CATÓLICA
FACULTY OF BIOTECHNOLOGY

PORTO

EVALUATION OF COMMERCIALLY AVAILABLE POST-CONSUMER RECYCLED PET TO PRODUCE BOTTLES FOR MINERAL WATER

by

Francisco Vasconcelos Brandão

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Thesis presented to Escola Superior de Biotecnologia of the Universidade Católica Portuguesa to fulfill the requirements of Master of Science degree in Food Engineering

by

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Resumo

O Polietileno Tereftalato (PET) é o principal polímero para a produção de garrafas de água e refrigerantes, sendo cada vez mais importante, no contexto global, o combate ao desperdício e descarte através da reciclagem deste importante recurso. Neste trabalho, seis resinas processo mecânicos aprovados pela EFSA foram avaliadas. As propriedades de cor, viscosidade intrínseca, temperatura de fusão, concentração de benzeno, limoneno, oligómeros e substâncias não intencionalmente adicionadas (NIAS) foram avaliadas. No que toca à determinação das concentrações de Benzeno, Limoneno e Oligómeros, foram encontrados valores superiores comparativamente ao reportado em bibliografia. As concentrações obtidas foram de 30 – 410 μg kg^{-1} PET para o benzeno, 20 – 66 μg kg^{-1} PET para o limoneno; 52 – 78 mg kg^{-1} PET para o dímero e 999 – 1394 mg kg^{-1} PET para o trímero. A concentração de NIAS detetada nas resinas conduz a um nível de exposição estimado (considerando uma garrafa de 8,5 g e 0,3 L) inferior ao correspondente à Classe 3 de Cramer da abordagem TTC para o limite de risco toxicológico.

A análise estatística dos dados pelo modelo paramétrico univariado agrupou as amostras em 3 sub-grupos de homogeneidade: o primeiro grupo compreende as amostras IN, NO e F, o segundo as amostras F, FBL e BA e o terceiro a amostra MO. A análise por componentes independentes (ICA) confirmou alguns dos resultados deste teste. Foi possível verificar a similaridade das amostras MO e BA pelos conteúdos em nonanal, F e FBL pelo etilhexilacetato, dodecano e o difenil éter e as amostras FBL e IN pelo farneceno. A amostra NO foi a única que não apresentou correlação com as restantes.

Palavras-Chave Polietileno tereftalato (PET), Benzeno, Limoneno, Oligómeros, substâncias não intencionalmente adicionadas (NIAS), materiais para contato com alimentos, SPME-GCMS, HS-GCMS, Análise individual de componentes (ICA), garrafas de água, reciclagem mecânica de PET.

Abstract

Polyethylene terephthalate (PET) is the most important polymer for the production of bottles for water and soft drinks, being increasingly important globally to reduce waste by recycling this material. In this work, six PET resins from different mechanical recycling processes, with positive opinions from EFSA, were evaluated for the properties: color, intrinsic viscosity, melting temperature and for the concentration of benzene, limonene, oligomers, and non-intentionally added substances (NIAS). Regarding the determination of Benzene, Limonene, and Oligomers, the samples in study have higher concentration values than those found in the literature. The obtained concentrations are 30 – 410 μg kg^{-1} PET for benzene, 20 – 66 μg kg^{-1} PET, for limonene and 52 – 78 mg kg^{-1} PET for PET dimer and 999 – 1394 mg kg^{-1} PET for trimer. The unknowns and NIAS concentration detected in the resins, yield and estimated exposure levels (considering a bottle of 8,5 g and 0,3 L) lower than that corresponding to the Cramer Class 3 of TTC approach for toxicology risk.

The statistical analysis by univariate approach grouped the samples into 3 subsets: one group including the samples IN, NO, and F, the second group including the samples F, FBL, and BA, and NO as the only sample in the third group. The ICA approach confirmed some results from the univariate model: it was found out that MO and BA correlate by nonanal, F and FBL by the ethylhexylacetate, dodecane and diphenyl ether, and FBL and IN by farnesene. NO showed no correlation with the remaining.

Keywords Polyethylene terephthalate (PET), Benzene, Limonene, Oligomers, Non-intentionally added substances (NIAS), Food contact material, SPME-GCMS, HS-GCMS, Independent components analysis (ICA), Water bottles, PET mechanical recycling.

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Table of Contents

Resumo 3

Abstract 4

Acknowledgments 5

List of Figures 9

List of Tables 10

Abbreviations 11

1. Introduction 12

    1.1 Goal 12

    1.2 Polyethylene terephthalate 12

    1.3 Bottle production 12

    1.4 Recycled PET Market 13

    1.5 New EU and Portuguese Frameworks for rPET 13

    1.6 Legislation for recycled PET in Food Contact Materials (FCM) 14

2. Literature Review 17

    2.1 PET Recycling processes 17

    2.2 PET Mechanical Recycling Process 19

3. Objectives 22

4. Materials and Methods 23

    4.1 Samples 23

    4.2 Sample Preparation 24

    4.3 Determination of resin color 24

    4.4 Determination of intrinsic viscosity 25

    4.5 Determination of melting temperature (T_m) 25

    4.6 Determination of limonene and benzene 25

        4.6.1 Standards preparation for calibration 25

        4.6.2 Head Space analysis 26

4.6.3 Gas chromatography – mass spectrometry 26
4.7 Oligomer Determination 26
4.7.1 Calibration standard preparation 27
4.7.2 Sample Preparation 27
4.7.3 High Performance Liquid Chromatography 27
4.8 Determination of NIAS 28
4.8.1 Standard preparation for semi-quantification 28
4.8.2 Solid Phase Microextraction (SPME) 29
4.8.3 Gas chromatography – mass spectrometry (GC-MS) 29
4.9 Data handling 29
4.9.1 SPSS analysis 29
4.9.2 Independent components analysis (ICA) 29
5. Results 31
5.1 Color 31
5.2 Intrinsic Viscosity 33
5.3 Differential scanning calorimetry 33
5.4 Limonene and Benzene 35
5.5 Oligomers 37
5.6 Non-intentionally added substances 40
5.7 Data handling 49
5.7.1 Statistical analysis of results for NIAS 49
5.7.2 Independent components analysis (ICA) 52
6. Conclusions 56
7. Further work 57
8. References 58
ANNEXES 67
ANNEX 1 - Summary of the recycling processes 68

1. Summary of the resins in study 68
2. Summary of the recycling process BA 70
3. Summary of the recycling process MO 71
4. Summary of the recycling process F 72
5. Summary of the recycling process NO 73
6. Summary of the recycling process IN 74

ANNEX 2 – Calibration curves for the detection of Benzene and Limonene 75

ANNEX 3 - Calibration curves for the detection of Oligomers 76

List of Figures

Figure 1 - Evolution of contamination of the PET throughout its lifespan. 18
Figure 2 - Visual representation of the colors corresponding to the mean values of L* a* b* obtained for each standard. 32
Figure 3 – Visual representation of the colors corresponding to the mean values of L* a* b* obtained for each sample. 32
Figure 4 - DSC thermograms of the samples during heating of the second cycle. 34
Figure 5 - Concentration of benzene and limonene on the samples. 37
Figure 6 - Results for oligomer content on the samples. 38
Figure 7 - The three resin groups from the Tuckey HSD test. 50
Figure 8 - Mean values comparison among the studied samples. 51
Figure 9 - Reduced TIC chromatograms overlay. 53
Figure 10- The three ICs with significant correlation. 54
Figure 11 - Interactions between the three ICs. 55
Figure 12 - Diagram of the BariQ recycling process. 70
Figure 13 - Diagram of the MOPET A recycling process. 71
Figure 14 - Diagram of the FENC recycling process. 72
Figure 15 - Diagram of the RPET Nosinyec recycling process. 73
Figure 16 - Diagram of the INDORAMA recycling process. 74
Figure 17 - Calibration curve for the benzene. 75
Figure 18 - Calibration curve for limonene. 75
Figure 19 - Calibration curve for the PET dimer. 76
Figure 20 - Calibration curve for the PET trimer. 76

List of Tables

Table 1 – Details of the recycled PET resins in study. 23
Table 2 - Decontamination efficiencies of the challenge test for the different samples (EFSA, 2013a, 2013b, 2013c, 2013d, 2014). (* - the concentration was below the detection limit; ** - not detected on the sample before the process; n.a.- not tested) 23
Table 3 - Values of L*a*b* for the standards. 24
Table 4 - Details of standard solution for NIAS semi-quantification. 28
Table 5 - Values for L* a* b* (mean) for samples. Presented ΔE values correspond to the color distance of the samples relative to Standard 1 / Standard 2. 31
Table 6 - Intrinsic viscosity obtained experimentally and specification values (dL g^{-1}). 33
Table 7 - Melting temperature in ºC (mean ± standard deviation) 34
Table 8 – Concentration (µg kg^{-1} PET) of Benzene on the rPET resins and total migration (µg kg^{-1} of water) on a worst-case scenario (8,5 g and 0,3 L). 35
Table 9 – Concentration (µg kg^{-1}) of limonene on the rPET resins and total migration (µg kg^{-1} of water) on a worst-case scenario (8,5 g and 0,3 L). 36
Table 10 - Results for the total concentration of oligomers (mg kg^{-1}PET) and the total migration (mg kg^{-1} of water) on the worst-case scenario (8,5g and 0,3L). 38
Table 11 - NIAS detected and their possible origin on the PET resin. 40
Table 12 – Concentration (µg kg^{-1}) of each compound on the respective PET resin. 43
Table 13 – Concentrations in polymer (µg kg^{-1}PET) for each class of NIAS 46
Table 14 - Total migration (µg kg^{-1} food) values for a worst-case scenario (bottle with 8,5 g and 0,3 L). 47
Table 15 – Normality and equality of variances tests. (a. Lilliefors Significance Correction; b. Based on mean; c. Tests the null that the error variance of the dependent variable is equal across groups.) 49
Table 16 - Test of between-subjects effects. 50
Table 17 - Information obtained from EFSA reports regarding the resins in study 68

Abbreviations

2,4DTBP – 2,4-Di-tert-butylphenol

DBP – Dibutyl phthalate

DiBP – Diisobutyl phthalate

DMP – Dimethyl phthalate

DSC – Digital scan calorimetry

EFSA – European Food Safety Authority

EPR – Extended producer responsibility

EU – European Union

FCA – Food contact article

FCM – Food contact materials

GC – Gas chromatography

HS – Head space

MeOH – Methanol

MS – Mass spectrometry

NIAS – Non-intended added substances

PET – Polyethylene terephthalate

rPET – Recycled polyethylene terephthalate

SPME - Solid Phase Microextraction

SUP – Single use plastics

Tg – Glass transition temperature

Tm – Melting temperature

1. Introduction

1.1 Goal

Super Bock Group (Leça do Balio, Portugal), previously known as Unicer Bebidas de Portugal SGPS SA, is the largest beverage player in Portugal. It is widely known for its beer, Super Bock, but the company also has other products and areas of business, such as bottled water and soft drinks. This work arises from Super Bock Group's intention to increase the content of recycled material in polyethylene terephthalate (PET) water bottles to meet future European Union requirements and, consequently, from the need to assess the impact of this measure on the quality and safety of the product.

1.2 Polyethylene terephthalate

Polyethylene terephthalate is considered one of the main polymers of the past two decades due to its extensive usage. It is considered an excellent material for a variety of applications, being widely used to produce bottles. When compared with glass bottles, it has a lower breakage probability and is lighter. It has excellent properties of tensile and impact strength, chemical resistance, clarity, processability, and reasonable thermal stability. It is an inert polymer, an important factor since it means that the interactions between the packaging material and the foodstuff are minimal when compared to other polymers used in packaging. Commercial PET has a range of intrinsic viscosity (η) values between 0.45 and 1.2 dL g^{-1}. The PET chain is stiff at temperatures higher than the glass transition temperature (Tg), unlikely other polymers. The inflexibility of the chain affects the PET's structural properties, such as thermal transitions (Awaja and Pavel, 2005; Nasser *et al.*, 2005; Welle, 2011).

1.3 Bottle production

The manufacturing process of PET bottles starts with the injection molding of the PET resin into a bottle preform. This is done in mold cavities under vacuum followed by rapid cooling, and then the preform, which has a test tube-like shape, is ejected. The second step, blow molding of the preform, involves heating and mechanical stretching of the preform on its axial direction and blow molding into the bottle shape using hot air (Konkol, 2004). During stretching and blow molding, polymer chains align themselves closely in the direction of the stretch, improving the gas barrier and mechanical properties such as tensile strength, Young's modulus, and elongation at break (Konkol, 2004).

1.4 Recycled PET Market

The market for PET packaging is extremely competitive. Major players are now focused on expanding their client/supplier relationship with mutual development agreements. However, environmental sustainability concerns, consumer awareness, and new EU approved measures are issues that have led to an increasing interest in recycled PET - rPET. In this context, in Europe, an average increase in rPET consumption is expected compared to the rest of the globe. Furthermore, an increase of 37% in PET bottle production relative to 2018 is expected by 2028 (Mordor Intelligence, 2016, 2018).

The availability of rPET in Europe depends on post-consumer bottle collection schemes implemented across the continent. There is a consensus that the market supply capacity of the PET flakes and pellets will increase as well as the demand. In several countries, legislation that may force the increase in recycled PET volumes applies. Clear (uncolored) recycled resin was the rPET with the largest market segment in 2018 and this position is expected to be maintained, as clear resin is more versatile regarding second-life applications. Companies are focused on securing a safe stock of rPET for food-grade applications for the coming years to meet demand (Grand View Research, no date; ICIS, no date). The competition between large players in the soft drinks sector also contributes to the scarcity of recycled resin, due to commercial deals with the suppliers that limit the opportunities of small players to access the recycled resin.

Also, regarding rPET, the demand from the textile industry has decreased for some years. However, a significant increase is expected in the next few years as a response of the industry to the EU actions to promote a circular economy, which will contribute further to the scarcity of the recycled material (Mordor Intelligence, 2016).

The European consumer market is characterized by their willingness to pay premium prices for greener materials, which is another incentive for companies to implement rPET in their packaging (Research and Markets, no date).

1.5 New EU and Portuguese Frameworks for rPET

In the coming years, the European Union will change the way it deals with plastic due to the approval of the Directive (EU) 2019/904. These new measures plan to act on the top 10 of Single Use Plastics (SUP) contributing to marine litter often found on European beaches, with plastic bottles present on the top tier.

Directives for municipal waste and plastic packaging waste have already been enacted. Each Member State is expected to achieve recycling rates of 65% for municipal waste and 55% for plastic packaging waste by 2030. Such targets will be achieved by setting up systems of differentiated collection for these products, being each Member State responsible for implementing the most convenient system (EU Commission, 2018).

Concerning beverage bottles, the new measures will act on the Extended Producer Responsibility programs (EPR), packaging design modifications and deposit refund systems (EU Commission, 2018). For EPR programs it is intended to introduce the obligation of producers to support the cleaning costs of items in the top 10 of SUP, complementing the Directive on Packaging Waste (EU Commission, 2018). Regarding product design modifications, the plastic bottle systems should have a non-removal plastic cap to avoid losing small plastic components that will fragment into microplastics (EU Commission, 2018; European Commission, 2018). Furthermore, regarding beverage bottles, the EU means to implement deposit refund systems (DRS) in at least 75 categories of beverage packaging. The amount of the refund may vary between the Member States. These measures may imply that the producers make investments in new infrastructures (EU Commission, 2018). These measures will allow for the reduction of 157 million beverage bottles on the beaches of the European Union, as well as the reduction of the value loss of these products, which is between 70 and 105 million euros per year (EU Commission, 2018).

In Portugal, the Portaria 202/2019 of 2019-07-03 defines the pilot program for the collection scheme of PET packages, to be operational until 30 June 2021. The packers and the importers of packaged products are responsible for the implementation of the recollection scheme, which will operate via deposit machines installed in large reseller stores, especially food resellers. The user will receive a reward for the deposited package. The program goals are 50% collection of PET packages, 97% of PET recycling, and 50% of rPET on new PET bottles composition (Patto, 2019).

1.6 Legislation for recycled PET in Food Contact Materials (FCM)

Prior to 2008, the use of post-consumer recyclates for applications in direct contact with food was regulated at a national level. Since May 2008, with the introduction of the Regulation (EC) No 282/2208, recycled plastic materials and articles for food contact can only be placed on the market if the recycled plastic was obtained from an approved recycling process. For the process to be approved, the company needs to submit the process to the European Food Safety

Authority (EFSA) for evaluation. After a positive scientific opinion from EFSA, the Commission may decide to grant an authorization for the recycling process, adding the process to a list of authorized processes from which recycled plastics can be obtained to produce food packaging and other food contact materials (European Commission, 2008; Welle, 2013).

The evaluation principle of EFSA starts with the cleaning efficiency of the recycling process. The cleaning efficiency is determined in a "Challenge Test" carried out on PET that has been deliberately contaminated with a set of surrogates (such as Toluene; Chloroform; Phenylcyclohexane; Benzophenone; Lindane; Chlorobenzene; Trichloroethane; Methyl stearate and o-Cresol). The intent is to simulate the improper use of PET bottles before collection and obtain a decontamination efficiency value as high as possible for the evaluated surrogates. The artificially contaminated plastic is subjected to the recycling process, and the difference between the initial concentration and the residual concentration of surrogates in the finished product is a measure of the cleaning efficiency of the recycling process.

