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Method for assessing lead, cadmium, mercury and arsenic in high-density polyethylene packaging and study of the migration into yoghurt and simulant

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The purpose of this paper was to assess the concentration of lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) in high-density polyethylene (HDPE) packaging intended for contact with yoghurt and the migration of these elements using the food itself and 3% acetic acid as a food simulant in accordance to ANVISA, the Brazilian Health Surveillance Agency. In order to perform this study, it was necessary to develop and validate a method by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. For method validation, the parameters linearity, limits of detection (LODs) and quantification (LOQs), accuracy and precision were determined. Fifteen commercial samples of yoghurt, marketed in Campinas – São Paulo (Brazil), were used for the analysis. The packaging and yoghurt were digested in high-pressure ashing equipment (HPA) and the migration of the elements into simulant were determined directly in the solution. The validated method proved adequate and the results obtained showed that all the packaging had levels of Hg and Cd below the LOQ, corresponding to 1.0 and 1.5 µg l^{-1}, respectively. The highest levels of As and Pb were 0.87 and 462.3 mg kg^{-1}, respectively. The migration of these elements to the yoghurt after 45 days of contact at 4ºC was below the LOQ for all the samples assessed. The results of specific migration into 3% acetic acid simulant showed the concentrations of Cd, Hg and As below 5, 5 and 10 µg kg^{-1}, respectively, which are the maximum limits set by ANVISA. However, for three samples the packaging lid showed migration of Pb into simulant ranging from 30.6 to 40.2 µg kg^{-1}, exceeding the limit set by ANVISA of 10 µg kg^{-1}.

Keywords: packaging; yoghurt; inorganic contaminants; migration; ICP-OES; high-pressure ashing

Introduction

Plastics additives, especially the inorganic pigments that are added to the polymers used in the manufacturing of food packaging, may contain lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) (Fordham et al. 1995; Zenebon et al. 2004; Cadore et al. 2008; Özer et al. 2011). Thus, migration of additives to the food may occur when a packaged product is in direct contact with a container that contains the additive (Munoz et al. 2002; Grob et al. 2008; Reinas et al. 2012; Simoneau et al. 2012; Haldimann et al. 2013; Van Goetz et al. 2013).

In Brazil, pigmented packaging and the pigments used are regulated by Resolution RDC No. 52, of 26 November 2010, published by the Brazilian Health Surveillance Agency (ANVISA), which sets limits and analytical methods to determine the concentrations of zinc (Zn), chromium (Cr), antimony (Sb), Hg, Cd, barium (Ba), selenium (Se), Pb, and As in pigments and dyes. This resolution also sets limits and analytical methods to the migration of the elements As, Ba, Cd, Cr, Hg, Pb, Sb, Zn, boron (B), copper (Cu), fluorine (F$^-$), silver (Ag) and tin (Sn) from the pigmented polymer packaging into a solution of 3% acetic acid (Brasil 2010).

One of the foodstuffs sold in many different coloured packaging is yoghurt, which is packaged mainly in high-density polyethylene (HDPE) bottles manufactured through blow moulding, dyed in many different colours (white, orange, green, yellow and red, among others) (Oliveira & Queiroz 2008).

In 2007, 665.3 million units of liquid yoghurt in 200 ml HDPE bottles were sold in Brazil, which would require the use of 7784 metric tons of polymer (Datamark 2009).

The analytical techniques used to determine the presence of trace elements in polymer packaging are atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), energy-dispersive X-ray spectroscopy (EDXRF) and neutron activation analysis (NAA). The chemical vapour generation added to ICP-OES, ICP-MS or fast sequential flame atomic-absorption spectrometry (FS-FAAS) are also used (Ernst et al. 2000; Nomura et al. 2000; Perring et al. 2001; Ritter et al. 2004; Soares et al. 2005; Sakurai et al. 2006; Cadore et al. 2008; Guerra et al. 2011; Butler et al. 2012).

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The ICP-OES technique has high sensitivity, good accuracy and is easy to operate, having as its main advantage simultaneous or sequential multi-element assessment. Consequently, analysis time is reduced and the amounts of sample and reagent which are required are minimised (Butcher et al. 2013).

