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Characterization of inorganic components in plastic materials

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Plastic products may contain high levels of trace elements, which, upon final incineration, may affect the environment. In the case of packing material, may affect food quality. In this work, instrumental neutron activation analysis was applied to the determination of As, Ba, Br, Cd, Co, Cr, Fe, Sb, Sc, Se, Ti and Zn in plastic materials originated from household and hospital wastes. Toxic elements such as Cd and Sb were found at the levels of $mg \cdot kg^{-1}$ in some food containers and also high levels of Ti were found in opaque packages. The accuracy and the precision of results were also evaluated by interlaboratory comparison.

Introduction

In recent years, plastics have had a large demand in manufacturing several kinds of products and in the packaging technology due to their excellent properties which facilitate protection of product quality, resistance, flexibility, light weight, etc. As a consequence, today plastics contribute about 4–7% to the weight of the municipal solid waste and are considered as one of major contributors to the volume of landfills.[1] For instance, the city of São Paulo produces, each day, about 12,000 ton of solid material in which about 700 ton are plastic packaging materials.[2] One solution to alleviate this volume of municipal solid waste is their incineration.

However, this process may cause a serious environmental problem since plastics may contain high amounts of toxic elements originating from additives, colouring agents, polymer stabilizing agents, catalyst residues and filling materials. Therefore, it is of great interest to analyse toxic elements in plastic materials using a reliable technique for further contribution to the investigation of possible sources of environmental contamination and in the migration study of these elements from the package to their contents.

Several techniques have been used in elemental analysis of plastic materials such as flame atomic absorption spectrometry,[3] X-ray fluoresce spectrometry,[4,5] inductively coupled plasma mass spectrometry[6,7] and neutron activation analysis.[8–13] In this work, instrumental neutron activation analysis was used because elements can be determined simultaneously with high accuracy and precision, without, on one hand, the need of digesting the sample, whilst, on the other hand, preserving the original test portion for either additional or repetitive analysis. The purpose of the research was to evaluate the analytical methodology and provide preliminary results of plastic materials used in Brazil.

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Experimental

Plastic samples and preparation for analyses

Plastic samples consisted of the packages of foods (soft drink, yoghurt, water, margarine, ice cream), of medical products (serum, blood, syringe) and of cleaning supplies. These samples were washed using, first, domestic detergent and water to remove content and paper or plastic labels. They were then wiped with a cotton pad soaked with hexane p.a. grade, diluted nitric acid solution and finally with distilled water. The samples were allowed to dry, and for irradiation they were cut or smashed into chips or strips smaller than 12 mm×12 mm.

The quality assurance of the analytical results was evaluated by analysing polyethylene reference material IMP-10 from Institute for Reference Materials and Measurements (IRMM), Belgium and also plastic samples which were also analysed by Interfaculty Reactor Institute (IRI) in Delft.

Standards

The standards for comparative neutron activation analysis were prepared by pipetting aliquots of multielement or single standard solutions onto sheets of Whatman No. 41 filter paper. The multielemental standards with the quantities of each element, in μg (in parentheses) were the following: Standard 1 with As (1.5), Cr (2.0), Sb (1.0) and Se (10.0); Standard 2 contained Cd (3.5 or 40), Co (1.0 or 20.0), and Sc (0.1); Standard 3 had Fe (300.0) and Zn (35). The quantities of the elements in single standards were the following: Ba (50); Br (5.7 or 10,000), Cl (200.0), Hg (8.0) and Ti (50.0). In the case of the Hg standard, an aliquot of 2% thioacetamide solution was also pipetted onto the sheet in order to avoid the loss of this element. After drying at room temperature in a desiccator, these sheets were placed in clean polyethylene bags and irradiated together with the samples.

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Instrumental neutron activation analysis (INAA)

About 150 mg of sample weighed and heat-sealed in polyethylene bags were irradiated at the IEA-R1m research nuclear reactor. Irradiations of 8 hours under thermal neutron flux of about 10^{12} n·cm^{-2}·s^{-1} were carried out for As, Ba, Br, Co, Cd, Cr, Sb, Cs, Se, Ti and Zn determinations. Irradiations of 30 minutes were also used for Br, Cl and Hg determinations in reference material IMEP-10 from the IRMM. After adequate decay times, the irradiated samples and standards were measured using a hyperpure Ge detector Model GX2020 coupled to Model 1510 Integrated Signal Processor, both from Canberra. Counting times of 10 minutes and of 10 hours were used, depending on the half-lives or activities of the radioisotopes considered. The radioisotopes measured were identified according to their half-lives and gamma-ray energies. The elemental concentrations were calculated by the comparative method.

