

Measurement of Hexavalent Chromium by UV-Vis Absorption Spectrophotometry -Analysis using "Water Analysis Program Pack"-

■ Prehistory of RoHS

The European Union issued the RoHS (Restriction of the use of Certain Hazardous Substance in Electrical and Electronic Equipment) directive in February 2003. The RoHS directive aims at eliminating heavy metals, including lead, mercury, cadmium, and hexavalent chromium, as well as polybrominated biphenyl (PBB) and polybromodiphenylether (PBDE) fire retardants from new electrical and electronic equipment and it will be implemented on 1 July 2006. Under these regulations, manufacturers of electrical and electronic

equipment are obliged to consider the concentrations of these toxic substances in products introduced into the European market. While the controlled concentrations are not clearly defined yet, for Japanese manufacturers those export them to Europe, RoHS is the question of growing concern.

This Application News focuses on hexavalent chromium. It presents examples of absorption spectrophotometry measurements of hexavalent chromium using the Shimadzu UVmini-1240 Spectrophotometer.

■ Quantitation of Hexavalent Chromium in Screw Samples

The system with UVmini-1240 introduced here includes the ready to use packed reagent which is based on the JIS(Japanese Industrial Standard) method using diphenylcarbazide as the coloring reagent. So, the complex pretreatments are not necessary anymore with this system. In addition, the preparation of calibration curve with the standard samples is not necessary (because the calibration curve is built in the system), this makes the measurements easier. We measured the hexavalent chromium in the commercially available chromate-treated screws with this system. We summarized the method in Fig. 3.

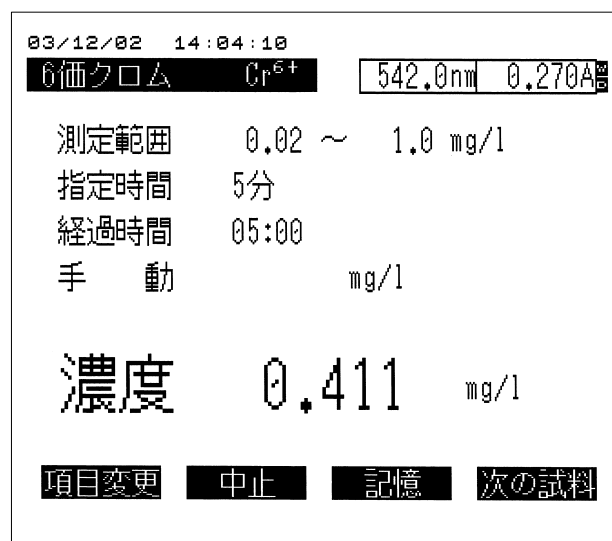


Fig.1 Example of printing

■ Results

The results of hot-water extraction on commercial screws are reported below.

While Unichrome is a chromate treatment, almost no hexavalent chromium was extracted from Unichrome plated screws. Unichrome is brilliance chromate treatment that is often seen as a shiny silver finish.

The greatest amount of hexavalent chromium was extracted from colored chromate-treated screws. those are also commonly seen and appear as a shiny yellow color.

General trends indicate that a longer extraction time or higher extraction temperature achieves a greater amount of hexavalent chromium extracted.

For example, Fig. 2 shows the differences in hexavalent chromium extraction due to different extraction times at an extraction temperature of 80°C. The extracted amount of hexavalent chromium is indicated as micrograms per gram of screw sample.

It is generally known that plating colored chromate-treated ones have high content of hexavalent chromium, while Unichrome plating contains almost none. The result of this analysis support this generality.

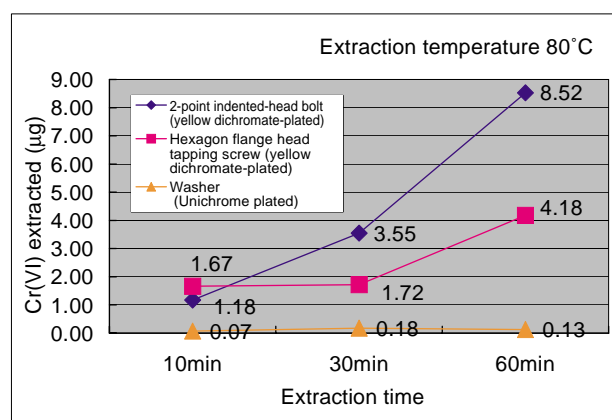


Fig.2 Quantitation of hexavalent chromium in different treatment time at 80°C

■ Comparison of Diphenylcarbazide Data with ICP (Inductively Coupled Plasma) Data

The sample solutions from the tests above were analyzed by using a Shimadzu ICPS-7000 Inductively Coupled Plasma Spectrometer. The resulting data showed a good correlation with absorption spectrophotometry (see Table 1). Iron (Fe) and zinc (Zn) were also measured by ICP. Although trivalent iron (Fe^{3+}) is an interfering ion in the diphenylcarbazide method, the ICP results suggest that iron has little affect.