With the results obtained for the decontamination efficiency in the challenge test, the residual concentration of each surrogate in recycled PET (Cres) is calculated, assuming a reference contamination level of 3 mg surrogate per kilogram of virgin PET (Equation 1).

$$Cres = 3\ mg\ surrogate \cdot kg^{-1}\ PET\ \times \left(1 - \frac{Decontamination\ efficiency\ (\%)}{100}\right) \quad (1)$$

The result is compared with a concentration obtained by mathematical modelling (Cmod), representing the concentration of surrogate in the recycled PET that, according to an accepted mathematical model, gives a specified migration value M (mg kg^{-1} PET). Cres should be lower than Cmod, which represents the concentration of surrogate in the recycled PET that, according to an accepted mathematical model, gives a specified migration value M (mg kg^{-1} PET). Cmod is estimated as the concentration in the polymer that migrates under certain conditions (1 year at 25 ºC), yielding an exposure of 0.0025 µg·kg bw^{-1}·day^{-1}. Different scenarios of consumption are considered depending on whether the packaging is intended to pack food for adults, toddlers, or infants. A fivefold multiplication to consider a worst-case scenario is applied. This migration value is determined using a mathematical model which involves the following variables: molecular weight of the surrogate, simulant, temperature, time and area of contact, packaging thickness, and surrogate solubility. The model parameters are the diffusion and partition coefficients.

If Cres<Cmod then PET recycled by the evaluated process can be fully incorporated into the production of new packages. However, if this condition is false, then the recycled PET can be incorporated in a mixture of virgin PET to lower the Cres, or the process can be redesigned for better values of decontamination efficiency.

Besides the efficiency of the process in removing contaminants from prior use and potential misuse, the fraction of PET packages in the recovered stream, coming from nonfood applications, should not be higher than 5% (EFSA, 2011).

2. Literature Review

2.1 PET Recycling processes

The PET recycling industry flourished due to environmental pressure for waste management. PET is a non-degradable plastic under normal conditions, and costly and complex processes are required to promote biological degradation (Awaja and Pavel, 2005). Therefore, the main options for closing the PET loop (circularity) are chemical recycling by depolymerization, or mechanical recycling, which mainly involves physical decontamination operations of the bottle fragments (flakes) and re-melting the PET. The increase of PET bottle-to-bottle recycling plants in operation in Europe has contributed to the increase in the quantity of post-consumer PET bottles that have been collected in Europe for recycling: 1.6 million tons of used PET were collected and sent off for recycling in 2011. These figures were equivalent to 51% of the PET bottles in the marketplace being recycled (Awaja and Pavel, 2005; Welle, 2013).

Bottle-to-bottle recycling of post-consumer PET requires a process capable of removing substances absorbed by the polymer during any stage of the material lifespan, and substances possibly formed during polymer processing and degradation, including contaminants and generally non-intentionally added substances (NIAS). The term NIAS includes all substances that have not been intentionally added to an FCM and food contact article (FCA). The origins are numerous, but these compounds can be grouped into a few main categories, such as side products, breakdown products, and contaminants. The introduction of NIAS in FCM and FCA may occur throughout the life cycle, from production to consumer. There is an increasing interest in NIAS as the analytical methods have increased in sensitivity, and are, therefore, capable of detection and identification of possible hazards that may migrate from FCMs and FCAs (Geueke, 2018). Figure 1 illustrates the potential for contamination throughout the material lifespan. During industrial processing, a much lower potential of contamination needs to be considered, and a simple re-extrusion process can be applied as a recycling step. In the transformation of the raw PET material (flakes or pellets) into a bottle (injection and blow molding), the scraps, leftovers or defects may be reintroduced on the melting step for new injection. It is performed on-site, and, therefore, the material is clean and without contamination, similar to the virgin input (Karayannidis and Achilias, 2007; Lettieri and Baeyens, 2009). In the industrial site where the bottle is filled, the recovered PET is necessarily contaminated with residues of the product it may have contacted with during filling, and those

must be removed during the recycling process. The recovery of post-consumer used bottles has the highest level of potential contamination, because of the longer time the product has contacted with its contents and the possible misuse of the bottles, such as storing automobile oils, household or garden chemicals, before sending them into the recovery stream.

The chemical safety of PET recycling has been extensively studied, with a focus on the evaluation of migration of several compounds, including NIAS, acetaldehyde, limonene, and surrogates foreseen by EFSA for the challenge test. Also, studies on the use of functional barriers in rPET to limit migration into the food, mathematical modeling to describe the decontamination process, the impact of cross-contamination in the process efficiency, and oligomer determination have been reported (Franz, Mauer and Welle, 2004; Cruz *et al.*, 2006; Bentayeb *et al.*, 2007; Welle and Franz, 2008; Welle, 2008, 2013, 2016; Cruz, Zanin and Nerin, 2009; Hurley *et al.*, 2013; Dutra *et al.*, 2014; Ubeda, Aznar and Nerín, 2018).

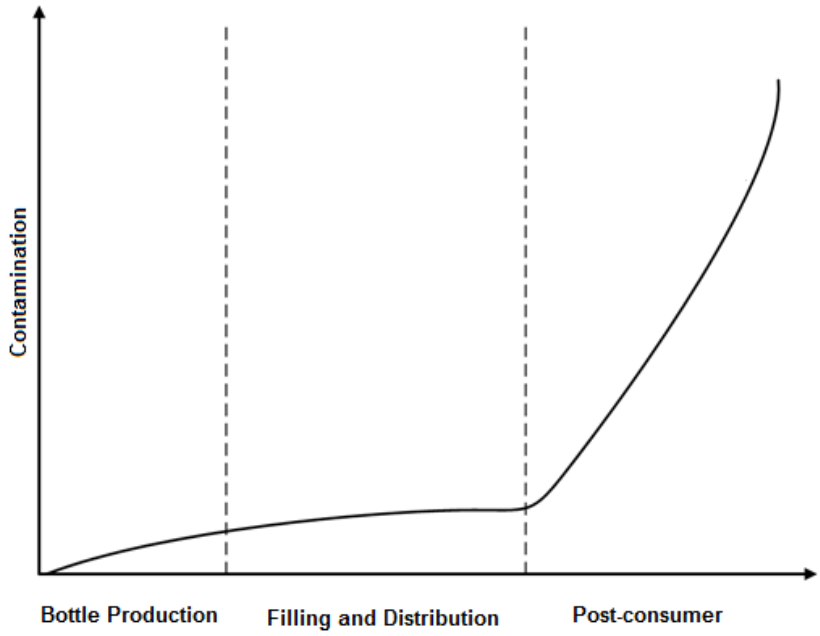

Figure 1 - Evolution of contamination of the PET throughout its lifespan.

Mechanical recycling is the process most widely used today for material recovered in the filler, at any point of the distribution chains and after consumer use. It started to be applied globally in the 1970s and includes the sorting and separation of different wastes with reduction of waste size. It can only be performed on single-type polymers, as PET. With the increase of complexity and contamination of the polymer, the harder its recycling becomes. The polymer does not change during the process, but in each recycling cycle, its properties can degrade due to the decrease of molecular weight via photo-oxidation and mechanical stress. Branching and

chain-scission can happen if water and impurities are present. For the bottles collected from post-consumer, a super clean mechanical recycling process should be applied since the bottles from this step can be heavily contaminated (Karayannidis and Achilias, 2007; Lettieri and Baeyens, 2009; Welle, 2011).

In the last 20 years there has been a great development in PET recycling processes, resulting in sophisticated decontamination processes capable of decontaminating post-consumer contaminants to concentration levels close to those present in virgin PET (Konkol, 2004; Welle, 2011).

Not all PET bottles are suitable for mechanical recycling: color, label type, inks, and glues may limit the capability of a process in separating and producing a good quality recycled stream. Opaque dark-colored packaging greatly restricts the use of rPET, while the recycling of clear or light blue PET allows greater versatility of applications in the production of new packaging with rPET resins. Polyvinyl chloride (PVC) sleeve type labels are difficult to be mechanically removed during the sorting process and are difficult to be separated from PET after milling by flotation, as they have similar density properties as PET. The use of insoluble inks and adhesives difficult to be removed by the alkaline wash process should also be avoided (ECOIBERIA, 2019).

Despite the existence of chemical recycling, this work will only address mechanical recycling processes for post-consumer PET.

2.2 PET Mechanical Recycling Process

The common recycling process of PET starts with the collection of PET bottles. These are processed into flakes and then subjected to two steps of aqueous washing: first, they are hot washed with a solution of 2 % NaOH and detergent at 80 °C followed by a cold wash only with water (Awaja and Pavel, 2005).

This washing step is followed by drying to minimize the water content of flakes, reducing hydrolytic degradation, and allowing higher quality of the rPET melt. For drying, the temperature used by the producers is 140 ºC to 170 °C for 3 to 7 hours. Under normal conditions, no more than 50 ppm of water is allowed in the PET flakes, which results from using dryers operating at 170 °C for 6 hours before they are fed to the extruder (Awaja and Pavel, 2005).

The post-consumer PET flakes can be processed in a regular extruder at 280 °C with vacuum degassing for decontamination. However, under these conditions, due to the presence of possible contaminants, the produced granules have low molecular weight caused by the action of degradation reactions, which is the main disadvantage of this type of processing. The main advantage of mechanical recycling is the simplicity of the process, the low investment required, as well as the fact that it is environmentally friendly (Awaja and Pavel, 2005). Stabilizers may be used to protect chain degradation and formation of by-products, to increase molecular weight and intrinsic viscosity. The application of vacuum during processing to remove volatile contaminants and water, as well as a step for solid-state polymerization (SSP), is included. The SSP step uses a lower melting temperature that significantly reduces the effect of degradation reactions, together with a vacuum / inert gas flow (Awaja and Pavel, 2005).

On April 2019 there were 109 processes from 93 companies with a favorable opinion published by EFSA. These companies are mainly present in Europe, with 16 companies located in Germany. Some recycling technologies have been licensed to several companies, for example, Starlinger Decon and EREMA Basic.

The recycling process can have flakes, pellets, or sheets as output, being pellets the most common one. According to the published information (EFS, 2016; EFSA, 2016a, 2016b, 2017), each output has its own processes with different decontamination efficiencies. Regarding flakes, the most efficient process is MOPET-FLAKE based on the technology MOPET-FLAKE. For film, the process RPC Cobelplast based on the technology RPC CobelPlast with Bandera superclean is the most efficient. For powder, the Phoenix-ESPS process, which is based on the technology Phoenix-ESPS, is the most efficient. For pellets, the process with higher efficiency is the Märkische Faser based on the technology NGR.

More information about all the approved processes by EFSA is available at https://tinyurl.com/yxwxrk9d and https://tinyurl.com/tqda9jc.

In this work different mechanical recycling processes, based on different technologies, were evaluated: EREMA Basic, Starlinger IV+, MOPET, Buhler, and RPET NOSINYEC/OHL. All these processes follow the typical steps of PET recycling:

- Washing
- Drying
- Extrusion
- Crystallization

- Solid-state-polymerization (SSP reactor)

All of them work with vacuum degassing except for Buhler C that includes one of the steps under inert gas flow. A step of SSP is common to every process of PET recycling, except for EREMA Basic, since it gives the rPET higher intrinsic viscosity values and aids in the decontamination (Cruz and Zanin, 2006; Starlinger & Co. Gesellschaft m.b.H., 2008; Thiele, 2016). Detailed information on the process conditions such as temperature, time, vacuum, and airflow were not available as they are considered confidential. Further information on the technologies can be found in respective EFSA opinions (EFSA, 2013a, 2013b, 2013c, 2013d, 2014).

3. Objectives

The present work had the following objectives:

(i) To evaluate the characteristics of different recycled PET commercially available, focusing on the parameters: color; intrinsic viscosity and melting temperature and concentration in limonene, benzene and oligomers.

(ii) To gather information on the level of other potential migrants present in actual commercially available recycled PET for food contact, focusing on NIAS.

The resins studied were recycled through different mechanical recycling processes with positive EFSA opinions for application as food contact materials.

4. Materials and Methods

4.1 Samples

Six samples of rPET pellets, from different recycling processes and technologies, were provided by Logoplaste (Cascais, Portugal): MO, NO, BA, and F were 100% recycled PET (rPET) and FBL and IN consisted of blends of virgin and recycled PET. These samples were selected because of their commercial availability for industrial use and different technologies of mechanical recycling of PET (*Table 1*). More details for each process can be found in *ANNEX 1 - Summary of the recycling processes*.

Table 1 – Details of the recycled PET resins in study.

Resin	***Technology***
MO	MOPET
NO	RPET NOSINYEC/OHL
BA	Starlinger IV+
F	Buhler C
IN	Erema Basic

Decontamination efficiencies for the surrogates obtained in the challenge tests, as reported in the respective EFSA opinions can be found on *Table 2*.

Table 2 - Decontamination efficiencies of the challenge test for the different samples (EFSA, 2013a, 2013b, 2013c, 2013d, 2014). *(* - the concentration was below the detection limit; ** - not detected on the sample before the process; n.a.- not tested)*

Surrogates	**Decontamination efficiency (%)**				
	BA	MO	F	NO	IN
Toluene	99,9	>99,8*	>99,4	99,9	98,4
Chloroform	99,9	n.a.	n.a.	99,9	98,6
Phenylcyclohexane	99,9	>99,4*	98,9	97,7	94,7
Benzophenone	98,4	>99,9*	99,3	96,5	92,4
Lindane	90,9	n.a.	n.a.	n.a.	n.a.
Chlorobenzene	n.a.	>99.4	>99,7	99,6	98,3
Trichloroethane	n.a.	**	n.a.	n.a	n.a.
Methyl stearate	n.a.	>99.9	99,2	98,2	95,5
o-Cresol	n.a.	>99.9	n.a.	n.a	n.a.
Methyl salicylate	n.a	n.a	n.a	99,8	94,0

EFSA recommends a set of surrogates representative of common PET contaminants: Toluene, Chlorobenzene, Methyl salicylate, Phenylcyclohexane, Benzophenone, Lindane, and Methyl stearate (EFSA, 2011). Toluene, Phenylcyclohexane, and Benzophenone were used as surrogates in all cases. Several surrogates were used in other cases: Chloroform, Lindane, Chlorobenzene, Trichloroethane, Methyl stearate, o-Cresol, and Methyl salicylate. IN resin has the worst efficiency decontamination percentages on average for the surrogates in study when compared with the other samples. This may be due to the absence of an SSP step. As an opposite, MO has the best efficiencies, being worth the mention that the process was capable of lowering the concentration of some surrogates to a level below the detection limit of the analysis.

4.2 Sample Preparation

Pellets from each sample were ground in a grinder (Retsch SM 100) with a 5 mm sieve to obtain a powder, increasing the contact area and improving extraction for the determination of NIAS, limonene, and benzene and increasing sample homogeneity. To minimize the heating effects of the grinding process, samples were ground with liquid nitrogen, added to the pellets before the process. After a sample was ground, the grinder surface was cleaned with compressed air, removing remaining particles to avoid cross-contamination.

4.3 Determination of resin color

For determination of color, the samples were prepared as in section 4.2. The CIELAB color space was used and the L*a*b* values were recorded with a colorimeter (CR-400 Chroma Meter from Konica Minolta). The colorimeter was calibrated with a CR-A43 Calibration Plate nº 19733078 with the coordinates Y = 93,47, x = 0,3140 and y = 0,3202 for the illuminant C and Y = 93,47, x = 0,3165 and y = 0,3330 for the illuminant D65.

Logoplaste currently uses two resins to produce water bottles for Super Bock Group according to the availability of resin stocks. These two resins were used as standards for the comparison of L*a*b* values with the samples in study. The standards have the color characteristics as shown in Table 3.

*Table 3 - Values of L*a*b* for the standards.*

	L*	a*	b*
Standard 1	78,00	-2,30	-1,25
Standard 2	83,97	3,43	-3,65

4.4 Determination of intrinsic viscosity

The determination followed the ASTM D4603 standard. A 60:40 w/w mixture of phenol and 1,1,2,2-Tetrachloroethane was used as a solvent to prepare the sample solutions at a concentration (C) of 0,5 g dL^{-1}. Two replicates of each sample solution were prepared and analyzed, to determine the relative viscosity (η_r), corresponding to the ratio between the flux time of the polymeric solution and solvent. The determination was made at 30 ºC, with a viscometer (Ubbelohde 50113/lc; SI Analytics), with an automatic flow time system and a thermostatic bath (Lauda Viscocoo16; Lauda). The intrinsic viscosity was calculated with Billmeyer Equation (1):

$$IV = 0{,}25 \times (\eta_r - 1 + 3 \times ln\, \eta_r)/C \qquad (2)$$

These tests were performed in the laboratory of Polo de Inovação em Engenharia de Polímeros – PIEP (Guimarães, Portugal).

4.5 Determination of melting temperature (T_m)

The melting temperature of the rPET resins was determined by differential scanning calorimetry (DSC) using aluminum dishes. A Shimadzu DSC-60 colorimeter was used and operated under a nitrogen flow of 20 cm^3 min^{-1}, in a temperature range of 25-350 ºC, with a 10 ºC min^{-1} rate. Results from the second heating cycle were considered.

4.6 Determination of limonene and benzene

The substances were quantified in the resins by head-space GC-MS and external calibration. An internal standard was also used.

4.6.1 Standards preparation for calibration

Two stock solutions, one with 10 mg benzene and the other with limonene both in methanol (MeOH), were prepared in volumetric flasks of 25 mL. From these two stock solutions were pipetted 0 (pad 0) to 5 mL (pad 5) of each stock solution in 5 mL volumetric flasks. The final concentrations of benzene in the calibration solutions were: 0,000; 0,066; 0,132; 0,198; 0,329, 0,659 mg mL^{-1}, for limonene: 0,000; 0,063; 0,125; 0,188; 0,314; 0,627 mg mL^{-1}.

