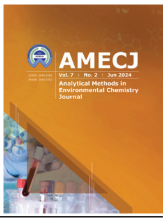
Anal. Methods Environ. Chem. J. 7 (2) (2024) 18-28

AMECJ

Research Article, Issue 2
Analytical Methods in Environmental Chemistry Journal
Journal home page: www.amecj.com/ir



Direct analysis of hexavalent chromium in water samples by UV-Vis spectrophotometry: Effects of pH and the presence of foreign ions

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ARTICLE INFO:

Received 10 Feb 2024
Revised form 14 Apr 2024
Accepted 17 May 2024
Available online 30 Jun 2024

Keywords:
Analytical method
Chromium (VI)
UV-Vis spectroscopy
Water samples

ABSTRACT

The present study aims to characterize the direct UV-Vis spectrophotometric analysis of hexavalent chromium (CrVI) in aqueous solution. The effects of pH and the presence of different ions are evaluated. The results obtained show that at pH ≤ 6, Cr(VI) analysis must be carried out at 350 nm. The Beer-Lambert law is respected for a concentration lower than 100mg Cr(VI) L^{-1}. At pH ≥ 8, the analysis must be performed at 372 nm. In this case, the linearity range of the standard curve does not exceed the concentration of 25 mg Cr(VI) L^{-1}. In the pH range 6 <pH < 8, the direct Cr(VI) analysis cannot be performed. Whatever the pH of the solutions, the presence of acetate, oxalate, citrate, and tartrate with a concentration ten times higher than that of Cr(VI), has no effect. At pH 2, only the presence of Fe(II) and Fe(III) ions prevents the direct determination of Cr(VI) ions. In the presence of metallic ions [Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)), Cr(VI)] analysis must be carried out at pH 2. At higher pH, these ions have a significant effect.

1. Introduction

Metal speciation is crucial to characterize their behavior and effects. Two forms of the same metal can be very different. Various methods are developed for toxic metal speciation in various samples [1, 2]. Chromium is one of the known toxic metals. It can exist in different oxidation states, ranging from the divalent to the hexavalent state. Generally, in water, chromium can be found as trivalent (Cr(III)) or hexavalent (Cr(VI)). The hexavalent form (Cr(VI)) is characterized by a high oxidative potential and a high solubility. It is considered to be the most toxic form of chromium. Cr(VI) forms species mainly with oxo or hydroxo ligands, which are readily absorbed from the gastrointestinal tract due to their high ability to diffuse across all types of cell membranes [3]. It is suggested that Cr(VI) exclusively impairs cellular energy production, disrupts the homeostatic metabolism of carbohydrate, protein, and lipid pathways; deregulates metabolically related enzymes, and impairs the structural and functional integrity of the liver and kidneys [4]. Potassium dichromate ($K_2Cr_2O_7$) and sodium chromate (Na_2CrO_4) are two hexavalent chromium salts widely used in industrial processes such as metallurgy, chromium plating, chemical industry, textile manufacturing, wood preservation, photography and photoengraving [5]. The main method used to analyze Cr(VI) in water is the 1,5-diphenylcarbazide method, which has been proposed for a long time [6]. This method is based on the formation, under acidic conditions of a red-violet

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https://doi.org/10.24200/amecj.v7.i02.278

color complex characterized by a UV-visible absorption band at 540 nm [7, 8]. However, it can only be used for low concentrations (< 0.3 mg L^{-1}), and dilution is often required. Consequently, several researchers have been interested in the direct determination of Cr(VI) ions in water using the UV-Vis spectrophotometric properties of Cr(VI) solutions. In a method developed for natural water, the concentration of Cr(VI) at pH 9 was determined by measuring the height of the absorption peak at 372 nm [9]. The Cr(VI) species were quantified by direct determination of Cr(VI) at 371nm at different pH values [10]. The direct multi-wavelength determination of Cr(VI) in natural waters, and urban and industrial effluents has given results comparable to those of the diphenylcarbazide method [11]. From the comparison of the dilution effect on the determination of Cr(VI) ions by the direct method and the diphenylcarbazide method, it has been suggested that the direct method is recommended for the quantification of Cr(VI) at concentrations higher than 1mg. L^{-1} [12]. Concerning the effect of the presence of foreign ions, it has been found that the presence of major ions such as Na^+, K^+, NO_3^- and Cl^-, does not affect the direct determination of Cr(VI) ions at 363 nm up to a concentration greater than 1000 mg L^{-1}. The tolerated concentration limit was 200 mg L^{-1} in the case of SO_4^{2-} and CO_3^{2-}, 100 mg L^{-1} in the case of $Al^{3+,}$ and 15 mg L^{-1} in the case of Mg^{2+} [13], experiments were carried out in the pH range 5-7. Recently, some methods such as isopropyl 2-[(isopropoxycarbothiolyl) disulfanyl ethane thioate, amino bimodal mesoporous silica nanoparticles, task-specific ionic liquid, and acetylcysteine based on dispersive liquid-liquid microextraction were used for chromium determination in different samples [14-19]. Also, the Raman analysis showed that the pH range 2-6 can be used for Cr(VI) [20]. The present study aims to optimize the direct determination of Cr(VI) in the presence of transition metals (Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)) and organic anions (oxalate, citrate, acetate, and tartrate).

2. Material and methods

2.1. Instrumental

Quantitative analysis of UV-visible spectrophotometry relies on the Beer-Lambert law which establishes a relation between the absorption of light by a substance and its concentration in a solution. The Beer-Lambert law is valid in the case of monochromatic light, diluted solutions, and in the absence of interferences from reflection, scattering, or fluorescence. In the present study, analyses were performed using Shimadzu 1610, UV-Vis spectrophotometer. A quartz cell was used for all analyses.