The application of this technique often requires extensive sample preparation. The digestion step is very important to avoid loss of analyte by volatilisation or precipitation, contamination of the sample and matrix effects – aspects that affect the quality of the results. Besides it is necessary to use quick digestion methods and low amounts of reagents (Korn et al. 2008; Krug 2008).

The sample preparation method can be classified as dry ashing or wet ashing. In the dry ashing method, the organic matter is removed from the samples by thermal decomposition using a muffle furnace. The degree of volatilisation loss is a limiting factor and elements such as Hg, As and Pb might be lost. Wet digestion methods are carried out in open vessels, in tubes, on a hot plate or heating block, or in a closed vessel at elevated pressure with thermal or microwave heating. For sample digestion, acids or mixtures of acids (hydrochloric acid, nitric acid, hydrofluoric acid and perchloric acid), and oxidising agents such as hydrogen peroxide are used. In open vessels, the boiling point of the acid or mixture of reagents determines the maximum temperature, which can be insufficient to eliminate all organic matter in polymeric and food samples and may also cause loss of the analytes by volatilisation. In closed vessels using the microwave is a viable technique for polymer and food digestion without loss by volatilisation, but the mass of the sample is a limiting factor because the internal pressure during digestion cannot exceed the maximum pressure of the equipment (Sneddon et al. 2006; Demirel et al. 2008; Korn et al. 2008; Krug 2008).

The system of high-pressure digestion is an alternative and it is used to digest complex samples. The technique has the advantage of reaching temperatures up to 320°C in 40 min. The digestion internal pressure is 130 bar (1920 psi), allowing a greater sample mass to be digested compared with the microwave technique, and different samples may be digested at the same time (White et al. 1998).

Thus, this study set out to develop and validate a method of analysis to determine the concentrations of Pb, Cd, Hg and As in HDPE yoghurt packaging, and to assess the migration of these elements into packaged yoghurt using a high-pressure digestion system and ICP-OES. The specific migration of these elements into 3% acetic acid was determined directly in the simulant by ICP-OES.

Materials and methods
Samples

Fifteen samples of different colours of yoghurt packaging made of HDPE were collected in supermarkets in Campinas – São Paulo, Brazil, as described in Table 1. The flavour of the yoghurt was not taken into consideration. The products were chosen with a production date no greater than 7 days in order to minimise the influence of the time of contact in the specific migration assays.

Instrumentation

All the measurements of elements were performed using ICP-OES, model OPTIMA 2000DV, from PerkinElmer Corporation (Shelton, CT, USA), coupled with a hydride generation and cold vapour system (Perkin Elmer – FIAS 400). The axial view was utilised and the cold recombination area was removed with a shear gas interface. The whole system was controlled by WinLab32™ software (Perkin Elmer).

For the measurement of Cd and Pb, a Mira Mist pneumatic parallel path nebuliser (Burgener Research Inc., Mississauga, ON, Canada) and a quartz cyclonic spray chamber were utilised. For As and Hg assessment, the hydride generation technique and the cold vapour generation technique were used, respectively, both using as a reducing agent a solution of sodium borohydride (1.2%) in an alkaline solution, and simultaneous readings. The parameters used for this ICP operation are listed in Table 2.

For the decomposition of the samples, high-pressure ashing equipment, model HPA-S (Anton Paar GmbH, Graz, Austria) equipped with an aluminium rotor and a quartz digestion vessel with 90 ml capacity was used.

Materials and reagents

Deionised water (resistivity of 18.2 MΩ cm^{-1}) was obtained with a Milli-Q system (Millipore, Bedford, MA, USA). The glassware used was previously washed with extran detergent (Merck, Darmstadt, Germany), decontaminated by immersion

Table 1. Descriptions of the analysed HDPE packaging.

Sample	Food manufacturer[a]	Packaging colour	Capacity (g)
A	1	White	100
B	1	Green	150
C	1	White	180
D	2	White	180
E	3	Red	170
F	3	Blue	180
G	3	Clear	75
H	4	White	180
I	5	White	200
J	6	White	900
K	6	Yellow lid	Lid
L	7	White	900
M	7	Red lid	Lid
N	8	Pink	900
O	8	Red lid	Lid

Note: [a]The same number corresponds to the same food manufacturer.

Table 2.   Experimental conditions used on ICP-OES equipment.

