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Application News

No. L528

High Performance Liquid Chromatography

Measuring Hexavalent Chromium Compounds in Atmospheric Dust

- Ion Chromatography Post-Column Absorption Spectroscopy Method -

In March 2018, Japan's Ministry of the Environment issued the "Manual of measurement methods for hazardous air pollutants - Measurement method for hexavalent chromium compounds in atmospheric dust" (in Japanese). In this manual, hexavalent chromium compounds are measured using the alkali-impregnated filter collection - ion chromatography post-column derivatization spectroscopic absorption method. Diphenyl carbonohydrazide, which specifically reacts with hexavalent chromium, is used as the post column derivatization reagent. The concentration of hexavalent chromium that can be measured by this method is 0.069 to 3.47 ng/m^3, in terms of concentrations in atmospheric dust. This article introduces an example measurement using the Prominence^{TM} HPLC.

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Overview of the Measurement Method

An alkali-impregnated cellulose filter is first prepared by using sodium bicarbonate solution. Air is passed through this filter at a flow rate of 5 L/min for 24 hours. The material collected on the filter is eluted with ultra-pure water and used as the measurement sample.

The hexavalent chromium ions in the sample solution are separated using an anion exchange column. Then, following post-column derivatization using a diphenyl carbonohydrazide/sulfate solution, absorbance at the wavelengths between 520 to 540 nm are to be measured.

Diphenyl carbonohydrazide, which is the reaction reagent, contacts hexavalent chromium ions and turns into diphenylcarbazone and then forms a diphenylcarbazide-chromium complex.

The measurement system requires plastic components for all liquid contact sections from the reaction reagent delivery pump and after, including the detector, since the reagent contains 0.5 mol/L sulfate. In addition, the detector light source must be a tungsten (W) lamp, which is suited for the wavelengths to be detected.

Fig. 1 shows the flow line diagram of the post-column system and Table 1 lists the measurement conditions.

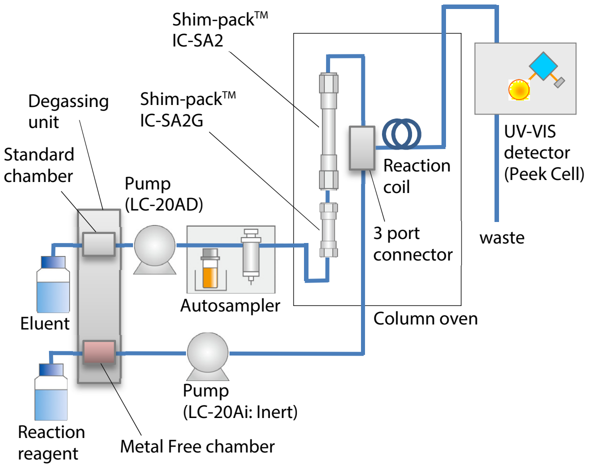


Fig. 1 Hexavalent Chromium Measurement System Flow Line Diagram

Table 1 Measurement Conditions

■	Separation	
	Column	: Shim-pack^{TM} IC-SA2 (250 mm L., 4.0 mm I.D.)
	Guard column	: Shim-pack^{TM} IC-SA2G (10 mm L., 4.6 mm I.D.)
	Eluent	: 10 mmol/L Sodium Carbonate/ 10 mmol/L Sodium Bicarbonate
	Flow rate	: 1.0 mL/min
	Column temp.	: 40 °C
■	Injection vol.	: 0.25 mL
■	Post Column Derivatization	
	Reaction reagent	: 2 mmol/L Diphenyl carbonohydrazide -10 %-Methanol-0.5 mol/L Sulfate
	Flow rate	: 0.2 mL/min
	Reaction temp.	: 40 °C
	Reaction coil	: 0.5 mm I.D.×8 m L. (PTFE)
■	Detection	: UV-VIS detector at 540 nm (SPD-20AV, W lamp, Inert Cell)

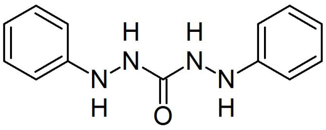


Fig. 2 Diphenyl Carbonohydrazide

Measurement of Standard Sample Solutions

Fig. 3 shows the chromatograms of potassium dichromate (JIS K8005) standard solutions diluted to between 0.1 and 5.0 ng/mL using ultra-pure water.

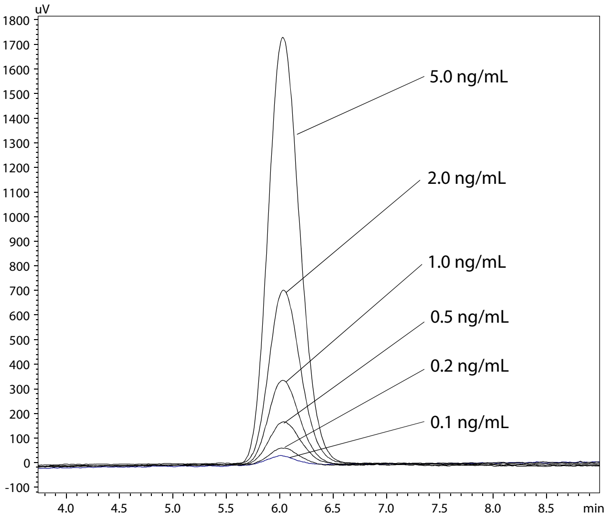


Fig. 3 Chromatograms of Standard Solutions

Linearity of Calibration Curve

Fig. 4 shows the calibration curve created using sample solutions of differing concentrations as shown in Fig. 3.

