VERSITA

Central European Journal of Chemistry
DOI: 10.2478/s11532-007-0038-4
Research article
CEJC 5(4) 2007 1084–1093

Quantitative determination of hexavalent chromium in aqueous solutions by UV-Vis spectrophotometer

Marie–Christine Fournier–Salaün*, Philippe Salaün

Laboratoire de Génie des Procédés et Environnement, INSA de Rouen
Place Emile Blondel, BP 8, 76131 Mont Saint Aignan cedex, France

Received 26 March 2007; accepted 11 June 2007

Abstract: In the last decade, different methods have been developed for the determination of chromium(VI) concentration in water. These methods use high cost equipment or they require a long preparation time. Because of their drawbacks, this paper describes an on-line, rapid and sensitive procedure for the determination of Cr(VI) concentrations in aqueous solutions via pH and absorption measurements. Only four Cr(VI) species are considered. The effects of pH and of total amount of chromium on the Cr(VI) speciation are investigated. The molar absorptivities of four chromium species at 371 nm are determined by minimising an objective function. The knowledge of these molar absorptivities and the measurements of pH and absorption at 371 nm lead to a rapid determination of total Cr(VI) concentration. The reliability and applicability of the method were confirmed using synthetic water samples.

Keywords: chromium(VI) concentration, water, spectrophotometry, analytical method, objective function

1 Introduction

Hexavalent chromium is widely used in many industries. It is used in refractory products, stainless and alloy steels, pigments, tanning agents, catalysts, electroplating and corrosion-resistant products. As a result, waste water from these industries contains significant quantities of waste hexavalent chromium solution and they are the main sources of contamination of chromium in natural water and the environment. Cr(VI) is a strong oxidizer and therefore harmful in environmental and biological systems. It can easily penetrate the cell wall and exert its noxious influence in the cell itself, also causing various forms of cancer. Hence, waste hexavalent chromium solutions have been strictly

* E-mail: fournier@insa-rouen.fr

regulated. For example in France their concentration does not exceed 0.1 mg of Cr per litre if there is more of 1 g of effluent per day. These effluents have to be treated before their discharge into natural water streams.

Cr(VI) recovery processes from waste solutions have been a major challenge for many years. For this purpose many different processes have been developed, for example ion exchange process [1], electrocoagulation [2] or pertraction [3]. For these continuous industrial processes, Cr(VI) concentrations have to be known by a simple and rapid method. At last, the pertraction process has the advantage to concentrate and extract Cr(VI) in the same apparatus. But because of the transport of counter-ions, the pH of the solution may vary. So in this process the Cr(VI) concentration determination has to take account of the pH of the solution.

In the last decade, different methods have been developed for the determination of chromium in water. Electrothermal atomic absorption spectrometric analyses [4] are not exempt from problems because the sample preparation is long and difficult. Preconcentration and determination by flame atomic absorption spectrometry are regarded as a useful technique for the determination of Cr(VI) [5, 6] but the preparation of the samples is long. An alternative is the spectrophotometric determination by solvent extraction of Cr(VI) using protriptyline [7], propylene carbonate [8], chitin [9] or ternary complexes [10]. These techniques require toxic solvents, a long preparation time and organic aqueous phases ratios must be maintained constant because of the mutual solubility of the two phases. Furthemore thermal lens spectrometry [11] can not be applied for routine analysis because of the high cost of the equipment.

Finally, all of these analytical procedures are not adapted to routine analyses. They are not simple and they do not permit the continuous determination of Cr(VI) concentration and they do not take into account the pH of the solution.

Because most processes are continuous, it is necessary to have a one-line rapid and reliable method to analyse the aqueous solutions and to control the processes. The present paper presents a work initiated to find an on-line, rapid, simple and reliable method for the determination of chromium (VI) concentration by spectrophotometry and pH measurements.

2 Experimental

2.1 Reagents and solutions

All chemicals are of analytical grade quality (Prolabo). According to Lide [12], buffer solutions are prepared. The pH values are: $2, 4.2, 4.6, 6, 7, 9, 10, 13.3$. All solutions are prepared with permuted water.