Elements: Pb and Cd	
RF power (W): 1300	Main argon flow rate (l min^{-1}): 15
Torch configuration: axial	Auxiliary argon flow rate (l min^{-1}): 0.2
Sample flow (ml min^{-1}): 1.5	Nebulising flow rate (l min^{-1}): 0.60
Integration and reading time (s): 10	Wavelength (nm): Pb: I 220.353 and Cd: I 228.802
Elements: As and Hg	
RF power (W): 1450	Main argon flow rate (l min^{-1}): 17
Torch configuration: axial	Auxiliary argon flow rate (l min^{-1}): 0.2
Sample flow rate (ml min^{-1}): 1.5	Nebulising flow rate (l min^{-1}): 0.50
Pump (rpm): 80	Wavelength (nm): As: I 193.696 and Hg: I 194.168

Note: (I) Analyte line atomic; and (II) analyte line ionic.

in a 20% (v/v) nitric acid solution for 12 h and rinsed with deionised water. All chemical reagents were of analytical grade. Nitric, sulfuric and acetic acids, hydrogen peroxide, and sodium hydroxide obtained from Merck and analytical-grade sodium borohydride (Vetec, Rio de Janeiro, Brazil) were used. The standard stock solutions of Pb, Cd, Hg and As (1000 mg l^{-1}) were obtained from Merck. Stock solution were diluted in HNO_3 (8%) and 1.0 ml of H_2SO_4 (96%) was added only in the analytical curve for analysis of the polymer. CRMs on low-density polyethylene from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium), for ERM-EC681k and ERM-EC680k, were also used.

Sample preparation

The digestion sample of HDPE packaging and yoghurt was performed in a closed system, using the HPA-S. Approximately 3 g of each sample (HDPE packaging) were cut into small pieces (10 × 10 mm, approximately)

and rinsed with deionised water. A 300 mg portion of each sample was weighed and introduced into the high-pressure, closed quartz decomposition vessel. To determine the digestion parameters, three digestion programmes and two different mixtures of reagents were tested, resulting in five procedures (Table 3). For the initial tests, a white and a red sample of HDPE were used (E and I samples).

The yoghurt sample was analysed on day 0 (the date on which the sample was acquired) and after 45 days of storage at 4°C. For samples K, M and O, the packaging was stored in an upside-down position with the purpose of studying whether migration of the elements from the lids into the food might occur. After homogenisation of yoghurt, 1.0 g of each sample was weighed and introduced into the quartz decomposition vessel. In order to set the parameters for digestion, two different reagent mixtures were tested (Table 3). After the digestion, all samples were diluted to a final volume of 25 ml with deionised water.

To determine the procedure for the digestion of the HDPE and of the yoghurt, the absence of opacity,

Table 3.   Procedures used in HDPE and yoghurt digestion.

Procedure	Reagent	Step	Ramp time (min)	Temperature (°C)	Duration (min)
1[a]	5 ml of HNO_3	1	45	250	30
		2	10	320	120
2[a]	5 ml of NO_3	1	45	250	15
		2	15	320	150
3[a]	3 ml of HNO_3 + 1.0 ml of H_2O_2	1	45	250	15
		2	15	320	150
4[a]	3 ml of HNO_3 + 1.0 ml of H_2O_2	1	45	250	15
		2	15	320	180
5[a]	3 ml of HNO_3 + 1.0 ml of H_2SO_4	1	45	250	15
		2	15	320	180
6[b]	3.5 ml of HNO_3	1	5	200	5
		2	10	320	30
7[b]	3.5 ml of HNO_3 + 0.5 ml of H_2O_2	1	5	200	5
		2	10	320	30

Notes: [a]Procedures used in the digestion of HDPE packages.
[b]Procedures used in yoghurt digestion.

supernatant and precipitate after the digestion was ascertained. In addition to the visual analysis of the digested material, the concentration of residual carbon was measured by ICP-OES in order to ascertain the efficiency of the samples digestion, using the method described by Gouveia et al. (2001), and a standard curve was drawn based on a glucose solution at a wavelength of 193.03 nm.

