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Determination of total Cr in wastewaters of Cr electroplating factories in the I.organize industry region (Kayseri, Turkey) by ICP-AES

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Abstract The wastewater pollution in industrial areas is one of the most important environmental problems. Heavy metal pollution, especially chromium pollution in the wastewater sources from electroplating, dyeing, and tannery, has affected the life on earth. This pollution can affect on all ecosystems and human health directly or by food chain. Therefore, the determination of total chromium in this study is of great importance. In this study, accurate, rapid, sensitive, selective, simple, and low-cost technique for the direct determination of total Cr in wastewater samples collected from the some Cr electroplating factories in March 2008 by inductively coupled plasma-atomic emission spectrometry has been developed. The analysis of a given sample is completed in about 15 min by this technique applied. As the result of the chromium analysis, the limit of quantification for the total Cr were founded to be over the limit value (0.05 mg L^{-1}; WHO, EPA, TSE 266, and inland water quality classification) as 1,898.78 ± 0.34 mg/L at station 1 and 3,189.02 ± 0.56 mg/L at station 2. The found concentration of total Cr has been determined to be IV class quality water according to the inland water classification. In order to validate the applied method, recovery studies were performed.

Keywords Chromium · Chromium-electroplating · Water pollution · Wastewater analysis · Determination · ICP-AES

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Introduction

Contamination with chromium (Cr) of the surface and ground waters is a persisting problem in many countries. Cr enter the environment as a result of discharge from steel industries, electroplating, tanning industries, oxidative dyeing, cooling water towers, refractory materials production, metallurgy, pigment, and mining (Prasada et al. 1998, p. 69; Rao and Sastri 1982, p. 607; Bobrowski et al. 2004, p. 1003; Oktor et al. 2008, p. 97).

Toxicological studies have indicated that the degree of toxicity of metals including Cr depends on the chemical form of chromium in wastewater (Kot and Namiesnik 2000, p. 69; Oktor et al. 2008, p. 97).

Chromium may appear in solution in the species of Cr (III) and Cr (VI). These species exist primarily as being related to the pH in forms Cr (VI) as CrO_4^{2-} and Cr (III) as Cr $(OH)^{2+}$ (Narin et al. 2002, p. 1437; Bağ et al. 2000, p. 895; Stein and Schwedt 1994, p. 38; Oktor et al. 2008, p. 97). Cr (VI) is toxic due it is highly oxidizing, and it penetrates easily to biological membranes. Therefore, this form is considered as a carcinogenic agent. On the other hand, Cr (III) is essential for the maintenance of the metabolism of lipids, glucose, and proteins. Although chromium is a biologically important metal, in concentrations greater than 0.05 mg L^{-1} is a very hazardous metal for living organisms, especially humans (Dominquez and Arcos 2002, p. 241; Oktor et al. 2008, p. 97). If there are high quantities of heavy metals such as Cr in the ambient water, the tissues or the organs of the aquatic organisms and especially fishes can be affected. Therefore, the wastewater in the industrial regions must be taken control, and the pollution must be considered continuously (Balcı and Türkoğlu 1993, p. 106; Polat 1997; Türkoğlu et al. 1992, p. 33; Türkoğlu and Parlak 1999, p. 47; Oktor et al. 2008, p. 97). Consequently, there is a need for investigation of accumulation of Cr, especially Cr^{+6} by means of human and other organisms' health.