2.2. Reagents

All chemical reagents used in this study are of analytical grade and have not been purified. All solutions were prepared in distilled water. The Cr (VI) solutions were prepared from potassium dichromate (ChemischeFabrick (Germany), CAS No:7778-50-9) and potassium chromate (Sigma-Aldrich (United States), CAS No:7789-00-6). Transition metals were used as chloride or nitrate salts. Iron (III) chloride (CAS No: 7705-08-0), manganese (II) chloride (CAS No: 7791-18-6), cadmium (II) nitrate (CAS No: 10022-68-1), and zinc (II) nitrate (CAS N°: 10196-18-6) were purchased from BIOCHEM (France). Nickel (II) chloride (CAS No: 7791-20-0) and cobalt (II) chloride (CAS No: 7791-13-1), were purchased from MERCK (Germany). Copper (II) chloride (CAS No: 10125-13-0) and iron (II) chloride (CAS No:13478-10-9) were purchased from NORMAPUR (Spain) and Sigma-Aldrich (United States) respectively. Organic ions were used as their potassium, sodium, or ammonium salts. Ammonium acetate (CAS No:8013-60-4), ammonium oxalate (H_2O, CAS No:6009-70-7), and potassium sodium tartrate (CAS No: 6381-59-5) were purchased from Thermo Scientific Chemicals (United States), NORMAPUR (Spain) and MERCK (Germany) respectively. Potassium citrate (CAS No: 6100-05-6) and sodium acetate (CAS No: 127-09-3) were purchased from BIOCHEM (France). Hydrochloric acid (CAS No:7647-01-0) and sodium hydroxide (CAS No: 1310-73-2) were purchased from BIOCHEM (France) and NORMAPUR (Spain) respectively.

2.3. Procedure

Cr(VI) stock solutions were prepared in distilled water. Cr(VI) solutions with various concentrations were obtained by dilution in distilled water. After pH adjustment using HCl (0.1M) or NaOH (0.1M), the absorbance of each prepared solution was measured (Figure 1). The same procedure was repeated in the presence of the foreign ions using Cr(VI) solution with a concentration of 10 mg L^{-1} and various foreign ions concentrations. Stock solutions of 20 mg L^{-1} in the case of cations and 200 mg L^{-1} in the case of anions were prepared and used. All the experiments were performed at least in triplicate.

3. Results and discussion

3.1. Cr(VI) solution characterization

The UV-vis spectra of an aqueous Cr(VI) solution at a concentration of 10 mg L^{-1} (Fig. 2) show two absorption bands corresponding to charge transfer transitions between oxygen and chromium. In water, Cr(VI) can be found as $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-}. In the three species, simple and double bonds between chromium and oxygen exist (Fig. 3). Increasing the pH causes a shift of the absorption bands towards higher wavelengths (batochrome effect) and an increase in the intensity of the bands (hyper chrome effect).