A stock solution of deuterated benzene (benzene-d6) was prepared as an internal standard, with 35 mg of deuterated benzene in MeOH on a volumetric flask of 5mL. 100 µL of

benzene-d6 were added to each calibration solution. The final volume of each solution was considered 5,1 ml.

One (1) µL of each calibration solution was analyzed as described in section 4.6.2.

A good linear fit was obtained for both calibration curves (R^2=0,9999 for benzene and R^2=0,9997 for limonene) with a limit of detection of 9,14 µg kg^{-1} of PET (benzene) and 9,36 µg kg^{-1} of PET (limonene), and limit of quantification of 30,46 µg kg^{-1} of PET (benzene) and 31,22 µg kg^{-1} of PET (limonene). In ANNEX 2 – Calibration curves for the detection of Benzene and Limonene.

4.6.2 Head Space analysis

One (1) gram of sample prepared as in section 4.2 with the addition of 1 µL of pad 0 calibration solution, was sealed in a 22 mL headspace vial and equilibrated at 200 ºC for 60 min following injection in the GC-MS. The analysis was performed in replicate. The calibration solutions were equilibrated and analyzed in the same conditions.

4.6.3 Gas chromatography – mass spectrometry

The gas chromatograph (GC 3800 Varian, USA) was equipped with an autosampler Combipal (CTC Analytics, Switzerland). Injections of 1 mL (split 1:10) were made at 250 ºC.

A separation column SLB-SMS column (30 m length, 0.25 mm internal diameter and df = 0.25 µm) was used. The oven temperature was kept at 40 ºC during the injection (10 min), then the temperature was increased to 280 ºC at 10 ºC min^{-1}. The gas carrier was helium with a total run time of 34 min.

A mass spectra detector (Saturn 2000, USA), with the source and carrier line kept at 220 ºC, operating in electron impact (EI) mode (70 eV) with ion monitoring fullscan between 45-140 m/z with Reconstructed Ion Current (RIC) at 78 m/z (benzene), 84 (IS) and 67+79+93+121+136 (limonene). Quantification was based on the ratio between the chromatographic peak area of the analyte and the internal standard (benzene-d6).

4.7 Oligomer Determination

Oligomers in the resins were determined by high-performance liquid chromatography (HPLC) with a UV/VIS spectrometer detector and external calibration.

4.7.1 Calibration standard preparation

An oligomer stock solution with 20 mg L^{-1} of PET 1st series cyclic dimer (CAS 24388-68-9) and PET 1st cyclic trimer (CAS 7441-32-9) was provided by JRC. From this solution, calibration solutions were prepared by dilution with acetonitrile. The volumes 0; 0,025; 0,05; 0,1 and 0,2 mL were pipetted into 10 mL volumetric glass flaks. The final concentration of dimers and trimers in the solutions were in the range 0 – 0,4 mg L^{-1}. The solutions were analyzed as described in section 4.7.3.

A good linear fit (R^2 = 0,9999 for PET dimer and R^2 = 1,0000 for PET trimer) was obtained with a limit of detection of 2,91 mg kg^{-1} of PET (PET dimer) and 1,60 mg kg^{-1} of PET (PET trimer), and a limit of quantification of 9,9 mg kg^{-1} of PET (PET dimer) and 5,33 mg kg^{-1} of PET (PET trimer). The calibration curves can be found in ANNEX 3 - Calibration curves for the detection of Oligomers**.**

4.7.2 Sample Preparation

The samples for this analysis were prepared as in section 4.2. Then, 2,5 g of each sample powder was extracted with 5 mL of dichloromethane at 40 ºC for 7 days following evaporation until dryness. Reconstitution in 10 mL of acetonitrile was performed with the assistance of an ultrasonic bath without heating for 15 minutes, to guarantee the total solubilization. The extract was filtered (0,45 µm PTFE filter) and analysed by HPLC in replicate. Samples were diluted 100 times to fit the calibration curve.

4.7.3 High Performance Liquid Chromatography

The samples were separated by liquid chromatography in a Beckman Coulter HPLC system equipped with an Agilent Zorbax Eclipse XDB-C18 column (150×4,6 mm), with 5 µm particle size. Acetonitrile HPLC Chromasolv gradient grade (A) and ultrapure water (B) were used as the mobile phase and a gradient program was applied: from 60% B to 25% B in 6 min, hold at 25% B for 13 min, from 25% B to 5% B in 2 min, from 5% B to 60% in 1 min and hold at 60% B for 1 min. The flow rate was 2,0 mL min^{-1} and the injection volume was 100 µL. The runs were performed at 40 ℃ (± 1,0 ºC). The column was coupled to a Beckman UV detector with an UV detection wavelength of 240 nm.

4.8 Determination of NIAS

NIAS were determined by SPME GS-MS in fullscan mode. The version 2.2 June 2014 of the NIST library was used to identify the substances. The criteria used for compound identification was made considering the highest similarity score and the NIST library guidelines for compound identification, where a match factor (SI) value between 800-900 is accepted as a good mass spectral match and values higher than 900 are an excellent match. A semi-quantification was performed using a standard mixture.

Methods available in the literature were searched and considered. Nerìn (2003) evaluated screening methods for contaminants in recycled PET flakes. Headspace, liquid extraction (LE), and supercritical fluid extraction followed by GC-MS were compared. Results indicated that head-space is a valid technique. Kassouf (2013) optimized the conditions of head-space/solid-phase microextraction following GC-MS. Preliminary analysis (not presented) was performed to compare the higher temperature (200 ºC) HS-GS-MS with the SPME-GC-MS at a lower temperature (85 ºC) and with LE-GC-MC. Results indicated that the best option was the SPME-GC-MS for the general NIAS analyses and that was followed in the present work.

4.8.1 Standard preparation for semi-quantification

A solution with 1µL of several standards representative of different chemical classes was prepared in methanol with a total volume of 25 mL. This mixture was used as calibration assuming that the response factor of each compound in the sample is the same of the standard assigned to that class of compounds. *Table 4* presents the concentration on the solution and the respective ion (or total ion count) used for semi quantification. Unknowns were semi-quantified in tetradecane.

Table 4 - Details of standard solution for NIAS semi-quantification.

Standard 1	***mg mL^{-1}***	***ions(s)***
DiBP	0,368	149
DBP	0,340	149
2,4DTBP	0,148	191 + 206
Benzophenone	0,200	105 + 182
Phenol	0,368	94
Ethyl benzene	0,640	91
Tetradecane	0,464	TIC

Standard 1	*mg mL^{-1}*	*ions(s)*
Nonanal	1,548	TIC
DMP	0,428	163
Naphthalene	0,056	128

4.8.2 Solid Phase Microextraction (SPME)

Three (3) grams of the sample prepared as in section 4.2, were sealed in a 22 mL headspace vial that was heated at 85 ºC for 45 min to allow extraction by the SPME fiber (Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS). The system was on a pre-heating program for 15 min at 85 ºC prior to the sample insertion for extraction. Two replicates were analyzed.

4.8.3 Gas chromatography – mass spectrometry (GC-MS)

A gas chromatograph (GC 456, SCION, UK) equipped with an autosampler (Combipal, CTC Analytics, Switzerland) operating in splitless mode was used.

A separation column SLB-SMS column (30 m length, 0.25 mm internal diameter and df = 0.25 μm). The desorption of the SPME fiber was made at 250 ºC for 15 min with a splitless injection time of 5 min. The oven temperature was kept at 40 ºC during injection (10 min), then the temperature was increased to 300 ºC at 5 ºC min^{-1} and held for 3 min. The gas carrier was helium, with a flow of 1 mL min^{-1} and a total run time of 65 min. The mass spectrometer was operated in electronic impact scan mode at 70 eV from 29 to 700 m/z.

4.9 Data handling

4.9.1 SPSS analysis.

The data obtained for the semi-quantification of NIAS was analyzed with SPSS (Version 24 from IBM), applying univariate general linear model and Tuckey tests for multiple comparisons, after the normality and variance equality tests.

4.9.2 Independent components analysis (ICA)

The data set consisted of 21 TIC chromatograms of the 6 recycled plastic samples, analyzed for 3 replicates each, in addition to 3 blanks. Therefore, the data matrix (21 × 3303) was composed of 21 rows corresponding to the 21 TICs and 3303 columns corresponding to retention times on which intensities were recorded. Before any chemometric treatment, the data

matrix was reduced by removing fiber and solvent peaks as well as the empty region at the end of the chromatogram. The new reduced matrix X (21 × 1983) was used for subsequent data analysis.

Independent components analysis (ICA) was applied on the reduced data matrix of the TIC chromatograms. These observed signals are considered to be linear mixtures of source signals. ICA aims to extract new latent variables, called Independent Components (ICs), which are linear combinations of the original variables and are assumed to correspond to source signals. ICA aiming to extract source signals from mixtures, means that the obtained ICs are easier to interpret and useful for qualitative and quantitative analyses.

The general model of ICA can be described as in Equation 3:

$$X=AS \tag{3}$$

Where X is the data matrix (21 × 1983), A is the matrix of coefficients (proportions) specifying the relative contributions of the source signals to each mixture and S is the matrix of extracted signals (the independent components, ICs). ICA aims to determine both A and S, knowing only X. The Joint Approximate diagonalization of Eigenmatrices (JADE) algorithm was used (Rutledge and Jouan-Rimbaud Bouveresse, 2013, 2015). The optimal number of ICs was calculated by ICA-by-blocks procedure and validated by Random_ICA (Kassouf, Jouan-Rimbaud Bouveresse and Rutledge, 2018).

5. Results

5.1 Color

Color is one of the first sensorial stimuli that the consumer has when interacting with the PET bottle, particularly for water, which is colorless. Typically, PET bottles have a blueish crystalline color, and a deviation from the standard can negatively impact the consumer's buying decision. *Table 5* presents the results for each coordinate of the LAB color space for the samples in study and for the two standards that Logoplaste uses to produce water bottles for Super Bock Group. Recycled PET tends to have a darker color than a virgin polymer. The L*a*b* values have the physical meaning: L* measures the luminosity, a* the redness, and b* the yellowness, when positive, and the blueness, when negative.

Table 5 - Values for L a* b* (mean) for samples. Presented ΔE values correspond to the color distance of the samples relative to Standard 1 / Standard 2.*

	L*	a*	b*	**ΔE**
MO	75,80	-1,53	-2,44	2,62 / 9,63
NO	77,60	-2,24	-2,00	0,85 / 8,69
BA	80,74	0,34	0,21	4,08 / 5,91
F	84,89	-0,04	-0,72	7,27 / 4,63
FBL	89,30	-0,40	-1,48	11,46 / 6,91
IN	79,20	-3,59	-2,15	1,98 / 8,62
Standard 1	78,00	-2,30	-1,25	- / -
Standard 2	83.97	3.43	-3.65	- / -

A b* value higher than 1,0 (more yellow) can be attributed to thermal or oxide degradation during drying or melting. According to the results for b* values (*Table 5*), none of the samples suffered thermal or oxide degradation during the drying and melting processes (Polisan Hellas, 2000). A visual representation of the results presented in *Table 5* are depicted in *Figure 2* and *Figure 3*. The results for the coordinates L* a* b* for the CIELAB color space can be used to compare a sample with a standard, using the ΔL, Δa and Δb values. A deviation value (ΔE) can be compared to the threshold for which the consumer notices the difference (Hunter Associates Laboratory Inc., 2012). ΔE measures the distance between two colors. A ΔE value of 1,0 is accepted as the lowest color difference the human eye can see. However, higher ΔE values can also be imperceptible to the human eye. Therefore, evaluations should be made by trained panels (Upton, 2005). Recycled PET is known to suffer from yellowing and greying with the introduction of post-consumer material. Optical brightening agents can be

added to minimize this problem, making rPET more similar to a virgin PET (Kalama, Falls and Prusak, 2016). Their use is a viable solution commonly applied by the PET bottle producers (Forrest, 2016).

Results for the color distance ΔE using Standard 1 and Standard 2 as references indicate that only the resin NO presents an acceptable color, but only when compared with Standard 1 (ΔE < 1). This sample belongs to the 100% of rPET resin group, and regarding the blended resins none meets the specification (ΔE < 1).

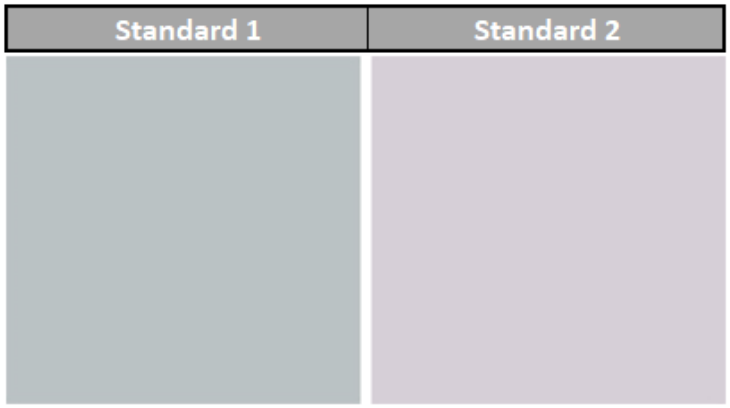

Figure 2 - Visual representation of the colors corresponding to the mean values of L a* b* obtained for each standard.*

Figure 3 – Visual representation of the colors corresponding to the mean values of L a* b* obtained for each sample.*

5.2 Intrinsic Viscosity

The determination of intrinsic viscosity is a common parameter in quality control since it extensively influences the final mechanical properties of the polymer. La Mantia and Vinci (1994) showed that with the increase of the number of extrusion steps, there is a decrease of the intrinsic viscosity, due to a decrease in molecular weight caused by thermal exposure and shear degradation. Some recycling technologies include in the process a step to increase the intrinsic viscosity. On blended resins (mixture with virgin PET), a higher value for intrinsic viscosity is expected when comparing this value with unmixed recycled resin. For the production of water bottles, the resin must typically present an intrinsic viscosity value of 0,78–0,85 dL g^{-1} (Anton Paar, no date; La Mantia and Vinci, 1994; Oromiehie and Mamizadeh, 2004; Silva Spinacé *et al.*, 2006).

Results for intrinsic viscosity are presented in *Table 6*. The values specified by the manufacturers are close to the values for the standards. The results indicate that NO, BA, F, and IN resins presented intrinsic viscosity values lower than the manufacturer specification but meet the typical range of intrinsic viscosity previously reported by other works.

Table 6 - Intrinsic viscosity obtained experimentally and specification values (dL g^{-1}).

	Experimental	Specification
MO	0,84 ± 0,00	0,82 ± 0,04
NO	0,77 ± 0,01	0,80 ± 0,02
BA	0,77 ± 0,01	0,80 ± 0,03
F	0,87 ± 0,00	0,81 ± 0,03
FBL	0,81 ± 0,00	0,82 ± 0,03
IN	0,77 ± 0,01	0,80 ± 0,02
Standard 1 and 2	-	0,80 ± 0,02

Only for the resin F, the measured values were considerably higher than specified. According to the information provided by the industry, these differences do not inhibit from choosing these resins to produce water bottles.

5.3 Differential scanning calorimetry

The thermograms of the samples are plotted in *Figure 4* and the values for melting temperature are presented in *Table 7*.

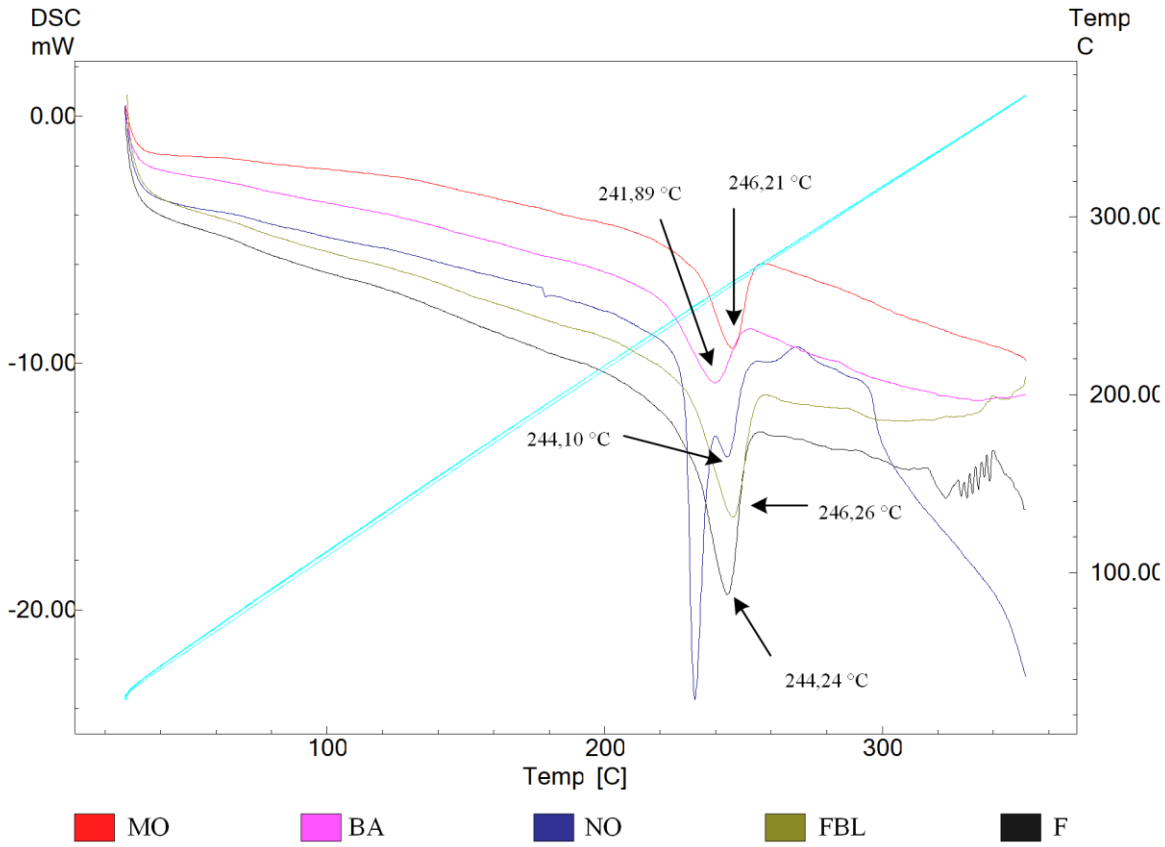

Figure 4 - DSC thermograms of the samples during heating of the second cycle.

