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The Influence of Foreign Ions on Determination and Speciation of Cr(VI) and Cr(III) from Water Samples

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Abstract: This study reports: a) the content of Ca, Cd, Co, Cr(III), Cr(VI), Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn in wastewater from metal industries and rivers that flow near the metal processing industries; b) the possibility of quantitative determination of Cr(III) and Cr(VI) in the presence of the following cations: Fe^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, $Mn^{2+;}$ and Zn^{2+} and anions Cl^-, NO_3^-, and SO_4^{2-}; c) speciation of Cr(III) and Cr(VI) on silica gel modified with Nb_2O_5 . Metals were determined by flame atomic absorption spectrometry, except for Na and K, which were determined by atomic emission spectrometry, and Cr(VI) by ultraviolet-visible spectrophotometry. When the concentration of cations is higher than Mg^{2+} (>25 mg/L), Ni^{2+} (>100 mg/L), Fe^{3+} (>250 mg/L), Zn^{2+} (>500 mg/L), and Mn^{2+} (>1000 mg/L), an error greater than 10 % is obtained in the measurement of Cr(III) . Silica gel modified with Nb_2O_5 can be considered as an effective solid phase extraction adsorbent for speciation of Cr species and simultaneous concentration of Cr(III). The proposed method was successfully applied to the speciation and determination of Cr(III) and Cr(VI) in the analyzed samples. The content of almost all analyzed metals has been below the permitted values for wastewaters.

INTRODUCTION

Despite different efforts to decrease it, the continuous pollution of surface water is a global issue that is not going away. The prosperous age of the industrial revolution and its modernization, along with reckless industrial operations, has sadly resulted in the degradation of the ecosystem, putting the environment in perilous conditions. As a result, harmful contaminants from diverse industrial processes have contaminated an increasing amount of surface water. Many ecosystems have disappeared as a result of this tragic issue, and many people have been left in excruciating health conditions that require constant medical monitoring (Rajput et al., 2017; Nkutha et al., 2021). The importance of chromium (Cr) speciation originates from the widespread participation of this element in various environmental and biological samples. The major sources of Cr in the environment are steel, electroplating, tanning, and chemical industries, oxidative dyeing, cooling water towers, corrosion inhibitors used in water pipes and containers, and sanitary landfill leaching (Kotas and Stasicka 2000; Dong, Chen, and Chen, 2013). The acidity and a significant concentration of Cr compounds in the wastewater make the Cr industry a high environmental concern. Industrial wastewater is the major source of pollutants that pollute the environment. Large amounts of industrial waste have been released into rivers, lakes, and coastal areas during the past century. This has resulted in a significant water contamination problem, as well as detrimental consequences for the ecosystem and human life. Increased metal concentrations in wastewater from the metal industry are hazardous to the aquatic ecology and can be lethal (Nkutha, Naidoo, and Shooto, 2021). It has been widely recognized that the impact of detrimental heavy metals on the ecological system, biological organisms, as well as human health does not only depend on the total amount of the element but also significantly depends on its chemical forms (Kot and Namiesnik, 2000). Cr(III) and Cr(VI), the two most stable oxidation states of Cr, have different biological activities and toxic effects on living organisms (Narin, Soylak, and Kayakirilmaz et al., 2002). Chromium (III) is less toxic and less soluble than Cr(VI) and is an essential micronutrient for most biota, including humans.

Chromium(VI) is generally soluble and toxic to many plants, animals, and microorganisms in the aquatic environment, and Cr(VI) is considered mutagenic and carcinogenic (Losi, Amrhein, Frankenberger, 1994). The Cr content in surface waters should be very low, usually between 0.3 and 6 µg/L (Rakhunde, Deshpande, Juneja, 2012). Due to all of the above mentioned, and mainly because of the toxicity of certain forms of Cr, it is necessary to perform Cr speciation. Chemical precipitation, ion exchange, and solid-phase extraction are methods used for Cr preconcentration and speciation (Sarzanini, Abolino, and Mentastri, 2001; Aydin and Soylak, 2007;Tuzen and Soylak 2007;Sulejmanović et al., 2015; Tiwari, Sharma, and Saxena, 2016; Pyrzynska, 2020). Adsorption has emerged as one of these techniques that is both effective and affordable. In trace element analysis, the two most common adsorbents are activated carbon and silica gel. Today, solid-phase extraction is a very useful technique, widely spread as part of sample preparation procedures for the determination of various inorganic and organic analytes (Chahal et al., 2012). A measurement procedure that provides quantitative and qualitative information on the chemical forms of an element in various samples is known as speciation analysis. Separation and determination are the two most common phases in speciation analysis (Kumral, 2007). The objectives of this study were: (1) to determine the content of the following metals: Ca, Cd, Co, Cr(III), Cr(VI), Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn in river waters that flow in the vicinity of metal processing industry and in wastewater of the metal industries (2); quantitative determination of Cr(III) and Cr(VI) in the presence of the following cations: Fe^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} which are added to model solutions as chloride or nitrate salts at the concentration range of 10 - 2000 mg/L; (3) the influence of Cl^-, NO_3^- on the quantitative determination of Cr(III) and Cr(VI) which are added to model solutions in the form of sodium, potassium and ammonium salts and SO_4^{2-} in the form of potassium salt so that their concentration range is 10 - 2000 mg/L; (4) speciation of Cr(III) and Cr(VI) on silica gel modified with Nb_2O_5.