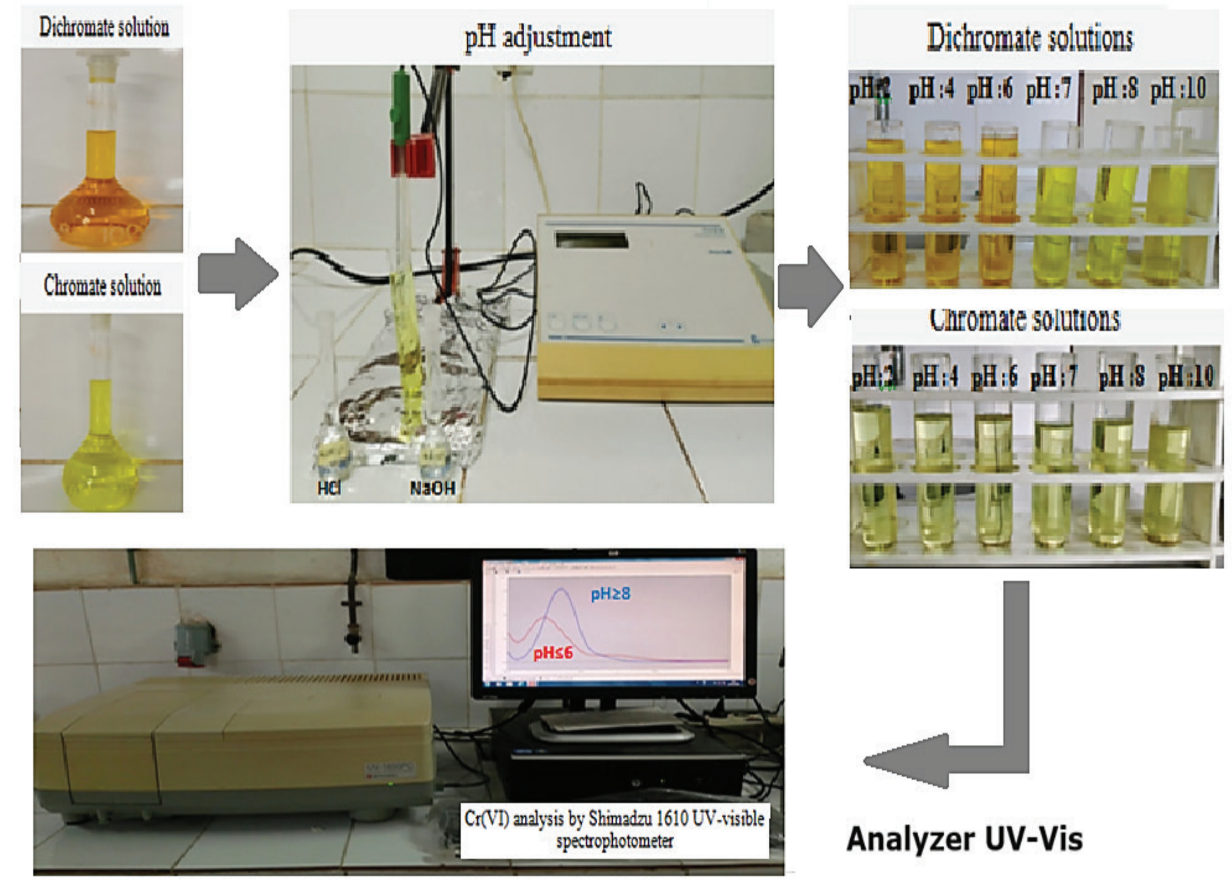

Fig. 1. Experimental procedure by UV-visible spectrophotometry

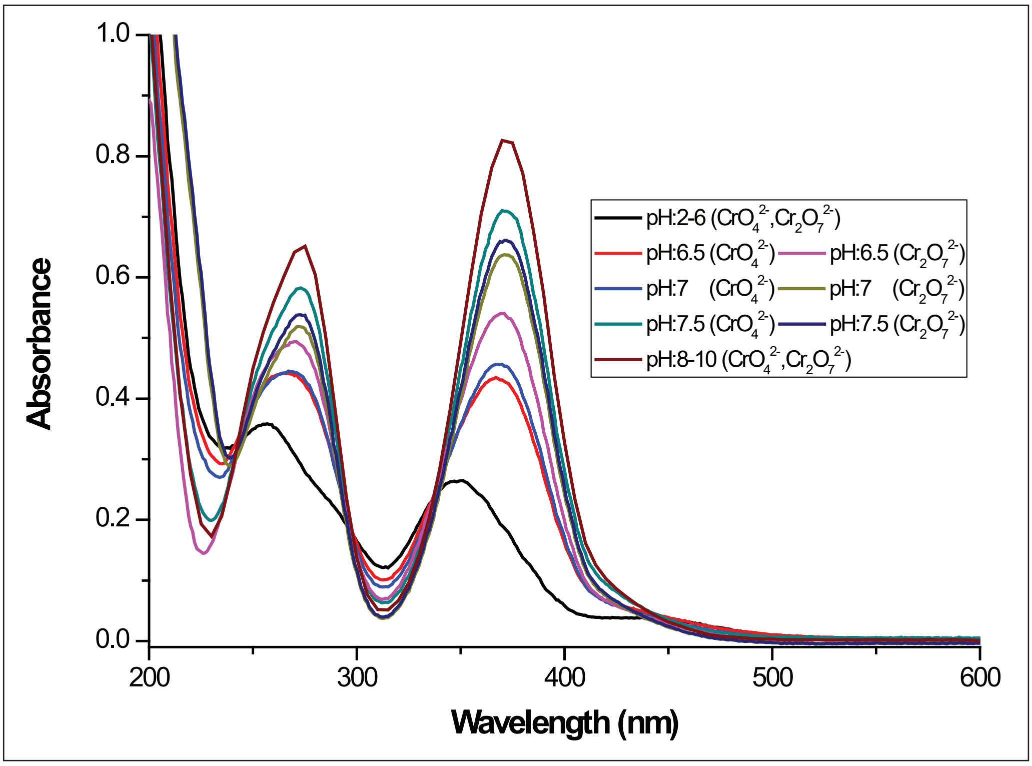

Fig. 2. Effect of pH on UV-Vis spectra of Cr(VI) solution (10 mg L^{-1})

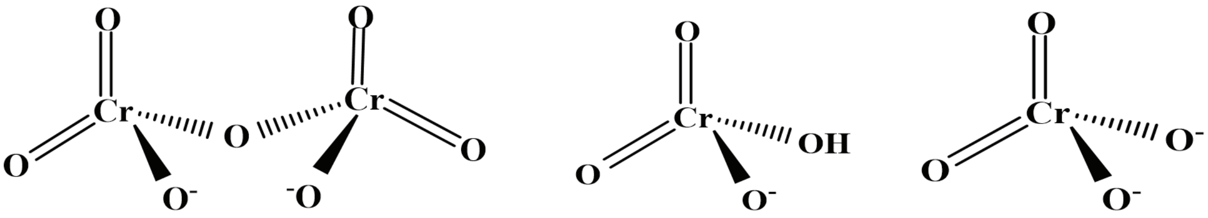

Fig. 3. Structures of Cr (VI) species

The intensity of the UV-Vis bands evolves according to three pH ranges (Fig. 4). Despite the possible presence of two Cr(VI) species ($HCrO_4^-$ and/or $Cr_2O_7^{2-}$), absorbance remains stable at pH ≤ 6. According to the results of Raman spectroscopic analysis [20], in the pH range 2-6, the dominant form of Cr(VI) at low concentration as is the case in our study is $HCrO_4^-$ rather than $Cr_2O_7^{2-}$. This can explain the observed stability of the optic density of the Cr(VI) solution in this pH range. At pH ≥ 8, where CrO_4^{2-} predominates, absorbance remains also stable. The wavelength of the maximum absorbance is 350 nm at pH≤6 and 372 nm at pH ≥ 8. In the pH range $6 < pH < 8$, where Cr(VI) speciation evolves from $HCrO_4^-$ to CrO_4^{2-}, the measured absorbance increases with increasing pH and varies with the nature of chromium salt (Fig. 4). Consequently, Cr(VI) speciation has a significant effect in this pH range. In the pH range $6<pH<8$, the same effect is also observed for Cr(VI) concentrations below or above 10 mg L^{-1} (Fig. 5); the measured absorbance increases with increasing pH.

