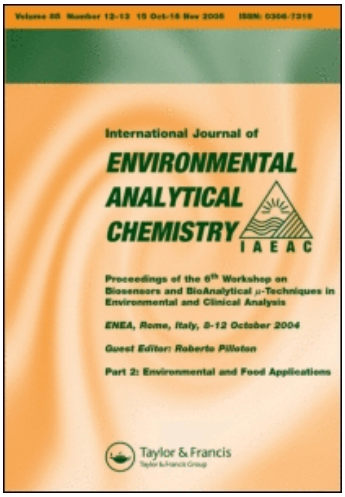

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Determination of Trivalent and Hexavalent Chromium in Waste Water by Flow Injection Chemiluminescence Analysis

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DETERMINATION OF TRIVALENT AND HEXAVALENT CHROMIUM IN WASTE WATER BY FLOW INJECTION CHEMILUMINESCENCE ANALYSIS

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Flow injection analysis (FIA) has been applied to the determination of both Cr(III) and Cr(VI) in waste water. The method is based on the measurement of Cr(III)-catalyzed light emission from luminol oxidation by hydrogen peroxide and the apparatus consists of a FIA system with a flow cell suitable for chemiluminescence detection. Cr(III) is determined directly by the chemiluminescence, meanwhile Cr(VI) is reduced previously to Cr(III) by H_2O_2 in acidic medium and then the total amount of chromium is determined. The concentration of Cr(VI) is obtained by the difference between the Cr(III) and Cr(VI) determinations. We have analyzed synthetic mixtures of both species, Cr(VI) and Cr(III), using this method and its application to waste water has been shown to be very efficient. The method is simple, inexpensive, sensitive (subnanomolar concentrations), selective and rapid. Tens of samples per hour can be performed with tolerance to potential interferants.

KEY WORDS: Flow injection analysis, chemiluminescence, chromium speciation, waste water.

INTRODUCTION

The oxidation state of an element can have an important effect on bioavailability and toxicity. Thus, Cr(III) is essential for the maintenance of glucose, lipid and protein metabolisms in mammals[1-5], meanwhile Cr(VI) is considered a toxic material for animals[6,7]. The presence of Cr(III) and Cr(VI) in the environment is a result of effluent discharges from tanning industries, steel works, oxidative dyeing and other industries. This metal may also enter drinking water supply systems from the corrosion inhibitors used in water pipes and containers[8,9].

There has been considerable activity associated with the determination and speciation of chromium in biological and environmental samples because its toxicity and benefits to health depend critically on its oxidation state[10,11].

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Traditionally, methods for speciation of chromium are relatively time consuming, involving species separation based on solvent extraction[12,13], co-oprecipitation[14,15], ion exchange[16] and electrochemical methods[17]. Speciation has also been achieved by coupling two different techniques such as column Chromatography-current Plasma Atomic Emission Spectrometry[18], Inductively Coupled Plasma Atomic Emission Spectrometry[19,20] or Co-oprecipitation Neutron Activation Analysis[14,21].

Additionally, FIA methods have been used for the analysis of chromium generally with spectrophotometric or atomic absorption detectors[22–29]. However, only very few analytical techniques with sufficient sensitivity for the direct determination and speciation of ultratrace levels of chromium in water are available. Chemiluminescence, in combination with flow injection system, provides sensitivity and selectivity for chromium determination in those samples. So far, luminol (5-amino,2,3-dihydrophthalazine,1,4-dione) has been the most frequently used chemiluminescence reagent[30–34]. Also, flavin mononucleotide as a chemiluminescence reagent has been used[35].

Recently, we have proposed a method for determination of Cr(III) in water and food samples by flow injection chemiluminescence analysis[36]. The method is based on the measurement of Cr(III)-catalyzed light emission from luminol oxidation by hydrogen peroxide. The specificity of this reaction for Cr(III) is achieved in the presence of EDTA, because the formation of Cr(III)-EDTA complex is kinetically slow and Cr(VI) does not catalyze the reaction at all[37,38]. Thus, this method can be used for the speciation of both chromium forms.

