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METHOD CORROBORATION FOR THE DETERMINATION OF HIGH CONCENTRATION OF CHROMIUM IN VARIOUS ALLOYS USING ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Atomic absorption spectrophotometric technique was employed to determine high concentration of chromium as usually found in alloys. Different instrumental parameters, such as wavelength, slit width, burner height and flow rate of fuel were optimized, for the minimum absorption signal with low background. The effect of cations (Al^{+3}, Ca^{+2}, Cd^{+2}, Co^{+2}, Cu^{+2}, Fe^{+2}, K^{+}, Li^{+}, Mg^{+2}, Mn^{+2}, Mo^{+6}, Na^{+}, Ni^{+2}, Sr^{+2}, V^{+5} and Zn^{+2}) and acids (HCl, HNO_3, $HClO_4$ and H_2SO_4) on the determination of chromium under the optimized conditions was studied. The reliability of the procedure was cross-checked by analyzing the alloy samples with other analytical techniques such as spectrometry, ICP-ES and neutron activation analysis and comparing the results, which are in quite good agreement with each other. The developed procedure was successfully applied for the determination of chromium in various types of alloys.

Keywords: High concentration, Chromium, Alloys, Atomic absorption spectrophotometry

1. Introduction

Chromium is one of the important alloy making metals, which is being used in manufacturing of stainless steels, oxidation and corrosion resistant alloys which are formed from chromium and its combination with iron, nickel, cobalt, aluminium, copper, molybdenum and tungsten. These alloys are mostly used in industries like thermocouple, furnaces, rocket thrust chambers, heat exchangers, parts of jet engine, strand annealing tubes, waste heat recuperators and chemical waste incinerators etc. In these alloys the concentration of chromium is in percentages and its accurate measurement is the prerequisite for quality assurance.

The determination of chromium in such materials could be carried out with various analytical techniques which include emission spectrography, polarography, spectrophotometry, atomic absorption spectrophotometry (AAS), X-ray fluorescence spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICP-ES) and neutron activation analysis (NAA). Each of these techniques has its own merits and demerits but the atomic absorption spectrophotometry is one of the preferred techniques due to its simplicity, rapidity and specificity. Moreover, the technique is readily available in almost every analytical laboratory.

One of the major problems commonly encountered in the atomic absorption spectrophotometric analysis while dealing with the solutions of high analyte concentrations is the excessive dilution of the sample solutions, resulting in poor accuracy and precision. To overcome this difficulty, different approaches have been adopted such as rotation of the burner head through a certain angle [1, 2] and the use of less sensitive line [3-5], as an alternate to excessive dilution of the sample solutions. The present study deals with the use of less sensitive absorption line for the determination of high concentration of chromium in various types of alloys like ferrochrome alloys, nickel and aluminium base alloys and low alloy steel, employing optimized parameters of flame atomic absorption spectrophotometry.

2. Experimental

2.1. Equipment

The atomic absorption spectrophotometric measurements were carried out with Hitachi Model Z-2000 polarized Zeeman instrument. A water cooled, premix, fish-tail type burner, having a slot of 10 × 0.05 cm, was used for the air-acetylene flame. Hollow cathode lamp of chromium from Hitachi was used as radiation source.

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2.2. Reagents

For preparing stock solution of chromium (1000 mg L^{-1}), appropriate amount of $K_2Cr_2O_7$ (Johnson Matthey Chemical, Limited) was dissolved in minimum amount of water. Calculated amount of distilled nitric acid [6] was then added to this solution to have a final acid concentration of 0.02 mol. L^{-1} when diluted to one liter. Standard working solutions were prepared by appropriate dilution of this stock solution immediately before use. High purity deionized water was used throughout this work. Glassware was cleaned by overnight soaking in nitric acid (1+1) followed by multiple rinses with water. All other chemicals used were of analytical reagent grade and were used without any pre-treatment unless otherwise mentioned in the text.

2.3. Procedure

About 100-200 mg samples were placed in triplicate in 100 mL beakers and were digested according to the recommended procedures [7] for a given matrix. The resultant solutions were quantitatively transferred to a 100 mL volumetric flasks and the volume was made up with water. Blank solutions were also prepared accordingly for each sample. The solutions were aspirated into an air-acetylene flame using the optimized instrumental parameters given in Table 1, in the order of deionized water, standards, sample blank and samples. The signal evaluation was made by subtracting the signal of blank from the signals of the samples.

Table 1. Optimized instrumental conditions used for the determination of chromium.