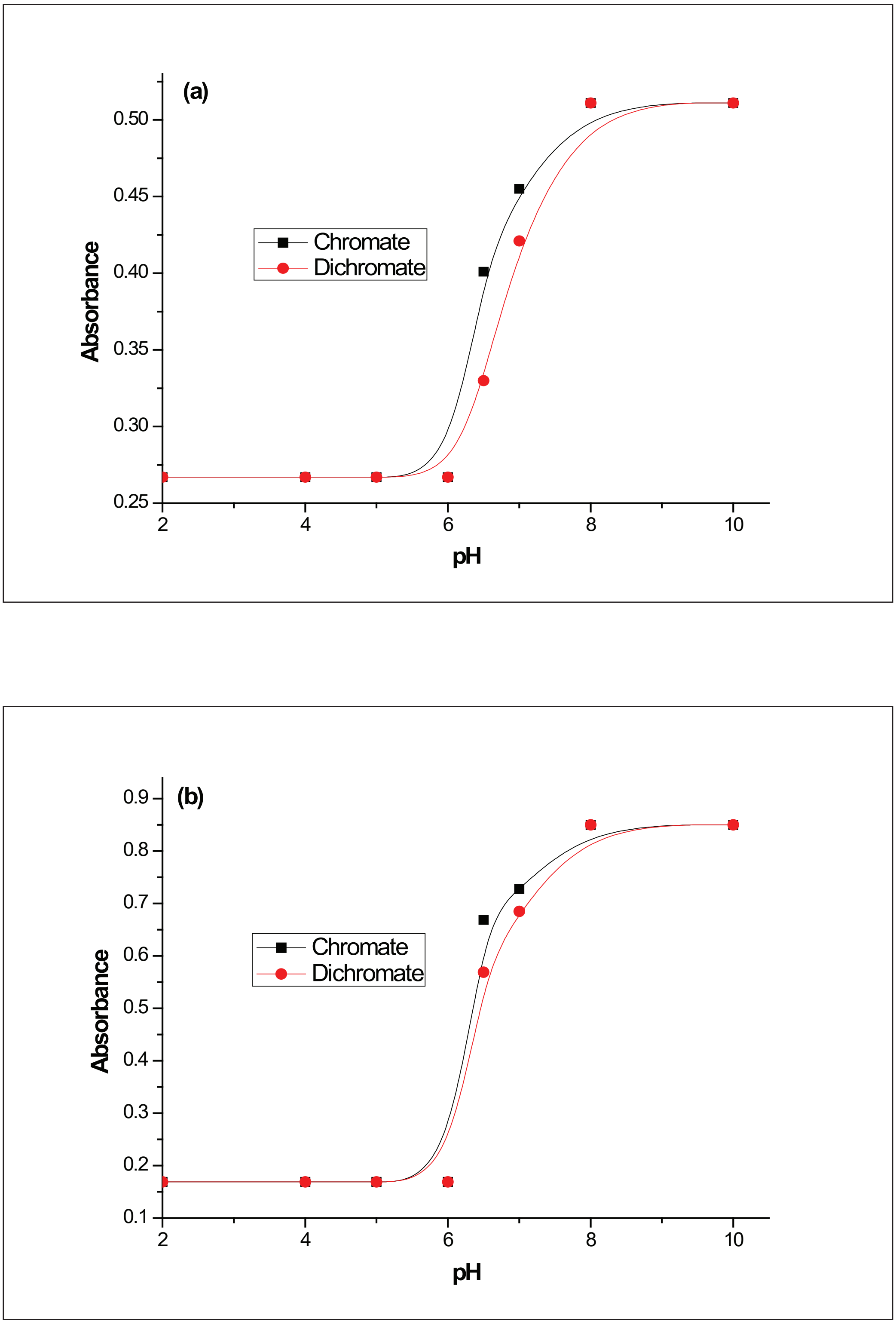

Fig. 4. Effect of pH on the absorbance of Cr(VI) solution (10 mg L^{-1}) at: a)350 nm and b)372nm

