

Evaluation of heavy metal migration from plastic food packaging materials to aqueous simulants by ICP-MS

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□ Overview

Heavy metal migration from different types of plastic food packaging materials was studied. The packaging materials were immersed into several mimic food solutions according to EU legislation to simulate the process of heavy metal migration onto foodstuffs. The concentrations of 14 metallic elements in aqueous simulants were accurately determined by the developed ICP-MS method. The migration of elements was observed to increase with contact time. The presence of heavy metals, especially toxic elements such as Pb, highlighted the importance of quality control measures for food packaging materials.

□ Introduction

Food packaging materials that contact with food directly may cause food contaminations due to toxic substances and elements leaching out and migrating onto the food. Plastics are heavily used in food packaging in the modern food industry. Heavy metal contamination caused by plastic packaging materials is one of the significant concerns in food safety [1]. Thus, accurately determining heavy metal migration from food packaging material is essential to evaluate the potential health hazards to humans. Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful tool to investigate the elemental migration from food packaging material due to its low detection limits, relatively few interferences and multi-element capacity. In this work, the release of heavy metals onto foodstuffs were evaluated by immersing the testing plastic packages in food simulants including pure water, 2% nitric acid and 3% acetic acid. 14 heavy metals (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb and Zn) in the leaching solutions were determined simultaneously by a high sensitivity ICP-MS method. The effect of contact time on heavy metal migration was investigated using the food simulants.

□ Experimental

Sample and Standards Preparation

Three different types of plastic food packages including polystyrene (PS) container, polypropylene (PP) container and polyethylene (PE) film were obtained from local food markets. 0.5 grams of each packaging material were weighed and immersed into 40 mL of aqueous solutions for heavy metal leaching at room temperature. The aqueous solutions used as leaching solvents were DI water (simulant A), 3% acetic acid (simulant B) [2] and 2% nitric acid. After immersion, 1 mL of soaking solution was taken out and 1 mL of 3% acetic acid was added before dilution to 10 mL as the analysis solution. Multi-element calibration standards were prepared up to 50 ppb (Al, As, Cd, Co, Mn, Ni, Sb) or 200 ppb (Ba, Cr, Cu, Fe, Li, Pb, Zn) in 0.3% w/v acetic acid from single element stock solutions (1000 mg/L). Concentrations of the 14 toxic and interest elements were determined by ICP-MS with internal standard correction. The internal standard solution containing Sc, Y, Rh and Bi were added using an online internal standard addition kit.

Analytical Conditions

All analyses was carried out on Shimadzu ICPMS-2030 coupled with mini torch and AS-10 autosampler. The detailed instrument configuration and operation parameters were summarized in Table 1. Helium collision cell provides an effective way to remove possible polyatomic spectral interferences. The cell gas mode was applied for all the elements except for Li and Sb as shown in Table 2. The instrument was tuned and optimized using a mixed tuning solution and warmed up to 30 minutes before measurement.



Figure 1: ICPMS-2030

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Table 1: Analytical conditions and parameters of ICPMS-2030

Parameter	Setting
RF Frequency Power	1.20 kW
Sampling Depth	6.0 mm
Plasma Gas	Ar 8.0 L/min
Auxiliary Gas	Ar 1.10 L/min
Carrier Gas	Ar 0.70 L/min
Torch	Mini-Torch, ICPMS
Nebulizer	Nebulizer, 07UES
Chamber	Cyclone Chamber
Chamber Temperature	5°C
No. of Scans	10 times
Cell Gas (He)	6.0 mL/min
Cell Voltage	-21.0 V
Energy Filter	7.0 V
Solvent Rinse Time	10 sec (Low), 30 sec (High)
Sample Rinse Time	30 sec (Low), 40 sec (High)

□ Results and Discussion

Calibration Linearity

Under the experimental conditions described in the section above, good linearity of calibration curves was achieved. The correlation coefficients are shown in Table 2 with $r > 0.9999$ for targeted elements. LODs and LOQs were calculated based on 3 and 10 times the standard deviations of 10 continuous measurement of the calibration blank. Sub ppb or ppt level of LODs and LOQs were achieved for all analytes especially for the potentially toxic elements such as As, Cd and Pb.

Recovery and Repeatability

The ICPMS method was evaluated by spiking a known concentration (10 ppb) of heavy metals into food simulant B soaked with two plastic packages samples (PS container and PP container). The spike recovery rates achieved were between 87% to 116% for 14 heavy metals as shown in Table 3. Good recovery rates indicated the method accuracy and absence of interference. The repeatability for three replicates were checked with RSD% obtained less than 3% for most of the elements as shown in Table 3.

