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A New Facile and Sensitive Method for the Spectrophotometric Determination of Chromium

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Abstract

A simple, rapid and sensitive spectrophotometric method for the indirect determination of trace amounts of chromium(VI) is described. The nitrite generated by the oxidation of hydroxylamine with chromium(VI) is used to diazotize *p*-aminophenol (PMP). The diazonium salt formed is coupled with isatin (IS) or isonipecotamide (ISO) or frusemide (FRU) in an alkaline medium to form azo dye showing absorption maxima at 524 or 533 or 558 nm respectively. Chromium(III) is determined after it is oxidized to Cr(VI) by bromine water. The range of linearity for PMP – IS, PMP-ISO and PMP-FRU couples are 0.02- 0.6 μg mL^{-1}, 0.04-2.0 μg mL^{-1} and 0.4-2.0 μg mL-1 of chromium respectively. The molar absorptivity, Sandell sensitivity for each system were calculated. The developed method is successfully applied to the determination of chromium in water samples, soil samples and dietary supplement.

Keywords: Spectrophotometry chromium; *p*-aminophenol; Isatin; Isonipecotamide; Frusemide

1. Introduction

Chromium is an essential nutrient required for normal sugar and fat metabolism and works primarily by potentiating the action of insulin. It is present in the entire body but with the highest concentrations in the liver, kidneys, spleen and bone. Chromium exists in the environment as chromium(III) and chromium(VI) oxidation states. Chromium(III) is an essential nutrient for maintaining normal physiological function [1], where as chromium(VI) is toxic [2]. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water [3]. The maximum concentration of chromium(VI) permitted in potable water is 5 μg/l [4]. The most important application of chromium in the metallurgic industry is its use as an alloying element in steels. In these materials, chromium contributes to increase the hardness, tempering and oxidation resistance [5].

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There are many sensitive techniques for chromium determination, such as ICP- MS [6 - 8], ICP-AES [9], HPLC [10], spectrophotometry [11,12] and AAS [11,12]. A survey of literature reveals that Cr(III) reacts with many organic reagents at high temperature due to the inert nature of $[Cr(H_2O)_6]^{3+}$ complex. The time required varied from 20 minutes to 2 hours depending on the nature of reagents [13-15]. The need to monitor chromium in the environment has led to the application of increasingly complex analytical techniques [16, 17]. The other reagents used for the spectrophotometric determination of chromium include methylene blue [18], N-m-tolyl-*p*-methoxybenzohydroxamic acid [19], leuco Xylene cyanol FF [20], iodnitrotetrazolium chloride [21], and trifluoperazine hydrochloride [22]. The determination of chromium using saccharin [23], variamine blue [24], azure B [25] were also reported by our group.

In the present work three new coupling agents isatin, isonipecotamide and frusemide are introduced. Chromium(VI) oxidizes hydroxylamine to nitrite in acetate buffer of pH 4.0, which then diazotizes *p*-aminophenol to form diazonium salt. The diazonium salt is then coupled with isatin or isonipecotamide or frusemide in alkaline medium to form azo dye. Chromium(III) is determined after it is oxidized to chromium(VI) by bromine water. The method has been successfully applied to the determination of chromium in various water samples, soil samples and dietary supplement.

2. Experimental

2.1. Reagents and Apparatus

All absorbance values were measured using a SHIMADZU UV 2550 UV-VIS spectrophotometer with 1 cm matching cells. All chemicals used were of analytical grade and distilled water was used for preparing reagent solutions. A standard chromium(VI) solution was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 100 ml of water. Standard chromium(III) stock solution was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ in 50 ml of water, adding 1 ml of saturated sodium sulphate solution, acidifying with 1 ml of 2.5 M sulphuric acid, then boiling for 2 min to remove excess SO_2 and diluting with water to 100 ml. *p*- Aminophenol (0.05%), isatin (0.2%), isonipecotamide (0.2%), frusemide (0.2%), NaOH (4 mol L^{-1}), hydroxylamine hydrochloride (0.1%), bromine water (saturated), sulphosalicylic acid (5%), KOH (4.5 mol L^{-1}), HCl (5 mol L^{-1}), sulphuric acid (2.5 mol L^{-1}) were also used.

