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Tetrahydrofuran (THF)-assisted alkaline extraction to determine hexavalent chromium (Cr(VI)) in retardant polymers containing Sb(III)

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Low recovery of the hexavalent chromium (Cr(VI)) in polymers due to the reduction to Cr(III) by Sb(III) has been a big issue for the implementation of the Regulation of Hazardous Substances (RoHS) directive. In this work, we developed a THF (tetrahydrofuran)-assisted alkaline extraction method to improve the extraction efficiency of Cr(VI) in the presence of Sb(III) by suppressing reduction through the formation of an Sb(III)-THF adduct. The adduct formed was identified as $Sb_2O_5Cl_5(THF)_3$ using various analytical techniques, such as XRD, NMR, and MALDI-TOF-MS, and by molecular simulation through the calculation of ground state energy. The efficiency of the developed method was demonstrated by the analysis of in-house manufactured reference polymers containing Sb(III), of which the recovery was obtained in the range of 48.9%-77.5%. Recovery was about 19.6-31.0 times more efficient than the current RoHS method. Furthermore, when the THF solvent was mixed with 2-propanol (Isopropyl alcohol, IPA) or 1-methyl-2-pyrrolidone (NMP), the recovery was significantly improved to over 95.2%, whereas a mixture with EDTA and NMP had a recovery of <20.0%.

Keywords: Hexavalent chromium, Trivalent antimony, Ethylenediaminetetraacetic acid Chelation, Tetrahydrofuran additive reaction, Organic-assisted extraction, RoHS Directive.

Introduction

Determination of hexavalent chromium Cr(VI) used as a pigment in plastics, has become one of the biggest issues for the implementation of the RoHS Directive. However, the current analytical method (IEC 62321:2008), which is based on an alkaline digestion followed by UV-Vis spectrometry has seriously suffered from poor accuracy and precision. [1] Recently, the organic-assisted alkaline method was introduced to extract Cr(VI) from plastics to overcome the drawbacks of the alkaline digestion method, in which a polar aprotic solvent, such as NMP, was used to dissolve the plastic samples, followed by alkaline extraction of the Cr(VI) ions from the organic solvent.[2] Nowadays, most common brominated flame retardants used in electronic polymers contain extensive amounts of antimony trioxide (Sb_2O_3) as a synergist to enhance the effectiveness of the flame retardants. However, the added Sb_2O_3 reacts with Cr(VI) during the treatment, converting it to Cr(III),[3] which resulted in serious analytical error, i.e., a low recovery of typically <2.5% for the ABS powder ground in the size of 1,000 μm using the current RoHS method. Therefore, the determination of Cr(VI) in plastics containing Sb(III) has been a great challenge for the effective implementation of the RoHS Directive.

So far, there have been several efforts to improve the recovery by preventing the reduction of Cr(VI) through the suppression of Sb(III) oxidation. For example, a formation of Sb(III) complex using a chelate, such as ethylenediaminetetraacetic acid (EDTA), one of the most common chelates for di- and trivalent metals, can be an excellent way to mask the Sb(III).[4,5,6,7,8,9,10,11] Lintschinger et al demonstrated the chelation of Sb(III) and Sb(V) species with EDTA, forming a negatively charged complex.[12]

An alternative way to suppress the reduction of Cr(VI) is formation of an Sb(III) adduct with an organic solvent, such as tetrahydrofuran (THF), a colorless, water-miscible organic liquid with low viscosity at standard temperature and pressure. THF has an oxygen atom that can coordinate to metal ion as a Lewis base. Sian C. James et al. characterized the structure of an $[SbI_3(THF)]$ compound, the first THF adduct of an antimony halide. The structure was comprised of a polymeric arrangement of $SbI_3(THF)$ units, with antimony centers being bridged alternately by pairs of I atoms and pairs of THF ligands, so that each Sb atom has an octahedral coordination geometry. [13] In addition, THF has the advantage of good solubility for various electronic polymers, such as ABS, HIPS, and PC. Hence, it can be used as a solvent for polymers as well as a chelating agent of Sb(III) without the reduction of Cr(VI).

Now, the aim of this study was to develop a new extraction method using THF to determine the amount of Cr(VI) with high recovery through the masking of Sb(III). For comparison, the chelating agent EDTA in NMP solvent was also tested on various polymers. Since no reference polymer material exists in the current market, in-house polymer reference materials (RMs) containing Cr(VI) and Sb(III) were specially manufactured for this work using an extrusion method. Under optimized conditions, analytical figures-of-merits of the developed method, such as calibration linearity, limit of detection, and recovery, followed by UV-Vis spectrometry were determined in this work.

