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Identification of volatile organic compounds (VOCs) in plastic products using gas chromatography and mass spectrometry (GC/MS)

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ABSTRACT

Plastic materials are widely used in daily life. They contain a wide range of compounds with low molecular mass, including monomeric and oligomeric residues of polymerization, solvent-related chemicals residues, and various additives. Plastic products made of expanded polystyrene (EPS) are currently employed as food containers. This study therefore sought to identify volatile organic compounds released by EPS from food packages and utensils used in Cartagena, Colombia. EPS-based plates, food and soup containers were subjected to various temperatures and released chemicals captured by solid phase microextraction, followed by on-column thermal desorption and gas chromatography/mass spectrometry analysis. The results revealed the presence of at least 30 different compounds in the EPS-based products examined; the most frequently found were benzaldehyde, styrene, ethylbenzene and tetradecane. The release of these molecules was temperature-dependent. It is therefore advisable to regulate the use of EPS products which may be subjected to heating in order to protect human health by decreasing the exposure to these chemicals.

Keywords: additives, expanded polystyrene (EPS), solid-phase microextraction (SPME), styrene.

Identificação de compostos orgânicos voláteis (COVs) em produtos plásticos por cromatografia gasosa acoplada a espectrometria de massa (CG/MS)

RESUMO

Os materiais plásticos são amplamente usados na vida quotidiana. Eles contêm uma grande variedade de compostos de baixa massa molecular, incluindo os resíduos monoméricos e oligoméricos de polimerização, relacionados com resíduos de solventes químicos, e diferentes aditivos. Atualmente, os produtos de poliestireno expandido (EPS) são empregados como recipientes para alimentos. Assim, o objetivo deste estudo foi identificar os compostos orgânicos voláteis liberados por objetos utilizados diretamente em contato com alimentos disponíveis em Cartagena, Colômbia. Produtos baseados em EPS tais como pratos, recipientes para alimentos e sopa foram submetidos a diferentes temperaturas de aquecimento e as substâncias químicas liberadas foram capturadas empregando-se a técnica de microextração em fase sólida, seguida de dessorção térmica e análise por cromatografia a gás/espectrometria de massa. Os resultados revelaram a presença de pelo menos 30 compostos diferentes relacionados aos produtos de EPS examinados, sendo o benzaldeído, estireno, etilbenzeno e tetradecano os mais frequentemente encontrados. A liberação dessas moléculas é dependente da temperatura a que o material é submetido. Portanto, para proteger a saúde humana, diminuindo a exposição a estes agentes químicos, é aconselhável regular o uso de produtos a base de EPS que poderão ser submetidos a aquecimento.

Palavras-chave: aditivos, estireno, micro extração em fase sólida (SPME), poliestireno expandido (EPS).

1. INTRODUCTION

The importance of plastic materials for many everyday life applications has increased steadily in recent years (Buchberger and Stiftinger, 2012). Manufactured products made of polymers are generally complex materials, composed of polymers or copolymers, with a variety of additives with different volatilities (Wampler, 2004). Currently, expanded polystyrene (EPS), used to make styrofoam containers, is the most widely used plastic in several countries; in fact, over 30 countries have signed an international agreement to maximize reuse and recycling of EPS (Kusch and Knupp, 2002; De Paula Pereira et al., 2004). These products are obtained by the polymerization of styrene monomer with the addition of pentane as blowing agent (Kusch and Knupp, 2002). Polystyrene is easy to manufacture, fragile, and softens at a temperature of approximately 100 °C, although it may degrade at elevated temperatures in a mixture of low organic molecular mass compounds. In addition, this material contains in its formulation antioxidants, UV stabilizers, lubricants, antistatic agents, plasticizers, and flame retardants (Smith and Taylor, 2002; Lattuati-Derieux et al., 2013).

