

Simultaneous Determination of Chromium(VI) and Aluminum(III) by Adsorptive Stripping Voltammetry with Pyrocatechol Violet

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A new methodology is presented for the simultaneous determination of chromium(VI) and aluminum(III) by differential-pulse adsorptive stripping voltammetry (DPAdSV) with Pyrocatechol Violet (PCV) as a complexing agent. In this procedure, a partial least-squares regression (PLS) is used for the resolution of the strongly overlapping voltammetric signals from mixtures of Cr^{VI} and Al^{III} in the presence of PCV. The procedure was successfully applied to the determination of these metals in river water.

Introduction. – Chromium is present in the environment in two oxidation states, Cr^{III} and Cr^{VI}. The toxicity of these two forms differs considerably. While Cr^{III} is considered to be essential for mammals, Cr^{VI} is very toxic and has been considered a carcinogenic agent [1].

It has been demonstrated that aluminum is involved in several neurological disorders such as *Alzheimer's* disease [2]. The presence of Al^{III} in natural waters is increasing due to acid rain, which dissolves soil-bound aluminum. Thus, the interest in the determination of this element at trace levels is increasing.

Cr^{VI} and Al^{III} in aqueous solution are usually analyzed by means of electrothermal atomic absorption spectrometry [3][4]. Applying electroanalytical techniques to the determination of trace elements can provide an interesting alternative to the traditional spectroscopic methods. Besides the relatively low cost of electrochemical instrumentation, one should bear in mind the high sensitivity of some of these methods, especially stripping voltammetry, which is based on the adsorption of numerous organic compounds in some electrodes.

Pyrocatechol Violet (PCV) has been used as a complexing agent for the determination of both Cr [5] and Al [6][7] by electrochemical techniques. There, Cr was considered to be an interferent in the determination of Al, and, in the same way, the presence of Al prevents the determination of Cr by differential-pulse adsorptive stripping voltammetry (DPAdSV). To solve this problem, different authors proposed the addition of masking reagents such as citrate [5] and NH₂OH · HCl [6]. However, it is known that the addition of such reagents represents a 'contamination' and, therefore, is a potential source of error in the analysis of metals at trace levels.

The simultaneous determination of Cr^{VI} and Al^{III} by means of voltammetric techniques is difficult because of signal overlapping, which prevents proper calibration. Fortunately, so-called 'partial-least-squares' (PLS) treatment is an effective tool in the resolution of electrochemical signals [8][9].

The aim of our studies has been to set up a method for the simultaneous determination of Cr^{VI} and Al^{III} in an aqueous medium by means of DPAdSV, using PCV as a complexing agent and applying multivariate calibration methodology.

Theoretical Aspects. – It is known that multivariate PLS calibration is achieved by constructing latent variables, which are linear combinations of the original variables. The number of latent variables is a meta-parameter of the procedure whose value is to be estimated from the calibration data. This can be accomplished by minimizing ‘PRESS’ as a function of k (internal validation):

$$\text{PRESS} = \sum_{i=1}^m (c_i - \hat{c}_{k/i})^2.$$

In this equation, c_i is the vector of concentrations corresponding to the i th sample, and $\hat{c}_{k/i}$ is the vector of concentrations estimated by PLS of k latent variables constructed without the i th sample.

PRESS is an estimation of the mean error expected in prediction. In practice, a more stable estimation is obtained if, instead of eliminating only one sample to calculate the concentration of k latent variables, the highest possible fraction of the samples is cancelled, *e.g.*, a third of a quarter. The importance of full cross-validation [10], compared with partial cross-validation [11][12], has been shown. In other words, it is essential that in the calculation process for the PLS model, neither the cancellation group nor an initial autoscaling that affects all the samples intervene in any way. If the data were autoscaled, the mean and variance of all the samples would intervene. In this work, the full cross-validation procedure, PLSC, is used instead of partial cross-validation.

