

An Investigation on the Extraction and Quantitation of a Hexavalent Chromium in Acrylonitrile Butadiene Styrene Copolymer (ABS) and Printed Circuit Board (PCB) by Ion Chromatography Coupled with Inductively Coupled Plasma Atomic Emission Spectrometry

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A hexavalent chromium (Cr (VI)) is one of the hazardous substances regulated by the RoHS. The determination of Cr (VI) in various polymers and printed circuit board (PCB) has been very important. In this study, the three different analytical methods were investigated for the determination of a hexavalent chromium in Acrylonitrile Butadiene Styrene copolymer (ABS) and PCB. The results by three analytical methods were obtained and compared. An analytical method by UV-Visible spectrometer has been generally used for the determination of Cr (VI) in a sample, but a hexavalent chromium should complex with diphenylcarbazide for the detection in the method. The complexation did make an adverse effect on the quantitative analysis of Cr (VI) in ABS. The analytical method using diphenylcarbazide was also not applicable to printed circuit board (PCB) because PCB contained lots of irons. The irons interfered with the analysis of hexavalent chromium because those also could complex with diphenylcarbazide. In this study, hexavalent chromiums in PCB have been separated by ion chromatography (IC), then directly and selectively detected by inductively coupled plasma atomic emission spectrometry (ICP-AES). The quantity of Cr (VI) in PCB was 0.1 mg/kg.

Key Words : Acrylonitrile butadiene styrene copolymer (ABS), Printed circuit board (PCB), Ion chromatography (IC), Inductively coupled plasma atomic emission spectrometry (ICPAES), Hexavalent chromium

Introduction

The chemical speciation of heavy metals has been very critical because their bioactivity and toxicity relies on the different chemical forms of heavy metals in a sample. Chromium is one of them because trivalent chromium (Cr (III)) is very essential in nutrition, but hexavalent chromium (Cr (VI)) is very toxic to human beings.¹⁻⁷ Thus, the concentration of Cr (VI) in drinking water has been restrictly regulated in the world. The RoHS (Directive on the Restriction of the use of Hazardous Substances in electrical and electronic equipment) also regulated the Cr (VI) in electrical and electronic products.⁸⁻¹⁰ Thus, the analytical method for the determination of Cr (VI) has been interested and important in many areas.¹¹⁻¹⁹

This work focused on the extraction and quantitation of the Cr (VI) in acrylonitrile butadiene styrene copolymer (ABS) and printed circuit board (PCB). The currently suggested detection method for the Cr (VI) is UV-Visible spectrometer, but the detection method has several limitations and interference problems. In this study, UV-Vis spectrometer was used for the determination of Cr (VI) in ABS. Inductively coupled plasma atomic emission spectrometry (ICP-AES) coupled with ion chromatography was also used for the detection method of the Cr (VI) in ABS. The analytical results obtained by UV-Vis spectrometry were compared with those by IC-ICP-AES.

The analytical method by UV-Visible spectrometer was not applicable to PCB because it contained lots of irons.^{20,21} The irons could interfere with the analysis of hexavalent chromium because those also could complex with diphenylcarbazide.²² In this study, hexavalent chromiums in PCB have been separated by ion chromatography (IC), then directly and selectively detected by inductively coupled plasma atomic emission spectrometry (ICP-AES).²³⁻²⁶

The speciation of Cr (VI) is still challenging. The certified reference material (CRM) needs to be developed. The standard analytical method for the determination of Cr (VI) should be established for various scientific and industrial areas.

Experimental

Instrumentation. UV-Vis Spectrometer was a model OPTIZEN 1412V (MECASYS Corp, Korea). The selected wavelength for a hexavalent chromium was 540 nm. Gradient pump 50 of Ion chromatograph (Dionex Corp., USA) with anion exchange column (250 × 4 mm, IonPac AS7, Dionex Corp., USA) and anion guard column (50 × 4 mm, IonPac AG7, Dionex Corp., USA) was used for the separation of Cr (VI). The effluent from the analytical column was introduced directly into the ICP-AES (SPECTRO, a model ARCOS, Germany). The operating parameters were shown in Table 1.