Migration of heavy metal from plastic packaging materials

Heavy metal migration from the three plastic packaging materials into food simulant B after soaking for 72 hours were determined and compared in Table 4. The leaching amounts were in ppb levels, but varied largely for different plastic packages. For example, for the PE film, the most leached element was zinc, followed by iron and aluminium with concentrations of 685.5, 142.5 and 135.5 µg/L, respectively. While for PS and PP container, the most leached element was aluminium, followed by zinc and copper. Migration of cobalt and lithium were not detected for any plastic materials. With regards to the toxic elements, arsenic and lead were detected with concentration ranges of 0.06 – 0.48 µg/L and 0.19 – 3.27 µg/L. Cadmium leaching was not found from PS and PP container, but 0.26 µg/L was detected from PE film. The measured concentrations shown in Table 4 are much lower than the restriction levels for Ba, Co, Cu, Fe, Li, Mn and Zn defined in EU No 10/2011 [2]. The MDLs indicates the superior sensitivity of ICP-MS to determinate heavy metal migration in food simulant.

Table 2: Analyte masses, acquisition modes, calibration correlation coefficients, LODs and LOQs

Element	Mass	Internal Standard	Cell gas	r	LOD (µg/L)	LOQ (µg/L)
Al	27	Sc	On	0.99992	0.201	0.670
As	75	Y	On	0.99996	0.005	0.018
Ba	138	Rh	On	0.99993	0.005	0.016
Cd	112	Rh	On	0.99999	0.001	0.004
Co	59	Sc	On	0.99999	0.001	0.002
Cr	53	Sc	On	1.00000	0.013	0.044
Cu	65	Y	On	0.99998	0.123	0.410
Fe	57	Sc	On	0.99998	0.104	0.348
Li	7	Sc	Off	0.99997	0.064	0.213
Mn	55	Sc	On	0.99995	0.008	0.027
Ni	62	Y	On	0.99999	0.067	0.223
Pb	208	Bi	On	0.99999	0.123	0.411
Sb	123	Y	Off	0.99999	0.001	0.002
Zn	68	Y	On	0.99996	0.073	0.243

Table 3: Spike recovery rates and RSD% (n=3) from food simulant B for PS container and PP container

Element	PS Recovery	PS RSD%	PP Recovery	PP RSD%
Al 27	114%	3.3	116%	2.1
As 75	108%	1.9	111%	1.5
Ba 138	99%	2.1	95%	3.7
Cd 112	102%	1.5	98%	2.6
Co 59	106%	2.2	105%	1.2
Cr 53	102%	1.3	101%	0.6
Cu 65	111%	2.5	112%	1.8
Fe 57	101%	3.9	100%	2.0
Li 7	87%	2.2	87%	0.2
Mn 55	101%	1.8	102%	1.5
Ni 62	102%	3.1	101%	0.5
Pb 208	98%	2.0	101%	0.9
Sb 123	112%	1.0	114%	1.7
Zn 68	103%	2.2	109%	2.0

Table 4: Heavy metal migration into food simulant B for different plastic packaging materials and MDLs

Element	PS container (µg/kg)	PP container (µg/kg)	PE film (µg/kg)	MDL (µg/kg)
Al	49.3	71.4	135.5	2.01
As	0.11	0.06	0.48	0.05
Ba	14.0	7.14	22.9	0.05
Cd	N.D.	N.D.	0.26	0.012
Co	N.D.	N.D.	N.D.	0.006
Cr	6.50	0.15	0.84	0.13
Cu	30.4	19.6	13.3	1.23
Fe	17.0	2.39	142.5	1.04
Li	N.D.	N.D.	N.D.	0.64
Mn	2.51	N.D.	52.8	0.08
Ni	8.81	1.86	2.14	0.67
Pb	2.22	0.19	3.27	0.06
Sb	0.08	0.04	0.40	0.006
Zn	34.60	23.50	685.5	0.73

Table 5: Comparison of heavy metal migration from PE film into different aqueous solutions. (unit in µg/kg)

