CHROMIUM, HEXAVALENT (DIFFERENTIAL PULSE POLAROGRAPHY)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium [Cr(VI)] in natural and waste waters and in EP extracts.

1.2 The method can quantitate chromium in concentrations of up to 1.0 mg/L to 5.0 mg/L, depending on the mercury drop size. Higher concentrations can be determined by dilution.

1.3 The lower limit of detection for Cr(VI) is 10 ug/L for the instrumental conditions given in this method. The limit of detection could be easily lowered by changing these conditions.

2.0 SUMMARY OF METHOD

2.1 Method 7198 measures the peak current produced from the reduction of Cr(VI) to Cr(III) at a dropping mercury electrode during a differential pulse voltage ramp.

2.2 The method described herein uses 0.125 M NH_4OH-0.125 M NH_4Cl as the supporting electrolyte. In this electrolyte, Cr(VI) reduction results in peak current occurring at the peak potential (Ep) of -0.250 V vs. Ag/AgCl.

2.3 Alternative supporting electrolytes, such as those given in Table 1, may be used.

2.4 The technique of standard additions must be used to quantitate the Cr(VI) content.

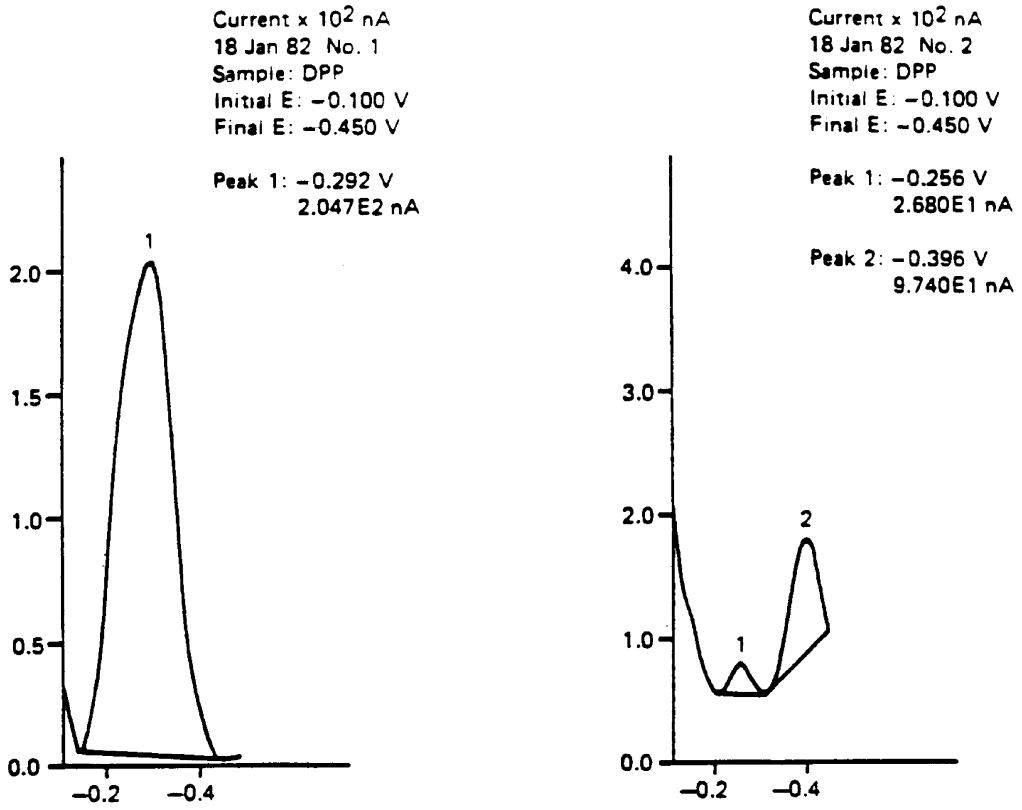
3.0 INTERFERENCES

3.1 Copper ion at concentrations higher than the Cr(VI) concentration is a potential interference due to peak overlap when using the 0.125 M ammoniacal electrolyte. Increasing the ammoniacal electrolyte concentration to 0.5 M shifts the copper peak cathodically (Ep = -0.4 V), eliminating the interference at a copper-to-chromium ratio of 10:1 (Figure 1).

3.2 Reductants such as ferrous iron, sulfite, and sulfide will reduce Cr(VI) to Cr(III); thus it is imperative to analyze the samples as soon as possible.

4.0 APPARATUS AND MATERIALS

4.1 Polarographic instrumentation: Capable of performing differential pulse analyses, including recorder or plotter.



A. 20 ppm Cu, 2.5 ppm Cr, 0.1 N buffer.

B. 20 ppm Cu, 2.5 ppm Cr, 0.5 N buffer.

Figure 1. Two polarograms illustrating shift in copper peak at higher ammoniacal electrolyte concentrations.

