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AN INDIRECT METHOD FOR THE DETERMINATION OF CHROMIUM SPECIES IN WATER SAMPLES BY SEQUENTIAL INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

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Summary—Determination of Cr(VI) and Cr(III) in water samples by inductively coupled argon plasma-atomic emission spectrometry (ICP-AES) was performed indirectly employing an on-line system. For this purpose a column with copper shavings was used to reduce Cr(VI) to Cr(III) in acidic media, generating Cu(II) ions in the flow path. This process permitted the evaluation of concentrations in the range of 1–50 mg/l. The protocol allowed a throughput of 100 samples per hour with 10% precision in the concentration

A literature search covering reports published in the last 10 years on chromium speciation in water samples revealed more than 140 entries. Of these, 60% were on analytical processes employing separation methods prior to the determination. Atomic emission spectrometry systems were used in 13 papers; nearly 55% of them employed a separation system: HPLC,[1] cationic or anionic exchange resins,[2–4] co-precipitation processes[5,6] or solvent extraction.[7] The others[8–13] determined only total chromium concentration.

Atomic emission spectrometry has been widely employed for water analyses, because this technique allows multielemental determination associated with a wide dynamic range. However, when chemical speciation is required, separation techniques must be employed. Simultaneous spectrometric emission determination associated with ion exchange separation, may be employed only for an on-line process. On the other hand, a batch determination can be performed making use of sequential inductively coupled argon plasma-atomic emission spectrometry (ICP-AES). The process, however, needs a long time for the retention and elution steps, typical of resin separations, resulting in a decrease of throughput. The use of an organic solvent in ICP-AES is not recommended because it causes a decrease in the plasma temperature in the torch in addition to an increase in the background signal,[14] leading to reduced precision and limit of detection. Finally, co-precipitation is a slow process that is susceptible to sample contamination.

In this study, the concept of a system for generation of ions (SGI) for spectrometric determination was developed. This system is based on the oxidative capacity of Cr(VI) ions in acidic media, which promote corrosion of copper shavings, producing Cu(II) ions in solution.[15] Finally, Cu(II) ions produced in solution were generated from the liquid–solid equilibrium sample, metallic copper. In this instance, this indirect process permitted the determination of dichromate ions, based on the following stoichiometry:

$$Cr_2O_7^{2-} + 3Cu^0 + 14H^+ \rightarrow 2Cr^{3+} + 3Cu^{2+} + 7H_2O.$$

Cr(III) ions did not react with metallic copper, allowing chromium species quantifications in aqueous samples.

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Table 1. Operation parameters

Observation height	12 *mm* above load coil
Plasma argon flow	8.5 *l./min*
Auxiliary argon flow	6.5 *l./min*
Aerosol argon carrier flow	1.5 *ml/min*
Nebulizer pressure	2.4 *bar*
Incident power	1.25 *kW*
Radio frequency	27.12 *MHz*
Integration time	5 *sec*
Wavelength	
Cu	324.75 *nm*
Cr	284.32 *nm*

EXPERIMENTAL

Apparatus

A Spectroflame sequential inductively coupled argon plasma emission spectrometer (Spectro, Germany) was employed for the Cr and Cu determinations. Table 1 shows the operational parameters for spectrometric determinations. A peristaltic pump connected to the spectrometer was used to introduce the sample stream into the nebulizer.

A home-made perspex column (3 mm × 4.9 cm) was built.

An ultrasonic bath (Microsonic SX-20, Arruda Ultra-Sons, Brazil) was employed to remove the dissolved gases from the solutions, and also as a mixer to improve reaction rates in the preliminary studies.

Reagents

Stock solutions with 1 g/l. of Cu(II), Cr(III) and Cr(VI) were prepared from metallic copper, metallic chromium and potassium dichromate (Merck, p.a.), respectively.

Working standards in the range of 1–100 mg/l. were prepared in solutions of nitric, sulphuric, phosphoric and hydrochloric acid (Merck, p.a.) of 1, 2 and 5% (v/v) concentration.

