

Photometric determination of chromium(III) and iron(III) with using Na₂EDTA

© Nikolay Yu. Kuzyakov, Viacheslav A. Veshnyakov,
Yury G. Khabarov,*[†] and Evgeny A. Skripnikov

Department of Pulp and Paper Technology. Northern (Arctic) Federal University. Severnoi Dviny St., 17.
Arkhangelsk, 163002. Russia. Phone: +7 (8182) 21-61-43. E-mail: khabarov.yu@mail.ru

*Supervising author; [†]Corresponding author

Keywords: EDTA, Na₂EDTA, iron(III), chromium(III), spectrophotometry.

Abstract

The method of photometric determination in solutions of chromium(III) and iron(III) in a simultaneous presence has been developed. The method is intended for the analysis of iron and chromium-containing technical products. The method is based on differences in the electronic spectra of chromium(III) and iron(III) complexes with Na₂EDTA. The electronic spectra of complexes with chromium(III) have absorption maxima at 394 and 584 nm. The electronic spectra of complexes with iron(III) have an absorption maximum at 470 and a shoulders at 540-560 nm and at 240-280 nm. The wavelength of 315 nm was chosen to determine iron(III), since chromium cations do not interfere. The wavelength of 660 nm was used to determine chromium(III), since iron cations do not interfere. The optimal conditions for the reaction and the metrological characteristics of the method are determined. The complex of the iron cation is formed at the moment of mixing the solutions. The complexation of the chromium(III) cation occurs slowly at room temperature. Therefore, a photometric reaction with Na₂EDTA is carried out in a boiling water bath for 5 minutes. The reaction mixture is then basified with ammonia water. Alkalization allows 2-3 times increase in absorption.

The calibration dependence for the determination of chromium(III) ions is direct (pair correlation 0.9999). To determine of iron(III), the calibration curve is parabole (Pair correlation 1). The accuracy of determining of chromium(III) and iron(III) ions is 99-104%. The results of the reaction are well repeated, the coefficient of variation does not exceed 1.4%.

References

- [1] Kirk-Othmer Encyclopedia of chemical technology: in 25 volumes. 4th Edition. Vol.6. New York: John Wiley & Sons, Inc. **2001**. 533p.
- [2] Ullmann's Encyclopedia of Industrial Chemistry. Chromium Compounds. G. Anger, J. Halstenberg, K. Hochgeschwender, C. Scherhag, U. Korallus, H. Knopf, P. Schmidt, M. Ohlinger. Wiley-VCH Verlag GmbH & Co. KGaA. **2002**. P.157-191.
- [3] J.M. Vidal, W.V. Evangelista, J. De Castro Silva, I.P. Jankowsky. Wood preservation in brasil: Historical, current scenario and trends. *Ciencia Florestal*. **2015**, Vol.25. No.1. P.257-270.
- [4] Darley H.C.H., Gray G.R. Composition and properties of drilling fluids. 5th Edition. Gulf Professional Publishing. **1988**. 643p.
- [5] F.A. Saad, M.M. Abou-Sekkina, A.M. Khedr, F.G. El-Metwaly. Synthesis, stability and DC-electrical conductivity of vanadium and chromium dual doped LiMn₂O₄ spinels as cathode material for use in lithium rechargeable batteries. *Int. J. Electrochem. Sci.* **2014**. Vol.9. P.3904-3916.
- [6] L.M. Rivera Gavidia, G. Garcia, V. Celorio, M.J. Lazaro, E. Pastor. Methanol tolerant Pt₂CrCo catalysts supported on ordered mesoporous carbon for the cathode of DMFC. *International Journal of Hydrogen Energy*. **2016**. Vol.41. No.43. P.19645-19655.
- [7] Y. Liu, Z. Feng, X. Zhou, G.E. Thompson, P. Skeldon, S.B. Lyon, S.R. Gibbon, D. Graham. Corrosion inhibition of pure aluminium and AA2014-T6 alloy by strontium chromate at low concentration. *Surface and Interface Analysis*. **2016**. Vol.48. P.804-808.
- [8] H.S. Akkera, D. Kaur. Effect of Cr addition on the structural, magnetic and mechanical properties of magnetron sputtered Ni-Mn-In ferromagnetic shape memory alloy thin films. *Applied Physics A: Materials Science and Processing*. **2016**. Vol.122. No.12. Article number 996.
- [9] P. Zhou, L. Xuepin, S. Bi. Preparation of lignosulfonate reduced chrome tanning agent and its tanning effect. *Journal of the Society of Leather Technologists and Chemists*. **2011**. Vol.25. Iss.1. P.257-270.

