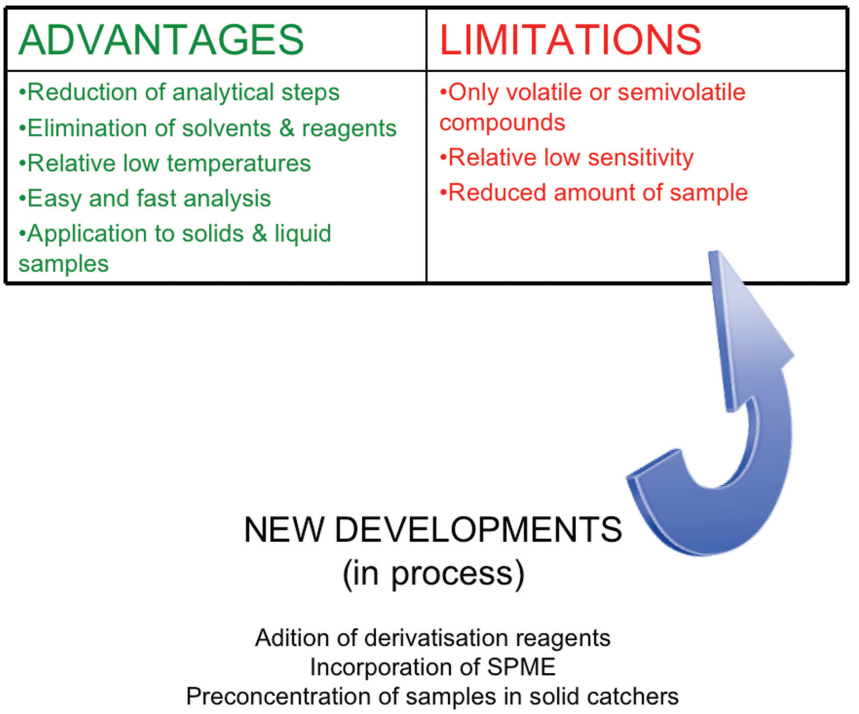

Figure 2: Advantages and limitations of static head space in GC

plasticiser in polymers may be released at relatively low temperatures allowing their detection within the polymer network. However, applying such high temperatures is very expensive and energy consuming making this approach not particularly green.

It can be concluded that headspace thermal desorption could be a valuable tool for direct analysis of volatile and semi-volatile compounds in samples. However the direct introduction of the vapour, in contact with the samples, after a short period of heating at a relatively low temperature does not result in a high sensitivity assay, and, because of that, pre-concentration of the analytes must be must be required in many cases (see Figure 2).

Thermal desorption of analytes from solids

Thermal desorption provides a viable alternative to solvent desorption, where the analytes are eluted from the trapping sorbent using an organic solvent. The use of solvents in analytical methodologies should be reduced as much as possible due to both the financial implications of using and disposing of organic solvents and also the environmental costs. The use of solvents in the extraction of the sample from the sorbent trap can also create challenges with both the sensitivity of the assay and also in the chromatographic noise generated which will also affect the limit of detection (see Table 1).

To avoid the extra step of pre-concentrating the sample (by blowing down and reconstituting in a lower volume of liquid), as well as reducing the environmental impact, thermal desorption of analytes retained on a suitable sorbent bed provides an obvious green and low cost alternative. The main advantages of thermal desorption over solvent desorption are: i) increased sensitivity, ii) lower detection limits, iii) elimination of toxic and interfering solvents, iv) fast analysis with reduced number of steps and v) the potential for automation (see Table 1).

Table 1 highlights the reasons why the most popular method used today for monitoring VOC´s in ambient indoor air is thermal desorption of the sample from a solid support [6].

There are three different types of thermal desorption sampling techniques which are commonly used: dynamic, passive and denuder.

Dynamic sampling techniques are based on the flow of samples through a tube which contains an adsorbent that traps the target analytes. In these systems the volume of air or water can be easily determined and, thus the amount of analyte retained in the sampler provides a direct measurement of their concentration in the original sample.