The total chromium content at trace levels was determined traditionally using graphite furnace atomic absorption spectrometry (GFAAS). However, in order to carry out speciation by this means, it is necessary to perform laborious prior extraction process (El Sokkary 1980, p. 493; Subramanian 1988, p. 11; Oktor et al. 2008, p. 97) which increases work time and manipulation of the sample, leading to possible sources of error and contamination. High-performance liquid chromatography has been successfully applied on several occasions for the speciation of chromium (Subramanian and Meranger 1979, p. 725; Bittner and Broekaert 1998, p. 31; Posta et al. 1996, p. 185; Oktor et al. 2008, p. 97). However, this technique still does not satisfy the requirements of routine analysis principally because of its complicated design (prior extraction and pre-concentration stages) and the need to be adapted to sophisticated techniques such as GFAAS or inductively coupled plasma-mass spectroscopy (ICP-MS) to obtain low detection limits (Posta et al. 1996, p. 185; Oktor et al. 2008, p. 97). Electrochemical techniques are a clear alternative for the determination of metals at trace level. Thus, chromium can be determined directly with no pretreatment in real samples using electrochemical techniques, particularly adsorptive stripping voltammetry, using different complexing agents (Andrle et al. 1997, p. 189; Elleouet et al. 1992, p. 301; Gao and Siow 1996, p. 602; Wang et al. 1992, p. 1913; Paneli et al. 1993, p. 205; Boussemart et al. 1992, p. 103; Vukomanovic et al. 1997, p. 86; Oktor et al. 2008, p. 97).

The variety of the instrumental techniques for Cr traces determination in water samples may be divided into two main groups (Krull 1991; Das et al. 2001, p. 1; Kotas and Stasicka 2000, p. 263; Margues and Salvador Morales-Robio 2000, p. 601; Oktor et al. 2008, p. 97): (1) Valence specific, spectrophotometric method of Cr (VI) determination with the diphenylcarbazide (Wrobel et al. 1997, p. 2136) or adsorptive stripping voltammetry, mainly utilizing the catalytic system Cr (III)-diethylenetriammine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid-NO_3^- (Golimowski et al. 1985, p. 315). The above methods are based on the different ability of complex formation by Cr (III) and Cr (VI). (2) Valence-nonspecific methods based on the preliminary valence-specific separation of both chromium form on selective removing of one chromium species from the sample and subsequent, nonspecific measurement of the separated form by means of AAS, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), or ICP-MS (Margues et al. 1998, p. 239; Oktor et al. 2008, p. 97).

There are only a few analytical techniques such as ICP-MS, ET AAS, and stripping voltammetry available that have sufficient sensitivity and selectivity for the direct determination and speciation of ultra-trace levels of Cr in water (Rao and Sastri 1982, p. 607; Bobrowski et al. 2004, p. 1177; Oktor et al. 2008, p. 97).

Gijerde et al. reported that the speciation Cr (III) and Cr (VI) has been determined with direct-injection nebulization and S-O-V ICP-AES (Gijerde et al. 1991; Gijerde et al. 1993, p. 73; Oktor et al. 2008, p. 97).

ICP-AES has been widely used for the determination of trace elements in various samples due to its high detection power, multi-element analysis, minor matrix effects, minor memory effects, high analysis speed, and tolerance to high salt concentrations. In the past, the atomization source of AES was only the side-on-plasma source for lateral observation. Recently, it has known that the detection limits of elements could be improved with the end-on-plasma source for axial observation of the plasma (Balosubramanion and Pugalenthi 1999, p. 457; Ivaldi and Tyson 1995, p. 1207; Emteborg et al. 1999, p. 1567; Oktor et al. 2008, p. 97).

According to literature investigations, the concentration of Cr has not been studied in wastewater samples of Cr electroplating factories in I.organize industry area (Kayseri, Turkey) by ICP-AES so far. Therefore, in this study, total Cr was successfully determined by applied ICP-AES technique.

Material and methods

Instrumentation and operating conditions

Spectroscopic determination of total Cr was performed with a Varian Liberty S series II AX Sequential Model ICP-AES with a glass nebulizer and SPS 5 Autosampler; operating parameters were given in Table 1.

