

A Rapid Spectrophotometric Method for the Determination of Chromium in Environmental Samples using Bis (salicylaldehyde) orthophenylenediamine

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Abstract

A very simple, ultra-sensitive and fairly selective spectrophotometric method is presented for the rapid determination of chromium at trace level using bis(salicylaldehyde)orthophenylenediamine (BSOPD). The method is based on the reaction of non-absorbing BSOPD in a strong acidic (5.0 M H_2SO_4) media with chromium(VI) to produce a highly absorbing orange colored chelate-product that has an absorption maximum at 478 nm. The reaction is instantaneous and the absorption remains stable for 6 hours. The average molar absorption coefficient and Sandell's sensitivity were found to be $1.67 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 10.0 ng cm^{-2} of chromium (VI), respectively. Linear calibration graphs were obtained for $0.02 - 4.0 \text{ mg L}^{-1}$ of Cr (VI). A large excess of over 50 cations, anions and complexing agents (e.g. EDTA, tartrate, oxalate, citrate, phosphate, thiocyanate etc.) do not interfere in the determination. The method was successfully used for the determination of chromium in several Standard Reference Materials (steels and alloys), environmental waters and solutions containing both chromium (III) and chromium (VI) as well as some complex synthetic mixtures. The method has high precision and accuracy ($s = \pm 0.0$ for 0.5 mg L^{-1}).

Keywords: Spectrophotometry; bis (salicylaldehyde) orthophenylenediamine; chromium; environmental.

Introduction

Chromium is the sixth most abundant element in the earth's crust and exists in three common stable valence states. In the environment hexavalent state is almost totally derived from human activities. Metallurgical, chemical and refractory industries are the most important industrial sources of chromium in the atmosphere. The reduction of Cr(VI) may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target organs¹. The balance that exists between extracellular Cr(VI) and intracellular Cr(III) is what ultimately dictates the amounts and rates at which Cr(VI) can enter cells and impart its toxic effects². There is a significant association between exposure to Cr(VI) and lung cancer³. Long-term workers had a higher lung cancer risk than short-term workers⁴. An analysis of lung cancer risk suggests a potential excess risk of death from lung cancer among U.S. workers exposed to the previous permissible exposure limit (PEL) for Cr(VI) of $52 \mu\text{g m}^{-3}$ ⁵. More recent studies also disclosed excess risk of lung cancer death resulting from occupational exposure to Cr(VI) compounds⁶.

The first defense against Cr(VI) after oral exposure is the reduction of Cr(VI) to Cr(III) in the gastric environment where gastric fluid⁷ and ascorbate⁸ play important roles. Approximately 10% of an absorbed dose is eliminated by biliary excretion, with smaller amounts excreted in hair, nails, milk and sweat⁹. Solubility and pH appear to be the primary determinants of the capacity of individual chromium compounds to elicit an allergic response¹⁰. The low solubility Cr(III) compounds are much less efficient contact allergens than Cr(VI)¹¹. The characteristic chrome sore begins as a papule, forming an ulcer with raised hard edges. Ulcers can penetrate deep into soft tissue or become the sites of secondary infection, but are not known to lead to malignancy¹². One study found increased blood chromium level after total hip replacement using metal-metal pairings where metal ions of the alloys are released¹³. Cr(VI) enters many types of cells and under physiological conditions can be reduced by hydrogen peroxide (H_2O_2), glutathione (GSH) reductase, ascorbic acid, and GSH to produce reactive intermediates, including Cr(V), Cr(IV), thiylradicals, hydroxyl radicals, and ultimately, Cr(III). Any of these

species could attack DNA, proteins, and membrane lipids, thereby disrupting cellular integrity and functions.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. Bis (salicylaldehyde) orthophenylenediamine (BSOPD) has never been used as a spectrophotometric reagent for the determination of chromium in aqueous medium. This paper reports in its use in a very sensitive, highly specific new spectrophotometric method for the trace determination of chromium. The method possesses distinct advantages over existing methods¹⁴⁻³⁰ with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH / acidity range, thermal stability, accuracy, precision and ease of operation. The method is based on the reaction of non-absorbent BSOPD in a strong acidic solution (5.0 M H₂SO₄) with Chromium (VI) to produce a highly absorbent orange chelate product followed by a direct measurement of the absorbance in an aqueous solution. With a suitable masking, the reaction can be made highly selective and the reagent blank solutions do not show any appreciable absorbance.

Materials and methods

Apparatus: A Shimadzu (Kyoto, Japan) (Model-1800) double beam UV-Visible recording spectrophotometer and Hanna Combo meter, Model-HI 255 pH-meter with a combination of electrode were used for the measurements of absorbance and pH respectively.

Reagents and the Solutions: All the chemicals used were of analytical reagent grade or the highest purity available. Doubly distilled deionized water, which is non-absorbing under visible radiation, was used throughout. Glassware were cleaned by soaking in acidic solutions of KMnO₄, followed by washing with concentrated HNO₃ and rinsed several times with demonized water. Stock solutions and environmental water sample (1000 mL each) were kept in a polypropylene bottles containing 1 mL of concentrated HNO₃. More rigorously contamination control was applied.