- [10] J. Jiang, J. Zhao. Hazards, regulations and alternatives of restricted substances in leather/textile industry: Hexavalent chromium. *Journal of the Society of Leather Technologies and Chemists*. **2014**. Vol.98. No.4. P.177-181.
- [11] P. Ma, Q. Geng, X. Gao, S. Yang, G. Liu. CuCr_2O_4 Spinel Ceramic Pigments Synthesized by Sol-Gel Self-Combustion Method for Solar Absorber Coatings. *Journal of Materials Engineering and Performance*. **2016**. Vol.25. No.7. P.2814-2823.
- [12] A.K. Lavrukhina, L.V. Yukina. Analytical chemistry of chromium. Series. Analytical chemistry of elements. Moscow: Science. **1979**. 219p. (russian)
- [13] H. Katsumata, N. Teshima, M. Kurihara, T. Kawashima. Potentiometric flow titration of iron(II) and chromium(VI) based on flow rate ratio of a titrant to a sample. *Talanta*. **1999**. Vol.48. No.1. P.135-141.
- [14] Y. Danzaki. Use of urea for eliminating chlorine formed in the determination of chromium by ammonium peroxodisulfate oxidation and potassium dichromate back titration. *Fresenius' Journal of Analytical Chemistry*. **1995**. Vol.352. No.6. P.603.
- [15] C.-Q. Li, L. Wang, C.-X. Yang. Determination of chromium in copper alloy by ferrous ammonium sulfate titration after perchloric acid treatment. *Yejin Fenxi/Metallurgical Analysis*. **2016**. Vol.36. No.2. P.71-74.
- [16] D.-X. Hu, D.-Q. Ma, H.-W. Pan, Z.-K. Wang, H. Wang, C.-G. Yao, H.-B. Wei. Study on microwave dissolution of sample for the determination of chromium sesquioxide in chrome ore by potentiometric titration. *Yejin Fenxi/Metallurgical Analysis*. **2011**. Vol.31. No.2. P.63-66.
- [17] M. Venezia, G. Alonzo, L. Palmisano. EDTA excess Zn(II) back-titration in the presence of 4-(2-pyridylazo)-resorcinol indicator and naphthol green β as inert dye for determining Cr(III) as Cr(III)/EDTA complex: Application of the method to a leather industry wastewater. *Journal of Hazardous Materials*. **2008**. Vol.151. No.2-3. P.356-363.
- [18] Y.-J. Zhang, X.-H. Li, H.-S. Li, L.-P. Pan. Determination of iron and zinc in zinc ferrite continuous titration with EDTA. *Yejin Fenxi/Metallurgical Analysis*. **2010**. Vol.30. No.3. P.53-56.
- [19] S.-P. Liu, L.-X. Yang, Y.-Z. Zhou. Determination of total iron in cold-compacted bulk for converter steelmaking with EDTA titration. *Yejin Fenxi/Metallurgical Analysis*. **2006**. Vol.26. No.1. P.72-74.
- [20] S.-F. Qi, J. Zhang, Y. Wang, S. Ning. Determination of total iron in iron ore by potentiometric titration with ascorbic acid as reducing titrant. *Yejin Fenxi/Metallurgical Analysis*. **2011**. Vol.31. No.5. P.63-66.
- [21] J. Kozak, J. Gutowski, M. Kozak, M. Wieczorek, P. Kościelniak. New method for simultaneous determination of Fe(II) and Fe(III) in water using flow injection technique. *Analytica Chimica Acta*. **2010**. Vol.668. No.1. P.8-12.