Passive sampling techniques are based on the concentration gradient of the analytes between the sample and the deployed sampler. This approach relies on a time

Methodology	Advantages	Drawbacks
Thermal Desorption	• no sample preparation step • easy reusability of sorbents • easily automated • no interference from the solvent • quantitative liberation of analytes • low detectable levels of VOC´s • reduced time of analysis	• additional cost of the instrumentation • relatively high temperature required • analytes may decompose and non volatile compounds may be lost • requires the use of thermally stable sorbents
Solvent Extraction	• cheap • no additional instrumentation required • useful for high-molecular weight compounds	• toxicity of solvents • interferences of solvents • dilution of samples. • potential for increase of matrix interferences • lack of greenness regeneration of sorbent bed before reuse

Table 1: Advantages and drawbacks of thermal desorption of analytes retained on solid sorbents, prior to solvent desorption.

based equilibrium state being reached, and provides an average concentration of the pollutants as a function of the exposure time [7].

Denuder sampling techniques were originally used to analyse inorganic pollutants in air. This technique has advanced over recent years, and as a consequence this approach can also be used to analyse organic pollutants in the atmosphere. This technique relies on drawing an atmospheric sample through a capillary or set of capillaries (these are typically coated GC column capillaries) which are coated with a material that traps the analyte of interest, whilst particulates and other non-volatile components, because of their lower diffusion coefficients, will tend to be drawn straight through the collection tube(s). The technique relies on a laminar flow of the sample through the tubes to ensure that particulates and other unwanted non-volatile components do not come into contact with the adsorbent wall of the tube.

For dynamic techniques, sorbents such as activated carbon, graphitised carbon black and porous polymers are used. The use of Carbopax X and Carboxen-56 has also been proposed [8]. The coatings used for denuders will typically reflect those found on GC capillary columns.

For passive sampling the type of sorbent employed strongly depends on the strategy used for analyte desorption and thus, for solvent extraction, triolein, silica gel, activated carbon or porous polymers are typically used. When thermal desorption is used, Tenax, graphitised carbon black and fluorisil are employed [7,9]. Table 2 provides a look into the recent applications of HS-GC for environmental, clinical and food analysis.

Matrix	Analytes	Procedure	Reference
Fennel	Volatile organic compounds	Heated to 145°C with an equilibration time of 35 min.	[11]
Ladybugs	Pheromones	Heated to 80°C with an equilibration time of 22 min and the addition of NaCl.	[12]
Soils	Hydrocarbons	Heated to 95°C with an equilibration time of 45 min.	[13]
Human blood	Amphetamine	In-matrix derivatisation of the analytes and heating conditions of 90°C for 20 min.	[14]
Blood and other human fluids	Cyanide	Heated to 95°C with an equilibration time of 25 min and occasionally vortexed.	[15]
Olive oil	BTEX*	Heated to 95°C with an equilibration time of 25 min.	[16]
Water	BTEX*	Heated to 70°C with an equilibration time of 20 min. and the addition of KCl and HNO3.	[17]
Passive samplers	Volatile organic compounds	After sampling in ambient air the semi-permeable membrane devices were heated to 150°C for 10 min to desorb the trapped molecules.	[18]
* BTEX: Benzene, Toluene, Ethylbenzene, Xylenes.			

Table 2: Selected applications of HS-GC for direct analysis.

Preconcentration of analytes in headspace vials

Many attempts have been made to enhance the sensitivity of HS-GC devices (see Table 3). One approach that is effective is the pre concentration and enrichment of analytes onto a fibre such as that used in a solid phase micro extraction (SPME) approach. The fibre consists of a coated fused silica capillary. The coating can vary in polarity, porosity and film thickness dependant on the compounds being analysed. Combinations of different materials are possible as well, offering the opportunity of extracting a broad range of molecules with different molecular mass, polarity and volatility [19,20]. The adsorption of the semi-volatile or volatile organic compounds takes place in the headspace above the sample, allowing for the extraction of the analytes over a wide range of concentrations. To limit the uptake of analytes and to avoid overload of the GC column, the fibre can be coated with a second layered coating restricting the adsorption.