Synthesis and characterization of BSOPD: The reagent was synthesized according to the method recommended by Salam et al.³².

BSOPD solution, 1.58 ×10⁻³ M: The reagent

solution was prepared by dissolving the requisite amount of bis (salicylaldehyde) orthophenylenediamine (BSOPD) in a known volume of N,N-dimethylformamide(DMF). More dilute solutions of the reagent were prepared as required.

Chromium(VI) standard solution, 1.9 ×10⁻² M
A 100 mL amount of stock solution (1 mg mL⁻¹) of chromium was prepared by dissolving 565.7 mg of potassium dichromate (K₂Cr₂O₇) in doubly distilled deionized water.

Other solutions: Solutions of a large number of inorganic ions and complexing agents were prepared from their AnalaR or equivalent grade water soluble salts (or the oxides and carbonates in hydrochloric acid).

Sample collection and preservation: Water samples were collected in polythene bottles from shallow tube-wells, rivers and tap water of different sources of Chittagong, Bangladesh. After collection, conc. nitric acid (1 mL L⁻¹) was added as preservative.

Procedure: A volume of 0.1–1.0 mL of a neutral aqueous solution containing 0.2–40.0 µg of chromium(VI) was taken in a 10 mL calibrated flask, then 1.5 –2.5 mL (preferably 1.5 mL) of 5M sulfuric acid and 1mL of EDTA solution was added. The mixture was mixed well and then 1:20–1:50 fold molar excess of bis (salicylaldehyde) orthophenylenediamine (BSOPD) reagent solution (preferably 0.7 mL of 1.58×10⁻³ M) was added. The mixture was diluted to the mark with deionized water. The absorbance was measured at 478 nm against a corresponding reagent blank. The chromium content in an unknown sample was determined using a concurrently prepared calibration graph.

Result and Discussion

Factors affecting the absorbance: Absorption spectra. The absorption spectra of a chromium (VI)-BSOPD system in a 5M sulfuric acid medium was recorded using the spectrophotometer. The absorption spectra of the chromium (VI)-BSOPD is a symmetric curve with maximum absorbance at 478 nm and an average molar absorption coefficient of 1.67 ×10⁴ L mol⁻¹ cm⁻¹ (Fig. 1). The reagent blank did not show any absorbance in the

range of determination. In all instances measurements were done at 478 nm against a reagent blank.

Effect of solvent: Because BSOPD is insoluble in water, an organic solvent was used for the system. The various solvents (benzene, chloroform, acetone, carbon tetrachloride, nitrobenzene, isobutyl alcohol, 1-butanol, isobutyl methyl ketone, ethanol, 1,4-dioxan and N,N-dimethylformamide (DMF) studied, DMF was found to be the best solvent for the system. No absorbance was found in the organic phase.

Effect of acidity: Of the various acids (nitric acid, sulfuric acid, hydrochloric acid and phosphoric acid) studied, sulfuric acid was found to be the best acid for the system. The variation of absorbance was noted after the addition of 0.5–3.0 mL of 5.0M sulfuric acid to every 10 mL of test solution. The maximum and constant absorbance was obtained in the presence of 1.5–2.5 mL of 5M sulfuric acid at room temperature (25 ± 5)°C. This corresponds to 0.75 – 1.25M acidity range (Fig. 3) in the final dilution. For all subsequent measurements, 1.5 mL of 5.00 M sulfuric acid (or pH 0.4) was added.

Effect of time: The reaction is very fast. A constant maximum absorbance was obtained just after dilution to volume and remained strictly unaltered for 6h.

Effect of reagent concentration: Different molar excess of BSOPD were added to a fixed metal ion concentration and the absorbance were measured according to the standard procedure. It was observed that at 1 mg L⁻¹ of chromium metal, the reagent molar ratios of 1:20 and 1:50 produced a constant absorbance of the Cr chelate (Fig. 4). For different chromium-concentration (0.5 and 1.0 mg L⁻¹) an identical effect of varying the reagent concentration was noticed. A greater excess of reagent were not studied. For all subsequent measurements, 0.7 mL of 1.58×10^{-3} M BSOPD reagent was added.

Effect of temperature: The absorbance of Cr-BSOPD complex was measured at different temperatures (0-40°C) and found to be strictly unaltered throughout the temperature range of 10-40°C. Therefore, all measurements were done at

room temperature (25 ± 5)°C).

Calibration graph (Beer's law and sensitivity):

The well-known equation for spectrophotometric analysis in a very dilute solution was derived from Beer's law. The effect of metal concentration was studied over 0.01 – 10 mg L⁻¹ distributed in three different sets (0.01– 0.1, 0.1– 1.0 and 1.0– 10.0 mg L⁻¹) for convenience of the measurements. The absorbance was found linear for 0.02 – 4.0 mg L⁻¹ of chromium at 478 nm. Of the three calibration graphs which shows the limit of linearity is shown in Fig. 5. The other graph was straight line passing through the origin. The molar absorption coefficient and the Sandell's sensitivity³³ were found to be 1.67×10^4 L mol⁻¹cm⁻¹ and 10.0 ng cm⁻² of Chromium (VI) respectively. The selected analytical parameters obtained with the optimization experiments are summarized in Table 2.

