

Application of Spectrophotometric Method for Estimation of Chromium in Effluents from Tanneries of Korangi Industrial Area

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ABSTRACT

The spectrophotometer method was employed for the determination of different oxidation state of chromium in effluents from different tanneries. The concentration ranges for are estimated for chromium (III) 1.63-3.85ppm and for chromium (VI) 1.69-21.00ppm. Whereas by atomic absorption spectroscopy (AAS) it is found to be 32.10- 86.25ppm. The difference in estimated values by two different techniques illustrate the reliability of spectrophotometric method. As effluents of leather treatment plants have the high concentration of other foreign ions interfere with determination of chromium. So AAS method is more reliable, specific, simple and inexpensive method for the determination of chromium from the tanneries effluent.

Keywords: Spectrophotometry, Atomic absorption Spectrometry, chromium.

1. INTRODUCTION

Chromium is a major water pollutant, usually as a result of some industrial pollution including tanning factories, steel work, dyeing or chromium plating, wood preservation, and artificial fertilizers¹. For this reason, determination ion of chromium in environmental samples and natural water, waste water samples and soil samples has become very important.

The USEPA has set concentration 0.1ng/L of total chromium for drinking water as "maximum contaminant level goals" WHO states that the guideline value of 50µg/L of chromium (VI) because of these importance of chromium species, their accurate and facile determinations are in important in the chemistry².

The sophisticated techniques, such as inductively coupled plasma- mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrochemical analysis, spectrophotometry, neutron activation analysis and atomic absorption spectrophotometry (AAS), been adopted for sensitive assays for both oxidation states of chromium. These methods have disadvantage of cost and instruments used in regular analysis. AAS often has low sensitivity due to the matrix effect of samples such as salinity³.

The presence of chromium in environmental samples at low levels and has matrix effects with detection limit of lead⁴. The traditional methods of spectrophotometers are employed with separation from matrix elements. Extractive and micellar sensitized spectrophotometer with ability to separate and preconcentrat of chromium solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as spectrophotometer. For this purpose various preconcentration

+method of chromium in micellar media are used⁵⁻⁶. The spectrophotometric and extraction method based on co-ordination with different ligands have been described for chromium determination⁷⁻¹¹. Many of these methods are time consuming and require complicated and expensive instrument and some of them has low reproducibility of results. Due to low concentration of chromium (III) ion content, new methods for selective, sensitive rapid and convenient determination are developed^{3,12,13}. The spectrophotometric determination and organic micellar media are employed as power full tools in analytical application^{3,14,15}. Absorbance and

fluorescence process are stable in aqueous solution and enhance sensitivity. Tetraalkylammonium bromide ($R_4N^+ Br^-$, $R=n$ -butyl and n -propyl) as a counter ion reacted very strongly with metal cyanides, alkyl sulfonate, sulfur oxides, inorganic anions and oxyanions, such as CrO_4^{2-} ¹⁶.

Tetrabutylammonium bromide [(n -But) $_4N^+ Br^-$] formed a stable ion-pair with chromate ions in an acidic aqueous solution. The ion-pair could be separated from other species present in the sample solution by extracting selectively into an organic solvent. Several organic solvents, such as chloroform, carbon tetrachloride and MIBK, were tested as testing solvents. Chloroform did not extract the ion-pair, and the extraction of this ion-pair with carbon tetrachloride was not quantitative. MIBK was recommended as a convenient solvent¹⁷.

The present study is related to application of the method developed by Noroozifar and Motlagh¹⁶ to effluents of tanneries. The results are compared with AAS method.

1. EXPERIMENTAL

Reagents

All reagents were analytical reagent grade or highly available purity. Potassium chromate (K_2CrO_4 , Merck), chromium chloride ($CrCl_3$), tetrabutylammonium bromide (TBAB, Merck), methyl isobutyl kenton (MIBK, Merck) and Sym_diphenylcarbazide (DPC, Merck), ethanol (Merck), nitric acid (HNO_3) and ammonium nitrate (Merck). Standard solution of chromium highly purified standard atomic absorption solutions were used for calibration curve.

Sampling

Samples were effluent, collected from tanneries of Korangi Industrial area, in clean polyethylene bottles. The sampling was done in November 2011.

Instrumentation

The pH of the samples was measured with Jenway 3320 pH meter. Conductivity values were determined by the use of Jenway 4010 conductivity meter. The absorbance was measured at Shimadzu UV-Vis spectrophotometer 160A at

548nm. All atomic absorption measurements were made on a double beam atomic absorption spectrophotometer. (Model: Perkin - Elmer AA3100).

Procedure

A chromium (III) standard solution was prepared by the dilution of stock solution of 0.27075g/L chromium chloride. A Chromium (IV) standard solution was prepared by diluting stock solution containing 0.48091g/L of potassium chromate. 250ml portion of (TBAB) 0.02M was prepared by dissolving 3.2568g of tetrabutylammonium bromide in methyl isobutyl ketone. A 100ml portion of $1.9 \times 10^{-3} M$ DPC was prepared daily by dissolving 0.1163g of sym_diphenylcarbazide in 150ml of ethanol and diluting up to 250ml with a 2.05mol/L HNO_3 solution. A solution of 0.4% (w/v) ceric ammonium nitrate was prepared by dissolving 4g of ceric salt in 0.5M HNO_3 (1L).