Granulated copper (spectroscopy grade) was used to load the perspex column.

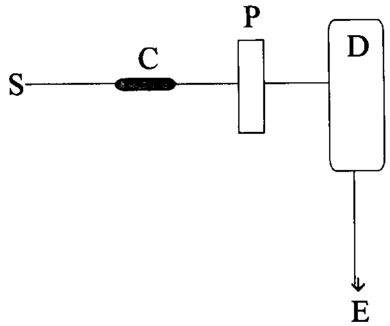

Fig. 1. Flow system diagram.

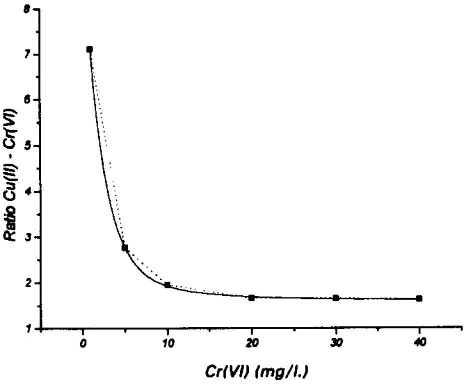

Fig. 2. Variation of the [Cu(II)] and [Cr(VI)] ratio with Cr(VI) concentration in the solution

Performance

Figure 1 shows the flow diagram. The samples (S) were pumped (1.5 ml/min) by a peristaltic pump (P), attached to the spectrometer, flowing through the perspex column (C), loaded with metallic copper shavings. The spectrometric detector (D) determined the total concentration of Cr and Cu, sequentially. The vapours went to the exhaustor (E) continuously.

RESULTS AND DISCUSSION

SGI

The electrochemical potential of Cr(VI) in acidic media permits the oxidation of several metals, whose reduction potentials are higher than those of hydrogen and lower than those of dichromate ions. In these instances, these metals can be used in SGI methodology. Metals such as zinc, iron and silver, can not be employed because of potential restrictions or affinity with the reagents (e.g. precipitation or complexation).

Cr(VI) concentration is calculated based on the stoichiometry of the reaction. The stoichiometric response (R) is defined as the ratio between Cu(II) and total chromium ion concentration. Figure 2 shows the variation of R over a wide range of Cr(VI) concentrations, where one can see the loss of linearity for concentrations lower than 10 mg/l. Ideally, R should be a constant, but competing oxidative processes may occur in diluted Cr(VI) solutions. Dissolved oxygen and some acids cause copper corrosion, increasing Cu(II) concentration. The reaction with dissolved oxygen may be expressed by the equation:

$$2Cu^0 + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O.$$

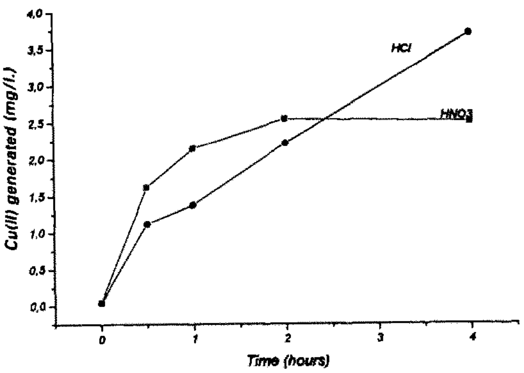

Fig. 3. Generation of copper ions in acidic solution [HNO_3, 1% (v/v) and HCl, 1% (v/v)] per unit time.

This oxidation process can be controlled by prior sonication of the sample or by bubbling an inert gas stream, such as N_2, Ar or He, through it for several minutes.

Effects of acids

Various acids, namely HCl, HNO_3, H_2SO_4 and H_3PO_4, were tested to find the most adequate for providing the acidic media necessary for the reaction conditions. The results indicated that nitric and hydrochloric media do not have adequate properties for this application, leading to copper corrosion, since the first is a strong oxidising agent and the latter has a high complexation capacity. Figure 3 shows the increase of Cu(II) ions generated per unit time, when metallic copper shavings were added to these acid solutions.