Experimental

Reagents and materials

All chemicals were of analytical reagent grade. All aqueous solutions were prepared using distilled water (DI water). The analytical working solutions of Cr(VI) were prepared from 1000 mgL^{-1} Cr(VI) standard stock solution (AccuStandard, USA) using DI water. Phosphate buffer (0.5 M K_2HPO_4/0.5 M KH_2PO_4) of pH 7 was prepared by dissolving 87.09 g K_2HPO_4 (Aldrich) and 68.04 g KH_2PO_4 (Sigma-Aldrich) in a 1 L beaker with DI water. The color developing agent was prepared by dissolving 0.25 g of 1,5-diphenylcarbazide (Aldrich) in a 50 mL volumetric flask and diluting with acetone, and was then stored in the freezer. The alkaline extraction solution was prepared by adding 20.0 (±0.05) g sodium hydroxide (Sigma-Aldrich) and 30.0 (±0.05) g sodium carbonate (Sigma-Aldrich) to a 1 L volumetric flask and diluting with DI water. The pH of this solution should be adjusted to 11.5 or greater prior to use. Magnesium chloride (Sigma-Aldrich) was used without any dilution. 35% (m/m) nitric acid was prepared by diluting 70% (m/m) nitric acid in a 100 mL volumetric flask and was stored in an amber Teflon bottle. 30% (m/m) sulfuric acid was prepared by diluting 30 mL of concentrated sulfuric acid to 100 mL with DI water in a volumetric flask. All glass, beakers, plastic bottles, etc., were soaked in a 5% (v/v) nitric acid solution for 24 h and rinsed with DI water prior to use.

Preparation of in-house polymer reference materials (RMs)

ABS (SD-0150, Cheil Industries Inc., Korea), HIPS (HR-1360, Cheil Industries Inc., Korea) and PC (SC-1220R, Cheil Industries, Korea) were used as base polymer materials for the in-house polymer RMs. Each base material contained a small amount of organic and inorganic additives at <2%. As additives, lead chromate ($PbCrO_4$, Sigma-Aldrich) and antimony trioxide (Sb_2O_3, Sigma-Aldrich) were added to each base material with a suitable dispersing agent. Then, the mixtures were extruded at melt temperature of about 200℃ using an extruder (TEK30, SM PLATEK Inc., Korea). The obtained granulates were mixed and extruded repeatedly to achieve optimum homogeneity. It was intended to produce two polymer samples (5 kg each) containing 322 and 1165 mg·kg^{-1} of Cr(VI). The resulting materials were cut into pieces of ca 10 mg and were stored in a 50 g bottle.

Instrumentation

An inductively coupled plasma-atomic emission spectrometer (ICP-AES, 7300DV, PerkinElmer-Sciex) was used to determine the total contents of chromium and antimony in the in-house RMs. A UV-Vis spectrophotometer (V-550, JASCO, Japan) equipped with a quartz cell was used to analyze the extracted Cr(VI) complex.

X-ray diffraction patterns were obtained using a PRO MPD diffractometer (Panalytical X'Pert). Unless otherwise stated, all runs were over a 2θ range of 10 to 70° at 0.02° increments using a Cu K_α radiation source at 40kV-30mA for vitreous samples.

All MALDI-TOF mass spectra were acquired using a MALDI SYNAPT G2 mass spectrometer (Waters, UK). The system utilizes a pulsed nitrogen laser (2.5 kHz), emitting at 337 nm. Acquisition mode was sensitive mode and polarity was positive. Mass range was from 100 to 1000 Da and there was no matrix material. NMR was performed with a Bruker Ascend^{TM} 600MHz wide bore NMR spectrometer operating at 151.06 MHz for the ^{13}C and 600.7 MHz for the ^{1}H resonance frequency. Cross-polarization with magic angle spinning (CPMAS) was applied at 35 kHz. A contact time of 1ms was used, with a pulse delay of 5 s.

Extraction procedure and method.

NMP-ASSISTED ALKALINE EXTRACTION WITH EDTA CHELATION. Samples were directly dissolved in 1-methyl-2-pyrrolidone (NMP) with EDTA. 0.15 g of sample and 10 g of NMP (with excess EDTA) were placed in 20 mL vials and dissolved by using a shaker for 3 h. About 5 g of the sample solution and 20 mL of the alkali solution with EDTA were added to a 150 mL beaker. Then, 1 mL of phosphate buffer solution and magnesium chloride was added. After adjusted to pH 7 - 8 with 35% nitric acid, the resulting solutions were diluted to 50 g. Then, 40 g was adjusted to pH 2.0 - 2.5. Finally, 2.5 mL of 0.5 M diphenylcarbazide (DPC, Special Grade, Merck), a colour developing agent, was added for chelation with Cr(VI) and the resulting violet solution was introduced into a UV-Vis spectrophotometer. The absorption peak of the Cr(III)-DPCO complex was observed at 540 nm. The absorbance reading of the sample was corrected by subtracting the absorbance of a blank carried through the color development procedures. From the corrected absorbance, the concentration of Cr(VI) was determined by referring to the calibration curve.

