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Article

Migration of Residual Nonvolatile and Inorganic Compounds from Recycled Post-Consumer PET and HDPE

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Foi determinada a migração de compostos residuais não voláteis e de inorgânicos provenientes do polietileno tereftalato (PET) pós-consumo reciclado, submetido a processos de descontaminação para produção de materiais destinados a contato com alimentos, bem como de material de embalagem multicamada contendo polietileno de alta densidade (HDPE) pós-consumo reciclado. Os ensaios foram realizados utilizando simulantes de alimentos. Os contaminantes orgânicos não voláteis do PET, determinados por cromatografia líquida-espectrometria de massas (UPLC-QqQ/MS), apresentaram redução significativa da migração como consequência da complexidade da tecnologia de descontaminação aplicada. No entanto, contaminantes não permitidos pelas legislações brasileira e europeia foram identificados, mesmo em amostras submetidas à tecnologia mais complexa. Os resultados do HDPE multicamadas mostraram maior número de contaminantes quando em comparação aos peletes reciclados. Os níveis de contaminantes inorgânicos, determinados por espectrometria de massa com fonte de plasma, se mostraram abaixo dos níveis recomendados. Estudos adicionais para identificar e quantificar as estruturas moleculares não identificadas neste estudo por UPLC-QqQ/MS são necessários para garantir a segurança do uso de material de embalagem pós-consumo reciclado.

Migration of nonvolatile and inorganic residual compounds from post-consumer recycled polyethylene terephthalate (PET) submitted to cleaning processes for subsequent production of materials intended to food contact, as well as from multilayer packaging material containing post-consumer recycled high-density polyethylene (HDPE) was determined. Tests were carried out using food simulants. Nonvolatile organic contaminants from PET, determined by liquid chromatography-mass spectrometry (UPLC-QqQ/MS), showed significant migration reduction as consequence of the more complex cleaning technologies applied. However, contaminants not allowed by Brazilian and European Union regulations were identified even in deep cleaning samples. Results from multilayer HDPE showed a greater number of contaminants when compared to recycled pellets. Inorganic contaminants, determined by inductively coupled plasma mass spectrometry were below the acceptable levels. Additional studies for identification and quantitation of unknown molecules which were not possible to identify in this study by UPLC-QqQ/MS are required to ascertain the safety of using post-consumer recycled packaging material.

Keywords: PET, HDPE, post-consumer recycled food packaging, migration studies, UPLC-QqQ/MS, ICP-MS

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Introduction

Packaging materials are currently considered an important source of environmental waste mainly due to their large volume fraction in the waste stream. Furthermore, the economic packaging sector maintains a high volume of polymeric materials consumption (mainly plastics). Plastic packaging offers several advantages to consumers; it is safe, lightweight, strong, easily processed and stored, and economical.[1]

The recycling of plastic packaging is one of the most effective methods for decrease the negative effects of waste disposal in the environment. Recycling can be performed using a variety of technologies that employ critical cleaning methods without affecting the chemical structure of the plastic.[2]

Several approaches have been proposed for recycling waste polymers including: primary, mechanical, chemical or feedstock recycling and energy recovery. Almost all the above techniques have been employed for the recycling of polymeric materials used for food packaging.[1]

Among the common plastics, polyethylene naphthalene (PEN), polyethylene terephthalate (PET), and rigid polyvinyl chloride (PVC) have more favorable material properties for packaging in comparison to other plastic materials, such as polyolefins and polystyrene (PS). In addition, these plastics are, in terms of compound migration, well suited for being reused in packaging applications. Polymers such as PS and high-density polyethylene (HDPE) may also be introduced into this closed loop recycling if the cleaning processes are efficient enough to remove contaminants.[3]

Stabilizers, such as antioxidants, ultraviolet (UV) absorbers, and processing stabilizers, are added to extend the lifetime of these types of polymers.[4-5] However, these additives might also decompose during processing or through the lifetime of the polymer. Concerning recycling, stabilizers may be added during each step to obtain a sufficient level in the end-product, subsequently maintaining its lifetime. As a result, accumulation of stabilizers and degradation products from the additives might occur.[6]

Regarding consumer safety, the composition and concentration of typical substances in post-consumer plastics and the ability of the applied recycling process to remove all post-consumer substances to concentrations similar to virgin materials is of interest.[3]

Hazardous components, flavorings, odors, monomers, oligomers, degradation products, and flame retardants are examples of compounds found in recycled materials. Some compounds might change the properties of the material or enhance degradation of the polymer. Colored inorganic salts produce visual defects on the recycled fraction. The presence of printing inks, paint residues, surfactants, and fatty materials can also lead to enhanced degradation of the polymer.[7] Inorganic elements, due to the presence of catalysts or environmental contamination, can influence the properties of recycled plastics and could reach toxic levels. Direct contact between recycled plastic materials and food can result in the migration of these contaminants from packaging materials into foodstuffs.

In the European Union, the materials for food packaging must comply with the Framework Regulation 1935/2004/EC which requires that the packaging material may not endanger human health. Furthermore, the recycled materials must also comply with the Regulation 10/2011/EU related to plastic materials and Regulation 282/2008/EC related to recycled plastic materials and articles intended to come into contact with food.[8-10] In Europe, the Regulation established the challenge test, which consists of contaminating materials with a series of surrogate representatives of the probable pollutants in PET and applying the cleaning and recycling procedures at an industrial scale. This test is intended to demonstrate the cleaning efficiency of a recycling process to remove chemical contamination from plastic materials.

In 2006, the United States Food and Drug Administration (US FDA) published a guidance for the industry ("Use of Recycled Plastics in Food Packaging: Chemistry Considerations"),[11] which provides recommendations for testing the cleaning efficiency of the investigated recycling processes. The maximum content of post-consumer substances in recycle-containing packaging materials and threshold limits for migration were also advised.[3]

In Brazil, the National Agency for Sanitary Surveillance (ANVISA) regulated the use of recycled post-consumer PET for direct contact with foods through Resolution No. 20, published on March 26, 2008.[12]

Regarding HDPE materials, researchers have demonstrated higher diffusion and sorption characteristics than PET. Development of food grade HDPE recycling process based on the super cleaning process applied to PET has been considered, particularly for milk bottles.[13,14]

In Brazil, some industries have demonstrated interest in the manufacture of multilayer packaging containing recycled post-consumer HDPE intended for pharmaceutical products and cosmetics. For pharmaceutical products, international regulatory authorities require that the package should not interact physically or chemically with their contents.[15-17] Although several studies deal with volatile compounds in recycled plastics,[18-21] only a few studies that identify nonvolatile compounds and inorganic elements in recycled