The alteration of sampling conditions influences the efficiency of the solid-phase microextraction in a similar way to static headspace sampling. The efficiency and thus the sensitivity depends on three parameters;

- the ratio between the volume of sample and the volume of the headspace vial
- extraction time
- extraction temperature.

The extraction can be performed under relatively low temperatures avoiding the desorption of trapped molecules and the potential degradation of compounds. This permits the collection of molecules with high molecular masses which cannot be collected with static headspace sampling. In the case of aqueous samples, warming the sample at a temperature below the boiling point of water is advantageous in order to avoid the vaporisation of water and consequently the contamination of the chromatographic column. In most cases static headspace sampling of aqueous samples needs a temperature above the boiling point of water to determine semi-volatile compounds and consequently a water peak, if the water is not previously separated from the analytes through further traps, will occur. To determine low concentrations of molecules in the presence of molecules in high concentrations and with high partition coefficients, it is useful to reduce extraction time. Agitation and the 'salting-out effect' often help to enhance sensitivity as well.

Solid phase micro-extraction is a powerful tool to pre-concentrate semi-volatile and volatile organic compounds from the headspace of complex sample matrices and to obtain a high sensitivity assay. The opportunity to automate the process and the omission of further preparation steps (since there is no need to cryo-focus the analytes prior to the injection onto the GC column), gives rise to fast method development for food and beverage samples [21].

Further developments to the technology have been made by increasing the amount of sorbent placed on the fibre resulting in higher loading capacities. These improvements led to techniques like stir bar sorptive extraction and headspace sorptive extraction.

Using the dispersive micro-solid phase extraction approach, a suspension of nanoparticles in an appropriate organic solvent is added to the liquid sample. After the desorption of the analyte onto the surface of the nanoparticles, the sorbent is separated from the liquid phase and collected on an interface which can be heated thermally to desorb the trapped analytes. In this case, there is no need to use organic solvents to extract the analyte from the sorbent. Here the analyte is thermally desorbed avoiding the dilution step and thus enhancing the sensitivity of this method [22].

The use of a programmable temperature vaporiser may be used to cryo-focus the analytes, which are adsorbed and finally desorbed from the diffusion denuder which

Matrix	Analytes	Pre-concentration strategy	Reference
Human blood	Acetone	SDME - 2 L of decane containing a derivatisation agent was exposed to the headspace above the sample at 60°C for 6 min.	[26]
Water	Organotins	SDME - 2 L of decane was exposed to the headspace above the sample at room temperature for 1 min.	[27]
Water	Chlorobenzenes	SDME - 2.5 L of toluene was exposed to the headspace above the sample at room temperature for 5 min.	[28]
Water	PAHs	SDME - 3 L of 1 butanol was exposed to the headspace above the sample at room temperature for 13 min.	[29]
Beer and beverages	Volatile sulphur compounds	SPME - The PDMS fibre was exposed in the headspace above the sample at 25°C for 30 min and thermal desorption was performed at 250°C for 3 min.	[30]
Water	BTEX	SPME – A portable device was used. The PDMS-DVB fibre was exposed in the headspace above the sample at room temperature for 1 min and thermal desorption was performed at 240°C for 10 sec.	[31]
Strawberry and cherry juices	Organophosphorous insecticides	SPME - The PDMS fibre was exposed in the headspace above the sample at 75°C for 45 min and thermal desorption was performed at 240°C for 2 min.	[32]
Water	Pesticides, PAHs; PCBs	SBSE - The PDMS stir bar was exposed for 14 h to the solution and the thermal desorption was performed at 280°C for 7 min.	[33]
Liquid solution	2,4,6-trinitrotoluene	TDS-CIS - Thermal desorption of the analytes and introduction into a cooled injection system to enrich and focus the analytes	[34]
Water	PAHs	DMSPE - Nanoparticles of RP C18 are used to adsorb the analyte out of the solution. Finally they are separated from the matrix and the analytes are thermally desorbed at 300°C for 2 min.	[22]
*SDME: Single-drop microextraction; SPME: Solid phase microextraction; SBSE: Stir-bar sorptive extraction; TDS-CIS: Thermal desorption system – cooled injection system; DMSPE: Dispersive micro solid phase extraction; PDMS: Polydimethylsiloxane; PDMS-DVB: Polydimethylsiloxane – divinylbenzene; PAH: Polycyclic aromatic hydrocarbon; BTEX: Benzen, Toluene, Ethylbenzene, Xylenes; PCB: Polychlorinated biphenyl.			