THF-ASSISTED ALKALINE EXTRACTION FOR ABS AND HIPS POLYMERS. ABS and HIPS polymer samples were directly dissolved in THF. 0.15 g of sample and 6 g of THF were placed into a 20 mL tube and dissolved by using a shaker for 1 h. After that, 3 g of isopropyl alcohol (IPA) was added to the solution. Then, the 7g sample solution and 20 mL of the alkali solution were mixed in a 150 mL beaker. The analytical procedure was then performed in accordance with the NMP-assisted alkaline extraction with EDTA chelation, mentioned in the section above.

THF-ASSISTED ALKALINE EXTRACTION FOR PC POLYMER. PC polymer samples were directly dissolved in 1-methyl-2-pyrrolidone (NMP). 0.15 g of sample and 6 g of NMP were placed into 20 mL tubes and dissolved by using a shaker for 1 h. After that, 3 g of IPA was added to the solution. Then, the 7g sample solution and 20 mL of the alkali solution were mixed together in a 150 mL beaker. The rest of the analytical procedure was performed in accordance with the NMP-assisted alkaline extraction with EDTA chelation, mentioned in the section above.

ADDITIVE REACTION BETWEEN Sb(III) AND Cr(VI). For the study of the additive reaction of Sb(III)-Cr(VI), 1.89 g of 10,000 mg/mL Sb(III) solutions and 2.2 g of 1,000 mg/mL Cr(VI) solution were charged in 20 mL sealable glass bottles. 8.4 g of distilled water was added to the tubes, which were then tightly capped and shaken in an air bath at 25℃ for 3 h. Similarly, the additive reaction was tested in THF, i.e., 2.1 g of 10,000 mg mL^{-1} Sb(III) solution and 2.00 g of 1,000 mg mL^{-1} Cr(VI) solution were charged in 20mL sealable glass bottles. 9.3 g of distilled water was added to the bottle and 1.5 g of THF was added drop-wisely. After the reaction, the bottle was tightly capped and adducted in an air bath at 25℃ for 3 h for suspension. The suspended particles were then collected by centrifugal separation at 20,000 rpm, filtered with a membrane filter (pore size 0.45 μm), and dried at 70℃ for 2 h. The total antimony and chromium content of the filtrates was determined by ICP-AES and the Cr(VI) content was determined by UV-Vis spectrophotometer. The solid phase was analyzed by X-ray diffraction (XRD), NMR and MALDI-TOF-MS.

Results and Discussion

Homogeneity test of the in-house manufactured polymer RMs.

Table 1. Analytical results (n=10) of homogeneity study of in-house RMs using ICP-AES.

Base Material	Standards	Expected Cr(VI) (mg kg^{-1})	Measured Cr(VI) (mg kg^{-1})	RSD (%)	F*	p-value	Fc**
ABS	RM-1	322	292	2.6	0.77	0.642	2.39
	RM-2	1165	1103	1.0	2.28	0.060	2.39
HIPS	RM-1	322	228	2.9	0.44	0.896	2.39
	RM-2	1165	862	1.1	0.39	0.926	2.39
PC	RM-1	322	284	3.0	0.34	0.950	2.39
	RM-2	1165	1076	4.1	2.19	0.069	2.39

*F=(between-group variability/within-group variability) = MS$_B$/MS$_W$ (Sb(III) Concentration : 2.5 ~ 4.3%)

**F$_c$ for α (significance level) = 0.05, ν$_1$ (between-group degrees of freedom) = 9, ν$_2$ (within-group degrees of freedom)= 20

