BASi
Tech Notes

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Determination of Cr(VI) in Natural and Waste Waters Using Differential Pulse Polarography: U.S. EPA (SW-846 Method 7198)

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Purpose

Speciation studies of chromium are very difficult to conduct due to the instability of its oxidation states and the variable composition of environmental samples. While Cr(III) is actually an essential biological element for many mammals, including humans, Cr(VI) is classified as toxic (1). The accurate determination of hexavalent chromium in such common environmental matrices as natural and waste waters is crucial for the safety of both human and wildlife populations.

The United States Environmental Protection Agency (U.S.EPA) has put forth SW-846, Method 7198, using differential pulse polarography for determination of Cr(VI) in natural and waste waters. (This Tech Note is intended to cover the general procedure of this particular method. For a more detailed description of the U.S. EPA-approved sample collection, preservation, handling, and quality control procedures, please consult the U.S. EPA manual, "Test Methods for Evaluating Solid Waste (SW-846), 3rd Edition").

Method

In Method 7198, the cathodic peak current resulting from the reduction of Cr(VI) to Cr(III) is measured. A standard addition procedure is used to quantitate Cr(VI). The concentration range for this method is listed as 10 ppb to 5 ppm Cr(VI). However, with the proper fine-tuning of experimental parameters and conditions, detection limits can be much lower (2).

Supporting Electrolyte	***Ep (vs. SCE)/ V***
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 $(NH_4)_2$ Tartarate	-0.24
0.2 M KCl, 0.3 M Triethanolamine, pH 9	-0.28
1 M Na_2SO_4	-0.23

T1. Supporting Electrolytes

A variety of supporting electrolytes can be used for this procedure, and are listed in T1 with the corresponding peak potential. The supporting electrolyte used in this application note is 0.125 M NH_4OH, 0.125 M NH_4Cl in which the peak potential is approximately -0.216 V vs. Ag/AgCl reference electrode.

Instrumentation and Equipment

All results were obtained using either the BAS 100 B/W Electrochemical Workstation or the CV-50W Voltammetric Analyzer and the Differential Pulse Polarography (DPP) technique. Equivalent results will be obtained using the BASi Epsilon, e2, Potentiostat/Galvanostat. The BASi Controlled Growth Mercury Electrode (CGME) in the Static Mercury Drop Electrode (SMDE) mode was used as the working electrode. The Ag/AgCl reference and Pt wire auxiliary electrodes were used throughout.

Procedure

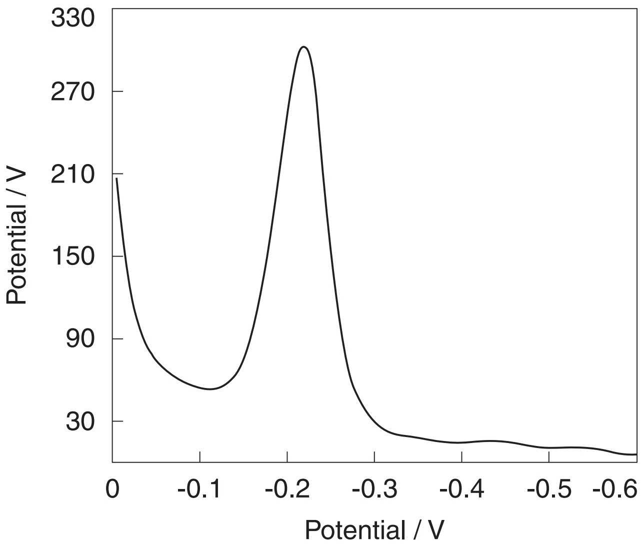
All glassware should be soaked in 50% nitric acid overnight and rinsed with distilled water (ASTM Type II water should be used and monitored for impurities throughout the procedure) before use. The instrumental parameters should be set as shown in T2.

