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Rapid and Efficient GC-MS Method for the Multiresidue Analysis of Contaminants from Recycled Polyethylene and Polypropylene

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Abstract

In the context of plastic recycling, legislation is evolving and varies across regions, but it remains largely nonspecific. In the European context, producers of post-industrial and post-consumer recycled plastics must guarantee the same wholesomeness as virgin materials. However, they cannot maintain such strict control over incoming materials, because, since the secondary raw materials derived from separate waste collection, they are subjected to high variability in composition and heterogeneity over time. In this frame, a rapid, and easy-to-apply GC-MS method was developed. It employs a liquid–liquid extraction with acetone, followed by quantitative analysis with gas chromatography coupled to mass spectrometry (GC-MS). A combination of total ion chromatograms (TICs) and extracted ion chromatograms (EICs) was used. Adequate sensitivity was demonstrated in the selected concentration ranges for most of the analytes, with limits of quantification (LOQs) lower than the legislative limit, when existing. The results showed that the method is sufficiently accurate with recoveries ever higher than 68.3% and relative standard deviations (RSDr) smaller than 4.2%. This method allows, for the first time, the simultaneous quantification of 40 molecules at levels of a few ng/g. It ensures the possibility of obtaining real-time data for the production control system about the safety of the input materials, allowing immediate corrective action in the event of anomalies. This method is focused on PE and PP recycled plastics and is to be considered a screening method that allows for highlighting batches of incoming materials that are too contaminated to control the output material. This method was successfully tested analyzing some batches of plastics both in input and post-recycling.

Keywords: plastics recycling; GC-MS method; SVHc list

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1. Introduction

Since the moment of our birth, we have been in contact with plastic materials, and it is currently impossible to think of a world without them. They are present in many of the objects that are used daily. Their discovery was certainly fundamental for the development of society, but unfortunately plastics also have disadvantages: The first issue is related to

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the use of fossil fuels, whose reserves are steadily declining, while the second pertains to the management of these materials at the end of their life, given that, if not managed correctly, they can persist in the environment for hundreds of years.

Managing the end-of-life of these materials has become mandatory, but the process is highly complex. There are plenty of types of plastic polymers, each with distinct functions and chemical compositions, which are often combined within a single material.

These polymers are frequently difficult or impossible to separate, and because each type requires specific recycling techniques, effective recycling can be extremely challenging. In cases where separation and recycling are feasible, the resulting material may require stringent safety standards if used for applications with higher added value [1].

In this context, legislation is evolving and varies across regions. In the European context, there are lists of compounds that are prohibited above a certain limit [1,2], i.e., the Restriction of Hazardous Substances (RoHS) [3] and lists and limits for specific substances when the material is to be used for food contact [4]. In addition, there is a list drawn up by the ECHA, the European Chemical Agency, that contains a series of substances that could have serious effects on human health and the environment, called Substances of Very High Concern (SVHC), that indicates substances that raise concerns for the effects they could have on human health or the environment [5–7]. Such substances are included in a candidate list of chemicals that require further study to assess their safety across different applications. This assessment is based on the collection of new scientific data or existing published studies, with the aim of increasing knowledge about these substances and, where necessary, implementing regulatory or restrictive measures.

This list was created with the aim of ensuring the control of the risks of problematic substances throughout their entire life cycle and to promote their replacement with less dangerous alternatives, where possible. This list already contains a very high number of analytes and is updated every six months based on new scientific discoveries. Currently, the latest update of the SVHC list dates to 25 June 2025, includes 241 analytes, and can be consulted on the official ECHA website [5].

Once the substance is included in the candidate list, companies, within the European Union and the European Economic Area, that manufacture, import, or use it are subject to certain legal obligations, leading to the reduced use of substances or their replacement and the obligation to provide recipients of the substance with the safety data sheet. There are currently no legal limits for the substances on the SVHC list, but many buyers of recycled materials require assurances that many of the compounds on this list are below the same RoHS limits when selecting suppliers. Consequently, producers of post-industrial and post-consumer recycled plastics must guarantee the same wholesomeness as virgin materials, but they cannot maintain strict control over incoming materials since, being secondary raw materials derived from separate waste collection, they are subject to high variability in composition and heterogeneity over time.

The onus of monitoring is, therefore, on those who produce recycled materials, especially if there is not a legal requirement.

Therefore, the aim of this work was to develop a rapid and easy-to-apply method that could provide the information needed in a small-to-medium industrial context. The method must be useful for monitoring both incoming and outgoing materials in a mechanical recycling plant. Consequently, it must be time-efficient and compatible with the processing cycles, which are on the order of a couple of hours.

To date, the literature does not report any studies focused on a similar objective; the list of SVHC is cited explicitly only once in works devoted to the analytical method development [8]. Most of them concern single categories of molecules (i.e., PAHs, Refs. [8–12] phthalates [10,13], and polychlorinated bisphenols [12] and more generally compounds classified as VOCs [10,14–16].

Another interesting work presents the results of the determination of many additives present in 59 commercial samples, but they were identified using complementary techniques, including spectroscopic, thermogravimetric, and chromatographic methods [17]. Unfortunately, such an approach is not compatible with the type of laboratory we are addressing. Many other works focus on volatile organic compounds (VOCs) and non-intentionally added substances (NIAS), without specifically referring to the SVHC list and with screening methods that only perform semi-quantitative determinations [15,18,19].