Stock standard solutions of Cr(VI) are prepared by dissolving the appropriate amount of potassium dichromate in buffer solutions. Calibration solutions of Cr(VI) are prepared in concentration range $0.15 - 1.5$ mmol L^{-1}. 68 synthetic solutions are thus prepared in order to determine the molar absorptivity of each component. Another set of experiments

(32 runs) was done by another person in order to validate the method.

2.2 Equipment

A Unicam model Helios Alpha spectophotometer was used for all spectra recording with matched 1 cm quartz cells. All the measurements were made at 25°C in triplicate and the results were expressed as mean value of these three measurements.

The pH measurements were made with a Hanna pH meter.

3 Results and discussion

3.1 Determination of Cr(VI) concentrations as a function of pH and total chromium concentration

Hexavalent chromium exists primarily as 7 forms depending upon the pH of the solution : chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$, hydrogen chromate $HCrO_4^-$, dihydrogen chromate H_2CrO_4, hydrogen dichromate $HCr_2O_7^-$, tetrachromate $Cr_4O_{13}^{2-}$, trichromate $Cr_3O_{10}^{2-}$. The last three ions do not exist in solutions of pH higher than 0 or at chromium concentrations lower than 1 mol L^{-1} [13]. The total amount of chromium and the pH of the solution are thus the main variables of the chromium species in an aqueous phase. According to pH and concentration ranges, three ions and one molecule have to be considered : CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$ and H_2CrO_4. If there is no other chemical species in the aqueous solution, the equilibrium reactions are

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \tag{1}$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \tag{2}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons HCrO_4^- \tag{3}$$

The equilibrium constants of the three reactions are K_1, K_2 and K_3 respectively and are thus expressed at 25°C

$$K_1 = \frac{[H^+][HCrO_4^-]}{[H_2CrO_4]} = 0.20[14] \tag{4}$$

$$K_2 = \frac{[H^+][CrO_4^{2-}]}{[HCrO_4^-]} = 1.87 \cdot 10^{-6}[13, 14] \tag{5}$$

$$K_3 = \frac{[HCrO_4^-]^2}{[Cr_2O_7^{2-}]} = 0.031[14] \tag{6}$$

From equations (4), (5) and (6) the concentrations of CrO_4^{2-}, $Cr_2O_7^{2-}$ and H_2CrO_4 can be expressed as a function of the concentration of $HCrO_4^-$ as follows

$$[H_2CrO_4] = \frac{[H^+][HCrO_4^-]}{K_1} \tag{7}$$

$$[CrO_4^{2-}] = \frac{K_2[HCrO_4^-]}{[H^+]} \tag{8}$$

$$[Cr_2O_7^{2-}] = \frac{[HCrO_4^-]^2}{K_3} \tag{9}$$

In a solution, total chromium concentration is equal to

$$C = [H_2CrO_4] + [HCrO_4^-] + [CrO_4^{2-}] + 2[Cr_2O_7^{2-}] \tag{10}$$

By substituting equations (7), (8) and (9) in equation (10), the total chromium concentration C can be evaluated

$$C = \frac{[H^+][HCrO_4^-]}{K_1} + [HCrO_4^-] + \frac{K_2[HCrO_4^-]}{[H^+]} + 2\frac{[HCrO_4^-]^2}{K_3} \tag{11}$$

For a total amount of hexavalent chromium, C in solution of known pH, the quadratic equation (11) is easily solved and leads to the determination of the four species concentrations.

For each prepared solution, equation (11) is solved and the four chromium species are determined. The results obtained by using different pH and initial hexavalent chromium concentrations are given in Table 1. At basic pH (9, 10 and 13.3) only chromate ions exist in the solution. At neutral pH the principal species in the solution are CrO_4^{2-} (75%) and $HCrO_4^-$ (25%). At acid pH (4.2, 4.6, 6) the principal species are CrO_4^{2-} (0.5% to 23%), $HCrO_4^-$ (95% to 25%) and $Cr_2O_7^{2-}$ (5% to 1%). At pH equal to 2 $HCrO_4^-$ (90%), $Cr_2O_7^{2-}$ (5%) and H_2CrO_4 (5%) are present. These results are consistent with those published before [14, 15].

