DETERMINATION OF TRACE ELEMENTS IN PLASTICS BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

In this paper instrumental neutron activation analysis was applied to the determination of As, Ba, Br, Cd, Co, Cr, Fe, Sb, Sc, Se, Sn, Ti and Zn in plastic materials coming mainly from household waste. In general, colored plastics presented higher concentrations of the elements than those found in colorless or transparent samples. High concentrations of Sb and Co were obtained in black and brown plastics, of Cd in yellow and cream-colored ones used in food packings, of Ti in opaque and various colors of plastics and Zn was found in most samples. These results indicate that colored plastics may constitute potentially serious problem from the standpoint of environmental contamination if the incineration process is used in municipal solid waste treatment.

INTRODUCTION

With the increase in the application of plastics for manufacturing several types of products and packing materials, the determination of trace elements in these materials is of great interest. Plastic materials could contain toxic elements originated from additives used as polymer stabilizers, coloring agents, catalysts, flame-retarding agents, filling materials and also from the contamination during their production or recycling process.

From the environmental monitoring point of view, analyses of plastics may contribute to the identification of possible sources of heavy metals present in municipal solid waste incinerator ashes and emissions. Also these materials have relatively short life cycles and increase the municipal solid waste. For instance, the city of São Paulo produces about 12,000 ton of solid waste per day in which approximately 700 ton per day are plastic packings (ref 1) At present the disposal of municipal solid waste is an increasing problem all over the world and in order to alleviate such problems the incineration process is being used as a feasible solution to reduce the great quantity of urban solid wastes.

Besides plastics are being extensively used in storage and packing of foods, drinks, blood and medicines. Due to the possibility of toxic compound migration from plastic to the stored material there is also much concern regarding the health hazards. In view of this problem the Brazilian government has enacted regulations for the use of plastics for packing both food and blood (ref 2 and 3).

In this paper toxic elements in plastic products were analyzed by instrumental neutron activation analysis since analyses data of such materials are very scarce in Brazil.

EXPERIMENTAL METHOD

Sampling and Preparation. Plastic samples from different original fields of use were divided in two groups. Group 1 for foils (bags, garbage bags), cleaning agent bottles, photograph film packings, personal hygiene products, etc and Group 2 for plastic products (food packings, water cups, soft drink bottles, packings for physiological serum) controlled

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by Brazilian legislation. Plastic packings were emptied of their contents and then washed using firstly domestic detergent and water to remove content and paper or plastic labels. Then they were cut or smashed in chips or strips smaller than approximately 10mmx2mm and washed using distilled water. The drying of these samples was carried out at room temperature inside a class 100 laminar flow hood.

Instrumental Neutron Activation Analysis. About 250 mg of sample weighed and heat sealed in clean polyethylene envelopes were irradiated for 8h under thermal neutron flux of about 10^{13} n cm^{-2} s^{-1} at the IEA-R1 nuclear research reactor, together with the elemental synthetic standards. These synthetic standards were prepared by drying multielement or single element standard solutions of appropriate concentrations pippeted onto pieces of Whatman No. 41 filter paper. After about 4 to 10 days of decay the irradiated samples and standards were measured using a HPGe detector coupled to an EG & G Ortec ACE8K card and an IBM PS-2 microcomputer. The counting system had a resolution (FWHM) of 0.90 keV for 122 keV gamma rays of ^{57}Co and 1.89 keV for 1332.5 keV gamma rays of ^{60}Co. Spectra data were saved in diskettes and then processed using a VISPECT computer program. The radioisotopes measured in this study (^{76}As, ^{131}Ba, ^{82}Br, ^{115}Cd, ^{60}Co, ^{51}Cr, ^{122}Sb, ^{46}Sc, ^{47}Sc for Ti analysis, ^{75}Se, ^{113}Sn, ^{117m}Sn and ^{65}Zn) were identified according to their half lives and gamma ray energies.