Prior to the development of a new method, reference materials (RM) should be prepared and verified by a proper analytical method. Unfortunately, since no commercialized polymer RM containing Cr(VI) with Sb(III) is currently available on the market, in-house RMs based on ABS, HIPS and PC polymers were specially produced for use in this work. The homogeneity was tested following the guidelines of ISO (guide 35, 2006) and the international harmonized protocol. Following the guidelines, the bulk RMs were divided into 10 bottles each containing 0.10g. All the RM samples were then treated using acid decomposition and ICP-AES was performed on the resulting solutions to determine the chromium and antimony content. Analytical results of the homogeneity tests are listed in Table 1. As shown in the table, the measured concentrations of total Cr in all the RMs were very close to the expected concentrations with a relative standard deviation (RSD) of <5 %. One-way analysis of variance (One-way ANOVA) using Excell 2007 software was performed on the results. The null hypothesis of the one-way ANOVA test, H$_0$, indicated that there was no difference among the mean concentration of the bottles, or, that the analytical results came from populations with the same mean. If the calculated statistic of the test, F, was lower than the critical F$_c$ value, there would be no evidence to reject H$_0$. Since F was indeed smaller than F$_c$, as shown in the table, it was concluded that the all the in-houses RMs were sufficiently homogeneous. However, F value and p-value of RM-2 for ABS and PC were not sufficient, compared to other RMs because of the high content of Sb$_2$O$_3$ (> 4.1 %).

Effect of EDTA complexation on the recovery of Cr(VI).

Table 2 Analytical results of Cr(VI) content using NMP-assisted alkaline extraction with EDTA masking.

Classification	ABS	HIPS	PC
Measured concentration of total Cr by ICP-AES (mg kg^{-1})	291.6 ± 3.9	228.0 ± 3.2	283.6 ± 3.9
Measured concentration of Cr(VI) by UV-Vis spectrometry (mg kg^{-1})	31.4 ± 8.3	45.7 ± 10.0	43.2 ± 26.0
Recovery rate (%) of Cr(VI)*	10.8	20.0	15.2

*[concentration of UV-Vis]/[concentration of ICP-AES] x 100

The stability constant of Sb(III)-EDTA complex was 24.80, and no report on Cr(VI), EDTA complexation has considered it as a way to suppress the oxidation of Sb(III) and to protect Cr(VI) from reduction. The making effect of EDTA on the recovery of Cr(VI) in NMP-assisted alkaline extraction was tested by UV-Vis spectrometry using the in-house manufactured RMs and the analytical results were compared with the results from ICP-AES. As listed in Table 2, the recovery of Cr(VI), as compared to the analytical result of ICP-AES, was <20.0% for all the polymers. This suggested that the addition of EDTA to the NMP-assisted alkaline extraction improved the recovery of Cr(VI), compared to the current RoHS method, which has a known recovery of <5%, but there was still large rooms for improvement, to obtain complete suppression of the redox reaction of Sb(III)-Cr(VI).

THF-assisted alkaline extraction to suppress the redox reaction.

EFFECT OF THE ADDITIVE REACTION OF THF WITH Sb(III) ON THE DETERMINATION OF Cr(VI). After screening various organic solvents, we found that THF possessed the superior extraction efficiency for Cr(VI) in the presence of Sb(III) without the polymer matrix. When THF was added, a solid adduct was formed. Conceptually, two additive reactions were possible for the adduct, i.e., the formation of Sb(III)-THF and/or Cr(VI)-THF. In order to clarify the adduct identity, the concentration of Cr(VI) in the filtrate was determined using ion chromatography and the precipitate was analyzed using ICP-AES after filtration. The results strongly indicated that the adduct identity was Sb(III)-THF, as the precipitates and the filtrate contained large amounts of Sb and Cr(VI), respectively. In addition, though the recovery rate of Cr(VI) obtained by the current RoHS method applied in this study was only about 2.5%, it increased to about 95.0% when THF was added. Therefore, we concluded that the use of THF in the alkaline extraction method uniquely suppressed the reduction of Cr(VI) by the formation of an Sb-THF complex.

IDENTIFICATION OF Sb(III)-THF ADDUCTS BY XRD AND NMR. For verification, XRD and NMR were carried out for the structural identification of the solid adduct. Fig 1 shows the XRD patterns, indicating the absence of crystalline content and the presence of an organometallic compound. To support the structure of the organometallic compound, the spectrum of ^{1}H and ^{13}C NMR were also obtained as shown in Fig. 1 (b) and (c), and the chemical shift was listed in Table 3.

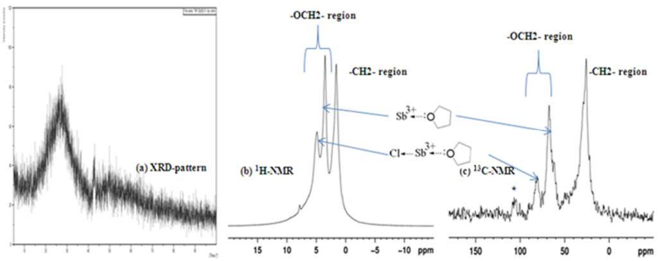
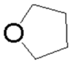
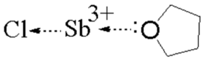
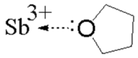


FIG. 1. THE SOLID STATE NMR SPECTRUM AND XRD PATTERNS OF THE SOLID PRODUCT OF Sb(III) AND THF ADDUCTION: (A) XRD PATTERNS; (B) ^{1}H-NMR; (C) ^{13}C-NMR.

