Meseguer-Lloret, S.; Campins-Falcó, P.; Tortajada-Genaro, LA.; Blasco-Gómez, F. (2003). A guide to avoid method bias of chromium(III, VI) chemiluminescence determination by luminol-hydrogen peroxide reaction. Application to unknown water samples. International Journal of Environmental & Analytical Chemistry. 83(5):405-416. doi:10.1080/0306731031000101383

A GUIDE TO AVOID METHOD BIAS OF CHROMIUM (III, VI) CHEMILUMINESCENCE DETERMINATION BY LUMINOL–HYDROGEN PEROXIDE REACTION – APPLICATION TO WATER SAMPLES

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Cr(III) and/or Cr(VI) determinations based on light emission produced by luminol oxidation by hydrogen peroxide in basic aqueous solution catalyzed by Cr(III) were studied in order to diagnose and/or avoid method bias. The calibration step was optimized, and the usefulness of the method for speciating chromium was tested. The use of the standard addition method in the linear interval concentration range made it possible to diagnose the accuracy of the method for real samples. Good results were obtained for several real water samples containing chromium at different concentrations. The proposed protocol made the method traceable with an appropriate certified reference material and with the reference method.

Keywords: Chromium(III, IV); Chemiluminescence; Luminol oxidation

INTRODUCTION

Metals are usually introduced in the water cycle by industrial wastes. Several of these ions are toxic for humans, and their release must be carefully monitored and controlled. Chromium is a common contaminant in natural and wastewater, and this metal can be found as Cr(III) and Cr(VI). The oxidation state of an element can have an important effect on its bioavailability and toxicity, and in fact Cr(VI) is more toxic than Cr(III). Cr(III) is nontoxic at low levels and is considered essential in mammals. Cr(VI) toxicity as an aerosol has been demonstrated; it produces damage to the skin and upper respiratory system, and can produce lung cancer [1]. However, the toxic effects of Cr(VI) in drinking water are not well documented. Cr(III) and Cr(VI) pollution is the result of effluent wastes from tanning industries, steel works, oxidative dyeing or from sectors that manufacture products such as paints, pigments or fungicides. This metal enters drinking water from the corrosion inhibitors used in water pipes and containers. Usually surface and underground water contains very low levels of chromium (for example, the maximum allowable concentration of Cr(III) in drinking water is 50 ug/L), but wastewater coming from the above mentioned industries exhibits much higher levels.

Determination of trace elements in environmental samples requires analytical techniques with high sensitivity and selectivity. In order to determine chromium in water samples, different methods such as spectrophotometry, fluorimetry, X-ray fluorescence spectroscopy, atomic absorption spectrometry, atomic emission sepctrometry, chromatography, electrochemical methods and chemiluminescence analysis have been employed. The chemiluminescence technique provides methods for trace analysis that are attractive because of their high sensitivity and low cost. Several procedures based on the luminol–hydrogen peroxide reaction can be used to measure Cr(III) in water samples and Cr(VI) by a previous reduction to Cr(III), as can be seen in Table I. In all cases, chemiluminescence detection at 425 nm has been used. A masking agent such as EDTA or chromatography is used in order to avoid interference caused

mainly by other metals. The detection limits depend on the procedure used, as can be seen in Table I.

In this study, the calibration step was examined and the effect of different interferents and matrix interference on these determinations were evaluated using EDTA as the masking agent. Different calibration models were studied: potential or log–log and linear. A discussion about the usefulness of the standard addition method (MOSA) depending on the calibration model chosen is also presented. This report shows how the MOSA method serves as an accurate diagnostic tool when real samples are processed in order to avoid method bias. The accuracy and precision of the procedure for quantifying both forms of chromium are tested.

EXPERIMENTAL SECTION

Apparatus and Reagents

A Hitachi F4500, 900v fluorescence spectrophotometer (Tokyo, Japan) was used for the measuring. The light emission was monitored at 425 nm.

The following reagents were used: chromium (III) nitrate (p.a., Panreac, Spain), potassium dichromate (p.a., Panreac, Spain), hydrogen peroxide (p.a., Panreac), luminol (98%, Fluka, Switzerland), sodium carbonate (p.a., Panreac) (p.a., Merk, Germany), sodium carbonate decahydrate (p.a., Probus, Spain), sodium hydrogencarbonate (p.a., Panreac) (r.a., Probus), sodium hydroxide (p.a., Probus), potassium hydroxide (r.a., Probus), chlorhydric acid 37% (puriss.p.a., Fluka) and 36% (trace pur, Merk). The solutions were prepared in water (nanopure, Sybron, Barnstead, Spain). For FI assembly, a Gilson Miniplus peristaltic pump was used to drive the reactants through the flow cell; it always worked at a flow rate of 15mL/min. The loop employed had a 200 mL internal volume. Tygon tubing (i.d. =0.8 mm) was used with the peristaltic pump. Other tubing was made of PTFE with i.d. =0.5 mm. The light emission intensity was recorded as a function of time. The flow injection assembly is shown in Fig. 1 and is similar to that reported by Escobar et al. [3,5]. Luminol and H2O2 streams were first mixed in the flow

system and then mixed with the sample, which was injected in a carrier containing the EDTA solution. The distance between the last T-junction and the detection cell was 4 cm.

