Determination of Toxic Elements in Polymer Materials Using Instrumental Neutron Activation Analysis

Kwangwon Park, Joung Hae Lee,* Kyunghaeng Cho, Hyung Sik Min, Myung Chul Lim, and Duk Soo Choi

Division of Metrology for Quality Life, Korea Research Institute of Standards and Science, Yuseong-Gu, Daejeon 305-340, Korea
*E-mail: ecljh@kriss.re.kr

Polymer materials are very difficult to decompose for the purpose of chemical analysis. Nondestructive analysis without pretreatment provides a suitable solution that will overcome this obstacle. In this study, CRM candidate samples that contained toxic elements such as As, Cd, Cr and Zn in a polypropylene (PP) were analyzed using instrumental neutron activation analysis (INAA). The analytical results were obtained from ten samples selected by random sampling at two different concentration levels (low and high). Particular attention was paid to reducing analytical errors and evaluating the associated uncertainty.

Key Words : INAA, Polypropylene, Toxic elements

Introduction

Polymers are the most important materials used as industrial products and the amount produced continues to grow. Heavy metals are often used in pigments or as stabilizers in polymer materials. Thus, polymers inevitably contain hazardous metals to a certain degree.

New electrical and electronic products that contain more than the agreed levels of Cd, Cr, Pb and Hg were banned by the European Union (EU) from July 1st, 2006. The various environmental regulatory directives include the restriction of hazardous substances in electrical and electronic products (RoHS)[1] and waste from electrical and electronic equipment (WEEE),[2] which act as technical barriers on international trade (TBT) of vehicles, electrical, and electronic products.

It is important to accurately determine the levels of hazardous metals and elements in polymers to comply with these regulations. Although elemental analysis of a polymer material is very common in field laboratories and the polymer industry, the analytical method and protocols currently used differ widely and are not standardized globally. This situation impedes mutual interpretation of analytical results among industrial, governmental and other private parties.

Certified reference materials (CRMs) are an ideal tool to improve the accuracy of the currently used analytical methods. Some new CRMs are being developed by the Korea Research Institute of Standards and Science (KRISS) for the determination of hazardous elements in polymers. The certified values of target elements in a CRM are usually determined using critically evaluated methods such as Isotope Dilution Inductively Coupled Mass Spectrometry (ID-ICPMS)[3] and Instrumental Neutron Activation Analysis (INAA).[4] INAA is a very sensitive, powerful analytical approach that qualitatively and quantitatively determines a number of elements of scientific and technical interest in laboratory and field samples. INAA allows the measurement of elements at trace levels from solid samples without any pretreatment such as chemical dissolution, separation or enrichment. This represents a major advantage of INAA over other instrumental analytical approaches such as gravimetric, calorimetric, spectrometric, and mass spectroscopic methods. Although INAA is a sensitive and accurate method for the determination of many trace elements, this method has some shortcomings. Pb cannot be determined because no suitable nuclides exist, and the determination of Hg is difficult due to volatilization during sample irradiation. This study presents analytical results and associated measurement uncertainties obtained after using INAA for the determination of As, Cd, Cr and Zn in a polypropylene, a typical polymer. The evaluation of uncertainty was performed according to the ISO guidelines.[5]

Theoretical Background

The principle of INAA is based on the irradiation of a stable nuclide ^AZ with neutrons using the $^AZ(n,\gamma)$ ^{A+1}Z nuclear reaction. If the production ^{A-1}Z occurs with a γ-ray emitter, a γ-ray detection system can be used to determine both the energy and intensity of the γ-rays, which are used to indicate the target nuclide ^AZ and find the concentration of the element in the sample, respectively. The analytical sensitivity depends mainly upon the abundance of the isotope ^AZ, the neutron capture cross section of ^AZ, the γ-ray emission branching ratio of ^{A+1}Z, and the interferences from other γ-rays in the sample. INAA is an absolute method that can be utilized without standard materials. Unless relevant uncertainty parameters are sufficiently known to obtain accurate analytical results, any absolute method could yield relatively large uncertainties. Therefore, high-accuracy INAA nearly always employs a relative method (comparator technique) by which a sample is compared to a comparator of the quantity being measured.

