Article

Quantification of the Synthetic Phenolic Antioxidant Cyanox 1790 in Bottled Water with SPE-HPLC/MS/MS and Determination of the Impact of the Use of Recycled Packaging on Its Generation

Joaquín Hernández-Fernández [1,2,3,*], Rodrigo Ortega-Toro [4] and John R. Castro-Suarez [5]

1 Chemistry Program, Department of Natural and Exact Sciences, San Pablo Campus, University of Cartgena, Cartagena 130015, Colombia
2 Chemical Engineering Program, School of Engineering, Universidad Tecnológica de Bolivar, Parque Industrial y Tecnológico Carlos Vélez Pombo Km 1 Vía Turbaco, Cartagena 130001, Colombia
3 Department of Natural and Exact Science, Universidad de la Costa, Barranquilla 080002, Colombia
4 Food Packaging and Shelf-Life Research Group (FP&SL), Food Engineering Department, Universidad de Cartagena, Cartagena de Indias 130015, Colombia
5 Exact Basic Area, Sinú University, Cartagena Section, Cartagena 130014, Colombia
* Correspondence: jhernandezf@unicartagena.edu.co; Tel.: +57-301-5624990

Abstract: One route of exposure to SPAs is through bottled water since the polymers used to make plastic bottles contain these SPAs, which migrate from the plastic to the water. Solid-phase extraction (SPE), HPLC-MS, FTIR, and DSC are used to identify and quantify these SPAs in water. Interday measurements of cyanox 1790 in water with HPLC showed RSD, error, and R^2 lower than 3.78, 9.3, and 0.99995, respectively. For intraday measurements of cyanox 1790 in water, the RSD, error, and R^2 were less than 4.1, 11.2, and 0.99995, respectively. Concentrations of Cyanox 1790 in water from non-recycled bottles ranged from 0.01 ± 0.0004 to 4.15 ± 0.14 ppm, while the levels of cyanox 1790 in water in recycled bottles ranged between 0.01 ± 0.0005 and 11.27 ± 0.12 ppm. In the tests carried out, an increase in the migration of Cyanox 1790 from plastic bottles to water was identified, since the ppm of Cyanox increased in the water as the days of storage increased at 40 °C.

Keywords: bottled water; synthetic phenolic antioxidant; Cyanox 1790; recycled packaging; non-recycled packaging; additive migration

1. Introduction

The global synthetic phenolic antioxidant (SPA) market size for 2020 was USD 3.9 billion; by 2022, the global market only registered an increase of 3.98%, and by 2028, the business growth is expected to exceed USD 6.5 billion [1]. SPAs are additives, and their high demand is because they can be used in manufacturing food, beverages, polymers, etc. SPAs [1] have the ability to protect polymers against oxidative degradation [2–6]; they inhibit free radicals and other oxidizing agents from preventing the degradation of polymer chains [2–4,7]. When these SPAs are not added to polymers such as polypropylene (PP), it can be observed that the polymers oxidize, become more fluid, and acquire yellow coloration and unpleasant odors [8]. SPAs help prevent thermal and mechanical processes from degrading polymers, which is why they became one of the fundamental additives in PP. Even so, due to their molecular structure (see Figure 1), these SPAs are also part of the families of emerging organic pollutants since their functional groups derived from phenols negatively affect the environment. Chemical bonds do not join SPAs and polymers; SPA–polymers are physically mixed in their multiple applications. This means that in various applications of plastics, these SPAs can separate from the polymeric matrix and migrate from the plastic to other materials such as water. Due to these migrations, SPAs

have been detected in different media and environments, such as marine sediments, river water, dust, and human secretions, including urine and serum, among others [3,9–35]. Due to the above, there is a global concern about the risks associated with these SPAs. Therefore, international control bodies, such as the European Union (EU), have determined that the amounts allowed for the use of SPAs in food must range between 100 and 200 mg L^{-1} [36,37]. It is observed that SPAs such as butylhydroxytoluene (BHT), butylated hydroxyanisole (BHA), and its by-products cause an estrogenic effect that could alter the correct sexual functioning of mice and zebrafish. Additionally, they can cause carcinogenesis and teratogenesis, thus generating DNA disruption. Concentrations higher than 9010 μg L^{-1} of BHA create diseases such as obesity and, in addition, cause a malfunction in the testes of male mice correlated with the dose supplied [38–53]. The impact of the SPAs is related to their chemical and structural nature. The structure of the SPA Cyanox 1790 is represented in Figure 1, where it can be observed that it has three fragments that are a variant of 2,6-di-tert-butylphenol. Therefore, since this 2,6-di-tert-butylphenol is a very toxic molecule, it is to be expected that Cyanox is equally or more toxic. In the literature, there is no evidence of more in-depth studies on the risk of Cyanox, so the information presented in this research will also serve as an input for other researchers to continue exploring its health risks. Concern about SPAs has increased as they have been identified in water samples [3,11,18–25], but their presence has not been linked to their migration from plastics and has not been linked to the use of recycled bottles. It is well-known that the current worldwide trend of bottled-water processing plants is to increase the recycling and reuse of these containers [54,55]. In water samples, it has been possible to identify other substances such as bisphenols, volatile compounds, microplastics, heavy metals, organophosphates, arsenic, nitrates, and manganese that have generated alarms about their risks [56–69]. The great concern arises given that the consumption of bottled water worldwide in 2011 reached the figure of approximately 232 billion liters, with an estimated growth of 7% per year. It is projected that by 2025 it will reach 513 billion liters [63,69]. It was found that the world region that consumes the most bottled water is North America with 30%, followed by Europe and Asia with 29% and 27%, respectively [70–73]. By 2020, 724 companies (INVIMA) dedicated to the sale and distribution of bottled water were created in Colombia, some without all the legal documents to operate, of which 14 are located in the city of Cartagena. It is estimated that this market has a growth rate of 12% per year; for example, by 2020, it was known that 53,000 families consumed bottled water [60]. The previous demand makes the identification and quantification of SPAs in water samples of vital importance. Thus, in these investigations, the selection of analytical techniques for the identification and quantification of contaminants is essential, observing the use of instrumental techniques such as liquid-phase microextraction (LPME), solid-phase extraction (SPE), and solid-phase microextraction (SPME). The relative standard deviation (RSD) and LOD for the determination of SPAs with HPLC are less than 10% in matrices with a low complexity of chemical content. Differential heat scanning (DSC) techniques have been used to determine the melting temperature of SPAs and examine the synergistic effects of antioxidants, including SPAs [3,42,74–79].
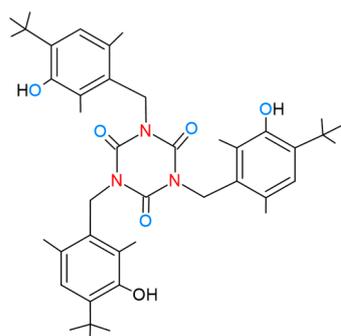
Figure 1. Spatial arrangement of the atoms of the Cyanox 1790 molecule.

In this research, an interday (different days) and intraday (same day) analytical measurement study of cyanox 1790 measurements were carried out by five analysts in the same laboratory to assess the reliability of the measurements. Water from three brands of non-recycled water bottles and water from three brands of recycled water bottles were then sampled. These commercial water bottles were stored in a local warehouse at 40 °C. The water bottles were monitored for 90 days to assess the effect of Cyanox 1790 migration. Cyanox monitoring is mainly performed with a previously calibrated HPLC-DAD/MS/MS. FTIR and DSC techniques have been used to verify that the water samples analyzed using HPLC did not have the presence of microplastics, which can form inside the bottles and affect the HPLC operation.

2. Materials and Methods

2.1. Reagents

To carry out the different tests, acetonitrile (99.99% HPLC grade, Merck, Darmstadt, Germany) and methyl alcohol (99.99% HPLC grade MeOH, Merck, Darmstadt, Germany) were used, as well as 1,3,5-tris[(4-tert-butyl-3-hydroxy-2,6-dimethylphenyl)methyl]-1,3,5-triazinane-2,4,6-trione (Cyanox 1790-Cytec, Asia, Singapore), ammonium chloride (Merck, Darmstadt, Germany), and sodium hydroxide (Merck, Darmstadt, Germany). A Milli-Q system (Milli-pore, Bed-ford, MA, USA) was used to purify the water. All solutions prepared for HPLC were filtered through a 0.45 μm nylon filter.

