Elemental Composition of Some Imported Toys and Handbags by X-ray Techniques

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Abstract: Some imported products such as toys and commercial handbags are collected and analyzed directly without sample preparation using X-ray Fluorescence (XRF) technique, Energy Dispersive X-ray (EDX) and Laser Ablation Inductively Coupled Plasma Mass spectrometer (LA-ICP-MS). The analysis showed a lot of elements with high concentrations whose values may exceed the permissible local values.
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1. Introduction

Polymers and mixtures of polymers are used in the manufacture of a large quantity of materials. Polypropylene (PP), low density polyethylene (LDPE), high density polyethylene (HDPE) and polystyrene (PS) can be used for toys fabrication. In general, additives are used in polymers for changing properties and pigments give color to the product. However, in many cases, the inorganic pigments may contain potentially heavy elements in their composition such as Ba, Cd, Cr, Pb, As and Sb among others. Some of these products are commercialized without legal ways [(1)]. These products have no safety or quality control and can release toxic contaminants. The contact of toys containing pigments can cause risk of intoxication in children.

Quantification of elements in polymeric materials can be done by atomic absorption spectrometry [(2–8)], x-ray fluorescence [(8–11)], total reflection x-ray fluorescence [(12,13)], inductively coupled plasma optical spectrometry [(8)], neutron activation analysis [(14)] and inductively coupled plasma mass spectrometry [(15)]. Few analytical techniques provide the ability for surface analysis, discriminating the ink and the base composition of a painted material in a non-destructive technique.

In the present work, toys and commercial handbags are analyzed by using x-ray and LA-ICP-MS analytical techniques. The concentrations of different toxic and heavy elements are presented.

2. Experimental

2.1. Materials

The samples are cleaned by distilled water and pure alcohol and then dried with air streaming for 5 minutes. Non-destructive elemental analysis studies were made on all samples. The used samples in this study are shown in figure (1).

2.2. EDX analysis

Microprobe EDX analysis is a non-destructive technique used for solid surfaces elemental analysis. The range of detection is from major to minor down to 100 part per million (ppm). The analysis can detect elements from carbon to uranium. Quantitative elemental analysis was done by using ZAF correction calculations.

Figure 1. Photographs of imported plastic products such as toys and handbags.

2.3. XRF analysis

Figure (2) represents the schematic diagram of the Energy Dispersive X-ray Fluorescence (EDXRF) system. The system consists of a low power air-cooled x-ray tube as an excitation source. The operating voltage and the current of the x-ray tube were 30 kV and 0.6 mA, respectively. The x-rays from the tube were exposed on a molybdenum secondary exciter and the generated characteristic x-rays of molybdenum were used to excite the elements present in the studied samples. The measurement time for the determination of the main components was 300 seconds. The characteristic x-rays emitted from the elements present in each sample were collected using a Si(Li) detector and a PC-based multi-channel analyzer. In the present work, EDXRF analysis was done for all samples to detect all the elements.

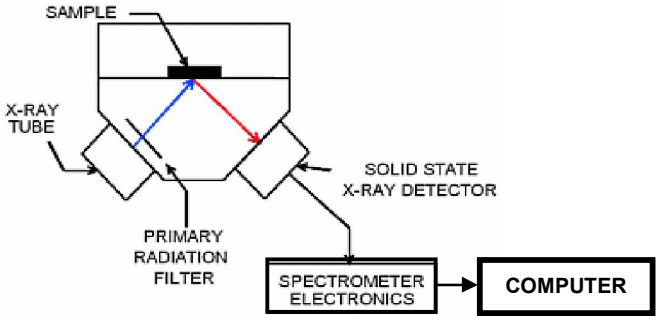

Figure 2. Schematic diagram of the XRF system.

2.4. LA-ICP-MS analysis

Laser ablation is a powerful tool for direct solid sampling in analytical chemistry and a valuable tool for non-destructive elemental analysis. It is regarded as a fast and accurate introduction system because it dose not need any chemical procedures for dissolution. During laser ablation, a laser beam removes tiny amounts of solid in the form of a dry aerosol that can be later transported into the ICP-MS for ionization and detection. These advantages make LA-ICP-MS a very attractive technique for sample analyses especially for trace examinations where the range of detection is trace or ultratrace and may reach to part per billion (ppb). The experimental conditions of Joel plasmax2 LA-ICP-MS which is used in the present measurements are shown in table (1).

3. Results and Discussion

Some commercial handbags are analyzed by EDX and x-ray fluorescence techniques to identify their elemental compositions where the hand of these bags from the same material of the bag.

Table (2) shows the elemental compositions of the hand and the belt of the bags. Raw white clean papers are swept on the body of the bag and analyzed.

The results of XRF are in an agreement with EDX technique and confirm the existence of heavy elements in the samples.

The results from the examination of the toys using EDX technique showed that there was Ti, Cu, Zn, As and Pb in the surface of the toys as shown in table (4).

Inspection of tables of elemental analyses of the commercial handbags and their belts in tables 2 and 3 showed the existence of many elements. Among them Pb, Cd and As whose have limitations in their concentrations to be daily handled.

Moreover, the easy released of some of these elements was investigated by sweeping the surface of the bag with white clean raw papers which was analyzed before and after sweeping.