The specific migration of Pb, Cd, Hg and As into 3% acetic acid solution followed the methodology established by norm EN1186 (European Committee for Standardization 2002), according to Resolution RDC No. 52/2010 (Brasil 2010). The packaging was emptied and rinsed with deionised water and was kept in contact with the 3% acetic acid solution at 40ºC for 10 days, using a standard relation of area of material per volume of simulant of 6 dm^2 kg^{-1}, and after contact an assessment of the elements was performed directly on the simulant by ICP-OES.

Validation parameters

Linearity

The linearity of analytical curve of each element was determined by the correlation coefficient (r), calculated by the WinLab32^{TM} software (Perkin Elmer) on each performed analysis and was considered acceptable when $r \geq 0.999$.

Detection and quantification limits

In order to determine the LODs and LOQs, seven independent readings of the blank after digestion were performed. The LODs and LOQs were calculated based on the average (X) and the standard deviation (s) of these assessments (LOD = X + 3.1s and LOQ = X + 10s), according to INMETRO (2011).

Accuracy and precision

The accuracy and precision of the method for assessing the elements in the packaging were determined utilising two CRMs (ERM-EC681k and ERM-EC680k) using procedure 5 (Table 3) for sample digestion, according to INMETRO (2011).

To verify the accuracy of the yoghurt digestion method, a recovery study was performed. Three standard concentrations were added to the food. After addition, the sample underwent the decomposition procedure in the HPA-S. In addition to the accuracy of the specific migration method in the 3% acetic acid simulant, a recovery study adding three standard concentrations to the solution was also performed before the ICP-OES reading.

Results and discussion

Evaluation of the efficiency of digestion

Method for polymer digestion

Procedures 1–4 were not efficient in completely eliminating organic matter. After digestion, the presence of a white precipitate and an opaque supernatant was observed. Procedure 5 produced a colourless solution without supernatant and precipitate only for the red packaging. However, the concentration of residual carbon, measured after the digestion for both samples, was less than 1%.

For the white HDPE packaging, despite the low level of residual carbon, the presence of titanium dioxide pigment was noted in the samples. Thus, for the white packaging samples, it was necessary to filter the digested sample with a porosity of 2.5 μm in order to remove the titanium dioxide before the ICP-OES reading.

Method for yoghurt digestion

The residual carbon for both procedures studied was lower than 0.6%, and the solutions after digestion were clear (Table 3). Thus, procedure 6 was chosen, as the use of peroxide did not produce any significant improvement in the digestion of the yoghurt samples.

Validation parameter for the analysis of inorganic contaminants

Linearity. It was observed that the correlation coefficients are above 0.999 for all elements, suggesting a good linearity in the concentration range between 2.0 and 20.0 μg l^{-1} for Cd, between 5.0 and 50.0 μg l^{-1} for Pb, and between 1.0 and 15.0 μg l^{-1} for both As and Hg.

Limits of detection and quantification. According to INMETRO (2011), for trace-level analyses it is recommended that the LOQ should be the lowest concentration on the analytical curve. For all the elements studied we prepared a solution with the same concentration of the value calculated. For the elements Hg and As, concentrations lower than 1.0 μg l^{-1} showed an error greater than 20%, thus for the elements Hg and As the lowest point on the analytical curve was adopted as the LOQ: 1.0 μg l^{-1}. For Cd in 3% acetic acid, concentrations lower than 2.0 μg l^{-1} showed error greater than 20%, thus the LOQ was adopted as 2.0 μg l^{-1} (Table 4). The LOQs expressed in micrograms (μg) per kilogram (kg) of polymer, considering 83.3 dilutions, were 1041.2, 124.9, 83.3 and 141.6 μg kg^{-1} for Pb, Cd, Hg and As, respectively.

Accuracy. The results obtained for the elements As, Pb, Cd and Hg, in the two reference samples, ERM-EC681k and ERM-EC680k, were within the confidence intervals of the certified reference materials and had a relative error

Table 4.   Limits of detection (LODs) and quantification (LOQs).