2.2. Calibration Curve

To evaluate the performance of the equipment and to be able to determine low concentrations in the water samples, a multi-point calibration curve was developed using a Cyanox 1790 stock solution of 100 mg L^{-1} as a reference. The 100 mg L^{-1} solution was prepared by weighing 10 mg of Cyanox 1790, adding it to a 100 mL volumetric flask, and bringing 100 mL of acetonitrile to the mark. The concentration ranges of Cyanox 1790 in ACN corresponded to 5.0, 2.5, 1.5, 0.5, 0.5, 0.25, 0.1, 0.05, 0.025, 0.001, and 0 mg L^{-1}. Each of these ten standards was prepared by multiple dilutions of the 100 mg L^{-1} stock solution. In the investigation, five laboratory analysts considered competent for the tests were selected, and the repeatability and reproducibility were evaluated. The repeatability was calculated with five analysts' measurements on the same day. The reproducibility was performed on different days by the five analysts. The repeatability and reproducibility studies were carried out as follows: (1) The standards were directly analyzed with HPLC and we performed 100 measurements corresponding to 50 repeatability measurements and 50 reproducibility measurements. (2) On the standards treated with solid-phase extraction (SPE), to study the variability provided by the SPE, we performed 100 measurements corresponding to 50 repeatability measurements and 50 reproducibility measurements. The test samples were only evaluated for reproducibility. To understand the efficiency of the SPE, the recovery percentage of Cyanox 1790 was calculated. This recovery was determined by taking as reference the theoretical concentration of the standards and the concentration calculated after the analysis of each standard in the SPE. The product of the division between the experimental concentration and the theoretical concentration was multiplied by 100, and this gave us the recovery percentage.

2.3. Sampling

The sampling point was chosen to consider the distribution logistics of these beverages in the city of interest. There is a central warehouse where the bottled hydrating drinks are received and transported to supermarkets, stores, warehouses, dispensers, etc. For the above in this investigation, a leading winery was selected as the sampling point. The main cellar had an average temperature of 40 °C. In this warehouse, bales of water bottles are placed on pallets on the ground. From there, six brands or six manufacturers of water were identified. Each was identified as A, B, C, D, E, and F. The marks A, B, and C correspond to water brands that use non-recycled plastic bottles. The D, E, and F brand waters use

recycled plastic bottles. The analyses of the water of brands A, B, C, D, E, and F were carried out by five analysts to determine the reproducibility of the measurement.

The sampling of drinks A, B, C, D, E, and F was carried out for 90 days on days 1, 5, 10, 15, 30, 45, 60, 72, and 90. For this activity, an analyst was assigned exclusively for sampling. This analyst went to the central warehouse to select the water bottles on days 1, 5, 10, 15, 30, 45, 60, 72, and 90. Each day he measured the temperature of the bottles and selected the brand A, B, C, D, E, and F bottles. The analyst stored the sampled water bottles in a HotLogic SKU-9137000 mini portable oven, ensuring that the samples maintained their temperature of 40 °C. The samples were transported by vehicle to the laboratory and delivered to each analyst, who proceeded to conduct their respective analysis. Each laboratory analyst removed the cap from the bottle and, with the help of a syringe, drew 50 mL of water from each bottle. When evaluating the samples, we made a total of 270 measurements, corresponding to analyzing 54 samples by five analysts. The experimental design is shown in Table 1.

Table 1. Experimental design for collection of samples of interest.

Bottled Water Sample Collection Information							
Beverage Brand	Sampling Frequency (days)	Container Recycling	Analyst 1	Analyst 2	Analyst 3	Analyst 4	Analyst 5
A	1/5/10/15/ 30/45/60/72/90	No	x	x	x	x	x
B	1/5/10/15/ 30/45/60/72/90	No	x	x	x	x	x
C	1/5/10/15/ 30/45/60/72/90	No	x	x	x	x	x
D	1/5/10/15/ 30/45/60/72/90	Yes	x	x	x	x	x
E	1/5/10/15/ 30/45/60/72/90	Yes	x	x	x	x	x
F	1/5/10/15/ 30/45/60/72/90	Yes	x	x	x	x	x

2.3.1. Solid-Phase Extraction (SPE) for Bottled Water Samples

Conditioning of the Stationary Phase of the SPE

Conditioning of the stationary phase was performed according to the protocol established by Phenomenex, provider of the referenced Strata-X33. This consisted of adding 5 mL of MeOH followed by 5 mL of HPLC grade water.

Pretreatment

The work sample was homogenized and tempered at 25 °C, and then filtered in a PTFE Teflon filter of 0.22 μm to facilitate the subsequent sample preparation and reduce microbial activity.

Preconcentration and Cleaning

At this stage, conditioning of Strata X-33 cartridges (6 mL, 500 mg) was performed with 5 mL of MeOH followed by 5 mL of distilled water. Subsequently, 15 mL of the sample was uploaded at a rate of 1 mL min^{-1}. Bottles of each brand (A, B, C, D, E, and F) were sampled every day of interest according to the experimental design of Table 1. Once the entire sample was percolated, the cartridges were washed with 3 mL of MeOH:H$_2$O 80:20. Elution of the compounds retained in the solid phase was performed with 10 mL of ACN. The eluate was evaporated until dry with a stream of nitrogen at 5 psi. The final extract was reconstituted with ACN to a final volume of 1 mL, obtaining a preconcentration of 10:1.

2.4. Liquid Chromatography with Diode Array Detector and Mass Spectrometry (HPLC-DAD/MS/MS)

For this analysis, an Agilent 1100 HPCL and a Micromass Quattro II triple quadrupole mass spectrometer were used. It is possible to acquire spectra using MS and MS/MS. As part of the system, a degasser (G1322A), a quaternary pump (G1311A), an automatic sampling system (G1313A), a column carrier (G1316A), a DAD detector (G1315B) with chemical station, a Lichrosorb RP-18 column (4.6 × 200 mm × 5 microns), 5 and 10 syringes and a precision balance were used. A separate double-pump system and self-sampler were also used for automatic injection into the MS with a Cyanox 1790 solution at ACN to establish chromatographic conditions. With the mixture of ACN and H_2O solvents, which were mixed in various proportions, the following separation was carried out: 84 and 16 percent (1 min, 15 mL/min); 92 and 8 percent (2 min, 2 mL/min); 96 and 4 percent (3.5 min, 3.5 mL/min); and 100 and 0 percent (8 min, 3.5 mL/min). The temperature, irrigation volume, and wavelength of the column were adjusted to 50 °C [9,26,80]. For the identification of the additive, the mass data of MS fragment and MS/MS ions are used.

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

This analysis used a Nicolet 6700 FTIR infrared spectrometer with values from 4000 to 600 cm^{-1} and a resolution of 2 cm^{-1} (reflection) [9,80]. With this equipment, plastic residues in the filtered water were monitored to prevent these small plastic particles from reaching the HPLC and generating obstructions in the equipment pump.

2.6. Differential Scanning Calorimeter (DSC)

A 6.1 mg sample was used to obtain the results under atmospheric nitrogen conditions. Nitrogen provides us with a controlled, inert environment that allows us to examine how decomposition affects the sample. This procedure was carried out in various circumstances, such as isothermy at 60 °C for 5 min, an atmosphere of 50 mL/min of nitrogen, and a temperature increase of 60 °C at 200 °C for 20 min. With this equipment, plastic residues in the filtered water were monitored to prevent these small plastic particles from reaching the HPLC and generating obstructions in the equipment pump.

2.7. Data Analysis

The Minitab program was used to perform the statistical studies (correlation analysis, linearity, and ANOVA). Tukey's test was employed for the analysis of variance of the data. One-way ANOVA was utilized to compare differences between groups. The threshold for statistical significance was set at $p \leq 0.05$.

