Forensic Science International 266 (2016) 462–468

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Volatile organic compounds in polyethylene bags—A forensic perspective

Rafał Borusiewicz*, Rafał Kowalski

Institute of Forensic Research, Westerplatte 9, 31-033 Krakow, Poland

ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form 6 July 2016
Accepted 9 July 2016
Available online 18 July 2016

Keywords:
Forensic science
Microtraces
Fire debris
Containers
Polyethylene
Background interferences

ABSTRACT

Polyethylene bags, though not recommended, are sometimes used in some countries as improvised packaging for items sent to be analysed for the presence of volatile organic compounds, namely ignitable liquids residues. Sometimes items made of polyethylene constitute the samples themselves. It is well known what kind of volatile organic compounds are produced as a result of polyethylene thermal decomposition, but there is a lack of information relating to if some volatile compounds are present in unheated/unburned items made of polyethylene in detectable amounts and, if so, what those compounds are. The aim of this presented research was to answer these questions. 28 different bags made of polyethylene, representing 9 brands, were purchased in local shops and analysed according to the procedure routinely used for fire debris. The results proved that in almost all bags a distinctive mixture of compounds is present, comprising of *n*-alkanes and *n*-alkenes with an even number of carbon atoms in their molecules. Some other compounds (e.g., limonene, 2,2,4,6,6-pentamethylheptane) are also often present, but the presence of even *n*-alkanes and *n*-alkenes constitutes the most characteristic feature.

1. Introduction

Fires cause not only great material losses but also suffering, mutilation and deaths of people. It is stated that about 50% of fires start by the acts of arson [1]. The aim of fire investigation is to establish the cause of fire. If arson is suspected, every information enabling the verification of this hypothesis and to connect a suspect with the crime is of value. Results from the chemical analysis of fire debris may provide valuable information helping to conclude the investigation. Ignitable liquids are most often used by arsonists to start and accelerate fire. In the absence of legitimate reason for the presence of ignitable liquid in the point of origin of the fire, finding ignitable liquid residues (ILR) in the samples taken from that point supports the hypothesis that the fire was started deliberately. Information about the kind of ignitable liquid (group identification) may help to explain the development of fire and to establish the possible sources of a specific liquid. Finding traces of the same kind of liquid in samples of fire debris and in the samples taken from the suspect (e.g., clothes, containers) supports the hypothesis that suspect person in fact committed the crime.

Chemical analysis of fire debris consists of four stages: choosing and properly packing the samples; isolating volatile organic compounds (VOC's) from the matrix; separating and identifying isolated compounds; interpretation i.e., stating if in the analysed sample ILR are present and what kind of liquid it is (group identification).

Interpretation is considered to be the most difficult step, as it requires experience and extensive knowledge, including information about possible interfering compounds i.e., VOC's which may be present in the sample but are not ignitable liquid. The source of these components is most often the material of the sample (matrix) as VOC's are normally present in various materials [2–12]. They can also be created during the fire as the result of pyrolysis and incomplete combustion [6,9,10,12–15].

It is important to know that materials used for packaging of the samples may also be a source of interfering compounds. Some research was already published which aimed to evaluate containers recommended in different countries for packaging of fire debris. Metal cans, glass jars with metal lids and rubber sealing, nylon bags and special "fire debris bags" were examined to check if they are clean, tight and impermeable for components of ignitable liquids [16–19]. Polyethylene bags were not included in these studies, as it is well known that they are able to adsorb VOC's and are permeable for these compounds and because of that they are not recommended as packaging for fire debris samples.

* Corresponding author. Fax: +48 124223850.
E-mail address: rborusiewicz@ies.krakow.pl (R. Borusiewicz).

http://dx.doi.org/10.1016/j.forsciint.2016.07.010

Nevertheless, polyethylene bags are quite often used in some countries by police technicians as improvised packaging, if items which must be packed (e.g., clothes of the suspect) are too big to fit recommended containers, e.g., glass jars or Ampac bags. In some countries experts conducting laboratory analyses have the authority to reject the samples if they are not packed properly. In other countries items are analysed even if they are not packed in the recommended container.

Garbage bags made of polyethylene are most often used as improvised packaging, because they are easily available and offered in different sizes. Sometimes polyethylene zip bags are also used. Comparative samples of packaging are rarely provided, therefore most often it is impossible to check what volatile compounds emanate from specific types of bags which were used to pack the evidences.

Sometimes items made of polyethylene (bottles, containers, bags) are also delivered to the laboratory as evidence to be analyzed for the presence of ILR.

It is therefore clear that information about volatile compounds which may emanate from polyethylene should be taken into consideration while interpreting results of the analysis.