PET and HDPE have been reported. Bentayeb *et al.*[22] screened samples of recycled PET and detected 36 chemical compounds that included common additives, such as *N*,*N′*-diβ-naphthyl-*p*-phenylenediamine (antioxidant) and 2,4-di-tert-butyl-6-(5-chloro-2*H*-benzotriazol-2-yl) phenol (light stabilizer), and degradation compounds, such as ethylene terephthalate dimers and trimers. Nerín *et al.*[23] screened recycled PET and reported very low levels of inorganic compounds and nonvolatile PET oligomers. Thereby, the aim of this study was to determine nonvolatile and inorganic compounds residual contaminants in post-consumer recycled PET submitted to cleaning processes. In addition, considering the lack of scientific information, in Brazil, about the use of post-consumer recycled HDPE intended for pharmaceutical and food products, multilayer packaging material containing recycled HDPE in the middle layer was evaluated for the potential migration of nonvolatile and inorganic compounds.

Experimental

Chemicals and solutions

Ethanol and acetic acid were HPLC-grade and were supplied by Scharlau (Barcelona, Spain). HPLC-grade methanol was obtained from Scharlau and Merck (São Paulo, Brazil). The water used throughout this study was obtained from a Milli-Q system from Millipore (Bedford, MA, USA).

For inductively coupled plasma mass spectrometry (ICP-MS), stock solutions were prepared in 1% (v/v) HNO_3 using a certified multi-element solution containing 100.0 mg L^{-1} of Al, As, Ba, Cr, Fe, Pb, Mn, Mo, Ni and Se. A standard solution containing 1000 mg L^{-1} of Sb was also prepared. All reagents for ICP-MS were obtained from Scharlau. Polyethylene containers and vials were used for samples and standard storage.

Samples

PET and HDPE samples are shown in the flowchart presented in Figure 1. The type of cleaning process applied to the PET and HDPE samples is pointed out in Tables 1 and 2, respectively. All samples were supplied by Brazilian packaging and recycling companies. PET post-consumer samples were obtained as flakes and pellets. HDPE multilayer packaging containing recycled HDPE was portioned to sample sizes of 4.0 × 3.0 cm.

Ultra performance liquid chromatography mass spectrometry (UPLC-QqQ/MS)

The UPLC-QqQ/MS system consisted of an ACQUITY™ UPLC chromatograph coupled to a Micromass® Quattro micro™ API mass spectrometer with a triple quadrupole mass analyzer (Waters, Milford, MA, USA). An electrospray ionization (ESI) interface was used for analyses. MassLynx (v. 4.0) software was

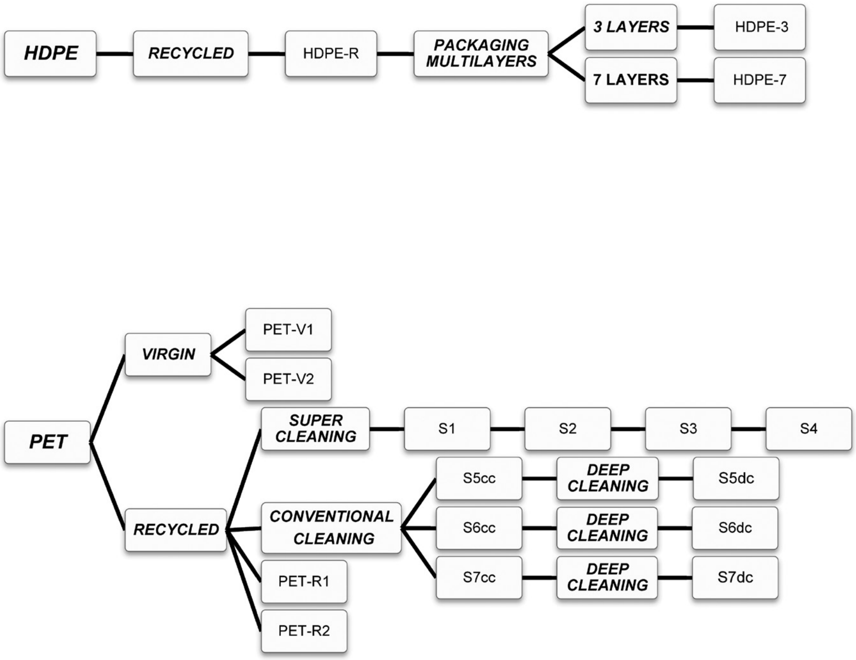

Figure 1. Flowchart of analyzed PET and HDPE samples. Description of the PET and HDPE samples analyzed and type of cleaning process they were submitted is presented in Tables 1 and 2, respectively.

Table 1. Description of the PET samples analyzed and type of cleaning process they were submitted

Material		Sample	Type of cleaning process
Virgin PET	Pellets	PET-V1	Virgin
	Flakes	PET-V2	Virgin bottle
Recycled PET	Flakes	S1	Conventional cleaning: flake washed with water
	Flakes	S2	S1 followed by deep cleaning (hot caustic washing with detergent, friction washing and drying)
	Pellets	S3	S2 followed by extrusion
	Pellets	S4	S1 followed by super cleaning (hot water and additives), extrusion and SSP (solid-state polycondensation)
	Flakes	S5cc	Conventional cleaning: flake washed with water
	Flakes	S6cc	Conventional cleaning: flake washed with water
	Flakes	S7cc	Conventional cleaning: flake washed with water
	Flakes	S5dc	Deep cleaning: hot caustic washing with detergent, friction washing and drying
	Flakes	S6dc	Deep cleaning: hot caustic washing with detergent, friction washing and drying
	Flakes	S7dc	Deep cleaning: hot caustic washing with detergent, friction washing and drying
	Pellets	PET-R1	Recycled conventional cleaning
	Pellets	PET-R2	Recycled conventional cleaning

PET-V1 and PET V-2: samples obtained from different suppliers. S1, S2, S3 and S4: samples obtained from the same supplier. S5cc, S6cc, S7cc: samples obtained from different suppliers. S5dc, S6dc, and S7dc: correspond, respectively, to samples S5cc, S6cc, S7cc submitted to deep cleaning process. PET-R1 and PET-R2: post-consumer recycled PET obtained from different suppliers.