Element	Sample	LOD ($\mu g \ l^{-1}$)	LOQ ($\mu g \ l^{-1}$)
Pb	HDPE container	5.5	12.5
	Yoghurt	3.9	8.2
	3% Acetic acid	3.0	7.9
Cd	HDPE container	0.6	1.5
	Yoghurt	0.3	0.8
	3% Acetic acid	0.2	2.0[1]
Hg	HDPE container	0.3	1.0[1]
	Yoghurt	0.3	1.0[1]
	3% Acetic acid	0.5	2.1
As	HDPE container	0.6	1.7
	Yoghurt	0.1	1.0[1]
	3% Acetic acid	2.2	8.4

Notes: [a]The lowest concentration on the analytical curve was considered. LOD = $X + t.s$; and LOQ = $(X + 10s)$, where X is the blank average; s is the standard deviation; and t is t-student.

below 4%. The accuracy of the method of adding 80 mg of titanium dioxide to 300 mg of the reference materials and digesting the samples using procedure 5 was also tested. After digestion, the digested material was filtered through filter paper with a porosity of 2.5 μm. The results in both certified polymer samples had relative errors lower than 13%. The filtration step and the presence of titanium dioxide increased the relative error for all elements, although only for Hg in the concentration band of 4.5 mg kg^{-1} was the obtained value outside the confidence interval (4.44 and 4.84 mg kg^{-1}) (Table 5).

The accuracy when adding the internal standards indium (In) and scandium (Sc), each with a concentration of 1 mg kg^{-1}, before the analysis of the ERM-EC680k reference material, was also assessed in order to determine the influence of sulfuric acid in signal suppression due to the increase in viscosity, as described by Ernst et al. (2000). For the same trial, the results were analysed in the presence and absence of an internal standard for the wavelengths 325.609 and 361.383 nm for In and Sc, respectively. The results obtained using internal standards of In and Sc showed no significant difference from the results without an internal standard (assessed through paired *t*-tests with a 95% confidence interval), and thus the use of an internal standard is not justified or necessary for this analytical method (Table 6).

Precision. Precision was assessed by comparing the coefficient of variation (CV) obtained by CRMs with the values calculated by the Horwitz equation (described by Horwitz 1982); INMETRO (2011) recommends that the CV of the sample should be lower than the value calculated by the Horwitz equation. The results of the assessments of the elements Pb, Cd, Hg and As, for the two CRM, presented CVs lower than the values calculated by the Horwitz equation. Therefore, the method showed good precision (Table 7).

Recovery study – yoghurt. For the migration of Pb, Cd, Hg and As into yoghurt, the recovery was assessed by adding three concentrations of each element to the strawberry-flavoured yoghurt before digestion. According to AOAC International (2013) the recovery assessment is a function of the concentration, and for a concentration of 10 μg kg^{-1} there is an acceptable range of variation between 70% and 125%. Therefore, the method utilised was acceptable, given that the recovery of all the analytes in the yoghurt was between 84.5% and 119.3% (Table 8).

Recovery study – 3% acetic acid. For the migration of Pb, Cd, Hg and As into 3% acetic acid solution, the recovery was assessed by adding three concentrations of each element to the simulant. The specific migration method in 3% acetic acid of the elements studied was accurate. The

Table 5.   Values of certified reference materials ERM-EC681k and ERM-EC680k; the values were obtained experimentally with the addition of titanium dioxide and experimentally obtained values.

	ERM-EC681k			ERM-EC680k		
Element	Certified value (mg kg^{-1})[c]	Obtained value (mg kg^{-1})[d]	Relative error (%)	Certified value (mg kg^{-1})[c]	Obtained value (mg kg^{-1})[d]	Relative error (%)
Pb	98 ± 6	99.8 ± 7.5[a]	1.8	13.6 ± 0.5	13.9 ± 0.6[a]	2.2
		89.3 ± 2.7[b]	8.9		12.7 ± 0.9[b]	6.9
Cd	137 ± 4	137.1 ± 4.5[a]	0.1	19.6 ± 1.4	19.9 ± 0.1[a]	1.5
		133.1 ± 1.4[b]	2.9		20.0 ± 0.6[b]	1.9
Hg	23.7 ± 0.8	23.3 ± 0.8[a]	1.7	4.64 ± 0.20	4.5 ± 0.2[a]	3.1
		23.6 ± 0.3[b]	0.6		4.1 ± 0.1[b]	12.6
As	29.1 ± 1.8	28.0 ± 1.5[a]	3.9	4.1 ± 0.5	4.1 ± 0.2[a]	0.4
		27.2 ± 2.8[b]	6.6		4.5 ± 0.4[b]	9.7

Notes: [a]Result from seven assessments.
[b]Result from six assessments with the addition of titanium dioxide.
[c]Average ± expanded uncertainty.
[d]Average ± standard deviation (SD).