3. Analysis and Results

3.1. Validation of Standards

The statistical analysis of repeatability and reproducibility was analyzed with ANOVA, and Tukey's test was applied to determine if all the means had an acceptable statistical behavior with a significance level of 95%. Tukey's test evaluates whether or not the data were grouped in the same group (A). Table 2 shows this ANOVA. Figure 2a,b show boxplots for the repeatability and reproducibility distributions of the standard data and the position of their means. To know the reliability of the analysis of the Cyanox 1790 standards by HPLC, Figure 2a,b show that the average of the analysts does not have significant differences at 95% confidence in repeatability and reproducibility for the performance of Cyanox 1790 measurement on HPLC on the same day or different days. Figure 2b,c show the performance of measurements by solid phase extraction (SPE). The performance of these measures was equal to that of the standards. RSD was achieved well below 5% for repeatability and reproducibility; repeatability errors were less than 5%, while reproducibility errors were less than 6.2%. These results were lower than those indicated by the literature, where it is observed that RSD and errors of 20% and 15%, respectively, were considered acceptable by the validation protocols [2,4,80].
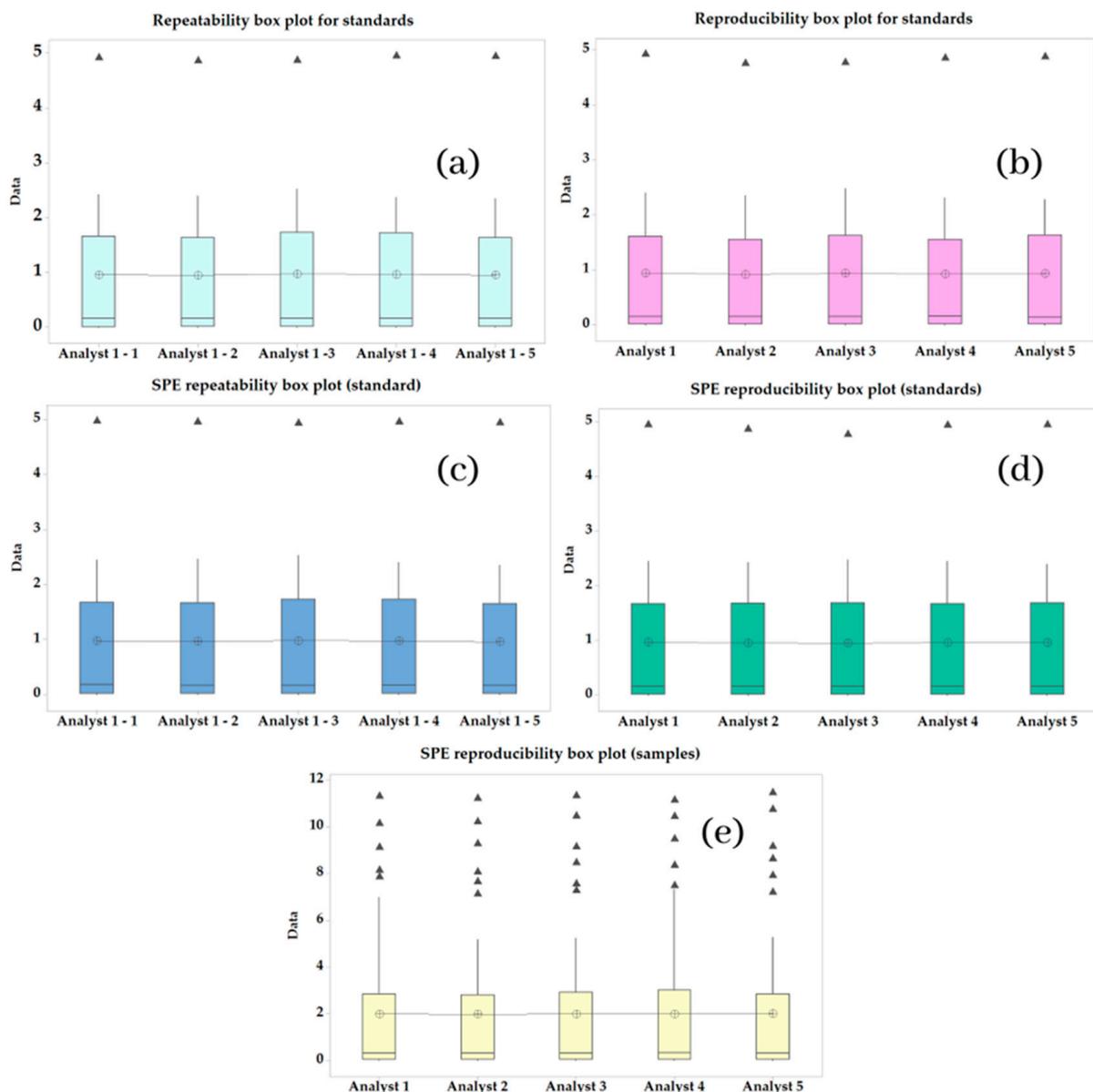
Figure 2. Repeatability and reproducibility behavior for standards (**a**,**b**), for SPE (**c**,**d**), and (**e**) for all bottled water samples.

For the SPE reproducibility tests, the recovery percentages were evaluated for the concentrations of 5, 2.5, 1.5, 0.5, 0.25, 0.1, 0.05, 0.025, and 0.001 mg L^{-1}, finding recoveries of 99, 98, 96, 95, 98, 97, 97, 95, and 98%, respectively. For the repeatability of SPE, the recoveries of all concentrations were higher than 94%.

Figure 3 shows an R^2 value of 0.99995 and a correlation coefficient (r) of 0.99998 for repeatability and reproducibility for the standards and SPE between 5.0, 2.5, 1.5, 0.5, 0.25, 0.1, 0.05, 0.025, 0.001, and 0 ppm Cyanox 1790 in ACN. These results are more accurate (0.04%) than similar studies for the determination of SPAs [22,80]. This coefficient shows a directly proportional relationship between the theoretical and experimental values.

Table 2. ANOVA analysis for standards and samples, using the Tukey method with 95% confidence.

Repeatability of standards with CH2Cl2				Reproducibility of standards with CH2Cl2			
Factor	**N**	**Average**	**Grouping**	**Factor**	**N**	**Average**	**Grouping**
Analyst 1–3	10	0.973	A	Analyst 1	10	0.946	A
Analyst 1–4	10	0.965	A	Analyst 3	10	0.939	A
Analyst 1–1	10	0.959	A	Analyst 5	10	0.933	A
Analyst 1–5	10	0.954	A	Analyst 4	10	0.928	A
Analyst 1–2	10	0.949	A	Analyst 2	10	0.921	A
Repeatability of standards with CH2CN in SPE				**Reproducibility of standards with CH2CN in SPE**			
Factor	**N**	**Average**	**Grouping**	**Factor**	**N**	**Average**	**Grouping**
Analyst 1–3	10	0.979	A	Analyst 1	10	0.971	A
Analyst 1–4	10	0.976	A	Analyst 5	10	0.967	A
Analyst 1–1	10	0.973	A	Analyst 4	10	0.967	A
Analyst 1–2	10	0.968	A	Analyst 2	10	0.959	A
Analyst 1–5	10	0.957	A	Analyst 3	10	0.955	A

Reproducibility of samples with CH2CN on SPE			
Factor	**N**	**Average**	**Grouping**
Analyst 1	40	1718	A
Analyst 4	40	1710	A
Analyst 5	40	1699	A
Analyst 2	40	1696	A
Analyst 3	40	1695	A
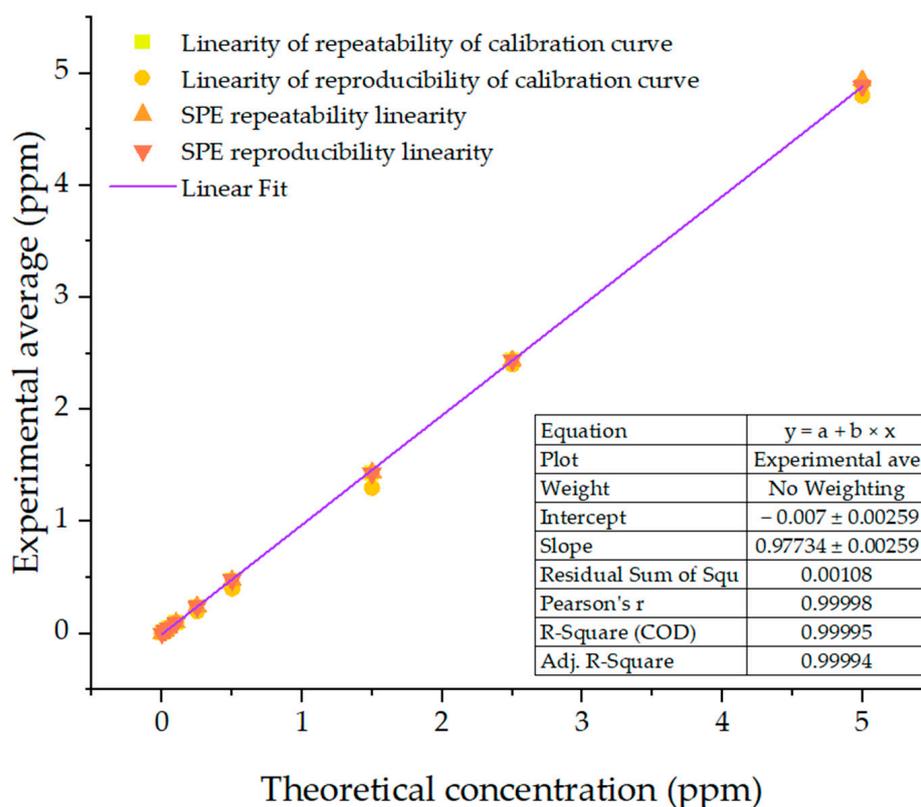
Figure 3. Graphical analysis of the linearity of the standards and SPE.