In this paper, we have determined Cr(VI) and Cr(III) in synthetic mixtures using that method. Cr(III) is determined directly as before[36], meanwhile Cr(VI) is reduced previously to Cr(III) by hydrogen peroxide in an acidic medium[39] and then the total amount of chromium is determined. The concentration of Cr(VI) is obtained by the difference between both determinations. This method has been applied to waste water, and the optimum experimental conditions have been determined.

EXPERIMENTAL

Instrumentation and procedures

The FIA apparatus used for chromium determination is shown in Figure 1. The reagent streams were sample solution, carrier water, luminol and H_2O_2. Luminol and H_2O_2 were first mixed in the flow system and then mixed again with the sample, which was injected and carried by water stream by operating the injection valve. The chemiluminescence was recorded and the concentration of Cr(III) was determined from the maximum emission intensity.

Reduction of Cr(VI) to Cr(III)

For the reduction of Cr(VI) to Cr(III), method as described by Bowling *et al.*[39] was used. A Cr(VI) standard solution or sample was added to a 100 ml beaker and diluted with 20 ml of water. Then 0.5 ml of 0.2 mol l^{-1} HCl and 0.1 ml of 30% H_2O_2 to reduce Cr(VI) to Cr(III) were added. After 5 minutes, the solution was heated at 80°C for 30 minutes to complete the reaction. Finally, some water was added to complete the 100 ml final volume.

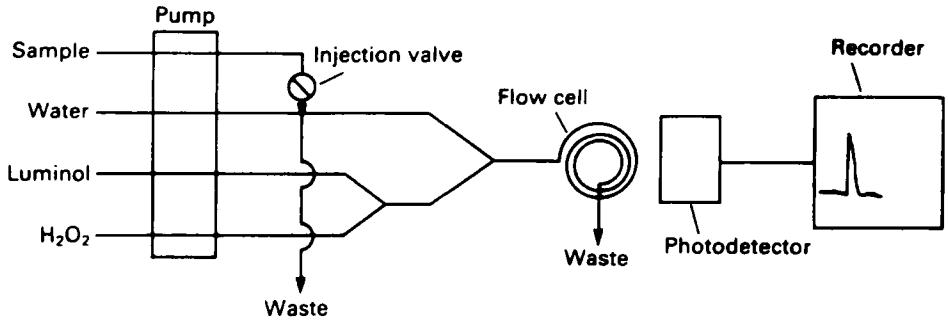

Figure 1 Schematic diagram of the FIA assembly for the determination of chromium speciation.

Reagents

All reagents were analytical reagent grade and water was obtained from a Milli-Q (Millipore S.A., Molsheim, France) deionization system.

Solutions

Chromium standard solutions, 1 mg ml^{-1}: 0.7696 g of $Cr(NO_3)_3.9\ H_2O$ for Cr(III) and 0.289 g of $K_2Cr_2O_7$ for Cr(VI) was dissolved in water and then diluted to 100 ml in a volumetric flask with water. Working solutions were prepared daily by appropriate dilution with water. The pH was adjusted to 4 with 0.5 mol l^{-1} H_3PO_4 in 250 ml volumetric flask.

Ethylenediaminetetraacetic acid (EDTA) solution, 0.1 mol l^{-1}: 3.72 g of EDTA was dissolved in 20 ml of 1 mol l^{-1} KOH solution and diluted to 100 ml with water. 1 x 10^{-3} mol l^{-1} EDTA was prepared by dilution from that solution with water.

Luminol stock solution, 1 x 10^{-2} mol l^{-1} : 0.1772 g of luminol was dissolved in 3.5 ml of 1 mol l^{-1} KOH solution, diluted to 100 ml in volumetric flask with water. For 1 x 10^{-3} mol l^{-1} luminol working solution, 10 ml of the solution was diluted to 100 ml in a volumetric flask with 2.7 ml of 0.2 mol l^{-1} $NaHCO_3$ and 87.3 ml of 0.2 mol l^{-1} Na_2CO_3 buffer to adjust the pH to 10.9.