- [22] A.V. Pereira, N. Valus, F.L. Beltrame, L.H. Garrido. Determinação de ferro (III) em produtos farmacêuticos por titulação fotométrica [Determination of iron (III) in pharmaceutical products photometric titration]. *Acta Scientiarum - Health Sciences*. **2011**. Vol.33. No.1. P.65-70.
- [23] J. Kozak, N. Jodłowska, M. Kozak, P. Kościelniak. Simple flow injection method for simultaneous spectrophotometric determination of Fe(II) and Fe(III). *Analytica Chimica Acta*. **2011**. Vol.702. No.2. P.213-217.
- [24] L.S. De Carvalho, A.C.S. Costa, S.L.C. Ferreira, L.S.G. Teixeira. Spectrophotometric determination of chromium in steel with 4-(2-Thiazolylazo)-Resorcinol (TAR) using microwave radiation. *Journal of the Brazilian Chemical Society*. **2004**. Vol.15. No.1. P.153-157.
- [25] A.C. Spínola Costa, J.C. Rosa Assis, A.L. Carvalho Torres, S.L. Costa Ferreira, M.D.G. Andrade Korn, L.S. Gomes Teixeira. Uso de irradiação de microondas na determinação espectrofotométrica de cromo com EDTA. *Química Nova*. **1999**. Vol.22. No.2. P.194-196.
- [26] L. Van Tan, T. Quang Hieu, N. Van Cuong. Spectrophotometric determination of Cr(III) and Pb(II) using their complexes with 5,11,17,23-Tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene. *Journal of Analytical Methods in Chemistry*. **2015**. Vol.2015. Article ID 860649. 7p.
- [27] P. Lazo, A. Cullaj, F. Lubonja. Spectrophotometric determination of hexavalent chromium after complex formation with EDTA using H-point method. *Asian Journal of Chemistry*. **2000**. Vol.12. No.3. P.745-752.
- [28] K.A. Stancheva, B.I. Bogdanov, D.P. Georgiev, Y.H. Hristov, I.G. Markovska. Spectrophotometric determination of hexavalent chromium content in commercial cement – an assessment of the optimal conditions for the analysis of chromium(VI). *Eurasian Journal of Analytical Chemistry*. **2013**. Vol.8. No.1. P.10-16.
- [29] M.A. Zayed, B.N. Barsoum, A.E. Hassan. Spectrophotometric determination of iron and chromium in Cr-electroplating baths at the Helwan Engineering Industrial Company using pyrocatechol as indicator. *Microchemical Journal*. **1996**. Vol.54. No.1. P.72-80.
- [30] K. Suwardhan, S. Ramanaiah, K. Suresh Kumar, D. Rekha, Umayur Bhagan, G.R.K. Naidu, G. Krishnamurthy Naidu, B.S. Sastry, P. Chiranjeevi. Spectrophotometric Determination of Chromium in Water and Pharmaceutical Samples Using 1-Naphthol. *E-Journal of Chemistry*. **2005**. Vol.2. No.1. P.6-14.
- [31] S. Chen, X. Zhang, L. Yu, L. Wang, H. Li. Simultaneous determination of Cr(III) and Cr(VI) in tannery wastewater using low pressure ion chromatography combined with flow injection spectrophotometry. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*. **2012**. Vol.88. P.49-55.