3.2. Analysis of Cyanox 1790 in Bottled Water Samples

Fifty-four samples were analyzed using the above methodology under the conditions described in Section 2.1. Cyanox 1790 ranged between 0.01 and 11.27 ppm for the water samples in recycled bottles (see Table 3). Water samples in non-recycled containers showed Cyanox 1790 concentrations between 0.01 and 4.16 ppm with an average of 1.06 ppm. The highest concentration of Cyanox 1790 was found in the water in recycled bottles of brand F at 90 days. The identified concentration was 11.27 ppm. For the standard deviation, values less than or equal to 0.2 were obtained, and for the relative standard deviation (RSD), values less than or equal to 5.3% were obtained. The ANOVA analysis presented in Table 2 shows that there is no significant difference between the means of the concentrations for the different analysts, which means that any analyst can perform the measurement and obtain reliable results in the measurement of Cyanox 1790 concentrations in bottled water.

Table 3. Reproducibility data for Cyanox 1790 in water samples using HPLC-MS.

				SPE with Acetonitrile (HPLC-MS Results)							
				Interday Test (Different Days) Samples							
Sample	Brand	Storage Time	Recycled Material	Analyst 1	Analyst 2	Analyst 3	Analyst 4	Analyst 5	Average	Deviation	RSD
1	A	1		0.010	0.010	0.010	0.010	0.011	0.01	0.0	4.4
2	B	1	NO	0.230	0.250	0.250	0.260	0.250	0.25	0.0	4.4
3	C	1		0.310	0.300	0.320	0.310	0.300	0.31	0.0	2.7
4	D	1		0.100	0.110	0.110	0.100	0.100	0.10	0.0	5.3
5	E	1	YES	0.210	0.220	0.200	0.210	0.200	0.21	0.0	4.0
6	F	1		0.300	0.310	0.280	0.300	0.290	0.30	0.0	3.9
7	A	5		0.020	0.019	0.021	0.020	0.019	0.02	0.0	4.2
8	B	5	NO	0.030	0.031	0.032	0.030	0.029	0.03	0.0	3.8
9	C	5		0.042	0.040	0.039	0.041	0.042	0.04	0.0	3.2
10	D	5		0.030	0.031	0.032	0.030	0.030	0.03	0.0	2.9
11	E	5	YES	0.050	0.051	0.052	0.050	0.050	0.05	0.0	1.8
12	F	5		0.060	0.061	0.063	0.060	0.060	0.06	0.0	2.1
13	A	10		0.030	0.031	0.032	0.030	0.030	0.03	0.0	2.9
14	B	10	NO	0.040	0.042	0.040	0.042	0.041	0.04	0.0	2.4
15	C	10		0.060	0.062	0.061	0.062	0.063	0.06	0.0	1.9
16	D	10		0.070	0.072	0.073	0.072	0.072	0.07	0.0	1.5
17	E	10	YES	0.080	0.081	0.083	0.084	0.084	0.08	0.0	2.2
18	F	10		0.090	0.093	0.092	0.093	0.092	0.09	0.0	1.3
19	A	15		0.050	0.053	0.052	0.051	0.052	0.05	0.0	2.2
20	B	15	NO	0.050	0.056	0.057	0.056	0.055	0.05	0.0	5.1
21	C	15		0.060	0.062	0.063	0.062	0.061	0.06	0.0	1.9
22	D	15		0.170	0.160	0.170	0.170	0.170	0.17	0.0	2.7
23	E	15	YES	0.180	0.190	0.170	0.180	0.190	0.18	0.0	4.6
24	F	15		0.240	0.220	0.230	0.240	0.220	0.23	0.0	4.3
25	A	30		0.110	0.120	0.120	0.110	0.120	0.12	0.0	4.7
26	B	30	NO	0.140	0.130	0.140	0.130	0.140	0.14	0.0	4.0
27	C	30		0.180	0.190	0.180	0.170	0.170	0.18	0.0	4.7
28	D	30		0.350	0.370	0.360	0.380	0.350	0.36	0.0	3.6
29	E	30	YES	0.440	0.450	0.470	0.460	0.480	0.46	0.0	3.4
30	F	30		0.500	0.530	0.520	0.540	0.550	0.53	0.0	3.6

Table 3. *Cont.*

| | | | | SPE with Acetonitrile (HPLC-MS Results) | | | | | | | |
| | | | | Interday Test (Different Days) Samples | | | | | | | |
Sample	Brand	Storage Time	Recycled Material	Analyst 1	Analyst 2	Analyst 3	Analyst 4	Analyst 5	Average	Deviation	RSD
31	A	45		0.860	0.890	0.870	0.850	0.840	0.86	0.0	2.2
32	B	45	NO	0.940	0.930	0.910	0.970	0.950	0.94	0.0	2.4
33	C	45		1.120	1.120	1.100	1.110	1.000	1.09	0.1	4.7
34	D	45		2.620	2.500	2.390	2.450	2.430	2.48	0.1	3.6
35	E	45	YES	2.710	2.730	2.860	2.940	2.760	2.80	0.1	3.5
36	F	45		3.240	3.090	3.160	3.240	3.100	3.17	0.1	2.3
37	A	60		1.710	1.630	1.840	1.730	1.700	1.72	0.1	4.4
38	B	60	NO	1.500	1.630	1.570	1.670	1.590	1.59	0.1	4.0
39	C	60		1.490	1.370	1.350	1.420	1.330	1.39	0.1	4.6
40	D	60		4.490	4.520	4.430	4.090	4.330	4.37	0.2	4.0
41	E	60	YES	5.330	5.190	5.240	5.310	5.270	5.27	0.1	1.1
42	F	60		5.160	5.090	5.200	4.990	5.190	5.13	0.1	1.7
43	A	72		2.270	2.190	2.240	2.340	2.110	2.23	0.1	3.9
44	B	72	NO	1.980	1.950	2.010	1.890	1.830	1.93	0.1	3.7
45	C	72		2.520	2.640	2.780	2.660	2.450	2.61	0.1	4.9
46	D	72		7.850	7.640	7.550	7.460	7.910	7.68	0.2	2.5
47	E	72	YES	8.120	8.060	8.450	8.330	8.610	8.31	0.2	2.7
48	F	72		6.990	7.120	7.260	7.330	7.190	7.18	0.1	1.8
49	A	90		4.510	4.260	4.010	4.110	4.260	4.23	0.2	4.5
50	B	90	NO	3.850	3.760	3.460	3.520	3.740	3.67	0.2	4.6
51	C	90		4.110	4.130	3.990	4.180	4.370	4.16	0.1	3.3
52	D	90		9.110	9.250	9.130	9.470	9.150	9.22	0.1	1.6
53	E	90	YES	10.120	10.190	10.450	10.420	10.720	10.38	0.2	2.3
54	F	90		11.280	11.190	11.310	11.120	11.430	11.27	0.1	1.1