Table 1 Instrument operating parameters for ICP-AES

Parameter	Description
Rf power	1.20 kW
Plasma gas flow rate	15.0 l/min
Auxiliary gas flow rate	1.50 l/min
Nebulizer gas flow rate	0.70 l/min
Sample uptake rate	1.8 ml/min
Argon gas (high purity)	99.99%
Torch type	High Solids Axıel (1.8 mm, quartz)
Nebulizer type	Concentric glass; cyclonic spray chamber
Nebulizer pressure	200 kPa
Pump rate	20 rpm
Replicates	3
Sample uptake delay	30 s
Wavelength	267.72

Chemicals

All reagents used were of analytical reagent grade (Merck, Darmstadt, Germany). Ultra-pure water obtained from Sartorius Arium Model Ultra Pure Water Systems was used through all experiments. Stock standard solution was prepared daily by appropriate dilution of AccuTrace, the reference standard (Item Number is ICP-07W-1, USA) in ultra-pure water with 1–5 drops concentrated nitric acid. This solution was appropriately diluted in ultra-pure water for prepared total Cr standard calibration solution concentrations of 1.00, 10.00, and 100 mg l^{-1}. In addition, the blank was prepared with ultra-pure water containing 1–5 drops concentrated nitric acid.

Chromic and sulfuric acid mix solution was used for the Cr plating. Then bisulfide solution (3–5%) was used for the reduction of Cr-VI to Cr-III. Hydrochloric acid was added for the cleaning. After the electrolytic Ni- and Cu-plating process, concentrated chromic acid solution was added for the Cr electroplating. Applied plating process forms wastewater at exit point of factory. Then, this wastewater dejars to Kayseri general cleaning facilities. Therefore, high-concentrated Cr wastewater must be diluted before this dejars process.

Study area and procedure of sampling

Kayseri I. Organize industry region is located in southwest of Kayseri in Iç Anadolu region (Turkey; Fig. 1). This region is one of the biggest industry regions of Turkey that many factories such as plating, furniture, metal, textile, plastic, food, machine, electric-electronic, chemistry, buildings, marble, carpet, and glass make many different produces. In this region especially, Cr plating of the surfaces of the metal table, chair, and furniture is important industrial facilities. For this aim, there are about 20 managements in this region.