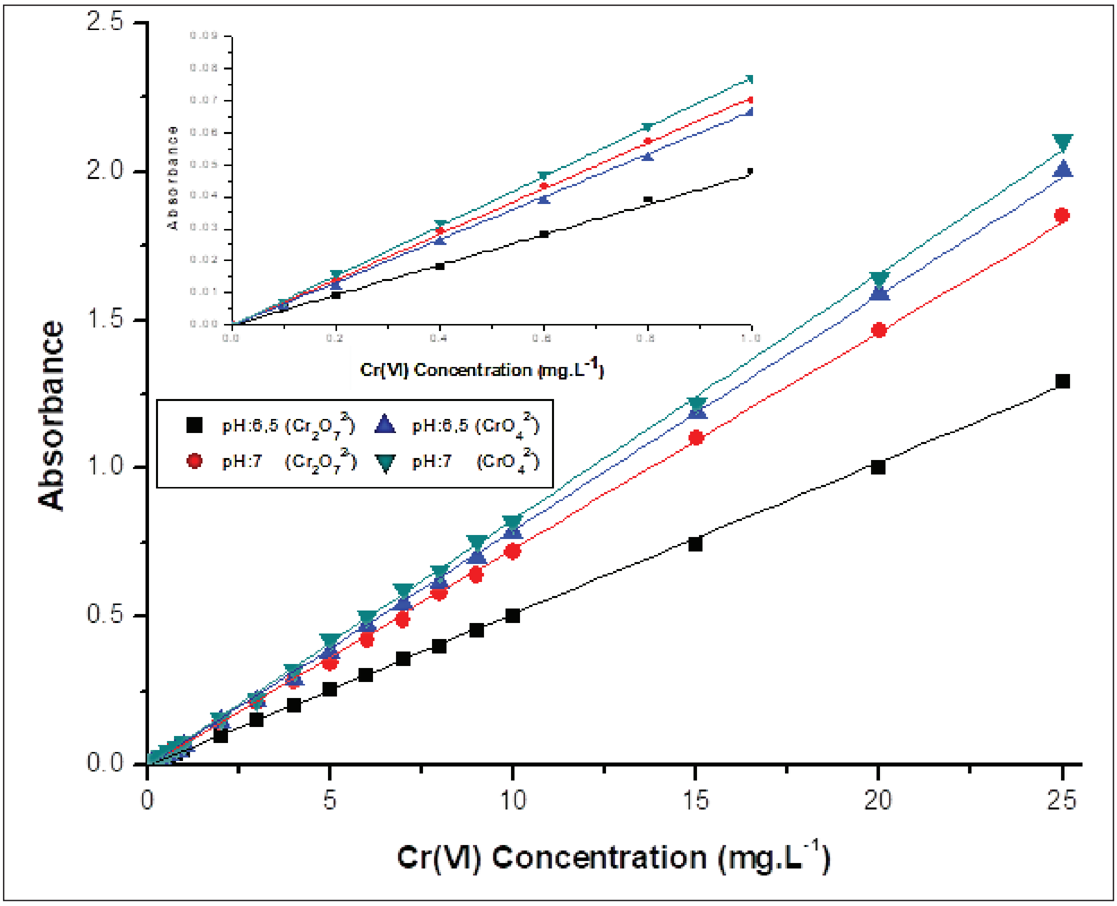

Fig. 5. Absorbance evolution of Cr(VI) solution for concentration below 10mg.L^{-1} in the pH range 6<pH<8 (372 nm)

3.2. Cr(VI) analysis

The above results imply that it is necessary to determine standard curves for acidic conditions (pH≤6) at 350 nm, and for alkaline conditions (pH≥ 8) at 372 nm. Contrary to what has been suggested in various studies, direct determination of Cr(VI) is not possible in the pH range (6 <pH<8). In these studies which were carried out at some pH values, it was suggested that Cr(VI) can be directly determined at pH< 6.4 [12] and at pH ≤7.4 [13]. The results obtained in the present study show that the Beer-Lambert law is valid for Cr(VI) concentrations up to 100 mg Cr(VI) L^{-1} at pH≤6 and up to 25 mg Cr(VI) L^{-1} at pH≥8. At higher concentrations, the absorbance does not respect the proportionality (Fig. 6). The absorbance measured at 372 nm at pH≥8, increases rapidly with the increase of Cr(VI) concentration. In these conditions, the absorbance measured for a solution with a concentration of 25 mg L^{-1} is reached for a concentration three times higher at 350nm at pH≤6.

In the two pH ranges, the proportionality is maintained up to a concentration of 0.1mg L^{-1} (Figures 7 and 8). The value of the mass absorption calculated from Beer Lambert's equation is 0.086 mg mol^{-1} cm^{-1} in acidic solutions and 0.028mg mol^{-1} cm^{-1} in alkaline solutions.