Table 1. The operating parameters (UV-Vis spectrometer, Ion Chromatography, Inductively Coupled plasma atomic emission spectrometry)

UV-Vis spectrophotometer	
System model	OPTIZEN 1412V
Wavelength range	200-1000 nm
Analysis wavelength	540 nm
Ion chromatography	
System	GP 50 Gradient Pump (Dionex Corp.)
Flow rate	1.3 mL/min
Column	IonPac AS7 anion exchange column (250 × 4 mm)
	IonPac AG7 guard column (50 × 4 mm)
	15 µm particles
Sample loop	100 µL
Pressure	1100-1200 psi
Eluent	250 mM Ammonium sulfate, (NH ₄) ₂ SO ₄
	100 mM ammonium hydroxide, NH ₄ OH
Inductively Coupled Plasma Atomic Emission Spectrometry	
System model	SPECTRO ARCOS
Generator Parameter	
Plasma power	1400 W
Addition flow	0.25 L/min
Coolant flow	12.00 L/min
Auxiliary flow	1 L/min
Nebulizer flow	0.75 L/min
Run time	500 s
Sampling rate	2.0 Hz
Integration interval	500 ms
Selected wavelength	283.563 nm

Chemicals and Reagents. All solutions were prepared with 18 MΩ·cm distilled deionized water (PURELAB Plus water purification system (ELGA, U.K)). All standard solutions for the chromium (III) and chromium (VI) were prepared from the stock solutions (1000 ± 3 µg/mL Cr (III) and 1000 ± 3 µg/mL Cr (VI), VHG Lab, USA). The complexing reagent for Cr (VI) was 1,5-Diphenylcarbazide (C₁₃H₁₄N₄O, 99.9%, Sigma-Aldrich Co., USA). Acetone (CH₃COCH₃, 99.99%, Sigma-Aldrich) was used to dissolve the 1,5-Diphenylcarbazide. *N*-methyl-2-pyrrolidone (NMP) (C₅H₉NO, 99.99%, Sigma-Aldrich) was used to dissolve the ABS.

Reagents of eluents were prepared from ammonium sulfate (99.99%, Aldrich Co., USA) and ammonium hydroxide (28%, Sigma-Aldrich). Alkaline digestion solvents of extraction were 0.5 M Sodium Hydroxide (99.99%, Sigma-Aldrich) and 0.28 M Sodium Carbonate (99.99%, Sigma-Aldrich). For the adjustment of pH of eluent, the pure nitric acid (70%, Aldrich) and sulfuric acid (95-98%, Aldrich) were used. A phosphate buffer (0.5 M K₂HPO₄/0.5 M KH₂PO₄) at pH 7 was prepared by dissolving 87.09 g K₂HPO₄ (99%, Sigma-Aldrich) and 68.04 g KH₂PO₄ (99%, Sigma-Aldrich) in a 1 L volumetric flask and diluting to mark with DDW.

ABS Samples and Preparation. Reference materials of ABS were made by polymer engineers of Jeil Industries Inc.

(Seoul, Koea). A blank of ABS was made for a hexavalent chromium. It did not contain any hexavalent chromium. A sample-A of reference material ABS contained 112 mg/kg of hexavalent chromium. It was spiked into the blank ABS. A sample-B of reference material ABS contained 482 mg/kg of hexavalent chromium.

Sample Preparation 1^{27,28}: Each of ABS 0.25 g was dissolved in a 20 mL of alkali digestion solution. In a 250 mL flask, 0.4 g of MgCl₂ and 2 mL of 0.5 mol/L phosphate buffer were added to the solution. The sample solution was shaken for 3 hours at the temperature of 90-95 °C, then it was cool down. The sample solution was adjusted at pH 7.0 ± 0.5 by 0.5 mol/L HNO₃, then it was filtered by 0.45 µm filter. A 2 mL of 0.5 mol/L diphenylcarbazide solution was added to the sample solution. The sample solution was adjusted to pH 2.0 ± 0.5 by slow adding of 30% H₂SO₄. The sample solution was transferred to a 100 mL volumetric flask, then added to the mark by DDW. The final solution was transferred to the cell of UV-VIS Spectrometer and the absorbance was measured at 540 nm.

