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Application News

No.A512

Spectrophotometric Analysis

Measurement of Hexavalent Chromium in Chromate Conversion Coating and Metal Ions in Eluate – Application of Water Analysis Program for the UV-1280 –

In the electrical and electronics sector, not only does a standard apply for industrial wastewater resulting from the manufacture of electrical and electronic equipment (JIS K 0102 Testing methods for industrial wastewater), manufacturers must also abide by restrictions on the use of specific toxic substances (RoHS Directive). These standards and restrictions brought about a change in the treatment agent used for chromate conversion coating used to improve corrosion resistance from hexavalent chromium to trivalent chromium, a change in the solder used to join metals to a lead-free type. The presence of these constituents and the amounts of these constituents present in waste liquids must also be managed.

The water analysis program for the UV-1280 UV-VIS spectrophotometer can be used with a PACKTEST series of products made by Kyoritsu Chemical-Check Lab., Corp. to easily test for 39 water quality items and 22 water quality species, including hexavalent chromium and lead.

This Application News describes the measurements of the amount of hexavalent chromium used in plating on screws, and the amounts of metal ions that elute from commercially available lead and copper products, using the water analysis program for the UV-1280.

Measurement of Hexavalent Chromium in Chromate Conversion Coating

The UV-1280 and a PACKTEST product from Kyoritsu Chemical-Check Lab., Corp. are shown in Fig. 1. The water analysis program displays analytical procedures on-screen, so the concentration of target constituents can be measured by simply following the on-screen instructions. An example on-screen view is shown in Fig. 2. A trend graphing function can also be used to observe daily changes in concentration levels. See Application News No. A503 for more information about trend graphing. The hot water extraction procedure described in IEC 62321 was performed on commercially available screws with different chromate conversion treatments, and measurements were taken using the PACKTEST Chromium (Hexavalent) product. Fig. 3 shows the screws analyzed, and Table 1 shows the analytical conditions used.

The surface area (cm^2) of the screws was calculated using the formulas shown in IEC 62321, and the amounts of pure water used for extraction were prepared with 1 mL for every 1 cm^2 of surface area[1]. Three of the colored chromate screws, and 4 of the glossy chromate screws and black chromate screws were used for a total surface area of at least 25 cm^2. The extraction solvent was boiled and test samples were inserted into the solvent. Test samples were removed after heating for 10 minutes, the extraction solvent was allowed to return to room temperature, a given volume was made up with dilution as required, and measurements were performed. Results of these measurements are shown in Table 2.

Table 1 Analytical Conditions

Instrument	: UV-1280 Water analysis program PACKTEST Chromium (Hexavalent)
Item Measured	: Hexavalent chromium (PACKTEST)

Fig. 1 UV-1280 and PACKTEST Product

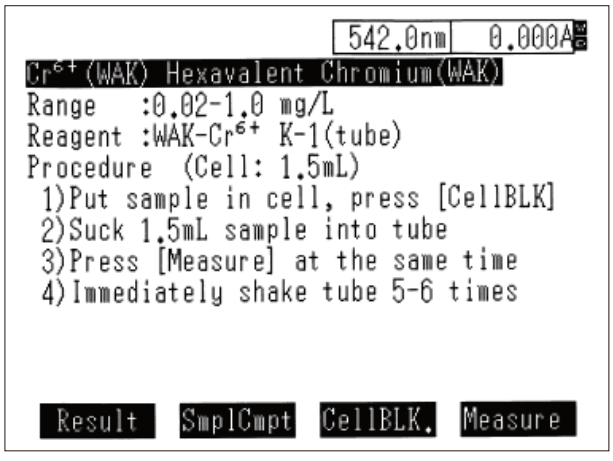

Fig. 2 Measurement Procedure for Hexavalent Chromium (PACKTEST)

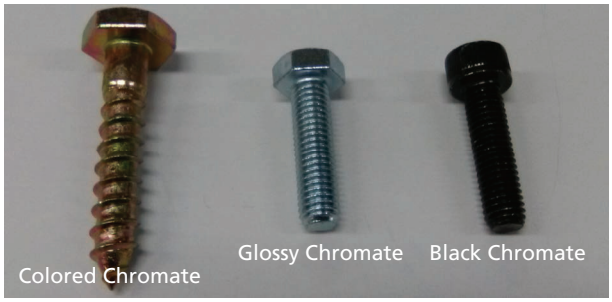

Fig. 3 Chromate-Coated Screws

Table 2 Concentrations of Extracted Hexavalent Chromium and Formula for Calculating Hexavalent Chromium Concentration

	Colored Chromate Screw Surface Area: 19.6 cm^2		Glossy Chromate Screw Surface Area: 12.1 cm^2		Black Chromate Screw Surface Area: 12.2 cm^2	
	Extraction Liquid (mg/L) *1	Extracted Amount ($\mu g/cm^2$)	Extraction Liquid (mg/L)	Extracted Amount ($\mu g/cm^2$) *3	Extraction Liquid (mg/L) *2	Extracted Amount ($\mu g/cm^2$)
1st time	0.37	3.73	< 0.02	-	0.49	0.97
2nd time	0.26	2.55	< 0.02	-	0.72	1.44
3rd time	0.48	4.79	< 0.02	-	1.03	2.06