Table 1. Optimized Experimental Parameters for LA-ICP-MS for analyzing of toys samples.

Parameter	Value
Rf power	1200 W
Coolant gas flow rate	14 L/min
Auxiliary gas flow rate	0.3 L/min
Nebulizer gas flow rate	0.85 L/min
Resolution	500
Laser power	10 mJ
Frequency	20 Hz

Table 2. Samples elemental analysis by EDX (%).

Element	Hand	Belt	Blank paper	Paper after sweeping the hand
C	39.68	98.11	37.39	38.27
O	17.82	--	60.25	53.45
Mg	0.48	--	0.76	0.49
Al	0.85	1.17	--	2.04
Si	1.48	0.09	1.16	1.35
S	0.25	--	0.1	0.13
Cl	24.69	0.05	0.06	2.05
K	0.10	0.15	--	0.05
Ca	13.45	--	0.11	1.19
Ti	0.18	--	--	0.03
Fe	0.36	0.09	0.07	0.13
Cu	--	0.25	0.1	0.11
As	0.28	0.08	--	0.27
Cd	0.09	--	--	--
Pb	0.28	--	--	--
Total %	100%	100%	100%	100%

Table 3. Samples elemental analysis by XRF % after normalization with C and O measured by EDX.

Element	Hand	Belt	Blank paper	Paper after sweeping the hand
C	39.68	98.11	37.39	38.27
O	17.82	--	60.25	53.45
Mg	0.28	--	0.42	1
Al	0.22	--	0.35	1.08
Si	0.81	0.27	1.4	4.17
S	--	--	--	0.16
Cl	22.28	--	--	--
K	--	0.07	--	--
Ca	17.6	0.75	0.12	1.48
Ti	0.3	0.35	--	--
Cr	0.02	--	--	--
Fe	0.6	0.26	0.06	0.37
Cu	0.02	0.05	--	--
Zn	0.08	--	--	--
As	0.27	--	--	--
Sr	0.02	--	--	--
Total %	100%	100%	100%	100%

Table 4. Toy samples elemental analysis by EDX (%).

Element	Red	Yellow	Pink	Black	Blue	Green
C	--	98.22	77.85	91.41	96.55	81.47
O	--	--	5.85	--	--	8.13
Na	--	0.7	0.09	0.1	--	--
Mg	--	--	--	0.31	--	0.82
Al	--	0.09	0.14	0.39	0.16	0.41
Si	2.4	0.08	0.09	0.63	0.25	0.96
P	--	--	0.06	0.03	0.02	0.05
S	--	0.03	0.04	0.15	0.04	0.24
Cl	--	--	0.02	0.81	0.13	0.37
K	--	--	--	0.06	0.05	0.03
Ca	10.39	0.06	15.33	5.39	2.15	3.95
Ti	0.15	0.19	0.32	0.2	0.31	2.51
Fe	--	--	--	0.26	0.08	0.22
Cu	--	0.23	0.09	0.07	0.08	0.35
Zn	11.18	0.23	--	0.13	0.06	0.33
As	--	0.18	0.1	--	0.01	--
Pb	--	--	--	0.07	0.11	0.14
Total %	100%	100%	100%	100%	100%	100%

Table 5. Elemental analysis by LA-ICP-MS for toys (ppm)*.

Element	Red	White	Blue	Pink	Rose	Green	Black	yellow	Light blue	Orange
Cr	4	2.2	2	11	2	3	1.3	--	26	8
Mn	58	85	47	58	45	59	77	70	220	228
Ga	14	104	5.8	63	--	2.4	--	--	--	0.4
Br	153	244	360	384	290	181	398	397	--	--
Cd	17	--	--	1	--	--	1.9	--	--	2.5
Sn	7	4	--	11	--	--	2.6	--	16	--
Ce	4	--	--	0.4	--	--	--	--	--	0.12
Hg	9	4	7	6	1.2	--	6.9	3.6	3.7	6.7
U	0.19	--	--	--	--	--	--	--	--	--
Ag	--	24	3	0.7	--	0.6	2.5	--	98	--
Sr	2.2	6	1.4	13.5	--	0.2	7.3	1	8	0.7

* Measurements are ± 20%.

Table 6. Concentrations of elements in toys according to the Egyptian standardizations (ppm).

Element	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Concentration (ppm)	60	25	500	75	60	90	60	500

Table 7. Brazilian legislation the max. permissible concentrations (ppm).

Element	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Concentration (ppm)	60	25	1000	75	60	90	60	500

The obtained results from the examination of the toys using LA-ICP-MS technique showed that there was Ti, Cd, Hg, and Ga in the surface of the toys as shown in table (5).

The results showed that the heavy and toxic elements such as As exist in all toys and plastic product while more heavy elements such as Cr, Ga, Cd, Sn, Hg and Pb were detected by LA-ICP-MS technique.

Local Egyptian standardization certification No. 4567/2004 for toys and commercial products and also some international standardization certifications for the minimum allowable values of some toxic and heavy elements are shown in tables (6,7). In addition to **Consumer Product Safety Commission (CPSC)** the limit for total Pb is 600 ppm.

According to the results of elemental analysis of toys and hand bags in the present work, it is clear that most of toxic and heavy elements concentrations are exceed the permissible values in all local and international certifications.

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