From a selected group, a part of the sample material was sent for analysis to the laboratory for INAA at the IRI in Delft. This interlaboratory comparison contributed to the quality assurance activities of the laboratory at IPEN, and, in fact, to the laboratory in Delft as well.

Results and discussion

In order to evaluate the homogeneity of the elements in the sample, subsamples obtained from three parts (bottom, lateral side and top) of two typical plastic containers were analysed. Table 1 shows the mean values obtained from 5 or 6 determinations from each part.The statistical *t*-test (95% confidence level) applied to these results showed the homogeneity of the Co, Cr, and Sb concentrations in the package samples analysed. Zn and Sc presented, respectively, the highest and the lowest concentrations in the subsamples obtained from the top of the margarine container.

Table 1. Means of the elemental concentrations obtained in different parts of a package

Element	Top	Lateral side	Bottom
Part of soft drink bottle			
Co, mg·kg^{-1}	29.9 ± 1.2*	28.3 ± 1.2	27.7 ± 1.2
Sb, mg·kg^{-1}	210 ± 5	198 ± 6	194 ± 6
Part of margarine container			
Cr, µg·kg^{-1}	10.9 ± 0.4	8.9 ± 1.1	9.8 ± 1.5
Sb, µg·kg^{-1}	146 ± 3	143 ± 4	148 ± 7
Sc, µg·kg^{-1}	26.0 ± 1.0	28.8 ± 1.7	30.7 ± 1.9
Zn, µg·kg^{-1}	11.8 ± 0.3	5.8 ± 0.6	5.8 ± 0.7

* Arithmetic mean and standard deviation of 5 or 6 determinations.

The precision and accuracy of the results were checked by analysing polyethylene reference material IMEP-10. The normalized values and the standardized difference or *z*-values for the elements analysed are presented in Figs 1 and 2, respectively. These results show a good precision and agreement between our results and those reference values presented by the IRMM.[14] Except for As, our results are systematically low but all the elements are in agreement when 2 standard deviation (95% confidence level) uncertainties are considered. For Ba and Sb the comparison was made with the data provided in the laboratory of INAA of the IRI for this material. The precision of the results was good, having relative standard deviations lower than 11%. The less precise result was obtained for As with relative standard deviation of 12.6% due to their low content in the sample.

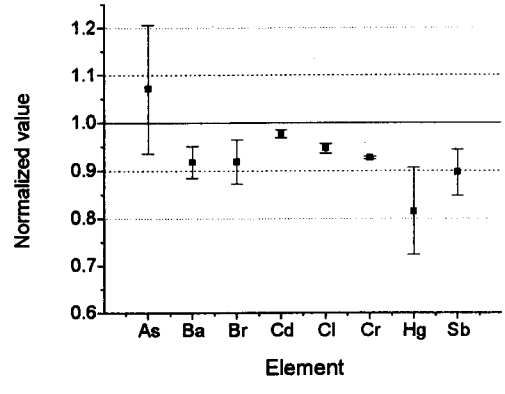

Fig. 1. Normalized values for elemental concentrations obtained in IMEP-10 reference material (Ratios between of the data obtained at IPEN and IRMM or IRI and the error bars in the figure are uncertainties of IPEN results)

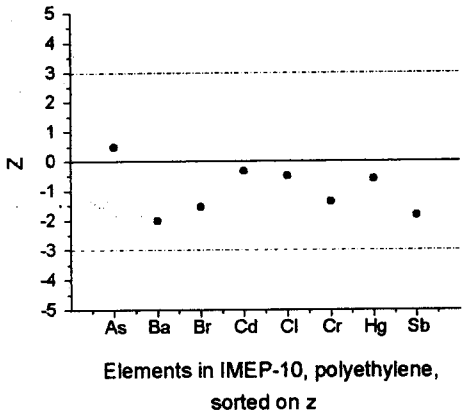

Fig. 2. Values of standardized differences (*z*-values) for elements analysed in IMEP-10