In its most common form, the use of a comparator technique with the INAA procedure compares by means of γ-ray spectrometry the neutron-induced activities in an unknown sample with the activities induced in a comparator of known

composition. This relationship is presented in the following equation[6]:

$$C_x = C_c \frac{m_c}{m_x} \frac{A_{0,x}}{A_{0,c}} R_\theta R_\phi R_\sigma R_\varepsilon$$

where C_x is the mass fraction of the sample ($\mu g/g$), C_c is the mass fraction of the comparator ($\mu g/g$), m_x and m_c are the masses of sample and comparator used in g, respectively. R_θ is the ratio of isotopic abundances for the sample and comparator. R_ϕ is the ratio of neutron fluences (including neutron self-shielding), R_σ is the ratio of effective cross sections. and R_ε is the ratio of counting efficiencies (differences due to geometry and γ-ray self-shielding). The decay-corrected counting rates for the indicator γ-ray of the sample $A_{0,x}$ and comparator $A_{0,c}$ are derived from the measurement. Therefore, the decay-corrected γ-ray counting rate (A_0) for a measured nuclide is calculated according to the following equation:

$$A_0 = N_c \lambda e^{\lambda t_D} / (1 - e^{-\lambda t_C}) \qquad (2)$$

where N_c is the number of counts in the indicator γ-ray peak. λ is the decay constant for the indicator nuclide, which is equivalent to ln $2/t_{1/2}$, t_D is the time elapsed between the end of activation and the start of counting, and t_C is the time of counting.

Experimental

Preparation of samples. New polypropylene CRMs representing two different concentration levels. 113-01-P03 (low level) and 113-01-P05 (high level), were developed by KRISS. These materials consist of pellets of variable size in which the contents of As, Cd, Cr and Zn were at two nominal levels: high-level bottles, 1000 mg/kg for As, Cr and Zn. 100 mg/kg for Cd; low-level bottles. 100 mg/kg for As, Cr and Zn, 10 mg/kg for Cd. The homogeneities of the materials were checked using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Homogeneity test results provided by KRISS indicated an approximate 0.3-1.6% relative standard deviation (RSD) using a sample size of about 0.1 g.

INAA procedure. Ten test portions (samples) of about 30 mg (high level) and 60 mg (low level) were weighed from each bottle. The test portions were embedded in about 300 mg of cellulose filter aid ashless powder (Whatman catalog # 1700025) and pressed into pellets of 13-mm diameter and 1.5-mm thickness under 2 tons of pressure. The test samples were sealed in bags made from 6-μm polypropylene (PP) film. These packaged samples were further sealed with linear polyethylene (LPE) film.

Portions of aliquots of the comparator as an assay standard taken from the KRISS certified reference solution were pipetted onto 55-mm diameter filter paper (Whatman # 41). After air-drying, the comparators were pelletized and sealed in LPE envelopes. The dimensions of pellets closely matched the size (13-mm diameter and 1.5-mm thickness) of the samples.

The irradiation was carried out for 4 hours in the IP-hole #4 of the KAERI research reactor. HANARO, at a neutron fluence rate of 1.30×10^{14} n·cm^{-2}·s^{-1}. The samples, comparators and blanks were stacked in the center of the irradiation container (rabbit). After irradiation, the outer PP film was removed and the samples, comparators and blanks were counted using a HPGe detector (GEM 30, EG&G Ortec, Oak Ridge. TN. 1.85-keV resolution at 1332.5 keV and 35% relative efficiency. 60 peak-to-Compton ratio) with a 16K channel analyzer. After approximately 1 day of cooling, a counting time of 20,000-40,000 seconds was used. Two weeks after irradiation, the level of Zn was measured for 20,000 seconds. All counts were conducted at a distance of 20 cm from the detector in order to minimize potential errors due to differences in counting geometry. The γ-ray energy used for the determinations was 559.1 keV, 336.3 keV, 320.1 keV and 1115.5 keV for ^{76}As ($t_{1/2} = 26.6$ h), ^{115}Cd ($t_{1/2} = 53.47$ h), ^{51}Cr ($t_{1/2} = 27.7$ d) and ^{65}Zn Cd ($t_{1/2} = 244.1$ d), respectively. The γ-ray spectra of the irradiated samples were counted at a very high counting rate in the γ-ray spectrometer. Since a counting loss often occurs due to a pulse pile-up from a high counting rate, a loss-free counting system was installed in the γ-ray spectrometer to correct this counting loss. The DSPEC system (DSPEC-PRO^{TM}, EG&G Ortec) was operated with a Gaussian amplifier using a 12-μs shaping time.