Parameters	Values
Lamp current (mA)	7.5
Resonance absorption line (nm)	429.0
Slit width (nm)	1.3
PMT voltage (V)	330.0
Signal mode	BKG Correct
Calculation mode	Integral
Type of burner	Standard*
Burner height (mm)	12.5
Oxidant gas (air) flow rate (L min.$^{-1}$)	15.0
Fuel gas (C_2H_2) flow rate (L min.$^{-1}$)	2.2
Delay time (sec.)	5.0
Measurement time (sec.)	5.0

* See experimental

3. Results and Discussion

In order to carry out direct determination of chromium at high concentrations by atomic absorption spectrophotometry, various instrumental parameters such as resonance absorption line, slit width, burner height and fuel gas flow rate were optimized by aspirating 20 mg L^{-1} of chromium solution into an air-acetylene flame. The criterion for the optimization of the instrument was the selection of instrumental parameters which produced minimum and reproducible absorption signal with low background. All the reported values, for the optimization purpose are averages of at least five readings with relative standard deviation less than 3%.

3.1. Selection of absorption line

The hollow cathode lamps emit a number of resonance lines. The degree of absorption differs according to the resonance, leading to variation in the sensitivity of the line. Therefore, the sensitivities of some major resonance lines were checked by measuring the absorption of 20 mg L^{-1} of chromium solution. The absorption was recorded at resonance lines of 357.9, 359.3, 360.5, 425.4, 427.5 and 429.0 nm by using the fixed conditions of silt width (1.3 nm), burner height (7.5 mm), oxidant gas flow rate (15 L min $^{-1}$) and fuel gas flow rate (2.5 L min $^{-1}$). The results are shown in Fig. 1. Among the resonance lines studied, the line at 429.0 nm was found to be the least sensitive and was, therefore, selected for its subsequent use regarding the optimization of rest of the parameters.

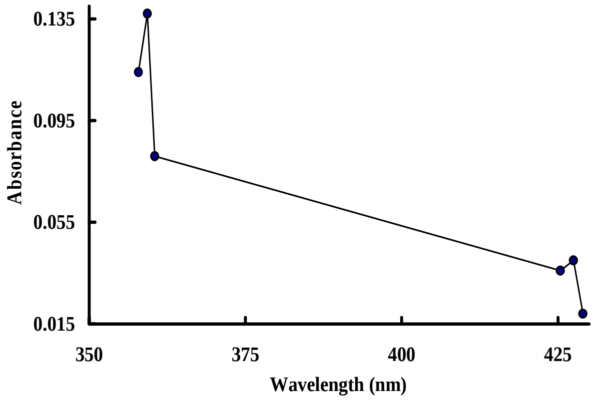

Fig. 1. Effect of wavelength on the absorption of 20 mg L^{-1} chromium solution in air-acetylene flame.

3.2. Effect of slit width

The absorption of a metal is also affected by the change of slit width of the instrument; therefore, the variation of absorption signal was studied with a chromium solution of 20 mg L^{-1} at 429.0 nm using different slit widths. The other instrumental parameters were kept constant as reported in the previous paragraph. Figure 2 shows that the minimum absorption was observed at a spectral slit width of 0.09 nm but the absorption signal was unstable resulting in poor precision of the results. Therefore, the slit width of 1.3 nm was thought to be the best suited for the present study.

3.3. Variation of burner height

The absorption sensitivity in the atomic absorption spectrometric measurements depends on the number of ground state atoms irradiated by the beam of light emitted from hollow cathode lamp. The atoms formed are distributed in an uneven density with in the flame profile; therefore, this parameter was also optimized for its minimum sensitivity. The absorption signals of 20 mg L^{-1} of chromium solution were recorded by the varying the burner height from 5.0 to 15.0 mm under the optimized wavelength (429.0 nm) and slit-width (1.3 nm). The oxidant and fuel gas flow rate used were 15 and 2.5 L min $^{-1}$ respectively. The results are reproduced in Fig. 3, which shows that the minimum absorption was observed at the burner height of 15.0 mm, but the signal was unstable leading to poor precision. Therefore, the burner height of 12.5 mm i. e., the next least sensitive position of burner height was considered suitable and used in all the subsequent experiments.

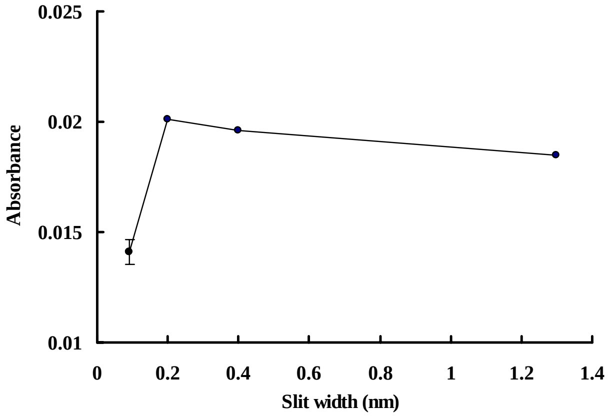

Fig. 2. Effect of slit width on the absorption of 20 mg L^{-1} chromium solution at 429.0 nm.