2.2. Determination of Chromium

An aliquot of a sample solution containing 0.02 to 0.6 µg $mL^{-1}$of chromium for PMP-IS system, 0.04-2.0 µg mL^{-1} of chromium for PMP- ISO system, 0.4-2.0 µg $mL^{-1}$of chromium for PMP-FRU system respectively was transferred into a series of 10 mL calibrated flasks, followed by addition of 0.5 mL of 0.1% hydroxylamine hydrochloride and 0.5 mL of the acetate buffer solution of pH 4. To this solution a volume of 0.5 mL of 0.05% *p*-aminophenol was added and the solution was allowed to stand for 2 minutes. Then, 2mL of isatin or isonipecotamide or frusemide was added followed by the addition of 1.5 mL of 4 mol L^{-1}sodium hydroxide solution, made up to the mark with distilled water, mixed thoroughly and after 5 minutes and the absorbance was measured at 524 or 533 or 558 nm respectively against the corresponding reagent blank. For the determination of Cr(III), suitable volume of an aliquot of sample solution of chromium(III) was transferred in to a series of 10 mL calibrated flasks. Volumes of 0.5 mL saturated bromine water and 0.5 mL KOH solutions were added to each flask and allowed to stand for 5minutes. Then 0.5 mL of sulfuric acid and 0.5 mL of sulfosalicylic acid were added and then above procedure for chromium(VI) was followed. The absorbance of the resulting solution was measured at 524 or 533 or 558 nm against the reagent blank

2.3. Determination of Chromium in water samples

Each filtered environmental water samples were analyzed for chromium. All the tested samples gave negative results. To these samples known amounts (not more than 0.02 to 0.6 μg mL^{-1} of chromium for PMP-IS system, 0.04-2.0 μg mL^{-1} of chromium for PMP- ISO system, 0.4-2.0 μg mL^{-1} of chromium for PMP-FRU) were spiked and analyzed for chromium by the proposed method (using PMP-IS, PMP-ISO and PMP-FRU) and also by the reference method [23].

2.4. Determination of chromium in soil samples

About 1 g of the soil sample (spiked with known amount of chromium samples) was weighed and placed in a 50 ml beaker and extracted triply with 5 ml of 1% sodium carbonate. The extract was filtered and made up to 100 mL in a standard flask. Suitable aliquot of the solution was transferred to a 10 mL calibrated flask and chromium content was determined directly according to the proposed method (Using PMP-IS, PMP-ISO and PMP-FRU) and also by the reference method [23].

2.5. Determination of chromium in tablets

Samples of the finely ground multivitamin- multimineral tablets containing chromium(III) were treated with 5mL of concentrated nitric acid, and the mixtures were evaporated to dryness. The residue was leached with 5mL of 0.5 mol L^{-1} H_2SO_4. The solution was diluted to a known volume with water. Suitable aliquots of the sample solution were analyzed according to the procedure for chromium(III).

3. Results and discussion

The nitrite generated by the oxidation of hydroxylamine by chromium(VI) is used to diazotize *p*-aminophenol. The diazonium salt formed is coupled with isatin or isonipecotamide or frusemide in an alkaline medium. The reactions are described in scheme 1.The reaction could be monitored spectrophotometrically and in the present work bromine water in an alkaline medium was used to oxidize Cr(III) to Cr(IV) and the excess oxidizer was removed by the addition of sulphosalicylic acid. In order to find the optimum reaction condition the effect of acidity, reagent concentrations were investigated. Optimum acidity for the formation of diazonium chloride was fixed to be 4 mol L^{-1} HCl. It was found that 1 mL of 0.05% solution of PMP was sufficient for complete diazotization. Isatin or isonipecotamide or frusemide was used as a 0.2% solution and 2 mL of IS or ISO or FRU was sufficient for maximum color development. Analytical parameters are evaluated by measuring the absorbance at 524 or 533 or 558 nm respectively against the reagent blank. The absorption spectra of azo dyes are presented in Fig. 1