Hydrogen peroxide working solution, 0.14 mol l^{-1}: 1.43 ml of 30% H_2O_2, 1 ml of 10^{-3} mol l^{-1} EDTA, 7.5 ml of water, 2.7 ml of 0.2 mol l^{-1} $NaHCO_3$ and 87.3 ml of 0.2 mol l^{-1} Na_2CO_3 buffer were mixed. The pH was also 10.9.

RESULTS AND DISCUSSION

Optimum experimental conditions

As discussed by us in the previous paper[36], the optimum experimental conditions for determination of Cr(III) were as following: 1 x 10^{-3} mol l^{-1} luminol (flow rate, 2.5 ml

min^{-1}); 0.14 mol l^{-1} H_2O_2 (flow rate, 2.1 ml min^{-1}); pH = 10.87; carrier water (flow rate, 11.1 ml min^{-1}); injection volume, 0.4 ml.

In order to reduce Cr(VI) to Cr(III), an appropriate amount of HCl and H_2O_2 must be added. The concentrations of 5 x 10^{-3} mol l^{-1} HCl (Figure 2) and 0.05 mol l^{-1} H_2O_2 were selected as the optimal experimental conditions.

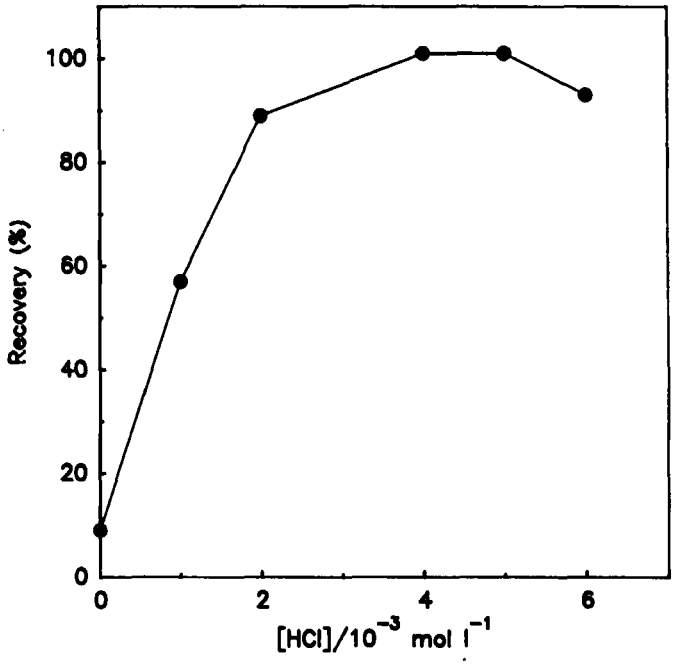

Figure 2 Effect of HCl concentration on Cr(VI) recovery. Conditions: 0.05 mol l^{-1} H_2O_2, 25 ng ml^{-1} Cr(III), 25 ng ml^{-1} Cr(VI).

Calibration graph

Appropriate volumes from Cr(III) standard solutions, plus 0.15 ml of 0.5 mol l^{-1} H_3PO_4 and 0.25 ml of 0.1 mol l^{-1} EDTA, were deposit into 250 ml volumetric flasks for determination of chemiluminescence intensity. The Cr(III) thus measured was linear from 0.01 ng ml^{-1} up to 6 ng ml^{-1} Cr(III).

Recovery and precision

In order to determine if the reduction of Cr(VI) was complete, we have prepared and analyzed a series of standard solutions, as shown in Table 1. The recoveries range was from 91% to 110%. Precision for chromium recovery was determined by 12 replicate analysis of 25 ng ml^{-1} Cr(VI) and 25 ng ml^{-1} Cr(III) mixed solution. The relative standard deviation was 6%.