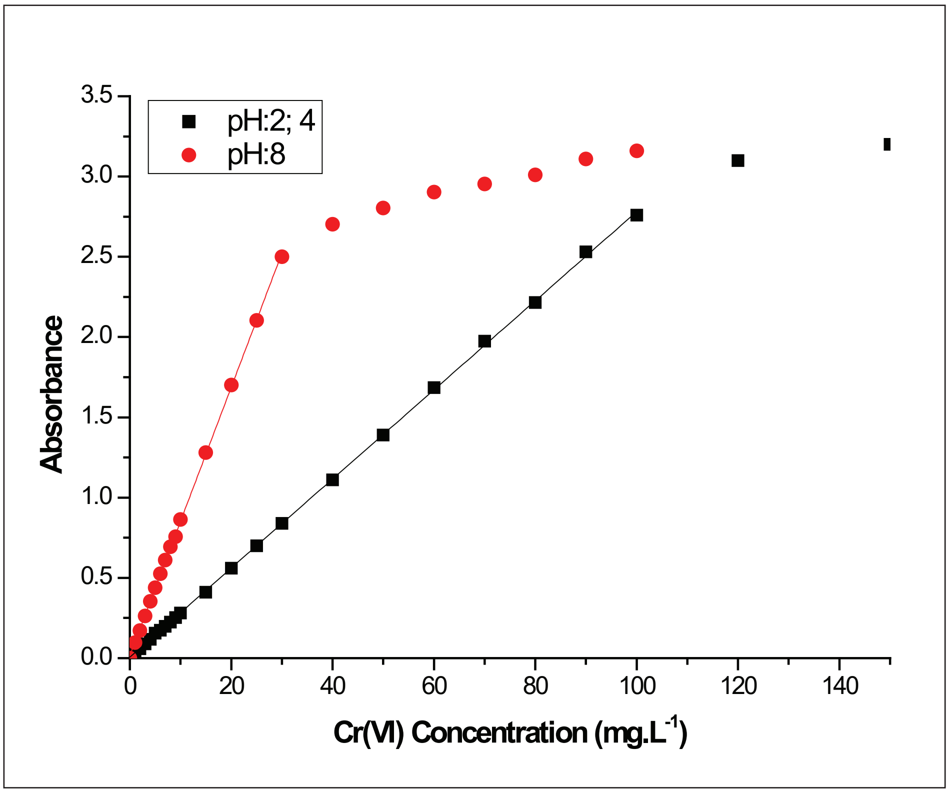

Fig. 6. Beer-Lambert law validity for Cr(VI) analysis

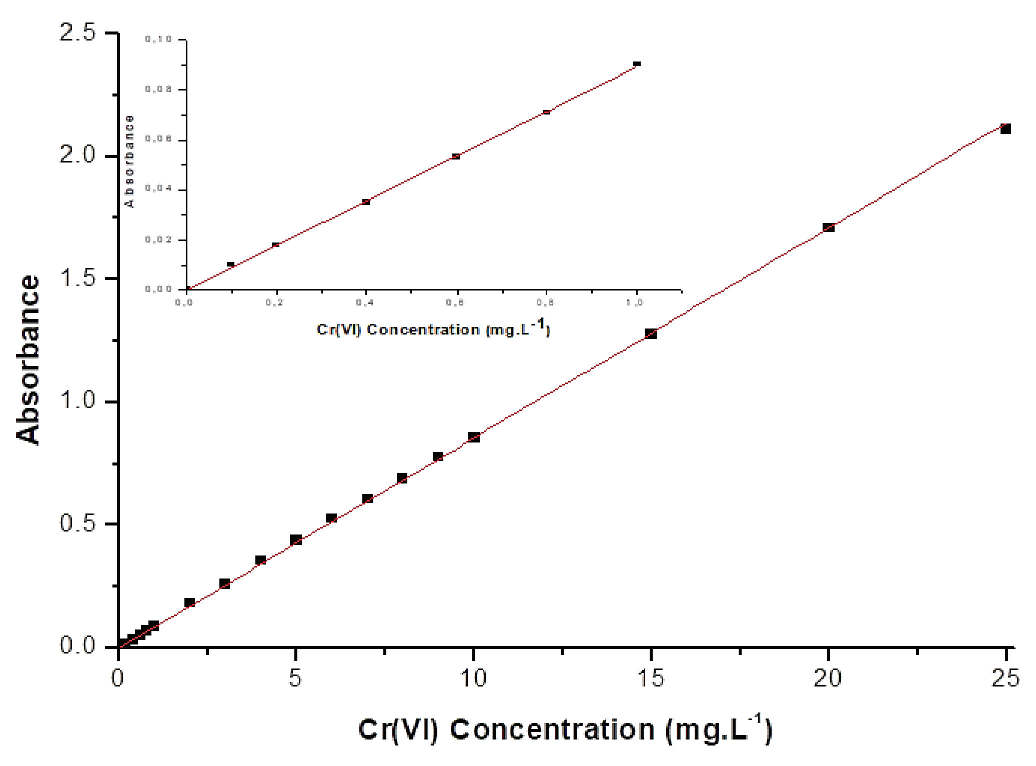

Fig. 7. Standard curve for Cr(VI) analysis at pH≤6.5 (350 nm)

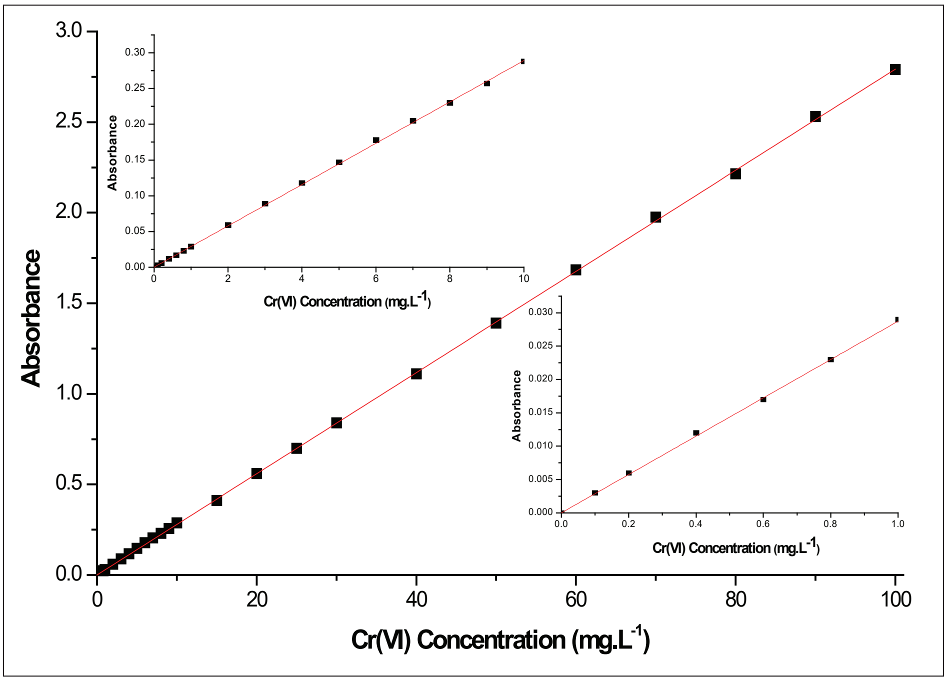

Fig. 8. Standard curve for Cr(VI) analysis at pH ≥ 8 (372nm)

At pH 2, the presence of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with a concentration five times higher than that of chromium, does not affect the direct determination of Cr(VI) whatever the salt used. With increasing pH, the nature of the chromium species seems to have an effect. At pH 4, no effect is observed in the case of dichromate salt. However, in the case of chromate salt, the presence of these metallic cations has a significant effect. At pH 8, whatever the chromium salt is used, the presence of metallic ions interferes with the direct Cr(VI) determination (Fig. 9).

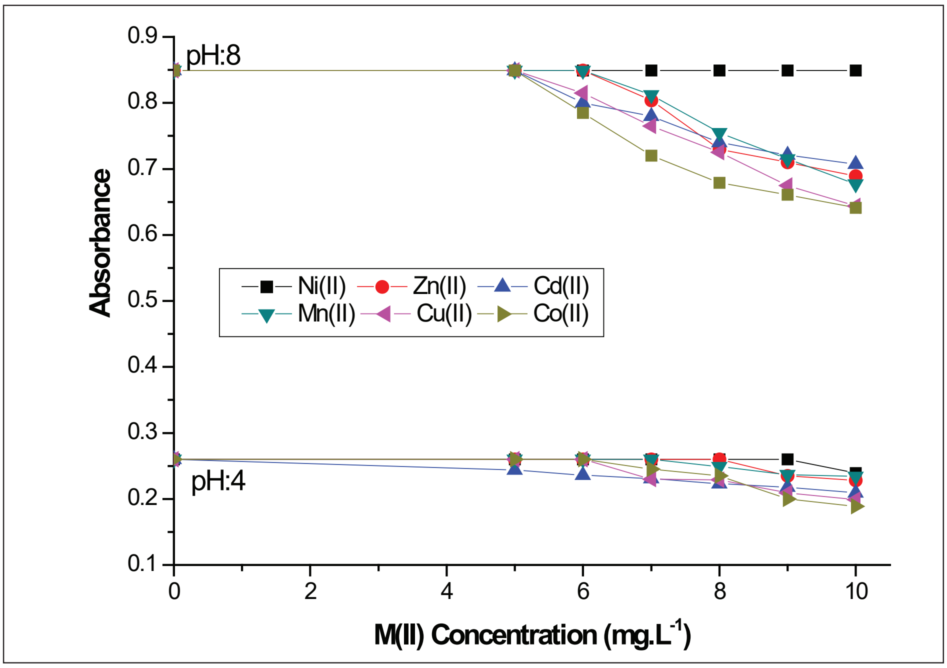

Fig.9. Effects of metallic cations (Cr(VI):10mg.L^{-1})