The working solutions were as follows: EDTA 0.01M in 0.02M KOH, luminol 1.2 10-3M in 0.3M carbonate buffer solution at pH 10.8 and hydrogen peroxide 0.1 M. The flow cell was a laboratory-made spiral cell, consisting of coiled transparent poly- (tetrafluoroethylene) tube measuring 50 cm in length and with i.d. =0.8 mm. The dimensions of the spiral cell were 1 cm of internal diameter and 3 cm of external diameter.

Procedures

Reagents Pollution Study

Diluted (1 : 3) solutions of each reagent and each component of the reagent are measured.

Cr(III) and/or Cr(VI) Calibration Curves

For the two HCL concentration conditions, 5, 10, 15 mg/L of Cr(III) or Cr(VI) standard solutions were prepared. Another calibration set (0, 3, 6, 10, 15 mg/L of Cr(VI)) was made using trace pure HCl reagent, and a third calibration set (0, 3, 6, 10, 15 mg/L of Cr(VI)) using trace pure HCl and Na2CO3 (p.a.) reagents. Cr(VI) and Cr(III) mixtures containing 3 mg/L of Cr(III) and 3, 8, 12, 15 mg/L of Cr(VI) were prepared. Light emission was measured before and after reduction treatment.

Interference Study

Cr(VI) Mixtures of 30 or 50 mg/L of Cr(III) and 50, 150, 250, 325, 500, 5000 mg/L Cr(VI) were prepared. Co(II) Standards of Co(II) containing 40, 100, 200, 600 mg/L of Co were measured. Mixtures of Co(II) and Cr(III) were prepared: 80 mg/L and 4, 7, 10, 13 mg/L, respectively; 50, 100, 150, 200 and 7 mg/L, respectively. A 1 mg/L Co(II) standard was treated by warming only with HCl or only with H2O2. Other Interferents Binary mixtures of 1mg L Cu(II), Mn(II), Ni(II), Mg(II), Ca(II), Fe(III), Cl, Br, SO24 and 10 mg L of Cr(III) were tested. Light emission was registered before and after reduction treatment.

Standard Addition Method (MOSA)

Tap Water Sample The following standard additions were prepared: SAI: 0, 4, 8, 12, 16, 20 mg/L Cr(VI) with 8mL of sample; SA2: 0, 4, 8, 12, 16, 20 mg/L of Cr(VI) with 5 mg/L of Cr(III) and 8mL of sample. HCl (puriss. p.a.%Cr 0.000002) The standard additions were the following: SA1: 0, 4, 8, 12, 16, 20 mg/L Cr(IV) with 90 mL of sample; SA2: 0, 4, 8, 12, 16, 20 mg/L Cr(IV) with 3 mg/L of Cr(III) and 90 mL of sample; SA3: 0, 4, 8, 12, 16 mg/L Cr(IV) with 2mL of sample 1M solution; SA4: 0, 4, 8, 12, 16 mg/L Cr(IV) with 3 mg/L of Cr(III) and 2mL of sample of 1M solution; SA5: 0, 4, 8, 12, 16 mg/L Cr(IV) with 5mL of sample 1Msolution; SA6: 0, 4, 8, 12, 16 mg/L Cr(IV) with 8mL of sample 1Msolution. All solutions were diluted up to 50 mL, and light emission was measured before and after reduction treatment.

Youden Method

For the tap water sample, 8, 16, 32mL of water sample were diluted up to 50mL with nanopure water. For HCl (puriss. p.a.) sample 0.3, 0.5, 0.7, 1.5, 2mL of a 1M HCl solution were diluted up to 50mL with nanopure water. In both samples, light emission was measured before and after reduction treatment.

Application to Real Samples

Samples of tap and mineral water were tested. 10mL were diluted up to 50mL. Three replicates were made for each solution. The trace elements in natural water, SMR1640 were diluted 6.4 times. Light emission was measured before and after reduction treatment.

RESULTS AND DISCUSSION

Cr(III) and/or Cr(IV) Calibration Curves

The chemiluminescence signal (S) can be generally described as a function of the analyte concentration (C). S =aCb, where a and b are constants. A linear representation is obtained for the plot of log S as a function of log C. Another option is to work with the linear interval of the potential graph. When trace pure HCl and Na2CO3 (p.a.) reagents were used, no signal was

obtained for the blank solution as can be seen in Fig. 2. However, significant signals were obtained for other kinds of reagents.