Among a large number of uses, EPS is employed for food packaging, product protection from damage during transport and storage, as well as for the building industry in the insulation of exterior walls and foundations (Kusch and Knupp, 2002; Shah et al., 2008). Under certain conditions, polystyrene is able to release residual styrene monomer, and other volatile organic compounds (VOCs) at room temperature (Garrigós et al., 2004), including pentane, benzene, toluene, ethylbenzene, xylene isomers, n-propylbenzene, 1,2,4-trimethylbenzene, o-methylstyrene, benzaldehyde, benzyl alcohol, and acetophenone, among others (Kusch and Knupp, 2002; Kusch and Knupp, 2004). These compounds, known environmental pollutants that affect air quality and human health (Lee et al., 2006; Wang et al., 2007), have the capacity of inducing deleterious effects on the mucous membranes of the nose, eyes, throat, skin the face, neck and hands, upper and lower airways (Yorifuji et al., 2012).

Styrene is one of the main compounds released from EPS products, and has been classified as a possible human carcinogen (Group 2B) by the International Agency for Research on Cancer (IARC) (EU, 2014). Therefore, there is a concern about the potential carcinogenicity of styrene, which comes largely from the ability of its metabolite, styrene-7,8-oxide (SO), to bind covalently to DNA, and its activity in a variety of genotoxicity tests. This chemical has also been classified by IARC in Group 2A, as probably carcinogenic to humans (Rueff et al., 2009). Styrene is harmful if inhaled, causing tissue irritation and neurological impairment (Kusch and Knupp, 2002). This study examined the release of VOCs from commercially available products made of EPS in Cartagena, Colombia, and discusses their probable impact on human health.

2. MATERIAL AND METHODS

EPS-based samples of different types, including plates, food and soup containers, were obtained from local stores at Cartagena city. The plastic material was cut into small pieces (≅ 0.05 g), and placed in 4 mL headspace amber glass vials with black, 13 x 425 caps, PTFE/silicone septum (Agilent Technologies, USA). Solid phase microextraction (SPME) was used for the extraction of analytes employing a 100 µm polydimethylsiloxane (PDMS) fiber (Supelco, Bellefonte, PA, USA). SPME fibers were previously conditioned for 30 minutes at 250 °C and then placed into the vials containing the samples. These vials were then heated at specific temperatures (55 - 85 °C, increasing 10° C) for 30 min to release chemicals. These temperatures were chosen taking into account the temperature of the food when placed in the container. Immediately after the extraction process, the SPME fiber was removed from the vial, and transferred into the injector of the gas chromatograph for complete thermal desorption, allowing the release and analysis of VOCs (Kusch and Knupp, 2004).

GC/MS analysis was carried out using an Agilent 7890A Gas Chromatograph coupled to an Agilent 5975C mass spectrometer equipped with an HP-5 capillary column, 30 m long, 0.25 µm i.d., and a 0.25 µm film thickness. The temperature of the column was programmed from 50 °C (2 min) to 120 °C, at a rate of 15 °C per minute, and the final ramp reached 300 °C, at an increasing temperature rate of 5 °C per minute. Helium grade 5.0 was used as carrier gas at a flow rate of 1 mL/minute. Split/splitless (splitless mode) inlet temperature was 280 °C as was that of the mass spectrometry transfer line (Fu and Kawamura, 2010). The temperature of the ion source was maintained at 230 °C. The mass spectrometer was operated under electron ionization mode at 70 eV. Mass spectra and the total ion chromatograms were obtained by automatic scanning a mass range (m/z) of 45-400. Three runs per sample (n=3) were performed. The volatile components were identified by comparing the mass spectrum with those available in the Nist08 spectra library. Chemical composition is reported as the percentage of relative area, after obtaining the sum of all peak areas in the chromatogram.

Data are presented as means ± SD (Standard deviation). Comparisons between groups were achieved using ANOVA, with Dunnett's post-test. Data normality and equality of variances were previously checked by Kolmogorov-Smirnov and Barlett tests, respectively. Statistical analysis was performed with GraphPad 3.00.