Table 2. Description of the HDPE samples analyzed

Material		Sample	Type of cleaning process
Recycled HDPE	Pellets	HDPE-R	Unknown recycling process
	Multilayer packaging	HDPE-3	Layers: polyethylene/polyethylene with maleic acid + post-consumer recycled polyethylene/ polyethylene
	Multilayer packaging	HDPE-7	Layers: polyethylene/polyethylene with maleic acid + post-consumer recycled polyethylene/ EVOH/post-consumer recycled polyethylene/polyethylene polyethylene with maleic acid + post-consumer recycled polyethylene/polyethylene

used to acquire and process the chromatographic and MS data. The extracts from simulants, prepared in duplicate, were directly infused into the MS or injected into the UPLC system, and analyzed in positive ionization mode. The following conditions were employed: a capillary voltage of 3.00 kV; a cone voltage of 40 V for samples directly infused into the MS and 30, 40 and 50 V applied simultaneously when the sample was injected throughout the UPLC system; a source temperature of 125 °C, a desolvation temperature of 350 °C; a cone gas (N_2) flow rate of 60 L h^{-1}; a desolvation gas (N_2) flow rate of 600 L h^{-1}; and an infusion flow rate of 20 µL min^{-1}. Parent-daughter spectra (MS/MS) were acquired in ESI positive mode using collision energies of 5, 15, 20 and 30 V applied simultaneously. The mass interval scan ranged from 100 to 1450 amu.

Some extracts were also analyzed using the UPLC-QqQ/MS system with an atmospheric pressure chemical ionization (APCI) interface, positive mode, and under the following conditions: a capillary voltage of 3.00 kV; a cone voltage of 40 V for samples directly injected into the MS and 30, 40 and 50 V applied simultaneously when the sample was injected throughout the LC system; a source temperature of 130 ºC; a desolvation temperature of 500 ºC; a cone gas (N_2) flow rate of 40 L h^{-1}; and a desolvation gas (N_2) flow rate of 125 L h^{-1}. The mass interval scan ranged from 100 to 1450 amu.

An UPLC™ BEH C18 column (2.1 × 100 mm, 1.7 µm particle size, and flow rate of 300 µL min^{-1}), an injection volume of 15 µL, and water (solvent A) and methanol (solvent B) mobile phases were used. Both solvents were filtered through 0.45 µm nylon membranes (Sartorius, Göttingen, Germany) and degassed for 5 min in an ultrasonic bath under vacuum. The separation was performed using a gradient elution with mobile phase A increasing linearly from 10 to 90% over 9 min. These conditions were maintained for 10 min and then returned to the original conditions for 5 min.

Inductively coupled plasma mass spectrometry (ICP-MS)

The ICP-MS system consisted of an Agilent 7500a series (Agilent Technologies Inc., Japan), equipped with a Babington nebulizer and nickel sampler and skimmer cones. An aqueous solution of HNO_3 (1%, v/v) was used as carrier solution at a flow rate of 1.2 mL min^{-1} and samples, prepared in triplicate, were introduced by a peristaltic pump.

A tuning of the instrument was carried out using a tuning solution provided by Agilent (10 µg L^{-1} Li, Co, Y, Ce and Tl solution). The radio frequency power (1290 W), sample depth (4.6 mm), plasma gas, and lens voltage were automatically optimized by the instrument during the tuning. Spray chamber temperature was 2 °C and carrier gas was 1.14 L min^{-1}. Plasma gas was argon (Alphagaz purity higher than 99.999%) supplied by Carburos Metálicos (Barcelona, Spain). Data acquisition parameters were as follows: 3 points *per* peak, 0.9 s integration time per mass and 3 repetitions. Isotopes selected for data acquisition were ^{27}Al, ^{55}Mn, ^{57}Fe, ^{62}Ni, ^{75}As, ^{76}Se, ^{138}Ba, ^{123}Sb, ^{98}Mo, ^{50}Cr and ^{207}Pb.

Migration tests

Migration tests were carried out by the total immersion of samples (0.5 g each, 17 samples) as follows: 20 mL of 3% (m/v) acetic acid aqueous solution (simulant B) and 10% (v/v) ethanol in water (simulant C), according to European and Brazilian Regulations.[9,24,25] Also, in accordance with Brazilian Regulations,[25] 20 mL 95% (v/v) ethanol in water was used as a simulant (simulant D). The experiment was performed in Teflon® capped vials. The vials were closed and incubated in an oven at 40 °C for 10 days before analysis.

For migration tests, blank samples were prepared using the same migration procedure without the presence of PET, HDPE, or the multilayer material.

Extracts from simulants B and C were concentrated eightfold by gentle evaporation under a nitrogen flow at 70 ºC and were analyzed by UPLC-QqQ/MS. The extracts from simulant D were concentrated eightfold by gentle evaporation under a nitrogen flow at room temperature and were analyzed by UPLC-QqQ/MS. After the concentration, all the extracts were stored at 4 ºC before analysis.

The extracts from simulants B and C, prepared in triplicate, were analyzed by ICP-MS after the migration test. However, the extracts from simulant D were diluted fivefold with water before the ICP-MS analysis. The same treatment was applied to the blank samples.

Inorganic elements were determined using certified solutions with concentrations of 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0, 30.0, 50.0, 120.0, 140.0, 160.0, 180.0, and 200.0 µg L^{-1}. The quantification was performed using an analytical curve. The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to Miller and Miller[26] using the following expressions: LOD = 3 $S_{y/x}$/m and LOQ = 10 $S_{y/x}$/m, where $S_{y/x}$ is the standard deviation of the residuals and m is the slope of the analytical curve.

Results and Discussion

Nonvolatile compounds by UPLC-QqQ/MS

For all evaluated samples, nonvolatile compounds were screened by UPLC- QqQ/MS analysis.

The migration was higher in simulant D than in simulants B and C for both PET and HDPE samples. Several non-identified compounds were also detected in the blank samples evaluated in simulant D. Their presence could be attributed to the presence of concentrated impurities from the solvent (95% ethanol in water), as well as contaminants from the Teflon® capped glass vials used for the migration test. Similar interferences have also been reported in other studies.[22] These compounds were not detected in simulants B and C.

Several additional compounds were detected for all evaluated samples when the extracts from simulant D were subject to chromatographic separation prior to MS analysis. The results obtained for simulant D using a cone voltage of 30, 40, and 50 V, positive mode, and ESI and APCI interfaces are listed in Table 3. In scan mode, the sensitivity is lower. Therefore, three injections were made for *m/z* 100-550, 550-1000, and 1000-1450 amu. MassLynx software was used to combine the obtained data. Overall, the ESI source provided better sensitivity than the APCI source.