Table 3: Selected applications of HS-GC after pre-concentration in the vial.

enhances the sensitivity of the analysis. To determine concentrations of organic compounds in environmental samples the interference from the background matrix and humidity has to be minimised.

Due to the potential to cause harm to the analytical column or potential to reduce method sensitivity, the measurement of aqueous samples is often difficult without a pre-extraction of the analytes with organic solvent. The combination of two programmable temperature vaporisers allows the fast separation of the water phase from the analytes. The first vaporiser evaporates the complete sample and the second vaporiser adsorbs and desorbs the analyte. Through this configuration the water can be vented out of the device and the extraction of the analyte out of an aqueous solution succeeds without the need to use organic solvents or further preparation steps. This method fulfils the requirement of robustness, the opportunity of automation and permits high sensitivity detection due to the cryo-focussing [23].

Large-volume-extraction uses a porous layer open tubular (PLOT) column to adsorb semi-volatile and volatile organic compounds from an aqueous solution. The trapped organics are thermally desorbed and injected onto the GC column. The injection of a large volume of the sample onto the trap enhances the sensitivity and low analyte concentrations may be detected. Nevertheless this technique provides only low reproducibility due to the inability of the analytical column to desorb the extracted analytes quantitatively [24].

The thermal desorption counter-flow introduction atmospheric pressure chemical ionisation mass spectrometer is a screening method which omits the separation step. The vaporised sample is introduced to the ion source under atmospheric pressure and the ionised molecules are accelerated in the same direction through the electric field from where they came. Due to the opposed flows of neutral and charged molecules an improvement of the efficiency of the ionisation can be achieved as well as a stable discharge for a long period of time. Hence there is almost no sample preparation or separation step prior to the analysis. This method can be used for the fast analysis of volatile and semi-volatile compounds. Furthermore there is no need for toxic organic solvents to create the spray and ionising the analytes as the residual water in the ambient air is sufficient enough to ionise them [25].

Evaluation of green parameters of HS-GC

In recent years efforts have been made to evaluate the environmental friendliness of a variety of alternative methods of analysis to long and multi-step traditional ones [35]. The overall goal is the reduction of unnecessary steps from sampling through to analyte measurement. Sample preparation typically requires the largest volume of reagents and consumes the most energy. The main criteria which should be considered for all green analytical methods are reagent consumption, waste generation, energy consumption and risks to both, operatives and the environment, being also obtained benefits concerning laboratory productivity, cost and time of analysis[36].

An important point to be considered on greening a method is the elimination or reduction of reagents and solvents. Pre-treatment, like sample extraction, cleanup and pre-concentration often consume large volumes of solvents. Thus solvent-free or solvent-less analytical methods should ideally be implemented. Additionally, less hazardous solvents should be used in the laboratory to avoid exposure of lab staff to harmful substances and to reduce analytical waste. If there is no alternative, the opportunity to recycle, degrade or decontaminate waste should be investigated. Another point is to avoid the chemical derivatisation of analytes whenever possible. If these measures are implemented, waste generation can be decreased. In addition reducing the energy consumption for sample analysis should be of interest. This goal can be achieved by reducing the chromatographic separation time and temperature, or by miniaturisation of the analytical devices [37].

A great advantage of HS-GC is that there is generally no need for sample preparation. The sample is heated inside a sealed vial and as there is no chemical treatment after measurement, the sample can be easily disposed of. It is highly desirable to avoid the use of reagents to solubilise analytes. Therefore direct volatilisation of compounds by heating at a relatively low temperature could be of great value in reducing the amount of reagents used, and reducing energy consumption.

The sensitivity of the HS-GC measurement depends on the partitioning constant of target analytes. Therefore it is important to optimise the parameters affecting the equilibrium between sample and vapour phase. Generally the sensitivity can be enhanced by increasing the temperature, the sampling time and controlling the nature of the sample matrix.