3. RESULTS AND DISCUSSION

Chromatographic analysis of VOCs released by EPS products revealed the presence of at least 30 major common compounds (Table 1). Typical chromatograms are presented at two different extraction temperatures (55 °C and 85 °C) (Figure 1). At the highest tested temperature, 85 °C, benzaldehyde, pentadecane, tetradecane, ethylbenzene, cumene, acetophenone, and styrene were released at least from 50% of all sampled materials. The relative frequency of these compounds is shown in Table 1. As expected, data showed the number of released compounds from EPS-based products and their abundance in the chromatogram is temperature-dependent (Table 1, Figure 2), with the greatest number of compounds released at the highest temperature. Several compounds released at 85 °C, in particular high molecular mass alkanes, did not appear at lower temperatures, such as dodecane, tridecane, pentadecane, heptadecane, octadecane, and undecane, among others (Table 1). Interestingly, some chemicals that appeared at lower temperatures did not show up at higher temperatures. The differences in these chromatograms can be attributed, at least in part, to the use of different processing conditions, materials or additives during the manufacture of the products.

Results presented here are similar to those reported by other authors that also showed that styrene monomer (De Paula Pereira et al., 2004) and other volatile organic compounds are released when EPS containers are heated, and therefore may be available to migrate into the food (Kusch and Knupp, 2002).