Several attempts were made to identify the compounds present in simulant D by taking into account the parent ions detected as sodium adducts, formed in the mobile phase due to the presence of sodium. Data are shown in Table 3. Very few data on nonvolatile compounds determined by UPLC-QqQ/MS are available in the literature for food packaging materials. Also, there are no libraries available which would allow a comparative analysis of the results. The main reason for that is the necessity of different analytical conditions in the mass spectrometer for the different substances found in the packaging materials.[27-29] Considering these aspects the tentative identification of substances in Table 3 was based on the mass weight of organic compounds. A series of compounds were identified as common additives employed in the transformation process of polymers, for example plasticizers, such as diisononyl adipate (bis(7-methyloctyl) hexanedioate) and diisononyl phthalate (diisononyl ester

Table 3. Compounds identified in the extracts from simulant D (PET and HDPE) analyzed by UPLC-QqQ using ESI and APCI in the positive mode at collision energies of 5, 15, 20 and 30 V and cone voltage of 30, 40 e 50 V

t_R / (min)	$[M+Na]^+$ *m/z*	Identified compounds	Commercial name	CAS No.	Formula	MW	Mode	Samples
6.170	129.1	diethylene glycol	–	111-46-6	$C_4H_{10}O_3$	106.1	ESI+	S2
–	351.4	2-(benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl) phenol	Tinuvin 328	25973-55-1	$C_{22}H_{29}N_3O$	351.2	ESI+	S5dc
6.689	441.4	diisononyl ester 1,2-benzenedicarboxylic acid	diisononyl phthalate	28553-12-0	$C_{26}H_{42}O_4$	418.6	ESI+	S2, S4, S5cc, S7cc, PET-R1, PET-R2, PET-V1, HDPE-3
6.808	214.0	*N*,*N*-diethyl-3-methyl-benzamide	diethyl toluamide	134-62-3	$C_{12}H_{17}NO$	191.3	APCI+	S7cc, S7dc
7.090	453.4	2,5-bis(5-*tert*-butyl-2-benzoxazolyl thiophene	Uvitex OB	7128-64-5	$C_{26}H_{26}N_2O_2S$	430.6	ESI+	S5cc, S5dc, S6dc, PET-R1, PET-V2
7.527	399.2	bis(7-methyloctyl) hexanedioate	diisononyl adipate	33703-08-1	$C_{24}H_{46}O_4$	398.6	ESI+	S2, PET-R1, PET-R2
9.458	304.3	(*Z*)-octadec-9-enamide	oleamide	94554-98-0	$C_{20}H_{39}NO_2$	281.3	ESI+	S1, S2, S3, S4, S7cc, S6cc, S5dc, S6dc, PET-R1, PET-R2, PET-V1, HDPE-R, HDPE-3, HDPE-5

1,2-benzenedicarboxylic acid); optical brightening agents, such as Uvitex OB (2,5-bis(5-*tert*-butyl-2-benzoxazolyl thiophene) and slip agents, such as oleamide ((*Z*)-octadec-9-enamide). As these nonvolatile substances are included in ANVISA and European Union positive lists, they can be found in plastic materials. Nevertheless, it is important that the residual levels accomplish the specific regulations.[9,25]

An UV stabilizer, Tinuvin 328 (2-(benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol); and the slip agent diethyl toluamide (*N*,*N*-diethyl-3-methyl-benzamide) were also identified. According to ANVISA and European Union regulations, these substances are not included in the positive lists; therefore, the presence in PET samples is quite unexpected.[9,25] These substances probably come from materials of different sources, suggesting that improvements must be worked out in the PET recycling chain in order to avoid undesirable contamination.

Oleamide is frequently found in HDPE; its presence in PET may have originated from contact with polyolefin.

The identification of substances in the samples submitted to several cleaning processes raises interest about the efficiency of each process in removing contaminants from the samples. Diethyl toluamide was found in recycled PET after conducting conventional cleaning (S7cc and S7dc), but it was not present after deep cleaning. This finding suggests that the final removal process is more efficient. Diisononyl phthalate and Uvitex OB were identified in virgin and several recycled PET samples submitted to conventional cleaning process. Uvitex OB is an additive used mainly for polyolefin, while diisononyl phthalate is employed as plasticizer of plastics and as component of printing inks and lacquers.[30] Those compounds were also present in virgin and recycled PET samples submitted to deep cleaning processes. Tinuvin 328 was also identified in PET samples submitted to deep cleaning (S5dc). Diisononyl phthalate, Uvitex OB and Tinuvin 328 were not expected to be found in PET, suggesting that they may have originated from a post-contamination source or from contact with other polymers. The occurrence of post-contamination enforces that improvements must be introduced in the recycling chain in order to obtain recovered materials suitable for food contact, regarding European and Brazilian legislation.

Diethylene glycol (DEG), a PET monomer, was found in samples submitted to conventional followed deep cleaning process (S2). The monomer did not appear in sample S4, which was treated by conventional and super cleaning, followed by extrusion and solid-state polycondensation (SSP) processes.

Detected organic compounds in samples submitted to conventional cleaning could not be identified, particularly for S5cc (*m/z* 149.0 and 158.0 amu for APCI+ mode; *m/z* 209.2, 227.2, 271.2, 285.3, 293.4, 301.3, 353.3, 365.3, and 455.4 amu for ESI+ mode). Samples S6cc and S7cc showed few unidentified organic compounds, expressed by the low number of ions present in the obtained UPLC-QqQ/MS spectra. Considering that the cleaning process was the same for these samples, these results demonstrate the heterogeneous characteristics of samples collected from different sources. The removal of such substances after deep cleaning (S5dc, S6dc, and S7dc) was verified by the UPLC-QqQ/MS spectra. These findings were also corroborated by the spectra obtained from direct infusion into the MS (extracts from conventional and deep cleaning). As expected, the number of substances identified in the extracts from conventional cleaning was greater than from deep cleaning processes. These results demonstrate that the purpose of more complex cleaning process is attained, since deep-cleansing process is employed to improve the quality of the recycled polymer and the migration thereof is directly proportional to its concentration in the food contact materials. To illustrate this result, the spectra of the extracts from simulant D, obtained by direct infusion into the mass spectrometer (QqQ/MS), from conventional (S5cc) and deep cleaning (S5dc) processes are shown in Figure 2.