Table II shows the influence of the quality of reagents used on parameters a and b of the potential curve for Cr(IV). As can be seen, a and b depend on the purity of the reagents used in the luminol solution. The linear interval plots obtained are also given. As can be observed, the signals obtained with HCl 5 10-3M are higher than with HCl 1 10-3M or without HCl (Cr(III) determination). This means that the HCl concentration present in the reduction step is a parameter that should be monitored. Figure 3 shows the FI peaks obtained for the Cr(IV) calibration with trace pure HCl and sodium carbonate (p.a.), treated with 5 10-3M HCl. Mixture samples of Cr(III) and Cr(VI) were processed using the reduction procedure in order to study the total determination of chromium. The calibration curves were obtained by plotting Signal (S) vs total chromium or added Cr(VI). For the potential model, coefficients a and b are similar to the Cr(VI) calibration curves only when total chromium is plotted because for the potential calibration curve C must be the total concentration. When the linear interval is used, b*should be the same regardless of the abscissa used, total or Cr(VI) concentration, respectively.

Figure 4 shows the potential calibration curves obtained for Cr(VI) and for mixtures of Cr(III) and Cr(VI) vs total chromium for the two different conditions of reduction. As the curves of Cr(VI) and mixture curves overlap, the degree of Cr(VI) conversion is 100%. Table III gives the equations of the calibration curves obtained for the mixtures assayed. It has been observed that b*coefficients are similar when we represent S vs total chromium or S vs added Cr(VI). Therefore, Cr(III) and Cr(VI) have similar behavior after the reduction treatment. The equations obtained are all similar to those shown in Table II.

Additionally, it is possible chromium speciation in water samples. The measurement of the signal without reduction step provides Cr(III) concentration. When the reduction treatment is performed, the total chromium concentration is calculated, as the sum of original Cr(III) and transformed Cr(VI).

157

158 Table IV shows figures of merit of the Cr(III), Cr(VI) and total Cr determinations. Better detection
159 limits are provided by the Cr(VI) and total chromium determination. Both findings can be
160 explained by the improvement in the chemiluminescence signal as a result of the presence of
161 HCl in the samples. Good precision and accuracy are shown in Table IV.
162 From this study it can be deduced that for estimating total chromium concentration, a
163 calibration graph obtained for solutions treated as in the reduction treatment is needed. If Cr(III)
164 and Cr(VI) determination is required, two calibration graphs are necessary, one for Cr(III)
165 determination and the other for total Cr. Another possibility is to add HCl to the samples and to
166 measure the chemiluminescence of Cr(III) in these conditions.
167

168 **Interference Study**

169 The effect of interferents in the reduction treatment and measurement step was evaluated
170 studying the presence of metal ions and common anions in samples. With this objective, the
171 procedure was performed for standard solutions described in experimental section. The
172 presence of Cr(VI) does not modify the direct determination of Cr(III) when the amount is lower
173 than 10 mg/L (>200 times normal level). The interference of Co(II) is important when its
174 concentration is higher than 50 mg/L. The Co(II) signal increases when reduction treatment is
175 applied. This increase is produced by the HCl used in reduction treatment because the signal is
176 not modified when treatment is done only with H2O2. The analytical signals of Cr(III), Cr(VI) and
177 Co(II) were additive. No influence of Mn(II), Ni(II), Cu(II), Mg(II), Ca(II), Fe(III), Cl, Br and SO24
178 was observed.

179 **Calibration Models to Test Matrix Effect**

180 A discussion with simulated data is presented in order to search for the suitable calibration
181 model for standard addition method. Potential, polynomial and linear interval curves are tested.

From Cr(III) calibration potential curve: y =32.985c1.2631, a matrix effect (P) between 80 and 120% was introduced and the change in a and b coefficients studied. The matrix effect is reflected in the a coefficient S =a(PC)b =(aPb)Cb. This could be a good model for studying the matrix effect, but these curves fail because the total concentration of the analyte is not known. We tested a two-order polynomial function as calibration model and concluded that a coefficient is conserved if different amounts of analyte are present (0–20 mg/L) in the unknown sample (see Fig. 5). This can be a good option for modeling the signals of the standard addition method, but the experimental data are not fitted to this model, as can be seen in Fig. 5. The conclusion is that potential curves and polynomial curves cannot be employed in the study of matrix effect, and only the concentration linear interval can be used in order to diagnose the matrix effect. The b*values must be tested.

HCl Sample

This sample was worked in order to study the standard addition method in presence of several potential interferents. This sample contains all the interferents discussed in the above section and others such as Hg and Mn. Different standard additions were made; slope values are given in Table V. SA6 gives different slope than Cr(VI) calibration curves because it is probably out of linear interval of chromium concentrations. The other obtained slopes are statistically consistent with the corresponding values obtained for chromium at 5 10-3 M HCl conditions. From this study it can be derived that it is only possible to work in the linear interval range of concentration in order to avoid or diagnose method bias. The slope value of the standard addition calibration graph can serve to guarantee that the linear interval of the chromium concentration is conserved.