*1: Measurement performed after diluting extraction liquid 10-fold
*2: Measurement performed after diluting extraction liquid 2-fold
All values in table are measurement results after dilution.
*3: Not calculated. Extraction liquid concentration below lower limit of detection

$$Cr(\mathrm{VI}) = \frac{C \times V}{S} \times DF$$

Cr (VI): Amount of hexavalent chromium ($\mu g/cm^2$) in chromate conversion coating
C: Concentration (mg/L), V: Extraction solvent (mL)
S: Surface area (cm^2), DF: Dilution ratio

Hexavalent chromium was detected on the colored chromate screws and black chromate screws, but was not detected on the glossy chromate screws. The liquid used for extraction from the colored chromate screws was diluted 10-fold before measurement, and the liquid used for extraction from the black chromate screws was diluted 2-fold before measurement. The variance in results obtained from the 3 repeated measurements shown in Table 2 is presumed to be caused by differences between individual sample screws, as well as differences in extraction times, amounts of extraction solvent, and temperature[2].

Measurement of Metal Ions Eluted from Products

Lead is used as an ingredient in fishing weights and solder due to its low melting point, good workability, and high specific gravity. Copper is used in electrical wires and cooking utensils due to its good electrical conductivity and thermal conductivity. Copper is also known to have antimicrobial properties[3].
Three lead weights (approximately 22.5 g) were immersed in 50 mL of pure water (room temperature), and amounts of lead ions eluted were measured at different elution times. A 10 yen coin, copper wire, and copper sheet were immersed in 50 mL of pure water for 1 day (room temperature), and the trace amounts of copper ions eluted were measured. Fig. 4 shows the samples used, Table 3 shows the analytical conditions, and Table 4 and 5 show the results obtained.

Table 3 Analytical Conditions

Instrument	: UV-1280 Water analysis program PACKTEST Lead set, Copper
Item Measured	: Lead and Copper

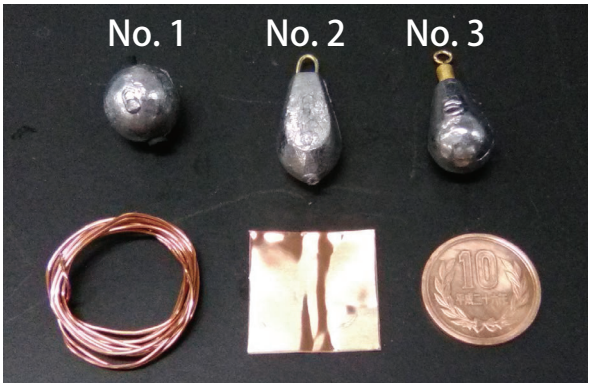

Fig. 4 Lead Samples and Copper Samples

Table 4 Relationship Between Concentration of Eluted Lead Ions and Elution Time

	Elution Time		
	1 minute	2 minutes*4	5 minutes*5
No. 1	0.31 mg/L	0.66 mg/L	1.68 mg/L
No. 2	0.41 mg/L	0.74 mg/L	2.15 mg/L
No. 3	0.32 mg/L	0.85 mg/L	3.76 mg/L

*4: Measurement performed after diluting elution liquid 2-fold
*5: Measurement performed after diluting elution liquid 10-fold
All values in table have been converted to elution liquid concentrations.

Table 5 Concentration of Eluted Copper Ions

Sample	Weight	Eluted Concentration
Copper wire	2.85 g	< 0.1 mg/L
Copper sheet	1.18 g	0.33 mg/L
10 yen coin	4.43 g	0.33 mg/L

The amount of lead ion eluted from the lead weights increased with elution time. Results also show the amount eluted varied depending on sample shape. We detected trace amounts of copper ion eluted from the copper sheet and 10 yen coin, but could not detect copper ions eluted from the copper wire. Copper wire is given an enamel coating treatment for insulation, which is presumed to be the reason that no copper ions were detected in the elution liquid.

Conclusions

The water analysis program for the UV-1280 and PACKTEST series of products from Kyoritsu Chemical-Check Lab., Corp. can be used to manage the amount of hexavalent chromium in chromate conversion coating, the amount of metal ions eluted from products, and the amounts of metal ions in plating solutions and waste liquids.

References
1) IEC 62321-7-1/Ed.1: Presence of hexavalent chromium (Cr (VI)) in colourless and coloured corrosion-protected coatings on metals by the colourimetric method
2) Naori Sasaki, Ryoji Nakazawa, Mami Tanaka, Tadashi Doi, Kaori Urasaki: Improved Repeatability of Hexavalent Chromium measurements in Chromate Conversion Coating, Bulletin of Tokyo Metropolitan Industrial Technology Research Institute No. 7 (2012)
3) Japan Copper Development Association web site http://www.jcda.or.jp/

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