Starting from the request of our industrial partner, a selection of the potential analytes from the RoHS e SVHC lists were performed. The first step of the selection consisted of removing, from the initial number of listed substances, the ones that were not available, as well characterized analytical standards. Gas chromatography was the chosen instrument approach, due to its versatility and availability in most control laboratories in small- and medium-sized mechanical recycling factories. In the second step, the substances considered as "inorganic" (oxides, hydroxides, silicates, etc.) were discarded together with the non-volatile substances, and the substances considered as "inorganic" (oxides, hydroxides, silicates, etc.) were removed. The resulting analytes were 40.

2. Materials and Methods

2.1. Reagents and Solvents

All the analytical standards were obtained from Merck (Sigma-Aldrich Chemie GmbH, Riedstraße 2, 89,555 Steinheim, Germany). All the relevant information regarding the target substances is presented in Table 1, including CAS numbers, purity (as stated by the supplier), chemical, and related hazard class. Purity (as stated by the supplier) was always >99% .

Table 1. Information about the substances under study. (Acronyms: PBT/vPvB: Persistent, bioaccumulative, and toxic substances/very persistent, very bioaccumulative substances; SVHC: Substance of very high concern; VOC: volatile organic compound; PAH: Polycyclic Aromatic Hydrocarbons; PVC:Polyvinyl Chloride.

CAS n°	Analyte	Chemical Class	Restriction List **	Toxicological Effects	Plastics Industry Use
138-86-3	Limonene	Terpene (VOC *)	No	Irritant/allergenic	Solvent, fragrance
78-70-6	Linalool	Terpenoid (VOC *)	No	Allergenic	Fragrance
149-57-5	2-Ethylhexanoic acid	Carboxylic acid	No	Irritant	Plasticizers intermediate
91-20-3	Naphthalene	PAH (VOC *)	No	Suspected carcinogen (Carc.2)	Petrochemical residue
149-30-4	2-Mercaptobenzothiazole	Benzothiazole	No	PBT, Skin sensitizer, Toxic to the aquatic environment	Rubber vulcanization
105-60-2	Caprolactam	Cyclicamide (VOC *)	No	Irritant	Nylon 6 monomer
1014-60-4	1,3-di-tert-butylbenzene	Alkylbenzene	No	Irritant	Antioxidant intermediate
128-39-2	2,6-di-tert-butylphenol	Phenol	No	Irritant	Antioxidant
208-96-8	Acenaphthylene	PAH	No	Toxic to the aquatic environment	Petrochemical residue
131-11-3	Dimethyl phthalate	Phthalate	RoHS	Irritant	Plasticizers
83-32-9	Acenaphthene	PAH	No	Toxic to the environment	Petrochemical residue
96-76-4	2,4-Di-tert-butylphenol	Phenol	No	Irritant	Antioxidant
128-37-0	Butylated hydroxy toluene	Phenol	No	Irritant, Toxic to the aquatic environment	Antioxidant
86-73-7	Fluorene	PAH	No	Environmental toxicity	Petrochemical residue
84-66-2	Diethyl phthalate	Phthalate (VOC *)	SVHC, RoHS	Irritant	Plasticizers

Table 1. *Cont.*

CAS n°	Analyte	Chemical Class	Restriction List **	Toxicological Effects	Plastics Industry Use
103-49-1	Dibenzylamine	Aromatic amine	No	Toxic	Synthesis intermediate (additives, stabilizers)
88-26-6	3,5-di-tert-butyl-4-hydroxybenzyl alcohol	Phenol	No	Irritant	Antioxidant
120-12-7	Anthracene	PAH	SVHC	PBT, toxic to the environment	Petrochemical residue
85-01-8	Phenanthrene	PAH	SVHC	vPvB	Petrochemical residue
301-02-0	Oleamide	Fatty amide	No	Low toxicity	Slip agent
84-74-2	Dibutyl phthalate (DBP)	Phthalate	SVHC RoHS	Endocrine disruptor, reproductive toxicity	Plasticizer (e.g., PVC)
206-44-0	Fluoranthene	PAH	SVHC	PBT, vPvB	Petrochemical residue
2440-22-4	Drometrizole	Benzotriazole	No	Irritant	UV stabilizer
129-00-0	Pyrene	PAH	SVHC	PBT, vPvB	Petrochemical residue
57-11-4	Octadecanoic acid	Fatty acid	No	Low toxicity	Lubricant/release agent
80-05-7	Phenol, 4,4′-(1-methylethylidene)bis-(Bisphenol A)	Bisphenol	SVHC RoHS	Endocrine disruptor, reproductive toxicity	Production of polycarbonate plastics and epoxy resins
80-09-1	Dioxydiphenylsulfone (Bisphenol S)	Bisphenol	SVHC RoHS	Endocrine disruptor, reproductive toxicity	Production of polycarbonate plastics and epoxy resins
85-68-7	Benzyl butyl phthalate (BBP)	Phthalate	SVHC RoHS	Endocrine disruptor, reproductive toxicity	Plasticizer (e.g., PVC)
57-10-3	n-Hexadecanoic acid	Fatty acid	No	Low toxicity	Lubricant
103-23-1	Hexanedioic acid, bis(2-ethylhexyl) ester	Adipate esters	No	Low toxicity	Plasticizer
56-55-3	Benz[a]anthracene	PAH	SVHC	Carcinogenic, PBT, vPvB	Petrochemical residue
218-01-9	Chrysene	PAH	SVHC	Carcinogenic, PBT, vPvB	Petrochemical residue
117-81-7	Bis(2-ethylhexyl) phthalate (DEHP)	Phthalate (VOC *)	SVHC	Endocrine disruptor, reproductive toxicity	Plasticizer (e.g., PVC)
117-84-0	Di-n-octyl phthalate (DNOP)	Phthalate	RoHS	Suspected of damaging fertility or the unborn child	Plasticizer (e.g., PVC)
205-99-2	Benzo[b]fluoranthene	PAH	No	Carcinogenic	Petrochemical residue
207-08-9	Benzo[k]fluoranthene	PAH	SVHC	Carcinogenic, PBT, vPvB	Petrochemical residue
50-32-8	Benzo[a]pyrene	PAH	SVHC	Carcinogenic, PBT, vPvB	Petrochemical residue
193-39-5	Indeno [1,2,3-cd]pyrene	PAH	No	Carcinogenic	Petrochemical residue
53-70-3	Dibenz[a,h]anthracene	PAH	No	Carcinogenic	Petrochemical residue
191-24-2	Benzo[ghi]perylene	PAH	SVHC	PBT, vPvB	Petrochemical residue