TABLE 1. POLAROGRAPHY OF HEXAVALENT CHROMIUM

Supporting electrolyte	Peak potential (vs. SCE)
1 M NaOH	-0.85
1 M Pyridine, 1 M NaOH	-1.48
1 M NH_4OH, 1 M NH_4Cl	-0.36
0.1 M NH_4OH, 0.1 M $(NH_4)_2$ Tartrate	-0.244
0.2 M KCl, 0.3 M Triethanolamine, pH 9	-0.28
1 M Na_2SO_4	-0.23
0.1 M NH_4OH, 0.1 M NH_4Cl	-0.25

4.2 Dropping mercury electrode assembly: Capable of performing differential pulse analyses.

4.3 Counter electrode: Platinum wire.

4.4 Reference electrode: Ag/AgCl or SCE, with a slow-leakage fritted tip (unfired Vycor).

4.5 Nitrogen gas and cell outgassing assembly.

4.6 Micropipets and disposable tips.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Chromium standard solution I, 1.0 mL = 100 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.3 Chromium standard solution II, 1.0 mL = 10 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.4 Chromium standard solution III, 1.0 mL = 1 ug Cr: Dilute 10 mL chromium standard solution II to 100 mL with Type II water.

5.5 Ammoniacal electrolyte, 2.5 N: Dissolve 33.3 g of NH_4Cl in 150 mL of Type II water, add 42.2 mL of concentrated NH_4OH, and dilute to 250 mL.

5.6 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Stability of Cr(VI) is not completely understood at this time. Therefore, the analysis should be carried out as soon as possible.

6.3 If the analysis cannot be performed within 24 hr, take an aliquot of the sample and add a known amount of Cr(VI) (0.1 mg/L for natural waters, 1 mg/L for wastewaters, and 5 mg/L for EP extracts). Analyze this known additional sample at the same time the sample is analyzed to determine whether Cr(VI) was reduced during storage.

6.4 To retard the chemical activity of Cr(VI), the sample should be transported and stored at 4°C until time of analysis.

7.0 PROCEDURE

7.1 Soak the voltammetric cells overnight in 1 + 1 HNO_3 and/or 1 + 1 aqua regia.

7.2 Rinse the electrode assembly with Type II water, then with 1 N HNO_3, and finally with Type II water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 **Mode:** Differential pulse.
7.3.2 **Scan rate:** 2 mV/sec.
7.3.3 **Drop time:** 1 sec.
7.3.4 **Initial potential:** -0.05 V $\pm$ 0.05 V vs. Ag/AgCl.
7.3.5 **Final potential:** -0.50 V $\pm$ 0.10 V vs. Ag/AgCl.
7.3.6 **Pulse height:** 0.05 V.
7.3.7 **Deaeration time:** 240 sec or less initially, 30 sec between standard additions.

7.4 Analysis:

7.4.1 Pipet a volume of sample containing less than 10 ug Cr(VI) into a voltammetric cell (the maximum volume depends on the voltammetric cell volume, usually 10 mL).

7.4.2 Add 0.5 mL of the ammoniacal electrolyte and adjust volume to 10 mL with Type II water.

7.4.3 Place the electrode assembly in the solution and outgas with nitrogen for at least 120 sec.

7.4.4 Engage the electrode assembly to the polarographic analyzer and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram.

7.4.5 Figure 2 gives typical differential pulse polarograms.

7.5 Prior to the analysis of any samples, and during analysis at a frequency of at least once every 10 samples, verify that the cell contamination is less than 10 ug/L Cr by analyzing demineralized water and the appropriate volume of supporting electrolyte in a manner similar to the procedure described in 7.4.3 and 7.4.4.

7.6 Calibration:

7.6.1 After running a differential pulse polarogram on the sample solution, quantitate the chromium using the technique of standard addition.