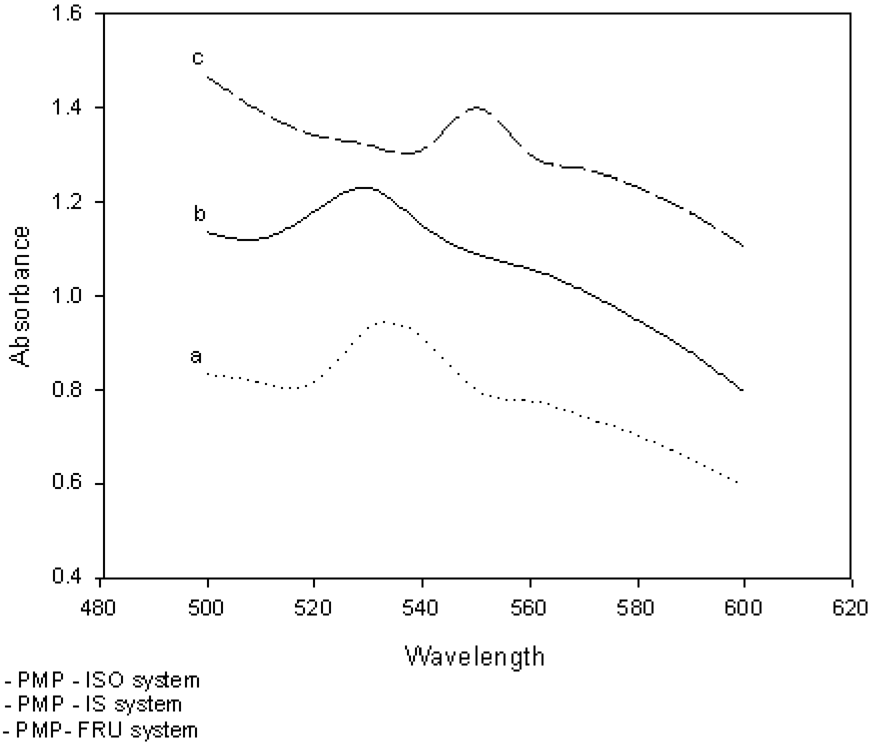
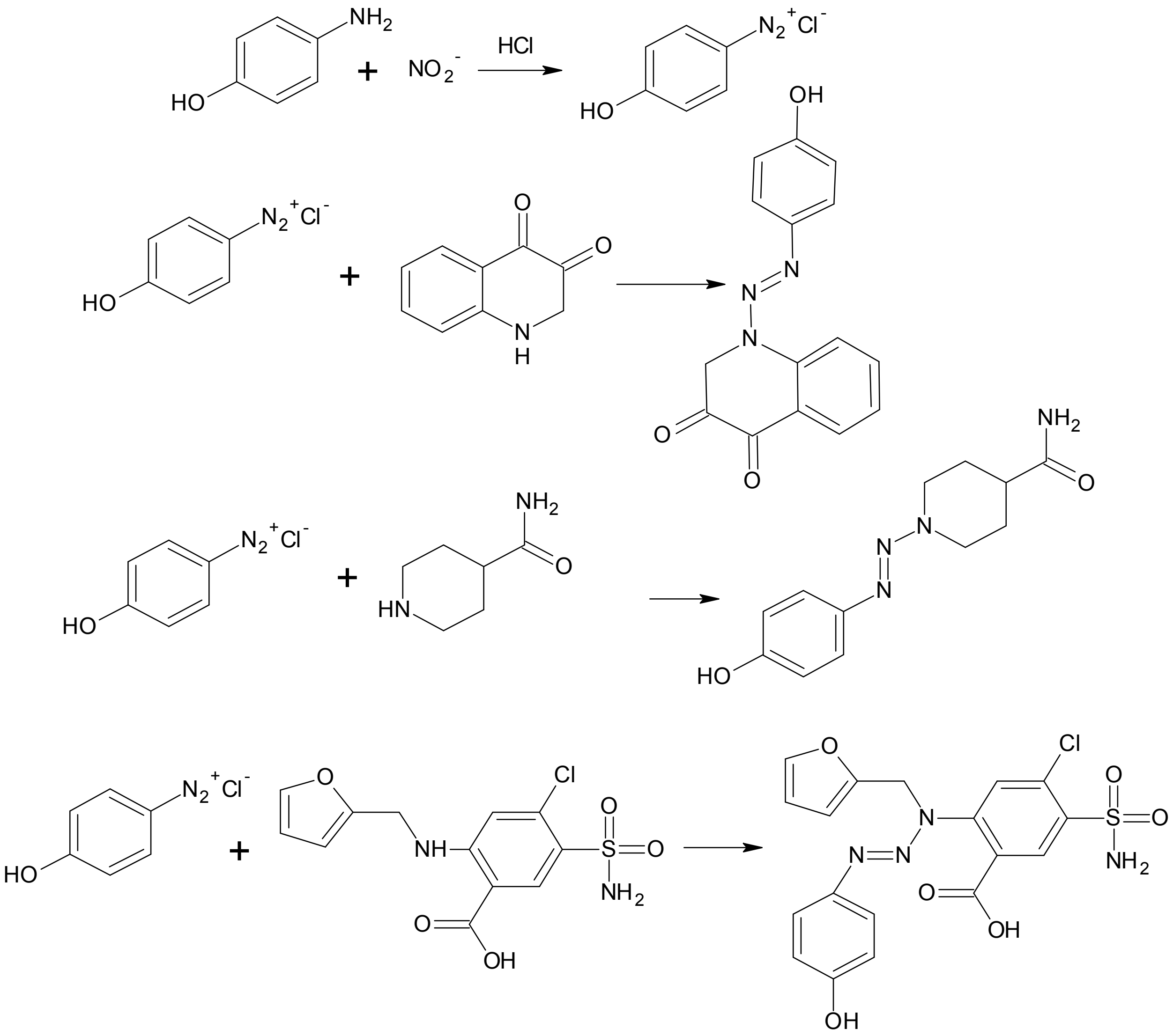