Acronyms: PBT/vPvB: Persistent, bioaccumulative, and toxic substances/very persistent, very bioaccumulative substances; SVHC: Substance of very high concern; VOC: volatile organic compound; PAH: Polycyclic Aromatic Hydrocarbons; PVC:Polyvinyl Chloride. * Classification from: A review on VOCs from recycled plastics. https://doi.org/10.1016/j.susmat.2020.e00179; ** European Chemicals Agency. Candidate List of substances of very high concern for Authorisation. ECHA. Available online: https://echa.europa.eu/it/candidate-list-table (accessed on 20 January 2026).

Stock solutions were prepared by dissolving the standard, as received in acetone, to obtain solution at 500 mg/L each. The working solutions were obtained by subsequent dilutions in acetone. Acetone, hexane, and dichloromethane were chromatographic grade and purchased by Merck (Steinheim, Germany).

2.2. Gas Chromatography-Mass Spectrometry (GC-MS) Apparatus

GC-MS analyses were carried out on a Shimadzu chromatographic apparatus comprising a HT-2800 autosampler (HTA, 25,131 (BS) Brescia, Italy) and a Shimadzu Nexis GC-2030 gas chromatograph equipped with a 30-m-long RTX-5MS capillary column, 0.25 mm in diameter and 0.25 µm thick, coupled to a QP2020 NX mass spectrometer. The carrier gas was ultra-pure hydrogen obtained using a HG pro 700 LN generator supplied by LNI Swiss Gas, employing MilliQ ultrapure water. The optimized chromatographic conditions were set as follows: ionization mode, EI at 70 eV; injector temperature, 250 °C; oven temperature gradient, 45.0 °C for 2 min and 10.0 °C/min up to 300.0 °C holding for 2.5 min, for a total of 30.0 min per run; injection volume, 3 µL. All analyses were performed in triplicate.

2.3. GC-MS Method Development and Calibration

Six concentration levels for each analyte, in the ranges reported in Table 2 were considered for the calibration step and five repetitions were carried out for each level. Models obtained with calibration have been evaluated with one-way ANOVA (analysis of variance), to assess regression models [20–22]. Lack of fit has been evaluated with an F-test, comparing the F_{tab} with the ratio F_{calc} = MSLOF/MSPE, considering the F distribution with *k-2* (*k* = number of concentration levels) and *n-k* (*n* = replicates) degrees of freedom. Two tailed Student's *t*-test at a 95% confidence level, has been performed to evaluate the significance of the intercepts, considering n-2 degrees of freedom. The limits of detection (LOD) and quantification (LOQ) were calculated with the standard deviation of the blank (r) and the slope of the regression lines (S), using the following equations: LOD = 3 r/S and LOQ = 10 r/S, respectively [23].

Table 2. Calibration ranges for the analytes under study.

Analyte	Calibration Range (mg/L)
Limonene	1.20–0.50
Linalool	1.20–0.50
Hexanoic acid, 2-ethyl-	1.04–0.50
Naphtalene	1.20–0.56
2-Mercaptobenzothiazole	1.04–0.52
Caprolactam	1.04–0.52
Benzene,1,3-bis(1,1-dimethylethyl)-	1.04–0.52
Phenol,2,6-bis(1,1-dimethylethyl)-	1.04–0.52
Acenaphthylene	1.20–0.56
Dimethyl phthalate	1.20–0.5
Acenaphthene	1.20–0.56
2,4-Di-tert-butylphenol	1.04–0.52
Butylated Hydroxytoluene	1.04–0.52
Fluorene	1.20–0.56
Diethyl Phthalate	1.20–0.50
Dibenzylamine	1.04–0.52
3,5-di-tert-Butyl-4-hydroxybenzyl alcohol	1.04–0.52
Anthracene	1.20–0.56
Phenanthrene	1.20–0.56
9-Octadecenamide, (Z)-	1.04–0.52
Dibutyl phthalate	1.20–0.50
Fluoranthene	1.20–0.56
Drometrizole	1.04–0.52
Pyrene	1.20–0.56
Octadecanoic acid	1.04–0.52