The calibration curve was drawn by using the previously reported method [13]. A regression equation was obtained using twelve point calibration.

$$Abs = 4.5 \times 10^{-3} + 6.747 C_{Cr}$$

Where the C_{Cr} concentration of chromium in $\mu g/L$. The correlation coefficient for the curve was obtained as 0.999.

The samples were filtered with Whatman Filter Paper 41, and then the analysis of chromium (III) and chromium (VI) was done by using extraction method. 100ml of diluted sample, 5ml of HNO_3 (65%) and 10ml of a TBAB solution were added. After mixing the solution was shake for 5min. The phases were allowed to separate and the organic phase was transferred into a new separatory funnels subsequently added 5ml of an acidic DPC solution and mixed thoroughly. The ion pair compound was back extracted from MIBK into an acidic DPC solution, which was used for spectrophotometric measurement of chromium (VI) in samples. The aqueous phase of ion pair extraction, 10ml of ceric ammonium nitrate (0.4%) was added to oxidize chromium (III) to chromium (VI) and shaken for 5min. Then, 5ml of HNO_3 and 10ml of a TBAB solution were added

and the new tetrabutylammonium (TBA^+) chromate, $\text{CrO}_4^{2-} (\text{TBA}^+)_2$ ion pair was extracted by shaking for 5 min. Again, the new ion pair from MIBK was back extracted into an acidic DPC solution and the chromium (III) concentration was measured.

For the analysis atomic absorption spectrophotometer was used. Nitric acid and perchloric acid were used as oxidizing agents to destroy matrix. 40 ml of sample solution was filtered through Whatman's 40. 10 ml nitric acid 60% was added to the filtrate and heated to get clear solution. Finally the volume of the filtrate was made up to the mark in 50.0 ml volumetric flask with double distilled de-ionized water.

2. RESULTS AND DISCUSSION

The pH has vast effect on solubility and toxicity many insoluble substance become soluble on the change in pH, The oxidation states are pH depended chromium (III) is water insoluble and predominant in alkaline pH while chromium (VI) is predominant in acidic pH, it is soluble form and serve as a strong oxidizing agent. The pH of the sample varies from 3.57 to 8.70 as shown in Table 3. All the samples have alkaline pH except sample T-1, has acidic pH. In alkaline pH means chromium (III) predominate and also insoluble while pH acidic means the oxidation state chromium(VI) is dominating¹⁹. Conductance of the sample varied from 6.9 to 175 mS. It indicates the presence of high concentration of salts. The expected major ions contributing ions are probably Na^+ , Cl^- and other metal ions. As NaCl salt is extensively used in tanneries for leather preservation. The values of the potential varied between -40 to +268 mV of different industrial effluent. Apil1 and Apil2 have high positive potential while T3 samples have negative potential. Potential can also give us idea about dominating oxidation state of chromium. The reduction reaction of chromium +6 to chromium +3 occurs at -170 mV but no clear picture can be obtained from these redox potential values [Table 3].

The concentration range of chromium (III) and chromium (VI) from samples of

industrial waste effluent by using spectrophotometric method was found to be lowest in the sample of industrial effluent in T-1 for chromium(III)= 1.64 ± 0.218 ppm and for chromium(IV)= 1.69 ± 0.14 ppm. The highest concentration found in the sample of industrial effluent of APIL-2 for chromium(III) = 3.85 ± 0.52 ppm and chromium(VI)= 21.00 ± 0.52 ppm [Table 4]. The concentration range of total chromium by using AAS method was found to be much higher than the spectrophotometric method, ranging from 32.10 ± 0.52 ppm to 86.833 ± 0.629 ppm [Table 4].

The accuracy and reliability of this method was evaluated by comparing the results obtained for the same samples by an AAS method. The results estimated by AAS and spectrophotometry are shown in Table 4. The results estimated by spectrophotometry are much less as compare to results obtained by AAS. It may be attributed to the interference of foreign ions in the determination of chromium. The interfering ions may be F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , CH_3COO^- , $\text{S}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_5^{2-}$, Ca^{+2} , Mg^{+2} , Co^{+2} , Al^{+3} , Cr^{+3} , Fe^{+3} , Ni^{+2} , Pb^{+2} , Cd^{+2} , Cu^{+2} , Mn^{+2} , Sn^{+2} , VO_3^- , MnO_4^- . These ions may interfere with chromium(III) and chromium (VI). The source of the ions are due to the use of different salts in leather industries like to remove hairs, nails, keratinous matters, natural grease and fats to some extent and some of the interfibrillary soluble proteins. The milk of lime with or without the addition of sharpening agents like sulfide, cyanides, amines etc are used to remove hairs. Similarly the other agents are used in tanneries in sodium sulphide, sodium hydroxide, sodium hydrosulfite, arsenic sulphide, calcium hydrosulfide, dimethyl amine and sodium sulphhydrate^{13,16-18} So all these salts may cause interference during the determination of chromium (III) and chromium (VI).