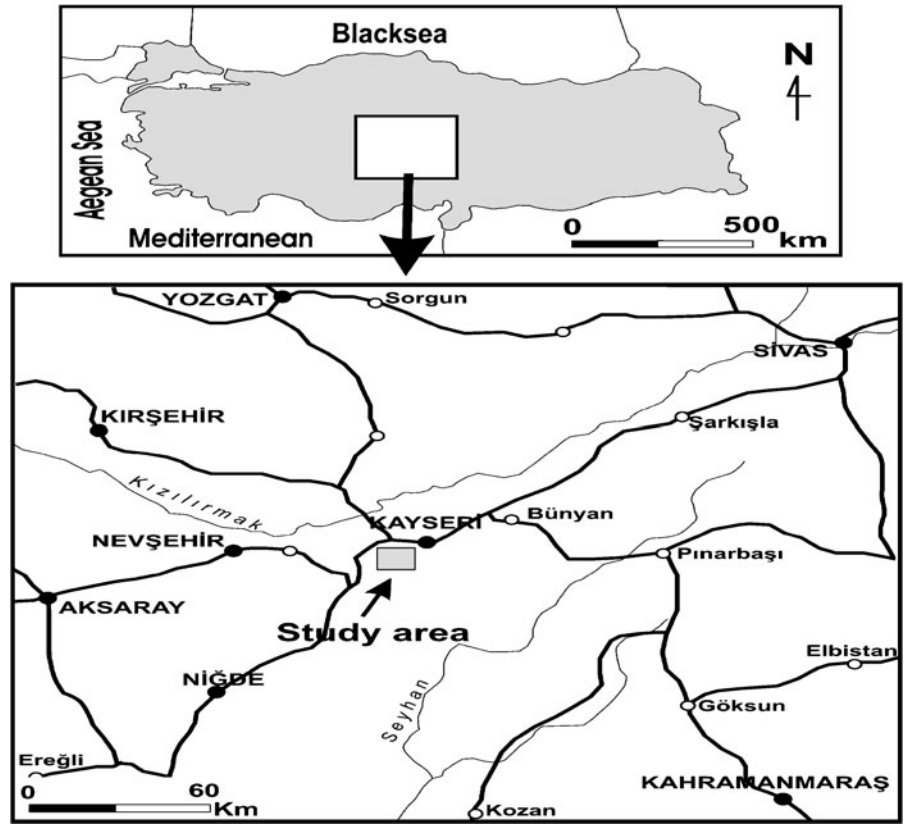

Fig. 1 Study area with indication of sampling station

In this study, Cr-plating wastewater samples from two stations which is the nearest to two Cr-plating factories in March 2008 (Fig. 1) were processed for spectroscopic analysis. The sampling stations are affected by especially electroplating factories known as a chromium source.

Wastewater samples of Cr plating were put into polyethylene bottles (250 ml volume) and immediately transported to the laboratory in the icebox; 3 ml concentrated HNO_3 was added to each bottle and stored in the refrigerator at +4°C until the measurements were carried out.

Procedure of sample mineralization

Industrial wastes cause serious pollution in the sampling area. Acid digestion (wet digestion) method was used to destroy the natural organic surfactants or complexing material in samples from polluted water before the ICP-AES measurements (UV digestion is only recommended for slightly polluted samples and as a post-treatment step wet digestion solutions; Metrohm 757VA Computrace Software Manual: 2001 Compu trace; Oktor et al. 2008, p. 97).

After the addition of 3 ml concentrated HNO_3 to each sample, they were evaporated on magnetic stirrer to dryness and then cooled to room temperature and digested again with 5 ml concentrate HNO_3. The samples were put into closed beaker and heated to dryness. After, samples were cooled, then 10 ml of HCl was (1:1) diluted, and 15 ml deionized water was added to each sample and evaporated for 15 min. Cooled samples were filtered from blue band (Whatman 42) and diluted to 25 ml ultra-pure water (USEPA 1994; Yayintaş et al. 2007a, p. 389; Süren et al. 2007, p. 91; Oktor et al. 2008, p. 97).

Spectroscopic measurements by ICP-AES method

After the mineralization, Cr-plating wastewater samples of 20 ml were appropriately diluted in

Table 2 Analytical parameters for the determination of total Cr in electroplating wastewater by ICP-AES

Parameters	Total Cr
Linear concentration range (mg/l)	1–100[a]
Slope (s/M)	15,986.5
SD of slope	0.0108
Intercept (s)	326.622
SD of intercept	0.0312
Correlation coefficient, *r*	0.999
Number of measurements (*n*)	5
LOQ (mg/l)	1,898.78–3,189.02
RSD %	0.34–0.56
Repeatability of intensity (RSD %)	1.5 for 10.00

LOQ limit of quantification, *RSD* relative standard deviation
[a]Linear concentration range after 100 fold diluted to wastewater samples

ultra-pure water and 1–5 drops of concentrated nitric acid were added. After this solution was put into the ICP-AES apparatus' samples tubes, spectroscopic measurement was made under optimum instrumental parameters (Table 1) using the standard addition method for the determination. Total Cr concentration was determined after 100-fold diluted to in reel wastewater samples using the calibration curve (Table 2).

Results and discussion

Determination of total Cr-plating wastewater samples and validation of proposed method

Proposed ICP-AES technique was applied to Cr-plating wastewater samples successfully. Analytical parameters for the determination and validation were evaluated for ICP-AES method using the proposed suitable set of experimental conditions (Table 2).