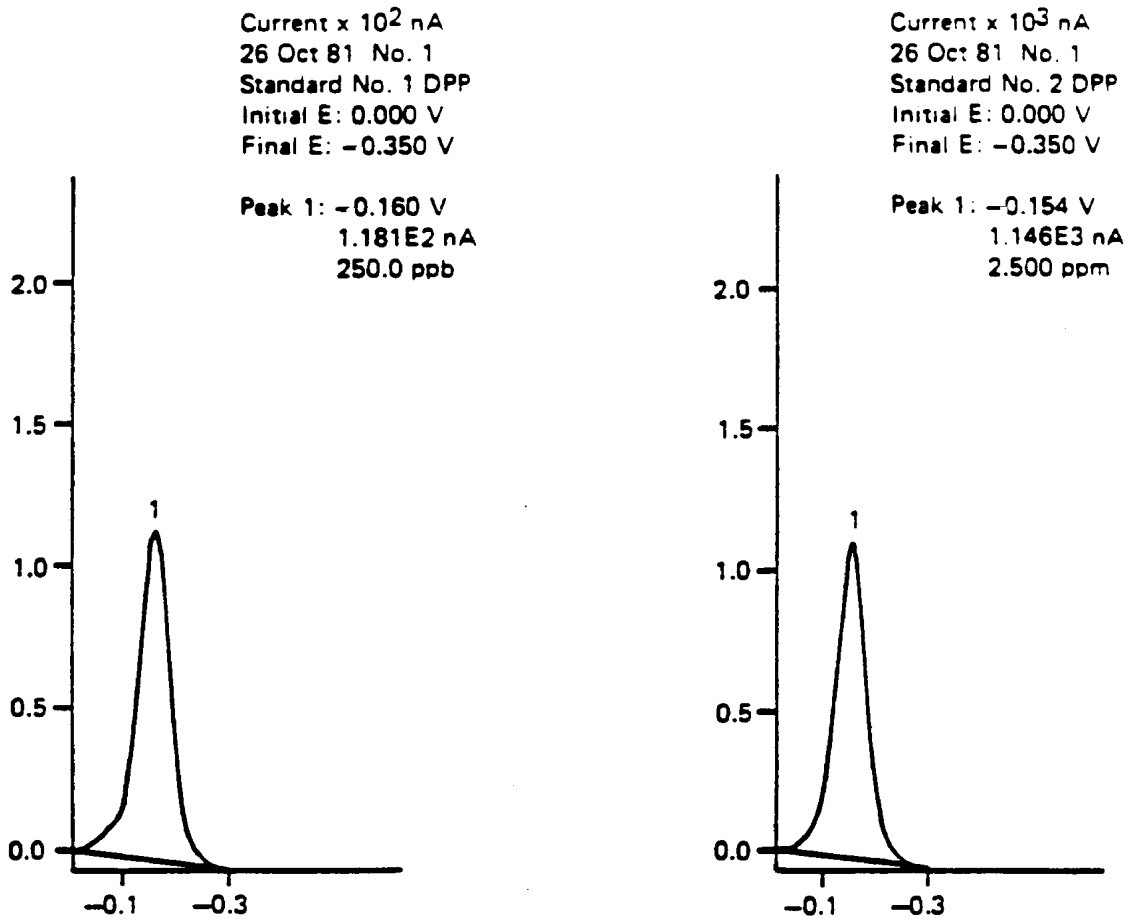


Figure 2. Typical differential pulse polarogram at 0.25 ppm and 2.5 ppm Cr in 0.1 N buffer.

7.6.2 Three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration of the sample, the second equal to that of the sample, and the third about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%.

7.6.3 Add an appropriate aliquot of chromium standard solution I, II, or III to the sample in the cell. Deaerate for 30 sec to mix the solution and remove oxygen added with the known addition.

7.6.4 Repeat the analysis procedure, beginning with Step 7.4.4 for each standard addition.

7.7 Calculations:

7.7.1 Calculate the concentration of chromium determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 V_i C_s}{i_1 V_i + (i_1 - i_1)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA);

i_i = Current peak height for the sample plus standard (nA);

V_u = Volume of sample in the cell (mL);

V_i = Volume of standard taken for spiking (mL);

V = Volume in cell prior to standard addition;

C_s = Concentration of standard used to spike (mg/L); and

C_u = Concentration of the unknown in the sample (mg/L).

7.7.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 If necessary, dilute samples so that they fall within the working range.

8.3 Quantitation must be performed by the method of standard additions (see Method 7000, Section 8.7).

8.4 Verify calibration with an independently prepared check standard every 15 samples (see Chapter One, Section 1.1.8).

8.5 Standards should be compared to a reference standard on a routine basis.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data for this method are summarized in Table 2.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4 and 218.5.