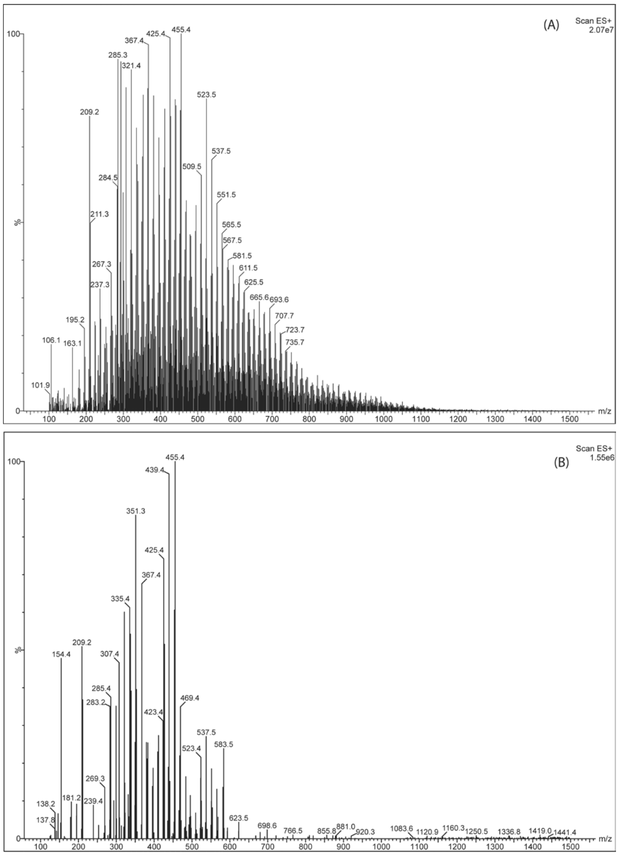

Figure 2. Direct infusion spectra of recycled PET sample S5cc (conventional cleaning) (A) and S5dc (deep cleaning) (B). Samples were obtained using 95% (v/v) ethanol in water (simulant D) as extraction solvent. Spectra were obtained under the following conditions: injection flow 20 µL min^{-1}, cone voltage 40 V, *m/z* scan range from 100 to 1500 amu, by UPLC-QqQ/MS, ESI positive mode.

Interesting results arise when the efficiency of the deep cleaning and the deep cleaning followed by extrusion are compared. Sample S2 possessed several organic compounds after deep cleaning (*m/z* 129.1, 149.0 301.3, 399.2, 451.0 and 497.1 amu for ESI+). These compounds were not detected in sample S3, which was subject to deep cleaning and extrusion, suggesting that this process is more effective in removing contaminants. The obtained data also showed that ion of *m/z* 149.0 amu was present in S5cc, S6cc and S7cc, submitted to conventional cleaning process, which shows that the introduction of detergent and friction were not enough to remove such substance.

The spectra obtained from the direct infusion into the MS indicates that the more rigorous the cleaning process, the higher the efficiency in removing organic contaminants from the samples. Nevertheless, some organic compounds were still detected in the deep cleaned samples that were not detected in virgin PET (flakes and bottles). Thus, this cleaning process did not remove all the impurities from recycled PET. On the other hand, it is important to notice that ions found in sample S4 are the same ones found in virgin PET, suggesting the good quality of the final product obtained in relation to nonvolatile contaminants. In relation to the recycled PET obtained from different companies (PET-R1 and PET-R2) both contained diisononyl phthalate and diisononyl adipate, and only PET-R1 contained Uvitex OB (Table 3). Nevertheless, in general, no difference in the detected organic compounds was observed between the materials. This behavior is corroborated by the spectra obtained by direct infusion into the MS.

Evaluated HDPE samples included recycled pellets (HDPE-R) and multilayer packaging materials (HDPE-3 and HDPE-7). Some compounds (*m/z* 701.6 amu for APCI+; *m/z* 149.0, 217.2, 245.1, 295.2, 304.3, 409.1, 441.4 and 928.0 amu for ESI+) were common in the extracts of simulant D for all HDPE materials (HDPE-R, HDPE-3, and HDPE-7). The multilayer packaging containing recycled HDPE (HDPE-3 and HDPE-7) showed a lower number of peaks when compared to the recycled HDPE pellets (HDPE-R). Considering that contaminants come from the post-consumer plastics, these results suggest a dilution effect for the contaminants present in the HDPE-R, since the global packaging structure of the HDPE multilayer materials contain other virgin polymers.

Taking into account the scenario presented in this research, it becomes clear that additional studies to identify and quantify the molecular structures of the *m/z* ions not identified by UPLC-QqQ/MS are required to ascertain the safety of using post-consumer PET and HDPE multilayer packaging for food and cosmetics, respectively.

Inorganic elements

The extracts from all the simulants (B, C, and D) in contact with all the recycled samples (PET, HDPE, and HDPE multi-layer) were also screened by ICP-MS to study the migration of inorganic elements (Tables 4-6). Table 4 shows the inorganic elements found in simulant B and the limits of detection (LOD) and quantification (LOQ) of the method of analysis. The linear ranges were from 2.23 to 360.45, 1.98 to 342.51, and 1.50 to 274.76 μg L^{-1} for simulants B, C, and D, respectively.

The inorganic elements with the highest migration were iron and aluminum. Aluminum and iron exhibited levels from 211 to 315 and 15.53 to 903 μg L^{-1}, respectively, for PET samples from conventional, deep, and super cleaning processes. For virgin, recycled PET, and HDPE samples, the iron concentrations ranged from 22 to 78 μg L^{-1}, and the levels of aluminum were 242 and 226 μg L^{-1} for PET-R1 and HDPE-R, respectively. These inorganic elements may have been originated from a number of sources, such as labels and glues, rather than from the PET. By analyzing the potential migration obtained for PET samples subject to conventional, deep, and super cleaning, in simulants B, C, and D, a decrease in element concentration, such as barium and lead, was observed while other inorganic elements were completely eliminated after the cleaning processes. In simulant B, for PET samples from conventional cleaning, the level of barium was 20 μg L^{-1} for S5cc, and the levels of lead ranged from 2.3 to 52 μg L^{-1}. After deep cleaning, the concentrations decreased to 2 and 1.66 μg L^{-1} for lead. Barium level was below the LOQ. For simulant C (S5cc), the barium concentration was 0.3 μg L^{-1} (Table 5).