Fig. 1. The absorption spectra of PMP-ISO, PMP-IS, PMP-FRU systems respectively against the reagent blank

3.1. Reaction Scheme

$$2Cr_2O_7^{2-} + 3NH_2OH + 13H^+ \longrightarrow 4Cr^{3+} + 3NO_2^- + 11H_2O$$



3.2. Analytical data

The linearity of the spectrophotometric method for the determination of chromium was evaluated under optimum conditions. All the optimization steps were carried out with a chosen chromium concentration. The effects of possible interference and the maximum tolerable concentrations are given in Table 4. Beer's law was obeyed in the range of 0.02– 0.6µg mL^{-1}, 0.04-2.0µg mL^{-1} and 0.4-2.0 µg $mL^{-1}$of chromium when PMP-IS, PMP – ISO and PMP-FRU were used as the reagent respectively. The molar absorptivity, Sandell sensitivity for PMP-IS, PMP-ISO system were found to be 4.4×10^4 $Lmol^{-1}$ cm^{-1}, 0.001 μgcm^{-2} and 2.0×10^4 $Lmol^{-1}cm^{-1}$,0.003 μgcm^{-2} , while that for PMP-FRU system was found to be 5.0 $\times10^4$ $Lmol^{-1}$ cm^{-1}, 0.001 µg cm^{-2}.