Element	Food Simulant A DI water	2% HNO3	Food Simulant B (3% Acetic acid)
Al	21.0	29.9	135.5
As	0.01	0.15	0.48
Ba	13.4	15.8	22.9
Cd	N.D.	0.05	0.26
Co	N.D.	N.D.	N.D.
Cr	0.03	0.69	0.84
Cu	1.94	3.86	13.3
Fe	3.72	73.0	142.5
Li	N.D.	N.D.	N.D.
Mn	1.09	15.9	52.8
Ni	0.91	1.37	2.14
Pb	0.02	2.54	3.27
Sb	0.04	0.08	0.40
Zn	31.4	127.5	685.5

Effects of food simulant type and contact time on heavy metal migration

Table 5 shows that heavy metal leaching was more significant from plastic materials exposed to the food simulant B as compared to DI water and 2% HNO₃. Note that simulant B is the acidic mimic food used mostly in heavy metal migration test and investigation. The solution of 2% nitric acid is to mimic acidic conditions of some preserved food.

The effect of contact time on migration of heavy metal were also evaluated for PS container and PE film using food simulant B. The results with different contact time (1h vs 72h) were compared and shown in Figure 2. For both plastic packaging materials, the migration of heavy metals increased significantly with extended contacting time, indicating that the contact time is an important factor for element migration evaluation.

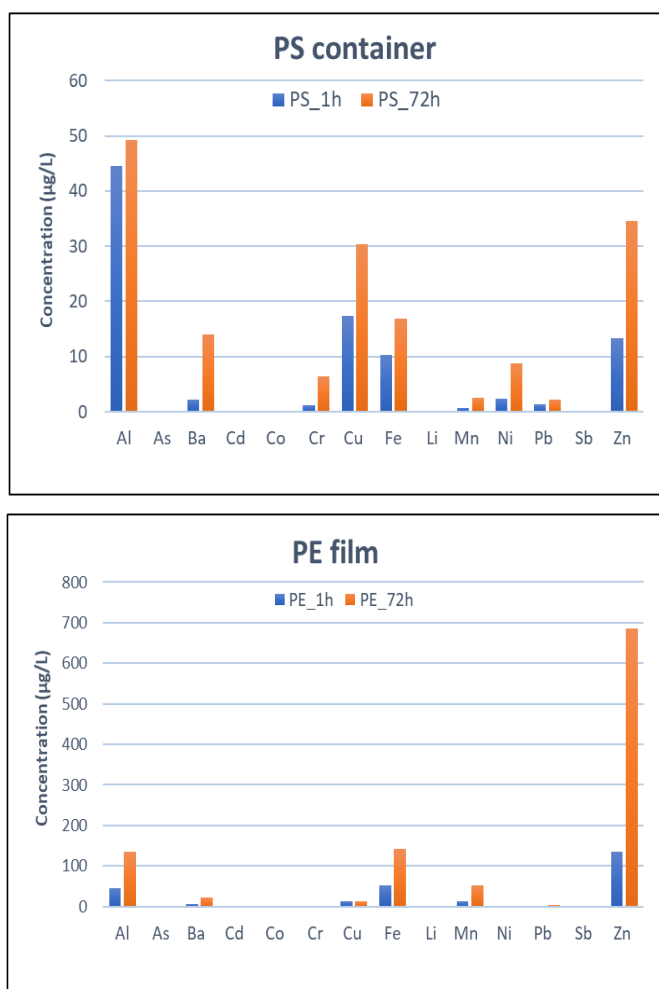


Figure 2: Effect of contact time (1h vs 72h) on heavy metal migration into food simulant B for PS container and PE film.

Conclusions

In the present work, we have studied the heavy metal migration from three different plastic materials used for food packaging with a developed ICP-MS method. The leaching amounts of 14 metallic elements from different plastics varied largely when 3% acetic acid was used as food simulant. Toxic elements such as As, Cd and Pb were detected in the leachate but in low levels. Significantly more heavy metal leaching into food simulant B than other aqueous solutions was observed. Obvious more metal migration was found with increasing contact time from 1h to 72h. The results showed good spike recovery rates and low RSD% for repeated measurements demonstrating the accuracy and precision of the determinations.

References

1. Zhanhua Dong, Lixin Lu, Zhigang Liu, Yali Tang, and Jun Wang, "Migration of Toxic Metals from Ceramic Food Packaging Materials into Acid Food Simulants," *Mathematical Problems in Engineering*, vol. 2014, Article ID 759018 7 pages, 2014.
2. COMMISSION REGULATION (EU) No 1935/2004 & No 10/2011 on plastic materials and articles intended to come into contact with food (OJ L 12, 15.1.2011, p. 1)