Figure 4 shows the percentage composition profile of the Cyanox 1790 concentrations found in the water samples using recycled and non-recycled plastic bottles. For the cases of brands A, B, and C in non-recycled bottles, the total variation of the concentration of Cyanox 1790 in the water was 3, 14, and 17%, respectively. Samples B and C had a decreasing trend. For the water samples of the D, E, and F brands that were characterized by having plastic bottles made with recycled plastic, we measured cyanox 1790 concentration variations of 13, 8, and 17%, respectively. However, it should be noted that the D, E, and F brands maintained the highest percentage concentration values obtained for Cyanox 1790. It should also be noted that the average percentage of Cyanox 1790 in bottled water made from recycled plastic was 60.93% higher than in bottled water made from non-recycled plastic. This allows us to deduce that the reuse of the container directly influences the concentration of Cyanox 1790 in the water. These concentration values obtained for this polymeric additive were approximately 13 times higher than the concentration found for other SPAs, such as BHT and BHT-Q, in bottled water [80], 4.5 times higher than a large group of SPAs found in different water bodies using the same analysis method [9], and 112,700 times higher than normal arsenic concentrations in the drinking water [67].
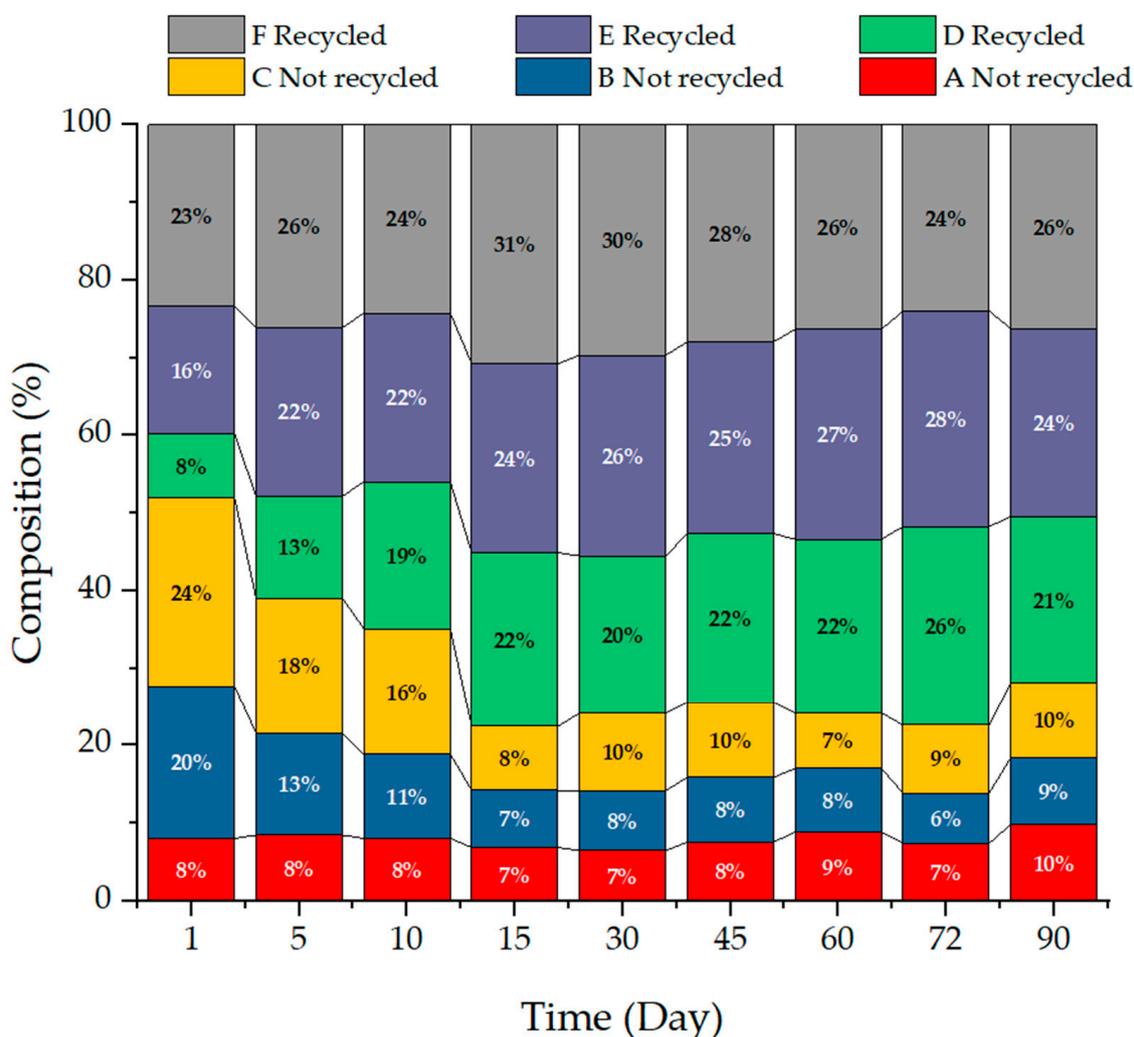
Figure 4. Cyanox 1970 concentration in bottled water stored in recycled and non-recycled plastic bottles.

3.3. Complementary Analysis of Cyanox 1790 in Bottled Water Samples

The Cyanox 1790 standard and the Cyanox 1790 sample extracted from bottled water had the same performance pattern in differential scanning calorimetry (DSC). The rising peak of the calorimetric curve shows that both Cyanox 1790 samples release heat between 155 and 176 °C. This heat release is due to the melting of the sample, which releases energy in the form of heat. The highest heat flux emitted for both Cyanox 1790 samples was 8.69 mW, as shown in Figure 5. This is one of the arguments supporting that Cyanox 1790 is the analyte isolated from the water bottles and that no other chemical species were found that could have caused interference in the measurements.

Pure Standard FTIR Analysis and Recovered Dust

The resulting spectrum (Figure 6) shows two bands between 1300 and 1050 cm^{-1} that correspond to the symmetric and asymmetric stretches of the Cyanox ester group and a peak around 1735 cm^{-1}, indicating the ester group (O=C) present in the Cyanox 1790 structure. The phenol functional group is present in the Cyanox 1790 structure, as indicated by the signal at 3670 cm^{-1}. Between 2950 and 2970 cm^{-1}, the typical band of the CH$_3$ group is observed. These classifications are also revealed by the chemical composition of Cyanox. Relatively strong absorption in the range of 1450–1500 cm^{-1} is characteristic of the spectra of aromatic compounds [80]. For this study, it is more convenient to measure the coupling. Figure 1 shows the molecular composition of Cyanox 1790. The overlap of the two FTIR spectra shows a high similarity between the two chemicals.
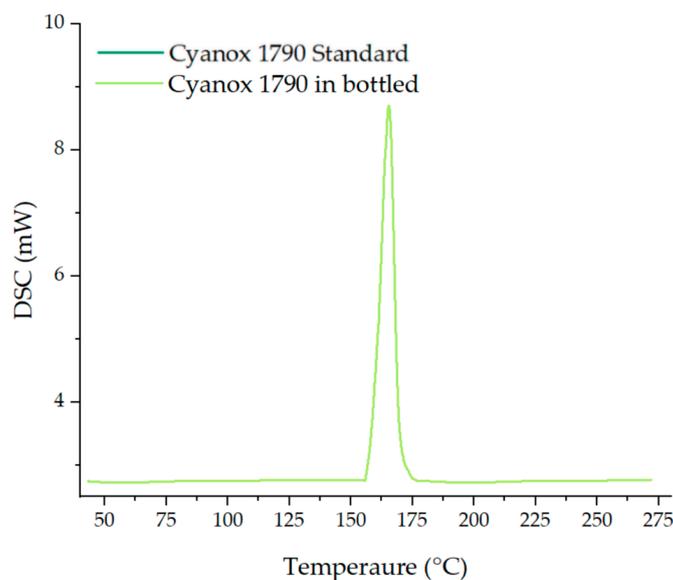
Figure 5. Standard and bottling Cyanox 1790 DSC charts.
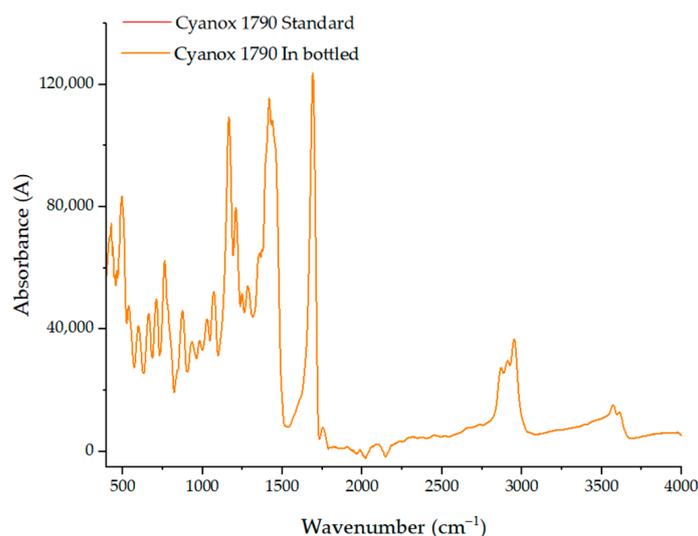

Figure 6. FTIR graphics for standard Cyanox 1790 and bottling.