Table 6. Accuracy using internal standard (IS) of indium (In) and scandium (Sc).[a]

Element	Certified value (mg kg^{-1})[b]	Results obtained with IS of In (mg kg^{-1})[c]	Results obtained with IS of Sc (mg kg^{-1})[c]	Results obtained without IS (mg kg^{-1})[c]
Pb	13.6 ± 0.5	13.2 ± 0.7	14.2 ± 0.8	13.9 ± 0.6
Cd	19.6 ± 1.4	19.5 ± 0.8	19.9 ± 0.1	19.9 ± 0.1

Notes: [a]Results of five assessments.
[b]Average ± expanded uncertainty.
[b]Average ± standard deviation (SD).

Table 7. Coefficient of variation (CV) of the analyses of the reference materials.[a]

Element	ERM-EC681k		ERM-EC680k	
	VHE (%)	Sample CV (%)	VHE (%)	Sample CV (%)
Pb	8.0	7.6	10.7	4.0
Cd	7.6	3.3	10.2	0.5
Hg	10.0	3.5	12.8	3.8
As	9.7	5.4	12.9	5.1

Notes: [a]Results of seven assessments.
VHE, values calculated by the Horwitz equation.

variation of the recovery of all the elements added to the 3% acetic acid solution remained within the acceptable range of 70–125% established by AOAC International (2013) (Table 8).

Results for the elements Pb, Cd, Hg and As in polyethylene yoghurt packaging

Of the 15 samples analysed, none of the packaging had levels of Cd or Hg above the LOQ, but 60% of the samples tested positive for the presence of either As or Pb above the LOQ (Table 9). Given that the positive list from Resolution RDC No. 17/2008 (BRASIL 2008) contains no As- or Pb-based additives, the only permitted source would be pigments used in the master batches for the manufacturing of this packaging.

The four samples (A, D, G and I) that tested positive for As above the LOQ (0.14 mg l^{-1}) were white; the white pigments and dyes used in the dying of polymers are

titanium oxide (TiO_2), zinc sulfide (ZnS), zinc oxide (ZnO) and white lead ($Pb(CO_3)_2).Pb(OH)_2$) (Cadore et al. 2008). These pigments do not contain As, so the presence of As may be attributed either to a problem with the purity of the resin, or the pigment or of other additives used in these packaging, or with a substance that is not on the positive list from Resolution RDC No. 17/2008 (Brasil 2008).

Two red lids and one yellow lid had levels of Pb approximately 400 times higher than the LOQ; the most commonly used red and yellow dyes and pigments for polymers dying are lead chromate, molybdate and sulfate ($PbCrO_4$, $PbMoO_4$ and $PbSO_4$) (Cadore et al. 2008). Lead-based pigments are permitted to be in contact with food as long as the migration quantity to an extraction solution of HCl 0.1 mol l^{-1} is no greater than 100 mg kg^{-1}. That is why it is necessary to demonstrate that the utilised pigments conform to the purity criteria established by Resolution RDC No. 52/10 (Brasil 2010). Because of the difficulty of obtaining the pigments used in these packaging for inspection, the importance of establishing total limits for contaminants in the final packagings rather than in the raw material (pigment) is evident.

Migration into yoghurt

For all samples evaluated, the concentrations of the elements Pb, Cd, Hg and As on day 0 were below the LOQ, and after 45 days of storage at 4ºC no migration above the LOQ of the elements studied was detected from the packaging to the food. Therefore, Pb and As present in samples A, D, E, I, J, K, M and O did not migrate into the yoghurt.

Table 8. Recovery of lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) in yoghurt and 3% acetic acid solution.