Water Samples

For the two sample volumes taken for the tap water, the obtained slope values were similar and the recoveries obtained were near 100%, as can be seen in Table V. This result is important

208 because the chromium concentration in the sample is unknown and this fact indicates that the
209 standard addition method can be employed with guarantee. The application of the Youden
210 method provides significant intercepts: ða tsa Þ for tap water are ð170 40Þ and ð100 40Þ
211 without or with treatment, respectively. Although these values are low and similar to the
212 ordinate values obtained in the calibration graphs, they should be considered in estimating the
213 chromium concentration. If direct measurements are made, differences in the
214 chemiluminescence signal are obtained as a function of the sample volume taken. The obtained
215 straight line was

216 $$S = (170 \pm 20) + (20 \pm 2)V$$

217 where V is the added volume of sample (syx = 20, n = 6, r2 = 0,985). When reduction treatment
218 is applied the same signal is obtained regardless of the sample volume (100+-40). This fact
219 implies that the measured signal for the direct determination of Cr(III) in this sample is due to
220 other species because it disappears when the reduction treatment is applied. In the cases in
221 which the behavior is the same as that indicated, it is only possible to estimate the total
222 concentration. the concentration obtained from the AE1 standard addition curve is 0.26 mg/L1,
223 which is below the detection limit of the method. For AE2 the concentration obtained was 3.5
224 mg/L, which is consistent with the fortified value, 5 mg/L of Cr(III). Direct measurements
225 interpolated in the calibration graphs provided similar results.
226
227 A still water sample was processed and no signal was obtained before or after the reduction
228 treatment. Another sample was analyzed by the diphenylcarbazide reference method [10] and
229 the chemiluminescence method. This sample was also spiked with 2.5 mg/L of Cr(III) and 2.5
230 mg/L of Cr(VI). The results obtained are shown in Table VI. As can be seen in this table, the found
231 concentrations for Cr(III), Cr total and Cr(VI) are consistent for both methods. The method was
232 traceable to the reference method. A reference material was also analyzed. The SMR1640 (NIST,
233 USA) is composed of natural fresh water collected from Cleark Creek CO. The Cr estimated for

234 the SMR1640 (certified value, 38.6+-1.6) was 38.2 (n =3). The method was also traceable to the
235 SMR. Operating as previously described the method bias was avoided as can be demonstrated.
236
237 **CONCLUSIONS**
238 Trace pure HCl and Na2CO3 (p.a.) must be employed to prepare luminol solution. Cr(III) has
239 different behavior before or after treatment due to the absence or presence of HCl in the
240 mixture, respectively. Mixtures of Cr(III) and Cr(VI) provided additive analytical signals after
241 treatment. The same calibration graph can be used for Cr(III) and Cr(VI) determination if HCl and
242 Cr(III) are employed in the standards. Cr(VI) to Cr(III) conversion is quantitative. From the
243 interference study it can be derived Co(II) is a strong interferent if pH and EDTA concentration
244 are uncontrolled. However, Cr(III) behavior is not affected by the presence of Co(II). In order to
245 study the matrix effect, linear calibration curves should be used. No matrix effect has been found
246 in all the samples analyzed. Robustness of the MOSA slope serves to avoid method bias. Also it
247 has been established that reduction treatment made for determining Cr(VI) increases selectivity
248 in Cr(III) determination. For some real samples the method only serves for the determination of
249 total chromium because it has been proved that it is interfered when the reduction treatment
250 is not made. The method was traceable to the reference method and to the standard reference
251 material SMR1640.
252
253 **Acknowledgments**
254 The authors are grateful to the DGICYT (Project n PB 97-1387) and to the Generalitat Valenciana
255 (GR-0036) for financial support.
256
257

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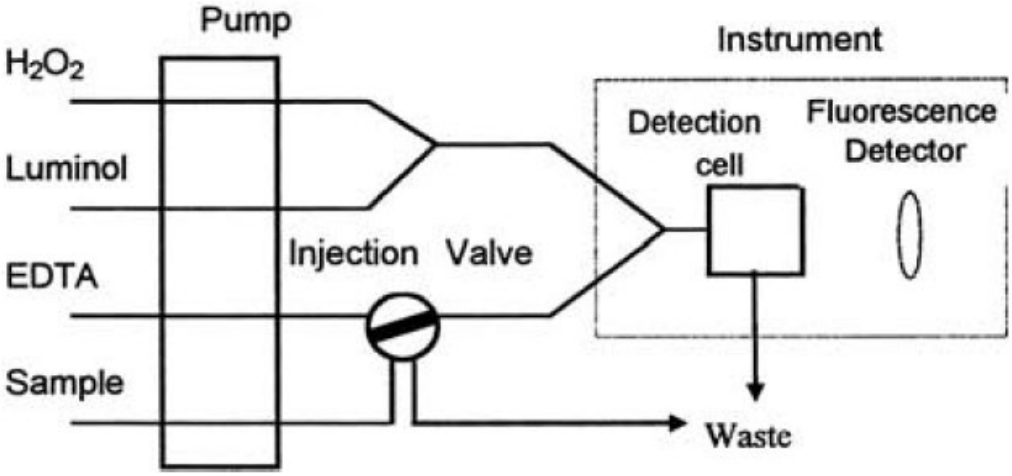

FIGURE 1 FIA system.