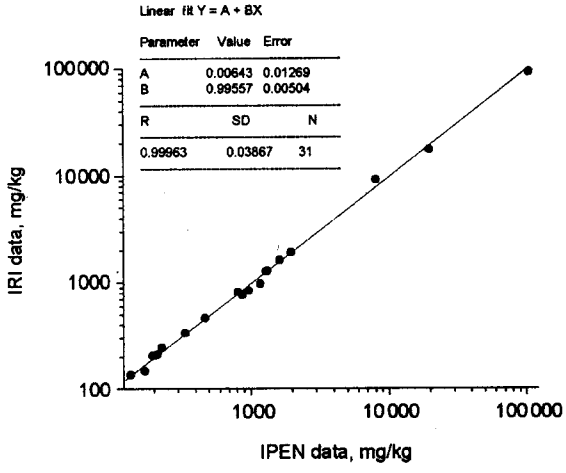

Fig. 3. Results of elemental concentrations obtained at IRI and IPEN

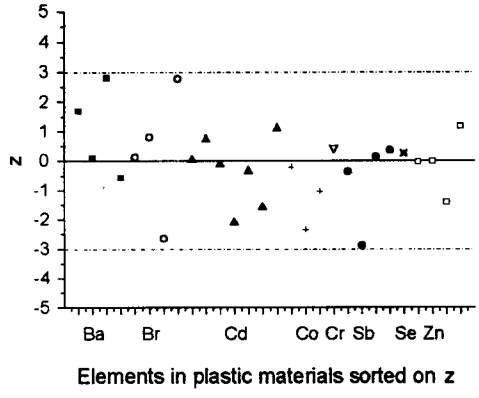

Fig. 4. Values of *z* obtained from elemental concentrations from IRI and IPEN

An addition, independent quality assurance of the data was obtained by comparison of the results obtained for plastic samples which were also analysed by IRI. These results exhibited a good agreement, as illustrated in Fig. 3. Figure 4 of *z*-values obtained for elements analysed in several plastic samples indicate that most of the results are in agreement when two standard deviation uncertainties are considered (95% confidence level).

The detection limits of the elements were evaluated according to CURRIE[15] in three different plastic samples and these values were lower than 1 $\mu g \cdot kg^{-1}$ for most of the elements and also dependent upon the sample composition.

Tables 2 and 3 present values of arithmetic mean and range of concentrations for As, Br, Cd, Co, Cr, Sb, Sc, Se, Ti and Zn obtained in plastics used as food package, cleaning supplies and as pharmaceutical or medical products. These results showed a large variability in the elemental concentrations, varying from a few $\mu g \cdot kg^{-1}$ to percentage levels, depending on the lot of sample analysed. For some samples, not all the elements were detected due to their low concentrations or to spectral interferences. For instance, in soft drink bottle only Br, Co and Sb were detected. It is interesting to notice that soft drink bottles made of PET material were found to contain high concentrations of Sb originating from the catalyst used in their manufacture. Also Cd was found in yellow and cream colour plastics, probably a compound of this element is used as pigment. Another element present in high level was Ti in opaque packages. In general, plastics used in pharmaceutical products presented very low concentrations of elements or they were not detected under the experimental conditions used in this work.

The number of samples analysed in this work was not large. However, a preliminary analysis of our results indicates that the toxic element levels in plastic samples are not high, except only for the result obtained for Sb in the PET bottle. Sb concentrations found in PET bottles were of about 200 $mg \cdot kg^{-1}$ and the legal standard limit for chemical waste is 50 mg/kg.[8] Cd was detected in some of our plastic samples but their concentrations were very low compared with those results found for plastics used in the Netherlands[8,9] where PVC articles comprise 80–90% of all products sampled for analysis and , in general, about 20% of this turns out to have too high Cd levels.[16]

Analytical data of plastics are very scarce in Brazil and this work has shown that the INAA procedure applied at IPEN can provide such information in a reliable way. The results obtained in this work provide motivation for more extensive inventory studies, taking advantage of the non destructive character of INAA and of the possibility of simultaneous evaluation of several elements present in a large range of concentrations.