4. Conclusions

The interday and intraday behavior of the SPA cyanox 1790 is studied. It is found that the interday measurements of cyanox in water using HPLC showed RSD, error, and R^2 less than 3.78, 9.3, and 0.99995, respectively. The intraday behavior of cyanox in water shows that the RSD, error, and R^2 were lower than 4.1, 11.2, and 0.99995, respectively. With this methodology, the content of Cyanox 1790 in six commercial brands of bottled water in Colombia was known. Concentrations of Cyanox 1790 in water from non-recycled bottles ranged from 0.01 ± 0.0004 to 4.15 ± 0.14 ppm, while the levels of cyanox 1790 in water in recycled bottles ranged between 0.01 ± 0.0005 and 11.27 ± 0.12 ppm. In the tests carried out, an increase in the migration of Cyanox 1790 from plastic bottles to water was identified, since the ppm of Cyanox increased in the water as the days of storage increased at 40 °C. It was observed that the reuse of containers drastically increases the presence of Cyanox 1790 in the water contained in these containers.

References

1. Fortune Business Insights. The Global Antioxidants Market Is Expected to Grow from \$4.13 Billion in 2021 to \$6.05 Billion in 2028 at a CAGR of 5.61% in the Forecast Period, 2021–2028. 2021. Available online: https://www.fortunebusinessinsights.com/industry-reports/food-antioxidants-market-100789 (accessed on 24 January 2023).
2. Hernández-Fernández, J.; Lopez-Martinez, J.; Barceló, D. Quantification and elimination of substituted synthetic phenols and volatile organic compounds in the wastewater treatment plant during the production of industrial scale polypropylene. *Chemosphere* **2021**, *263*, 128027. [CrossRef]
3. Hernández-Fernandez, J.; Rodríguez, E. Determination of phenolic antioxidants additives in industrial wastewater from polypropylene production using solid phase extraction with high-performance liquid chromatography. *J. Chromatogr. A* **2019**, *1607*, 460442. [CrossRef]
4. Hernández-Fernández, J. Quantification of oxygenates, sulphides, thiols and permanent gases in propylene. A multiple linear regression model to predict the loss of efficiency in polypropylene production on an industrial scale. *J. Chromatogr. A* **2020**, *1628*, 461478. [CrossRef]
5. Wiles, D.M.; Scott, G. Polyolefins with controlled environmental degradability. *Polym. Degrad. Stab.* **2006**, *91*, 1581–1592. [CrossRef]
6. Al-Malaika, S. Perspectives in stabilisation of polyolefins. *Adv. Polym. Sci.* **2004**, *169*, 121–150. [CrossRef]
7. Pospíšil, J. Mechanistic Action of Phenolic Antioxidants in Polymers—A Review. *Polym. Degrad. Stab.* **1988**, *20*, 181–202. [CrossRef]
8. Coreño-Alonso, J.; Méndez-Bautista, M.T. Relación estructura-propiedades de polímeros. *Educ. Quím.* **2010**, *21*, 291–299. [CrossRef]
9. Liu, R.; Ruan, T.; Song, S.; Lin, Y.; Jiang, G. Determination of synthetic phenolic antioxidants and relative metabolites in sewage treatment plant and recipient river by high performance liquid chromatography–electrospray tandem mass spectrometry. *J. Chromatogr. A* **2015**, *1381*, 13–21. [CrossRef]
10. Liu, R.; Song, S.; Lin, Y.; Ruan, T.; Jiang, G. Occurrence of synthetic phenolic antioxidants and major metabolites in municipal sewage sludge in China. *Environ. Sci. Technol.* **2015**, *49*, 2073–2080. [CrossRef]
11. Wang, W.; Xiong, P.; Zhang, H.; Zhu, Q.; Liao, C.; Jiang, G. Analysis, occurrence, toxicity and environmental health risks of synthetic phenolic antioxidants: A review. *Environ. Res.* **2021**, *201*, 111531. [CrossRef]
12. Wang, J.; Wang, J.; Liu, J.; Li, J.; Zhou, L.; Zhang, H.; Sun, J.; Zhuang, S. The evaluation of endocrine disrupting effects of tert-butylphenols towards estrogenic receptor α, androgen receptor and thyroid hormone receptor β and aquatic toxicities towards freshwater organisms. *Environ. Pollut.* **2018**, *240*, 396–402. [CrossRef]
13. Wang, W.; Kannan, K. Inventory, loading and discharge of synthetic phenolic antioxidants and their metabolites in wastewater treatment plants. *Water Res.* **2018**, *129*, 413–418. [CrossRef]
14. Tang, J.; Tang, L.; Zhang, C.; Zeng, G.; Deng, Y.; Dong, H.; Wang, J.; Wu, Y. Different senescent HDPE pipe-risk: Brief field investigation from source water to tap water in China (Changsha City). *Environ. Sci. Pollut. Res.* **2015**, *22*, 16210–16214. [CrossRef]
15. Shao-Yang, H. Toxicity effects of the environmental hormone 4-tert-octylphenol in zebrafish (Danio rerio). *Int. J. Mar. Sci.* **2016**, *6*, 4–5. [CrossRef]
16. Honda, M.; Kannan, K. Biomonitoring of chlorophenols in human urine from several Asian countries, Greece and the United States. *Environ. Pollut.* **2018**, *232*, 487–493. [CrossRef]
17. Wang, W.; Kannan, K. Quantitative identification of and exposure to synthetic phenolic antioxidants, including butylated hydroxytoluene, in urine. *Environ. Int.* **2019**, *128*, 24–29. [CrossRef]
18. Liu, R.; Mabury, S.A. Synthetic Phenolic Antioxidants: A Review of Environmental Occurrence, Fate, Human Exposure, and Toxicity. *Environ. Sci. Technol.* **2020**, *54*, 11706–11719. [CrossRef]
19. Dương, T.-B.; Dwivedi, R.; Bain, L.J. 2,4-di-tert-butylphenol exposure impairs osteogenic differentiation. *Toxicol. Appl. Pharmacol.* **2023**, *461*, 116386. [CrossRef]
20. Liu, R.; Mabury, S.A. Synthetic phenolic antioxidants and transformation products in dust from different indoor environments in Toronto, Canada. *Sci. Total Environ.* **2019**, *672*, 23–29. [CrossRef]
21. Makahleh, A.; Saad, B.; Bari, M.F. Synthetic phenolics as antioxidants for food preservation. In *Handbook of Antioxidants for Food Preservation*; Elsevier Inc.: Amsterdam, The Netherlands, 2015; pp. 51–78. [CrossRef]

22. Gonçalves-Filho, D.; De Souza, D. Detection of Synthetic Antioxidants: What Factors Affect the Efficiency in the Chromatographic Analysis and in the Electrochemical Analysis? *Molecules* **2022**, *27*, 7137. [CrossRef]

23. Chen, Y.; Chen, Q.; Zhang, Q.; Zuo, C.; Shi, H. An Overview of Chemical Additives on (Micro)Plastic Fibers: Occurrence, Release, and Health Risks. *Rev. Environ. Contam. Toxicol.* **2022**, *260*, 22. [CrossRef]

24. Wang, W.; Asimakopoulos, A.G.; Abualnaja, K.O.; Covaci, A.; Gevao, B.; Johnson-Restrepo, B.; Kumosani, T.A.; Malarvannan, G.; Minh, T.B.; Moon, H.-B.; et al. Synthetic Phenolic Antioxidants and Their Metabolites in Indoor Dust from Homes and Microenvironments. *Environ. Sci. Technol.* **2015**, *50*, 428–434. [CrossRef] [PubMed]