Full Paper

- N.Yu. Kuzyakov, V.A. Veshnyakov, Yu.G. Khabarov, and E.A. Skripnikov
- [32] H. Vašková, K. Kolomazník. Determination of trivalent and hexavalent chromium by Raman spectroscopy. *CORALS–2013 (Conference on Raman and Luminescence Spectroscopy in the Earth Sciences)*. **2013**. P.105-106.
- [33] H. Vašková, K. Kolomazník. Spectroscopic measurement of trivalent and hexavalent chromium. *17th International Carpathian Control Conference (ICCC)*. **2016**. P.775-778.
- [34] O.P. Shvoeva, V.P. Dedkova, S.B. Savvin. Adsorption-spectroscopic method for multielement analysis: Determination of Cr(VI), V(V), Ni(II), and Cu(II) from one sample using a two-layer adsorbent. *Journal of Analytical Chemistry*. **2010**. Vol.65. No7. P.699-703. (russian)
- [35] V.P. Dedkova, O.P. Shvoyeva, S.B. Savvin. Sorption-spectrometric determination of zirconium and chromium (VI) from one sample on a two-layer carrier with reagents of arsenazo III and 1,5-diphenylcarbazide. *Journal of Analytical Chemistry*. **2013**. Vol. 68. No 2. P.130. (russian)
- [36] H. Filik, D. Giray. Cloud point extraction for speciation of iron in beer samples spectrophotometry. *Food Chemistry*. **2012**. Vol.130. No.1. P.209-213.
- [37] T.F. Rudometkina, V.M. Ivanov. Spectrophotometric determination of macroquantities of iron and titanium in real-world objects. *Moscow University Chemistry Bulletin*. **2011**. Vol.66. No5. P.315-317. (russian)
- [38] T. Shamspur, I. Sheikhshoaei, M.H. Mashhadizadeh. Flame atomic absorption spectroscopy (FAAS) determination of iron(III) after preconcentration on to modified analcime zeolite with 5-((4-nitrophenylazo)-N-(2',4'-dimethoxyphenyl)) salicylaldimine column method. *J. Anal. At. Spectrom.* **2005**. Vol.20. No.5. P.476-478.
- [39] E.O. Jorge, M.M. Rocha, I.T.E. Fonseca, M.M.M. Neto. Studies on the stripping voltammetric determination and speciation of chromium at a rotating-disc bismuth film electrode. *Talanta*. **2010**. Vol.81. No.1-2. P.556-564.
- [40] M. Grabarczyk. Protocol for extraction and determination of Cr(VI) in solid materials with a high Cr(III)/Cr(VI) ratio using EDDS as a leaching agent for Cr(VI) and a masking agent for Cr(III). *Electroanalysis*. **2008**. Vol.20. No.17. P.1857-1862.
- [41] H.A. Zamani, S. Sahebnasagh. Potentiometric detection of Cr³⁺ ions in solution by a chromium(III) electrochemical sensor based on diethyl 2-phthalimidomalonate doped in polymeric membrane. *International Journal of Electrochemical Science*. **2013**. Vol.8. P.3708-3720.
- [42] P. Kubáň, P. Kubáň, V. Kubáň. Speciation of chromium(III) and chromium(VI) by capillary electrophoresis with contactless conductometric detection and dual opposite end injection. *Electrophoresis*. **2003**. Vol.24. No.9. P.1397-1403.
- [43] A. Manova, S. Humenikova, M. Strelec, E. Beinrohr. Determination of chromium(VI) and total chromium in water by in-electrode coulometric titration in a porous glassy carbon electrode. *Microchimica Acta*. **2007**. Vol.159. No.1-2. P.41-47.
- [44] O.V. Popova, V.V. Sursyakova, G.V. Burmakina, A.I. Rubaylo. Determination of iron and copper ions in cognacs by capillary electrophoresis. *Journal of Analytical Chemistry*. **2015**. Vol.70. No.2. P.198-202. (russian)
- [45] J. Threeprom, W. Som-Aum, J.-M. Lin. Determination of Pb(II), Cu(II) and Fe(III) with capillary electrophoresis using ethylenediaminetetraacetic acid as a complexing agent and vancomycin as a complex selector. *Analytical Sciences*. **2006**. Vol.22. No.9. P.1179-1184.
- [46] F. Wei, J.S. Huo, J. Huang, W.X. Li. Capillary zone electrophoretic determination of NaFeEDTA in iron fortified soy sauce. *Wei sheng yan jiu = Journal of hygiene research*. **2006**. Vol.35. No.1. P.103-106.
- [47] R. Michalski. Trace level determination of Cr(III)/Cr(VI) in water samples using ion chromatography with UV detection. *Journal of Liquid Chromatography & Related Technologies*. **2005**. Vol.28. No.18. P.2849-2862.
- [48] A.F. Geddes, J.G. Tarter. The ion chromatographic determination of Cr(III)-Cr(VI) using an edta eluant. *Analytical Letters*. **1988**. Vol.21. No.5. P.857-867.
- [49] W.-D. Xu, R. Sun, X.-Q. Wen. Study on the adsorption behavior of ion exchange chromatographic microcolumn to chromium(VI) and its analytical application. *Yejin Fenxi/Metallurgical Analysis*. **2010**. Vol.30. No.7. P.72-75.
- [50] E.H. Borai, E.A. El-Sofany, A.S. Abdel-Halim, A.A. Soliman. Speciation of hexavalent chromium in atmospheric particulate samples by selective extraction and ion chromatographic determination. *TrAC - Trends in Analytical Chemistry*. **2002**. Vol.21. No.11. P.741-745.
- [51] W.-P. Yang, Z.-J. Zhang, W. Deng. Speciation of chromium by in-capillary reaction and capillary electrophoresis with chemiluminescence detection. *Journal of Chromatography A*. **2003**. Vol.1014. No.1-2. P.203-214.
- [52] L. Zheng, D.G. Watson, J.N.A. Tettey, C.A. Clements. The determination of iron as its EDTA complex in *Helix aspera* hydrophilic interaction liquid chromatography coupled to Fourier transform electrospray ionisation mass spectrometry. *Talanta*. **2008**. Vol.76. No.5. P.1165-1169.