3.2 Determination of molar absorptivity

According to Beer-Lambert law, the concentrations C_i of each species i being low, the absorbances of the solution at wavelength λ are a linear function of each species concentrations, such as

$$\mathrm{ABS}(\lambda) = \sum_i \varepsilon_i(\lambda) l C_i \tag{12}$$

in which l is the cell pathlength and $\varepsilon_i(\lambda)$ is the molar absorptivity of the i^{th} specie (L mol^{-1} cm^{-1}). Relation (12) is available if all species absorb independently and if there are no interference.

Table 1 Effect of pH and total amount of chromium on Cr(VI) concentration species.

pH	$[Cr(VI)]_{ini}$ (mmol/L)	$[CrO_4^{2-}]$ (mmol/L)	$\%_{CrO_4^{2-}}$	$[HCrO_4^-]$ (mmol/L)	$\%_{HCrO_4^-}$	$[Cr_2O_7^{2-}]$ (mmol/L)	$\%_{Cr_2O_7^{2-}}$	$[H_2CrO_4]$ (mmol/L)	$\%_{H_2CrO_4}$
13.3	0.2536	0.2536	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
13.3	0.1516	0.1516	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
13.3	0.4643	0.4643	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
13.3	0.3916	0.3916	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
13.3	0.3256	0.3256	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
13.3	0.1700	0.1700	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
13.3	0.2006	0.2005	100.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
10	0.1666	0.1665	99.97	0.0001	0.03	0.0000	0.00	0.0000	0.00
10	0.2794	0.2793	99.97	0.0001	0.03	0.0000	0.00	0.0000	0.00
10	0.5901	0.5899	99.97	0.0002	0.03	0.0000	0.00	0.0000	0.00
10	0.5187	0.5185	99.97	0.0002	0.03	0.0000	0.00	0.0000	0.00
10	0.3420	0.3418	99.97	0.0001	0.03	0.0000	0.00	0.0000	0.00
10	0.4011	0.4010	99.97	0.0001	0.03	0.0000	0.00	0.0000	0.00
10	0.6118	0.6117	99.97	0.0002	0.03	0.0000	0.00	0.0000	0.00
10	0.6798	0.6796	99.97	0.0002	0.03	0.0000	0.00	0.0000	0.00
9	0.2679	0.2670	99.67	0.0008	0.31	0.0000	0.02	0.0000	0.00
9	0.4324	0.4309	99.65	0.0013	0.31	0.0000	0.02	0.0000	0.00
9	0.3535	0.3523	99.66	0.0011	0.31	0.0000	0.02	0.0000	0.00
9	0.1822	0.1816	99.67	0.0006	0.31	0.0000	0.02	0.0000	0.00
9	0.4045	0.4031	99.65	0.0013	0.31	0.0000	0.02	0.0000	0.00
9	0.2611	0.2602	99.67	0.0008	0.31	0.0000	0.02	0.0000	0.00
9	0.1210	0.1206	99.68	0.0004	0.31	0.0000	0.02	0.0000	0.00
9	0.4011	0.3997	99.65	0.0012	0.31	0.0000	0.02	0.0000	0.00
9	0.1795	0.1789	99.67	0.0006	0.31	0.0000	0.02	0.0000	0.00
9	0.4290	0.4275	99.65	0.0013	0.31	0.0000	0.02	0.0000	0.00
9	0.5847	0.5825	99.64	0.0018	0.31	0.0000	0.02	0.0000	0.00
9	0.2719	0.2710	99.67	0.0008	0.31	0.0000	0.02	0.0000	0.00
9	0.4738	0.4722	99.65	0.0015	0.31	0.0000	0.02	0.0000	0.00
9	0.5099	0.5081	99.65	0.0016	0.31	0.0000	0.02	0.0000	0.00
9	0.3474	0.3462	99.66	0.0011	0.31	0.0000	0.02	0.0000	0.00
