



# Application of multi-factorial experimental design to successfully model and optimize inorganic chromium speciation by square wave voltammetry



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## ARTICLE INFO

### Article history:

Received 18 May 2015

Received in revised form 28 July 2015

Accepted 30 July 2015

Available online 8 August 2015

### Keywords:

Chromium speciation

Square wave voltammetry

Experimental design

Desirability profile

## ABSTRACT

Response surface methodology (RSM) was used to optimize voltammetric signal of hanging mercury drop electrode (HMDE) for inorganic chromium determination and speciation. Initial solution pH, DTPA (Diethylenetriaminepentaacetic acid) concentration, SWV frequency, pulse height, step potential, accumulation time and accumulation potential were considered as important operating factors through experimental design methodology for Cr(VI) quantification. The central composite and a Box–Behnken designs as response surface design coupled with numerical optimization technique was applied for obtaining the optimum chemical and SWV instrumental conditions as well as the maximum height of chromium reduction peak. Optimum conditions were set as follow: pH 6.5, DTPA concentration 5.5 mmol L<sup>-1</sup>, SWV parameters: frequency 500 Hz, step potential 0.005 V, pulse height 0.1 V, accumulation time 120 s and accumulation potential -1.10 V. Speciation is performed in two separate samples, in the first one Cr(VI) is measured after 40 min and DTPA addition. While in the second one, Ce(IV) is added and all Cr(III) is oxidized to Cr(VI) allowing total chromium determination, finally Cr(III) is obtained by difference. Under the optimal experimental conditions, the current reduction peak was proportional to chromium(VI) concentration in the 5–105 nmol L<sup>-1</sup> range, with detection and quantification limits of 3.77 and 8.47 nmol L<sup>-1</sup>, respectively. Using the proposed method, inorganic chromium speciation was successfully determined in water samples with standard addition method, suggesting that this method can be applied to the quantification of inorganic chromium speciation in water samples.

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## 1. Introduction

Chromium (Cr) presence in the environment mainly owing to industrial production became an important threat for plant productivity and food safety [1,2]. It exists in two stable forms, as trivalent (Cr(III)) and hexavalent (Cr(VI)) species, but various intermediate states have also been detected [3–5]. Generally reduction of Cr(VI) to Cr(III) is favored in nature and in plants by naturally present antioxidants [6,7] but its re-oxidation may take place by the action of microorganisms [8]. In this view, Cr redox changes are dynamic process which do not allow for distinguishing between toxicity of individual chemical forms [1].

The measurement of the total Cr content in environmental samples does not provide sufficient information about possible health hazards as toxicity and bioavailability of the chromium species depend on their oxidation states and complexes composition [9]. A detailed knowledge of the concentration of chromium at different oxidation states in environment is important for the following reasons: (i) the geochemical behavior and consequently the transport pathways are different for Cr(III) and Cr(VI) [10]; (ii) impact of chromium on living organisms depends strongly on its oxidation state; Cr(VI) is reported as toxic for

mammals due to its solubility and reactivity, however, high concentrations of Cr(III) can also adversely affect water organisms [11]; (iii) the limits of the Cr(III) and Cr(VI) contents are separated in all the legislations, such as World Health Organization (WHO) that establish for Cr(VI) in groundwater a limit of 50 ppb [12].

Many analytical procedures using different techniques have been reported in the literature to quantify chromium species, atomic absorption spectroscopy (AAS) and inductive coupled plasma mass spectrometry (ICP-MS) being the most frequently employed [13]. In general, previous treatment of samples involving preconcentration and separation schemes is required, such as chromatography [14], coprecipitation [15], extraction [16], X-ray fluorescence spectroscopy [17] or ion-exchange resins [18]. However, these methods are not profitable enough to be adapted to routine analysis, since they are somewhat complicated, and usually involve expensive instrumentation.

Electrochemical methods appear very attractive for analytical purposes because they are reliable, sensitive and require less expensive equipment [19]; for chromium in particular, they allow direct redox speciation with no separation step [20–27]. While Cr(VI) has been successfully determined with detection limits below nanomolar [28–30], the determination of Cr(III) is not such an easy task, since a continuous decrease of the voltammetric signal has been observed [20–27]. Using diethylenetriaminepentaacetic acid (DTPA) as a complexing agent, Li

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**Table 1**  
Central Composite design for chemical variables and obtained response.

Runs	Variables		ip ( $\mu\text{A}$ )
	Buffer pH	[DTPA] ( $\text{mmol L}^{-1}$ )	
1	6.5	5.5	1.596
2 (C)	5.75	3.5	1.402
3	6.5	1.5	1.187
4	4.69	3.5	0.300
5	5.75	3.5	1.420
6	5	1.5	0.470
7	5.75	0.67	0.779
8	5.75	3.5	1.097
9	5.75	3.5	1.048
10	6.81	3.5	1.158
11	5.75	3.5	1.317
12	5	5.5	0.480
13	5.75	6.33	1.279

and Xue [23] developed an entire protocol for chromium speciation at subnanomolar level, which was applied to natural samples. In other works [20–27], reaction schemes were proposed for the complexation and redox reactions of Cr(III) and Cr(VI) with DTPA in the presence of nitrate at mercury electrodes, under catalytic adsorptive stripping voltammetric (CAdSV) electrode surface where it is rapidly reduced to Cr(III) at potentials as low as  $-0.05\text{ V}$  [23]. An interesting review presented not only the mechanisms for Cr(III) and Cr(VI) reduction but also indicate the use of other electrode surfaces [27]. A Cr(III)–DTPA complex is then formed and adsorbed; its reduction to a Cr(II)–DTPA species takes place, originating a well-defined reduction peak. On the other hand, Cr(III) is easily complexed in bulk solution with DTPA; the complex diffuses to the electrode surface where it is weakly adsorbed and then reduced. However, this process is hindered because only a small fraction of the complex reaches the electrode; during its transport, the conversion to a non-electroactive complex species occurs.