Mode:	***Differential Pulse Polarography (DPP)***
Initial E (mV)	0
Final E (mV)	-600
Scan Rate (mV/s)	2
Drop Time (s)	1
Pulse Height (mV)	50
Deaeration Time (s)	300

T2. Instrumental Parameters for DPP

Perform a background check of the supporting electrolyte for impurities by repeating the procedure below, using D.I. water in place of the natural or waste water. A background check should be performed prior to the first sample, as well as after every ten samples to ensure the accuracy of the analysis.

A 10 mL sample is prepared and analyzed as follows: Transfer 0.5 mL of ammoniacal electrolyte (33 g of NH_4Cl in 150 mL of Type II water + 42.2 mL of concentrated NH_4OH, dilute to 250 mL) into a clean CGME low-volume cell and dilute to 10 mL with sample (natural or waste water). Place the cell and sample into the CGME cell assembly and deaerate the solution by sparging with nitrogen for at least 5 minutes. Record the polarogram. A typical polarogram is shown in F1.

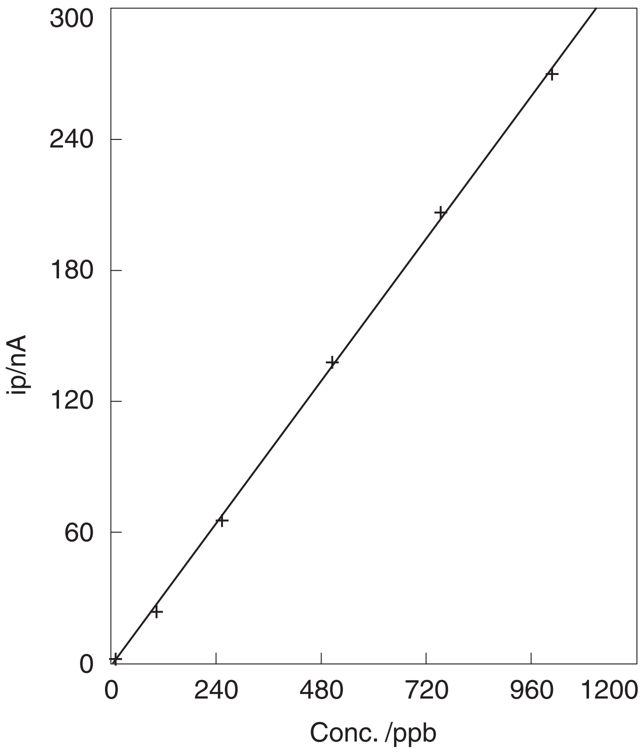


F1. Polarogram of 1 ppm Cr(VI) in .125M ammoniacal electrolyte.

Results and Discussion

The lower limit of detection for this procedure is listed by the EPA as 10 µg/L (10 ppb) depending on the instrumental conditions, with a stipulation stating that this limit "could be easily lowered by changing these conditions." A calibration curve from 10 ppb to 1 ppm Cr(VI) in 0.125 M ammoniacal electrolyte was linear, as shown in F2. Peak to peak noise was estimated to be about 0.25 nA for a background scan of the supporting electrolyte. Using a signal to noise ratio of 3 and the sensitivity obtained from the calibration curve, the detection limit is estimated to be 7ppb.

There are certain interferences that have the potential for hampering the accuracy of this method. Cu(II), in certain supporting electrolytes, produces a peak that overlaps the Cr(VI) peak. Various compounds of iron and sulfur can reduce Cr(VI) to Cr(III). Reduction of Cr(VI) by organic matter, commonly present in environmental samples, is also a major interference. Therefore it is imperative to analyze environmental samples as quickly as possible. Method 7198 suggests that if the sample can not be analyzed within 24 hours from the time of collection, an aliquot of the sample should be spiked with a known amount of Cr(VI) ion immediately after collection, in order to check for significant reduction of the Cr(VI) during storage.



F2. Calibration curve for Cr(VI) from 10 ppb to 1 ppm in .125 M ammoniacal electrolyte.

References

1. A.C. Harzdorf, Intern. J. Environ. Anal. Chem., 1987, Vol. 29, pp. 249-261.

2. U.S. EPA, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods. SW-846, 2nd Ed. Washington, D.C. U.S. EPA Office of Solid Waste and Emergency Response, 1984.