

Analysis Method of Dissolved Hexavalent Chromium According to EPA 218.6

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User Benefits

- ◆ Trace concentrations of hexavalent chromium (Cr(VI)) can be analyzed according to EPA 218.6.
- ◆ Cr(VI) is chromatographically separated from potential interferences and selectively detected using post-column derivatization.

■ Introduction

The method for analyzing dissolved Cr(VI) in drinking water, groundwater, and industrial wastewater is described in EPA 218.6. This article demonstrates analysis of Cr(VI) with the Shimadzu Prominence Inert System.

Dissolved Cr(VI) is separated by an anion exchange column. The colored complex formed between Cr(VI) and diphenylcarbazide in the post-column derivation is then detected at 530 nm. The flow path diagram is shown in Fig. 1.

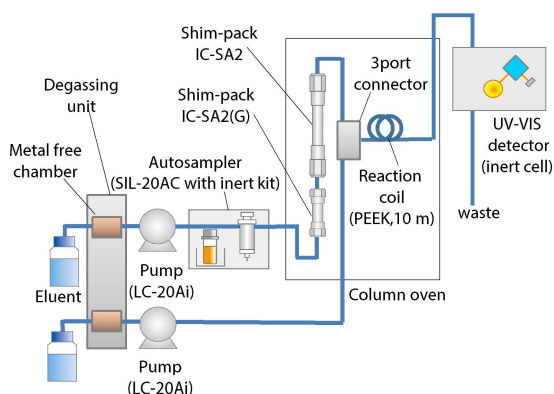


Fig. 1 Flow Path Diagram of Cr(VI) Analysis System

■ Analysis of Standard Sample

An example chromatogram of a 1 µg/L Cr(VI) is shown in Fig. 2. Table 1 shows the analytical conditions. Mobile phase conditions were optimized for the exchange capacity of the column used in this study. The standard sample was prepared by diluting sodium chromate tetrahydrate with ASTM Type 1 water. Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. To minimize this transformation, EPA 218.6 states that the sample pH should be adjusted to 9-9.5 with an aqueous solution of ammonium sulphate-ammonia prior to final dilution.

In this article, the pH was adjusted prior to the final dilution of the sample according to the procedure described in EPA 218.6.

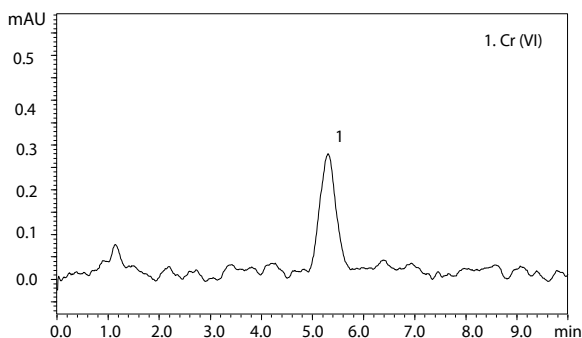


Fig. 2 Analysis Result of 1 µg/L Cr(VI) Standard Sample

Table 1 Analytical Conditions

Column:	Shim-pack IC-SA2 ^{*1} (250 mm × 4.0 mm I.D., 9 µm)
Guard Column:	Shim-pack IC-SA2(G) ^{*2} (10 mm × 4.6 mm I.D., 9 µm)
Mobile Phase:	25 mmol/L Ammonium sulphate, 10 mmol/L Ammonium hydroxide
Mobile Phase Flowrate:	1.5 mL/min
Post Column Reagents:	2 mmol/L Diphenylcarbohydrazide 10 %(v/v) Methanol 0.5 mmol/L Sulfuric acid
Post Column Reagents Flowrate:	0.5 mL/min
Column Temp.:	40 °C
Injection Volume:	250 µL
Vial:	Shimadzu Vial, LC, 4 mL, Polypropylene ^{*3}
Detection:	UV-VIS (530 nm, Inert cell)
Reaction Coil:	10 m × 0.5 mm I.D., (PEEK)

*1 P/N: 228-38983-91 *2 P/N: 228-38983-92 *3 P/N: 228-31537-91

■ Coefficient of Determination and Repeatability

EPA 218.6 states that the coefficient of correlation for the calibration curve which is created from at least three points should be 0.999 or greater. Fig. 3 shows the calibration curve created in the range of 5 µg/L to 50 µg/L. Also, table 2 shows the repeatability of area and retention time for seven repeated analyses of each standard sample.