RESULTS AND DISCUSSION

Tables 1 and 2 present the results of As, Ba, Br, Cd, Co, Cr, Fe, Sb, Sc, Se, Sn, Ti and Zn determinations obtained in plastics belonging to Groups 1 and 2, respectively. For some samples, not all these elements were detected due to their low concentrations or to interferences. As indicated in these Tables, the ranges of the concentrations of many elements for the samples of same type, color and original field of use were large, varying from few ppb to percentage level. Colored and opaque plastics, in general, presented higher concentrations of the elements than those obtained for colorless and transparent or milky plastics. High concentrations of Sb and Co were obtained in black and brown plastics, of Cd in yellow and cream-colored ones used for food packings and Ti in opaque and several colors of samples. Element Zn was obtained pratically in all the samples analyzed.

These results indicate that incineration of some types of plastics from household waste may constitute a possible source of environmental contamination with heavy metals. Also we can conclude that instrumental neutron activation analysis is an useful method for analyzing plastic materials due to its nondestructive character and to the possibility of simultaneous determination of several elements present in a large range of concentrations.

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Table 1. Range and mean of the elemental concentrations in plastic samples from Group I.

Elemental concentration	Plastic Samples (Color, Type and Number of samples analyzed)						
	Softener for clothes, bottle (blue, a, 5)	Film packing (black, b, 1)	Garbage bag (black, c, 1)	Detergent bottle(colorless, d, 4)	Instant cleaner bottle (blue, b, 3)	Bag (colorless, a, 1)	Desinfectant bottle (colorless, d, 4)
As (ppb)	221 - 333 291 ± 44	nd	180 ± 5*	nd	32 - 49 38 ± 8	nd	4.5 - 17 8.8 ± 5.8
Ba (ppm)	0.85 - 9.1 4.3 ± 3.4	nd	17 ± 2*	nd	4.3 - 5.1 4.7 ± 0.3	nd	nd
Br (ppb)	48 - 132 93 ± 35	124 ± 37*	5266 ± 11*	1265 - 3506 2701 ± 862	151 - 265 202 ± 47	75.6 ± 1.5*	523 - 2317 1429 ± 770
Cd (ppb)	nd	499 ± 434*	1439 ± 82*	nd	41 ± 6*	nd	nd
Co (ppb)	3.5 - 14 7.7 ± 4.1	229 ± 9*	55 ± 4*	13 - 22 18 ± 3	22 - 33 26 ± 5	nd	3 - 122 39 ± 49
Cr (ppb)	131 - 3329 1991 ± 1496	4794 ± 100*	40263 ± 205*	118 - 211 156 ± 34	164 - 2102 139 ± 846	79 ± 2*	58 - 240 143 ± 67
Fe (ppm)	6.1 - 9.6 7.5 ± 1.5	nd	78 ± 2*	4.6 - 7.3 5.9 ± 1.0	3.3 - 18.3 8.9 ± 6.7	2.3 ± 0.2*	3.1 - 5.2 4.2 ± 0.8
Sb (ppb)	33 - 57 42 ± 10	68922 ± 81*	22012 ± 45*	21 - 125 55 ± 42	18 - 21 19 ± 1	3.78 ± 0.09*	166 - 1136 521 ± 392
Sc (ppb)	15 - 51 33 ± 11	3.3 ± 0.4*	29.3 ± 0.3*	0.88 - 1.03 0.97 ± 0.06	10 - 16 14 ± 3	nd	0.6 - 1.0 0.78 ± 0.6
Se (ppb)	413 - 874 736 ± 171	nd	1107 ± 37*	nd	140 - 392 299 ± 113	5.6 ± 1.6*	nd
Sn (ppm)	nd	nd	nd	2150 - 2415 2255 ± 113	229 ± 6*	nd	1308 - 2511 1836 ± 450
Ti (ppm)	2225 - 5739 4121 ± 1151	nd	2686 ± 54*	nd	1531 ± 23*	nd	nd
Zn (ppm)	18 - 650 265 ± 300	7.5 ± 0.3*	56.8 ± 0.3*	300 - 360 332 ± 25	3.6 - 6.5 5.5 ± 1.4	0.60 ± 0.02*	0.3 - 0.4 0.35 ± 0.04

nd - not detected; (*) - Result of one sample and standard deviation calculated using statistical counting errors
Type of plastics: a - polyethylene; b - polypropylene; c - low density polyethylene; d - polyvinyl chloride.