It is well known that polyethylene decomposes while heated, and volatile products of thermal decomposition are created. In polyethylene all C—C bonds are of the same strength, therefore they are broken according to "random scission mechanism". Characteristic chromatograms obtained for pyrolysis products (triplets of homologous *n*-alkadienes, *n*-alkenes and *n*-alkanes) are depicted [9,10,12,13,20], but in the literature there is a lack of information about volatile compounds which may emanate from unburned items made of polyethylene. To the best of our knowledge, the problem of VOC's present in packages made of polyethylene was only addressed briefly in three sources [10,21,22]. In the first, one unburned piece of plastic bottle made of high-density polyethylene (HDPE) was analysed using passive adsorption from the headspace (carbon strip method, 80 °C, 4 h) with subsequent solvent extraction and GC–MS analyses. In the extract dodecene, tetradecene and hexadecene were identified [10]. In the second study, concerning degradation of polyethylene during extrusion process, VOC's were directly desorbed from polyethylene film in 100 °C using a thermal desorber with cold trap, and analysed with GC–MS. It was found that in foils made of HDPE and linear low-density polyethylene (LLDPE), aside from volatile products of PE degradation and oxidation, other chemicals such as: decane, dodecane, tetradecane, hexadecane and octadecane were present [21].

The aim of presented research was to check what volatile organic compounds emanate from polyethylene bags, analysed according to the procedure routinely used in the analysis of fire debris.

2. Materials and methods

2.1. Bags samples

Garbage bags consisting of 26 rolls of different bags, representing 8 different brands, were purchased from local shops. Additionally two zip bags of different sizes, made of transparent polyethylene foil were analyzed. From each of the rolls the first bag, constituting the external layer, was discarded, to avoid the influence of incidental pollution, and the second one was analysed.

Bags were first analysed using infra-red spectroscopy (IR) to check their composition. After that they were analysed for the presence of VOC's.

2.2. IR analyses

The IR analyses were performed using spectrometer Nicolet IS 50 FT-IR (Thermo Scientific, Waltham, MA, USA) equipped with DTGS detector. Details of spectrometer setup are as follows: sample introduction mode: ATR diamond single bounce; number of scans co-added: 32; spectral resolution: 4 cm^{-1}; scan range: 400–4000 cm^{-1}; software used in data processing: OMNIC 9. Information about analyzed bags and results of IR analyses are given in Table 1.

Table 1
Properties of analysed bags and their composition on the basis of IR analysis.

Sample No.	Brand and item No.	Capacity and quantity in the roll	Appearance	Additional information	Composition
1	1_1	60 dm^3, 18 pcs	Blue		PE + calcium carbonate
2	2_1	60 dm^3, 16 pcs	Black		PE, calcium carbonate
3	2_2	60 dm^3, 15 pcs	White and red stripes		talcum powder
4	2_3	20 dm^3, 40 pcs	Transparent	Strawberry scented	PE
5	2_4	60 dm^3, 10 pcs	Navy blue	Strong, 2 layers	both layers: PE, calcium carbonate
6	3_1	60 dm^3, 26 pcs	Black		PE, calcium carbonate
7	3_2	60 dm^3, 20 pcs	Green		PE, calcium carbonate
8	3_3	20 dm^3, 40 pcs	Black		PE, calcium carbonate
9	3_4	60 dm^3, 20 pcs	Violet		PE, calcium carbonate
10	3_5	35 dm^3, 30 pcs	Orange		PE, calcium carbonate
11	3_6	35 dm^3, 20 pcs	Brown	For bio waste segregation	PE, calcium carbonate
12	3_7	35 dm^3, 20 pcs	Yellow	For plastic segregation	PE, calcium carbonate
13	3_8	60 dm^3, 10 pcs	Black	Strong	PE, calcium carbonate
14	4_1	60 dm^3, 10 pcs	Black		PE, calcium carbonate
15	5_1	60 dm^3, 20 pcs	Transparent		PE
16	6_1	60 dm^3, 10 pcs	Black		PE, calcium carbonate
17	6_2	20 dm^3, 40 pcs	White		PE, calcium carbonate
18	6_3	60 dm^3, 15 pcs	Blue		PE
19	6_4	35 dm^3, 20 pcs	Black		PE, calcium carbonate
20	7_1	60 dm^3, 10 pcs	Red	For metal segregation	PE
21	7_2	60 dm^3, 10 pcs	Green	For glass segregation	PE, polyamide
22	7_3	60 dm^3, 10 pcs	Blue	For paper segregation	PE, polyamide
23	7_4	60 dm^3, 18 pcs	Brown	For bio waste segregation	PE
24	8_1	20 dm^3, 40 pcs	Transparent		PE
25	8_2	30 dm^3, 25 pcs	White		PE + calcium carbonate + titanium dioxide
26	8_3	60 dm^3, 20 pcs	Green		PE + calcium carbonate
27	9_1	23 cm x 16 cm	Transparent	Zip bag	PE
28	9_2	41 cm x 30 cm	Transparent	Zip bag	PE