Sample Preparation 2: Each of ABS 0.25 g was dissolved in 10 g of NMP in glass vial. The sample solution was shaken for 60 minutes. A aliquot 5 g of the dissolved solution was added to a 20 mL of alkali digestion solution in a 250 mL flask. In a 250 mL flask, 0.4 g of MgCl₂ and 1 mL of 0.5 mol/L phosphate buffer were added to the solution. The sample solution was shaken for 1 hours at the room temperature. The sample solution was adjusted at pH 7.0 ± 0.5 by 0.5 mol/L HNO₃. A 2 mL of 0.5 mol/L diphenylcarbazide solution was added to the sample solution. The sample solution was adjusted to pH 2.0 ± 0.5 by slow adding of 30% H₂SO₄. The sample solution was transferred to a 100 mL volumetric flask, then added to the mark by DDW. It was filtered by 0.45 µm filter. The final solution was transferred to the cell of UV-VIS Spectrometer. The absorbance was measured at 540 nm.

Sample Preparation 3: Each of ABS 0.25 g was dissolved in 10 g of NMP in glass vial. The sample solution was shaken for 60 minutes. A aliquot 5 g of the dissolved solution was added to a 20 mL of alkali digestion solution in a 250 mL flask. In a 250 mL flask, 0.4 g of MgCl₂ and 1 mL of 0.5 mol/L phosphate buffer were added to the solution. The sample solution was shaken for 1 hours at the room temperature. The sample solution was adjusted at pH 7.0 ± 0.5 by 0.5 mol/L HNO₃. The sample solution was transferred to a 100 mL volumetric flask, then added to the mark by DDW. It was filtered by 0.45 µm filter. The sample was analyzed by IC-ICP-AES.

PCB Sample Preparation. PCB was obtained from the old computers, then all electrical parts on PCB were removed. The PCB was broken down into the powder by a pulverizer (FRITSCH GmbH, Vibratory Micro Mill, Germany). The particles that were under the size of diameter 250 µm were collected for the sample. Each 2 g samples were dissolved in the 20 mL of alkali digestion solution. The samples were digested at 90-95 °C for 3 hours, then those were adjusted at pH 7 by 5 M nitric acid. A 0.4 g of MgCl₂

(Sigma-Aldrich Co., USA) and 1 mL of phosphate buffer solution were added. At last, the samples were filtered by 0.45 μm filter for analysis.

Results and Discussion

The Result of ABS. Samples of ABS were prepared by a method of sample preparation 1 described in experimental section. Hexavalent chromiums were determined in the ABS samples by UV-Vis spectrometer. The results are shown in Table 2. For the sample-A and sample-B, the measured amounts of hexavalent chromium were far lower than those of reference materials. The extraction method of sample preparation 1 might be not enough for ABS. The results suggested that the sample preparation 1 was not suitable for ABS.

Another samples were prepared by a method of sample preparation 2 described in experimental section. Hexavalent chromiums were determined in the ABS samples by UV-Vis spectrometer. As the results are shown in Table 3, the measured amounts of hexavalent chromium were close to those of reference materials. It indicated that the sample preparation 2 was much better than sample preparation 1. In

Table 2. Hexavalent chromium in ABS by Sample preparation 1

Sample	Result (mg/kg)	Average (mg/kg)	Spike concentration (mg/kg)
Sample A	1 22.8	22.3 ± 1.4	112
	2 20.8		
	3 23.3		
Sample B	1 89.9	87.3 ± 6.3	482
	2 91.8		
	3 80.3		