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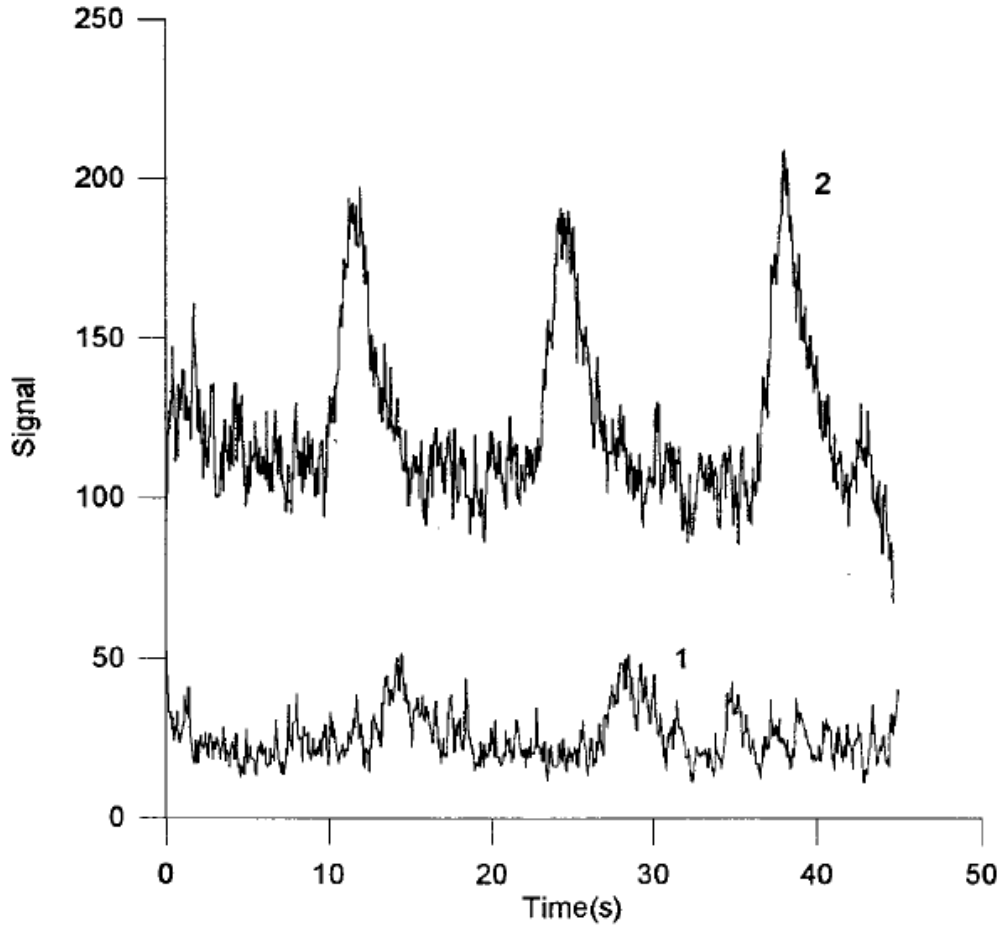

FIGURE 2 Luminol mixture register with pure (**1**) and nonpure (**2**) reagents.