Results and Discussion

The comparator INAA method was applied for the direct analysis of As, Cd, Cr and Zn in solid polypropylene samples. In general, the sources of measurement uncertainty associated with INAA that result from the individual steps of the analysis can be grouped into three categories: sample preparation, irradiation, and γ-ray spectrometry. A measurement uncertainty estimate takes into account all recognized effects that influence the final results. A representative example of uncertainty components and their relative contributions in the determination of low-level Cr (a total of 10) in a polypropylene sample is shown in Table 1. The four Type A uncertainties were measurement precision for determination of sample mass and comparator mass, counting statistics for the sample and comparator. The remaining uncertainties were all considered to be Type B. The chromium comparator mass fraction (standard) was prepared from the KRISS chromium certified reference solution with a relative standard uncertainty of 0.066%. The comparator mass of Cr was measured gravimetrically (about 60 mg) and the relative standard uncertainty of the comparator mass deposited onto filter paper was 0.085%. The relative standard uncertainty of the sample mass for KRISS 113-01-P03-3001 was 0.013%.

Isotopic abundance is equal in the comparators and samples, and thus the ratio of isotopic abundance (R_θ) = 1. The uncertainty of this parameter is therefore zero. The uncertainty of the ratio of neutron flux (R_ϕ) is influenced by the spatial gradient and/or neutron flux self-shielding. Neutron flux differences between the comparators and

Determination of Toxic Elements

Bull. Korean Chem. Soc. **2008**, Vol. 29, No. 7   1393

Table 1. Standard uncertainty components for the determination of Cr in KRISS candidate PP CRM 113-01-P03 -3001 at low level using INAA

Parameter	Source of uncertainty	Relative standard uncertainty (%)
C_c	Comparator mass fraction (mg/kg)	0.0066
m_x	Sample mass* (mg)	0.013
m_c	Comparator mass* (mg)	0.085
N_x	Sample counts*	0.178
N_c	Comparator counts*	0.225
λ	Decay constant	0.072
$t_{D,x}$	Decay time of sample	0.00176
$t_{D,c}$	Decay time of comparator	0.00023
$t_{C,x}$	Elapsed time of sample	0.00397
$t_{C,c}$	Elapsed time of comparator	0.00994
R_θ	Ratio of isotope abundance	0
R_ϕ	Ratio of neutron flux	0.3
R_σ	Ratio of cross section	0
R_ε	Ratio of efficiency	0.012
Result		
Measurement standard uncertainty u_c (mg/kg)		**0.638**

*indicates Type A uncertainty; remaining uncertainties are Type B

samples were caused by the flux gradients of the irradiation position. These differences were eliminated by correction with a sandwich monitor (Au foil). The largest flux difference for irradiation position of samples for PTS-3 of the HANARO research reactor was approximately 5%. The residual uncertainty after correction was less than 0.3% (assuming a maximum correction error of 6% relative to the largest flux difference of ~5%). No uncertainty is produced from differences of neutron energy duration of irradiation if samples and comparators are irradiated together. The uncertainty of the ratio of effective cross section (R_σ) will be zero. The uncertainty of the ratio of counting efficiency (R_ε) may cause the differences in counting position and γ-ray self-absorption for the comparators and samples. The uncertainty in γ-ray self-absorption can be neglected in samples and comparators made of filter paper.[7] All counts were made at a distance of 20 cm from the detector surface. If comparators and samples are pressed into pellets of similar thickness, corrections can be made for differences in geometry. The differences in thickness between samples and comparators were measured to within 0.1 mm. The ratio of counting efficiency (R_ε) from a $1/r^2$ counting geometry yields the ratio $(200.0/200.2)^2$ or 0.998. Thus, the relative standard uncertainty for the ratio of counting efficiency (R_ε) is 0.012%.