Table 3. Hexavalent chromium in ABS by Sample preparation 2

Sample	Result (mg/kg)	Average (mg/kg)	Spike concentration (mg/kg)
Sample A	1 132.3	133.9 ± 2.3	112
	2 133.0		
	3 136.5		
Sample B	1 601.1	594.0 ± 6.5	482
	2 588.4		
	3 592.4		

Table 4. Hexavalent chromium in ABS by Sample preparation 3

Sample	Result (mg/kg)	Average (mg/kg)	Spike concentration (mg/kg)
Sample A	1 113.9	114.1 ± 2.9	112
	2 111.3		
	3 117.1		
Sample B	1 416.9	434.0 ± 6.5	482
	2 437.2		
	3 448.0		

this method, NMP played an very important role for the extraction of hexavalent chromium from ABS samples.

In addition, the hexavalent chromiums in the ABS samples were determined by IC-ICP-AES without the diphenylcarbazide solution after those were prepared by sample preparation 3. The results are shown in Table 4. It clearly indicated that the best results were obtained with sample preparation 3 and IC-ICP-AES. The chromatograms are shown in Figure 1. The better results by IC-ICP-AES might be due to the simple sample preparation without the diphenylcarbazide solution.

Results of PCB. First, the analytical method by UV-Vis spectrometer was applied to PCB. When PCB was prepared by sample preparation 1, many precipitates formed in the sample solution after it was dissolved in the diphenylcarbazide solution. It was not possible to measure the hexavalent chromium in a PCB sample by UV-Vis spectrometer. An additional experiment was designed to investigate which elements could form precipitate with diphenylcarbazide. Each 10 mg/kg of Ni, Pb, Fe, Cu, Zn, Hg, Sn, Cd and W were prepared, it was adjusted to pH 2.0 by nitric acid and sulfuric acid. Then, it was reacted with diphenylcarbazide. Color of the solution was changed with irons right after the reaction, it was also changed with copper and lead in 12 hours after reaction. In the case of copper and lead, it could be controlled by time, but it was not possible for iron. In the

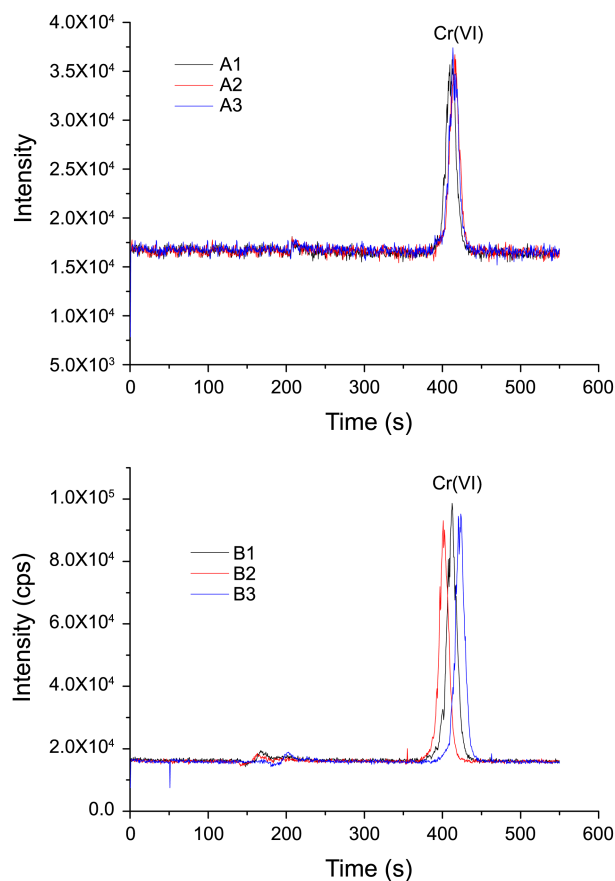


Figure 1. IC-ICP-AES Chromatogram of hexavalent chromium in ABS.