Experimental. – *Materials and Equipment.* All solns. were prepared with deionized H₂O obtained via a *Barnstead NANO Pure II* system. N₂ (99.99%) was used to remove dissolved O₂. Stock standard solns. of Cr^{VI} were prepared by dissolving the adequate amount of K₂Cr₂O₇ (anal.-reagent grade, *Merck*) in H₂O. Al^{III} solns. were obtained from Al(NO₃)₃·9 H₂O (anal.-reagent grade, *Merck*) in H₂O. Solns. of the chelating agent, Pyrocatechol Violet (PCV; *Fluka*), were prepared by dissolving the appropriate quantities. As support electrolyte, acetate buffer was used, obtained by dissolving adequate quantities of AcOH (anal.-reagent grade, *Merck*) and AcONa (anal.-reagent grade, *Fluka*) in H₂O. H₂O₂ (30% in H₂O; *Merck*) and HCl (*Merck*) used in the ‘digestion’ were of anal.-reagent grade. Voltammetric measurements were carried out with a *Metrohm Model 746 VA Trace Analyzer* (*Metrohm*, Switzerland) and a *Model 747 VA* electrode stand with a multimode electrode (MME) operating in the hanging-mercury-drop-electrode (HMDE) mode. An Ag/AgCl, 3M KCl reference electrode, and a platinum-wire auxiliary electrode were used. Water-sample digestion was performed in a *Model 705 UV digester* (*Metrohm*, Switzerland) with a high-pressure Hg lamp (radiation source power: 500 W). pH-Values of the solns. were measured with a *Crison Model 2002* (*Barcelona*, Spain) pH meter. Data analysis was performed with PARVUS [13].

Voltammetric Procedure. – Voltammetric measurements were performed as follows: once the soln. had been deoxygenated, the stirrer was connected, and deposition began according to a time and potential determined for each experiment. When the time had elapsed, the stirrer was switched off, and the soln. was left to settle for an equilibrium time of 5 s. The voltammogram was then recorded by making a cathodic sweep. The following values for the instrumental parameters were used to provide the most-reproducible signal: amplitude, – 62 mV; staircase size, 4 mV; duration of the pulse in the staircase potential sweep, 500 ms. Mercury-drop-size and stirring rates in the accumulation period were fixed at 0.4 mm² and 1290 rev min⁻¹, resp.

Results and Discussion. – *Vukomanovic et al.* [5] demonstrated that Cr^{VI} can be determined by DPAdSV in the presence of PCV. These authors found that the addition

of Cr^{VI} to acetate buffer (pH 6) containing PCV gives rise to a reduction peak at a potential of -0.73 V and a decrease of the free PCV reduction peak at -0.53 V. When Cr^{III} was added, no reduction peak was observed, and the free PCV reduction peak did not decrease. This is explained by the fact that the $\text{Cr}^{\text{III}}/\text{pcv}$ complex formed with Cr^{III} originally present in solution is *not* electroactive, whereas the complex with Cr^{III} arising from the chemical reduction of Cr^{VI} is electroactive.

Al^{III} was found to give rise to well-defined reduction peaks at nearly the same potential as that for the reduction of the adsorbed $\text{Cr}^{\text{III}}/\text{pcv}$ complex. The interference of Al was completely eliminated by addition of 3×10^{-7} M citrate solution. However, several tests carried out in our laboratory have shown that citrate has a negative influence on the determination of Cr^{VI} with PCV; it reduces the intensity of the reduction peak of the complex by *ca.* 20%.

The determination of Al^{III} using DPAdSV [6] is also affected by the presence of Cr^{VI} . To eliminate this interference, it is necessary to add $\text{NH}_2\text{OH} \cdot \text{HCl}$ in the electrochemical reduction of Cr^{VI} to Cr^{III} . The addition of such reagents to the medium is always a source of contamination and error, though. Hence, one needs to look for a way to carry out the simultaneous determination of the two analytes without having to add any reductor or masking reagent. Interestingly, Cr^{III} does interfere only of concentrations above 10^{-6} M, causing the appearance of a reduction peak at a potential close to that for the reduction of the $\text{Cr}^{\text{III}}/\text{pcv}$ complex made from Cr^{III} and arising from the chemical reduction of Cr^{VI} [14]. When Cr^{VI} is added to a solution containing PCV, the chemical oxidation of the pcv ligand takes place. This modification of the ligand can explain the different behavior of the complex formed from Cr^{VI} compared to that formed from Cr^{III} .