Figure 4 presents the results obtained when sulphuric and phosphoric acid were used in 1% (v/v) concentration. For acid concentrations between 1 and 5% (v/v) a significant difference in copper ions generated was not observed. The Cr(VI) reaction requires a high concentration of H^+ ions in solution, and the partial dissociation of the weak phosphoric acid does not provide it. Thus, sulphuric acid was found to be most suitable for the reaction.

Agitation and flow features

Interaction of the dichromate solution with copper shavings was enhanced by increasing the mass transfer between solution and metallic surface. This was achieved through mechanical agitation, sonication or turbulent flow.

A system employing mechanical agitation, with constant rotation, was used with granulated copper immersed in the sample solution. The concentration of Cu(II) ions generated increased linearly with Cr(VI) concentration in the sample solution. The slope revealed that the stoichiometry of the reaction was not reached after 60 min of agitation ([Cu(II)] = 1.57 + 0.75[Cr(VI)]). On increasing this time stoichiometry would be reached but the process would become too slow for routine analyses.

When sonication was employed, the results presented anomalous behaviour, because of the effect of the sonic radiation. It broke up the metal into submicrometric particulate material, transferring it, as slurry, to the nebulizer of the ICP-AES. Another possibility is surface area modification, caused by friction forces, which can generate more Cu(II) ions in solution in a chaotic way.

In a flow process, it is necessary to employ a column with granulated metal, increasing the efficiency of the solid–liquid interaction. The reaction occurs quickly in the inner column, consuming the copper shavings present and, unfortunately, wasting the packed column. Therefore, the column load needs to be changed every day.

Chromium concentration response

The process was evaluated for standard samples with the following concentrations of dichromate ions: 5, 10, 20, 30 and 40 mg/l., in 1% sulphuric media. An analytical curve in sulphuric medium is shown in Fig. 5. The slope calculated applying a linear regression on the curve was 1.85. Since the theoretical ratio is 1.83, stoichiometry was reached in the flow system and the reaction was completed.

Application in synthetic samples

Figure 6 shows three analytical curves in different matrices, with different slopes. Fe(III) ($\epsilon^0 = 0.77$ V) modifies the curve's behaviour because it can oxidize Cu^0 to Cu(II) ($\epsilon^0 = 0.35$ V) with Fe(II) generation and ferrous ion oxi-

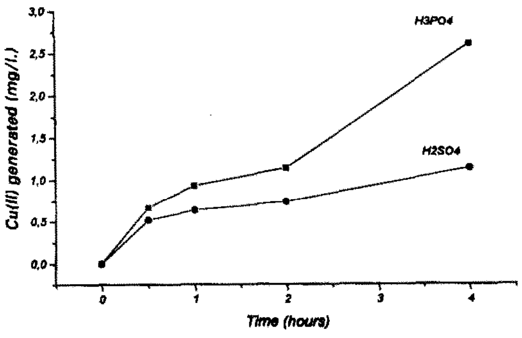

Fig. 4. Generation of copper ions in acidic solution [H_2SO_4 1% (v/v) and H_3PO_4 1% (v/v)] per unit time.

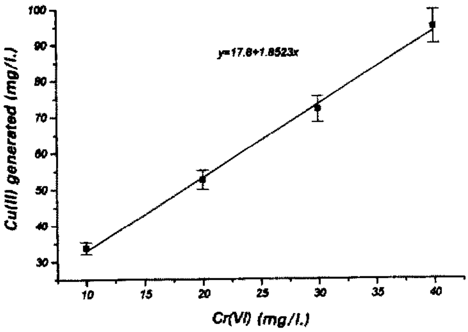

Fig. 5. Analytical curve in sulphuric media.