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Table 2. *Cont.*

Analyte	Calibration Range (mg/L)
Phenol,4,4′-(1-methylethylidene)bis- (Bisphenol A)	1.04–0.52
Dioxydiphenylsulfone (Bisphenol S)	1.04–0.52
Benzyl butyl phthalate	1.20–0.50
n-Hexadecanoic acid	1.04–0.52
Hexanedioic acid, bis(2-ethylhexyl) ester	1.20–0.50
Benz[a]anthracene	1.20–0.56
Chrysene	1.20–0.56
Bis(2-ethylhexyl) phthalate	1.04–0.50
Di-n-octyl phthalate	1.20–0.50
Benzo[b]fluoranthene	1.20–0.50
Benzo[k]fluoranthene	1.20–0.50
Benzo[a]pyrene	1.20–0.50
Indeno [1,2,3-cd]pyrene	1.20–0.50
Dibenz[a,h]anthracene	1.20–0.50
Benzo[ghi]perylene	1.20–0.50

Precision evaluation was performed in terms of repeatability (RSDr) that was calculated for each analyte at 5 mg/L. Six replicates were performed. RSDr values were calculated as % standard deviation, as reported in the AOAC guidelines [24].

2.4. Real Samples Extraction Procedure and Analysis

Real samples were PE or PP pellets obtained from a real process of plastic waste recycling carried out at Mottin S.r.l. in Cassano Magnago (VA), Italy. The factory treated post-consumer wastes with a mechanical treatment of extrusion followed by a deodorization process. The samples in this study are both the input materials and the resulting materials after the deodorization process.

Solid–liquid extraction was performed, and 10.0 g of pellet sample was put in contact with 30.00 mL of acetone for 30 min in a sonication bath. The obtained extract was then filtered and 3.00 µL was injected in the GC-MS apparatus. In the preliminary experiments, hexane and dichloromethane were also used.

Recovery was calculated using a spike procedure on virgin polyethylene pellets with a solution containing all the analytes while performing the entire extraction and analysis procedure. As virgin polyethylene may already contain some of the analytes, it was treated and analyzed both before and after the standard addition. Recovery % values were calculated following the AOAC guidelines [24], as expressed in Equation (1):

$$\text{Recovery } \% = \text{Cadd} - \text{Cb}/\text{Ccalc} * 100 \tag{1}$$

where Cb is the analyte concentration obtained without the standard addition, Cadd is the analyte concentration obtained with the standard addition, while Ccalc is the expected concentration.

3. Results

3.1. GC-MS Method Optimization

To obtain a gas chromatographic method suitable for the separation of all analytes, we started from the method developed by Radulović et al. [25] and used this method in our laboratories for the determination of numerous organic compounds within real matrices. It is characterized by a long, slightly steep temperature ramp that makes it very useful in the preliminary phase because of its adaptability to very different cases. Preliminary injections of solutions containing few analytes at a time led to obtaining the information about identification and the mass spectra of all the analytes. A temperature gradient slightly different from Radulović et al.'s work [25] allowed for obtaining the separation in 32.5 min of analysis time (it starts at 45 °C and held for two minutes, followed by an increase of 10 °C/min until reaching 300 °C and held for five minutes). Employing the optimized gradient method and the acquisition of full scan mode (from 40 to 500 m/z), the chromatogram of Figure 1 can be obtained. The separation is almost satisfactory, but, as evidenced in the same figure, some coelutions were still registered.

Even after several attempts to optimize the separation, no better results were obtained. To achieve the necessary resolution, the selected ion monitoring (SIM) acquisition mode was implemented using the characteristic fragments of each analyte obtained by observing the mass spectra. The NIST mass spectral libraries were helpful in this case, but, with H_2 as the carrier gas, the attribution was not achieved automatically but only after associating the spectrum with the possible fragmentation of the molecules under study. In this way, it was possible to identify, for each analyte, a fragment to be used for identification (qualify ion) and at least two fragments useful in the quantification phase (quantify ions). The values obtained are reported in Table S1. Therefore, the final acquisition method involves carrying out the detection in mass spectrometry by acquiring both in full scan mode (40–500 m/z) and in selected ion monitoring (SIM) mode by acquiring the signal of both the qualify ions and the quantify ions.

Since the simultaneous acquisition of all SIM signals during the entire analysis did not allow for sufficient sensitivity, the chromatographic run was divided into six consecutive events, in each of which the ionic currents of both the full scan and the SIM signals of only the analytes eluting in the specific window were acquired, as outlined in Table 3.