EXPERIMENTAL

Instruments

A Varian model Fast Sequential Atomic Absorption Spectrometer, AA240FS was used for the determination of Ca, Cd, Co, Cr(III), Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn. Spectrophotometer type Cary 50 (Varian) was used for spectrophotometric determination of Cr(VI) at $\lambda = 545$ nm using 1 cm glass cells.

Chemicals and reagents

All chemicals used were of analytical grade purchased from Merck (Darmstadt, Germany). Doubly distilled water was used throughout the experiment.

Stock solutions (1.000 mg/L) of Cr(VI) were prepared by dissolving 0.7856 g of $K_2Cr_2O_7$, previously dried for 2 hours at 175 °C, and diluted in doubly distilled water to 250 mL A working solution with a concentration of Cr (VI) of 50 mg/L was prepared by diluting the stock solution. Stock solutions of cations (5.000 g/L): Fe^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}were prepared by dissolving appropriate amounts of the chloride and nitrate salts.

Stock solutions of anions (5.000 g/L): Cl^-, NO_3^-, SO_4^{2-}, were prepared by dissolving appropriate amounts of the following salts: NaCl, $NaNO_3$, NH_4Cl, NH_4NO_3, KNO_3, KCl, K_2SO_4. A 0.5 % solution of 1,5-diphenylcarbazide was prepared by dissolving appropriate amounts of this reagent in acetone. A fresh solution was prepared every day.

General procedure

Silica gel was modified with Nb_2O_5 according to the procedure by Music (2010), since this study described the used sorbent as an effective sorbent for the speciation of Cr because it acts as a cationic ion exchanger. of silica gel (250 mg) modified with Nb_2O_5 (sorbent) was weighed on an analytical balance (Mettler Toledo New Classic MF, model: ML204/01, Switzerland), which was then quantitatively transferred to the columns. Solutions containing a mixture of Cr(III) and Cr(VI), then a solution of Cr(III) or Cr(VI), and solutions containing Cr(III) and the metal being tested as an interference were passed through the columns. According to Musić (2010) the optimal pH value for Cr speciation analysis is pH 9. In the process of speciation of Cr(III) and Cr(VI) ions, a self-made glass tube column filled with 250 mg of silica gel modified with Nb_2O_5 was used. The solutions that passed through the columns contained metals at a concentration of 0.1 mg/L in a 100 mL volumetric flask. According to Musić (2010), in order to achieve efficient retention of the metal of interest on the given sorbent and to adjust the analyte flow through the column, the specified buffer (pH 9) was first passed through the column. The buffer solution was prepared by dissolving an appropriate amount of disodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in distilled water, and the pH was adjusted using 0.1 mol/L HCl. After that, standard metal solutions were passed through the columns at a flow rate of 2 mL/min. The adsorbed metals were eluted with 8 mL HNO_3 (1 mol/L), in a 10 mL measuring vessel. During the speciation analysis, Cr(III) is retained on the sorbent, and Cr(VI) passes through the column unhindered because it is present in aqueous solutions as CrO_4^{2-}, $Cr_2O_7^{2-}$ and $HCrO_4^-$ (Martendal et al., 2009).

A series of model solutions containing Cr(III) and Cr(VI) and metals in varied concentrations (10 mg/L–2000 mg/L) were created and treated according to the devised method (Musić, 2010) for the determination and speciation analysis of Cr species.

Wastewater and river water analysis

The ISO standard method was used for sampling (ISO, 2014). Water samples were collected in polyethylene bottles. River samples were taken during stable weather conditions at four locations in Bosnia and Herzegovina (BiH): Ilijaš, Misoća, Vogošća and Vareš. The sampling sites were in rivers flowing near industries. Wastewater samples, from the electroplating industries, were collected before discharge into the recipient (river water). The concentrations of Cr(III), Cu, Mn, Fe, Co, Ni, Cd, Pb, Zn, Ca, and Mg were determined using flame atomic absorption spectrometry (FAAS), and the concentrations of Na and K by flame atomic emission spectrometry

(FAES). Cr(VI) was determined from the original samples by ultraviolet and visible (UV/Vis) spectrophotometry.