Table 7 - Melting temperature in ºC (mean ± standard deviation)

Resin	T_m, ºC
MO	245,22 ± 1,00
NO	245,53 ± 1,43
BA	240,79 ± 1,10
F	243,25 ± 0,99
FBL	244,86 ± 1,41
IN	*
Standard	245.00 ± 5,00

* This sample was not possible to be analysed due to equipment malfunction.

The NO thermogram exhibits two close peaks in the annealing zone instead of only one peak for the melting temperature. This is due to a reorganization of the crystalline structure during the heating run. The first peak corresponds to the melting of small and imperfect crystals formed at constant crystallization temperature, while the second peak represents the real T_m value where the melting of the more perfect crystals that suffered a reorganization during the run occurs. Furthermore, the last peaks of the DSC heating cycle are associated with the

dominant branches of the polymer, which can recrystallize during heating (Kong and Hay, 2002).(Kong and Hay, 2002) The intensity of the peak is related to the percentage of crystallinity: peaks with a stronger signal have a higher percentage of crystallinity (Scheirs, 2000a; Kong and Hay, 2002; Elamri *et al.*, 2015). On this parameter, all the resins meet the standard value even when taking into consideration the standard deviation.

5.4 Limonene and Benzene

The determination of Benzene in recycled PET during the evaluation of the recycling process started in 1992 when the Food and Drug Administration (FDA) issued the document "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations" (updated in 2006) where benzene was one representative contaminant of PET. Benzene is known to be a carcinogenic agent, therefore its presence in the bottles needs to be controlled. In the European Union, the limit for benzene in bottled water is 1 μg kg^{-1} (Komolprasert, Hargraves and Armstrong, 1994; EU Council Directive, 1998; FDA, 2006).

The concentration of benzene found in the samples is presented in *Table 8*. The total migration, i.e., the migration assuming that the whole benzene present in the polymer migrates into the water is also presented in *Table 8*. For this calculation, a bottle of 0.3 L and 8.5 g was assumed.

Table 8 – Concentration (μg kg^{-1} PET) of Benzene on the rPET resins and total migration (μg kg^{-1} of water) on a worst-case scenario (8,5 g and 0,3 L).

	MO	**NO**	**BA**	**F**	**FBL**	**IN**
Replicate 1	57,32	35,53	342,67	372,59	30,46	124,94
Replicate 2	50,75	36,42	281,41	447,87	30,46	67,22
Mean	54,03	35,97	312,04	410,23	30,46	96,08
Standard deviation	4,64	0,63	43,31	53,23	0,00	40,81
Total migration	1,53	1,02	8,84	11,62	0,86	2,72

According to the results obtained for a worst-case scenario, the resin FBL is the one with the lowest total migration value for benzene and F the one with the highest concentration, followed by BA. It is worth mentioning that the rPET of F and FBL follows the same recycling process, but FBL is a blend. However, the obtained values differ on a large scale. From the available data obtained for this study, it is impossible to know if the rPET produced was

obtained from the same batch of post-consumer PET. IN is the only process without an SSP step and is the third sample with the highest benzene concentration. It was expected that this sample would stand out, but samples BA and F have an SSP step and their concentration values were higher than IN on a large scale.

Thoden van Velzen *(2016)* determined the concentration of benzene in rPET after a mechanical recycling process of post-consumer PET bottles. This study also determined the benzene concentration before and after the SSP step to evaluate its importance. The range of benzene concentrations before the SSP reactor was 4 – 14 μg kg^{-1} PET, and after 0 – 0,2 μg kg^{-1} PET. The concentrations for the samples in this study exceed the values obtained in the previously mentioned study (Thoden van Velzen, Brouwer and Molenveld, 2016), with higher values than those obtained even without applying the SSP reactor (step present in all samples except IN). Benzene is a known substance that can be formed during the heating of PET, with its formation well documented in PET pyrolysis. The results obtained for the samples in study are pertinent, and it would be interesting to evaluate if they are replicated when taking into account the input batch of the recycling process (Du *et al.*, 2016).

Regarding the possible detection by the consumer of this substance, all the obtained values are lower than the reported sensory thresholds of benzene in water: 840-53000 μg kg^{-1} for odor and 500-4500 μg kg^{-1} for taste (Cotruvo, 2019). As for the legal limit of benzene in bottled water, only the sample FBL meets the criteria. Nevertheless, it is well known that the estimation based on the total migration assumption tends to overestimate by far the real migration value.

The concentration of limonene in the samples is presented in *Table 9*. The determination of limonene concentration is also a typical analysis of quality control of rPET. Limonene is commonly present in soft drinks. It can be absorbed into the bottle wall with other flavor compounds, so it is necessary to evaluate the capacity of the recycling process to remove it, preventing the migration into the water during the post recycling life with consequences regarding taste and odor (Welle, 2009).

Table 9 – Concentration (μg kg^{-1}) of limonene on the rPET resins and total migration (μg kg^{-1} of water) on a worst-case scenario (8,5 g and 0,3 L).

	MO	**NO**	**BA**	**F**	**FBL**	**IN**
Replicate 1	19,73	65,77	19,73	31,22	31,22	49,78

	MO	NO	BA	F	FBL	IN
Replicate 2	19,73	65,77	19,73	31,22	31,60	32,05
Mean	19,73	65,77	19,73	31,22	31,41	49,78
Standard deviation	0,00	0,00	0,00	0,00	0,27	12,54
Total migration	0,56	1,86	0,56	0,88	0,89	1,41

Regarding the possible detection by the consumer of limonene, all the obtained values are lower than the reported sensory thresholds. The minimum detection threshold is 200 µg kg^{-1} for orthonasal odor, 34 µg kg^{-1} for retronasal odor, and 35 µg kg^{-1} for taste (Buettner and Schieberle, 2001; Welle, 2014).

There have been reports of limonene content in rPET flakes, being the average concentration of 2,9 µg kg^{-1} PET and the maximum concentration of 20 µg kg^{-1} PET (Franz, Bayer and Welle, 2004). The obtained concentrations are higher than 2,9 µg kg^{-1} PET, except for MO and BA that are close to the maximum concentration reported.

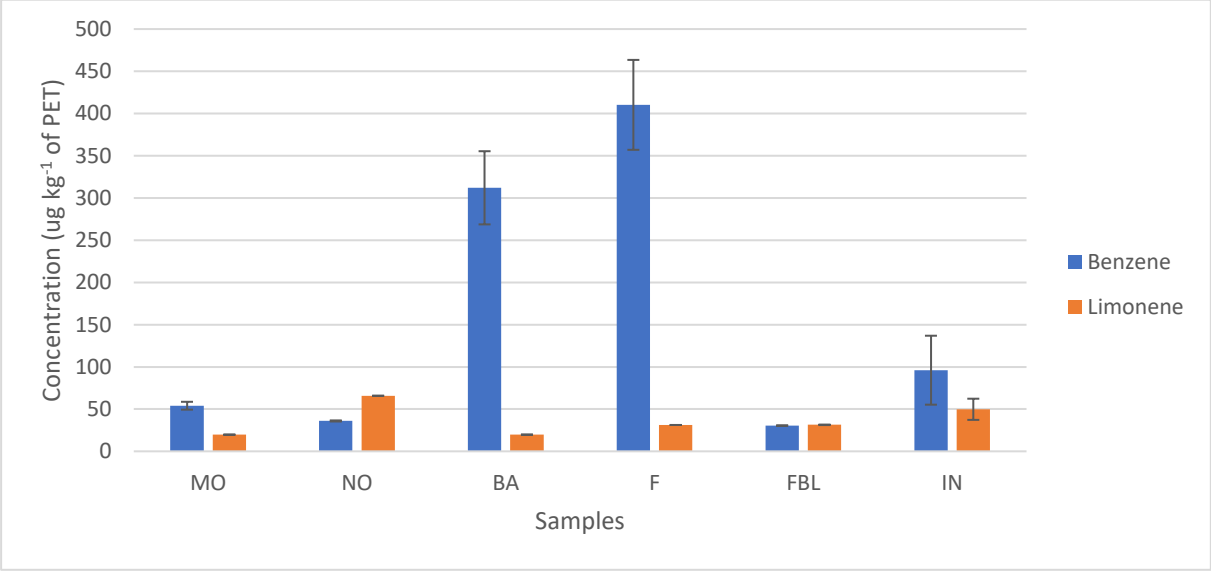

Figure 5 - Concentration of benzene and limonene on the samples.

5.5 Oligomers

The concentration of oligomers (dimer and trimer) in the samples is presented in *Table 10*. The total migration, i.e., the migration assuming that the total amount of oligomers present in the polymer migrates into the water is also presented in *Table 10*. For this calculation, a bottle of 0.3 L and 8.5 g was assumed.

Table 10 - Results for the total concentration of oligomers (mg kg^{-1}PET) and the total migration (mg kg^{-1} of water) on the worst-case scenario (8,5g and 0,3L).

		MO	NO	BA	F	FBL	IN
Dimer	Replicate 1	39,71	83,94	47,86	39,98	83,89	55,74
	Replicate 2	63,78	71,30	51,93	63,95	67,87	67,84
	Mean	51,74	77,62	49,89	51,96	75,88	61,79
	Standard deviation	17,02	8,94	2,88	16,95	11,33	8,56
	Total migration	1,47	2,20	1,41	1,47	2,15	1,75
Trimer	Replicate 1	1191	1599	1196	800	1198	1194
	Replicate 2	1196	1188	1198	1199	1198	1197
	Mean	1193,49	1393,58	1197,39	999,33	1198,08	1195,82
	Standard deviation	0,03	2,90	0,01	2,82	0,00	0,02
	Total migration	33,82	39,48	33,93	28,31	33,95	33,88

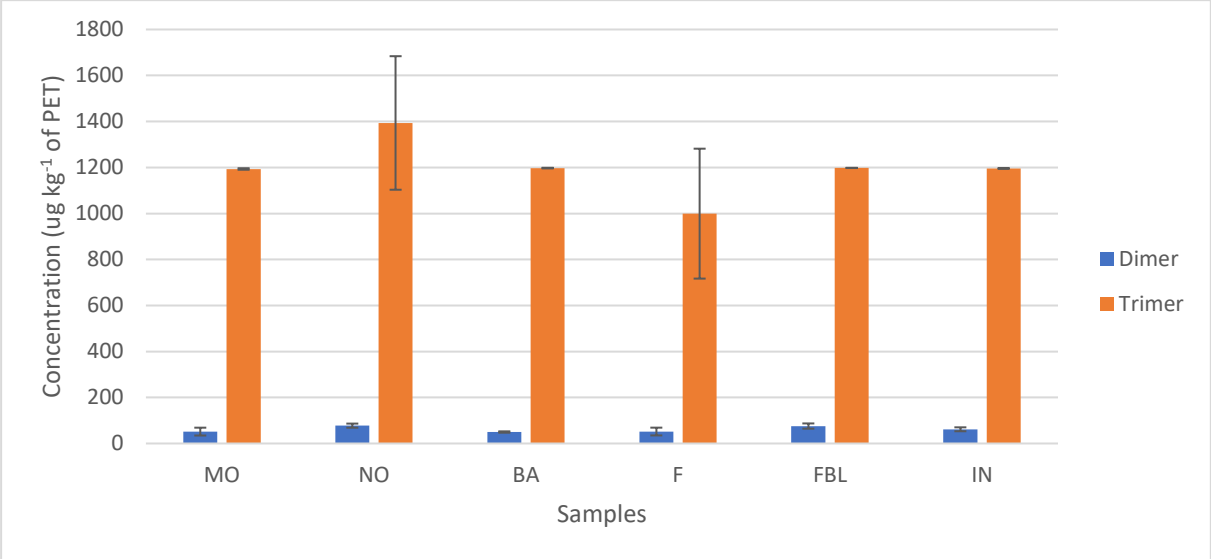

Figure 6 - Results for oligomer content on the samples.

The results for the trimer oligomer were similar between resins. Although the results regarding dimer oligomers are alike, it is possible to notice that NO and FBL have the highest concentrations for each group of rPET content. Because of the low concentrations and the small

standard deviation, BA has the lowest migration values within the unblended rPET resins and IN has the lowest concentration for the blended PET resins.

PET oligomers are not contaminants of the recycling process, but instead chemical substances inherent to the PET matrix. They appear during the manufacturing process of the polymer chain, but their concentration can increase if the polymer chain suffers depolymerization by degradation processes. This can originate oligomers with various molecular weights. It is known that oligomers can migrate into beverages. In previous studies of the determination of linear and cyclic PET oligomers, the predominance of dimers and trimers was found. The increase of cyclic oligomers was also observed for PET that had been reprocessed up to five times. (Stoski *et al.*, 2016; Geueke, Groh and Muncke, 2018; Ubeda, Aznar and Nerín, 2018).

There is no specific limit for PET oligomers on the regulation (EU) No. 10/2011, on plastic intended to come into contact with food. It is only considered that oligomers must comply with the global migration limit of 10 mg of total constituents released per dm^2 food contact surface. Recently, EFSA specified a limit of 50 $\mu g\ kg^{-1}$ for the total oligomer migration of two new co-monomers but for polyester, introduced on the 6^{th} Amendment 1416/2016 of Regulation (EU) No. 10/2011. If this limit were to be applied to the oligomers of PET, some of the reported results in the literature would exceed this limit (Hoppe *et al.*, 2017).

In addition to food safety aspects, it is worth taking into consideration that oligomers can influence the recycling process by changing the intrinsic viscosity, so it is crucial to prevent processes that can increase their concentration during recycling (Awaja and Pavel, 2005). Previous works show that the oligomer content decreases with the use of a SSP reactor and that the oligomer concentration is lower on rPET (Scheirs, 2000b; Scheirs and Long, 2003; Ubeda, Aznar and Nerín, 2018).

A previous work by Ubeda, Aznar and Nerín (2018) on oligomer content on rPET reports concentration values of 0,03 – 1,00 $\mu g\ kg^{-1}$ PET for the dimer and 4,51 – 5,39 $\mu g\ kg^{-1}$ PET for the trimer, while for virgin PET reports values ranging from 0,18 – 1,25 $\mu g\ kg^{-1}$ for dimer and 0,67 – 7,0 $\mu g\ kg^{-1}$ for trimer. The values are much lower than the ones obtained in the present work.

5.6 Non-intentionally added substances

From the analyses by the SPME-GCMS, 45 substances were identified by comparison with NIST and owned laboratory libraries of spectra. The identified substance name, CAS, possible reasons for its presence on rPET and maximum migration limits from the Regulation (EU) 10/2011, if applicable, are presented in *Table 11*.

Table 11 - NIAS detected and their possible origin on the PET resin.

Number	***Name***	***CAS***	***Uses***	***Limits (mg kg^{-1} food)***
1	Octanal	124-13-0	Very common in flavored soft drink containers (Nerìn *et al.*, 2003)	Not listed
2	D-Limonene	5989-27-5	Sorption from food and non-food application (Geueke, Groh and Muncke, 2018)	Not listed
3	1-Hexanol, 2-ethyl-	104-76-7	Contamination by PVC during recycling (Vitali *et al.*, 1993)	30
4	Benzyl alcohol	100-51-6	Information not found	Listed but no limit
5	1-octanol	111-87-5	Information not found	Listed but no limit
6	Possible Alkane	n.a.	Degradation product (Achilias *et al.*, 2007)	n.a.
7	Nonanal	124-19-6	Very common in flavored soft drink containers (Nerìn *et al.*, 2003)	Not listed
8	Triethyl phosphate	78-40-0	Information not found	Not listed
9	Acetic acid, 2-ethylhexyl ester	103-09-3	Information not found	Not listed
10	Unknown	n.a.		n.a.
11	Possibly Naphthalene	n.a.	Information not found	n.a.