25. Xu, X.; Liu, A.; Hu, S.; Ares, I.; Martínez-Larrañaga, M.-R.; Wang, X.; Martínez, M.; Anadón, A.; Martínez, M.-A. Synthetic phenolic antioxidants: Metabolism, hazards and mechanism of action. *Food Chem.* **2021**, *353*, 129488. [CrossRef]

26. Hernández-Fernández, J.; Ortega-Toro, R.; López-Martinez, J. A New Route of Valorization of Petrochemical Wastewater: Recovery of 1,3,5-Tris (4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)–1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (Cyanox 1790) and Its Subsequent Application in a PP Matrix to Improve Its Thermal Stability. *Molecules* **2003**, *28*, 2003. [CrossRef]

27. Pavon, C.; Aldas, M.; López-Martínez, J.; Hernández-Fernández, J.; Arrieta, M.P. Films based on thermoplastic starch blended with pine resin derivatives for food packaging. *Foods* **2021**, *10*, 1171. [CrossRef] [PubMed]

28. Hernández-Fernández, J.; Puello-Polo, E.; Castro-Suarez, J.R. Characterization of the Morphological and Chemical Profile of Different Families of Microplastics in Samples of Breathable Air. *Molecules* **2023**, *28*, 1042. [CrossRef]

29. Pavón, C.; Aldas, M.; Hernández-Fernández, J.; López-Martínez, J. Comparative characterization of gum rosins for their use as sustainable additives in polymeric matrices. *J. Appl. Polym. Sci.* **2021**, *139*, 51734. [CrossRef]

30. Bonachela, S.; López, J.; Granados, M.; Magán, J.; Hernández, J.; Baille, A. Effects of gravel mulch on surface energy balance and soil thermal regime in an unheated plastic greenhouse. *Biosyst. Eng.* **2020**, *192*, 1–13. [CrossRef]

31. Hernández Fernández, J.; Cano, H.; Guerra, Y.; Puello Polo, E.; Ríos-Rojas, J.F.; Vivas-Reyes, R.; Oviedo, J. Identification and Quantification of Microplastics in Effluents of Wastewater Treatment Plant by Differential Scanning Calorimetry (DSC). *Sustainability (Switzerland)* **2022**, *14*, 4920. [CrossRef]

32. Hernández-Fernández, J.; Guerra, Y.; Espinosa, E. Development and Application of a Principal Component Analysis Model to Quantify the Green Ethylene Content in Virgin Impact Copolymer Resins During Their Synthesis on an Industrial Scale. *J. Polym. Environ.* **2022**, *30*, 4800–4808. [CrossRef]

33. European Parliament and Council Directive No 95/2/EC. 1995. Available online: https://eur-lex.europa.eu/eli/dir/1995/2/oj (accessed on 14 December 2022).

34. Nurerk, P.; Bunkoed, O.; Jullakan, S.; Khongkla, S.; Llompart, M.; Poorahong, S. A dumbbell-shaped stir bar made from poly(3,4-ethylenedioxythiophene)-coated porous cryogel incorporating metal organic frameworks for the extraction of synthetic phenolic antioxidants in foodstuffs. *J. Chromatogr. A* **2021**, *1655*, 462497. [CrossRef] [PubMed]

35. Wang, W.; Wang, X.; Zhu, Q.; Zhou, Q.; Wang, Y.; Liao, C.; Jiang, G. Occurrence of synthetic phenolic antioxidants in foodstuffs from ten provinces in China and its implications for human dietary exposure. *Food Chem. Toxicol.* **2022**, *165*, 113134. [CrossRef]

36. Ham, J.; Lim, W.; Park, S.; Bae, H.; You, S.; Song, G. Synthetic phenolic antioxidant propyl gallate induces male infertility through disruption of calcium homeostasis and mitochondrial function. *Environ. Pollut.* **2019**, *248*, 845–856. [CrossRef] [PubMed]

37. Ham, J.; Lim, W.; You, S.; Song, G. Butylated hydroxyanisole induces testicular dysfunction in mouse testis cells by dysregulating calcium homeostasis and stimulating endoplasmic reticulum stress. *Sci. Total Environ.* **2019**, *702*, 134775. [CrossRef] [PubMed]

38. Scientific Opinion on the re-evaluation of butylated hydroxyanisole—BHA (E 320) as a food additive. *EFSA J.* **2011**, *9*, 2392. [CrossRef]

39. Scientific Opinion on the re-evaluation of butylated hydroxytoluene BHT (E 321) as a food additive. *EFSA J.* **2012**, *10*, 2588. [CrossRef]

40. Statement on the refined exposure assessment of tertiary-butyl hydroquinone (E 319). *EFSA J.* **2016**, *14*, 4363. [CrossRef]

41. Scientific Opinion on the re-evaluation of propyl gallate (E 310) as a food additive. *EFSA J.* **2014**, *12*, 3642. [CrossRef]

42. Hernández-Fernández, J.; Guerra, Y.; Puello-Polo, E.; Marquez, E. Effects of Different Concentrations of Arsine on the Synthesis and Final Properties of Polypropylene. *Polymers* **2022**, *14*, 3123. [CrossRef]

43. Joaquin, H.-F.; Juan, L.-M. Autocatalytic influence of different levels of arsine on the thermal stability and pyrolysis of polypropylene. *J. Anal. Appl. Pyrolysis* **2021**, *161*, 105385. [CrossRef]

44. Hernández-Fernández, J.; Cano, H.; Aldas, M. Impact of Traces of Hydrogen Sulfide on the Efficiency of Ziegler–Natta Catalyst on the Final Properties of Polypropylene. *Polymers* **2022**, *14*, 3910. [CrossRef]

45. Hernández-Fernández, J.; Vivas-Reyes, R.; Toloza, C.A.T. Experimental Study of the Impact of Trace Amounts of Acetylene and Methylacetylene on the Synthesis, Mechanical and Thermal Properties of Polypropylene. *Int. J. Mol. Sci.* **2022**, *23*, 12148. [CrossRef] [PubMed]

46. Hernández-Fernández, J.; Cano-Cuadro, H.; Puello-Polo, E. Emission of Bisphenol A and Four New Analogs from Industrial Wastewater Treatment Plants in the Production Processes of Polypropylene and Polyethylene Terephthalate in South America. *Sustainability* **2022**, *14*, 10919. [CrossRef]

47. Hernández-Fernández, J.; Castro-Suarez, J.R.; Toloza, C.A.T. Iron Oxide Powder as Responsible for the Generation of Industrial Polypropylene Waste and as a Co-Catalyst for the Pyrolysis of Non-Additive Resins. *Int. J. Mol. Sci.* **2022**, *23*, 11708. [CrossRef]

48. CYTEC. Cyanox 1790 Material Safety Data Sheet. 2019. Available online: https://www.echemi.com/sds/tris4-tert-butyl-3-hydroxy-26-dimethylbenzylisocyanurate-pid_Seven42940.html (accessed on 27 October 2022).

49. Altaf, M.; Najam, T.; Jabeen, S.; Wattoo, M.; Bashair, M.; Ahmad, S.; Rehman, A. Facile synthesis of Tri-metallic layered double hydroxides (NiZnAl-LDHs): Adsorption of Rhodamine-B and methyl orange from water. *Inorg. Chem. Commun.* **2022**, *145*, 110008. [CrossRef]

50. Altaf, M.; Najam, T.; Jabeen, S.; Wattoo, M.; Bashair, M.; Ahmad, S.; Rehman, A. Heterointerface engineering of water stable ZIF-8@ZIF-67: Adsorption of rhodamine B from water. *Surf. Interfaces* **2022**, *34*, 102324. [CrossRef]

51. da Silva Costa, R.; Fernandes, T.S.M.; Almeida, E.D.S.; Oliveira, J.T.; Guedes, J.A.C.; Zocolo, G.J.; de Sousa, F.W.; Nascimento, R.F.D. Potential risk of BPA and phthalates in commercial water bottles: A mini review. *J. Water Health* **2021**, *19*, 411–435. [CrossRef]

52. Parto, M.; Aazami, J.; Shamsi, Z.; Zamani, A.; Savabieasfahani, M. Determination of bisphenol-A in plastic bottled water in markets of Zanjan, Iran. *Int. J. Environ. Sci. Technol.* **2021**, *19*, 3337–3344. [CrossRef]