Square wave voltammetry (SWV) is rapid, sensitive and consume less analyte than other pulsed techniques [30]. Most of the optimization of SWV also deals with the traditional one-factor-at-a-time (OFAT) approach, examining SWV parameters such as frequency, step potential and pulse height [31–33]. If the factors are independent (which is rarely the situation), the most common practice is OFAT while holding all others parameters constant. However, the result of this univariate analysis shows inadequate optimization toward response(s). Recently, some statistical designs of experiment methods have been employed in electrochemical sensors optimization [34–36]. Using statistical design of experiment imparts advantages, as it allows obtaining the optimum conditions through relatively smaller numbers of experiments. A proper design matrix can lead to obtain a regression equation which highlights effect of individual factors and their relative importance in given operation process. The possibility of evaluating the interaction effect between the variables on the signal can also be known which are not readily

possible in a classical method [37]. Until now, a few reports of the optimization of SWV signal using response surface methodology (RSM) have been published [38–40]. Nevertheless, there is lack of reports on optimization of voltammetric signal for chromium determination using RSM. In an attempt to overcome these problems a new approach is proposed in this research, where the speciation is still carried out in two steps, but in a different way. Influence of important variables was investigated and optimized by experimental design. We focused on the enhancement of the intensity of chromium current by response surface experimental designs as improved optimization methodology. Derringer's desirability function, was used for the evaluation the SWV parameters.

## 2. Experimental

### 2.1. Equipment

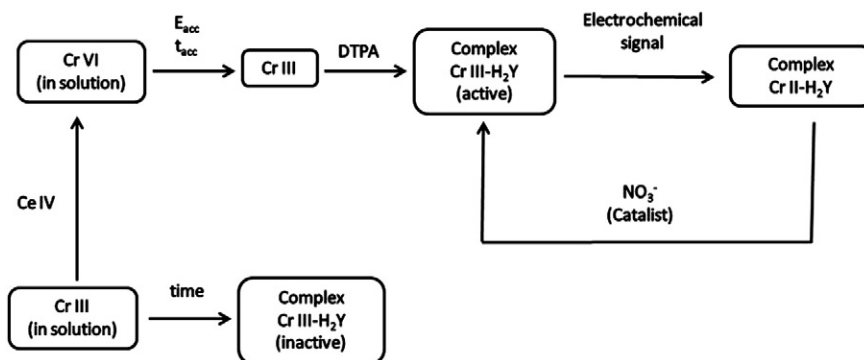
Cataytic cathodic square wave stripping voltammetry (CCSSWV) measurements were performed with an Autolab (Eco-Chemie, Utrecht, Netherlands) equipped with a PSTAT 20 potentiostat and the GPES 4.8 software package. A static mercury drop (VA663 Metrohm, Switzerland) with a small drop having a  $4.0\text{ mm}^2$  surface area was used as the working electrode, in hanging mercury drop electrode (HMDE) mode. A glassy carbon rod was the counter electrode and all potentials in the text are referred to Ag/AgCl ( $3\text{ mol L}^{-1}$  KCl) reference electrode. Each scan was done on a separate drop at room temperature.

### 2.2. Data analysis

The STATISTICA statistical package software version 7.0 (StatSoft Inc., Tulsa, USA) was used for experimental design analysis and data processing. The adequacy of the developed models were tested by performing coefficient of determination ( $R^2$ ), adjusted coefficient of determination ( $R^2_{\text{adj}}$ ) and predicted coefficient of determination ( $R^2_{\text{pre}}$ ) analysis, and its statistical significance was checked by a Fisher F-test. The level of significance was given as values of the probability less than 0.05.

### 2.3. Chemicals and solutions

Acetic buffer ( $0.5\text{ mol L}^{-1}$ , pH 6.5) was prepared by mixing the corresponding amounts of acetic acid and NaOH (both Suprapure®, Cicarelli). Diethylenetriaminepentaacetic acid (DTPA) was purchased from Sigma. A DTPA solution ( $20\text{ mmol L}^{-1}$ ) was prepared by dissolving the appropriate amount of the reagent and the addition of 25% ammonia (Suprapur®, Merck) until pH 6.0.  $\text{KNO}_3$  ( $0.5\text{ mol L}^{-1}$ ) was prepared by dissolving the corresponding amount of the salt (Sigma) in deionized water. Solution of Ce(IV) was prepared by dissolving  $\text{Ce}(\text{SO}_4)_2$  salt (Anedra) ( $3\text{ mmol L}^{-1}$ ) and adjusted to pH 2 by  $\text{H}_2\text{SO}_4$  (Cicarelli) addition. Stock solution of Cr(III) was prepared by dissolving Chromium potassium sulfate (Mallinckrodt) while stock solution of Cr(VI) by



**Scheme 1.** Proposed reactions in bulk solution and at the electrode interface to describe the electrochemical Cr(VI) and Cr(III) speciation and quantification in the presence of DTPA and Ce(IV).

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