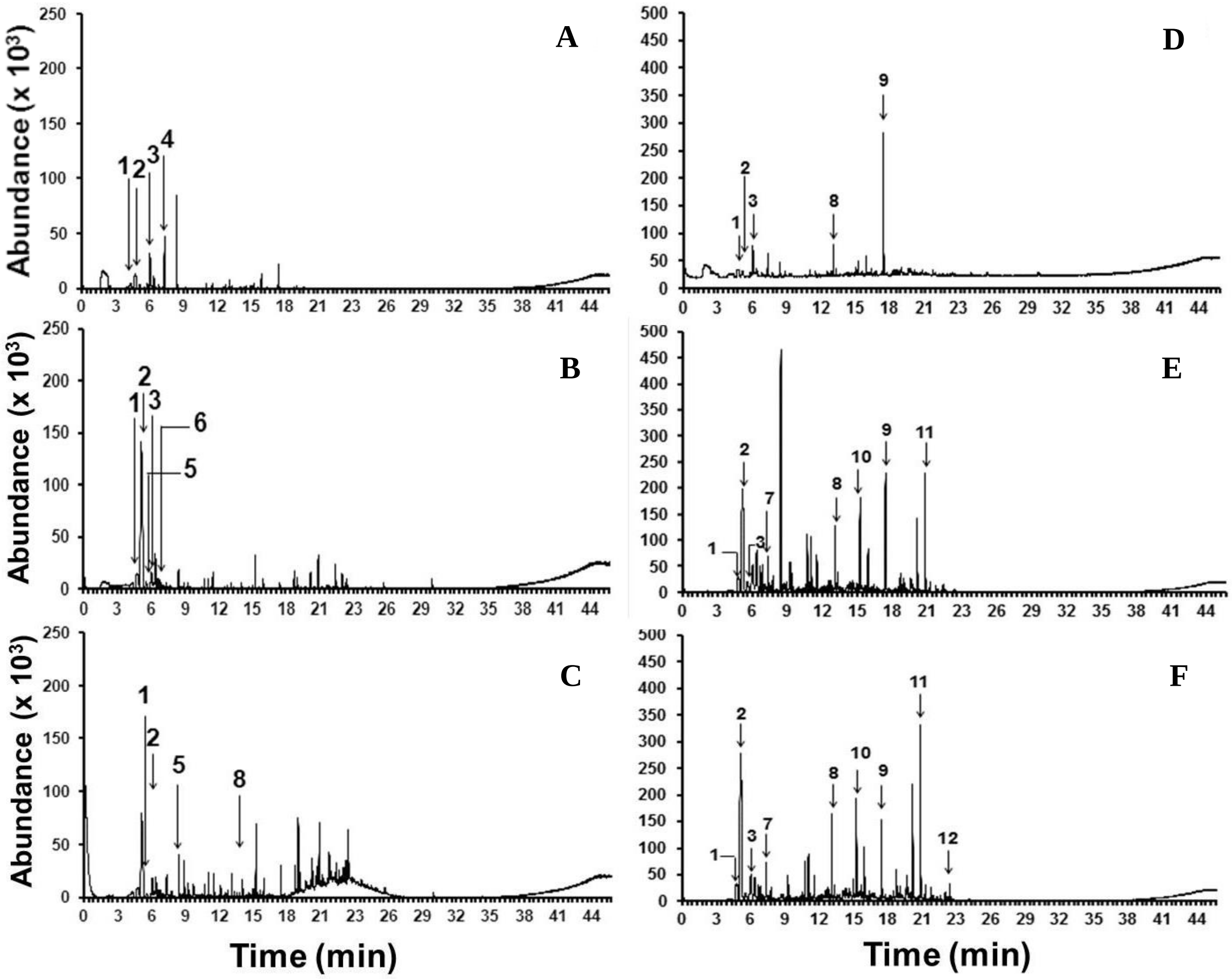

Figure 1. Typical SPME-GC/MS chromatograms of EPS-based products. Soup containers (**A, D**), food containers (**B, E**) and plates (**C, F**) at extraction temperatures of 55 °C and 85 °C, respectively. 1. Ethylbenzene. 2. Styrene. 3. Benzaldehyde. 4. Benzene, (1,1-dimethylethoxy). 5. Cumene. 6. Benzene, (1-methylpropyl). 7. Acetophenone. 8. Tetradecane. 9. Diethyl Phthalate. 10. Pentadecane. 11. Benzene, 1,1'-(1,2-cyclobutanediyl)bis, trans. 12. Nonanal.

The presence of particular VOCs released from EPS has been related to the extraction conditions of the analytes (Kusch and Knupp, 2002). An increase in temperature leads to a raise the diffusion of small molecules in the polymer core, promoting the transfer of these compounds in the headspace phase (Vilaplana et al., 2010). At 55 °C, on average, 19 compounds were detected from tested EPS-based products, whereas at 85 °C this number increased to 55 (Figure 2a). Moreover, the extraction temperature also determined the relative peak area of the compounds identified in the analyzed EPS-based products (Figure 2b). Kusch and Knupp (2002) also reported the influence of temperature on peak area, in agreement with these results.

Table 1. Relative frequency of major components identified in EPS-based products at different extraction temperatures.

Components	Temperature (°C)							
	55±5 °C		65±5 °C		75±5 °C		85±5 °C	
	Relative Frequency*	% Area	Relative Frequency	% Area	Relative Frequency	% Area	Relative Frequency	% Area
Benzene, 1,1'-(1,2-cyclobutanediyl)bis	6/9	5.1±2.7	---	---	4/9	9.7±6.4	---	---
Styrene	5/9	36.6±20.1	5/9	45.9±19.4	5/9	37.1±12.0	7/9	25.4±14.1
Ethylbenzene	5/9	21.2±33.3	5/9	19.5±27.9	4/9	6.3±1.6	8/9	3.3±2.7
δ-Cadinene	3/9	2.0±0.9	3/9	1.6±0.7	7/9	2.2±1.0	7/9	2.9±1.5
Benzaldehyde	3/9	15.0±14.1	7/9	3.4±1.3	7/9	9.7±7.3	8/9	7.1±5.4
Isocumene	1/9	17.0±0.0	3/9	4.0±2.7	3/9	5.9±4.4	4/9	0.9±0.2
Tetradecane	---	---	4/9	1.0±0.9	7/9	2.9±1.7	9/9	3.5±1.8
Cumene	---	---	3/9	6.4±7.9	3/9	5.9±7.9	5/9	3.6±5.1
DiethylPhthalate	---	---	2/9	2.7±1.8	3/9	8.9±6.0	6/9	11.0±11.3
Acetophenone	---	---	2/9	1.0±0.5	---	---	5/9	2.1±0.3
Diphenylether	---	---	---	---	4/9	1.5±1.3	6/9	1.6±0.9
Tridecane	---	---	---	---	3/9	2.7±0.1	3/9	1.6±0.9
Benzene, (1-methylpropyl)	---	---	---	---	3/9	1.7±0.5	2/9	1.1±0.1
Dodecane	---	---	---	---	3/9	1.1±0.2	6/9	0.9±0.4
Nonanal	---	---	---	---	1/9	2.1±0.0	---	---
Pentadecane	---	---	---	---	---	---	6/9	3.1±0.8
Heptadecane	---	---	---	---	---	---	4/9	1.0±0.4
1,3-diphenylpropane	---	---	---	---	---	---	4/9	1.0±0.3
Benzene, 1-methyl-4-propyl	---	---	---	---	---	---	3/9	1.6±0.3
Octadecane	---	---	---	---	---	---	3/9	0.7±0.4
Octane, 1,1'-oxybis	---	---	---	---	---	---	3/9	0.6±0.2
n-Heptadecanol-1	---	---	---	---	---	---	2/9	1.0±0.2
Undecane	---	---	---	---	---	---	2/9	0.4±0.1
Othercompounds	---	3.3±0.8	---	14.5±7.4	---	2.5±1.1	---	25.7±8.3