Number	*Name*	*CAS*	*Uses*	*Limits (mg kg^{-1} food)*
12	Terpineol	n.a.	Aroma compound	Not listed
13	Possible Alkane	n.a.	Degradation product (Achilias *et al.*, 2007)	n.a.
14	Decanal	112-31-2	Very common in flavored soft drink containers (Nerìn *et al.*, 2003)	n.a.
15	Unknown	n.a.	n.a.	n.a.
16	Unknown	n.a.	n.a.	n.a.
17	Possible Alkene (Olefin)	n.a.	Contamination from bottle cap (Cincotta *et al.*, 2018)	n.a.
18	Possible Alkane	n.a.	Degradation product (Achilias *et al.*, 2007)	n.a.
19	Possible Aldehyde	n.a.	Information not found	n.a.
20	Unknown	n.a.	n.a.	n.a.
21	Possible Aldehyde	n.a.	Information not found	n.a.
22	Possible Alkane	n.a.	Degradation product (Achilias *et al.*, 2007)	n.a.
23	4-tert-Butylcyclohexyl acetate	32210-23-4	Fragrance in perfumes and cleaning products (European Chemicals Agency, no date)	Not listed
24	Triacetin	102-76-1	Main compound in plastic laminated paper (Guazzotti *et al.*, 2015)	Not listed
25	2-Propenoic acid, 2-methyl-, 3,3,5-trimethylcyclohexyl ester	7779-31-9	Inks	Not listed
26	4-tert-Butylcyclohexyl acetate (Same as previous)	32210-23-4	Fragrance in perfumes and cleaning products (European Chemicals Agency, no date)	Not listed
27	Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester	77-68-9	Inks	Not listed

Number	*Name*	*CAS*	*Uses*	*Limits (mg kg^{-1} food)*
28	Biphenyl	92-52-4	Degradation product (Achilias *et al.*, 2007)	Not listed
29	Possible Alkene	n.a.	Information not found	n.a.
30	Alkane	n.a.	Side product from polymerization of HDPE and PP(Franz and Welle, 2008)	Not listed
31	Diphenyl ether	101-84-8	UV absorver (Bentayeb *et al.*, 2007)	Not listed
32	Benzene, 2-isocyanato-1,3-bis(1-methylethyl)-	28178-42-9	Contamination from other polymers during recycling	Not listed
33	5,9-Undecadien-2-one, 6,10-dimethyl-, (Z)-	3879-26-3	Side product from polymerization of HDPE and PP(Franz and Welle, 2008)	Not listed
34	(E)-β-Farnesene	18794-84-8	Aroma compound absorbed by PET (Forrest, 2016)	Not listed
35	Propanedioic acid, ethyl(3-methylbutyl)-, diethyl ester	77-24-7	Information not found	Not listed
36	Dimethyl phthalate	131-11-3	Contamination from PVC or by labelling (Pivnenko *et al.*, 2016)	Not listed
37	2,4-Di-tert-butylphenol	96-76-4	Assumed to be a break-down product from a polyolefine antioxidant (Bach *et al.*, 2013)	Not listed
38	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	Information not found	5
39	Diethyl Phthalate	84-66-2	Contamination from PVC or by labelling (Pivnenko *et al.*, 2016)	Not listed
40	DIPN pattern	n.a.	Contamination from recycled office paper applied on food packaging (Geueke, Groh and Muncke, 2018)	n.a.
41	Unknown	n.a.	n.a.	n.a.
42	Unknown	n.a.	n.a.	n.a.
43	Dibutyl phthalate	84-74-2	Contamination from PVC or by labelling (Pivnenko *et al.*, 2016)	0,3

Number	*Name*	*CAS*	*Uses*	*Limits (mg kg^{-1} food)*
44	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	Information not found	Not listed
45	Dichlofluanid	1085-98-9	Fungicide (National Center for Biotechnology Information, no date)	Not listed

The mean of concentrations for the three replicates and respective standard deviation for each substance obtained from the SPME-GCMS chromatogram are present in *Table 12*.

Table 12 – Concentration (µg kg^{-1}) of each compound on the respective PET resin.

Number	*Name*	*MO*	*NO*	*BA*	*F*	*FBL*	*IN*
1	Octanal	2,215 ± 0,282	0,861 ± 0,138	1,442 ± 0,109	0,520 ± 0,150	0,509 ± 0,125	0,875 ± 0,102
2	D-Limonene	0,058 ± 0,012	0,057 ± 0,016	0,041 ± 0,001	0,018 ± 0,002	0,016 ± 0,003	0,037 ± 0,007
3	1-Hexanol, 2-ethyl-	0,969 ± 0,103	0,889 ± 0,109	1,094 ± 0,160	1,464 ± 0,086	1,275 ± 0,122	1,308 ± 0,146
4	Benzyl alcohol	5,937 ± 0,637	11,215 ± 1,311	-	-	-	-
5	1-octanol	0,947 ± 0,049	0,129 ± 0,046	0,378 ± 0,072	0,345 ± 0,069	0,271 ± 0,050	0,142 ±0,034
6	Possible Alkane	0,397 ± 0,037	0,199 ± 0,025	0,333 ± 0,062	0,306 ± 0,031	0,364 ± 0,089	0,192 ±0,063
7	Nonanal	154,985 ± 6,680	46,120 ± 3,162	103,513 ± 8,315	30,221 ± 4,463	25,957 ± 3,030	42,622 ± 1,705
8	Triethyl phosphate	0,049 ± 0,013	0,009 ± 0,002	-	-	-	-
9	Acetic acid, 2-ethylhexyl ester	-	-	-	0,563 ± 0,043	1,411 ± 0,133	-
10	Unknown	0,563 ± 0,080	-	-	-	-	-
11	Possibly Naphthalene	-	0,459 ± 0,055	0,160 ± 0,028	0,203 ± 0,028	0,081 ± 0,029	0,084 ± 0,009
12	Terpineol	0,288 ± 0,022	0,124 ± 0,003	0,124 ± 0,008	0,216 ± 0,035	0,123 ± 0,017	0,122 ± 0,012
13	Dodecane	0,110 ± 0,001	0,031 ± 0,002	0,044 ± 0,004	0,041 ± 0,006	0,105 ± 0,008	0,038 ± 0,001
14	Decanal	1,492 ± 0,133	1,288 ± 0,191	1,047 ± 0,080	0,402 ± 0,179	0,332 ± 0,109	0,624 ± 0,180
15	Unknown	0,069 ± 0,018	0,030 ± 0,009	0,050 ± 0,006	0,042 ± 0,016	0,051 ± 0,012	0,054 ± 0,008

Number	*Name*	*MO*	*NO*	*BA*	*F*	*FBL*	*IN*
16	Unknown	0,018 ± 0,003	0,014 ± 0,002	0,013 ± 0,003	-	-	0,014 ± 0,003
17	Possible Alkene/Olefin	0,049 ± 0,056	-	-	-	-	-
18	Possible Alkane	0,409 ± 0,087	0,404 ± 0,044	0,470 ± 0,160	0,181 ± 0,063	0,260 ± 0,059	0,295 ± 0,009
19	Possible Aldehyde	0,120 ± 0,071	0,272 ± 0,064	0,159 ± 0,038	0,099 ± 0,036	0,114 ± 0,027	0,198 ± 0,036
20	Unknown	0,122 ± 0,009	0,070 ± 0,001	0,090 ± 0,004	0,088 ± 0,011	0,085 ± 0,010	0,039 ± 0,015
21	Possible Aldehyde	0,151 ± 0,010	0,096 ± 0,007	0,095 ± 0,013	0,033 ± 0,010	0,093 ± 0,022	-
22	Possible Alkane	0,308 ± 0,011	0,365 ± 0,034	0,406 ± 0,002	0,135 ± 0,036	0,234 ± 0,060	0,182 ± 0,034
23	4-tert-Butylcyclohexyl acetate	0,274 ± 0,023	0,111 ± 0,020	0,052 ± 0,008	0,156 ± 0,012	0,109 ± 0,028	0,117 ± 0,007
24	Triacetin (Or diacetin)	0,776 ± 0,391	0,892 ± 0,268	0,580 ± 0,259	0,239 ± 0,117	0,208 ± 0,071	0,344 ± 0,290
25	2-Propenoic acid, 2-methyl-, 3,3,5-trimethylcyclohexyl ester	0,782 ± 0,100	-	0,247 ± 0,040	0,889 ± 0,173	0,311 ± 0,100	0,458 ± 0,051
26	4-tert-Butylcyclohexyl acetate	0,519 ± 0,031	0,226 ± 0,003	0,215 ± 0,007	0,321 ± 0,072	0,312 ± 0,089	0,273 ± 0,032
27	Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester	0,622 ± 0,036	0,479 ± 0,015	0,435 ± 0,132	0,203 ± 0,064	0,242 ± 0,110	0,474 ± 0,048
28	Biphenyl	-	-	-	0,670 ± 0.214	4,534 ± 4.774	8,786 ± 2,915
29	Possible Alkene	0,219 ± 0,024	0,072 ± 0,015	0,051 ± 0,009	-	-	-
30	Alkane	1,197 ± 0,058	0,445 ± 0,060	0,519 ± 0,035	0,315 ± 0,054	0,714 ± 0,203	0,521 ± 0,047
31	Diphenyl ether	-	-	-	44,439 ± 9,361	61,217± 26,429	0,676 ± 0,571
32	Benzene, 2-isocyanato-1,3-bis(1-methylethyl)-	4,212 ± 0,016	-	0,040 ± 0,015	-	-	-
33	5,9-Undecadien-2-one, 6,10-dimethyl-, (Z)-	0,296 ± 0,037	0,120 ± 0,015	0,121 ± 0,015	-	-	-
34	(E)-β-Famesene	0,224 ± 0,104	2,165 ± 0,203	0,514 ± 0,187	0,014 ± 0,005	0,016 ± 0,005	0,325 ± 0,050
35	Propanedioic acid, ethyl(3-methylbutyl)-, diethyl ester	0,421 ± 0,137	0,237 ± 0,087	6,365 ± 7,904	0,015 ± 0,006	0,031 ± 0,013	0,045 ± 0,006
36	Dimethyl phthalate	-	-	-	-	5,293 ± 2,371	-
37	2,4-Di-tert-butylphenol	0,525 ± 0,061	0,089 ± 0,007	0,229 ± 0,024	0,053 ± 0,019	0,407 ± 0,111	0,688 ± 0,117
38	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	0,258 ± 0,049	0,113 ± 0,012	0,225 ± 0,024	0,167 ± 0,033	0,415 ± 0,145	0,203 ± 0,035
39	Diethyl Phthalate	0,232 ± 0,029	5,656 ± 0,575	0,580 ± 0,156	0,362 ± 0,154	0,184 ± 0,121	0,303 ± 0,097

Number	*Name*	*MO*	*NO*	*BA*	*F*	*FBL*	*IN*
40	DIPN pattern	0,020 ± 0,003	0,051 ± 0,004	0,053 ± 0,008	0,016 ± 0,003	0,023 ± 0,010	0,054 ± 0,006
41	Unknown	0,116 ± 0,005	0,067 ± 0,014	0,052 ± 0,004	0,085 ± 0,009	0,062 ± 0,013	0,060 ± 0,028
42	Unknown	-	-	-	0,057 ± 0,019	0,177 ± 0,059	-
43	Dibutyl phthalate	0,546 ± 0,123	0,564 ± 0,016	0,636 ± 0,115	0,372 ± 0,237	0,438 ± 0,224	0,861 ± 0,192
44	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	0,215 ± 0,052	0,199 ± 0,036	0,214 ± 0,030	0,109 ± 0,045	0,074 ± 0,034	0,184 ± 0,038
45	Dichlofluanid	0,276 ± 0,076	0,083 ± 0,029	0,175 ± 0,060	0,010 ± 0,018	0,057 ± 0,020	0,145 ± 0,046

From the results shown in *Table 12*, the substances were grouped considering the functional chemical group. Some substances of specific interest were evaluated independently. The unknows were grouped by class considering the potential functional group. These observations are presented in *Table 13*.

Table 13 – Concentrations in polymer (μg kg^{-1}PET) for each class of NIAS.

Substance or class	MO	NO	BA	F	IN	FBL
(E)-β-Famesene	0,22	2,17	0,51	0,01	0,32	0,02
4-tert-Butylcyclohexyl acetate	0,79	0,34	0,27	0,48	0,39	0,42
Carboxylic acid	1,82	0,72	7,05	1,67	0,98	2,00
Alcohol	8,38	12,32	1,70	1,86	2,14	1,95
Aldehydes	158,69	48,27	106,00	31,14	44,12	26,80
Biphenyl	0,00	0,00	0,00	8,79	0,67	4,53
Dichlofluanid	0,28	0,08	0,18	0,01	0,15	0,06
Diphenyl ether	0,00	0,00	0,00	44,44	0,68	61,22
DIPN pattern	0,02	0,05	0,05	0,02	0,05	0,02
D-Limonene	0,06	0,06	0,04	0,02	0,04	0,02
Hidrocarbons	1,86	0,71	0,91	0,52	0,83	1,17
Isocyanate	4,21	0,00	0,04	0,00	0,00	0,00
Phthalates	0,78	6,22	1,22	0,73	1,16	5,92
Terpineol (or related)	0,29	0,12	0,12	0,22	0,12	0,12
Triacetin (Or diacetin)	0,78	0,89	0,58	0,24	0,34	0,21
Triethyl phosphate	0,05	0,01	0,00	0,00	0,00	0,00
Unknowns	0,89	0,18	0,20	0,27	0,17	0,38
Unknowns (possible Alkanes)	1,11	0,97	1,21	0,62	0,61	0,92
Unknowns (possible Alkenes)	0,27	0,07	0,05	0,00	0,00	0,00
Unknowns (possible Naphthalene)	0,00	0,00	0,16	0,20	0,08	0,08
Unknowns (possible Aldehyde)	0,27	0,37	0,25	0,13	0,20	0,21
Others	0,22	0,20	0,21	0,11	0,18	0,07
Total	180,98	73,74	120,76	91,49	53,23	106,11
Total Unknowns	3,08	1,62	1,91	1,26	1,16	1,63

The main class in terms of concentration is the aliphatic aldehydes, being the most common detected octanal, nonanal, and decanal. Aldehydes with a second double bond are present at much lower significance, which can be due to the thermo-oxidation of PE waxes used as lubricants in PET production (Saldívar-Guerra and Vivaldo-Lima, 2013). Future studies should evaluate the influence of this group on the sensorial characteristics of the water due to its flavoring properties.

Table 14 shows the global migration of NIAS for all samples, as well as the migration of unknowns, dibutyl phthalate, and all phthalates. It is important to evaluate these migrations since some of these substances present adverse toxicological effects therefore requiring safety evaluation.

Table 14 - Total migration (μg kg^{-1} food) values for a worst-case scenario (bottle with 8,5 g and 0,3 L).

	MO	NO	BA	F	IN	FBL
Global maximum migration	5,13	2,09	3,42	2,59	1,51	3,01
Total maximum migration for unknowns	0,08	0,05	0,05	0,04	0,03	0,05
Dibutyl Phthalate	0,016	0,016	0,018	0,011	0,012	0,024
All Phthalates	0,022	0,018	0,035	0,021	0,033	0,168

For the global NIAS content and unknowns, the threshold of toxicological concern (TTC) approach was followed. TTC is a tool for risk assessment based on the principle of establishing a human exposure threshold value for all chemicals, below which there is a very low probability of an appreciable risk to human health. If the chemical structure of a substance is known, its likely health risk can be evaluated based on generic human thresholds of exposure for chemicals. These are called “TTC values”. Depending on the chemical structure, substances classes corresponding to the Cramer classes for non-genotoxic compounds are defined with different TTC values:

- Class 1: substances with simple chemical structures efficiently metabolized to innocuous products; anticipated low order of oral toxicity, such as normal constituents of body and simply branched acyclic aliphatic.
- Class 2: substances which possess intermediate structures that are less innocuous than substances in Class 1, but do not contain structural features suggestive of toxicity like those in Class 3, such as Cyclopropane or cyclobutane with aliphatic side chains or only alcohol, aldehyde, acid, ester; Most substances in Class II belong to either of two categories; one includes substances with functional groups that are similar to, but somewhat more reactive than functional groups in Class 1 (e.g. allyl and alkyne); the other includes substances with more complex structures than substances in Class 1 but that are common food components.
- Class 3: substances with chemical complex structures that permit no strong initial presumption of safety or may even suggest significant toxicity (e.g. acetonitrile, 2,4-dinitrotoluene, chlorobenzene or p-aminophenol) or have reactive functional groups; metabolism to reactive products suggestive of potential toxicity, such as aliphatic secondary amine, cyano-nitroso, diazo, triazeno or quaternary nitrogen and ring bearing any substituents.

Human exposure thresholds of 1800, 540, and 90 μg person day^{-1} (corresponding to 30, 9, and 1.5 μg kg bw^{-1} day^{-1}) were proposed for class 1, 2, and 3, respectively, using the 5^{th} percentile of the lowest no observed effect level (NOEL) for each group of chemicals, a body weight of 60 kg, and a safety factor of 100 (Munro *et al.*, 1996).

In the present work, the indicative structure of these substances, not positively identified, are probably aldehyde, alkanes, alkenes, and naphthalene. Therefore, they correspond to structures with no genotoxicity alert. The estimated exposure can thus be compared to the values applicable for substances with structure Cramer Class 2 – 540 μg person day^{-1} or Cramer Class 3 of TTC approach - 90 μg person day^{-1}. Unknowns maximum concentration, in this work, was of 3,08 ng g^{-1} on MO resin. Regarding the total migration of these compounds, all the studied resins would give a value lower than 1 μg kg^{-1} as in *Table 14*, which translates to an exposure level lower than 1 μg person day^{-1}, which meets the Cramer Class 3 exposure level. The estimated exposure was found considering the total migration calculated from the concentration in the resin and the consumption of 1 kg food per day per person.

For the overall concentration of NIAS, the sample MO had the highest concentration, which will give a maximum migration value of 5,13 μg kg^{-1} and an exposure value of 5,13 μg person day^{-1} while the other samples have lower exposure levels. This exposure value meets the Cramer Class 3 exposure level, which establishes a threshold of 90 μg per person day^{-1}. The estimated exposure was found considering the total migration calculated from the concentration in the resin and the consumption of 1 kg food per day per person.