Quality control

Recovery evaluations were conducted to ensure the accuracy of the research. Real samples of river water and wastewater were spiked with the standard solution of each metal at three different levels of concentration to cover the measurement range. The recovery values for all metals determined ranged from 86% to 104%. Recovery values are presented in table 1. For model solutions, the results are presented as recovery values in Tables 2 and 3, and on Fig. 2 – Fig. 7.

Table 1. Recovery values of spiked real river water and wastewater samples

Metals	**Recovery (%)**	
	River water	**Wastewater**
Cr(III)	97	98
Cr(VI)	90	91
Cu	95	96
Mn	98	99
Fe	95	95
Co	86	86
Ni	88	88
Cd	93	93
Pb	98	97
Zn	103	103
Ca	101	104
Mg	99	100
Na	93	93
K	96	97

The detection limits (LOD) were calculated as three times standard deviation of the blank solution signal. The LOD values were: Ca (0.001 mg/L), Cd (0.002 mg/L), Co (0.005),Cr(III) (0.006 mg/L), Cr(VI) (0.02),Cu (0.003 mg/L), Fe (0.006 mg/L), K (0.003 mg/L), Mg (0.0003 mg/L), Mn (0.002 mg/L), Na (0.0002 mg/L), Ni (0.01 mg/L), Pb (0.01 mg/L), Zn (0.001 mg/L).

Influence of cations and anions on determination of Cr(III)

First, 25 µL of the sample solution containing 1000 mg/L Cr(III) and 1000 mg/L Cr(VI) was placed in a 25 mL volumetric flask, then the tested cations (Fe^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}) were added separately to the volumetric flasks so that their concentrations were 10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 250 mg/L, 500 mg/L, 1000 mg/L, 1500 mg/L and 2000 mg/L. The same procedure described above was performed with anions (Cl^-, NO_3^-, SO_4^{2-}). For each model solution, a blank solution containing the interfering metal or anion as well as doubly distilled water was prepared. The concentration of Cr(III) in the prepared solutions was determined by FAAS.

Influence of cations and anions on determination of Cr(VI)

For the spectrophotometric determination of Cr(VI), an absorption spectrum was first recorded with the objective to determine the wavelength (λ) of the maximum absorption of the colored complex Cr(VI) and diphenylcarbazide (DPC) in a range of (450–650) nm (Fig. 1). Measurements were performed using a standard solution containing 0.5 mg/L of Cr(VI), 1 mL of (1:1) H_2SO_4 (*v*/*v*), and 1 mL of 0.5% DPC. The reaction is selective for Cr(VI) and very sensitive. that The maximum absorption for Cr(VI)-DPC colored complex was found to be at 545 nm. The influence of cations and anions on the direct spectrophotometric determination of Cr(VI) was also investigated for determination of Cr(III). First, 250 µL of the working solution (50mg/L Cr(VI)) was placed in a 25 mL volumetric flask, the tested cations and anions were added separately to the volumetric flasks in the same concentration range as for the determination of Cr(III), and Cr(VI) was complexed with 1 mL of 0.5% DPC in the presence of 1 mL of (1:1) H_2SO_4 (*v*/*v*). A blank solution was prepared for each model solution (interfering metal or anion, 1 mL (1:1) H_2SO_4 (*v*/*v*), 1 mL 0.5% DPC, and doubly distilled water).

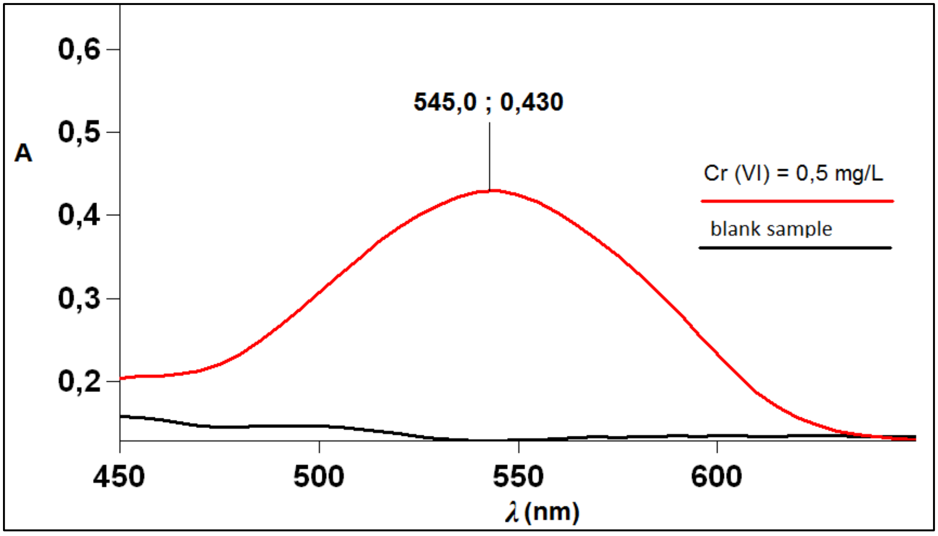

Fig. 1 - Spectral responses of Cr(VI) solution in the range from 450 to 650 nm.