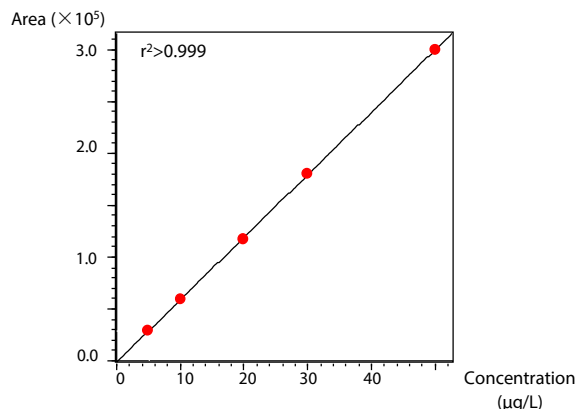


Fig. 3 Calibration Curve of Cr(VI)

Table 2 Repeatabilities of Area and Retention Time

Concentration (mg/L)	Retention time repeatability (%RSD)	Area repeatability (%RSD)
5 µg/L	0.04	2.16
20 µg/L	0.02	0.56
50 µg/L	0.04	0.16

■ Calculation of Method Detection Limit

The method detection limit (MDL) was calculated from the results of the seven repeated analyses of 1 µg/L Cr(VI) standard sample. Fig. 4 shows the results of the seven repeated analyses of 1 µg/L Cr(VI) standard sample. Table 3 shows the method detection limit calculated from the analysis results in Fig. 4 and the calculation method described in EPA 218.6.

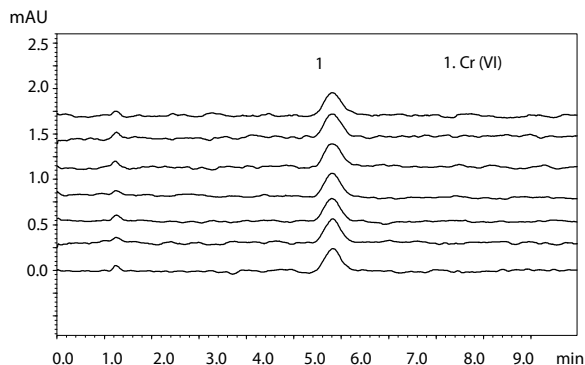


Fig. 4 Seven Repeated Analyses of 1 µg/L Standard Sample

Table 3 Method Detection Limit Calculated from Seven Repeated Analyses of 1 µg/L Standard Sample

MDL: 0.1 µg/L

$$MDL = (t) \times (s)$$

t = Student's t value for n-1 degrees of freedom at the 99 % confidence level;
t = 3.143 for six degrees of freedom
s = standard deviation of the replicate analyses

■ Analysis Example of Simulated Wastewater

Simulated wastewater (3 g of sea salt added 1 L of reagent water (ASTM Type I water : 18 Mohm low TOC)) and the sample obtained by adding 1 µg/L Cr(VI) standard to the simulated wastewater were analyzed according to the procedure described in EPA 218.6. Fig. 5 shows the results of the analyses.

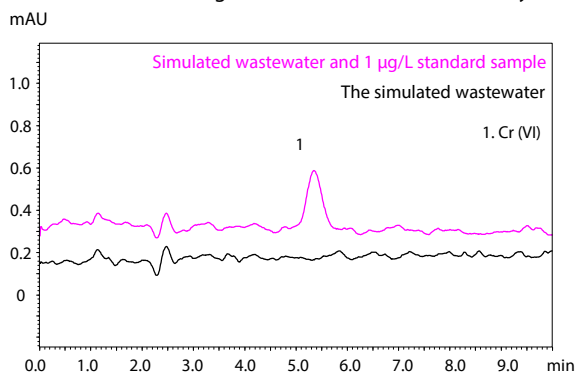


Fig 5 Analysis Results for the Simulated Wastewater and the Simulated Wastewater Plus 1 µg/L Standard Sample

■ Calculation of Percent Recovery

Table 4 shows the percent recovery obtained from the analysis results of the simulated wastewater and the simulated wastewater plus 1 µg/L standard sample shown in Fig. 5. The percent recovery calculation method was in accordance with EPA 218.6.

Table 4 Percent Recovery

R: 106.7 %

$$R = \frac{C_F - C}{F} \times 100$$

R = percent recovery

CF = fortified sample concentration

C = sample background concentration

F = concentration equivalent of Cr (VI) added to sample

■ Conclusion

The analysis example of Cr(VI) according to EPA method 218.6 with the Shimadzu Prominence Inert System is introduced in this article. Cr(VI) can be selectively analyzed with the post-column reaction. Also, this analysis method can be applied to drinking water, groundwater, and industrial wastewater.

<References>

1) EPA Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography, Rev. 3.3

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