Table 4: Effect of diverse ion on the determination of chromium

Foreign ion	Tolerance limit (µg mL-1)
Oxalate, tartrate, acetate, citrate	1200
Ba^{2+}, Cd^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}	>1600
Mg^{2+}, Mn^{2+}, Al^{3+}	600
EDTA	1000
Na^{+}, Cl^{-}, NO_3^{-}	>1500

3.3. Applications

The proposed method has significant advantage over the reported method in terms of simplicity, sensitivity and rapidity [22-24,26,27].When compared with other existing methods, the developed method retains the specific interaction of Cr(VI) with PMP-IS, PMP-ISO and PMP-FRU to form color derivatives and good sensitivity is achieved at room temperature without the need for extraction. Accurate and reproducible results are obtained with permissible standard deviation. The precision and accuracy of the method was studied by analyzing the coupling solution containing known amounts of the cited reagents within Beer's law limit. The law values of the relative standard deviation in percentages and the error indicated the high accuracy of the methods. The method has been successfully applied to the determination of chromium in various water samples, soil samples and dietary supplement (Tables 1, 2 and 3).

Table 1: Determination of chromium in different water samples, soil samples and dietary supplement (*p*-aminophenol with isatin)

Samples		Standard method		Proposed method		[b]t - test	[c]F-test
				PAP+ ISA			
	Chromium Added µg mL^{-1}	[a]Chromium Found µg mL^{-1}±SD	Relative Error (%)	[a]Chromium found µg mL^{-1}±SD	Relative Error(%)		
Sample1	0.2	0.196±0.006	0.66	0.201±0.010	0.50	0.236	2.78
	0.4	0.410±0.020	2.50	0.404±0.010	1.00	0.894	4.00
	0.6	0.601±0.010	0.13	0.596±0.007	0.56	1.270	2.04
Sample2	0.2	0.201±0.010	0.25	0.207±0.008	0.92	2.060	1.56
	0.4	0.396±0.005	0.66	0.402±0.002	0.50	2.230	6.25
	0.6	0.606±0.007	1.00	0.605±0.007	0.70	1.560	1.00
Sample3	0.2	0.204±0.004	0.66	0.201±0.010	0.06	2.845	6.25
	0.4	0.418±0.010	2.25	0.407±0.008	0.92	2.060	1.56
	0.6	0.598±0.010	-1.00	0.606±0.010	3.00	1.340	1.00
Soil samples	0.4	0.404±0.004	1.00	0.402±0.002	0.25	2.236	4.00
	0.6	0.606±0.007	1.00	0.406±0.010	1.00	1.346	2.04

Table 1 (continued)

Tablets	Chromium certified in mg	Chromium found in mg	Relative Error (%)	Chromium found in mg	Relative Error(%)	[b]t - test	[c]F-test
	0.4	0.401±0.010	0.06	0.403±0.004	0.40	1.700	6.25
	0.6	0.603±0.004	0.50	0.604±0.003	0.55	2.810	1.77

[a]Mean ± Standard deviation (n=5)
[b]Tabulated t- value for 5 degrees of freedom at 95% probability level is 2.31.
[c]Tabulated F- value for (4,4) degrees of freedom at 95% probability level is 6.39
Tablets – Chromoplex (Label claim, 0.2 milligram per tablet) Aristo Pharmaceuticals Ltd., India.

Table 2: Determination of chromium in different water samples, soil samples and dietary supplement (*p*-aminophenol with isonipecotamide)