In simulant B, the levels of antimony in PET samples from conventional cleaning processes (from 1.2 to 3.0 μg L^{-1}) did not change even after applying deep and super cleaning processes (from 1.7 to 3.7 μg L^{-1}) (Table 4). In virgin and recycled PET samples, the levels of antimony ranged from 0.5 to 14.0 μg L^{-1}. In simulant C, the antimony concentration was below the LOQ in PET samples from conventional cleaning. The deep and super cleaning processes reduced the level to 0.8 μg L^{-1} (Table 5). The virgin and recycled PET samples exhibited levels of antimony ranging from 8 to 8.9 μg L^{-1}.

In simulant D, the concentration of antimony was 4 μg L^{-1} for PET samples from conventional cleaning (Table 6). Also, the maximum level of antimony determined in PET samples submitted to deep and super cleaning processes was 3 μg L^{-1}.

Antimony trioxide is the preferred polycondensation catalyst for the production of PET. The Sb concentration of commercialized PET resin ranges between 190 and 300 μg g^{-1}.[31] Moreover, antimony is widely used in plastics and commonly found in many laboratories.[32] The concentration of antimony in the samples was below the limits established by the Regulation 10/2011/EU, as well as by the Brazilian Resolution No. 17, from March 17, 2008 (40 mg kg^{-1}).[9,33]

In simulant B, the only element that showed a significant increase after deep and super cleanings was chromium, possibly due to contamination during these processes. Chromium was quantified in PET sample S4 (46.2 μg L^{-1}), due to solid-state polycondensation (SSP), which was also

Table 4. Inorganic elements quantified in the simulant B (n = 3)

Inorganic elements / (μg L^{-1})	^{27}Al	^{50}Cr	^{55}Mn	^{57}Fe	^{62}Ni	^{76}Se	^{138}Ba	^{207}Pb	^{123}Sb
LOD[a] / (μg L^{-1})	11.2	0.053	0.022	1.08	0.045	2.56	0.064	0.026	0.027
LOQ[b] / (μg L^{-1})	37.4	0.176	0.075	3.60	0.15	8.55	0.21	0.087	0.089
S1	–	–	1 ± 0.8	223 ± 17	30 ± 1	–	6 ± 1	7.8 ± 0.9	1.4 ± 0.4
S2	–	< LOQ	1.0 ± 0.3	108 ± 12	–	–	0.3 ± 0.1	–	17 ± 1
S3	292 ± 69	–	–	22 ± 5	0.5 ± 0.2	< LOQ	–	–	0.50 ± 0.07
S4	253 ± 67	46.2 ± 0.9	–	15.53 ± 0.01	–	< LOQ	–	–	3.7 ± 0.3
S5cc	260 ± 8	4 ± 2	5.4 ± 0.5	903 ± 60	–	–	20 ± 1	52 ± 10	1.2 ± 0.4
S6cc	211 ± 69	–	3 ± 2	156 ± 25	–	–	–	4 ± 3	3.0 ± 0.9
S7cc	293 ± 90	–	2 ± 1	–	–	–	–	2.3 ± 0.6	1.2 ± 0.3
S5dc	–	12 ± 2	3 ± 1	71 ± 17	–	< LOQ	–	–	1.7 ± 0.5
S6dc	315 ± 24	–	0.9 ± 0.5	59 ± 3	–	–	–	2 ± 1	3.1 ± 0.5
S7dc	–	10 ± 1	1.9 ± 0.6	152 ± 20	–	–	–	1.66 ± 0.01	3.2 ± 0.4
PET-V1	–	–	–	42 ± 3	–	–	–	0.53 ± 0.09	9 ± 1
PET-V2	–	–	–	41.4 ± 0.5	–	–	–	0.790 ± 0.005	13 ± 2
PET-R1	242 ± 28	–	–	78 ± 13	–	–	–	–	14.0 ± 0.4
PET-R2	–	< LOQ	–	26 ± 11	2.53 ± 0.08	–	–	3.8 ± 0.5	0.5 ± 0.1
HDPE-R	226 ± 38	2 ± 0.8	–	22 ± 10	–	< LOQ	–	0.30 ± 0.05	–
HDPE-3	–	–	–	36 ± 10	–	< LOQ	1.32 ± 0.01	–	–
HDPE-7	–	–	–	32 ± 14	0.4 ± 0.2	–	3.6 ± 0.7	–	–

[a]limit of detection; [b]limit of quantification.

Table 5. Inorganic elements quantified in the simulant C (n = 3)

Inorganic elements / (μg L^{-1})	^{27}Al	^{55}Mn	^{57}Fe	^{62}Ni	^{75}As	^{76}Se	^{138}Ba	^{123}Sb
LOD[a] / (μg L^{-1})	17.8	1.25	11.8	3.43	0.036	10.2	0.075	0.072
LOQ[b] / (μg L^{-1})	59.2	4.17	39.3	11.4	0.12	34.1	0.25	0.24
S1	< LOQ	–	< LOQ	–	1.59 ± 0.03	< LOQ	–	–
S2	< LOQ	–	< LOQ	< LOQ	–	< LOQ	–	12.6 ± 0.4
S4	< LOQ	–	< LOQ	–	–	< LOQ	–	1.1 ± 0.3
S5cc	< LOQ	< LOQ	< LOQ	–	–	< LOQ	0.3 ± 0.1	–
S6cc	< LOQ	–	< LOQ	–	–	< LOQ	–	< LOQ
S7cc	< LOQ	–	< LOQ	–	0.7 ± 0.5	< LOQ	–	–
S5dc	< LOQ	–	–	–	–	< LOQ	–	0.4 ± 0.2
S6dc	–	–	–	–	–	< LOQ	–	0.8 ± 0.1
S7dc	< LOQ	–	–	–	–	< LOQ	–	0.5 ± 0.2
PET-V1	–	–	< LOQ	–	< LOQ	< LOQ	–	8 ± 6
PET-V2	< LOQ	< LOQ	–	< LOQ	< LOQ	–	–	8.7 ± 0.6
PET-R1	< LOQ	–	< LOQ	–	< LOQ	< LOQ	–	8.9 ± 0.5
PET-R2	< LOQ	< LOQ	< LOQ	–	< LOQ	–	–	–
HDPE-R	< LOQ	34 ± 4	< LOQ	–	< LOQ	–	–	–
HDPE-3	< LOQ	–	< LOQ	15 ± 6	< LOQ	–	–	–
HDPE-7	68 ± 28	–	< LOQ	< LOQ	< LOQ	–	–	–

[a]limit of detection; [b]limit of quantification.