7	0.3392	0.1370	40.39	0.0428	12.62	0.0797	46.99	0.0000	0.00
7	0.3671	0.1445	39.37	0.0452	12.30	0.0887	48.32	0.0000	0.00
7	0.6404	0.2080	32.48	0.0650	10.15	0.1837	57.37	0.0000	0.00
7	0.2305	0.1047	45.42	0.0327	14.20	0.0465	40.38	0.0000	0.00
7	0.9824	0.2715	27.64	0.0848	8.64	0.3130	63.72	0.0000	0.00
7	0.1183	0.0638	53.93	0.0199	16.85	0.0173	29.22	0.0000	0.00
7	0.1972	0.0936	47.46	0.0292	14.83	0.0372	37.71	0.0000	0.00
7	0.8158	0.2422	29.68	0.0757	9.28	0.2490	61.04	0.0000	0.00
6	0.3134	0.0169	5.40	0.0529	16.89	0.1218	77.71	0.0000	0.00
6	0.3957	0.0193	4.88	0.0603	15.24	0.1580	79.89	0.0000	0.00
6	0.4249	0.0201	4.72	0.0627	14.76	0.1711	80.51	0.0000	0.00
6	0.3834	0.0190	4.94	0.0592	15.45	0.1526	79.60	0.0000	0.00
6	0.2441	0.0147	6.02	0.0459	18.82	0.0917	75.16	0.0000	0.00
4.6	0.8804	0.0012	0.14	0.0950	10.79	0.3921	89.07	0.0000	0.00
4.6	0.6764	0.0011	0.16	0.0826	12.21	0.2964	87.64	0.0000	0.00
4.6	0.7628	0.0011	0.15	0.0880	11.54	0.3368	88.31	0.0000	0.00
4.6	0.2903	0.0007	0.23	0.0522	18.00	0.1187	81.77	0.0000	0.00
4.6	0.4772	0.0009	0.18	0.0685	14.35	0.2039	85.46	0.0000	0.00
4.6	1.1523	0.0014	0.12	0.1094	9.50	0.5207	90.38	0.0000	0.00
4.6	0.2787	0.0007	0.23	0.0511	18.33	0.1135	81.43	0.0000	0.00
4.2	0.4494	0.0003	0.07	0.0663	14.76	0.1913	85.16	0.0000	0.01
4.2	0.4344	0.0003	0.08	0.0651	14.99	0.1845	84.92	0.0000	0.01
4.2	0.5656	0.0004	0.07	0.0751	13.27	0.2451	86.65	0.0000	0.00
4.2	0.6547	0.0004	0.06	0.0812	12.40	0.2865	87.53	0.0000	0.00
2	0.3800	0.0000	0.00	0.0603	15.87	0.1582	83.25	0.0034	0.88
2	0.4059	0.0000	0.00	0.0625	15.40	0.1699	83.74	0.0035	0.86
2	1.4249	0.0000	0.00	0.1221	8.57	0.6480	90.96	0.0068	0.48
2	0.7927	0.0000	0.00	0.0896	11.30	0.3491	88.07	0.0050	0.63
2	0.5779	0.0000	0.00	0.0757	13.10	0.2490	86.18	0.0042	0.73
2	0.7791	0.0000	0.00	0.0888	11.40	0.3427	87.97	0.0049	0.63
2	0.9443	0.0000	0.00	0.0983	10.41	0.4203	89.01	0.0055	0.58
2	0.9198	0.0000	0.00	0.0970	10.54	0.4087	88.87	0.0054	0.59
2	1.0605	0.0000	0.00	0.1045	9.86	0.4751	89.60	0.0058	0.55
2	1.1285	0.0000	0.00	0.1080	9.57	0.5073	89.90	0.0060	0.53
2	0.4147	0.0000	0.00	0.0633	15.25	0.1740	83.90	0.0035	0.85
2	0.8756	0.0000	0.00	0.0945	10.79	0.3880	88.61	0.0052	0.60
2	1.0401	0.0000	0.00	0.1035	9.95	0.4655	89.50	0.0057	0.55
2	1.1496	0.0000	0.00	0.1091	9.49	0.5172	89.98	0.0061	0.53

Aqueous solutions of hexavalent chromium compounds absorb the light in the ultraviolet and violet regions of the spectrum, as shown in Figure 1. Spectra depend on pH and thus on the chemical form of the chromium (VI). In acid media, the spectrum has two maxima: at 257 nm and at 349 nm. In basic media, the absorption spectrum showed two maxima at 275 nm and at 371 nm. Absorbance was measured at 371 nm.