The uncertainty of the γ-ray count (N) is influenced by the error in counting statistics (counting error. $Er = 100(C_N + 2B)^{1/2}/C_N$, where B is the background area, C_N is the net peak area of activity of ^{51}Cr) and calculation (integration) of the analytical peak area in γ-ray spectra of the comparators and samples. The relative standard uncertainty of the γ-ray count (N) for samples and comparators was 0.178% and 0.225%. respectively. In addition to the counting uncertainty. the

uncertainty of the calculation of the peak area in γ-ray spectra was evaluated from the difference between peak areas using the Gamma Vision-32 software program and hand integration performed channel by channel. Correction was not needed in this step since each spectrum was visually inspected to search for γ-ray interference.

The half-life (^{51}Cr) used in the calculation was taken from the evaluation in the Table of Isotopes.[8] The half-life of ^{51}Cr was 27.701 days with an uncertainty (1s) of 0.004 days. The uncertainty and the relative standard uncertainty of the decay constant, λ (ln $2/t_{1/2}$), were 0.025% and 0.072%, respectively. The system clock drift was 0.80 seconds per day. The sample and comparator decayed 1.31 days and 9.92 days prior to the start of counting, respectively. The relative standard uncertainty of the decay time (t_D) for sample and comparator results was 0.00176% and 0.00023%. respectively. The counting time (live time) of all samples and comparators was 50,000 and 20,000 seconds, respectively. The relative standard uncertainty of the counting time (t_C) for sample and comparator results was 0.000397% and 0.00994%, respectively.

The uncertainty from the pile-up effect in γ-ray spectrum collections could be held at a negligible level by keeping a low count rating and using proper hardware and software to obtain highly accurate results. This investigation revealed that the dead time for both samples and comparators did not exceed 3%. A live-time extension mode was used in dead-time correction. No chromium was recorded in the blank. Since Eq. (1) and Eq. (2) contain multiplication and division of quantities. the measurement standard uncertainty can be expressed as the square-root of the sum of the squares of each relative standard uncertainty. The measurement standard uncertainty calculated for the Cr mass fraction in

Table 2. Individual data for Cr mass fraction in KRISS candidate PP CRM 113-01-P03 at low level using INAA

	Mass fraction (mg/kg)	Measurement standard uncertainty (mg/kg)
113-01-P03 -3001	149.19	0.638
113-01-P03 -3051	147.84	0.627
113-01-P03 -3101	147.61	0.624
113-01-P03 -3151	151.47	0.639
113-01-P03 -3201	150.54	0.633
113-01-P03 -3251	153.04	0.641
113-01-P03 -3301	149.86	0.627
113-01-P03 -3351	150.99	0.630
113-01-P03 -3401	148.04	0.617
113-01-P03 -3451	149.67	0.623
Pooled measurement standard deviation		0.630
Mean of mass fractions (C_x), mg/kg	149.8	
Standard deviation of mass fractions (u_R), mg/kg	1.75	
Combined uncertainty (u_C), mg/kg	1.86	
Coverage factor, k	2	
Expanded uncertainty (U), mg/kg	3.72	

Table 3. Analytical results and their uncertainties for KRISS candidate PP CRM using INAA

Element	113-01-P03 (Low level)				113-01-P05 (High level)			
	As	Cd	Cr	Zn	As	Cd	Cr	Zn
Certified value, mg/kg	119.7	15.8	149.8	149.8	753	102	960	963
Standard uncertainty, mg/kg	0.44	0.076	0.63	0.47	2.70	0.49	3.98	2.99
Relative uncertainty, %	0.37	0.48	0.42	0.31	0.36	0.48	0.41	0.31
Measured between-bottle standard deviation, mg/kg	1.24	0.387	1.75	2.43	10.12	3.72	13.38	11.85
Relative standard uncertainty, %	1.04	2.44	1.16	1.62	1.34	3.64	1.39	1.23
Combined uncertainty, mg/kg	1.31	0.39	1.86	2.47	10.47	3.76	13.96	12.22
Relative uncertainty, %	1.11	2.49	1.24	1.65	1.39	3.67	1.46	1.27
Coverage factor[a]	2	2	2	2	2	2	2	2
Expanded uncertainty, mg/kg[a]	**2.62**	**0.79**	**3.72**	**4.95**	**20.94**	**7.52**	**27.93**	**24.44**

[a]approximately 95% level of confidence

KRISS 113-01-P03-3001 was 0.638 mg/kg.