RESULTS AND DISCUSSION

Influence of coexisting cations on determination of Cr(III)

Matrix effects are a very problematic point in the instrumental detection of trace metal species (Unsal, Tuzen, and Soylak, 2014). The influence of cationic chloride and nitrate salts on the recovery values of Cr(III) was investigated separately. The results obtained are given in Figs. 2 and 3.

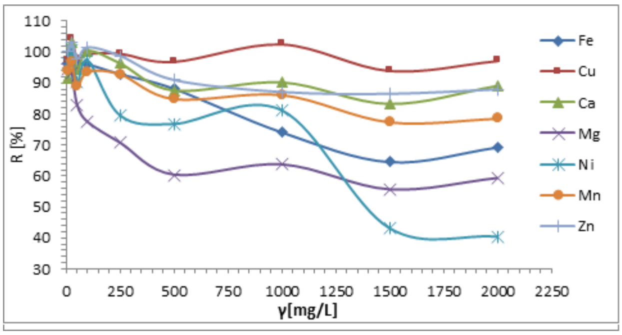

Fig. 2 - Recovery values for Cr(III) in presence of cation chloride salts.

Figure 2 shows that Ca^{2+} and Cu^{2+} in all concentration ranges (10-2000 mg/L) do not affect the measurement of Cr(III), since the error in the determination of Cr(III) was lower than 10%. The error in the measurement of the Cr(III) is higher than 10% in the presence of these cations: Mg^{2+} (> 25 mg/L), Ni^{2+} (> 100 mg/L), Fe^{3+} (> 250 mg/L), Zn^{2+} (> 500 mg/L) and Mn^{2+} (> 1000 mg/L).

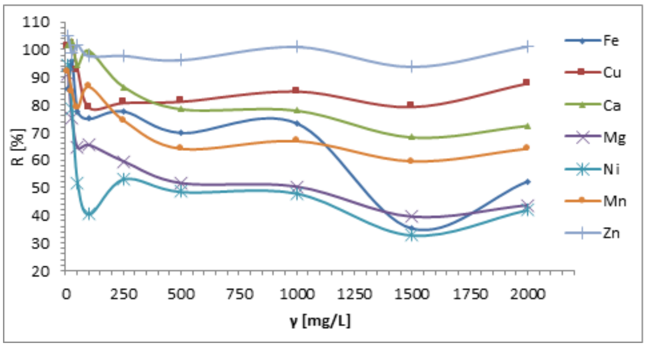

Fig. 3- Recovery values for Cr(III) in presence of cation nitrate salts.

The obtained results for cations in nitrate salts (Fig. 3) show that only in the presence of Zn^{2+}, the recovery values for Cr(III) are at the maximum recovery value (~100%). The error of Cr(III) measurement is higher than 10% when the concentration of metal ions is higher than Mg^{2+}, Ni^{2+}, and Fe^{3+} (> 25 mg/L), Cu^{2+} and Mn^{2+} (> 50 mg/L), and Ca^{2+} (> 100 mg/L). The lowest recovery values for Cr(III) were achieved in the presence of nickel as $Ni(NO_3)_2$. If the Ni^{2+} concentration is 25 mg/L, the recovery value for Cr(III) is 78.55%, and if the Ni^{2+} concentration is 1500 mg/L, the recovery value is only 32.95%.

Influence of coexisting anions on determination of Cr(III)

Recovery values for Cr(III) in the presence of Cl^-, NO_3^-, and SO_4^{2-} ions are presented in Table 2.

It is clear from the results that chloride ions do not interfere with the determination of Cr(III) because the recovery values ranged from 95% to 106% whether chloride ions were added as potassium, sodium, or ammonium salt in all ranges of concentration (10 mg/L to 2000 mg/L).