Phthalates should not be present in PET bottles since they are not used on bottle production, but these substances are ubiquitous on the environment and some are known for their endocrine disruptor behavior (Casals-Casas and Desvergne, 2011; Mariana *et al.*, 2016). From the phthalates detected, only dibutyl phthalate is authorized by the Regulation (EU) 10/2011 as a substance to be used in food contact materials, being 0,3 mg kg^{-1} food the migration limit authorized. For the phthalates not authorized a default limit of 10 μg kg^{-1} applies.

Moreover, in the rPET analysed the following compounds were not detected: ethylbenzene, xylene, toluene (products of PET degradation), ethylene glycol (monomer and also product of PET degradation); if present, these compounds would be at levels below the detection limit. The following compounds also remained undetected: methyl dioxolane and acetaldehyde (probably due to the high volatility and chromatographic conditions used).

5.7 Data handling

5.7.1 Statistical analysis of results for NIAS

Table 15 presents the results for the normality test and the test of equality of variances for the concentration data of NIAS. These tests are required to check whether the data meet the requirements for a parametric test.

Table 15 – Normality and equality of variances tests. (a. Lilliefors Significance Correction; b. Based on mean; c. Tests the null that the error variance of the dependent variable is equal across groups.)

	Kolmogorov-Smirnov[a]			**Shapiro-Wilk**			**Levene Statistic[b,c]**			
	Statistic	df	Sig.	Statistic	df	Sig.		df1	df2	Sig.
Concentration	,455	810	,000	,163	810	,000	2,883	221	588	,000

From the sig. value present in *Table 15*, it is possible to conclude that this data does not follow normality and equality of variances, so the results obtained from a univariate general linear model analysis are not valid. However, the analysis was performed as a preliminary

interpretation of the results, and these will be compared to the ICA results to confirm the assumptions speculated in this section.

Table 16 - Test of between-subjects effects.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	138594,043[a]	269	515,219	88,693	,000
Intercept	4518,241	1	4518,241	777,796	,000
Substance	82178,210	44	1867,687	321,514	,000
RESIN	710,283	5	142,057	24,454	,000
Substance * RESIN	55705,550	220	253,207	43,588	,000
Error	3136,879	540	5,809		
Total	146249,162	810			
Corrected Total	141730,921	809			

a. R Squared = ,978 (Adjusted R Squared = ,967)

With the data presented in *Table 16*, it is possible to conclude that there is statistical significance between the groups since all sig. values are lower than 0,05. The null hypothesis is false, so there are differences between the mean values of the samples and these differences were evaluated with a Tuckey test.

The Tuckey test for multiple comparisons allows the identification of homogenous subsets of the samples tested. The samples within a subset have no statistical differences, although they have statistical differences when compared to the means of samples on other groups. This is represented in *Figure 7*.

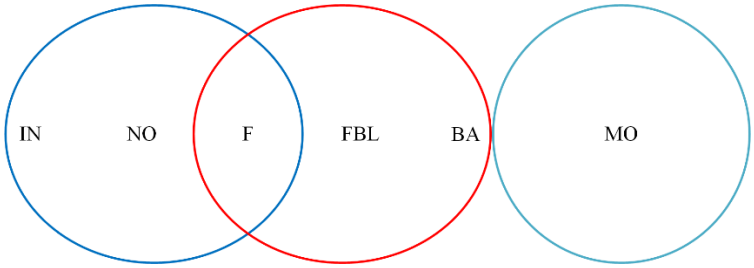

Figure 7 - The three resin groups from the Tuckey HSD test.

The Tuckey test shows that the MO sample is the one that stands out from the other samples, as it alone represents a group with statistical differences compared to the others. This sample is the one with the highest concentration of NIAS compounds, which can justify its isolated position.

The samples F, FBL, and BA form another group. It is possible to verify that the F sample is also present in the IN and NO group, showing that this sample has no significant differences, relative to the mean values, with the samples present in both groups. Thus, the use of a 100% rPET F will get the same response compared to an FBL and an IN (also blend), which can offer considerable insights on the use of blends in bottle production.

These previous results can be presented in a plot highlighting the compounds that differentiate the samples: *Figure 8* shows that most of the substances present have little effect since they are mostly present on the baseline of the graph. However, it is noteworthy that two compounds are isolated from the others, these substances being nonanal and diphenyl ether. Since nonanal is a flavoring agent on soft drinks, it is important to evaluate if it can be perceived by the consumer on the bottled water even on samples where its presence is small, like FBL and F. Diphenyl ether used as a UV absorber causes more concerns on the toxicologic safety for humans.

This analysis is based on the mean values for concentration and therefore, only the highest values are considered. The ICA approach is following presented.

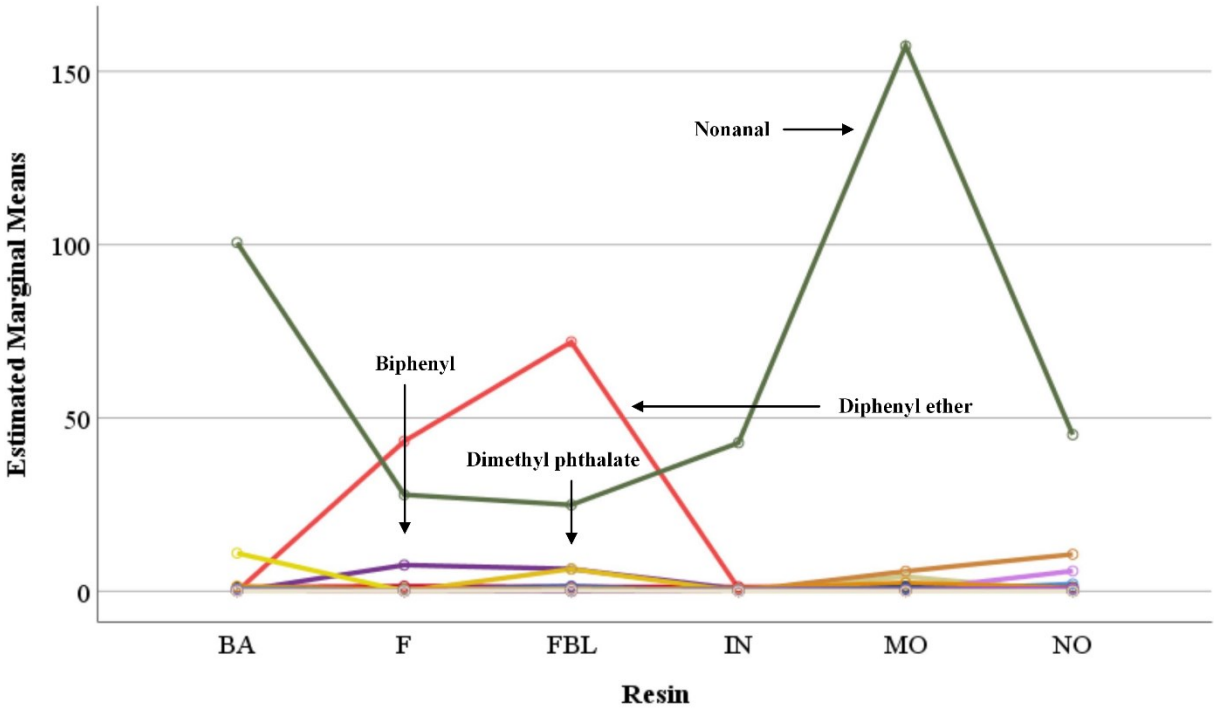

Figure 8 - Mean values comparison among the studied samples.

5.7.2 Independent components analysis (ICA)

IC analysis was applied to the reduced TIC chromatograms (*Figure 9)* and three ICs extracted were found to correspond to significant signals. These are shown in *Figure 10*, for each IC, scores for the three replicates analyzed and corresponding loadings are presented.

IC1 allows the discrimination of samples MO and BA due to nonanal (CAS 124-19-6), a common substance in flavored soft drinks containers (Nerìn *et al.*, 2003). With the results of the SPSS analysis and the graph in *Figure 8* shows that nonanal is the most prominent substance when compared to the remaining, most notably in samples MO and BA. The data obtained from the semi-quantification of NIAS proves once again that this substance has the highest concentration in these two samples. The data obtained by ICA confirm the results previously obtained.

IC3 discriminates samples F and FBL from the other samples due to 2-ethylhexylacetate (CAS 103-09-3) which may be used as a flavoring, dodecane (CAS 112-40-3) an alkane commonly found in recycled PET, and diphenyl ether (CAS 101-84-8). This latter can be used as a processing aid in polyesters production or be related to flame retardants. Samples F and FBL are related to each other as FBL is a blend of resin F and virgin PET. Dodecane is present in all samples, 2-ethylhexylacetate is only present in these two samples, with a significant concentration when compared with the remaining substances, and diphenyl ether is only present in the blends (FBL, IN) and F. Regarding the SPSS analysis, F and FBL were grouped together as shown in *Figure 7*, implicating the absence of statistical significance between these two samples, while the results from the IC appear to agree with this observation.

Moreover, IC4 seems to discriminate samples FBL and IN due to a terpenoid compound (farnesene, CAS 18794-84-8), related to fruit flavors, which were present in completely different concentration on the semi-quantification of NIAS. The SPSS analysis grouped these two samples into different groups, but the SPSS analysis is subject to errors, thus being the ICA analysis a better tool to analyze the data.

Figure 11 presents the IC scores relationships (IC1 versus IC3, IC1 versus IC4, and IC3 versus IC4). These plots show clearly that resins can be discriminated with the three ICs.

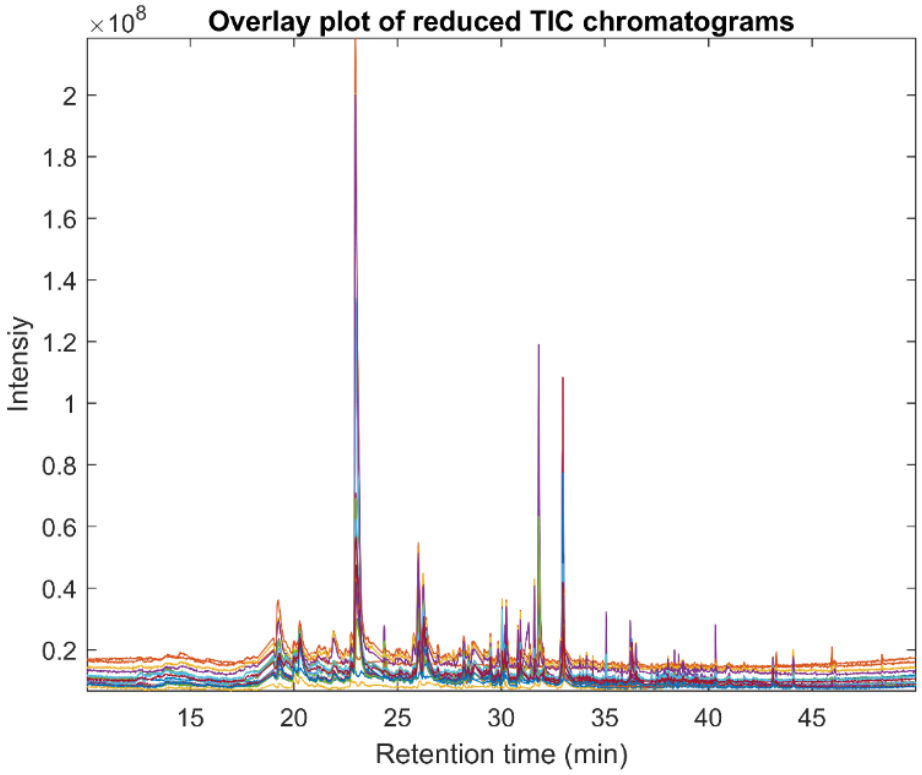

Figure 9 - Reduced TIC chromatograms overlay.

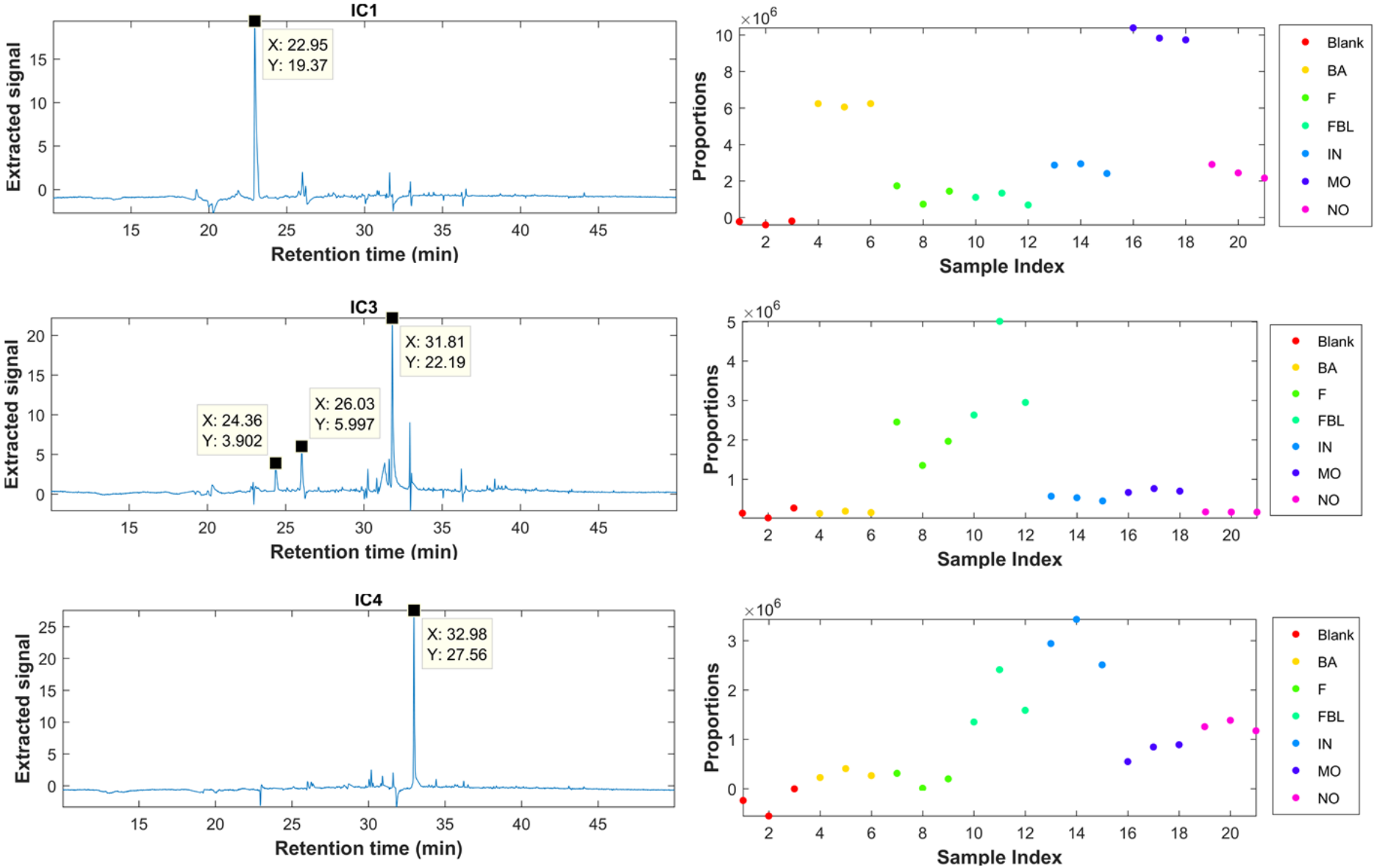

Figure 10- The three ICs with significant correlation.

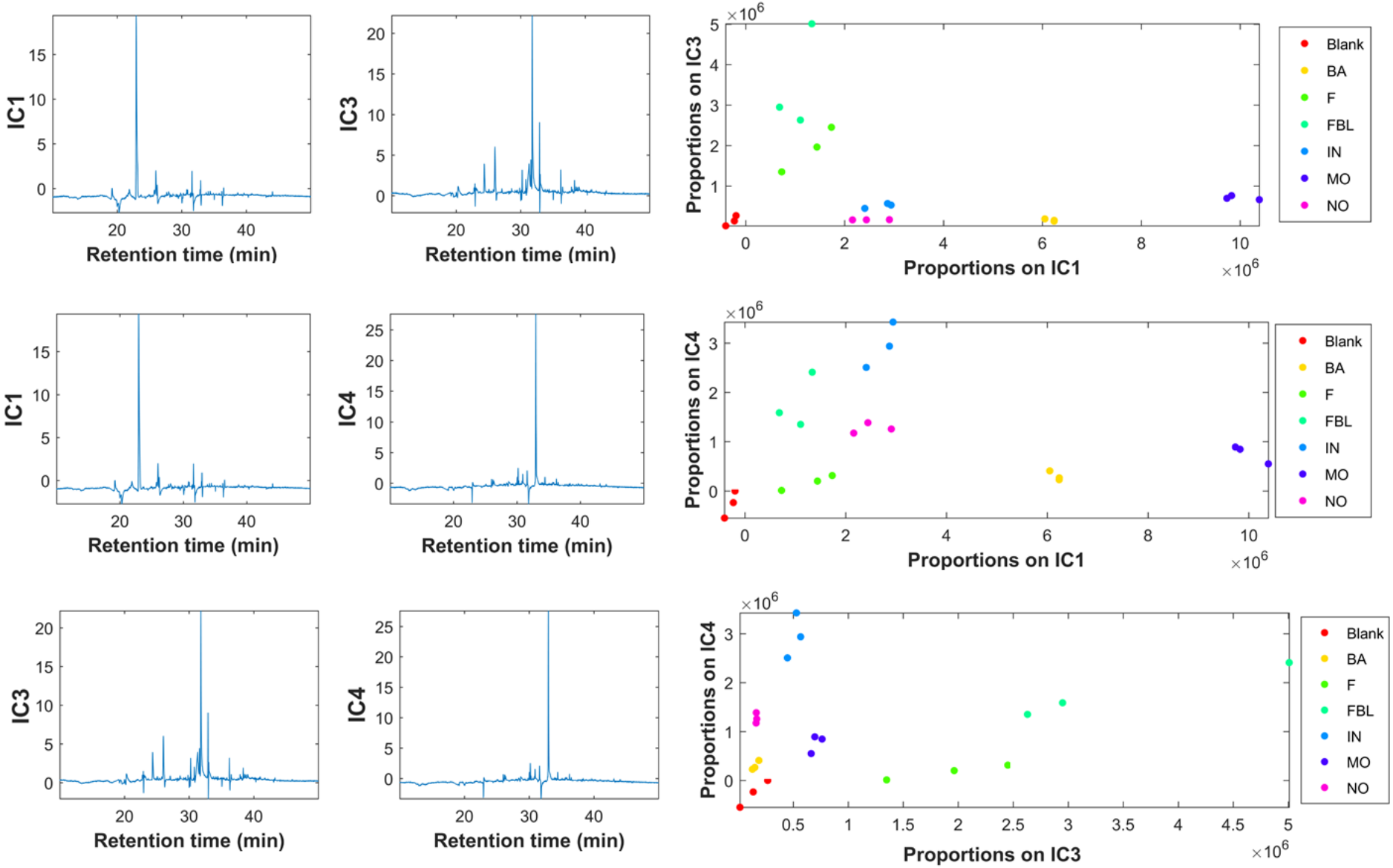

Figure 11 - Interactions between the three ICs.