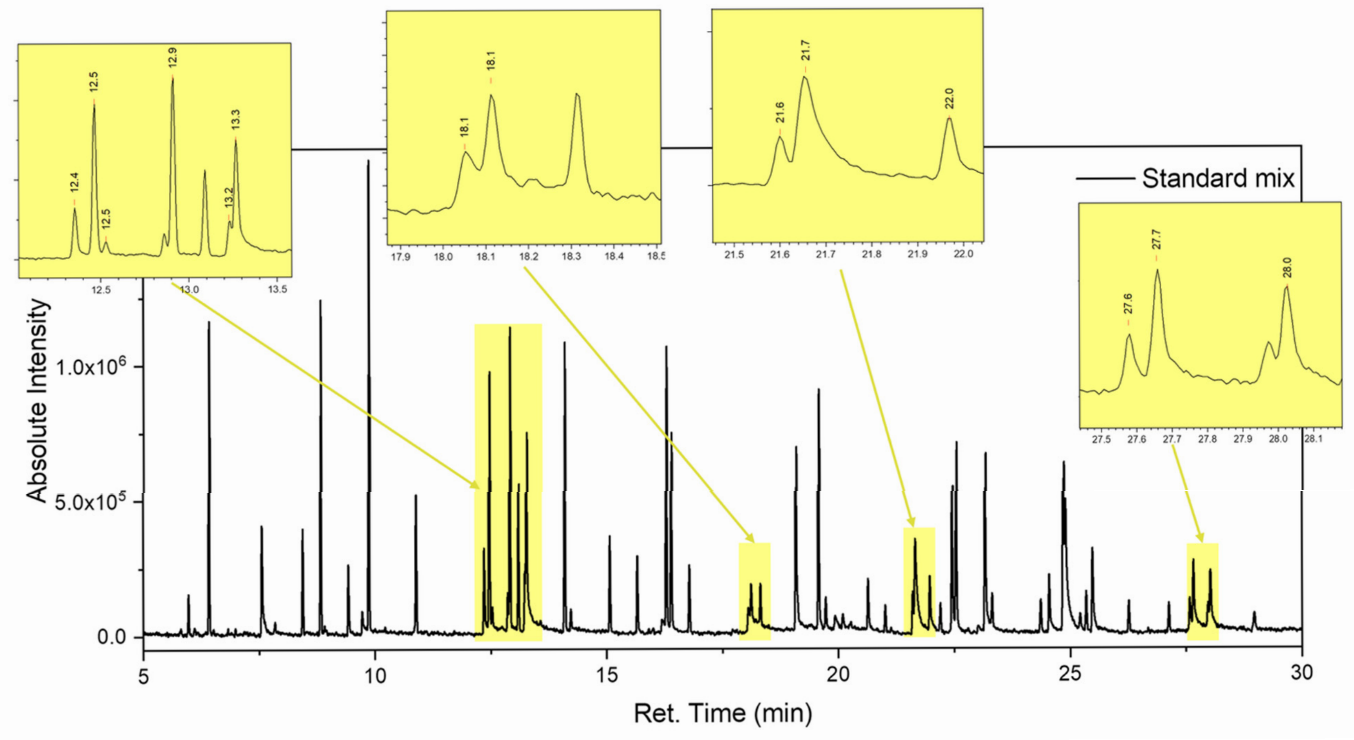

Figure 1. Chromatogram of the standard mixture at concentration of 1 mg/L with zooms on the overlapped peaks.

Table 3. Scan mode parameters and SIM values.

Start Time (min)	End Time (min)	Acq. Mode	Event Time (s)	Start m/z	End m/z	Ch1 m/z	Ch2 m/z	Ch3 m/z	Ch4 m/z	Ch5 m/z	Ch6 m/z	Ch7 m/z	Ch8 m/z	Ch9 m/z	Ch10 m/z	Ch11 m/z	Ch12 m/z	Ch13 m/z
4.0	10.0	Scan	0.10	40	500													
4.0	10.0	SIM	0.20			68	41	73	105	128	135	55	175					
10.0	15.0	Scan	0.10	40	500													
10.0	15.0	SIM	0.30			191	152	163	153	191	205	166	149	168				
15.0	20.0	Scan	0.10	40	500													
15.0	20.0	SIM	0.30			91	205	176	179	135	149	200	225	100	43			
20.0	25.0	Scan	0.10	40	500													
20.0	25.0	SIM	0.30			213	112	273	149	55	57	114	113	70	42	250	252	83
25.0	30.0	Scan	0.10	40	500													
25.0	30.0	SIM	0.30			252	276	278	277									
30.0	32.5	Scan	0.10	40	500													

Acquisition in SIM mode also allows for increased selectivity by allowing for the separate ionic currents to be obtained and, therefore, for the reconstruction of different chromatograms (Figure 2) for the coeluting analytes, guaranteeing the possibility of accurate identification and quantification of all analytes.

The optimized method was then validated and calibrated. All the data obtained are reported in Table 3. The calibration curves were calculated by analyzing standard solutions of the analytes at six concentrations ranging from 0.10 to 1.20 mg/L. Three replicates were performed for each concentration. The calibration curves were all found to be linear, with linearity intervals between 1.2 mg/L and the LOQ value for all analytes. Only a few, as can be seen in Table 3, had a slightly lower upper value.

The LOD and LOQ values obtained are reported in Table 4. The highest obtained LOQ values are about 0.5 mg/L that reported in the unit of measurement required by law correspond to 0.015% *w*/*w*. Consequently, and in the worst case, the proposed method's analytical sensitivity results are largely satisfactory.