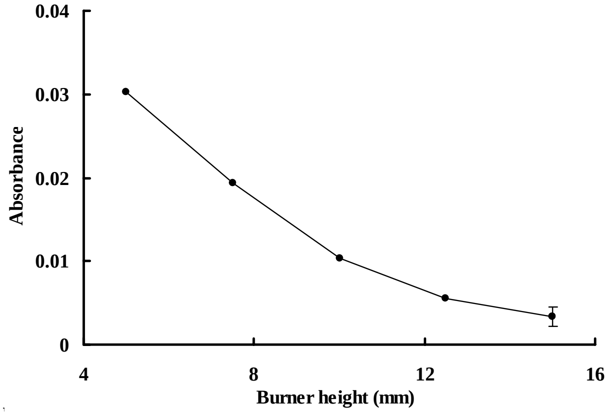

Fig. 3. Effect of burner height on the absorption of 20 mg L^{-1} chromium solution at 429.0 nm.

3.4. Effect of fuel gas flow rate

The atomization process is also related to flame temperature which is dependent upon fuel to oxidant ratio, therefore, the variation of the fuel flow rate was optimized by recording the absorption signal of 20 mg L^{-1} of chromium solution using the fixed oxidant flow rate of 15 L min^{-1} and other optimized instrumental conditions. The fuel gas flow rate was varied from 2.0 to 3.0 L min^{-1} and the results are reproduced in Fig. 4, which shows that the minimum absorption was observed at a fuel gas flow rate of 2.0 L min^{-1}, with a large fluctuation of the signal, therefore, the fuel gas flow rate of 2.2 L min^{-1} was considered to be the most favorable for present study.

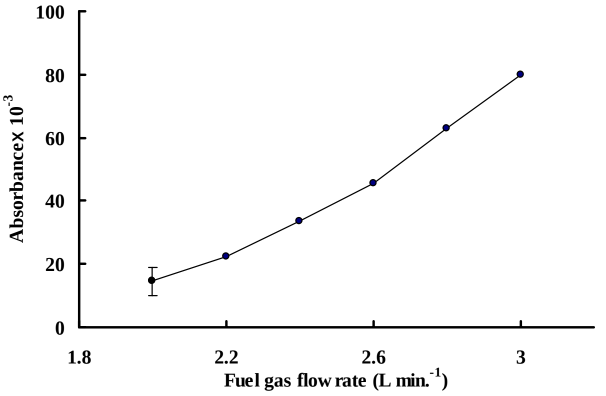

Fig. 4. Effect of fuel gas flow rate on the absorption of 20 mg L^{-1} chromium solution at 429.0 nm.

Table 2. Effect of cations on the absorption of chromium (50 mg L^{-1})

Cation	50 mg L^{-1} of cation		500 mg L^{-1} of cation	
	Abs. × 10^{-4}	Deviation (%)	Abs. × 10^{-4}	Deviation (%)
Nil	59	–	–	–
Al^{+3}	58	1.69	58	–1.69
Ca^{+2}	57	–3.39	54	–8.47
Cd^{+2}	61	3.39	57	–3.39
Co^{+2}	61	3.39	58	–1.69
Cu^{+2}	59	0.00	57	3.39
Fe^{+2}	62	5.08	60	1.69
K^{+}	60	1.69	58	1.69
Li^{+}	60	1.69	59	0.00
Mg^{+2}	59	0.00	55	–6.78
Mn^{+2}	60	1.69	59	0.00
Mo^{+6}	57	3.39	56	–5.08
Na^{+}	59	0.00	59	0.00
Ni^{+2}	60	1.69	61	3.39
Sr^{+2}	59	0.00	59	0.00
V^{+5}	63	7.29	63	6.78
Zn^{+2}	64	8.47	60	1.69

3.5. Sensitivity and detection limit

The sensitivity expressed as the concentration of metal which produces an absorbance value of 0.0044, was determined under the optimized conditions and was found to be 35 mg L^{-1} of chromium. The detection limit, defined as the concentration of chromium that gives a signal three times the value of standard deviation of ten determinations of blank, was determined to be 5 mg L^{-1}.