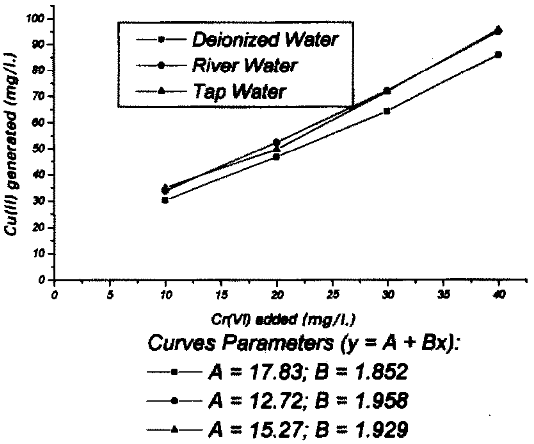

Fig. 6. Analytical curves in three different matrices.

dation by dichromate ions, regenerating ferric ions and producing Cr(III). In this way, ferric ions give the same product as the prinicpal reaction leading to a positive error.

To overcome this drawback, it is necessary to know or to determine copper, chromium and iron concentrations without employing SGI. For chromium (VI) speciation a matrix matching procedure can be used. In water samples containing chromium ions, the Cr(VI) species can be determined following this analytical protocol. A comparison of chromium (VI) data with and without matrix matching is shown in Table 2.

The application of the standard addition method was useless, since the copper–chromium ratio, as depicted in Fig. 2, increased for Cr(VI) concentrations lower than 10 mg/l. This abnormal response was due to the presence of sulphuric acid.

The results in Table 3 show that the method can be applied to water samples under different conditions, using a matrix matching procedure. In this table data are concentrations of Cr(III) and Cr(VI) ions obtained, compared with Cr(III) and Cr(VI) concentrations added to the sample. The relationship of accuracy in different matrices can be seen too.

Table 2. Cr(VI) data using SGI with and without matrix matching

		Cr(VI) concentration (*mg*/*l*.)		
Sample	Fe(III) concentration (*mg*/*l*.) in matrix	Expected	Obtained using matrix matching	Obtained without matrix matching
Deionized water + Fe(III)	10.0	30.0	29.0	31.8
Tap water	0.10	30.0	29.4	31.2

Table 3. Results obtained for chromium species determined in synthetic samples by the SGI process

Sample	Matrix	Cr(III) obtained (*mg*/*l*.)	Cr(VI) obtained (*mg*/*l*.)
Tap water + 15 *mg*/*l*. Cr(III) + 15 *mg*/*l*. Cr(VI)	H_2SO_4 + HCl + Fe(III)	14.0	15.5
Tap water + multielemental standard + 20 *mg*/*l*. Cr(VI)	H_2SO_4 + HNO_3 + Fe(III)	5.3	21.8
River water + 15 *mg*/*l*. Cr(III) + 15 *mg*/*l*. Cr(VI)	H_2SO_4 + HCl + Fe(III)	14.5	15.6
River water + multielemental standard + 20 *mg*/*l*. Cr(VI)	H_2SO_4 + HNO_3 + Fe(III)	5.1	20.5
Deionized water + 15 *mg*/*l*. Cr(III) + 15 *mg*/*l*. Cr(VI)	H_2SO_4 + HCl	14.0	14.4
Deionized water + multielemental standard + 20 *mg*/*l*. Cr(VI)	H_2SO_4 + HNO_3 + Fe(III)	4.8	20.6

The multielemental standard was composed of 5.0 *mg*/*l*. of Ca(II), Mg(II), Cd(II), Cr(III), Fe(III), Pb(II), Zn(II), Mn(II), Ba(II), Al(III), Cu(II) and Ni(II). All synthetic samples were prepared in 1% sulphuric acid.

CONCLUSIONS

Satisfactory results for Cr(VI) determination in synthetic water samples was obtained by the SGI employing a matrix matching process. The very high throughput (100 samples per hr) and a precision of 10%, allow the application of the proposed method in water samples with different composition in routine laboratory analysis.

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