LOQ value for total Cr was given in Table 2, which was calculated for the intensity for ICP-AES using the following equations (Riley and Rosanske 1996; Swartz and Krull 1997; Oktor et al. 2008, p. 97).

$$\mathrm{LOD} = 3s/m;\ \mathrm{LOQ} = 10s/m$$

The sensitivity was calibrated by standard additions to the sample, and the initial total Cr concentration was calculated by extrapolation; *s* is the standard deviation of the intensity for ICP-AES (five runs) of the sample, whereas *m* is the slope of the calibration curve.

As can be seen from Table 3, the found concentrations of total Cr at both stations (station I = 1,898.78 ± 0.34 and station II = 3,189.02 ± 0.56) indicate "IV. Quality Water" according to the inland water quality classification (Table 4). Also Cr concentration is found very high according to limit values of TSE 266, WHO, and EPA (Yigit

Table 4 Limit values of some heavy metals (μg/l) according to the inland water quality classification

Heavy metals	Water quality classes			
	I. Quality	II. Quality	III. Quality	IV. Quality
Cd	3	5	10	>10
Pb	10	20	50	>50
Cu	20	50	200	>200
Zn	200	500	2,000	>2,000
Cr^{+6}	<20	20	50	>50
Cr (total)	20	50	200	>**200**
Fe	300	100	5,000	>5,000
Ni	20	50	200	>200

Table 3 The concentration of total chromium in Cr-plating wastewater of I.organize industry region (Kayseri, Turkey) by ICP-AES

	Limit values			Found value in Cr-plating wastewater (March 2008)		
	TSE 266 (mg/L)	WHO (mg/L)	EPA (mg/L)	Station I (mg/L)	Station II (mg/L)	Quality class (mg/L)
Cr	0.050	0.050	0.05	1898.78[a] ± 0.34[b]	3189.02[a] ± 0.56[b]	IV. Quailty[c]

$n = 5$, $p = 0.95$; mean with standard deviation
[a]Mean found value
[b]Standard deviation
[c]According to the inland water quality classification (Table 4)
n number of measurement

Table 5 Recoveries % of total Cr in Cr-electroplating wastewater samples by ICP-AES method

Total Cr (station I)			Total Cr (station II)		
Added (mg/L)	Found[a] (mg/L)	Recovery %	Added (mg/L)	Found[a] (mg/L)	Recovery %
0[b]	1898.78 ± 0.65	(% RSD = 0.34)	0[b]	3,189.02 ± 0.18	(% RSD = 0.56)
10[c]	1908.68 ± 0.60	99.00	10[c]	3,198.87 ± 0.13	98.50
100[d]	2008.48 ± 0.10	99.80	100[d]	3,298.87 ± 0.10	99.50

RSD relative standard deviation
[a]Each value is the mean (± standard deviation) of five experiments
[b]Sample (Cr-electroplating wastewater)
[c,d]Added standard solution of total Cr

et al. 2002; Yayintaş et al. 2007b, p. 389; Oktor et al. 2008, p. 97).

The concentrations of total Cr found as IV. Quality at both stations indicates that Cr-electroplating wastewaters can have high negative effects on the environment.

In order to validate the applied method, recovery studies were performed after the spiked addition of a certain amount total Cr standard solution to the Cr-electroplating wastewater. The results are given in Table 5. A good agreement was obtained between the added and measured amounts. The recovery values calculated for the added standards were always higher than 95%, thus, confirming the accuracy of the procedure and its independence from the matrix effects applied spectrometric method validated with these good results (Table 5).

Conclusions

In this study, the concentrations of total Cr in the Cr-electroplating wastewater samples of I.organize industry area (Kayseri, Turkey) were determined successfully by ICP-AES technique.

The found excessively total Cr concentrations at the both studied stations indicated that studied area was so much polluted in view of the total Cr concentration. This pollution causes various serious high negative effects on environment, and these are carried over to the human body by means of the web food. Therefore, there is a need for investigation of accumulation of total Cr in view of human health.

It is necessary to clean wastewaters by purification procedures and the controlling of pollution sources as well as maintaining water quality controls. At the same time, full purification systems should be established to remove the risk in the area.

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