The dependence of temperature on sensitivity was investigated by Kolb and Ettre [38]. The partitioning constant was found to increase when the sample was heated due to the easier release of the analytes from the sample matrix. The general trend is the higher the temperature the higher the sensitivity. However the increase of temperature also involves the degradation of some compounds and could increase the number of unidentified peaks in sample chromatograms. Nevertheless several reasons limit the use of temperature to increase sensitivity such as degradation of the target compounds [39] or the achievement of maximum response due to reaching equilibrium [40]. The application of low temperatures may lead to high selectivity as only a small number of compounds are injected into the GC. Thus the observance of interferences may be suppressed and the sensitivity for selected substances increased. An example of this approach is the successful suppression of a false positive determination of benzene by applying low temperature volatilisation and the use of a suitable solvent [41].

In HS analysis, the heating of each vial to vaporise compounds consumes energy. Through the use of an appropriate solvent, the partitioning constant between sample and vapour phase can be increased by reducing interactions between analyte and solvent. Optimisation of the headspace sample dilution medium leads to an increase in the sensitivity and permits the use of low sampling temperatures [42]. Furthermore the degradation of polar or high molecular mass compounds, which are often sensitive to heat, can be suppressed. Obviously the use of solvents has some disadvantages like the appearance of a solvent peak in the chromatogram, which could interfere with analyte peaks leading to decreased selectivity and sensitivity. When reagents are used to transport the analytes out of a solid phase there is the risk of contamination and/or the loss of the target compounds. In the context of green analytical chemistry the extraction of the analyte from the sample is undesirable because of the addition of a further steps in the analytical procedure. As a consequence the additional sample treatment consumes energy, solvents and produces additional waste.

Future Perspectives

HS-GC is a powerful tool to directly determine the presence of volatile and semivolatile compounds in environmental, clinical and food samples without significant sample preparation. A combination of HS-GC with passive samplers allows us to monitor air and waste quality. The low cost and simple methodology means this method is often preferable compared to other complex procedures like the use of active samplers and denuders. HS-GC strongly reduces the consumption of reagents and solvents and also has a relatively low energy consumption compared to other strong heating alternatives. Important developments have been made on alternative solid phases for passive sampling, miniaturisation of analytical devices as well as developments allowing faster analytical measurements. Additional investigations are also looking at pre-concentration steps like the use of traps prior to injection of the headspace onto the GC column, or the use of SPME in HS vials.

References

[1] S. Armenta, S. Garrigues, M. de la Guardia, TrAC 27 (2008) 497 511.

[2] M.Tobiszewski, J. Namiesnik, TrAC 35 (2012) 67-73.

[3] N.H. Snow, G.P. Bullock, J. Chromatogr. A 1217 (2010) 2726-2735.

[4] S. de Koning, H.-G. Janssen, U. A. T. Brinkman, Chromatographia 69 (2009) 33-67.

[5] C. Camarasu, C. Madichie, R. Williams, TrAC 25 (2006) 768-767.

[6] D. L. Heavner, M. W. Ogden, P. R. Nelson, Environ. Sci. Technol. 26 (1992) 1737-1746.

[7] E. Magi, M. Di Carro, C Liscio, Anal. Bioanal. Chem. 397 (2010) 1335-1345.

[8] S. Król, B. Zabiegala, J. Namiesnik, TrAC 29 (2010) 1092-1112.

[9] R. A. Hallama, E. Rosenberg, M. Grasserbauer, J.Chromatogr.A 809 (1998) 47-63.

[10] K. M. Hart, L. M. Isabell and J. F. Pankow, Environ. Sci. Technol. 26 (1992) 1048-1052.

[11] M. Križmana, D. Bariče̊vič̊b, M, Prošeka, Anal. Chim. Acta 557 (2006) 267–271.

[12] E. Cudjoe, T. B. Wiederkehr, I.D. Brindle, Analyst 130 (2005) 152-155.

[13] J.L. Pérez Pavón, A. Guerrero Peña, C. García Pinto, B. Moreno Cordero; J.Chromatogr. A 1047 (2004) 101–109.

[14] K. Watanabe, N. Okamoto, I. Yamagishi, H. Nozawa, A. Ishii, O. Suzuki; Chromatographia 58 (2003) 455-458.