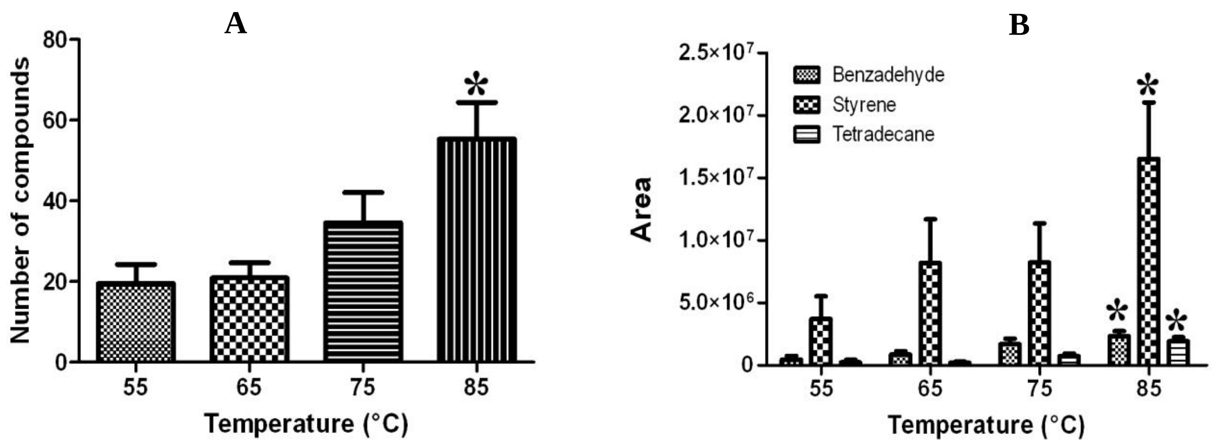

Figure 2. Effect of temperature on the number of compounds released from EPS-based products **(A)**, and on the peak area for specific compounds **(B)**. *****Significantly different as compared to 55 °C (P< 0.05).