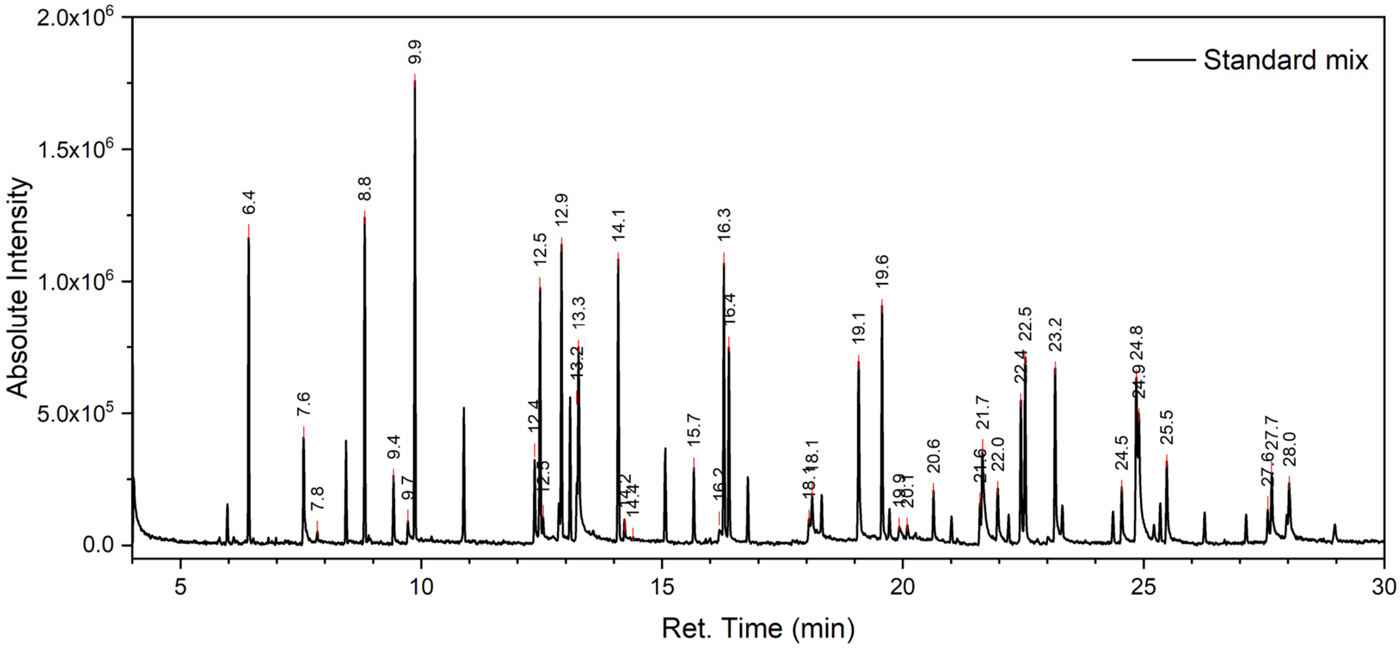

Figure 2. Reconstructed SIM chromatograms of the mixture containing all the analytes at the concentration of 5 mg/L each. The red lines highlight the point at which the retention time is taken.

Table 4. Calibration and validation parameters.