Table 3. Structural identification of the solid product using solid state ^{1}H and ^{13}C NMR.

	Chemical Shift (ppm)				Structure
	^{1}H-NMR		^{13}C-NMR		
	OCH$_2$-	CH$_2$-	OCH$_2$-	CH$_2$-	
Pure THF	3.6	2.5	67.4	25.3	
Solid product (adducts)	4.9	1.6	81.1	25.9	
	3.7		67.7		

The chemical shift of the –OCH$_2$- region was slightly different from that of pure THF and new peaks were also observed in the region of –OCH$_2$- on the ^{1}H NMR (4.9 ppm) and ^{13}C NMR (81.1 ppm) spectrum. In the ^{1}H-NMR spectrum, peaks at 4.9 ppm and 3.7 ppm indicated the presence of two types of –OCH$_2$- with another peak at 1.6 ppm corresponding to –CH$_2$-. The existence of two -OCH$_2$- peaks specially indicated that the oxygen atom in THF had a lone pair of electrons donated to Sb(III) as a Lewis base ligand. When this happened, the peak for –OCH$_2$- in THF was shifted down-field due to the deshielding effect. In the ^{13}C-NMR spectrum, the peak assignment was nearly the same as that obtained by ^{1}H-NMR.

IDENTIFICATION OF Sb(III)-THF ADDUCTS BY MALDI-TOF-MS. For further structural confirmation, the structure of the Sb(III)-THF adduct was analyzed using MALDI-TOF-MS (Fig 2). From the fragment pattern, the molecular weight of the Sb(III)-THF adduct was identified at 717 mass-to-charge ratio (m/z), because the pattern of all molecular ion clusters showed a separation of 2 mass units due to the presence of chlorine atom. Generally, compounds containing the chlorine atom can be readily recognized in mass spectrometry, and the numbers of chlorine atoms can also be determined by the chlorine rule. The assignment of 717 m/z as the molecular weight (MW) was very important because it can be considered as conclusive evidence of the presence of Sb(III)-THF adduct, formed by the additive reaction.

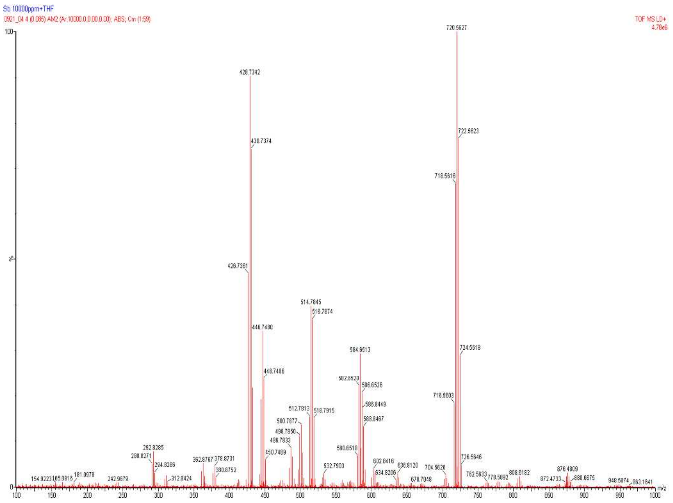


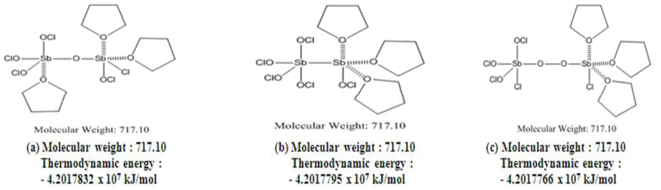
Fig. 2. Positive ion MALDI-TOF-MS spectrum of the solid product formed in the reaction between Sb(III) and THF. The peak at 716.6 (m/z) was identified to be the molecular weight of the Sb(III)-THF adduct.

The number of split isotope patterns, molecular weight (observed), expected fragment structure, and molecular weight (calculated) in each mass range are listed in Table 4.

In the m/z range of 716 to 726, the peak was split into 6 molecular ions (MW of 716, 718, 720, 722, 724, 726), which strongly implied that the solid product contained 5 chlorine atoms by the (n-1) chlorine rule. The presence of 3 THF units was identified from the mass spectra of 3 regions at 586 to 514, 518 to 446, 362 to 290 m/z, which showed a difference of molecular weight of 72 mass units.