53. Ghanem, A.; Maalouly, J.; Saad, R.A.; Salameh, D.; Saliba, C.O. Safety of Lebanese Bottled Waters: VOCs Analysis and Migration Studies. *Am. J. Anal. Chem.* **2013**, *4*, 176–189. [CrossRef]

54. Al-Mudhaf, H.F.; Alsharifi, F.A.; Abu-Shady, A.-S.I. A survey of organic contaminants in household and bottled drinking waters in Kuwait. *Sci. Total Environ.* **2009**, *407*, 1658–1668. [CrossRef]

55. Gambino, I.; Bagordo, F.; Grassi, T.; Panico, A.; De Donno, A. Occurrence of Microplastics in Tap and Bottled Water: Current Knowledge. *Int. J. Environ. Res. Public Health* **2022**, *19*, 5283. [CrossRef]

56. Welle, F.; Franz, R. Microplastic in bottled natural mineral water—Literature review and considerations on exposure and risk assessment. *Food Addit. Contam. Part A* **2018**, *35*, 2482–2492. [CrossRef]

57. Maxwell, O.; Olusegun, O.A.; Emmanuel, S.J.; Sociis, T.O.; Efemena, A.O.; Akinwumi, A.; Theophilus, E.A. Potential Health Risks of Heavy Metal Contents in Bottled Water from Lagos State and Its Environs, Nigeria. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, *173*, 012021. [CrossRef]

58. Nazir, M.A.; Yasar, A.; Bashir, M.A.; Siyal, S.H.; Najam, T.; Javed, M.S.; Ahmad, K.; Hussain, S.; Anjum, S.; Hussain, E.; et al. Quality assessment of the noncarbonated-bottled drinking water: Comparison of their treatment techniques. *Int. J. Environ. Anal. Chem.* **2020**, *102*, 8195–8206. [CrossRef]

59. Leavey-Roback, S. Heavy Metals in Bottled Natural Spring Water Article. 2011. Available online: https://www.researchgate.net/publication/51213966 (accessed on 3 January 2023).

60. Ding, J.; Shen, X.; Liu, W.; Covaci, A.; Yang, F. Occurrence and risk assessment of organophosphate esters in drinking water from Eastern China. *Sci. Total Environ.* **2015**, *538*, 959–965. [CrossRef]

61. Josyula, A.B.; McClellen, H.; Hysong, T.A.; Kurzius-Spencer, M.; Poplin, G.S.; Stürup, S.; Burgess, J.L. Reduction in Urinary Arsenic with Bottled-water Intervention. *J. Health Popul. Nutr.* **2006**, *24*, 298–304.

62. Mostafa, M.G.; Cherry, N. Arsenic in Drinking Water, Transition Cell Cancer and Chronic Cystitis in Rural Bangladesh. *Int. J. Environ. Res. Public Health* **2015**, *12*, 13739–13749. [CrossRef]

63. Ward, M.H.; Jones, R.R.; Brender, J.D.; De Kok, T.M.; Weyer, P.J.; Nolan, B.T.; Villanueva, C.M.; Van Breda, S.G. Drinking Water Nitrate and Human Health: An Updated Review. *Int. J. Environ. Res. Public Health* **2018**, *15*, 1557. [CrossRef]

64. Hafeman, D.; Factor-Litvak, P.; Cheng, Z.; Van Geen, A.; Ahsan, H. Association between Manganese Exposure through Drinking Water and Infant Mortality in Bangladesh. *Environ. Health Perspect.* **2007**, *115*, 1107–1112. [CrossRef]

65. Carvalho, S.M.; Santos, D. Consumo de agua embotellada en envases plásticos y sus consecuencias para la salud familiar y comunitaria. 2020. Available online: https://repositorio.unbosque.edu.co/bitstream/handle/20.500.12495/4410/Carvalho_DosSantos_Sandra_Mar%25C3%25ADa_2020.pdf?sequence=1&isAllowed=y (accessed on 12 January 2023).

66. Aslani, H.; Pashmtab, P.; Shaghaghi, A.; Mohammadpoorasl, A.; Taghipour, H.; Zarei, M. Tendencies towards bottled drinking water consumption: Challenges ahead of polyethylene terephthalate (PET) waste management. *Health Promot. Perspect.* **2021**, *11*, 60–68. [CrossRef]

67. Díez, J.R.; Antigüedad, I.; Agirre, E.; Rico, A. Perceptions and Consumption of Bottled Water at the University of the Basque Country: Showcasing Tap Water as the Real Alternative towards a Water-Sustainable University. *Sustainability* **2018**, *10*, 3431. [CrossRef]

68. Jain; Singh, A.K.; Susan, M.A.B.H. The World around Bottled Water. *Bottled Packaged Water* **2019**, *4*, 39–61. [CrossRef]

69. Hernández-Fernández, J.; Puello-Polo, E.; Trilleras, J. Characterization of Microplastics in Total Atmospheric Deposition Sampling from Areas Surrounding Industrial Complexes in Northwestern Colombia. *Sustainability* **2022**, *14*, 13613. [CrossRef]

70. Farzadkia, M.; Shahamat, Y.D.; Nasseri, S.; Mahvi, A.H.; Gholami, M.; Shahryari, A. Catalytic Ozonation of Phenolic Wastewater: Identification and Toxicity of Intermediates. *J. Eng.* **2014**, *2014*, 520929. [CrossRef]

71. Guo, L.; Hu, Y.; Lei, Y.; Wu, H.; Yang, G.; Wang, Y.; Wei, G. Vitrification of petrochemical sludge for rapid, facile, and sustainable fixation of heavy metals. *J. Environ. Chem. Eng.* **2022**, *10*, 108812. [CrossRef]

72. Wang, S.; Kalkhajeh, Y.K.; Qin, Z.; Jiao, W. Spatial distribution and assessment of the human health risks of heavy metals in a retired petrochemical industrial area, south China. *Environ. Res.* **2020**, *188*, 109661. [CrossRef]

73. Kanu, I.; Achi, O. Industrial Effluents and Their Impact on Water Quality of Receiving Rivers in Nigeria Medical Microbiology View Project Fermented Food Development View Project. 2011. Available online: https://www.researchgate.net/publication/287104597 (accessed on 13 January 2023).

74. Radelyuk, I.; Tussupova, K.; Klemeš, J.J.; Persson, K.M. Oil refinery and water pollution in the context of sustainable development: Developing and developed countries. *J. Clean. Prod.* **2021**, *302*, 126987. [CrossRef]

75. Rodil, R.; Quintana, J.B.; Basaglia, G.; Pietrogrande, M.C.; Cela, R. Determination of synthetic phenolic antioxidants and their metabolites in water samples by downscaled solid-phase extraction, silylation and gas chromatography–mass spectrometry. *J. Chromatogr. A* **2010**, *1217*, 6428–6435. [CrossRef]

76. Spectrabase. Cyanox 1790-FTIR-Spectrum-SpectraBase, 22 August 2022. Cyanox 1790 Antioxidant. Available online: https://spectrabase.com/spectrum/I3g5xqi3f4q (accessed on 18 January 2023).

77. Casagrande, M.; Kulsing, C.; Althakafy, J.T.; Piatnicki, C.M.S.; Marriott, P.J. Direct Analysis of Synthetic Phenolic Antioxidants, and Fatty Acid Methyl Ester Stability in Biodiesel by Liquid Chromatography and High-Resolution Mass Spectrometry. *Chromatographia* **2018**, *82*, 271–278. [CrossRef]

78. Alladio, E.; Amante, E.; Bozzolino, C.; Seganti, F.; Salomone, A.; Vincenti, M.; Desharnais, B. Effective validation of chromatographic analytical methods: The illustrative case of androgenic steroids. *Talanta* **2020**, *215*, 120867. [CrossRef] [PubMed]

79. Fernández, J.H.; Rincón, D.; López-Martínez, J. Development and validation of a prototype for the on-line simultaneous analysis of quality caprolactam synthesized on an industrial scale. *Methodsx* **2022**, *10*, 101952. [CrossRef] [PubMed]

80. McMurry, J.E. Synthetic Polymers. In *Organic Chemistry*; ACS Publications: Washington, DC, USA, 2011; p. 1242. Available online: https://www.aspu.edu.sy/laravel-filemanager/files/31/McMurry%20Organic%20Chemistry%208th%20txtbk_compressed.pdf (accessed on 4 January 2023).