Table 2 - Recovery values for Cr(III) in presence of anions

Concentration of anion	**10 mg/L**	**25 mg/L**	**50 mg/L**	**100 mg/L**	**250 mg/L**	**500 mg/L**	**1000 mg/L**	**1500 mg/L**	**2000 mg/L**
Salts	**R for Cr(III)(%)**								
KCl	102.25	98.90	96.55	94.35	98.95	101.35	103.80	102.15	106.45
NH_4Cl	98.45	98.10	99.25	99.10	96.45	97.55	97.85	94.60	96.85
NaCl	96.35	97.30	99.90	100.60	102.50	101.50	104.01	103.50	102.40
KNO_3	98.85	98.45	100.55	100.25	101.05	100.45	101.55	102.45	105.80
NH_4NO_3	87.35	87.55	84.55	81.05	87.15	86.45	93.40	89.10	94.95
$NaNO_3$	111.90	110.65	113.95	118.25	113.10	112.20	110.35	112.10	109.50
K_2SO_4	96.35	114.90	116.30	115.15	115.30	114.70	118.75	117.15	113.30

The lowest recovery values for Cr(III) were in the presence of NH_4NO_3. The recovery values in this case ranged from 87.35% for 10 mg/L of NO_3^- anion to 94.95% for 2000 mg/L of NO_3^- anion. If the nitrate anion was added to the solution as potassium salt, the recovery values for Cr(III) were 98.85% when the concentration of NO_3^- was 10 mg/L and increased with increasing nitrate concentrations.

Recovery values for Cr(III) are higher than 110% if the nitrate anion is present in the solution in the form of a sodium salt. Table 2 shows that SO_4^{2-} anion has an influence on the recovery values for Cr(III) if it is present in a concentration higher than 10 mg/L.

Influence of coexisting cations on determination of Cr(VI)

After it was established that Cr(VI) ions have no affinity to be retained on silica gel modified with Nb_2O_5, the influence of the cations and anions on the quantitative determination of Cr(VI) was investigated using model solutions. The results are presented in Fig.4 (chloride salts), and Fig.5 (nitrate salts).

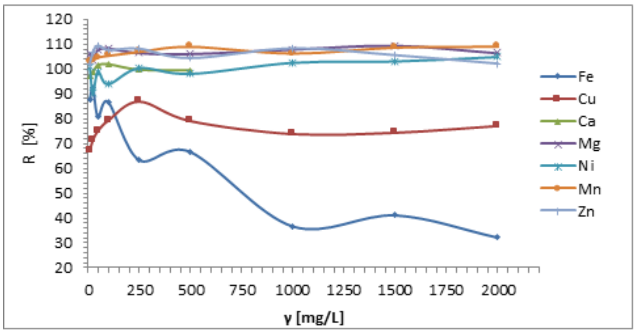

Fig. 4 - Recovery values for Cr(VI) in presence of cation chloride salts.

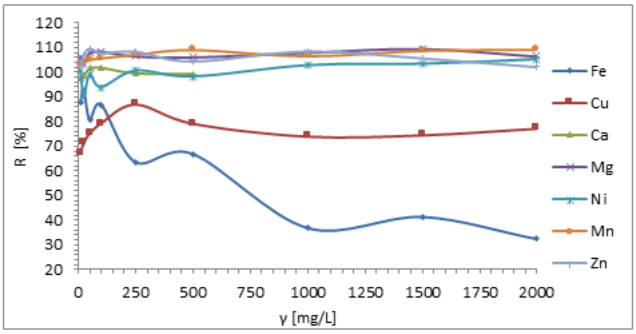

Fig. 5 - Recovery values for Cr(VI) in presence of cation nitrate salts.

As a result, Fe^{3+} ions clearly interfere with the determination of Cr(VI). Since the recovery values are around 80%, the quantitative determination of Cr(VI) is not possible if the concentration of Fe^{3+} is greater than 250 mg/L (chloride salts) or 100 mg/L (nitrate salts). Also, the color of the solutions changed from purple to red as the concentration of Fe^{3+} ions increased.

When copper ions were added to the solution, the recovery values for Cr(VI) were approximately 80% when the copper concentration was less than 500 mg/L; when the concentration of Cu(II) increased to 2000 mg/L, the recovery value for Cr(VI) was 52.16% (this occurs in the presence of chloride salt). When the Ca^{2+} ion concentration exceeds 500 mg/L, a white precipitate is formed, which makes quantitative determination of Cr(VI) impossible; Ca^{2+} concentrations less than 500 mg/L have no effect on the determination of Cr(VI). The error in the measurement of Cr(VI) is not higher than 10% in the presence of these ions Mg^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}.

Recovery values for Cr(VI) in the presence of Cl-, $NO_3^-$and SO_4^{2-} ions are presented in Table 3.