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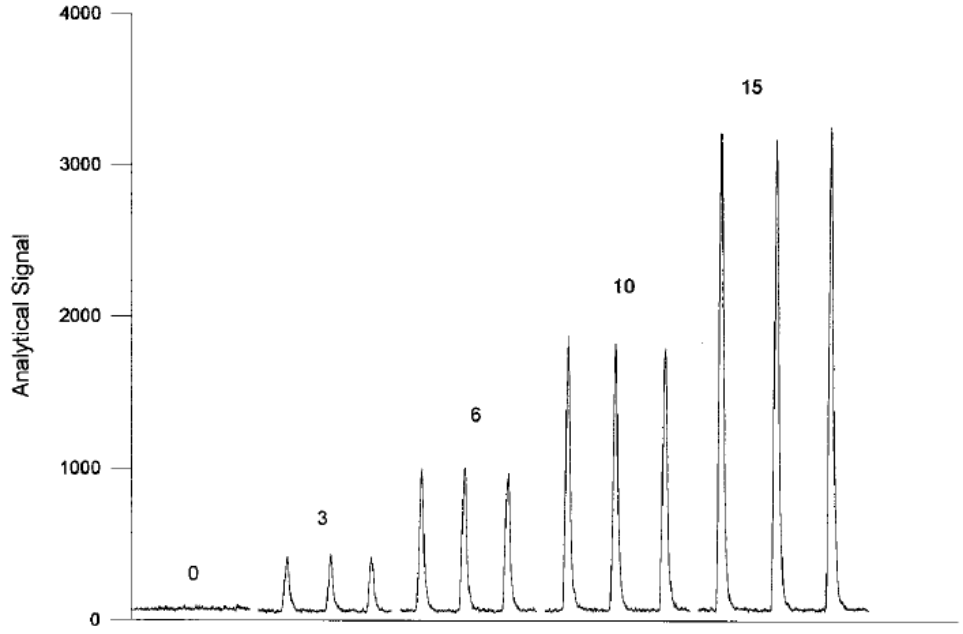

279 FIGURE 3 Signal register for Cr(VI) calibration curve with HCL 5 · 10E-3M (0, 3, 6, 10, 15 µg/L).

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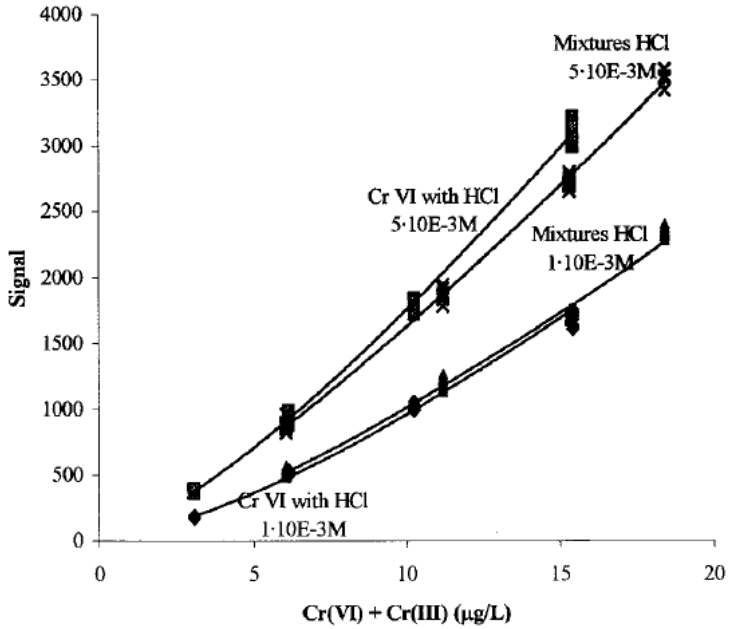

FIGURE 4 Cr(VI) and mixture calibration curves with sodium carbonate (p.a.) and HCl (trace pure).

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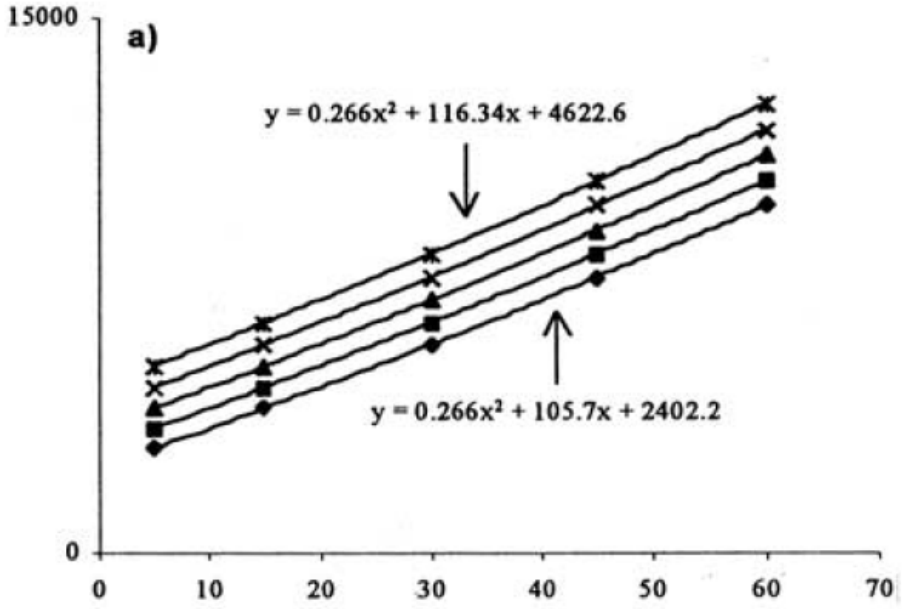