Linearity in the range from 0.1 to 5.0 ng/mL was favorable at above $r^2 = 0.999$.

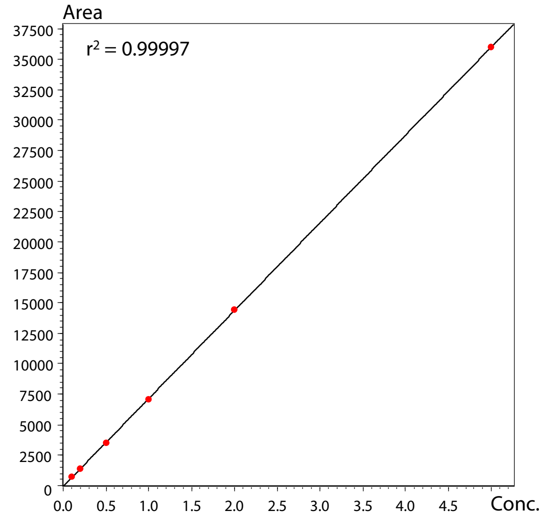


Fig. 4 Linearity of Calibration Curve

Repeatability of the Standard Solutions

Fig. 5 shows the chromatograms obtained by measuring the 0.1 ng/mL standard solution five times repeatedly. Table 2 lists the peak area, quantitation value (concentration) based on the calibration curve shown in Fig. 4, and the accuracy of each measurement.

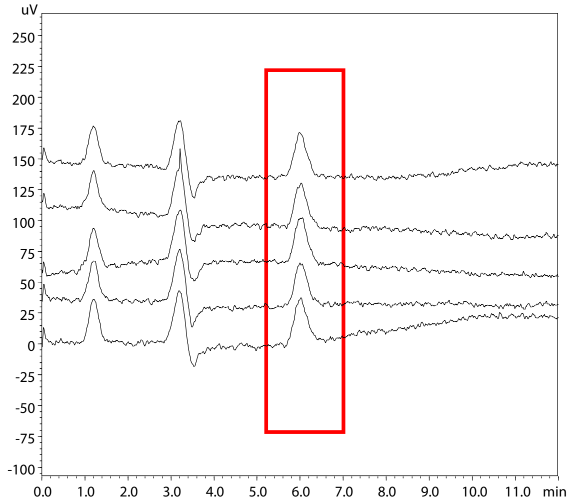


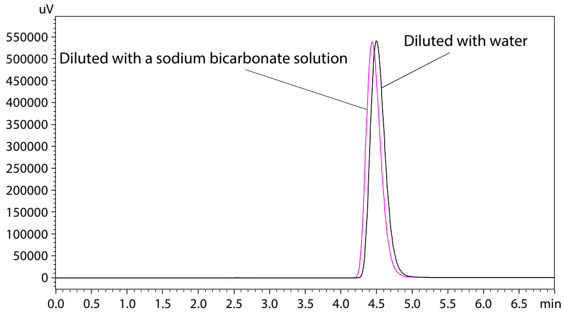
Fig. 5 Chromatograms from Repeated Measurements of 0.1 ng/mL Standard Solution

Table 2 Results from Repeated Measurements of 0.1 ng/mL Standard Solution

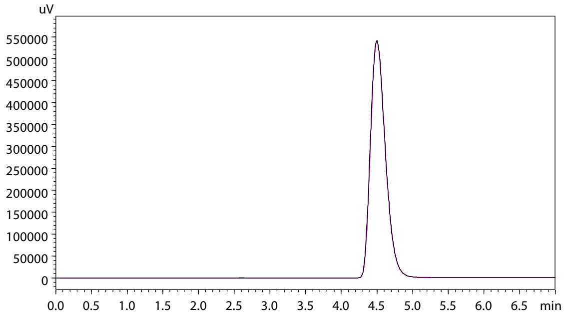
Measurement	Area	Concentration (ng/mL)	Accuracy (%)
1	724	0.099	99.1
2	719	0.098	98.5
3	743	0.102	101.7
4	731	0.100	100.0
5	736	0.101	100.8
Average	731	0.100	
%RSD	1.3	1.6	

Influence of Sample Matrix

Fig. 6 compares the chromatograms of the standard solution when diluted, respectively, with water and with sodium bicarbonate solution, which is used to prepare the alkali-impregnated filter. Sodium carbonate released from the alkali-impregnated filter is a matrix and the elution strength becomes slightly stronger, causing a change in the elution time by a few seconds. However, we can see that the peak shapes are the same. The chromatograms are shown in (a) before retention time alignment and in (b) after retention time alignment to compare the peak shapes.



(a) Before retention time alignment



(b) After retention time alignment

Fig. 6 Comparison of Dilution Solvents with a 1000 ng/mL Standard Solution

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