Table 3 - Recovery values for Cr(VI) in presence of anions

Concentration of anion	10 mg/L	25 mg/L	50 mg/L	100 mg/L	250 mg/L	500 mg/L	1000 mg/L	1500 mg/L	2000 mg/L
Salts	**R for Cr(VI) (%)**								
KCl	96.22	101.30	97.66	101.12	103.20	101.88	103.90	103.28	105.78
NH_4Cl	100.96	99.28	94.62	94.14	95.34	97.62	96.96	98.82	96.23
NaCl	102.50	97.50	100.80	98.90	102.60	101.10	100.70	99.20	102.00
KNO_3	103.64	100.48	96.90	95.84	99.64	95.76	100.78	97.42	100.28
NH_4NO_3	100.44	98.52	97.66	97.72	96.32	97.30	99.56	95.90	98.80
$NaNO_3$	91.48	92.36	94.00	99.78	92.88	92.70	98.26	97.42	99.88
K_2SO_4	101.58	97.80	100.18	99.54	101.74	98.66	104.32	102.14	103.76

The recovery values for Cr(VI) were around 96% when the Cl^- ion was added to the solution as KCl (the concentration of Cl^- ion was 10 mg/L), and recovery values increased with increasing chloride concentrations up to 105.78% for 2000 mg/L of Cl^- ions. The concentration of Cl^-ions had no effect on the recovery values of Cr(VI) when chloride ions were added in the form of potassium and ammonium salt. The presence of NO_3^- ion in the form of sodium salt results in the lowest recovery values. The recovery values are in the range of 91.48% - 99.88%, and the recovery values increase with the increase in nitrate concentrations. From the results shown in Table 3, SO_4^{2-} anion does not affect the recovery values for Cr(VI).

Effect of interfering ions on speciation of Cr(III) andCr(VI)

The effect of common coexisting ions in river water and wastewater that could interfere with the speciation process (Cr(III) and Cr(VI)) and Cr(III) and adsorption on SiO_2-Nb_2O_5 were studied. Solutions of 0.1 mg/L of Cr(III) in the presence of interfering ions (Cu^{2+}, Mn^{2+}, Fe^{3+}, Zn^{2+}, $Mg^{2+}$and Ni^{2+} individually and in a mixture were analyzed according to the recommended procedure (Musić, 2010). If the recovery value of Cr species in the presence of a standard solution of metal ions is ± 10%, then the metal or a mixture of metal solutions is considered an interfering species. The recovery value for Cr(VI) was determined based on its concentration in the eluate from the sample that passed through a column filled with SiO_2-Nb_2O_5. It was found that interfering metals do not interfere with the determination of Cr(VI) because Cr(VI) does not adsorb on the SiO_2-Nb_2O_5 (Fig. 6).

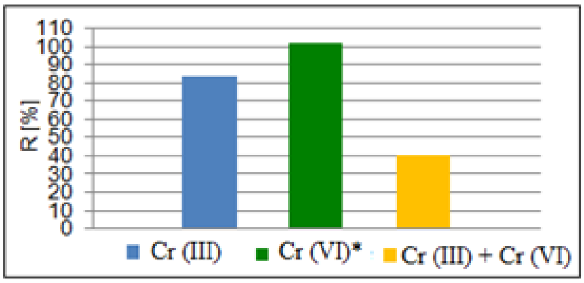

Fig. 6 - Results of preconcentration of Cr(III), Cr(VI) and mixture solution of Cr(III) and Cr(VI) on silica gel modified with Nb_2O_5.

The result of preconcentration of Cr(III) (0.1 mg/L) in the presence of metals (0.1 mg/L) individually and in a mixture is presented in Fig. 7.

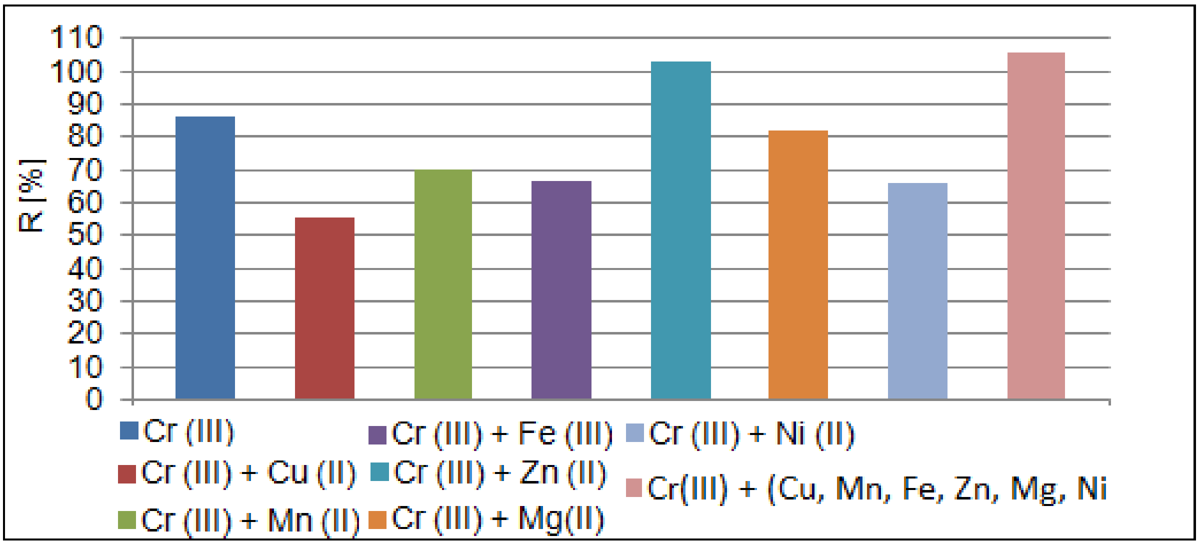

Fig. 7 - Recovery values of Cr(III) preconcentration and in a mixture with metals