Table 6. Inorganic elements quantified in the simulant D (n = 3)

Inorganic elements / (μg L^{-1})	^{55}Mn	^{75}As	^{98}Mo	^{123}Sb	^{207}Pb
LOD[a] / (μg L^{-1})	6.57	2.26	0.915	0.377	0.428
LOQ[b] / (μg L^{-1})	21.9	7.55	3.05	1.26	1.43
S1	–	–	5 ± 1	–	–
S2	–	–	5 ± 2	3 ± 1	–
S4	–	–	–	2.0 ± 0.7	–
S5cc	48 ± 4	–	–	–	4 ± 2
S5dc	–	–	10 ± 2	2.5 ± 0.7	3 ± 1
S6dc	–	13.3 ± 0.5	12 ± 0.8	3 ± 1	3.0 ± 0.9
S7dc	–	–	9.5 ± 0.7	–	3.0 ± 0.9
PET-V1	–	–	6 ± 2	–	–
PET-V2	–	–	9.7 ± 0.8	4 ± 2	2.0 ± 0.5
PET-R1	–	–	–	5 ± 1	–
PET-R2	–	–	5 ± 1	2.0 ± 0.6	–
HDPE-R	–	–	6.3 ± 0.5	–	2.0 ± 0.3
HDPE-3	–	–	5 ± 3	–	2.0 ± 0.5
HDPE-7	–	–	7.28 ± 0.07	2 ± 1	4 ± 2

[a]limit of detection; [b]limit of quantification.

responsible for increasing the levels of antimony.[34] After deep cleaning, the maximum level of chromium was 12 μg L^{-1}.

The HDPE samples exhibited low concentrations of inorganic elements (maximum concentration found was 226 μg L^{-1}). The HDPE-R exposed to simulant B exhibited concentration levels of 226, 2, 22, and 0.30 μg L^{-1} for aluminum, chromium, iron, and lead, respectively. A greater number of inorganic elements were identified in HDPE-7 compared to HDPE-R and HDPE-3; however, a lower nickel concentration of 0.4 μg L^{-1} in simulant B was observed (Table 4). Manganese (34 μg L^{-1}) and nickel (15 μg L^{-1}) were found in HDPE-R and HDPE-3, respectively, when exposed to simulant C (Table 5). Aluminum was observed in HDPE-7 at 68 μg L^{-1}. In simulant D, HDPE samples exhibited levels from 2 to 4 and 5 to 7.28 μg L^{-1} for lead and molybdenum, respectively (Table 6).

Considering the European Regulation 10/2011/EU,[9] as well as the Brazilian Resolution No. 17, of March 17, 2008,[33] for the inorganic elements the migration levels found were below the specific migration limits. Some

Table 7. Specific migration limits (SML) established by European and Brazilian Regulations

Element SML / (mg kg^{-1})	Regulation 10/2011 European Union[9]	Regulation 17/2008 ANVISA[33]	Regulation 52/10 ANVISA[35]
Aluminum	–	up to 25.0	–
Antimony	0.04	0.04	0.04
Arsenic	–	–	0.01
Barium	1.0	1.0	1.0
Chromium	–	–	0.05
Iron	48.0	up to 30.0	–
Lead	–	–	10
Manganese	0.6	0.6	–

of them are regulated for colorants in plastic packaging materials, according to Resolution No. 52, 2010.[35] Specific migration limits are shown in Table 7. For elements, such as aluminum and lead, the Regulation 10/2011/EU[9] considers limits in the plastic material. Nickel and selenium are not mentioned in these European and Brazilian regulations.

Conclusions

A reduction of migration of nonvolatile compounds as a consequence of the cleaning process was verified in the PET post-consumer samples studied. As expected, this reduction was more evident when more sophisticated technologies were applied, such as deep and super cleaning. It is important to notice that the super cleaning technology is recommended for post-consumer selected materials. Thus, considering that in this study there was used recycled PET and HDPE originally collected from unknown origin and, consequently, there was not any form of sample contamination control (a real scenario employed in the recycling of plastic packaging material), our results suggest that the usage of such technologies for decontamination of post-consumer PET material intended for food contact is very promising. Nevertheless, none of the cleaning process, including deep and super cleaning, was able to eliminate all the organic compounds present in the post-consumer PET samples. In addition, taking into account that contamination of recycled plastic materials can occur in several steps of the recycling chain, it can be suggested that improvements should be worked out starting by a more efficient control of post-consumer materials source to the cleaning process employed.

The recycled HDPE pellets (HDPE-R) showed a greater number of nonvolatile compounds when compared to the multilayer packaging material, probably due to a dilution effect of the compounds present in the HDPE-R, since the global packaging structure of the HDPE multilayer materials contain other virgin polymers. In general, additional studies are required to identify and quantify the molecular structures of the nonvolatile compounds (*m/z* ions) not identified when UPLC-QqQ/MS was used, in order to ascertain the safety of using post-consumer PET and HDPE multilayer packaging for food contact material and cosmetic packaging material, respectively.

The inorganic element levels found in the recycled PET were below the tolerable levels, according to the European Union and Brazilian legislation. The reduction in migration level of contaminants according to the different cleaning processes employed suggests differences in efficiency among the applied technologies.

In general, the HDPE samples presented low concentrations of inorganic elements. However, the multilayer (seven layers) HDPE samples demonstrated higher levels of inorganic elements, probably as a consequence of the manufacturing process.

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References

1. Achilias, D. S.; Giannoulis, A.; Papageorgiou, G. Z.; *Polym. Bull.* **2009**, *63*, 449.
2. Meran, C.; Ozturk, O.; Yuksel, M.; *Mater. Des.* **2008**, *29*, 701.
3. Franz, R.; Welle, F. In *Novel Food Packaging Techniques*, 1st ed.; Ahvenainen, R., ed.; CRC Press: Boca Raton, 2003, ch. 23.
4. Lau, O. W.; Wong, S. K.; *J. Chromatogr. A* **2000**, *882*, 225.
5. Piotrowska, B. In *Toxins in Food*; Sikorski, Z. E.; Dabrowski, W. M., eds.; CRC Press: Boca Raton, 2005, ch. 14.
6. Coulier, L.; Orbons, H. G.; Rijk, R.; *Polym. Degrad. Stab.* **2007**, *92*, 2016.