[15] B. Desharnais, G. Huppé, M. Lamarche, P. Mireault, C.D. Skinner, Forensic Science International 222 (2012) 346–351.

[16] F.Peña, S. Cárdenas , M. Gallego , M. Valcárcel, J.Chromatogr. A 1052 (2004) 137–143.

[17] A. Serrano, M. Gallego ;J.Chromatogr. A 1045 (2004) 181-189.

[18] S. Ly-Verdu, F. A. Esteve-Turrillas, A. Pastor, M. de la Guardia, Talanta 80 (2010) 2041–2048.

[19] L. Pillonela, J.O. Bosseta, R. Tabacchib, LWT-Food science and Technology 35 (2002) 1-14.

[20] J. Gromadzka, W. Wardencki, Chromatographia 71 (2010) 81-86.

[21] E. Schaller, S. Zenhäusern, T. Zesiger, J.O. Bosset, F. Escher, Analusis 28 (2000) 743-749.

[22] F. Galán-Cano, R. Lucena, S. Cárdenas, M. Valcárel, Anal. Methods 3 (2011) 991-995.

[23] W. Ziemer, M. Wortberg, C. Eichberger, J. Gerstel, W. Kerl, Anal. Bioanal. Chem. 397 (2010) 1315-1317.

[24] S. M. Pyle, G. W. Sovocool, L. A. Riddick, Talanta 69 (2006) 494-499.

[25] H. Inoue, H. Hashimoto, S. Watanabe, Y. T. Iwata, T. Kanamori, H. Miyaguchi, K. Tsujikawa, K. Kuwajama, N. Tachi, N. Uetake, J. Mass Spectr. 44 (2009) 1300-1307.

[26] L. Dong, X. Shen, C. Deng, Anal. Chim. Acta 569 (2006) 91–96.

[27] V. Colombini, C. Bancon-Montigny, L. Yang, P. Maxwell, R. E. Sturgeon, Z. Mester, Talanta 63 (2004) 555–560.

[28] L. Vidal, A. Canals, N. Kalogerakis, J.Chromatogr A 1089 (2005) 25–30.

[29] S. Shariati-Feizabadi, Y. Yamini, N.Bahramifar, Anal. Chim. Acta 489 (2003) 21–31.

[30] Q. Xiao, C. Yu, J. Xing, B. Hu, J. Chromatogr.A 1125 (2006) 133–137.

[31] J. Ji, C. Deng, W. Shen, X. Zhang, Talanta 69 (2006) 894–899.

[32] D. A. Lambropoulou, T. A. Albanis, J. Agric. Food Chem. 50(2002) 3359-3365.

[33] E. Pérez-Carrera , V. M. León, A. G. Parra, E. González-Mazo, J.Chromatogr. A 1170 (2007) 82 90.

[34] C. R. Fielda, B. C. Giordanoa, D. A. Rogersa, A. L. Lubranob, S.L. Rose-Pehrssona, J. Chromatogr. A 1227 (2012) 10-18.

[35] M. de la Guardia, S. Garrigues, Challenges in Green Analytical Chemistry, Royal Society of Chemistry, Cambridge, 2011.

[36] A. Galuszka, P.Konieczka, Z. A.Migaszewski, J.Namiesnik, TrAC 37 (2012) 61–72.

[37] J. Namiesnik, J. Sep. Sci. 24 (2001) 151–153.

[38] B. Kolb, L. S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, Wiley-VCH, New York, 1997, p. 20.

[39] L. Lucentini, E. Ferretti, E. Veschetti, V. Sibio, G. Citti, M. Ottaviani, Microchem. J. 80 (2005) 89–98.

[40] J. Tian, J. Food Compost. Anal. 23 (2010) 475–479.

[41] H. K. Ju, J. H. Park, S. W. Kwon, Biomed. Chromatogr. 22 (2008) 900-905.

[42] Y. Sitaramaraju, A. van Hul, K. Wolfs, A. Van Schepdael, J. Hoogmartens, E. Adams,J Pharm. Biomed. Anal. 47 (2008) 834-840.