The results showed that the lowest recovery values for Cr(III) were in the presence of Cu 55 %. For Fe, Mn, and Ni, the recovery was below 70% and for Mg below 80%. Ions that are already known to interfere with the determination of Cr(III) are Cu^{2+} and Fe^{3+} (Wiryawan et al. 2018; Handbook, 2007). Based on the results of this study, Ni, Mn, and Mg also interfere. The best recovery values for Cr(III) are achieved in the presence of either zinc (102.6%) or all metals (105.9%). One of the reasons for this could be the formation of metal hydroxide on the surface of the sorbent, considering that in these two samples a thin yellow-colored layer was observed on the surface of the sorbent, which is lost during the elution of the columns. The results from this study were compared with the results of other studies that also analyzed the concentration of common coexisting ions that could affect the determination of Cr(III) and Cr(VI): NO_3^{-} and Cl^{-} were tolerated above 5000 mg/L, SO_4^{2-} and Ca mg/L were tolerated between 1000 and 100 mg/L, while those tolerated below 100 mg/L were Zn^{2+}, Cu^{2+}, Mg^{2+}, and Cd^{2+} (Tiwari et al. 2016). Zhang et al. (2008) in their study found that: Na^{+}, K^{+},and Cl^{-} were tolerated for Cr(III) up to 10, 000 mg/L and for Cr(VI) up to 2000 mg/L. Mg^{2+}, Ca^{2+}, Zn^{2+} were tolerated for Cr(III) and Cr(VI) up to 1000 mg/L, and Fe up to 100 mg/L, NO_3^{-} can be tolerated up to 2000 mg/L for Cr(III) and for Cr(VI) up to 1000 mg/L. SO_4^{2-} is tolerated up to 3000 mg/L for Cr(III) and for Cr(VI) up to 1000 mg/L.Ca^{2+}, Mg^{2+}, Zn^{2+}, and Na^{+} do not interfere with the determination of Cr(III) if their concentrations are less than 50 mg/L (Sulejmanović et al., 2015).

The results of this study were in good agreement with other previous published studies related to this investigated topic and also indicated that the use of silica gel or other sorbents for Cr speciation can also have an effect on the reduced interfering influence of foreign ions present in the sample. Therefore, the presence of major coexisting ions had no obvious influence on the determination of Cr(III) and Cr(VI).

River water and wastewater analysis

The methods for Cr(III) and Cr(VI) determinations were applied to the river water and wastewater samples. Two wastewater samples were analyzed. The samples were filtered through a 0.45 μm membrane filter (Whatman), and concentrated HNO_3 was added to prevent metal ion losses and the formation of microorganisms. The concentrations of the following interfering metals (Ca, Cd, Co, Cr(III), Cu, Fe, Mg, Mn, Ni, Pb, and Zn by FAAS, and Na and K by AES, while Cr(VI) by UV/Vis spectrophotometry) were determined from real samples. The results are shown in Table 4.

Table 4 -Average concentration of metals in wastewater and river water

Samples	Wastewater I	Wastewater II	River water Ilijaš	River water Vogošća	River water Misoća	River water Vareš
Metals	**Concentration mg/L**					
Cr(III)	0.031	0.106	< LOD	< LOD	< LOD	< LOD
Cr(VI)	0.162	0.204	0.038	0.035	0.04	0.04
Cu	0.064	0.419	< LOD	< LOD	< LOD	< LOD
Mn	21.52	40.7	0.011	0.009	0.018	0.064
Fe	449.75	1810	0.156	0.29	0.177	0.086
Co	0.165	0.301	< LOD	< LOD	< LOD	0.012
Ni	1.258	2.437	0.017	< LOD	< LOD	< LOD
Cd	0.011	0.013	0.002	0.002	0.003	0.004
Pb	< LOD	5.212	0.053	0.056	0.015	0.043
Zn	2675	5250	0.636	0.299	1.763	1.908
Ca	2775	4625	63.05	66.01	73.5	79.5
Mg	80.00	120.00	7.5	9.5	7.00	22.5
Na	9.00	14.00	3.4	3.62	3.45	4.52
K	2.512	5.025	0.937	1.087	1.255	1.575

The concentrations of Ca and Fe in the wastewater samples were higher than the concentration that affects Cr(VI) determination. The obtained concentrations for Ca, Mn, Mg, Fe, and Zn in the tested samples were higher than the concentration that has an influence on Cr(III) determination. Ca concentrations in wastewater can be high as a result of the use of CaO or $Ca(OH)_2$ as flocculants in the wastewater treatment process. The concentrations of all other investigated cations do not affect the Cr(III) and Cr(VI) determinations in wastewater samples. The results for the metal content in the river water samples showed that the concentration of all determined metals was lower than the concentrations that could affect the accuracy of the determination of Cr(III) and Cr(VI).