6. Conclusions

Several commercial resins rPET to be used for bottles for water were evaluated. Regarding the color, the resin NO is the one with the lowest mean deviation of ΔE followed by BA. The intrinsic viscosity of all samples tested meets the values typical of virgin PET, and the same can be said about the melting temperature.

On the benzene content, the results from this work are higher than what has been reported in other works. The migration was estimated assuming a total mass transfer. Only FBL meets the migration criteria set by the council directive 98/83/EC of 1 μg kg^{-1}, although it is recognized that the approach followed may largely overestimate the real migration. The limonene content of the samples evaluated is also higher than the reported concentrations from other works. However, the obtained migration values will not affect the sensorial proprieties of the product, according to the sensory thresholds. BA and MO were the samples with the lowest concentration of limonene.

The oligomer concentration in the samples is higher than what has been reported in previous works. Trimer concentration was higher than the dimer concentration for rPET, corroborating data from previous studies. The concentration values are even higher than the concentration on virgin PET. IN is the only resin without an SSP step, a process known for the reduction of oligomer concentration. However, this sample is the third with the highest concentration for both compounds. BA is the sample with the lowest concentrations when considering the standard deviation, while NO is the sample with the highest content.

Regarding the NIAS evaluation and specifically for the identified substances - unknown substances - migration estimation is lower than 1 μg kg^{-1}. This corresponds to an exposure lower than 1 μg person day^{-1}, much lower than the values applicable for substances with structure corresponding to Cramer Class 3 of TTC (90 μg person day^{-1}). For identified NIAS the exposure level estimated, is lower than 5,13 μg person day^{-1} which also is lower than the correspondent to Cramer Class 3. The sample with the lowest NIAS content was IN for the blended group and NO for the unblended rPET group.

The obtained concentration data for NIAS does not meet the criteria for the normality and equality of variances test. Therefore, the parametric test performed is just indicative. This analysis grouped the samples into three subsets: the first group comprehends the resins IN, NO, and F, the second group has F, FBL, and BA, and the last only has the sample MO. By the estimated marginal means plot it is possible to see that two substances are isolated from the

remaining - nonanal and diphenyl. However, other two substances are worth mentioning even if only on specific resins - biphenyl in resin F and dimethyl phthalate in resin FBL.

ICA analysis, a more robust approach, confirms that nonanal and diphenyl ether are key substances for sample discrimination. Regarding nonanal, the samples MO and BA can be grouped together, for the ethylhexylacetate, dodecane and diphenyl ether the samples F and FBL are correlated which has been previously shown by the SPSS approach. Samples FBL and IN are correlated by farnesene. Only the sample NO does not correlate with any other sample.

As a major conclusion, the results indicate the preference for resins NO and BA for bottle production. It would be important to validate these results with data from inter batches variability.

7. Further work

Regarding inter batch variability, it would be important to assess whether these results are constant or dependent on the post-consumer PET that is undergoing the recycling process. The properties of the virgin resins currently used by Logoplaste to produce bottles for the Super Bock Group should have been simultaneously analyzed.

The evaluation of bottles blown with these resins would be important to accurately assess color properties and mechanical strength. Filling the same bottles would allow the evaluation of the possible impact of these resins on the sensory properties of water, as well as to determine the possible migrations of benzene, limonene, oligomers, and NIAS.

8. References

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ANNEXES

ANNEX 1 - Summary of the recycling processes

1. Summary of the resins in study

Table 17 - Information obtained from EFSA reports regarding the resins in study.

Date of Publication	*Process*	*Company*	*Submission by*	*INPUT*	*OUTPUT*
06 December 2012	F	Far Eastern New Century Corporation (Taipei, Taiwan)	Ministère de l‟Economie de l‟Industrie et de l‟Emploi (DGCCRF), France	**PET Flakes** obtained from post-consumer PET containers, coming from post-consumer collection systems, are hot caustic washed and dried. PET originate from non-food applications in a fraction below **5%**.	**rPET Pellets,** intended to be used **up to 100%** on the manufacture of new food articles and packages. The trays produced with this rPET are not intended to be used either in microwave or in a conventional oven.
18 February 2013	MO	Morssinkhof Plastics BV (The Netherlands)	Ministry of Health, Welfare and Sport, The Netherlands	**PET Flakes** obtained from post-consumer PET containers, mainly bottles, are hot caustic washed and dried. PET originate from non-food applications in a fraction below **5%**. **PET flakes** bought from the market from approved suppliers.	**rPET Pellets**, intended to be used up to **100%** on the manufacture of new food articles and packages. The trays produced with this rPET are not intended to be used either in microwave or in a conventional oven.

Date of Publication	*Process*	*Company*	*Submission by*	*INPUT*	*OUTPUT*
05 December 2012	NO	Nosinyec SL	Ministerio de Sanidad, Servicios Sociales e Igualdad, Spain	**PET Flakes** obtained from post-consumer PET bottles are hot caustic washed and dried. PET originate from non-food applications in a fraction below **5%**. **PET flakes** bought from the market from approved suppliers.	**rPET Pellets**, intended to be used up to **100%** on the manufacture of new food articles and packages. The trays produced with this rPET are not intended to be used either in microwave or in a conventional oven.
05 December 2012	BA	BariQ (Egypt)	Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, Germany	**PET Flakes** obtained from post-consumer PET containers, mainly bottles, are hot caustic washed and dried. PET originate from non-food applications in a fraction below **5%**. **PET flakes** processed in house.	**rPET Pellets**, intended to be used up to **100%** on the manufacture of new food articles and packages. The trays produced with this rPET are not intended to be used either in microwave or in a conventional oven.

2. Summary of the recycling process BA

Technology: Starlinger IV+

Drying and crystallization (step 2): In this step the flakes are dried and crystallized at high temperature in a reactor under inert gas or desiccant air flow, in a continuous process.

Extrusion and crystallization (step 3): The flakes from the previous step are fed to an extruder under high temperature and vacuum for a predefined residence time. Further decontamination occurs in this step. The extruded pellets are then crystallized at high temperature in a further reactor under atmospheric pressure.

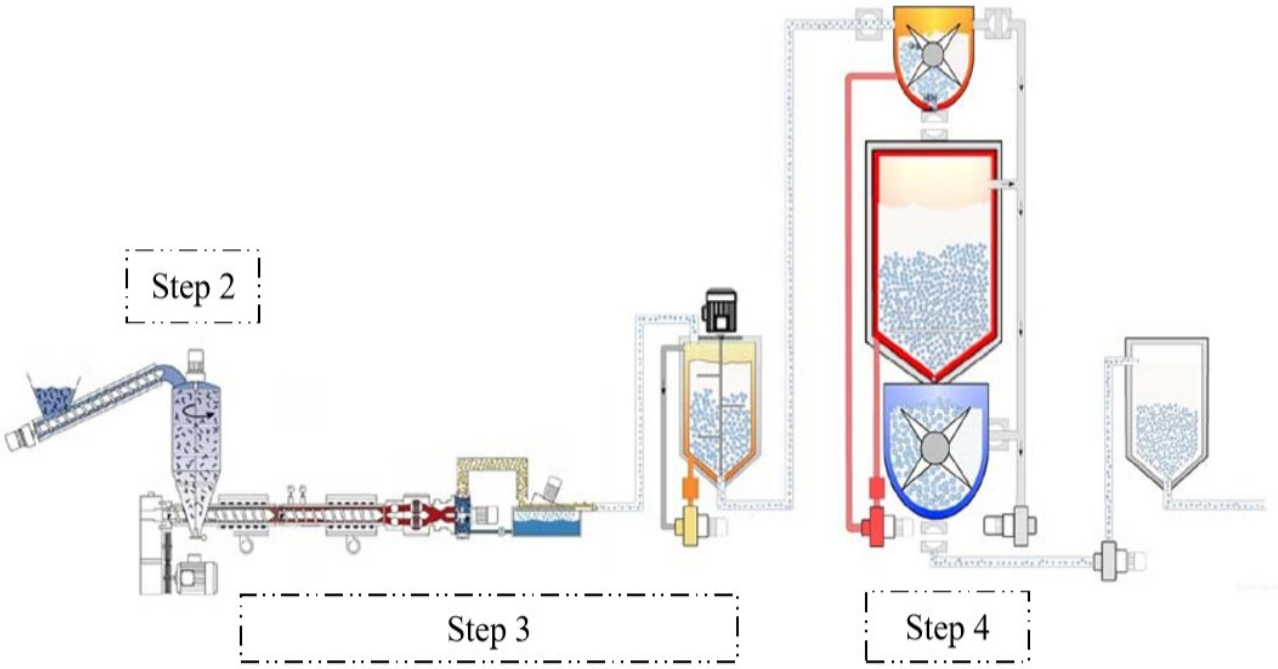

Figure 12 - Diagram of the BariQ recycling process.

SSP reactor (step 4): The crystallized pellets are continuously pre-heated in a reactor before being introduced in the solid-state polymerization reactor running under vacuum for a predefined high temperature and residence time.

3. Summary of the recycling process MO

Technology: MOPET®

Extrusion of flakes into pellets (step 2): Flakes are processed on a twin-screw extruder into amorphous pellets with multiple vacuum degassing under high temperature. In the first section flakes are further dried and heated with degassing operating under atmospheric pressure. In the second section the melted material is processed under high temperature and vacuum degassing (two vent zones). In this step, some volatile contaminants are removed, and the polymer is melt filtered to remove residual solid particles (e.g. paper, aluminum, etc.).

Crystallization and solid-state polymerization (SSP) (step 3): The amorphous pellets are loaded into a rotary reactor (also called tumble drier) in which they are first crystallized then solid state polymerized under vacuum, temperature and nitrogen flow to achieve the desired intrinsic viscosity.

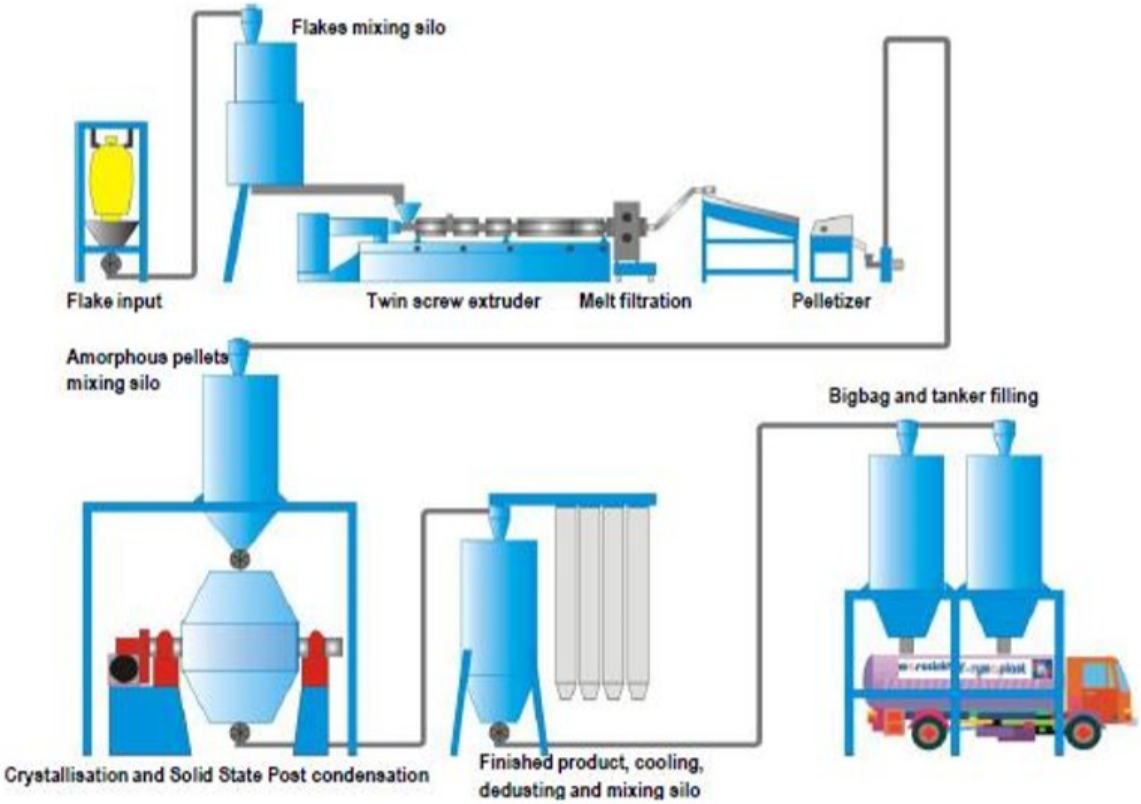

Figure 13 - Diagram of the MOPET A recycling process.

4. Summary of the recycling process F

Technology: Buhler C

Extrusion (step 2): The flakes are introduced into a ring extruder in which they are firstly dried and degassed at solid state before being melted and further degassed. Finally, residual solid particles (e.g. paper, aluminum, etc.) are filtered out before pellets are produced.

Drying and crystallization (step 3): The pellets are crystallized at high temperature in a gastight fluid bed reactor in a continuous process.

SSP reactor (step 4): The crystallized pellets are continuously introduced in the solid-state polymerization reactor running under gas flow (e.g. nitrogen) for a predefined high temperature, pressure and residence time.

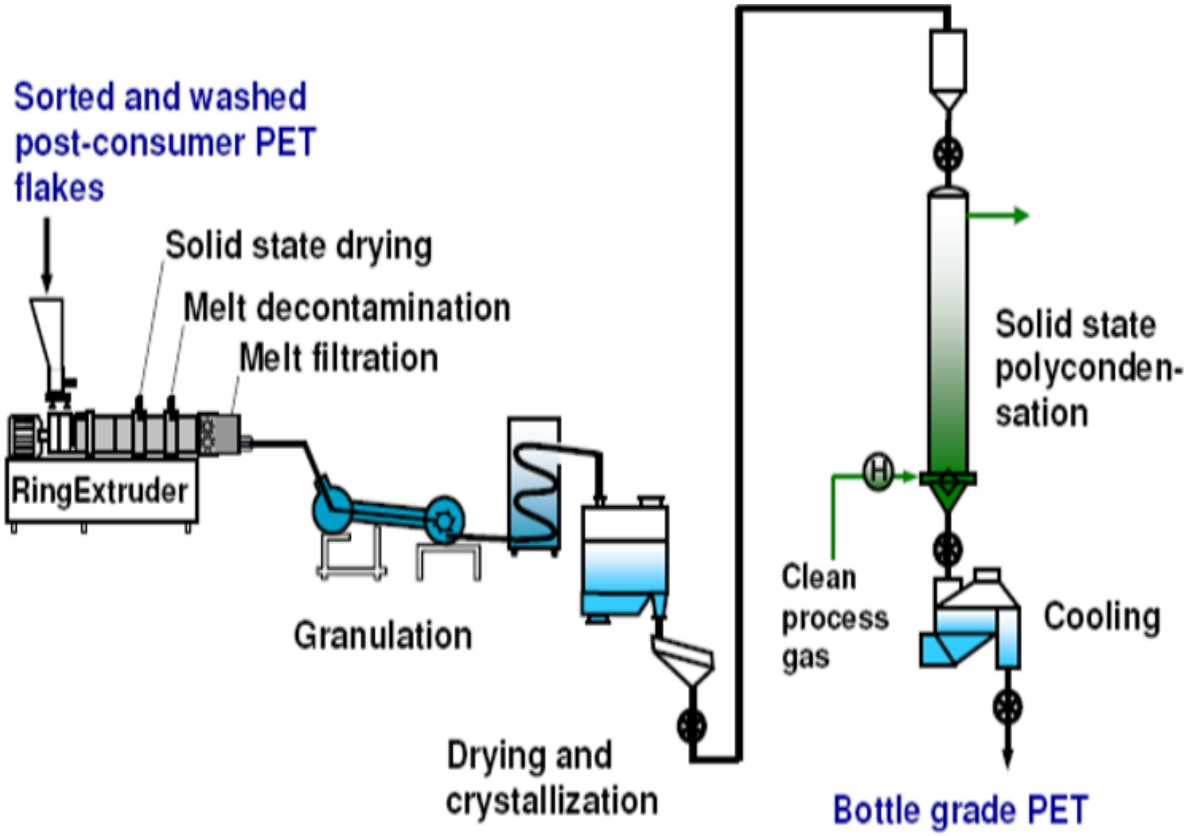

Figure 14 - Diagram of the FENC recycling process.