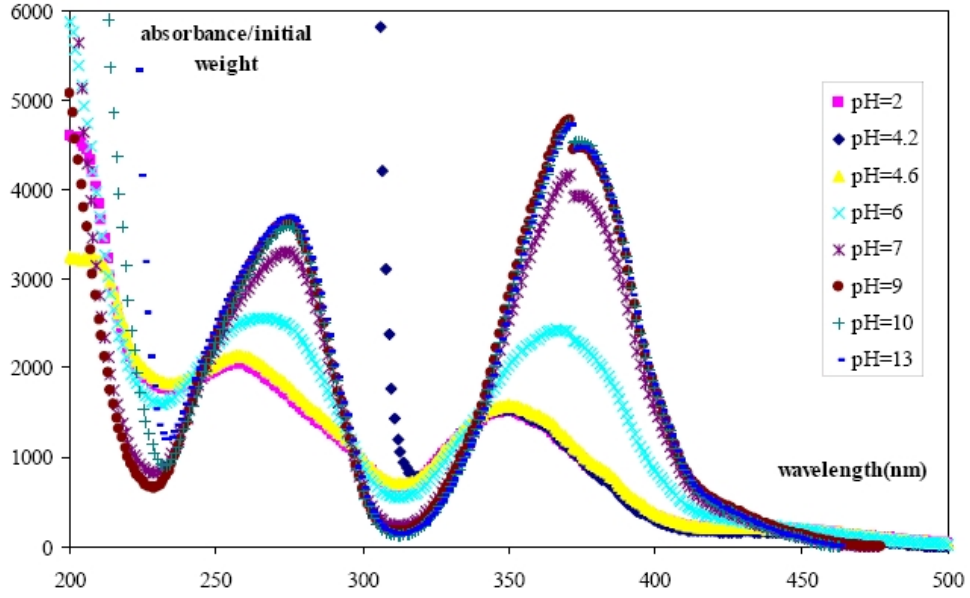

Fig. 1 Effect of pH of the solution on absorption spectra.

If all compounds absorb separately, the calculated absorbance at 371 nm, ABS (371 nm) is expressed 371 nm

$$\begin{aligned}\mathrm{ABS_{calc}}(371\ \mathrm{nm}) = 1(&\varepsilon_{\mathrm{H_2CrO_4}}(371\ \mathrm{nm})[\mathrm{H_2CrO_4}] + \varepsilon_{\mathrm{HCrO_4^-}}(371\ \mathrm{nm})[\mathrm{HCrO_4^-}] + \\ &\varepsilon_{\mathrm{CrO_4^{2-}}}(371\ \mathrm{nm})[\mathrm{CrO_4^{2-}}] + \varepsilon_{\mathrm{Cr_2O_7^{2-}}}(371\ \mathrm{nm})[\mathrm{Cr_2O_7^{2-}}])\end{aligned} \tag{13}$$

in which $\varepsilon_i(371\ \mathrm{nm})$ is the molar absorptivity of the i^{th} compound at 371 nm.

From four initial molar absorptivities and concentrations of four species an absorbance, called $\mathrm{ABS_{calc,j}}(371\ \mathrm{nm})$ for the j^{th} run is calculated. With the intention of determining these molar absortivities the objective function F has to be minimised

$$F = \sum_{j+1}^{n} \left| \frac{\mathrm{ABS_{calc,j}}(371\ \mathrm{nm})}{\mathrm{ABS_{exp,j}}(371\ \mathrm{nm})} - 1 \right| \tag{14}$$

in which $\mathrm{ABS_{exp,j}}$ is the absorbance corresponding to the j^{th} calibration sample and $\mathrm{ABS_{calc,j}}$ is its calculated absorbance.

The best set of molar absorptivity is given in Table 2. As it can be seen in Figure 2, calculated and experimental absorbances are in good agreement.