- [53] J.-F. Jen, C.-S. Chen. Determination of metal ions as EDTA complexes reversed-phase ion-pair liquid chromatography. *Analytica Chimica Acta*. **1992**. Vol.270. No.1. P.55-61.
- [54] R. Ripan, I. Chetyanu. Inorganic chemistry. Chemistry of metals. Vol. 2. Moscow: Mir. **1972**. 871p. (russian)
- [55] M. Wacker, A. Seubert. Determination of stability constants of strong metal-ligand complexes using anion or cation exchange chromatography and atomic spectrometry detection. *J. Anal. At. Spectrom.* **2014**. Vol.29. P.707-714.
- [56] S. Pozdniakova, A. Padarauskas. Speciation of metals in different oxidation states by capillary electrophoresis using pre-capillary complexation with complexones. *Analyst*. **1998**. Vol.123. No.7. P.1497-1500.
- [57] T.F. Rudometkina, V.M. Ivanov. Photometric determination of chromium in natural and industrial objects in the form of ethylenediaminetetraacetates. *Moscow University Chemistry Bulletin*. **2013**. Vol. 68. No.3. P.151-153. (russian)
- [58] H. Bennett, K. Marshall. The separation and determination of chromium sesquioxide in chrome ores and chrome-bearing refractories. *Analyst*. **1963**. Vol.88. No.1052. P.877-881.
- [59] P. Jeffery. Chemical methods of rock analysis. Moscow: Mir. **1973**. 470p. (russian)
- [60] Yu.V. Karyakin, I.I. Angelov. Pure chemicals. Moscow: Chemistry. **1974**. 408p. (russian)
- [61] H. Von Brintzinger, H. Tiefe, U. Müller. Komplexverbindungen und Salze der Äthylendiamintetraessigsäure. *Zeitschrift fur anorganische und allgemeine Chemie*. **1943**. Bd.251. P.285-294.
- [62] K. Kanamori, K. Kawai. Raman spectral study on the solution structure of the chromium(III)-edta complex. *Inorganic Chemistry*. **1986**. Vol.25. No.20. P.3711-3713.
- [63] R. Meier, F.W. Heinemann. Structures of the spontaneously resolved six-coordinate potassium chloro-(ethylenediaminetriacetato acetic acid) iron(III) monohydrate and the seven-coordinate potassium (ethylenediaminetetracetato) iron(III) sesquihydrate. *Inorganica Chimica Acta*. **2002**. Vol.337. P.317-327.