5. Summary of the recycling process NO

Technology: RPET NOSINYEC/OHL

Extrusion of flakes into pellets (step 2): Flakes are processed in a ring extruder with three zones of degassing to produce pellets under high temperature and vacuum for a predefined residence time. Degassing of the melt removes some volatile contaminants and residual un-melt particles (e.g. paper, aluminum, etc.) are filtered out.

Pre-crystallization of pellets (step 3): The extruded pellets are then crystallized in line in a further reactor under atmospheric pressure for a short residence time before being stored in a silo.

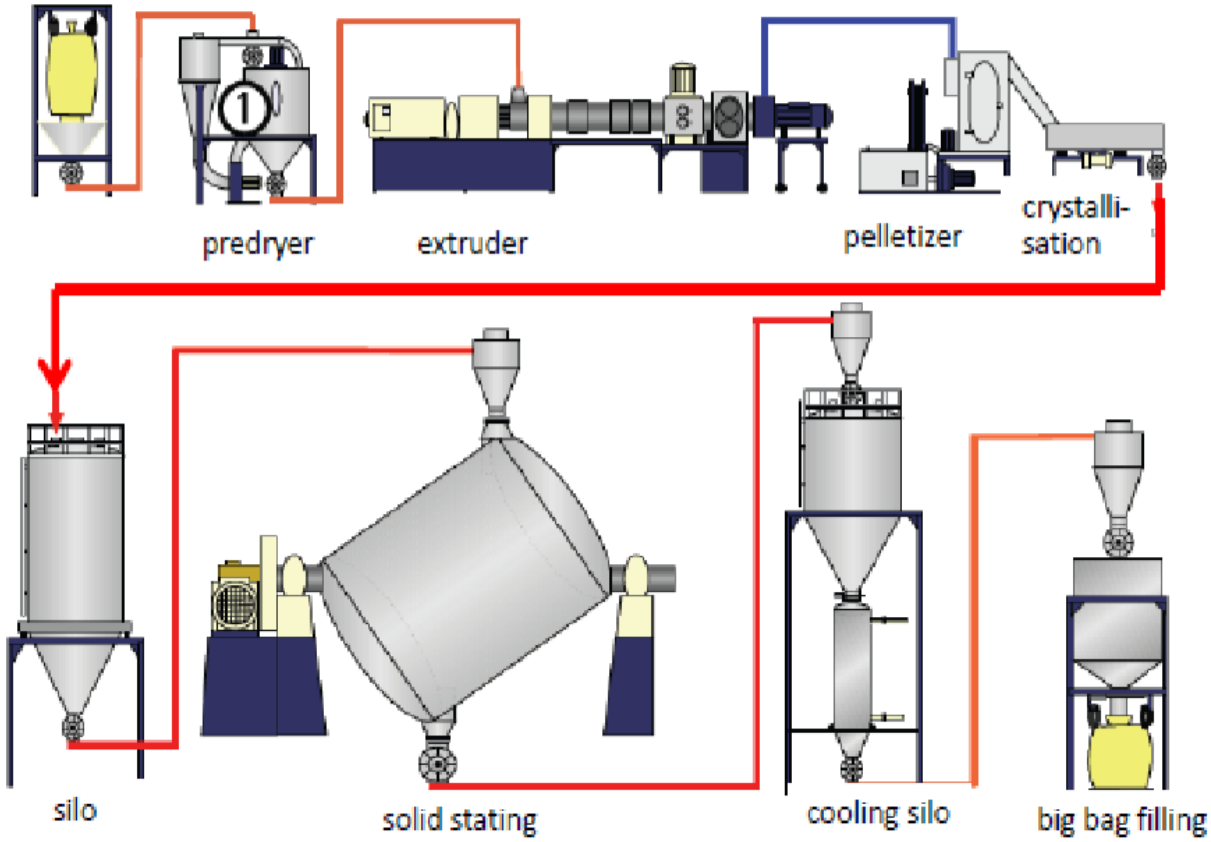

Figure 15 - Diagram of the RPET Nosinyec recycling process.

SSP reactor (step 4): The pre-crystallized pellets are loaded into a batch tumble dryer for further crystallization and solid-state polymerization (s) at high temperature under vacuum for the time necessary to achieve the desired intrinsic viscosity.

6. Summary of the recycling process IN

Technology: EREMA BASIC

Crystallization and decontamination in a continuous reactor (step 2): In this step the flakes are introduced into a continuous reactor equipped with a bottom-mounted rotating mixing device, in which vacuum and temperature are applied for a predefined residence time. These process conditions favor the vaporization of possible contaminants and crystallization of PET flakes.

Re-extrusion of the decontaminated flakes (step 3): The flakes continuously coming from the previous reactor are melted in the extruder. Residual solid particles (e.g. paper, aluminum, etc.) are filtered out of the extruded plastic before the final pellets are produced.

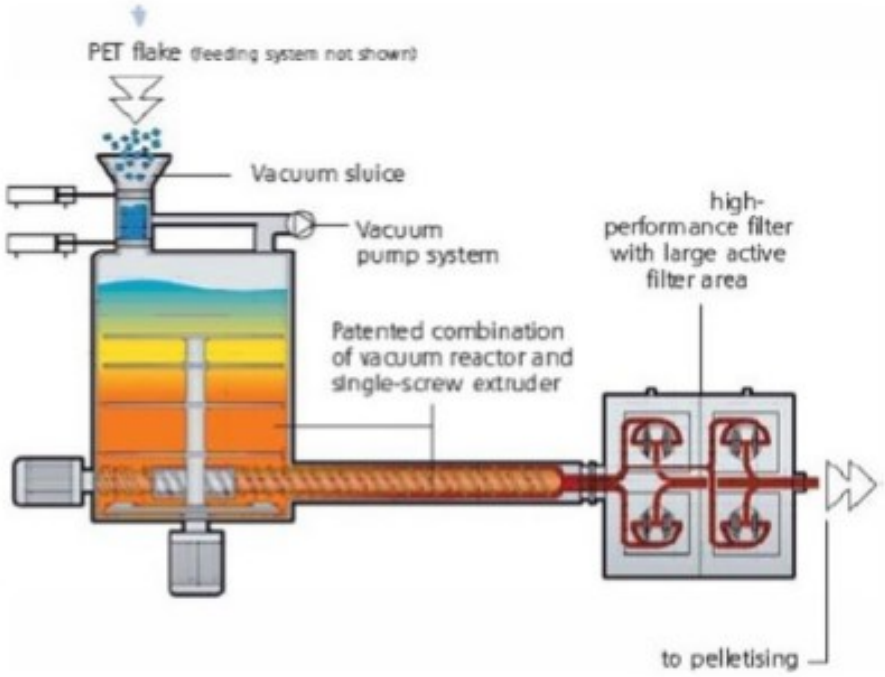

Figure 16 - Diagram of the INDORAMA recycling process.

ANNEX 2 – Calibration curves for the detection of Benzene and Limonene

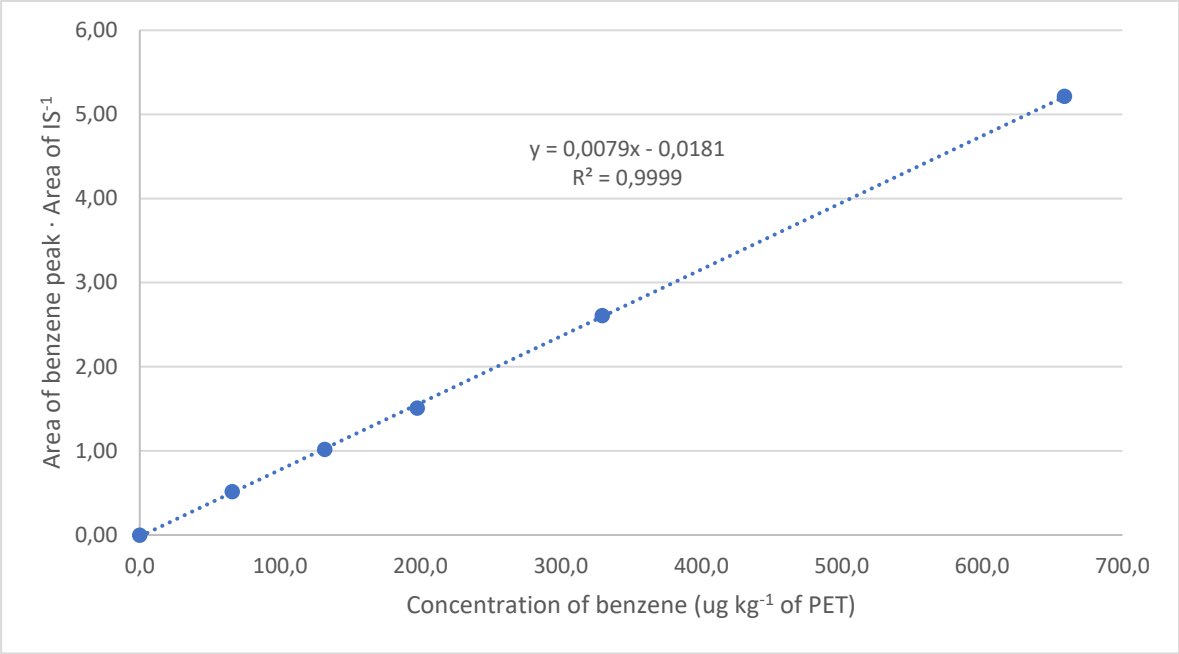

Figure 17 - Calibration curve for the benzene.

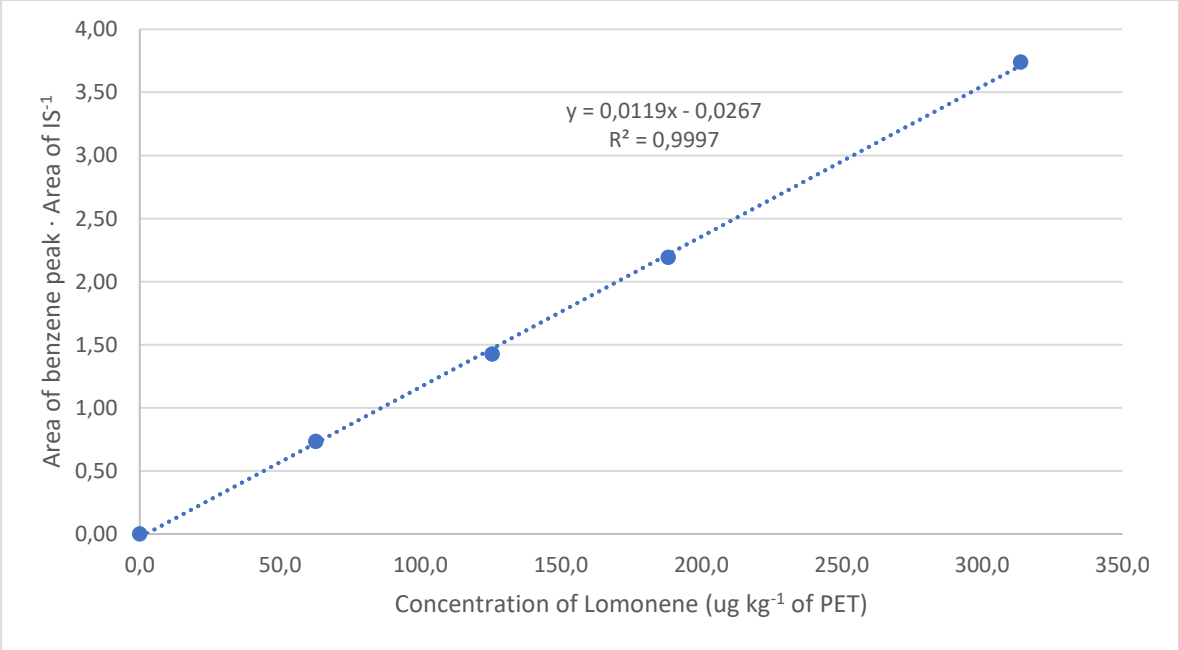

Figure 18 - Calibration curve for limonene.

ANNEX 3 - Calibration curves for the detection of Oligomers

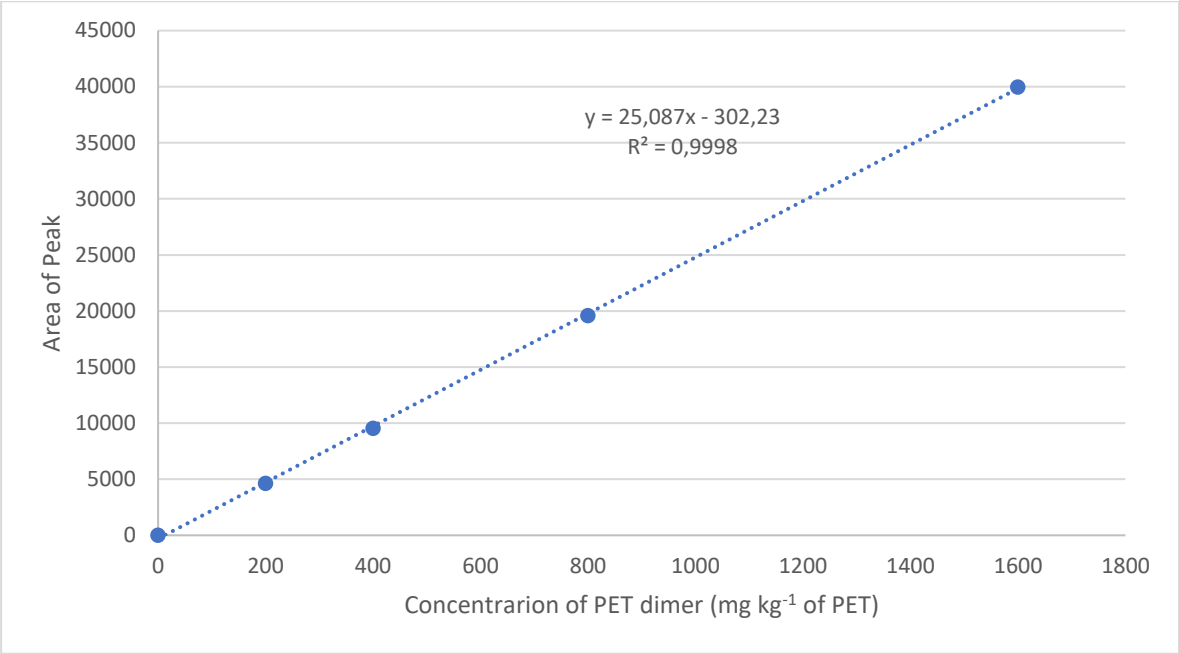

Figure 19 - Calibration curve for the PET dimer.

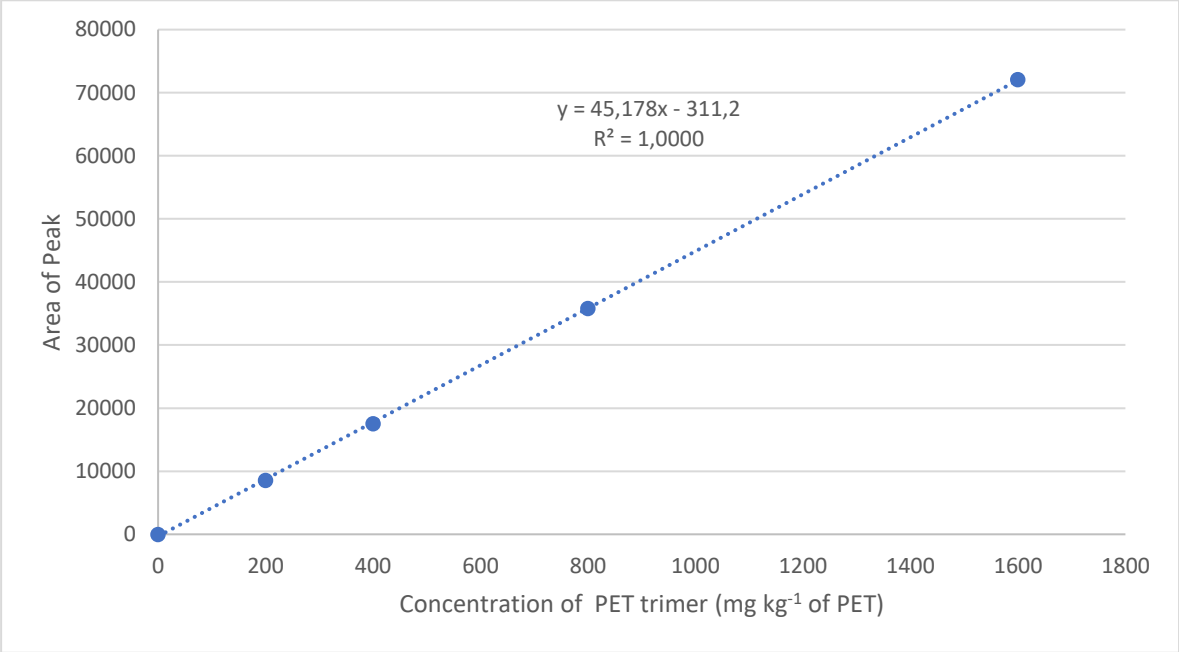

Figure 20 - Calibration curve for the PET trimer.