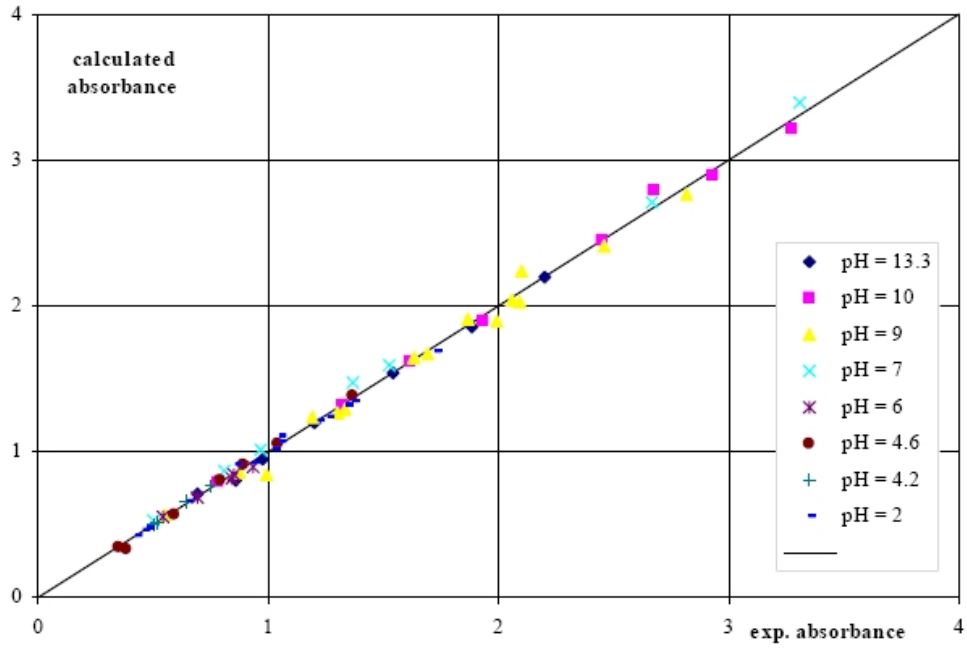

Fig. 2 Calculated absorbance as a function of experimental absorbance.

Table 2 Molar absorptivity of Cr(VI) species at 371 nm ($F = 190$).

species	ε (L · mol^{-1}· cm^{-1})
CrO_4^{2-}	4730
$HCrO_4^-$	590
$Cr_2O_7^{2-}$	2490
H_2CrO_4	1000

3.3 Analytical application

The proposed method was applied to the determination of Cr(VI) concentration in a synthetic wastewater. A new set of experiments are then used.

Now the molar absorptivities of four hexavalent chromium species are known. Knowing them as well as the absorbance and pH of the solution permits the determination of the concentration of the four hexavalent chromium species. By replacing the chromate, $Cr_2O_7^{2-}$ dichromate and dihydrogen chromate concentrations with the hydrogen chromate concentration the equation (13) is written as

$$\mathrm{ABS_{calc}}(371\ \mathrm{nm}) = 1(\varepsilon_{\mathrm{H_2CrO_4}}(371\ \mathrm{nm})\frac{[\mathrm{H^+}][\mathrm{HCrO_4^-}]}{\mathrm{K_1}} + \varepsilon_{\mathrm{HCrO_4^-}}(371\ \mathrm{nm})[\mathrm{HCrO_4^-}] + \varepsilon_{\mathrm{CrO_4^{2-}}}(371\ \mathrm{nm})\frac{\mathrm{K_2}[\mathrm{HCrO_4^-}]}{[\mathrm{H^+}]} + \varepsilon_{\mathrm{Cr_2O_7^{2-}}}(371\ \mathrm{nm})\frac{[\mathrm{HCrO_4^-}]^2}{\mathrm{K_3}}) \quad (15)$$

The resolution of the equation enables firstly the determination of hydrogen chromate concentration. Secondly equations (7) to (9) allow the calculation of the chromate, $Cr_2O_7^{2-}$ dichromate and dihydrogen chromate concentrations. The value of total chromium (VI) concentrations is then compared with the initial concentration of the solution. The relative standard derivation is calculated by equation (16)

$$\left| 1 - \frac{\mathrm{Cr(VI)_{calc}}}{\mathrm{Cr(VI)_{exp}}} \right| \tag{16}$$

As shown in Table 3, good agreement was obtained between the concentrations found and the value of total Cr(VI). Experimental and predicted chromium(VI) concentrations are given with 3.50% maximum deviation. Results are shown in Figure 3.