Table 4. Assignment of fragment structure for the solid adduct from the data obtained using MALDI-TOF/MS.

Peak pattern (mother ion)	Number of split isotope pattern	Chlorine Atoms contained	Molecular Weight (Observed)	Expected fragment structure	Molecular Weight (Calculated)
716 ~ 726(716)	6	5	716.56	$Sb_2O_5Cl_5(THF)_3$	716.77
580 ~ 588(580)	6	5	580.65	$H_1Sb_2O_1Cl_5(THF)_2$	581.77
512 ~ 518(512)	4	3	512.78	$H_4Sb_2O_1Cl_3(THF)_2$	513.87
496 ~ 502(496)	4	3	496.78	$H_3Sb_2Cl_3(THF)_2$	496.87
444 ~ 450	4	3	444.74	$H_6Sb_2O_1Cl_3(THF)_1$	444.97
426 ~ 432	4	3	426.74	$H_5Sb_2Cl_3(THF)_1$	426.87
360 ~ 364	3	2	360.87	$Sb_2O_3Cl_2$	362.42
308 ~ 312	3	2	308.84	$H_4SbO_7Cl_2$	308.66
290 ~ 294	3	2	290.83	$H_4SbO_6Cl_2$	292.66



(a) Molecular weight : 717.10
Thermodynamic energy :
- 4.2017832 x 10^7 kJ/mol

(b) Molecular weight : 717.10
Thermodynamic energy :
- 4.2017795 x 10^7 kJ/mol

(c) Molecular weight : 717.10
Thermodynamic energy :
- 4.2017766 x 10^7 kJ/mol

Fig. 3. Predicted structures of the Sb(III)-THF adduct based on MALDI-TOF/MS and the ground state energy calculation using a molecular simulation by Density functional theory (DFT)- Generalized Gradient Approximation (GGA).

From the interpretation, the structure was narrowed down to three possibilities, as shown in Fig. 3. Since the predicted structures had five coordination numbers, it provided no chance to reduce Cr(VI), which agreed with the analytical results of UV-Vis measurement. Among the structures, structure (a) (-Sb-O-Sb-) was found to be the most stable from the calculation of ground state energy using the molecular simulation by density functional theory (DFT)-generalized gradient approximation (GGA). As listed in the figure, the calculated thermodynamic energy of structure (a) was 4.2017832 x 10^7 kJ mol^{-1}, which was the largest of the three. Based on all the analytical results and the calculations, we conclude that the product of the additive reaction, $Sb_2O_5Cl_5(THF)_3$, clearly has the structure shown in Fig. 3 (a).

Application of the THF-assisted alkaline extraction to polymer samples.

Table 5. Analytical results of Cr(VI) in polymer samples using the developed THF-assisted alkaline extraction.

Classification	ABS	HIPS
Measured concentration of total Cr by ICP-AES (mg kg^{-1})	291.6	228.0
Measured concentration of Cr(VI) by UV-Visible spectrometry (mg kg^{-1})	142.5	176.6
Recovery rate of Cr(VI) (%)	48.9	77.5

When the developed THF-assisted alkaline extraction method was applied to ABS and HIPS polymers, recoveries of 48.9 % and 77.5 % were obtained, respectively, in comparison to the results obtained by ICP-AES (Table 5). Although those results were significantly larger than the recoveries obtained by the current RoHS method or by the NMP-assisted alkaline extraction with the addition of EDTA, the recovery was still significantly low, compared to that without polymer matrix.

Optimization of the developed THF-assisted alkaline extraction.

In order to maximize the recovery of Cr(VI), the amount of THF extraction solvent was optimized using the mixture of IPA or NMP, varying the solvent ratio to THF while the extraction time and pH of the final solutions were fixed at 60 min and 2.0, respectively (supplementary figure S-1 and S-2). The optimum ratio of 6:3 for both THF/IPA and NMP/THF mixtures was chosen for ABS/HIPS and PC polymers, respectively. When the optimized solvent was used, the recovery was raised to >95.2%, as shown in the figures, which was nearly 19-38 folds better than that obtained by the current RoHS method.

Analytical figures-of-merits.

All the analytical figures-of-merits of the developed THF-assisted alkaline extraction (6:3=THF/IPA) were determined by UV-Vis measurements, following the requirements of the ICH Guideline Q2B,[14,15,16,17] for linearity, precision, accuracy, limit of detection (LOD) and limit of quantification (LOQ). Linearity was estimated at the desired concentration range of 0-1.5 mg L^{-1} of Cr(VI) under the optimum conditions, as described above. Six-point calibration curves with matrix matching were obtained, of which the linear regression coefficient (R^2) was >0.999 (supplementary figure S-3).