In *Fig. 1*, one can see the high degree of overlapping of the electrochemical signals of the two elements present in the same medium. It is, therefore, unviable to jointly determine Al^{III} and Cr^{VI} using univariate calibration techniques. Rather, we propose to use a multivariate regression by partial least-squares (PLS) analysis.

DPAdSV is a very sensitive technique, yet, i_p , the response obtained, is notably influenced by variables such as time (t_{dep}) and potential (E_{dep}) of deposition, the concentration of the complexing agent (PCV), and the pH. Therefore, it is necessary to optimize all parameters that may influence the measurement of the current.

The accumulation potential (E_{dep}) strongly affects the size of the reduction peak. Previous experiments had shown that, for E_{dep} values different from 0.0 V, no result is obtained. Therefore, we decided to fix E_{dep} at this value.

We have shown before [14] that pH 5.5 is most adequate for the determination of Cr^{VI} by DPAdSV with PCV. Bearing in mind that the optimum pH for the determination of Al^{III} using this same technique is in the range of pH 4–6 [15], a final value of 5.5 was taken as optimal for the joint determination of the two analytes. The concentration of the complexing agent chosen to carry out the calibration was fixed at 10^{-4} M. Finally, the accumulation time was set to 100 s, following previous optimization of the experimental parameters [14].

PLSC Calibration. With the aim of determining the viability of PLSC calibration, 105 samples containing Cr^{VI} and Al^{III} concentrations of 1.99×10^{-7} to 9.89×10^{-6} M were analyzed. The PLSC model constructed with the entire set of samples gave poor results (explained variance < 99%). For that reason, different PLSC models were

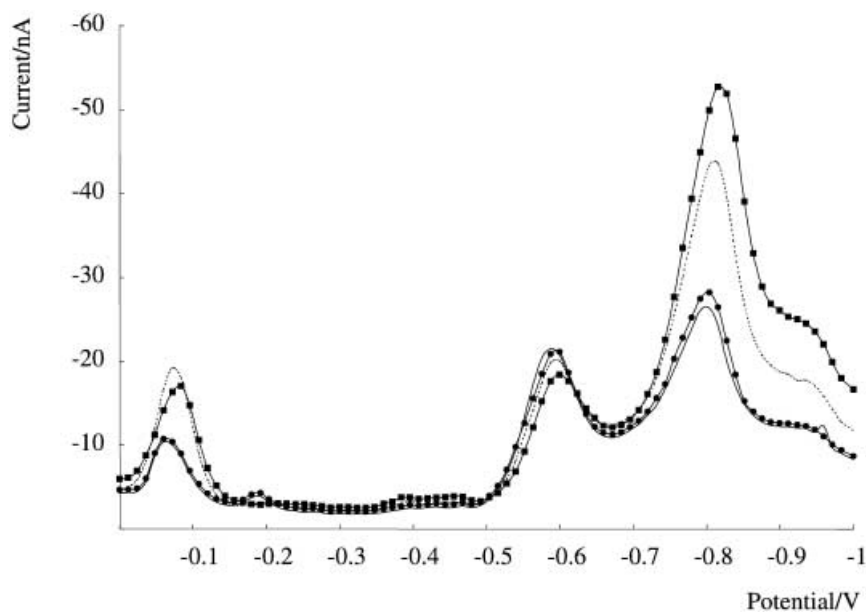


Fig. 1. Adsorptive stripping voltammograms obtained for Cr and Al using PCV as complexing agent in aqueous acetate buffer (pH 5.5). $E_{\text{dep}} = 0$ V, $t_{\text{dep}} = 100$ s, $[\text{PCV}] = 10^{-4}$ M. Designations: —, $[\text{Cr}^{\text{VI}}] = 10^{-7}$ M; —●—, $[\text{Al}^{\text{III}}] = 10^{-7}$ M; ···, $[\text{Cr}^{\text{VI}}] = [\text{Al}^{\text{III}}] = 10^{-7}$ M; —■—, $[\text{Cr}^{\text{VI}}] = 10^{-7}$, $[\text{Al}^{\text{III}}] = 2 \times 10^{-7}$ M.