3.6. Linearity range

The linearity range of the calibration curve for chromium was also determined by measuring the absorbance values of standard solutions of chromium upto 900 mg L^{-1} using the optimized instrumental parameters (Table 1). The graph of absorbance verses concentration of chromium was a straight line. It was found that the Lambert-Beer law was obeyed up to 500 mg L^{-1}. To obtain an empirical relationship for chromium determination, least square fitting was done on the calibration standards. The best regression coefficients come out to be 0.00011 and 0.00054 for slope and intercept respectively with r^2 value of 0.999. The regression equation for chromium determination comes out to be:

$$y = 0.00011x + 0.00054$$

3.7. Interference studies

Under the optimized conditions (Table 1) the interference effects of different concentrations (50 and 500 mg L^{-1}) of various cations as contaminants on the absorption signal of 50 mg L^{-1} of chromium was studied and the results are reproduced in Table 2. The data in Table 2 reveal that at low concentrations (50 mg L^{-1}) almost all the contaminants have insignificant effect on the absorption signal of chromium except for Fe, V and Zn, which increased the absorption to 5.0, 7.3 and 8.5% respectively. However, higher concentrations (500 mg L^{-1}) of Ca, Mg and Mo suppressed the absorption of chromium to 8.5, 6.8 and 5.0 % respectively, which could probably be due to the inclusion of chromium atoms in the crystal lattices of the relatively more stable oxides of these metals and are not completely released and atomized. Similar argument has also been reported by Alkemade [8] for the suppression of the strontium signal in the presence of high concentration of calcium.

The influence of different acids (HCl, HNO_3, $HClO_4$ and H_2SO_4) on the absorption of 50 mg L^{-1} of chromium solution was also determined under the optimized instrumental parameters. The acid concentration was varied from 0.01 to 1.0 M

Table 3. Comparison of results for chromium with different analytical techniques.

S. No.	Sample	Concentration of chromium (%)		
		AAS	ICP-ES / INAA	Spectrometry
1.	Ferrochrome alloy	28.90 ± 1.40	29.30 ± 0.56*	25.9 ± 1.0
2.	Aluminium base alloy	0.17 ± 0.01	0.20 ± 0.01	–
3.	Low alloy steel	2.37 ± 0.08	2.47 ± 0.06	–

* ICP-ES

Table 4. Determined concentration of chromium (%) in various alloys.

S. No.	Name of sample	Sample code	Conc. of chromium
1.	Ferrochrome alloy[1]	F 1	63.16 ± 2.45
2.	Ferrochrome alloy[2]	F 2	35.20 ± 1.31
3.	Ferrochrome alloy[3]	F 3	28.90 ± 1.40
4.	Aluminium base alloy	A 1	00.17 ± 0.01
5.	Low alloy steel[1]	L 1	1.02 ± 0.02
6.	Low alloy steel[2]	L 2	1.79 ± 0.10
7.	Low alloy steel[3]	L 3	2.37 ± 0.08
8.	Nickel base alloy	N 1	28.50 ± 0.20

and the results are summarized in Figure 5. The data in Figure 5 indicate that the addition of acids decreased the absorption of chromium with the gradual increase in the acid concentration. The decrease in the absorbance of chromium signal at higher acid concentrations could probably be due to the increase in viscosity of the resultant acidic solution, which decreases the neubilizing efficiency [9].

3.8. *Reliability of the procedure*

The reliability of the adopted procedure was checked by analyzing a few samples for their chromium contents with some other analytical techniques such as instrumental neutron activation analysis, ICP-ES and spectrometry [10]. The comparison of the results with different techniques is shown in Table 3 which are in good agreement with each other. The data in Table 3 reveal that the established method is applicable to the samples having low as well as high concentration of chromium in different matrices.

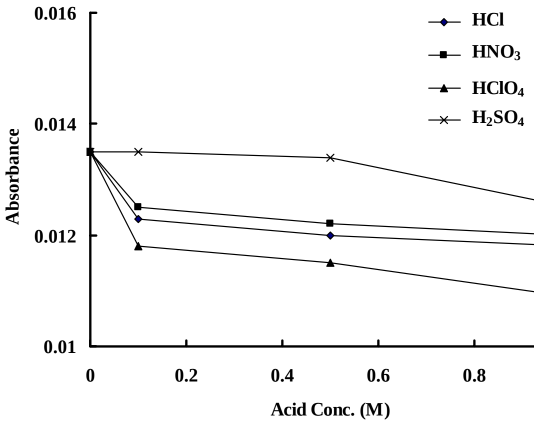

Fig. 5. Effect of acids on the absorption of 50 mg L^{-1} chromium solution at 429.0 nm.

3.9. *Analysis of alloys*

The established method was applied for the determination of chromium in eight samples of various types of alloys such as ferrochrome alloys, aluminium base alloy, low alloy steel and nickel base alloy. The results are shown in Table 4. The average relative standard deviation was found to be 3.74 %.

4. Conclusion

The method described is simple, rapid and almost interference free. There is no need to use matrix-matched standard solutions in the presence of contaminants at comparable and at high concentrations. It is equally applicable to samples containing low as well as high chromium contents in different matrices. Another advantage of this procedure is the minimum volumetric manipulation, thereby resulting in high precision and low standard deviation.

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