Analyte	Quantify Ion	Calibration Range (mg/L)	LOD (mg/L)	LOQ (mg/L)	Precision RSDr %
Limonene	67.00; 93.00	1.20–0.50	0.055	0.183	2.1
Linalool	69.00–67.00	1.20–0.50	0.155	0.345	3.2
Hexanoic acid, 2-ethyl-	88.00–41.00	1.04–0.50	0.30	0.502	2.1
Naphtalene	127.00–129.00	1.20–0.56	0.021	0.071	2.4
2-Mercaptobenzothiazole	108.00–69.00	1.04–0.52	0.155	0.422	3.6
Caprolactam	56.00–85.00	1.04–0.52	0.139	0.383	2.6
Benzene,1,3-bis(1,1-dimethylethyl)-	57.00–41.00	1.04–0.52	0.015	0.050	2.2
Phenol,2,6-bis(1,1-dimethylethyl)-	57.00–206.00	1.04–0.52	0.064	0.212	2.2
Acenaphthylene	153.00–154.00	1.20–0.56	0.017	0.056	2.6
Dimethyl phthalate	77.00–164.00	1.20–0.5	0.074	0.247	4.2
Acenaphthene	154.00–152.00	1.20–0.56	0.010	0.033	3.1
2,4-Di-tert-butylphenol	57.00–206.00	1.04–0.52	0.011	0.036	1.6
Butylated Hydroxytoluene	57.00–220.00	1.04–0.52	0.030	0.102	1.8
Fluorene	165.00–82.00	1.20–0.56	0.025	0.084	1.1
Diethyl Phthalate	177.00–150.00	1.20–0.50	0.155	0.407	2.8
Dibenzylamine	106.00–92.00	1.04–0.52	0.050	0.166	3.1
3,5-di-tert-Butyl-4-hydroxybenzyl alcohol	57.00–161.00	1.04–0.52	0.153	0.410	2.2
Anthracene	179.00–176.00	1.20–0.56	0.014	0.046	2.8
Phenanthrene	179.00–180.00	1.20–0.56	0.007	0.022	1.5
9-Octadecenamide, (Z)-	56.00–55.00	1.04–0.52	0.120	0.222	4.2
Dibutyl phthalate	41.00–56.00	1.20–0.50	0.190	0.434	1.3
Fluoranthene	203.00–178.00	1.20–0.56	0.073	0.242	2.2
Drometrizole	93.00–55.00	1.04–0.52	0.263	0.878	3.4
Pyrene	203.00–101.00	1.20–0.56	0.042	0.139	3.5
Octadecanoic acid	43.00–55.00	1.04–0.52	0.388	0.534	2.3
Phenol,4,4′-(1-methylethylidene)bis-(Bisphenol A)	119.00–228.00	1.04–0.52	0.374	0.454	3.3
Dioxydiphenylsulfone (Bisphenol S)	78.00–112.00	1.04–0.52	0.031	0.103	2.5
Benzyl butyl phthalate	149.00–92.00	1.20–0.50	0.168	0.561	2.2
n-Hexadecanoic acid	55.00–43.00	1.04–0.52	0.042	0.141	1.1
Hexanedioic acid, bis(2-ethylhexyl) ester	41.00–70.00	1.20–0.50	0.160	0.533	1.3
Benz[a]anthracene	229.00–230.00	1.20–0.56	0.083	0.276	1.1
Chrysene	229.00–226.00	1.20–0.56	0.023	0.078	3.2
Bis(2-ethylhexyl) phthalate	41.00–70.00	1.04–0.50	0.165	0.351	2.2
Di-n-octyl phthalate	41.00–56.00	1.20–0.50	0.299	0.502	2.7
Benzo[b]fluoranthene	253.00–55.00	1.20–0.50	0.101	0.338	2.1
Benzo[k]fluoranthene	253.00–126.00	1.20–0.50	0.068	0.227	3.4
Benzo[a]pyrene	253.00–126.00	1.20–0.50	0.320	0.534	1.1
Indeno [1,2,3-cd]pyrene	138.00–277.00	1.20–0.50	0.320	0.534	4.3
Dibenz[a,h]anthracene	279.00–139.00	1.20–0.50	0.009	0.030	2.2
Benzo[ghi]perylene	138.00–277.00	1.20–0.50	0.302	0.534	2.5

3.2. Application to Real Sample Cleaning and Deodorizing Procedure Evaluation

The entire optimized method was tested on real samples. The samples were PE pellets obtained with extrusion from materials derived from post-consumer plastic recycling.

Specifically, a material was analyzed that had undergone a deodorization process, a treatment used to remove the most volatile compounds contained in the material to be recycled. This material, initially solid, underwent solvent extraction using ultrasound to extract leachable substances and obtain a solution analyzable with the instrument.

Acetone was the solvent chosen for the procedure for several reasons. In preliminary tests of the standards dissolution, we also tested hexane and dichloromethane, which are also used in similar studies in the literature. Acetone proved to be the solvent that dissolved all the analytes and produced the best chromatographic results in terms of signal-to-noise ratio and sensitivity. Furthermore, acetone is a fairly common solvent in industrial settings, making it easier to implement and include in laboratory protocols.

Two samples were analyzed: the material entering the deodorization plant (PE_pre) and the material obtained after the deodorization process (PE_post). Three genuine replicates of the analysis were performed for each sample.

Critical for the data accuracy is the evaluation of the recovery of the developed method. The percent recoveries were calculated as detailed in the Materials and Methods section and are reported in Table 5. The values vary between 68 and 101% but are all adequate. From now on, the values obtained from the analyses of the real samples are always corrected for the total recovery.

Table 5. Concentration of the analytes in real samples.