constructed with distinct subsets within the overall set of samples. The best results were obtained for concentrations ranging between 3.97×10^{-7} and 9.80×10^{-7} M. Table 1 shows the results in percentages of explained variance and cross-validation as a function of the number of latent variables. The minimum PRESS is reached for the number of latent variables that give the maximum cross-validation variance. According to this criterion, more than 99.2% of the cross-validation variance is explained by taking six latent variables for Cr^{VI} and two for Al^{III} , respectively. In the calibration of

Table 1. Variance (in %) Explained in the Blocks of Predictors and of the Response and Cross-validation Variance (CV) for the Concentration of Cr^{VI} and Al^{III}

Chromium(VI)				Aluminum(III)			
LV ^{a)}	Explained variance of Y block	CV Explained variance of Y block	Variance of X block	LV	Explained variance of Y block	CV Explained variance of Y block	Variance of X block
1	90.57	90.71	93.79	1	99.50	90.83	93.78
2	94.18	91.53	95.97	2 ^{b)}	99.19	99.20	98.02
3	99.05	98.98	99.19				
4	99.64	99.49	99.40				
5	99.95	99.81	99.52				
6 ^{b)}	99.98	99.89	99.62				

^{a)} Latent variables index. ^{b)} Number of the latent variables needed to reach the maximum of the cross-validated variance.

Cr^{VI} , the average relative absolute error was 0.94%. For Al^{III} , the average relative absolute error was 8.03%.

To check the performance of the PLSC-calibration model base, it was applied to a set of 3 additional samples (t1, t2, and t3) containing Cr^{VI} and Al^{III} at trace levels, which are more difficult to analyze. The standard error of prediction (SEP) for the test set can be calculated according to the following expression:

$$\text{SEP}(k) = \sqrt{\frac{\sum_{i=1}^e (c_i - \hat{c}_i(k))^2}{e}}$$

in which c_i is the concentration corresponding to the i th evaluation sample and $\hat{c}_i(k)$ is the concentration estimated by the PLS model with only k latent variables for the same sample. In Table 2, the true and estimated values obtained for the calibration of Cr^{VI} and Al^{III} are compared. The results suggest that multivariate PLSC regression allows Cr^{VI} and Al^{III} concentrations to be jointly calibrated with PCV, despite the high degree of overlapping signals.

Table 2. Concentrations and Standard-Error-of-Prediction (SEP) Values Obtained with the PLSC Model in the Determination of Cr^{VI} and Al^{III} in the Three Test Samples

Sample	Concentration of Al^{III} [M]		Concentration of Cr^{VI} [M]	
	True	Found	True	Found
t1	4.96×10^{-7}	5.32×10^{-7}	3.96×10^{-7}	3.93×10^{-7}
t2	3.95×10^{-7}	3.68×10^{-7}	7.91×10^{-7}	8.00×10^{-7}
t3	8.83×10^{-7}	9.25×10^{-7}	9.81×10^{-7}	9.59×10^{-7}
SEP	3.55×10^{-8}		1.38×10^{-8}	

Analytical Application. The new PLSC model constructed was applied to the determination of Cr and Al in samples of river water from an industrial area. The voltammetric response obtained from the direct measurement of this water in the presence of the complexing agent is depicted in Fig. 2. The peak due to the reduction of the complexes of $\text{Cr}^{\text{III}}/\text{pcv}$ and $\text{Al}^{\text{III}}/\text{pcv}$ is of low intensity. This is due to the high concentration of organic matter present in the sample, which acts as an interferent in the determination, preventing the reduction of the complexes.