7. Möller, J.; Strömberg, E.; Karlsson, S.; *Eur. Polym. J.* **2008**, *44*, 1583.
8. Official Journal of the European Union, Comission Regulation 1935/2004/EC of the European Parliament and of the Council of 27 October 2004, L 338/4-17; Brussels, 2004.
9. Official Journal of the European Union, Commission Regulation 10/2011/EU of 14 January 2011, L12/1-89; Brussels, 2011.
10. Official Journal of the European Union, Commission Regulation 282/2008/EC of 27 March 2008, L86/9-18; Brussels, 2008.
11. US Food and Drug Administration (FDA), Center for Food Safety an Applied Nutrition; *Recycled Plastics in Food Packaging*, 2006. http://www.fda.gov/food/ingredientspackaginglabeling/packagingfcs/recycledplastics/ucm093435.htm accessed in December 2013.
12. Agência Nacional de Vigilância Sanitária (ANVISA); Resolução No. 20, de 26 de março de 2008; Diário Oficial da República Federal do Brasil, Brasília. http://portal.anvisa.gov.br/wps/wcm/connect/beed8180474597599feddf3fbc4c6735/RDC_20.pdf?MOD=AJPERES accessed in December 2013.
13. Davidson, P.; *Plastics Resource*, **2013**, *35*. http://www.resource.uk.com/article/Plastics/ARCHIVE_lot_bottle accessed in December 2013.
14. Welle, F.; *Food Addit. Contam., Part A, Chem. Anal. Control Expo. Risk Assess.* **2005**, *22*, 999.
15. Agência Nacional de Vigilância Sanitária (ANVISA); *Farmacopéia Brasileira Vol. 1*, **2010**. http://www.anvisa.gov.br/hotsite/cd_farmacopeia/pdf/volume1.pdf accessed in December 2013.
16. European Medicines Agency Inspections (EMEA); *Guideline on Plastic Immediate Packaging Materials*, **2005**. http://www.ema.europa.eu/docs/en_GB/document_library/Scientific_guideline/2009/09/WC500003448.pdf accessed in December 2013.
17. World Health Organization (WHO); *Guidelines on Packaging for Pharmaceutical Products,* **2002**. http://www.who.int/medicines/areas/quality_safety/quality_assurance/GuidelinesPackagingPharmaceuticalProductsTRS902Annex9.pdf accessed in December 2013.
18. Salafranca, J.; Cacho, J.; Nerín, C.; *Polym. Rec.* **1999,** *1*, 13.
19. Fabris, S.; Freire, M. T. A.; Wagner, R.; Reyes, F. G. R.; *Ciênc. Tecnol. Aliment.* **2010,** *30*, 1046.
20. Dutra, C.; Pezo, D.; Freire, M. T. A.; Nerín, C.; Reyes, F. G. R.; *J. Chrom. A* **2011**, *1218*, 1319.
21. Félix, J.; Alfaro, P.; Nerín, C.; *Anal. Chim. Acta* **2011**, *68*, 767.
22. Bentayeb, K.; Battle, R.; Romero, J.; Nerín, C.; *Anal. Bioanal. Chem.* **2007,** *388*, 1031.
23. Nerín, C.; Albiñana, J.; Philo, M. R.; Castle, L.; Raffael, B.; Simoneau, C.; *Food Addit. Contam.* **2003,** *20*, 668.
24. Official Journal of the European Union, Commission Regulation 97/48/EC of 29 July 1997, L222/10; Brussels, 1997.
25. Agência Nacional de Vigilância Sanitária (ANVISA); Resolução RDC No. 51, de 26 de novembro de 2010; Diário Oficial da República Federal do Brasil, Brasília. http://portal.anvisa.gov.br/wps/wcm/connect/d29d1c804d8b6e73aa7eebc116238c3b/ALIMENTOS+RESOLU%C3%87%C3%83O+RDC+N%C2%BA+51%2C+DE+26+DE+NOVEMBRO+DE+2010+-+Migra%C3%A7%C3%A3o.pdf?MOD=AJPERES accessed in December 2013.
26. Miller, J. C.; Miller, J. N.; *Statistics for Analytical Chemistry*, 3rd ed.; Ellis Horwood: New York, 1993.
27. Buchalla, R.; Begley, T. H.; *Radiat. Phys. Chem.* **2006**, *75*, 129.
28. Block, C.; Wynants, L.; Kelchtermans, M.; De Boer, R.; Compernolle, F.; *Polym. Degrad. Stab.* **2006**, *91*, 3163.
29. Silva, S. A.; Gárcia, R. S.; Cooper, I.; Franz, R.; Losada, P. P.; *Trends Food Sci. Technol.* **2006**, *17*, 535.
30. Fierens, T.; Servaes, K.; Van Holderbeke, M.; Geerts, L.; De Henauw, S.; Sioen, I.; Vanermen, G.; *Food Chem. Toxicol.* **2012**, *50*, 2575.
31. Duh, B.; *Polymer* **2002,** *43*, 3147.
32. Shotyk, W.; Krachler, M.; Chen, B.; *J. Environ. Monit.* **2006**, *8*, 288.
33. Agência Nacional de Vigilância Sanitária (ANVISA); Resolução No. 17, de 17 de março de 2008; Diário Oficial da República Federal do Brasil, Brasília. http://portal.anvisa.gov.br/wps/wcm/connect/0cbc4d804d8b67e6a9f7e9c116238c3b/ALIMENTOS+RESOLU%C3%87%C3%83O+-+RDC+N%C2%BA+17%2C+DE+17+DE+MAR%C3%87O+DE+2008.pdf?MOD=AJPERES accessed in December 2013.
34. Agencia para Sustancias Tóxicas y el Registro de Enfermedades (ATSDR), Departamento de Salud y Servicios Humanos de EE. UU, Servicio de Salud Pública; *Resumen de Salud Pública Cromo CAS#: 7440-47-3*; Septiembre 2000. http://www.docstoc.com/docs/46578717/ATSDR---Resumen-de-Salud-Pública-Cromo accessed in December 2013.
35. Agência Nacional de Vigilância Sanitária (ANVISA); Resolução No. 52, de 26 de novembro de 2010; Diário Oficial da República Federal do Brasil, Brasília. http://portal.anvisa.gov.br/wps/wcm/connect/cdc282004d8b6ee0aa87ebc116238c3b/ALIMENTOS+RESOLU%C3%87%C3%83O+RDC+N%C2%BA+52%2C+DE+26+DE+NOVEMBRO+DE+2010+-+Corantes.pdf?MOD=AJPERES accessed in December 2013.

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