Analyte	CAS n°	Recovery (%)	PE_pre (%*w*/*w*)	PE_post (%*w*/*w*)
Limonene	138-86-3	82	7.1×10^{-3}	1.6×10^{-3}
Linalool	78-70-6	79	-	-
Hexanoic acid, 2-ethyl-	149-57-5	77	-	-
Naphtalene	91-20-3	92	16.8×10^{-3}	1.8×10^{-3}
2-Mercaptobenzothiazole	149-30-4	88	-	-
Caprolactam	105-60-2	85	-	-
Benzene, 1,3-bis(1,1-dimethylethyl)-	1014-60-4	92	19.3×10^{-3}	5.9×10^{-3}
Phenol, 2,6-bis(1,1-dimethylethyl)-	128-39-2	75	13.2×10^{-3}	2.2×10^{-3}
Acenaphthylene	208-96-8	88	16.2×10^{-3}	6.2×10^{-3}
Dimethyl phthalate	131-11-3	87	16.3×10^{-3}	4.4×10^{-3}
Acenaphthene	83-32-9	79	17.3×10^{-3}	0.7×10^{-3}
2,4-Di-tert-butylphenol	96-76-4	93	11.0×10^{-3}	2.2×10^{-3}
Butylated Hydroxytoluene	128-37-0	99	2.3×10^{-3}	-
Fluorene	86-73-7	101	6.7×10^{-3}	1.9×10^{-3}
Diethyl Phthalate	84-66-2	79	-	-
Dibenzylamine	103-49-1	68	9.2×10^{-3}	2.8×10^{-3}
3,5-di-tert-Butyl-4-hydroxybenzyl alcohol	88-26-6	79	-	-
Anthracene	120-12-7	78	16.7×10^{-3}	3.6×10^{-3}
Phenanthrene	85-01-8	83	13.8×10^{-3}	4.8×10^{-3}
9-Octadecenamide, (Z)-	301-02-0	84	-	-
Dibutyl phthalate	84-74-2	91	<LOQ	-
Fluoranthene	206-44-0	88	5.4×10^{-3}	0.5×10^{-3}
Drometrizole	2440-22-4	79	-	-
Pyrene	129-00-0	86	6.3×10^{-3}	0.6×10^{-3}
Octadecanoic acid	57-11-4	88	<LOQ	-
Phenol, 4,4′-(1-methylethylidene)bis- (Bisphenol A)	80-05-7	89	<LOQ	-
Dioxydiphenylsulfone (Bisphenol S)	80-09-1	76	41.1×10^{-3}	1.3×10^{-3}
Benzyl butyl phthalate	85-68-7	77	17.1×10^{-3}	1.7×10^{-3}
n-Hexadecanoic acid	57-10-3	69	56.1×10^{-3}	15.4×10^{-3}
Hexanedioic acid, bis(2-ethylhexyl) ester	103-23-1	67	55.0×10^{-2}	3.7×10^{-3}
Benz[a]anthracene	56-55-3	88	16.1×10^{-3}	0.4×10^{-3}
Chrysene	218-01-9	89	33.0×10^{-3}	0.65×10^{-3}
Bis(2-ethylhexyl) phthalate	117-81-7	75	-	-
Di-n-octyl phthalate	117-84-0	76	-	-
Benzo[b]fluoranthene	205-99-2	88	15.3×10^{-3}	6.5×10^{-3}
Benzo[k]fluoranthene	207-08-9	89	16.0×10^{-3}	11.3×10^{-3}
Benzo[a]pyrene	50-32-8	96	<LOQ	-
Indeno [1,2,3-cd]pyrene	193-39-5	94	<LOQ	-
Dibenz[a,h]anthracene	53-70-3	95	15.4×10^{-3}	12.4×10^{-3}
Benzo[ghi]perylene	191-24-2	94	-	-

The analysis of PE_pre and PE_post samples highlighted the presence of many of the compounds under study (Table 4). By the calibration curves and the recovery values, the concentrations were calculated. In Table 5, it is reported as a weight/weight percentage (%w/w) to allow the comparison between the concentrations in the real samples and the legal limit for the concentration of the substances present in the RoHs restriction list, which corresponds to 0.1%w/w. As previously said, there isn't a legal limit for the SVHC list, but buyers do not accept products that are not under this limit for SVHC.

As can be seen from Table 5, the analytes detected are always found in quantities much below the legal limit, 0.1%w/w.

As expected, many PAH and phthalate compounds are present. Their presence had already been detected in many previous studies [10–13]. As regards the concentrations found, it was not always easy perform a comparison, because, in the literature, the quantification is only semi-quantitative since the sampling is performed with the solid phase micro-extraction (SPME) technique [14–16,26,27], or the studies are purely for screening purposes [28].

Furthermore, with respect to the 12 new that were analyzed and quantitively determined to be PAH, the concentrations are totally in agreement. As an example, naphthalene was found in our work at about 16 ng/g, which fully agrees with the values comprised between 25 and 138 ng/g of the cited work.

The same argument can be made for other compounds, particularly those present in the SVHC list, for which very few data are reported in the literature. In fact, most of the works often relied on migration or extraction experiments using a special extractant mixture (food simulants), whereas the present work focuses on a rapid multiresidue screening directly applicable to recycled PE and PP materials. In Figure S1, the comparison between the pre- and post-deodorization samples highlight that the process was extremely efficient, as it is capable of further reducing the concentrations of the analytes under investigation.

4. Conclusions

This optimized work proposes a rapid and efficient GC–MS multiresidue method specifically designed for the simultaneous screening and quantification of a broad range of contaminants in recycled PE and PP materials. Unlike previous studies, the proposed method is optimized for routine application, enabling the detection of 40 contaminants of multiple classes within a single analytical run and supporting the industrial quality control of recycled polyolefins. This method allows for providing the information needed in the industrial context for the determination of the presence and concentration of compounds contained in recycled plastics, in particular compounds belonging to the SVHC list. Thanks to its high sensitivity with optimal LOD and LOQ values, the method allows for providing reliable data to the production process control system in real time about the safety of the input products of factories, allowing for immediate corrective action in the event of anomalies. In fact, the method provides the possibility to determine 40 analytes potentially present in recycled plastics with a single chromatographic run. This method is to be considered a screening method that allows for highlighting batches of incoming material that are too contaminated to control the output material. This method was tested to analyze various batches of plastics both to be recycled and post-recycling to certify the safety and non-toxicity of the products obtained.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jox16020042/s1, Table S1. Analyte retention times and acquisition parameters. Figure S1. Comparison of the chromatograms of the samples pre- and post-deodorization process.

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