Table 1 Comparison of Data from ICP and the Diphenylcarbazide Method

Hexagon flange head tapping screw (yellow dichromate-plated)	10min	30min	60min
Diphenylcarbazide method	4.07	4.20	10.19
ICP (total Cr)	3.42	3.59	9.45
ICP (Fe)	0.04	0.04	0.04
ICP (Zn)	0.37	0.17	2.19
2-point indented-head bolt (zinc yellow dichromate-plated)	10min	30min	60min
Diphenylcarbazide method	6.36	19.20	46.11
ICP (total Cr)	5.16	16.94	49.15
ICP (Fe)	0.07	0.07	0.07
ICP (Zn)	0.16	3.05	13.90

Extraction temperature 80°C, Units: mg/sample

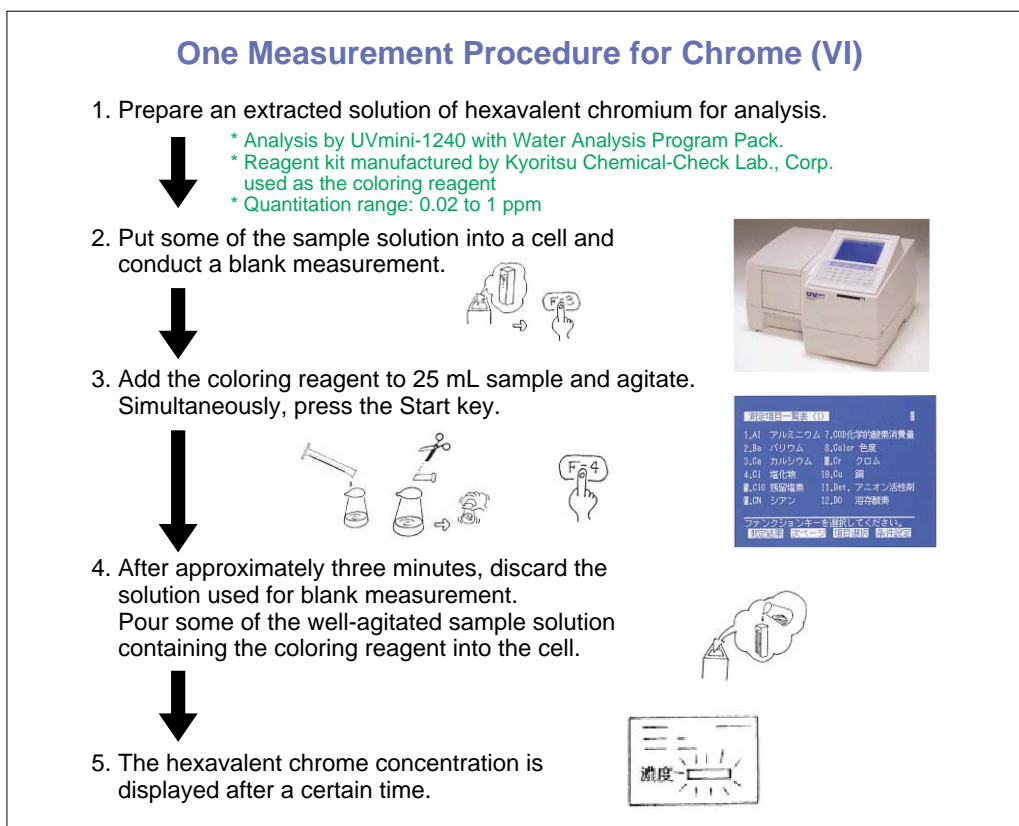


Fig.3 Analysis Procedure Using the Water Analysis Program Pack

■ Summary

Japanese manufacturers are starting to investigate products containing no hexavalent chromium or other toxic substances, based on the RoHS regulations.

Conversely, in Europe the limit value is simply defined as "hexavalent chromium 1000ppm max." but the conditions under which this restriction applies still remain partly unclear.

Bolts and screws come in an infinite variety of shapes. As the chromate layer is applied to the surface only, the problem remains of how to calculate concentration

values for solid shapes.

The larger the sample surface area, the greater the volume of hexavalent chromium extracted to the solution. Consequently, when using this method to compare different types of screws with different shapes, the affects of the surface area and plating-layer thickness must also be considered. This Application News simply determines the amount of hexavalent chromium(μg)extracted per gram of screw sample.



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