Whatever the pH of the solution and the Cr(VI) salt used, the presence of iron ions [Fe(III) or Fe(II)] interferes with the direct determination of Cr(VI). In their presence, the measured absorbance of the Cr(VI) solution increases significantly (Fig. 10). This is due to the interference of the absorption of the two iron chlorides which are characterized by an absorption band at about 334 nm in the case of Fe(III) and 367 nm in the case of Fe(II)._Whatever the pH, the presence of oxalate, citrate, acetate, and tartrate anions with a concentration ten times higher than that of Cr(VI) does not affect its direct determination (Fig. 11).

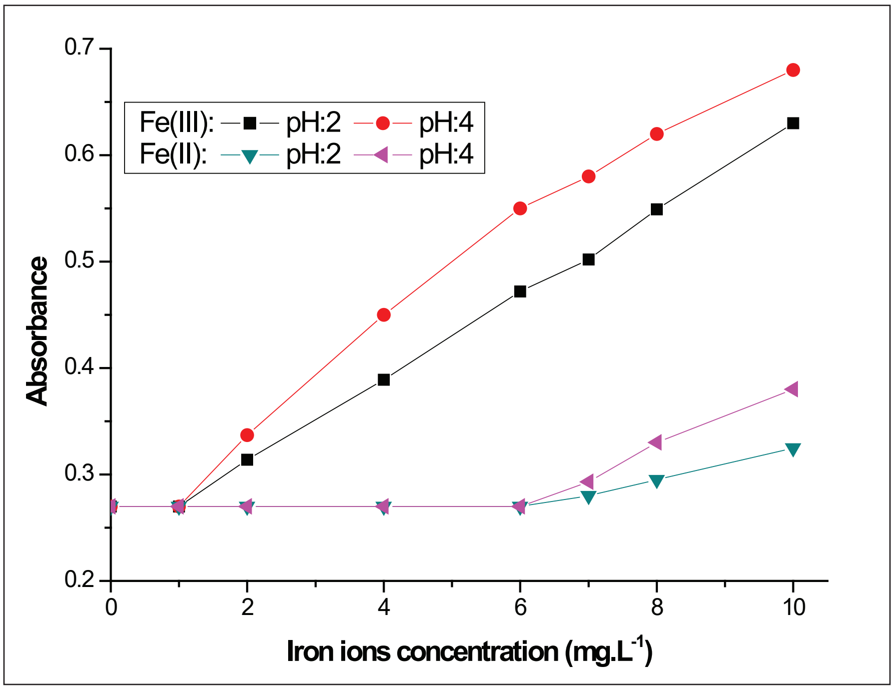

Fig. 10. Effects of iron ions (Cr(VI):10 mg L^{-1})

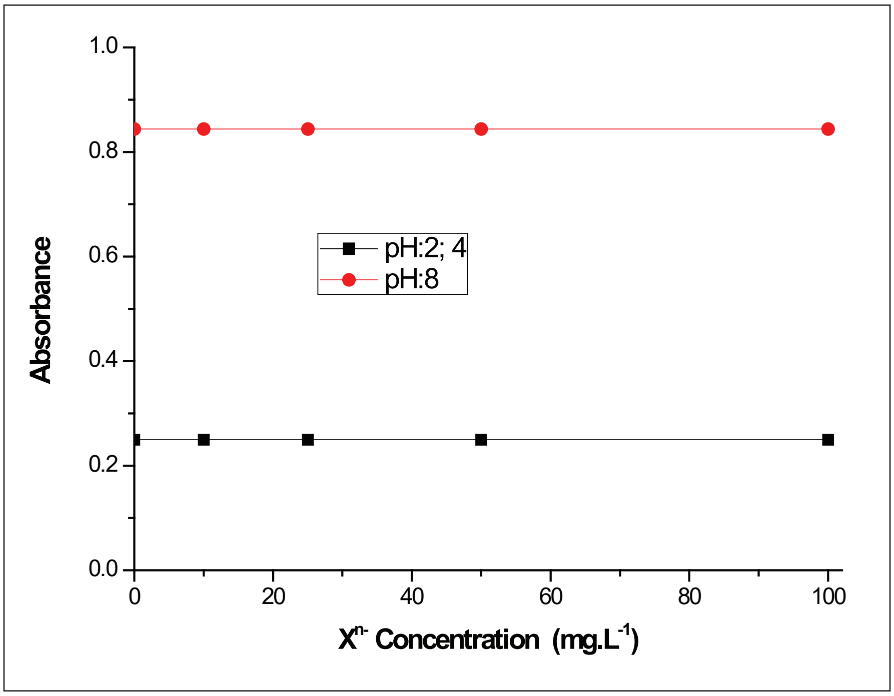

Fig. 11. Effects of anions (oxalate, citrate, tartrate, acetate) (Cr(VI):10mg.L^{-1})

4. Conclusion

The direct determination of Cr(VI) by UV-Vis spectrophotometry can be successfully applied in acidic solutions at pH≤6 and in alkaline solutions at pH ≥ 8. The presence of organic anions (oxalate, citrate, acetate, tartrate) has no effect. In the presence of metallic cations (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)), the method must be carried out at very acid pH (pH: 2). The direct determination of Cr(VI) cannot be used in the pH range 6.5<pH<8 and in the presence of Fe(II) and Fe(III).