Table 2. Range and mean of the elemental concentrations in plastic samples from Group 2.

	Plastic Samples (Color, Type and Number of samples analyzed)							
Elemental Concentration	Water Cup (colorless, b, 5)	Yoghurt bottle (green, e, 1)	Soft drink bottle (brown, f, 1)	Serum packing (milky, a, 1)	Yoghurt bottle (pink, e, 2)	Margarine packing (cream, b, 5)	Margarine packing (white, b, 4)	Ice cream packing (yellow, b, 3)
As (ppb)	1.5 ± 0.4*	7948 ± 199*	90 ± 21*	0.45 ± 0.05*	98 - 115 106 ± 8	122 - 223 171 ± 42	126 - 164 150 ± 14	41 - 89 62 ± 20
Ba (ppm)	nd	nd	nd	nd	nd	6.9 - 694 350 ± 344	1.1 ± 0.5*	nd
Br (ppb)	86 - 196 115 ± 41	6518 ± 16*	nd	43.9 ± 0.3*	200 - 224 212 ± 12	153 - 408 259 ± 86	78 - 600 247 ± 208	65 ± 106 82 ± 16
Cd (ppb)	77 ± 5*	nd	nd	nd	1768 ± 25*	36 - 331483 $(1.3 \pm 1.4)10^5$	21 - 40 30 ± 9	7111 - 7637 7374 ± 263
Co (ppb)	11 - 30 22 ± 6	45 ± 2*	81876 ± 616*	nd	80 - 128 104 ± 24	7.8 - 240 80 ± 83	18 - 856 422 ± 404	6.0 ± 0.7*
Cr (ppb)	73 - 172 100 ± 38	201 ± 7*	nd	19 ± 2*	2473 - 629 451 ± 178	113 - 139 128 ± 10	84 - 147 115 ±22	150 - 180 165 ± 15
Fe (ppm)	4.9 - 13 7.9 ± 2.9	65 ± 1*	nd	0.49 ± 0.18*	15 - 62 38 ± 24	1.5 - 11 21 ± 14	1.5 - 7.6 4.2 ± 2.2	1.6 ± 0.4*
Sb (ppb)	2.9 - 3.9 3.6 ± 0.6	73 ± 1*	144139 ± 376*	0.34 ± 0.03*	70 - 91 80 ± 10	54 - 159 113 ± 37	70 - 119 93 ± 17	26 - 52 37 ± 11
Sc (ppb)	0.7 - 4.6 1.9 ± 1.3	nd	nd	nd	32 - 45 39 ± 6	37 - 102 65 ± 25	54 - 60 57 ± 2	24 - 27 25 ± 1
Se (ppb)	4.3 ± 2.5*	1505 ± 9*	nd	nd	1331 - 1955 1643 ± 312	1438 - 3361 2737 ± 774	1724 - 2163 1916 ± 153	717 - 2045 1564 ± 600
Sn (ppm)	nd	nd	nd	nd	1235 ± 42*	1956 ± 66*	nd	nd
Ti (ppm)	17 - 26 23 ± 4	5204 ± 93*	nd	nd	4454 - 602 5238 ± 784	5201 - 11755 8411 ± 2551	7718 - 8534 8076 ± 312	2792 - 3518 3129 ± 298
Zn (ppm)	0.3 - 0.4 0.36 ± 0.07	121 ± 1*	nd	nd	119 - 150 135 ± 16	119 - 150 135 ± 16	29 - 40 34 ± 4	16 - 42 25 ± 12

nd - not detected: (*) - Result of one sample and standard deviation calculated using statistical counting errors
Type of plastics: a - polyethylene; b - polypropylene, e - polystyrene, f - polyethylene terphthalate