Another factor which affects the determination of chromium (III) and chromium (VI) may be the influence of shaking time on the efficiency of the extraction process because the shaking time of 5 min was required for extraction when shorter times were used the

chromium (III) and chromium (VI) was not quantitatively extracted.

3. CONCLUSION

The spectrophotometer method is not too much reliable as compare to AAS for the determination of chromium (III) and chromium (VI) from the effluents of leather treatment plants because of the high concentration of other foreign ions may

successively effect on the determination of chromium. So AAS method is more reliable, specific, simple and inexpensive method for the determination of chromium from the industrial effluent.

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Table 1: GPS locations of samples

Degree	Inches	Centimeter	Locations
T-1			
24° 67°	57' 07'	19.18" 07.07"	North East
T-2			
24° 67°	51' 07'	19.69" 09.79"	North East
T-3			
24° 67°	51' 07"	13.44" 15.37"	North East
T-4			
24° 67°	51' 07"	09.82" 11.31"	North East
T5			
24° 67°	51' 07'	18.02" 11.66"	North East
T-6			
24° 67°	57' 07'	14.80" 14.80"	North East
AE-1			
24° 67°	57' 07'	23.75" 16.78"	North East
AE-2			
24° 67°	57' 07'	23.75" 16.48"	North East
AE-3			
24° 67°	57' 07'	20.29" 11.43"	North East
APIL-1			
24° 67°	51' 07'	20.29" 11.43"	North East
APIL-2			
24° 67°	51' 07'	22.28" 10.92"	North East

Table 2: Physical parameter of the samples; potential, conductance, pH and colour

Samples	Potential(mV)	Conductance (mS)	pH	Colour
T-1				
Sample1	132	55.8	3.57	Grey
Sample2	134	50.0	4.96	
Sample3	122	55.9	4.92	
T-2				
Sample1	125	64.6	8.61	Cream
Sample2	135	54.4	8.05	
Sample3	110	40.5	8.01	
T-3				
Sample1	40	89.5	7.94	Grey
Sample2	36	90.0	8.01	
Sample3	34	89.6	8.08	
T-4				
Sample1	234	69.0	8.62	Pale Yellow
Sample2	209	67.0	8.68	
Sample3	222	66.2	8.71	
T-5				
Sample1	150	31.4	8.34	Yellow
Sample2	178	11.5	7.99	
Sample3	169	26.8	7.90	
T-6				
Sample1	177	279.9	7.07	Green
Sample2	180	175.5	7.09	
Sample3	169	115.0	7.21	
AE-1				
Sample1	102	50.6	8.50	Grey
Sample2	98	92.0	7.95	
Sample3	99	33.7	7.85	
AE-2				
Sample1	157	37.2	8.72	Transparent
Sample2	159	49.7	8.41	
Sample3	110	44.6	8.70	
AE-3				
Sample1	138	61.2	7.58	Black
Sample2	130	64.8	7.52	
Sample3	140	64.2	7.63	
APIL-1				
Sample1	250	58.2	7.90	Cream
Sample2	252	59.7	7.99	
Sample3	251	62.6	7.97	
APIL-2				
Sample1	268	65.6	7.44	Cream
Sample2	264	69.0	7.01	
Sample3	266	68.5	7.92	

Table 3: Absorbance of Cr (IV)DPC complex for calibration curve at 548nm

Concentration($\mu\text{g/L}$)	Absorbance
0.002	0.001
0.004	0.023
0.006	0.033
0.008	0.049
0.010	0.067
0.02	0.089
0.04	0.210
0.06	0.499
0.08	0.539
0.10	0.692
0.12	0.813
0.13	0.951

Table 4: Spectrophotometric determination of chromium by diphenylcarbazide

Sites	Concentration of Cr(VI)/ ppm	Concentration of Cr(III)/ppm	Total concentration of chromium by AAS/ ppm
T-1	1.619 ± 0.14	1.637 ± 0.22	81.11 ± 0.94
T-2	1.69 ± 0.13	1.55 ± 0.14	86.25 ± 1.61
T-3	2.53 ± 0.11	2.31 ± 0.108	62.25 ± 0.85
T-4	14.83 ± 0.54	2.24 ± 0.18	75.50 ± 0.83
T-5	2.72 ± 0.18	2.71 ± 0.18	58.61 ± 0.87
T-6	18.72 ± 0.19	2.82 ± 0.13	82.15 ± 0.98
AE-1	21.00 ± 0.52	3.17 ± 0.17	60.12 ± 1.30
AE-2	3.16 ± 0.18	3.15 ± 0.25	32.10 ± 0.89
AE-2	2.96 ± 0.13	3.10 ± 0.22	56.12 ± 0.88
APIL-1	3.43 ± 0.125	3.54 ± 0.21	42.13 ± 0.30
APIL-2	3.71 ± 0.11	3.856 ± 0.74	49.13 ± 0.74

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