The LOD and LOQ were calculated as follows:

$$LOD = \frac{3.3\sigma}{S}$$

and

$$LOQ = \frac{10\sigma}{S}$$

, where σ is the standard deviation of the blank and S is the slope of the calibration curve. The calculated LOQ for ABS, HIPS and PC polymers were 0.058, 0.044 and 0.040 mg kg^{-1}, respectively. The dilution factor for the developed extraction method was about x500, thus the final LOQ multiplied by the dilution factor was less than about 30 mg kg^{-1}. The results indicated that the new quantitative method with the proposed extraction method was sufficiently sensitive to determine accurate Cr(VI) composition for the evaluation of RoHS compliance, which requires the threshold of <1,000 mg kg^{-1} for electronic products.

The accuracy and precision of the method were also assessed by analyzing the recovery and repeatability. The repeatability was calculated as the relative standard deviation (RSD). For repeatability, the quantitative analysis was carried out on ten identical RM samples under the same experimental conditions. The results are listed in Table 6, showing recoveries in the range of 95.2 to 100.3% with RSD of <5%, as compared to the analytical results obtained by ICP-AES (Table 1) for method validation.

Table 6. Comparison of the analytical result from UV-Vis spectrometry for the optimized alkaline extraction method with ICP-AES results.

Base material	Standards	Measured total Cr conc. by ICP-AES* (mg kg^{-1})	Measured Cr(VI) conc. by UV-Vis** (mg kg^{-1})	Recovery*** (%)	RSD (%)
ABS	RM-1	292	278 ± 5	95.2	1.7
	RM-2	1103	1082 ± 21	98.1	2.0
HIPS	RM-1	228	228 ± 11	100.3	4.8
	RM-2	862	829 ± 11	96.1	1.4
PC	RM-1	284	270 ± 9	95.3	3.1
	RM-2	1076	1043 ± 18	97.0	1.7

*Table 1.

**Number of analytical replicates: 10

***[Cr(VI) concentration by UV-Vis]/[total Cr concentration by ICP-AES] x 100

Conclusions

In this work, the THF-assisted alkaline extraction method was developed to improve the recovery of Cr(VI) in plastic materials in the presence of Sb(III). The developed method achieved recoveries >95.2%, which showed significant improvement, over the current RoHS method, typically obtaining <5% in our work. From experimentation, we also proved that THF efficiently suppresses the conversion of Cr(VI) to Cr(III) by the formation of a Sb(III)-THF adduct, and identified the structure to be $Sb_2O_5Cl_5(THF)_3$ based on the analytical results of XRD, NMR, and MALDI-TOF-MS. In addition, all the analytical figures-of-merits using UV-Vis measurement were determined satisfactorily, and the method was verified by ICP-AES. Therefore, this new extraction technique should be suitable as a successful new sample preparation method to determine Cr(VI) in IEC62321 for the

International Electrotechnical Commission's Technical Committee 111 (IEC TC111). A new edition of IEC 62321 is currently in progress, with reflection of the method developed in this work.