The content of Zn, Mn, Ni, Fe, and Cr(VI) in both wastewater samples was above the values allowed according to the Regulation on the limit values of hazardous and harmful substances for technological wastewater before their discharge into the public sewage system or into another receiver according to the Law on Water in the the Federation of Bosnia and Herzegovina ("Official Gazette of the Federation of Bosnia and Herzegovina "number 18/98; a and b).The level of Cu and Pb in Wastewater II were higher than the allowed values in the abovementioned Regulation. The metal concentration in all river water samples was below the values specified in the Regulation on limit values of hazardous and harmful substances in the waters that are discharged from the public sewage into a natural recipient after purification , except for Zn in river water collected at Misoča and Vareš sites. The obtained values are almost two times higher than the limit value for Zn (1 mg/L) ("Official Gazette of the Federation of Bosnia and Herzegovina" number 18/98; a and b).

CONCLUSIONS

The effect of some cations and anions on the determination of Cr(III) and Cr(VI) was investigated in this study. Chloride salts of calcium and copper, as well as nitrate salts of zinc do not interfere with the determination of Cr(III). The concentration of Cr(III) in the presence of cation nitrate salts (except calcium) was lower compared to the presence of their chloride salts. Nitrate salts showed a lower recovery value for Cr(III) compared to chloride salts: nickel nitrate salts showed a 30% lower recovery value for Cr(III), iron and magnesium 17%, 16% manganese, 11% copper, and zinc with 7%. In the case of anions, chloride ions had no effect on the determination of Cr(III), and the nitrate ion had the same effect, but only if it was added as a potassium salt.

If the nitrate anion is added as the sodium salt, the recovery values for Cr(III) are 10 % lower, but in the case of ammonium salt, they are 10% - 20% lower. Investigated anions in the concentration range of 10 mg/L up to 2000 mg/L do not affect the determination of Cr(III). The majority of the investigated cations have no effect on Cr(VI) determination, but recovery values are 10% lower if the cation concentration is higher than: Fe^{3+} (> 10 mg/L), Cu^{2+} (> 25 mg/L), and Ca^{2+} (500 mg/L). Investigated anions in concentration range of 10 mg/L up to 2000 mg/L do not affect the determination of Cr(VI). In subsequent research, the concentration range and number of metals as potential interferers in chromium speciation could be expanded. Also, the potential use of sorbent (silica gel with Nb_2O_5) for the speciation of other metals that occur in two or more oxidation states could be investigated.

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Summary/Sažetak

U ovoj studiji je predstavljen: a) sadržaj Ca, Cd, Co, Cr(III), Cr(VI), Cu, Fe, K, Mg, Mn, Na, Ni, Pbi Zn u otpadnim vodama metalske industrije i rijeka koje teku u blizini metaloprerađivačke industrije; b) mogućnost kvantitativnog određivanja Cr(III) I Cr(VI) u prisutnosti sljedećih kationa: Fe3+, Cu2+, Ca2+, Mg2+, Ni2+, Mn2+; i Zn2+ i anioni Cl-, NO3- i SO42-; c) specijacija Cr(III) I Cr(VI) na silikagelu modificiranim sa Nb2O5. Specijacijska analiza Cr(III) i Cr(VI) provedena je na silikagelu modificiranim sa Nb2O5. Metali su određeni atomskom apsorpcionom spektrometrijom - plamena tehnika, osim Na i K koji su određeni atomskom emisijskom spektrometrijom, i Cr(VI) ultraljubičastom-vidljivom spektrofotometrijom. Kada je koncentracija kationa veća od: Mg2+ (>25 mg/L), Ni2+ (>100 mg/L), Fe3+ (>250 mg/L), Zn2+ (>500 mg/L) i Mn2+ (>1000 mg /L), dobiva se pogreška veća od 10% u određivanoj koncentraciji Cr(III), Cr(VI). Silikagel modificiran s Nb2O5 može se smatrati efikasnim adsorbensom za ekstrakciju specija hroma na čvrstoj fazi i istovremeno koncentriranje Cr(III). Predložena metoda uspješno je primijenjena na specijaciju i određivanje Cr(III) i Cr(VI) u analiziranim uzorcima. Sadržaj skoro svih određivanih metala je bio ispod dozvoljenih vrijednosti za otpadne vode.