TABLE 2. PRECISION AND ACCURACY OF THE DPP OF HEXAVALENT CHROMIUM

2a. Precision

Sample type	No. of replicates	Average value	% RSD
Leachate[a]	3	1.87	0.69

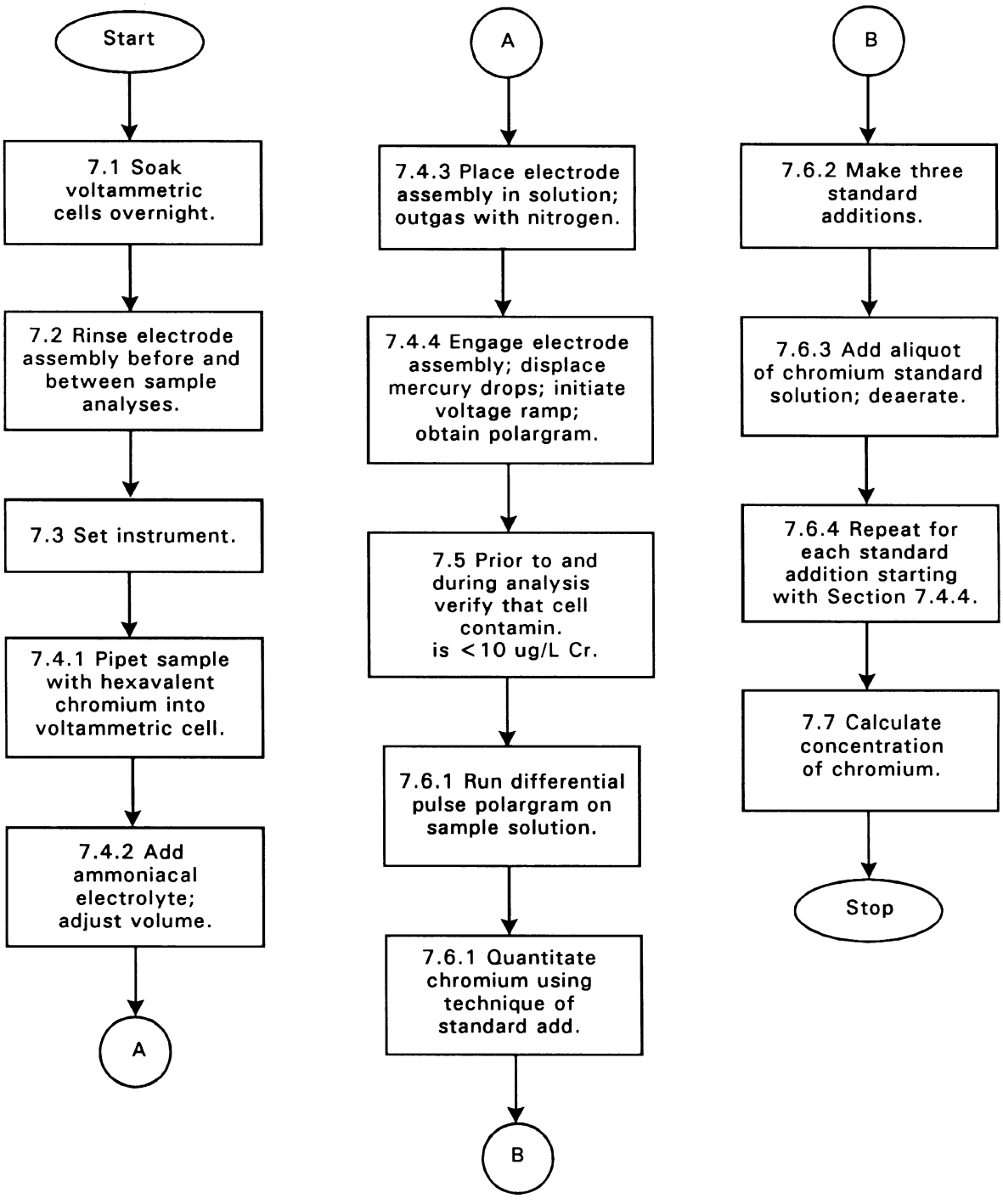
2b. Accuracy (spike recovery data)

Sample type	Spike level (mg/L)	No. of samples	Average % recovery	Standard deviation of % recovery
EP extracts	5.0	8	92.8	6.4

2c. Methods comparison

	Diff. pulse polarography	APDC extraction ICAP-OES	Ion chromatography coupled to ICAP-OES
Value[a]	1.87	1.84	1.91

[a]Leachate sample from a waste disposal site.


Start
7.1 Soak voltammetric cells overnight.
7.2 Rinse electrode assembly before and between sample analyses.
7.3 Set instrument.
7.4.1 Pipet sample with hexavalent chromium into voltammetric cell.
7.4.2 Add ammoniacal electrolyte; adjust volume.
A
A
7.4.3 Place electrode assembly in solution; outgas with nitrogen.
7.4.4 Engage electrode assembly; displace mercury drops; initiate voltage ramp; obtain polargram.
7.5 Prior to and during analysis verify that cell contamin. is <10 ug/L Cr.
7.6.1 Run differential pulse polargram on sample solution.
7.6.1 Quantitate chromium using technique of standard add.
B
B
7.6.2 Make three standard additions.
7.6.3 Add aliquot of chromium standard solution; deaerate.
7.6.4 Repeat for each standard addition starting with Section 7.4.4.
7.7 Calculate concentration of chromium.
Stop