Notes and references

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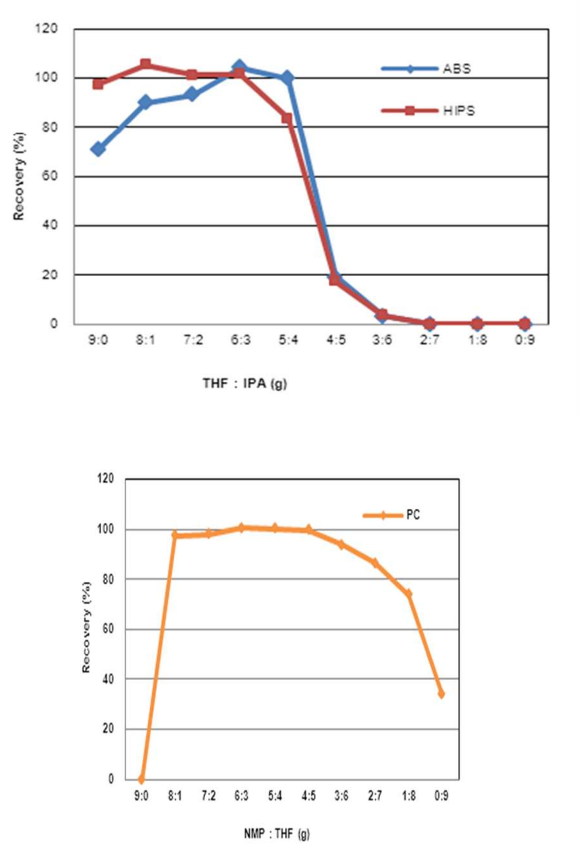
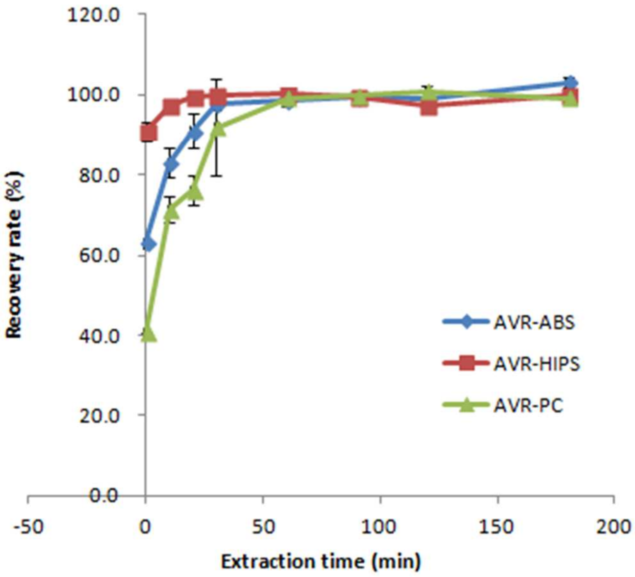
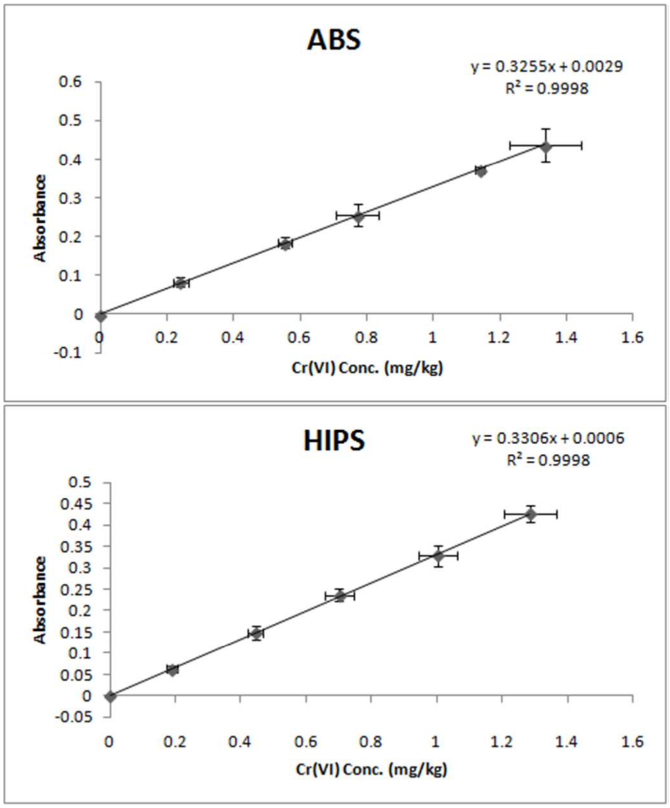
Supplementary figures.

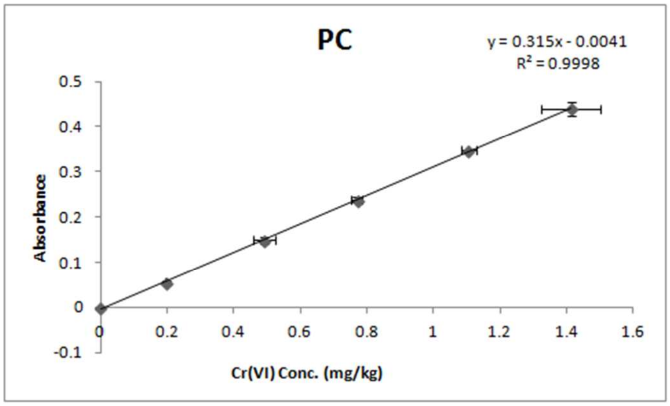


Supplementary figure S-1. Effect of extraction solvent ratio on recovery of Cr(VI) in ABS and HIPS polymers.



Supplementary figure S-2. Effect of extraction time on recovery of Cr(VI) in polymers.





Supplementary figure S-3. Matrix-matched calibration curve for the quantitation of Cr(VI) in ABS, HIPS and PC using UV-Vis spectrometry.

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