Table 3 Deviation data on the determination of Cr(VI) concentration.

pH	$[\mathrm{Cr(VI)}]_{\mathrm{calc}}$ (mmol L^{-1})	$[\mathrm{Cr(VI)}]_{\mathrm{ini}}$ (mmol L^{-1})	Deviation
13.3	0.5745	0.5765	0.34%
13.3	0.0831	0.0829	0.15%
13.3	0.2561	0.2570	0.33%
13.3	0.3392	0.3617	6.22%
9	0.0857	0.0823	4.14%
9	0.2832	0.2753	2.87%
9	0.4770	0.4765	0.09%
9	0.3845	0.3651	5.34%
7	0.6585	0.6608	0.35%
7	0.6031	0.5996	0.59%
7	0.6244	0.6193	0.81%
7	0.5607	0.5439	3.09%
7	0.4193	0.4079	2.80%
6	0.3082	0.2882	6.94%
4	0.2030	0.2162	6.09%
4	0.3882	0.4133	6.08%
4	0.2107	0.2141	1.59%
4	0.2918	0.2896	0.76%
4	0.2918	0.2882	1.23%
4	0.1040	0.1027	1.31%
4	0.4244	0.4160	2.02%
2	0.2208	0.2203	0.26%
2	0.3663	0.3875	5.46%
2	0.3229	0.3277	1.45%
1.73	0.6259	0.6254	0.07%
1.73	0.9041	0.8980	0.68%
1.73	0.1009	0.1033	2.32%
1.73	0.3685	0.3651	0.94%
1.73	1.3290	1.2869	3.28%
1.73	0.2358	0.2298	2.64%
1.73	0.7557	0.7709	1.98%
1.73	0.4647	0.4731	1.79%

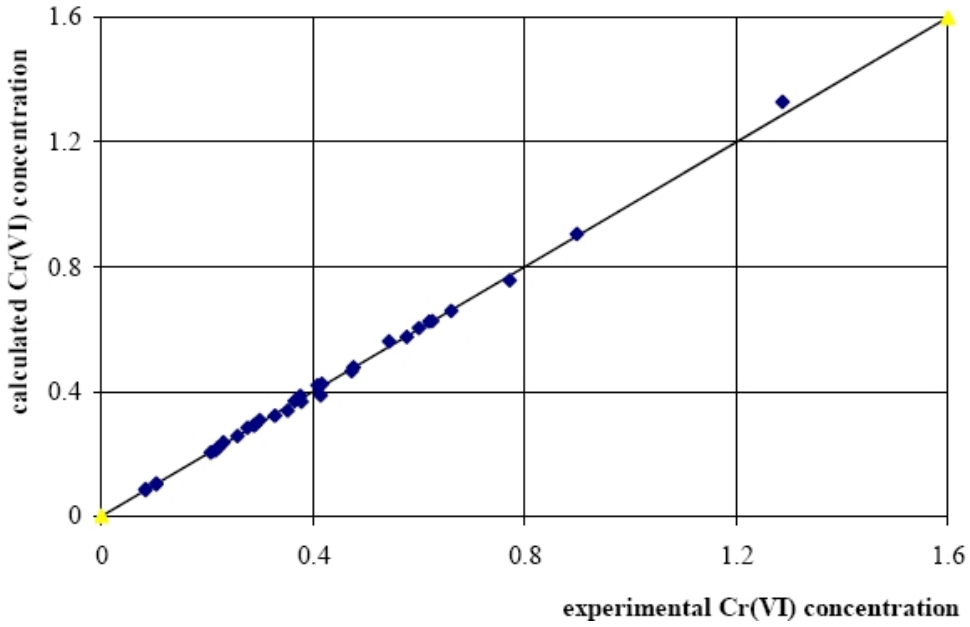

Fig. 3 Calculated Cr(VI) concentration as a function of experimental Cr(VI) concentration.