Table 2. Mean and range values of As, Br, Cd, Co and Cr concentrations in plastic materials

Plastic product	Plastic type	*n*	As, $\mu g \cdot kg^{-1}$	Br, $\mu g \cdot kg^{-1}$	Cd, $mg \cdot kg^{-1}$	Co, $mg \cdot kg^{-1}$	Cr, $\mu g \cdot kg^{-1}$
Soft drink bottle	PET[a]	12	n.d.	219±162 (6) 28.5–442	n.d	44±34 (11) 0.15–93	n.d.
Yoghurt bottle	PS	8	96±108 5–342	54±32 2–108	n.d	n.d	148±122 31–436
Water glass	PP	5	2 (1)[b]	115±41 86–196	0.077 (1)	$(22\pm6)\cdot10^{-3}$ $(11–30)\cdot10^{-3}$	100±38 73–172
Margarine container	PP	14	176±37 98–218	208±210 65–882	26±45 (7) 0.056–103	n.d	183±111 (10) 54–298
Ice cream container	PP	3	62±20 41–89	82±16 65–106	7.4±0.3 7.11–7.64	6.0 (2)	165±15 150–180
Detergent bottle	PVC	4	n.d.	$(2.7\pm0.9)\cdot10^{3}$ $(1.3–3.5)\cdot10^{3}$	n.d	$(18\pm3)\cdot10^{-3}$ $(13–22)\cdot10^{-3}$	156±34 118–211
Serum package	PE	1	0.5	13.9	n.d.	n.d.	19
Blood plastic bag	?	2	n.d.	$(13.0\pm0.6)\cdot10^{3}$ $(12.4–13.6)\cdot10^{3}$	n.d.	$(104\pm29)\cdot10^{-3}$ $(75–134)\cdot10^{-3}$	n.d.
Plastic syringe	PE	2	6.8±0.1 6.6–6.9	248.0±0.5 247–294	n.d.	n.d.	27±4 31–54

[a] PET – Polyethylene terephthalate; PS – polystyrene; PP – polypropylene; PVC – polyvinil chloride; PE – polyethylene.
[b] Value in parenthesis indicates the number of samples in which the element was detected.
n – Total number of samples analysed.
n.d. – Not detected.

Table 3. Mean and range values of Sb, Sc, Se, Ti and Zn concentrations in plastic materials

Plastic product	Plastic type	*n*	Sb, $mg \cdot kg^{-1}$	Sc, $\mu g \cdot kg^{-1}$	Se, $\mu g \cdot kg^{-1}$	Ti, %	Zn, $mg \cdot kg^{-1}$
Soft drink bottle	PET	12	190±16 155–211	n.d.	n.d.	n.d.	n.d.
Yoghurt bottle	PS	8	0.14±0.27 0.012–0.814	27±18 16–49	165±146 (6) 5.8–348.3	0.45±0.05 (3) 0.40–0.50	81±73 0.7–178
Water cup	PP	5	$(3.6\pm0.6)\cdot10^{-3}$ $(2.9–3.9)\cdot10^{-3}$	2±1 0.7–4.6	4.3 (1)	$(23\pm4)\cdot10^{-4}$ $(17–26)\cdot10^{-4}$	0.36–0.07 0.3–0.4
Margarine container	PP	14	0.13±0.07 0.08–0.35	59±30 (13) 13–110	2151±866 (13) 90–3400	1.0±0.2 (2) 0.73–1.28	224±511 2–1540
Ice cream container	PP	3	$(37\pm11)\cdot10^{-3}$ $(26–52)\cdot10^{-3}$	25±1 24–27	1564±600 717–2045	0.31±0.03 0.28–0.35	25±12 16–42
Detergent bottle	PVC	4	$(55\pm42)\cdot10^{-3}$ $(21–125)\cdot10^{-3}$	0.97±0.06 0.88–1.03	n.d.	n.d.	332±25 300–360
Serum package	PE	1	0.003	n.d.	n.d.	n.d.	n.d.
Blood plastic bag	?	2	3±1 1.9–3.9	n.d.	n.d.	n.d.	49.2±0.2 49–50
Plastic syringe	PE	2	$(4.7\pm0.4)\cdot10^{-3}$ $(4.3–5.2)\cdot10^{-3}$	n.d.	n.d.	$(3\pm1)\cdot10^{-3}$ $(1.6–3.7)\cdot10^{-3}$	1.7±0.1 1.6–1.9

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