5. References

[1] N. Esmaeili, J. Rakhtshah, E. Kolvari, H. Shikhanoo, Ultrasound assisted-dispersive-modification solid-phase extraction using task-specific ionic liquid immobilized on multiwall carbon nanotubes for speciation and determination mercury in water samples, Microchem. J., 154 (2020) 104632. https://doi.org/10.1016/j.microc.2020.104632.

[2] H. Shikhanoo, M. Habibnia, A. Rashidi, A. Faghihi Zarandi, Simultaneously speciation of mercury in water, human blood and food samples based on pyrrolic and pyridinic nitrogen-doped porous, graphene nanostructure, Food Chem., 403 (2023) 134394. https://doi.org/10.1016/j.foodchem.2022.134394

[3] T. W. Clarkson, Molecular and ionic mimicry of toxic metals, Ann. Rev. Pharmacol., 33 (1993) 545-571. https://doi.org/10.1146/annurev.pa.33.040193.002553

[4] K. Shil, S. Pal, Metabolic adaptability in hexavalent chromium-treated renal tissue: an in vivo study, Clin. Kidney J., 10 (2017) 1-8. https://doi.org/10.1093/ckj/sfx069

[5] R. M. Park, J. F. Bena, L. T. Stayner, R. J. Smith, H. J. Gibb, P. S. Lees, Hexavalent chromium and lung cancer in the chromate industry: a quantitative risk assessment, Risk Anal., 24 (2004) 1099-1108. https://doi.org/10.1111/j.0272-4332.2004.00512.x

[6] P. Cazeneuve, Sur la diphénylcarbazide, réactif très sensible de quelques composés métalliques; cuivre, mercure, fer, acide chromique, Bull. Soc. Chim., 23 (1900) 701-706. http://www.societechemicaldefrance.fr

[7] A. Wiryawan, R. Retnowati, P. Burhan, S. Syekhfani, Method of analysis for determination of the chromium (cr) species in water samples by spectrophotometry with diphenylcarbazide, J. Environ. Eng. Sustain. Technol., 5 (2018) 37-46. http://jeest.ub.ac.id

[8] A. Lace, D. Ryan, M. Bowkett, J. Cleary, Chromium monitoring in water by colorimetry using optimized 1,5-Diphenylcarbazide method, Int. J. Environ. Res. Public Health, 16 (2019) 1803-1818. https://doi.org/10.3390/ijerph16101803

[9] A. Oumedjbeur, O. Thomas, Dosage rapide du chrome (VI) dans les eaux naturelles, Analusis, 17 (1989) 221-224. https://hal.univ-smb.fr/hal-02869678v1

[10] M. C. Fournier-Salaün., P. Salaün, Quantitative determination of hexavalent chromium in aqueous solutions by UV-Vis spectrophotometer, Cent. Eur. J. Chem., 5 (2007) 1084-1093. https://doi.org/10.2478/s11532-007-0038-4

[11] O. Thomas, S. Gallot, E. Naffrechoux, Ultraviolet multiwavelength absorptiometry (UVMA) for the examination of natural waters and wastewaters, Part III. Determination of Chromium(VI), Fresenius J. Anal. Chem., 338 (1990) 241-244. https://doi.org/10.1007/BF00323016

[12] A. Sanchez-Hachair, A. Hofmann, Hexavalent chromium quantification in solution: Comparing direct UV–visible spectrometry with 1,5-diphenylcarbazide colorimetry, C. R. Chim., 21 (2018) 890-896. https://doi.org/10.1016/j.crci.2018.05.002

[13] D. Kim, J. Om, Direct spectroscopic determination of aqueous phase hexavalent chromium, Univers. J. Eng. Sci., 1 (2013) 1-4. https://doi.org/10.13189/ujes.2013.010101

[14] M.M. Eskandari, Cloud point assisted dispersive ionic liquid-liquid microextraction for chromium speciation in human blood samples based on isopropyl 2-[(isopropoxy-

carbothiolyl) disulfanyl] ethane thioate, Anal. Chem. Res., 10 (2016) 18-27. https://doi.org/10.1016/j.ancr.2016.10.002

[15] A. Khaligh, F. Golbabaei, A Vahid, On-line micro column preconcentration system based on amino bimodal mesoporous silica nanoparticles as a novel adsorbent for removal and speciation of chromium (III, VI) in environmental samples, J. Environ. Health Sci. Eng., 13 (2015) 47. https://doi.org/10.1186/s40201-015-0205-z

[16] A.A.Miran Beigi, M.M. Eskandari, Dispersive liquid-liquid microextraction based on task-specific ionic liquids for determination and speciation of chromium in human blood, J. Anal. Chem., 70 (2015) 1448-1455. https://doi.org/10.1134/S1061934815120072

[17] H.Z. Mousavi, Chromium speciation in human blood samples based on acetyl cysteine by dispersive liquid–liquid biomicroextraction and in-vitro evaluation of acetyl cysteine/cysteine for decreasing of hexavalent chromium concentration, J. Pharm. Biomed. Anal., 118 (2016) 1-8. https://doi.org/10.1016/j.jpba.2015.10.018

[18] M. Arjomandi, A review: analytical methods for heavy metals determination in environment and human samples, Anal. Methods Environ. Chem. J., 2 (2019) 97-126. https://doi.org/10.24200/amecj.v2.i03.73

[19] A. Rouhollahi, Preconcentration and determination of heavy metals in water, sediment and biological samples, J. Serb. Chem. Soc., 76 (2011) 1583-1595. https://doi.org/10.2298/JSC101024139S

[20] JD. Ramsey, L. Xia, MW. Kendig, RM. McCreery, Raman spectroscopic analysis of the speciation of dilute chromate solutions, Corros. Sci., 43 (2001) 1557-1572. https://doi.org/10.1016/S0010-938X(00)00145-1