Element	Pb			Cd			Hg			As		
Yoghurt												
Added concentration (µg l^{-1})	10.0	20.0	30.0	2.5	5.0	7.5	2.5	5.0	7.5	2.5	5.0	7.5
Recovery (%)	114.8	101.4	102.7	110.3	119.3	113.3	94.5	84.5	96.2	105.9	103.2	104.2
3% Acetic acid												
Added concentration (µg l^{-1})	9.0	10.0	11.0	4.0	5.0	6.0	2.0	4.0	6.0	7.5	10.0	12.5
Recovery (%)	108.9	107.4	105.5	93.1	94.3	95.6	91.0	85.8	84.1	94.8	91.9	92.8

Table 9.　Levels of elements lead (Pb), cadmium (cd), arsenic (As) and mercury (Hg) in the HDPE yoghurt containers in mg kg^{-1}.[a]

Samples	Pb	Cd	As	Hg
A	≤LOQ	≤LOQ	0.87 ± 0.01[b]	≤LOQ
B	≤LOQ	≤LOQ	≤LOQ	≤LOQ
C	≤LOQ	≤LOQ	≤LOQ	≤LOQ
D	≤LOQ	≤LOQ	0.60 ± 0.01[b]	≤LOQ
E	2.73 ± 0.12[b]	≤LOQ	≤LOQ	≤LOQ
F	≤LOQ	≤LOQ	≤LOQ	≤LOQ
G	≤LOQ	≤LOQ	0.38 ± 0.02[b]	≤LOQ
H	≤LOQ	≤LOQ	≤LOQ	≤LOQ
I	≤LOQ	≤LOQ	0.32 ± 0.03[b]	≤LOQ
J	2.11 ± 0.14[b]	≤LOQ	≤LOQ	≤LOQ
K	393.65 ± 25.67[b]	≤LOQ	≤LOQ	≤LOQ
L	≤LOQ	≤LOQ	≤LOQ	≤LOQ
M	366.10 ± 23.05[b]	≤LOQ	≤LOQ	≤LOQ
N	≤LOQ	≤LOQ	≤LOQ	≤LOQ
O	462.35 ± 19.02[b]	≤LOQ	≤LOQ	≤LOQ

Notes: [a]Results of two assessments.
[b]Average ± standard deviation (SD).
LOQ, limit of quantification.

Results of the specific migration test in 3% acetic acid

The results obtained in the study of the migration of the elements Pb, Cd, Hg and As into 3% acetic acid solution were below the LOQ; however, for the three lids (K, M and O samples), the levels of Pb that migrated into 3% acetic acid solution were 30.6, 40.2 and 32.4 μg l^{-1}, respectively.

The limits set by Resolution RDC No. 52/10 (Brasil 2010) for the specific migration of the elements Pb, Cd, As and Hg are 10, 5, 10 and 5 μg l^{-1}, respectively.

The levels of the elements Cd, Hg and As that migrated from the HDPE packaging into an aqueous solution of 3% acetic acid were below the limits established by Resolution RDC No. 52/10 (Brasil 2010); however, the migration levels of Pb from the lids were above the limit established by ANVISA. In spite of that, the level of Pb that migrated into yoghurt that was in direct contact with these lids for 45 days at 4ºC was below the LOQ.

Conclusion

The methods developed for the determination of Pb, Cd, As and Hg in HDPE polymer and yoghurt were suitable. The proposed methods of decomposition of the HDPE packaging and yoghurt were shown to be efficient. The procedures had adequate sensitivity, precision and accuracy. Addition and recovery studies indicated that the method can be applied to the determination of elements in HDPE polymers, yoghurt and 3% acetic acid by ICP-OES. About the analysed samples, 60% had levels of As and Pb above the LOQ of the method, which points to the use of pigments and additives containing these elements. Given the difficulty of inspecting the pigment utilised in these packaging, it is important to set limits of inorganic

contaminants in the final packaging. Three lid samples used on 900 ml yoghurt bottles contained a high concentration of Pb, which migrated into 3% acetic acid at levels above the limit set by Brazilian legislation. The other elements were within the established limits. There was no migration of Pb, Cd, Hg and As into yoghurt above the LOQ. Although ANVISA recommends using a simulant for the study of migration, it is worth noting that the migration testing into food will consider specific and intrinsic parameters that are important to the study of migration. The intentional use of Pb-based pigments in food packaging is a matter of public health and must be inspected by public health officials, just as it is necessary institute environmental legislation in order to establish limits to total inorganic contaminants in food packaging.

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