Samples	Chromium added $\mu g\ mL^{-1}$	Standard method		Proposed method		[b]t-test	[c]F-test
				PMP+ ISO			
		[a]Chromium Found $\mu g\ mL^{-1}$±SD	Relative Error (%)	[a]Chromium found $\mu g\ mL^{-1}$±SD	Relative Error(%)		
Sample1	0.8	0.803±0.004	0.40	0.806±0.008	0.72	1.620	4.00
	1.0	0 .078±0.020	1.30	1.020±0.020	2.00	2.236	1.00
	2.0	2.026±0.040	0.51	2.046±0.080	0.05	1.162	4.00
Sample2	0.8	0.812±0.003	1.50	0.804±0.003	0.55	2.810	1.00
	1.0	0.078±0.060	1.30	1.079±0.060	1.33	1.321	1.00
	2.0	0 .074±0.040	1.84	2.052±0.080	0.43	1.341	4.00
Sample3	0.8	0.804±0.004	0.55	0.806±0.007	0.70	1.916	3.06
	1.0	1.039±0.050	3.90	1.024±0.050	1.35	1.079	1.00
	2.0	2.054±0.030	1.35	2.038±0.040	0.95	2.12	1.78
Soil samples	1.0	1.004±0.010	0.40	1.026±0.004	0.51	2.980	6.25
	2.0	2.052±0.040	0.43	2.018±0.020	0.02	2.310	4.00
	Chromium certified in mg	Chromium found in mg	Relative Error (%)	Chromium found in mg	Relative Error(%)	[b]t-test	[c]F-test
Tablets	0.6	0.606±0.007	0.70	0.604±0.003	0.66	2.980	5.44
	0.8	0.804±0.004	0.55	0.805±+0.007	0.72	1.620	3.06

[a] Mean ± Standard deviation (n=5)
[b]Tabulated t- value for 5 degrees of freedom at 95% probability level is 2.31.
[c]Tabulated F- value for (4,4) degrees of freedom at 95% probability level is 6.39
Tablets – Chromoplex (Label claim, 0.2 milligram per tablet) Aristo Pharmaceuticals Ltd., India,

Table 3: Determination of chromium in different water samples, soil samples and dietary supplement (*p*-aminophenol with frusemide)

Samples	Chromium Added µg mL^{-1}	Standard method		Proposed method		[b]t - test	[c]F-test
				PAP + FRU			
		[a]Chromium Found µg mL^{-1}±SD	Relative Error (%)	[a]Chromium found µg mL^{-1}±SD	Relative Error(%)		
Sample1	0.8	0.803 ±0.004	0.40	0.807±0.008	0.93	2.060	4.00
	1.0	0 .078±0.035	1.30	1.078±0.080	0.65	2.180	5.22
	2.0	2.026±0.020	0.51	2.034±0.030	0.57	2.710	2.25
Sample2	0.8	0.812±0.020	1.50	0.798±0.008	0.25	0.550	6.25
	1.0	0.078 ±0.060	1.30	1.014±0.030	0.23	2.000	4.00
	2.0	2.074 ±0.030	1.84	2.046±0.080	0.58	1.162	7.11
Sample3	0.8	0.804±0.004	0.55	0.796±0.006	0.66	1.400	2.25
	1.0	0.039±0.040	3.90	1.102±0.060	2.56	3.816	2.25
	2.0	2.014±0.030	1.35	2.016±0.040	0.82	0.960	1.78
Soil samples	1.0	1.004±0.020	0.40	1.034±0.030	0.57	2.710	2.25
	2.0	2.052±0.040	0.43	1.024±0.020	2.40	2.680	4.00

	Chromium certified in mg	Chromium found in mg	Relative Error (%)	Chromium found in mg	Relative Error(%)	[b]t - test	[c]F-test
Tablets	0.6	0.606±0.007	0.70	0.612±0.010	1.50	2.720	2.04
	0.8	0.804±0.004	0.55	0.807±0.008	0.92	2.000	4.00

[a] Mean± Standard deviation(n=5)
[b] T abulated t- value for 5 degrees of freedom at 95% probability level is 2.31.
[c] Tabulated F- value for (4,4) degrees of freedom at 95% probability level is 6.39
Tablets –Chromoplex, (Label claim, 0.2 milligram per tablet) Aristo Pharmaceuticals Ltd., India

4. Conclusion

The results from this study show that proposed work is simple, rapid and sensitive for the determination of chromium(VI). The introduction of new coupling agents isatin, isonipecotamide and frusemide, determination of Cr(IV) and Cr(III) individually make the method more advantages. No extraction step is required and hence, the use of organic solvents, which are generally toxic pollutants, is avoided. The results of the parallel determination with the standard method confirm the precision and accuracy of the method.

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