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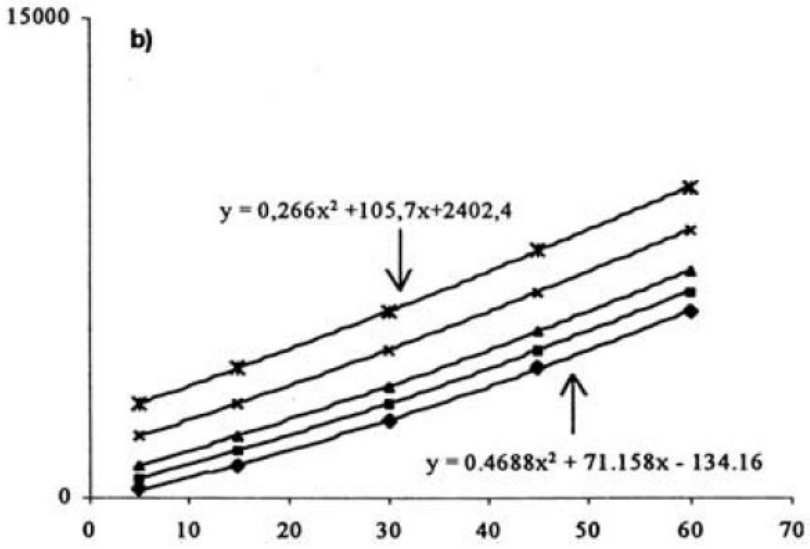

FIGURE 5 (a) Simulated polynomial curves: analyte 0–20 µg/L. (b) Real data: analyte 0–20 µg/L.

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TABLE I Recent studies based on luminol–hydrogen peroxide reaction for chromium

Reference	*Method*	*Detection limit* ($\mu g L^{-1}$)
[2]	Cr(III) and Co determination. Chromatographic separation	15
[3]	Flow injection Cr(III) determination. EDTA as masking agent	0.01
[4]	Cr(VI) and Cr(III) determination. SO_2 as reductor. Chromatographic separation	Cr(III): 50 Cr(VI): 100
[5]	Flow injection Cr(VI) and Cr(III) determination. H_2O_2 in HCl as reduction agent. EDTA as masking agent	0.01
[6]	Cr(III) and Cr(VI) determination by ionic chromatography. Sodium sulphite as reductor	Cr(III): 120 Cr(VI): 90
[7]	Flow injection Cr(III) determination	500
[8]	Cr(VI) and Cr(III) determination with chromatographic separation and a second chromatographic column for reduction Cr(VI) to Cr(III)	2
[9]	Flow injection Cr(III) determination	5.2

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TABLE II Calibration curves obtained for chromium

Cr	*HCl (M)*	*Type of reagents*	*Calibration curve*	
			Potential or log–log*: $a \pm s_a$; $b \pm s_b$ (n,s_{yx}, r^2)*	*Linear $a^* \pm s_{a^*}$; $b^* \pm s_{b^*}$ (n, s_{yx}, r^2)*
Cr(III)	–	HCl (trace pure) Na_2CO_3 (p.a.)	1.70±0.07; 1.06±0.07 (10, 0.04, 0.9861)	−330±70; 97±6 (10, 80, 0.9689)
Cr(VI)	1 · 10E-3	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	2.000±0.004; 1.113±0.004 (45, 0.02, 0.9924)	−170±30; 148±3 (45, 80, 0.985)
Cr(VI)	5 · 10E-3	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	1.637±0.019; 1.77±0.02 (43, 0.03, 0.995)	−1500±40; 433±3 (43, 90, 0.9974)
Cr(VI)	1 · 10E-3	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	2.17±0.03; 1.07±0.03 (36, 0.9, 0.975)	0±40; 174±4 (36, 110, 0.9824)
Cr(VI)	5 · 10E-3	HCl (trace pure) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	2.274±0.009; 1.080±0.010 (36, 0.015, 0.9972)	−120±20; 240±2 (36, 60, 0.9972)
Cr(VI)	1 · 10E-3	HCl (trace pure) Na_2CO_3 (p.a.)	1.576±0.012; 1.403±0.013 (40, 0.02, 0.9967)	−189±8; 115.9±1.1 (30, 17, 0.9976)
Cr(VI)	5 · 10E-3	HCl (trace pure) Na_2CO_3 (p.a.)	1.927±0.008; 1.314±0.009 (40, 0.014, 0.9984)	−252±17; 197±2 (30, 40, 0.996)

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TABLE III Calibration curves for mixtures