To improve the response signal, a ‘digestion’ process was carried out. The most commonly used method for the digestion of samples is their irradiation with ultraviolet (UV) light in an oxidizing medium [16][17]. In this way, the attached organic matter is destroyed, and Cr^{III} eventually present in the medium is oxidized, which allows one to determine the total Cr content of the sample.

Digestion by UV radiation for the determination of Cr must be performed in a neutral or slightly basic medium (pH 6–8), which is the normal pH of natural waters. If this is done in previously acidified waters, then Cr^{VI} may be reduced to CrO_2 via formation of volatile CrO_2Cl_2 , which would lead to sample losses [15]. In contrast, for the digestion of Al-containing samples, a medium acidified with HCl or HNO_3 is recommended to avoid the adsorption of Al on the quartz walls of the digestion tube [17]. Therefore, in our case, digestion of the sample was performed at approximately

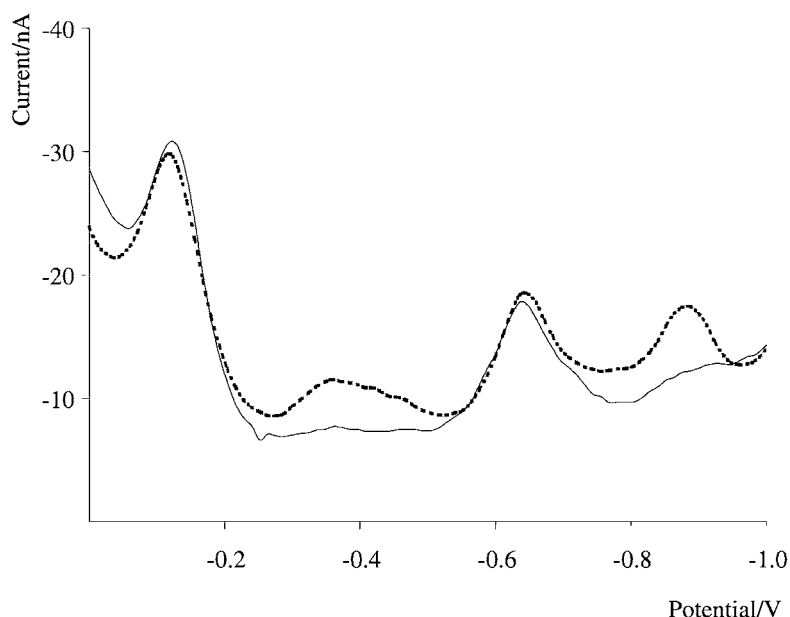


Fig. 2. Adsorptive stripping voltammograms obtained for Cr and Al in river water using PCV as complexing agent in aqueous acetate buffer (pH 5.5). $E_{\text{dep}} = 0$ V, $t_{\text{dep}} = 100$ s, $[\text{PCV}] = 10^{-4}$ M. Designations: —, without digestion; ···, with digestion.

pH 6, and the medium was later acidified to collect the Al possibly adsorbed on the walls of the digestion tube.

To determine the best experimental conditions for digestion, a series of tests was performed by varying the sample volume and the acid used to collect the residual Al. The digestion time was set at 4 h according to [8]. The optimum conditions were found to be: 5 ml of sample, 1 ml of H_2O_2 , and addition of 100 μl of HCl. The voltammogram obtained under these conditions is shown in Fig. 2. Clearly, the peak intensity increases markedly with respect to that of the undigested sample.

In our river-water samples, the total concentration was found to be $4.45 \pm 0.08 \times 10^{-6}$ M ($n = 3$, $\alpha = 0.05$) for Cr and $4.17 \pm 0.02 \times 10^{-5}$ M ($n = 3$, $\alpha = 0.05$) for Al. This result is in good agreement with that found by ICP-MS ($3.70 \pm 0.05 \times 10^{-6}$ and $3.95 \pm 0.03 \times 10^{-5}$ M for Cr and Al ($n = 3$, $\alpha = 0.05$)), respectively.

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