4 Conclusions

UV-vis spectrophotometer associated with pH measurement can be successfully applied to the determination of total Cr(VI) concentration.

The method is well suited for the speciation of chromium (VI). This inexpensive and relatively simple method gives good precision and accuracy. Moreover this method can be used for continuous determination of Cr(VI) concentrations.

From the results it can be considered that the method is a suitable technique for routine analysis of chromium (VI) solutions whose pH can change.

Acknowledgements

The authors wish to thank Stéphane Dubois for technical support.

References

[1] S.H. Lin and C.D. Kiang: "Chromic acid recovery from waste acid solution by an ion exchange process : equilibrium and column ion exchange modelling", *Chem. Eng. J.*, Vol. 92, (2003), pp. 193–199.

[2] S. Reussard: *Study of an electrochemical reactor using a change in pH : application for the recovery of chromium(VI) by electro-coagulation (Contribution à l'étude d'un réacteur électrochimique mettant en œuvre une évolution de pH : application á l'épuration de solutions d'acide chromique par électrocoagulation*, PhD thesis INPT France (2003).

[3] M.C. Fournier-Salaün and C. Vauclair: "Recovery of chromic ions from aqueous effluents by liquid membrane in continuous mode", *Desalination*, Vol. 144, (2002), pp. 227–229.

[4] P. Vinas, N. Campillo, I. Lopez–Garcia and M. Hernandez–Cordoba: "Electrothermal atomic absorption spectrometric determination of molybdenum, aluminium, chromium and manganese in milk", *Anal. Chim. Acta*, Vol. 356, (1997), pp. 267–276.

[5] A. Gaspar and J. Posta: "On-line sorption preconcentration of chromium(VI) and its determination by flame atomic absorption spectrometry", *Anal. Chim. Acta*, Vol. 354, (1997), pp. 151–158.

[6] R.M. Crespon–Romero, M.C. Yebra–Biurrun and M.P. Bermejo–Barrera: "Preconcentration and speciation of chromium by the determination of total chromium and chromium (III) in natural waters by flame atomic absorption spectrometry with a chelating ion-exchange flow injection system", *Anal. Chim. Acta*, Vol. 327, (1996), pp. 37–45.

[7] D.T. Burns and M.D. Dunford: "Spectrophotometric determination of chromium(VI) by extraction of protriptylinium dichromate", *Anal. Chim. Acta*, Vol. 319, (1996), pp. 205–207.

[8] D.T. Burns and C.D.F. Dangolle: "Spectrophotomeric determination of chromium(VI) by extraction of the dichromate anion into propylene carbonate", *Anal. Chim. Acta*, Vol. 356, (1997), pp. 145–148.

[9] S. Hoshi, K. Konuma, K. Sugawara, M. Uto and K. Akatsuka: "The simple and rapid spectrophotometric determination of trace chromium(VI) after preconcentration as its colored complex on chitin", *Talanta*, Vol. 47, (1998), pp. 659–663.

[10] P. Gao, X. Gu and T. Zhou: "New separation method for chromium(VI) in water by collection of its ternary complex on an organic solvent-soluble membrane filter", *Anal. Chim. Acta*, Vol. 332, (1996), pp. 307–312.

[11] M. Sikovec, M. Franko, F.G. Cruz and S.A. Katz: "Thermal lens spectrometric determination of hexavalent chromium", *Anal. Chim. Acta*, Vol. 330, (1996), pp. 245–250.

[12] D.R. Lide: *CRC Handbook of Physics and Chemistry*, 84^{th} ed., Academic Press, New York, 2003.

[13] G. Charlot: *Chemical reactions in solution (Les réactions chimiques en solution*), Masson ed., 1970.

[14] J.D. Neuss and W. Rieman: "The application of the glass electrode to a study of chromic acid", *J. Am. Chem. Soc.*, Vol. 56, (1934), pp. 2238–2243.

[15] R.K. Tandon, P.T. Crisp, J. Ellis and R.S. Baker: "Effect of pH on chromium(VI) species in solution", *Talanta*, Vol. 31, (1984), pp. 227–228.