Calibration curve	*Conditions*	*Reagents*	*a or* ($a^* \pm s_{a^*}$)	*b or* ($b^* \pm s_{b^*}$)	*n*	r^2
Potential	Total chromium. HCl 1×10^{-3} M	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	92.428	1.2467	36	0.9976
Linear	Total chromium. HCl 1×10^{-3} M	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	(−310±30)	(195±3)	18	0.9958
Linear	Cr(VI) added. HCl 1×10^{-3} M	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	(270±20)	(195±3)	18	0.9958
Potential	Total chromium. HCl 5×10^{-3} M	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	186.29	1.1107	36	0.9977
Linear	Total chromium. HCl 5×10^{-3} M	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	(−310±20)	(277±2)	18	0.9974
Linear	Cr(VI) added. HCl 5×10^{-3} M	HCl (p.a.) $NaHCO_3$ (r.a.) $Na_2CO_3 \cdot 10H_2O$ (p.a.)	(520±20)	(277±4)	18	0.9974
Potential	Total chromium. HCl 1×10^{-3} M	HCl (trace pure) Na_2CO_3 (p.a.)	46.845	1.3307	40	0.9945
Linear	Total chromium. HCl 1×10^{-3} M	HCl (trace pure) Na_2CO_3 (p.a.)	(−270±20)	(129±3)	20	0.9906
Linear	Cr(VI) added. HCl 1×10^{-3} M	HCl (trace pure) Na_2CO_3 (p.a.)	(120±20)	(129±3)	20	0.9906
Potential	Total chromium. HCl 5×10^{-3} M	HCl (trace pure) Na_2CO_3 (p.a.)	90.704	1.2507	40	0.9971
Linear	Total chromium. HCl 5×10^{-3} M	HCl (trace pure) Na_2CO_3 (p.a.)	(−300±50)	(193±4)	20	0.9932
Linear	Cr(VI) added. HCl 5×10^{-3} M	HCl (trace pure) Na_2CO_3 (p.a.)	(270±20)	(193±4)	20	0.9932

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TABLE IV Figures of merit of the Cr(III), Cr(VI) and total chromium determinations

				*Precision (%cv)***			*Accuracy (%Er)****		
Cr, HCL	*Cal**	*D.L.*	*Q.L.*	$\%cv_{8.162}$	$\%cv_{10.203}$	$\%cv_{20.405}$	$\%Er_{8.16}$	$\%Er_{10.2}$	$\%Er_{20.4}$
Cr(III)	P	3	7	17	13	12	14	9	17
	L-L	3	7	3	40	40	3	1.5	2
	LI	4	7	17	13	12	6	6	–
				$\%cv_{5.137}$	$\%cv_{10.273}$	$\%cv_{15.410}$	$\%Er_{5.137}$	$\%Er_{10.273}$	$\%Er_{15.410}$
Cr(VI),	P	1.1	3	4	3	5	16	30	20
HCl	L-L	1.1	3	0.6	0.4	0.7	3	6	3
1-10E-3M	LI	1.9	4	4	3	5	–	30	18
Cr(VI),	P	1.8	4	3	1.3	2	3	15	50
HCl	L-L	1.8	4	0.5	0.17	0.3	0.6	3	6
5-10E-3M	LI	1.8	4	4	3	5	30	30	–
				$\%cv_{30.131}$	$\%cv_{35.268}$	$\%cv_{50.678}$	$\%Er_{30.131}$	$\%Er_{35.268}$	$\%Er_{50.678}$
Total Cr,	P	2	5	6	4	2	4	7	1.8
HCl	L-L	2	5	0.9	0.5	0.3	0.6	0.9	0.3
1-10E-3M	LI	3	5	6	4	–	5	5	0.9
Total Cr,	P	1.3	3	5	3	1.8	5	5	1.6
HCl	L-L	1.3	3	0.7	0.3	0.2	0.6	0.7	0.2
5-10E-3M	LI	2	4	5	3	–	5	5	0.8

*P: Potential calibration curve, L-L: double logarithm calibration curve, LI: linear interval;
**Variation $\text{coefficient}_{\text{concentration added (µg/L)}}$; ***Relative $\text{error}_{\text{concentration added (µg/L)}}$.

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TABLE V Standard additions for HCl and water samples

Sample	*Standard addition*	$b \pm s_b$	*% Recovery*
Water	SA1	165±7	83.7%
Water	SA2	206±4	104.6%
HCl	SA1	185±5	93.9%
HCl	SA2	200±7	101.5%
HCl	SA3	216±3	109.6%
HCl	SA4	225±12	114.2%
HCl	SA5	193±4	98%
HCl	SA6	268±12	136%

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TABLE VI Results obtained in the chromium determination in water samples

	Reference method			*Chemiluminescence method*		
	Cr(III)	*Total Cr*	*Cr(VI)*	*Cr(III)*	*Total Cr*	*Cr(VI)*
Sample	(1.5±0.4)	(1.7±0.2)	–	(1.56±0.05)	(1.83±0.09)	–
Spiked sample	(3.2±0.3)	(6.1±0.3)	(2.9±0.3)	(3.7±0.1)	(5.97±0.07)	(2.3±0.2)

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