Table 2 shows the overall results regarding Cr in the polypropylene sample at the low level from a group of 10 samples. For the other groups (As, Cd, Zn of low level and As, Cd. Cr, Zn of high level), the measurement standard uncertainties were calculated (see Table 3 for final results) in the same manner using the calculation procedures presented in Tables 1 and 2. The final combined standard uncertainty (u_c) of the low-level Cr mass fraction in polypropylene samples was estimated by combining the pooled measurement standard uncertainty and the standard deviation of mass fractions of 10 low-level Cr samples. The pooled measurement uncertainty due to systematic effects was obtained by averaging the measurement standard uncertainties of the 10 samples. The standard deviation (1.75 mg/kg) of mass fractions of the 10 samples in Table 2 reflects the uncertainty associated with homogeneity between sample bottles. Thus, it appears that this relative standard deviation (1.16%) was located within the reported range of approximately 0.3-1.6% as obtained by ICP-OES. This discrepancy may be due primarily to the smaller number of samples. Finally, the expanded uncertainty was obtained by multiplying the combined uncertainty with a coverage factor (k) of 2 at an approximate 95% level of confidence. The analytical results and uncertainties of As. Cd. Cr and Zn in polypropylene at low and high levels were calculated using the aforementioned procedures and are summarized in Table 3.

In order to validate the analytical results for our polypropylene samples, the standard reference materials polyethylene BCR 680 (high level) and BCR 681 (low level) from the Bureau Communautaire de Reference (BCR) were analyzed in the same manner. The reference values using BCR materials yielded the following results for mass frac-

tions: 30.9 ± 0.7 mg/kg (As), 140.8 ± 2.5 mg/kg (Cd) and 114.6 ± 1.9 mg/kg (Cr) at the high level; 3.93 ± 0.09 mg/kg (As), 21.7 ± 0.7 mg/kg (Cd) and 17.7 ± 0.6 mg/kg (Cr) at the low level. Our measured results were 30.1 ± 0.6 mg/kg (As). 139.5 ± 1.9 mg/kg (Cd) and 112.9 ± 1.8 mg/kg (Cr) at the high level, and 4.1 ± 0.1 mg/kg (As). 22.3 ± 0.7 mg/kg (Cd) and 18.2 ± 0.6 mg/kg (Cr) at the low level. A comparison of these two sets of results indicates acceptable agreement.

The results of this study show that the comparator INAA method may be appropriate for the determination of toxic elements in polymer materials. Analytical procedures used in this investigation were designed to evaluate the accuracy and uncertainties of INAA measurements. Our future efforts will include the determination of Hg using the INAA method.

References

1. Official Journal of the European Union. L37/19. *Directive 2002/95/EC of the European Parliament and of the Council on the Restriction of the Use of Hazardous Substances in Electrical and Electronic Equipment*. 2003.
2. European Commission Environment Directorate-General XI, *Proposal for a Directive on Waste from Electrical and Electronic Equipment (WEEE)*. 3rd Draft Version: 1998.
3. Park. C. J.; Cho. K. H.; Suh. J. K.; Han. M. S. *J. Anal. At. Spectrom.* **2000.** *14*, 567.
4. Balla, M.; Molnar. Z.; Karos. A. *J. Radioanal. Nucl. Chem.* **2004.** *259*, 395.
5. ISO/IEC Guide 34, *Quality System Guidelines for the Production of Reference Materials*. ISO. Geneva. 1996.
6. Zeisler. R.; Vajda. N.; Lamaze. G.; Molnar. G. L. *Handbook of Nuclear Chemistry*. Kluwer Academic Publishers: 2003: Vol. 3. p 303.
7. Zikovsky, L. *Nucl. Instr. Meth. Phys. Res.* **1984.** *B4*. 421.
8. Firestone, R. B.; Shirley, V. S. *Table of Isotopes*, 8th ed.: Wiley: New York. 1996.