Table 1 Recoveries for a series of Cr(VI) standard solutions.

Solution	*Cr(VI) added (ng ml^{-1})*	*Cr(III) added (ng ml^{-1})*	*Cr(VI) found (ng ml^{-1})*	*Recovery (%)*
#1	5	25	4.6	92
#2	10	25	9.56	96
#3	25	25	22.8	91
#4	50	25	50.0	100
#5	100	25	91.2	91.2
#6	1	0	0.95	95
#7	50	0	55	110
#8	200	0	209.4	104.7

Results are averages of three replicates.

Interferences

At the presence of EDTA, the most of metal ions do not interfere with the determination of Cr(III). Thus, the addition of 5 ng ml^{-1} Cr(VI) only increases 5% of chemiluminescence intensity in 1 ng ml^{-1} Cr(III) solution. In Table 2 is shown the results of the analysis on interferences by several metal ions.

On the other hand, some organic compounds, which are present in waste water, could interfere enhancing the chemiluminescence which must be considered in order to determine accurately Cr(III). This chemiluminescence intensity contributed by the organic compounds must be determined previously adding appropriate amount of EDTA and heating to 80°C for 30 minutes to mask cations included Cr(III). Also, during the treatement with H_2O_2 in an acid medium for Cr(VI) reduction, the organic compounds are destroyed. Thus, the chemiluminescence is contributed only by the total amount of Cr(III). It is important to note that searched literature does not contain reference to the interference of organic compounds relative to Cr(III) determination by chemiluminescence methods.

Table 2 Tolerance of interferant ions in the determination of Cr(III) and Cr(VI).

Sample	*Cr and ions added*	*Cr determined*		
		Cr(III) (ng ml^{-1})	*Total Cr (ng ml^{-1})*	*Cr(VI) (ng ml^{-1})*
#1	1 ng ml^{-1}:Cr(III), Cr(VI) 0.1 μg ml^{-1}:Cu(II), Mn(II), Ni(II), Mg(II), Ca(II), Fe(III), Cl^-, Br^-, $SO_4^=$	1.05	2.0	0.95
#2	0.5 ng ml^{-1}:Cr(III), Cr(VI) 0.01 μg ml^{-1}:Cd(II), Al(III), Pb(II), Hg(II) 5 ng ml^{-1}:CO(II)	0.51	1.05	0.54

Results are averages from three replicates.

Applications

The method has been applied to four waste water samples from waste pipe of Seville. The amount of Cr(III) was determined by direct application of calibration graph. Then, samples were treated as indicated in Experimental for the reduction of Cr(VI) to Cr(III). The amount of Cr(VI) was obtained by the difference between the total amount of chromium after the reduction with H_2O_2 and the amount of Cr(III). The results are shown in Table 3.

Table 3 Results of the determination of Cr(III) and Cr(VI) in different samples of waste water.

Sample	*Cr(III)* ($ng\ ml^{-1}$)	*Total Cr* ($ng\ ml^{-1}$)	*Cr(VI)* ($ng\ ml^{-1}$)	*Cr(VI) added* ($ng\ ml^{-1}$)	*Recovery* (%)
#1	45	41	not found	0.5	100
#2	10	17	7	0.5	110
#3	52.5	53	not found	0.5	94
#4	0.35	7.5	7.5	0.5	106

The four samples are from waste pipe of the city of Seville. Results are averages from three replicates.

CONCLUSIONS

The proposed method is useful for the determination of Cr(III) and Cr(VI) in natural and waste waters. Their high sensitivity and tolerant of interferents permit the determination of subnanomolar concentrations of both Cr(III) and Cr(VI) in complex matrices in which interferences may be severe limitations to accuracy and realibility. On the other hand, the method is simple, inexpensive, sensitive, selective and rapid, being analyzed several tens of samples per hour.

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