Table 5. The recovery efficiency of hexavalent chromium in standard solution by IC-ICP-AES

Certified value (mg/kg)	Measured value (mg/kg)	Efficiency (%)
0.40	0.39	97.5

Table 6. The detection limits of Cr (III) and Cr (VI) by IC-ICP-AES

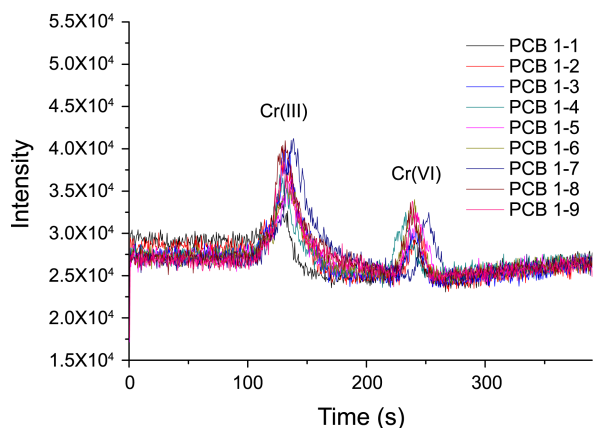
	Cr(III) (mg/kg)	Cr(VI) (mg/kg)
Detection Limits	0.081	0.021

case of iron, the positive absorbance at the wavelength of 540 nm was also observed after the iron was complexed with diphenylcarbazide. It indicated that iron could interfere with the analysis of Cr (VI) because PCB contained lots of irons.

The analytical method by IC-ICP-AES was applied to PCB. First of all, recovery efficiency of Cr (VI) by IC-ICP-AES was examined with a standard of 0.4 mg/kg Cr (VI) because there was no certified reference material (CRM) of Cr (VI). The results are shown in Table 5. The recovery efficiency was about 97.5%.

The detection limits of Cr (III) and Cr (VI) were investigated with IC-ICP-AES. The detection limits were obtained as the concentration giving a signal equivalent to three times the noise that was calculated from the standard deviation of the background. The pneumatic nebulizer was used in ICP-AES. The results are shown in Table 6. The detection limit of Cr (III) was higher than that of Cr (VI).

Three PCB samples were prepared as it was described in

**Figure 2.** IC-ICP-AES Chromatogram of chromium species in PCB.**Table 7.** Hexavalent chromium species in PCB by IC-ICP-AES

Sample Number	Concentration (mg/kg)	
	Cr(III)	Cr(VI)
PCB No.1	4.396 ± 0.132	0.108 ± 0.008
PCB No.2	4.216 ± 0.017	0.102 ± 0.007
PCB No.3	4.137 ± 0.033	0.099 ± 0.007
Average	4.200 ± 0.057	0.103 ± 0.004
RSD(%)	1.361	4.234

PCB preparation method, and the quantities of Cr (III) and Cr (VI) in PCB with IC-ICP-AES were measured repeatedly by three times. The average concentration of Cr (VI) in PCB was obtained. The chromatogram of Cr (III) and Cr (VI) are shown in Figure 2. The results are shown in Table 7. Fortunately, the quantity of Cr (III) in PCB was higher than that of Cr (VI) which is harmful to human.

Conclusion

The extraction and quantitation of a hexavalent chromium from ABS were successfully performed with the new extraction method and IC-ICP-AES. The determination of chromium (VI) in PCB including lots of iron has been difficult with UV-VIS spectrometer because it could cause much error by interference of iron in PCB. Chromium (VI) in PCB could be quantized with IC-ICP-AES without any interferences. For the first time, the chromium (III) and chromium (VI) in PCB were determined by IC-ICP-AES. Fortunately, the chromium (III) that was not harmful to human was much higher than the harmful chromium (VI) in PCB. The detection capability of the analytical method by IC-ICP-AES was enough for the determination of Cr (VI) in PCB. The recovery efficiency of Cr (VI) was 97.5%. The quantity of Cr (VI) in PCB was about 0.1 mg/kg.

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