Many studies have been conducted on volatile emissions during processing and thermal degradation of polymers (Ciucanu et al., 2002; Watanabe et al., 2007; Vilaplana et al., 2010). As shown here, EPS-based products release different chemicals when heated. These substances may migrate into food, and as a consequence, jeopardize the safety of these containers (Date et al., 2002). However, for many of these compounds, little is known about their health effects and most are not regulated by local authorities. The European Union (Regulation No 10/2011) has imposed several restrictions and even banned some substances in certain articles intended for contact with food; however, permissible levels of VOCs released, and possible migration into food, are not included in this regulation (EU, 2014). This problem is not unique to EPS products; several plastic types used as containers release monomers as well as impurities and oxidation products (Camacho and Karlsson, 2000; Kusch and Knupp, 2002; Skjevrak et al., 2003; Kusch and Knupp, 2004; Vilaplana et al., 2010a; Vilaplana et al., 2010b; Lattuati-Derieux et al., 2013) (Figure 3). In fact, some of the identified VOCs may also be formed by thermo-oxidative degradation of EPS when exposed to high temperatures and solar irradiation (Kusch and Knupp, 2004).

Since plastics are highly used in many countries to store and carry different food products, it is evident that their use may pose some risks for human health. The technique of gas chromatography coupled with mass spectrometry allows the identification of the compounds released by these materials, and based on this information, it is possible to perform text mining to identify possible adverse effects linked to their use. Accordingly, this process was carried out to visualize possible health problems associated with different molecules released from tested polystyrene containers, such as styrene, cumene, tretadecane, pentadecane, acetophenone and ethylbenzene (Figure 4) (Leibman, 1975; USEPA, 1988; 2000a; 2000b; Arnedo-Pena et al., 2003; Sliwinska-Kowalska et al., 2003; Seeber et al., 2004; Muhammad et al., 2005; WHO, 2005; ASTDR, 2007; Dusseldorp et al., 2007; OSHA, 2010). These chemicals do possess a broad spectrum of toxicities. In fact, several studies have reported that some are estrogenic (Yang et al., 2011), carcinogenic (Lithner et al., 2011), and also originate human ototoxicity and effects on color discrimination (Gelbke et al., 2014), among other problems.

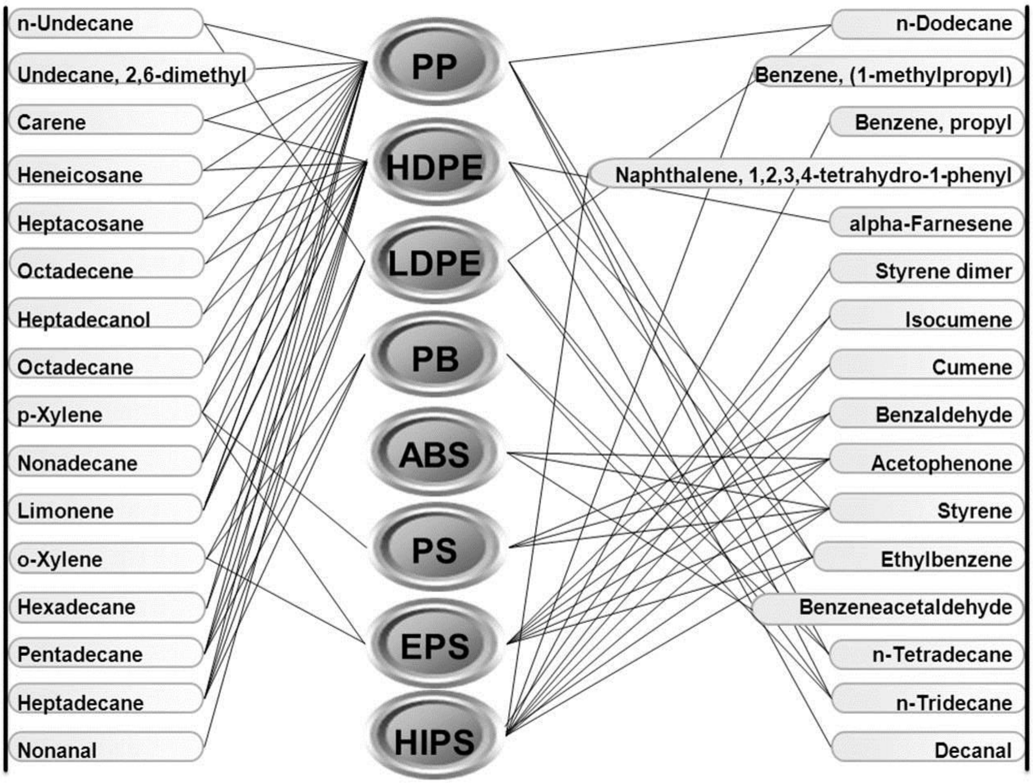

Figure 3. Compounds identified in different plastic-based products (3,4,8,19,14,15,20). PP: Polypropylene, HDPE: High density polyethylene, LDPE: Low density polyethylene, PB: Polybutylene, ABS: Acrylonitrile-Butadiene-Styrene, PS: Polystyrene, EPS: Expanded polystyrene, HIPS: High-impact polystyrene.

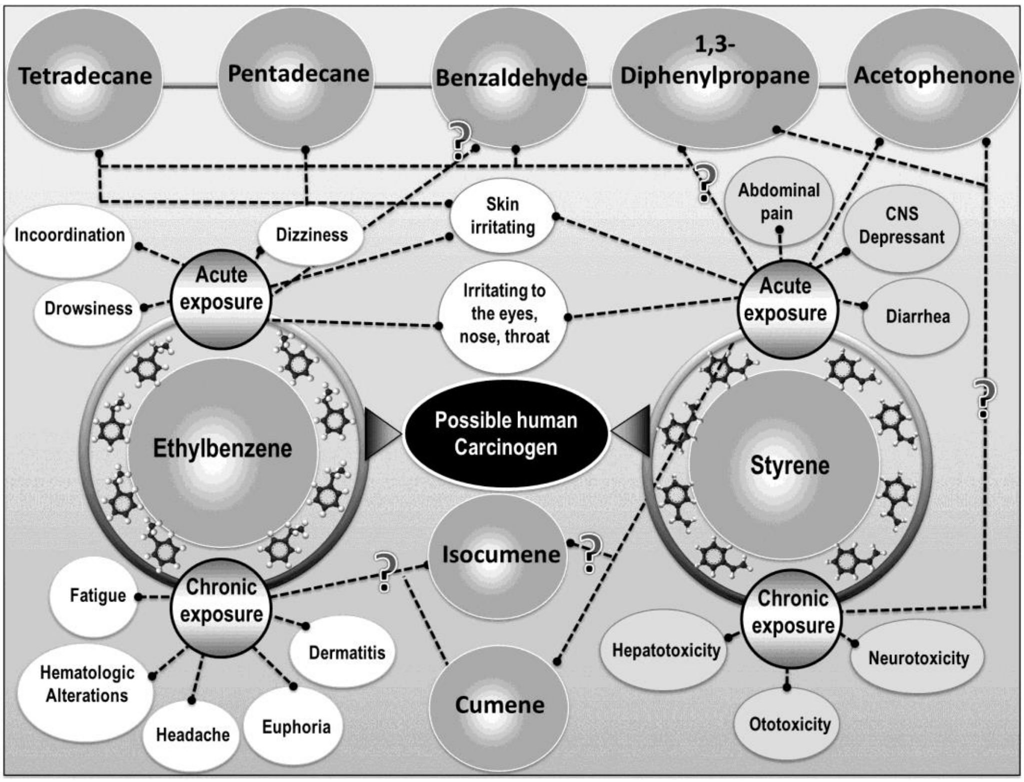

Figure 4. Results from text mining on several chemicals released from EPS-based containers. ?= No information available.

4. CONCLUSION

In conclusion, EPS-based products available in Colombia release several chemicals when heated; some of the most frequently observed are benzaldehyde, pentadecane, tetradecane, ethylbenzene, cumene, isocumene, acetophenone, 1,3-diphenylpropane, and styrene. The emission of these molecules was temperature-dependent; therefore, the use of these materials to store food and hot drinks should be carefully controlled. This preliminary report is sufficient to encourage the development of public policies aimed at protecting people from exposure to these chemicals. Therefore, mandatory legislation should establish appropriate quality characteristics for these EPS-based products.

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