Effect of foreign ions

The effect of over 50 cations and complexing agents on the determination of only 1 mg L⁻¹ of chromium (VI) was studied (Table 3). The criterion for interference³⁴ was absorbance value varying ± 5 % from the expected value for chromium alone. The results are summarized in Table 3. As can be seen, a large number of ions have no significant effect on the determination of chromium. The most serious interference was from Fe (II) ion. Interference from this ion is probably due to complex formation with BSOPD. The greater tolerance limits for these ions can be achieved by using masking methods. In order to eliminate the interference of Fe(II), 10 mg L⁻¹ EDTA was added and the precipitation formed in any case was filtered off. As stated above, the proper masking and precipitating agents may be added by while aiming at different interfering ions according to actual comparison of the sample. For this reason, the selectivity of the proposed method is greatly improved and practically is increased. Particularly, the chromium amounts in complex samples may be determined by using the proposed method. Moreover, the tolerance limits of NO₃⁻, ClO₄⁻, SO₄²⁻ are especially high which is advantageous with respect to the digestion of the samples.

Precision and accuracy: The precision of the present method was evaluated by determining different concentrations of chromium (each

analyzed at least five times). The relative standard deviation ($n=5$) was 2–0% for 0.2– 40.0 μg of chromium in 10 mL, indicating that this method is highly precise and reproducible (Table 2). The detection limit ($3s$ of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for chromium (VI) were found to be 1.0 ng mL^{-1} and 10.0 ng cm^{-2} respectively. The results for total chromium were in good agreement with the certified values (Table 5). The reliability of our chromium-chelate procedure was tested by adding chromium(VI) spike to some environmental water samples and the results were quantitative, as shown in Table 6. The method was also tested by analyzing several synthetic mixtures containing chromium (VI) and divers' ions (Table 4).

Application: The present method was successfully applied to the determination of chromium (VI) in a series of synthetic mixtures of various composition (Table 4), and also in a number of real samples, e.g., several Certified Reference Materials (CRMs) (Table 5). The method also extended to the determination of Chromium in a number of environmental, water samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such sample were analyzed for Chromium content; the recoveries in both the 'spiked' (added to the samples before the mineralization or dissolution) and the 'unspiked' samples are in good agreement (Table 6). The precision and accuracy of the method were excellent.

Determination of chromium in synthetic mixtures: Several synthetic mixtures of varying composition containing Chromium(VI) and diverse ions of known concentrations were determined by the present method using tartrate or EDTA as a masking agent; and the results were found to be highly reproducible as shown in Table 4. Accurate recoveries were achieved in all solutions.

Determination of chromium in alloy and steel (certified reference materials): A 0.1 g amount of alloy or steel sample containing (0.02 to 1.45) % of chromium was accurately weighed and placed in a 50-mL Erlenmeyer flask following a method recommended by Parker³⁵. To it 10 mL of concentrated HNO_3 and 2 mL concentrated H_2SO_4 were carefully added and then covered with a watch-glass until the brisk reaction subsided. The

solution was heated and simmered gently after the addition another 5 mL of concentrated HNO_3 until all carbides were decomposed. The solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen, and the cooled to the room temperature (25 ± 5)⁰C. After suitable dilution with deionized water, the content of Erlenmeyer flask were warmed to dissolve the soluble salts. The solution was cooled and neutralized with dilute NH_4OH solution in the presence of a 0.1 % (w/v) EDTA solution. The resulting solution was filtered, if necessary, through Whatman No. 40 filter paper into a 25-mL calibrated flask. The residue was washed with a small volume of (5 mL) hot (1:99) H_2SO_4 followed by water; the volume was made up to the mark with deionized water. A suitable aliquot (1-2 mL) of the above mentioned solution was taken into a 10-mL calibrated flask and the Chromium content was determined as described under procedure using EDTA as masking agent. Based on five replicate analyses, the average chromium concentration determined by spectrophotometric method was in close agreement with the certified values. The average percentage recovery obtained for addition of a chromium(VI) spike to some certified reference materials was quantitative. The results are shown in Table 5.

Determination of chromium in environmental water samples: Each filtered samples (1000 mL) was evaporated nearly to dryness with a mixture of 5 mL of concentrated H_2SO_4 and 10 mL of concentrated HNO_3 in a fume cupboard, following a method recommended by Clesceri et al.³⁰ and was then cooled to room temperature. The residue was then heated with 10 mL of deionized water in order to dissolve the salts. The solution was then cooled and neutralized with dilute NH_4OH in the presence of a 1-2 mL of 0.1% (w/v) EDTA solution. The resulting solution was then filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with deionized water. An aliquot (1-2 mL) of this pre-concentrated water sample was pipetted into a 10-mL calibrated flask and then Chromium content was determined as described under the procedure using EDTA as a masking agent. The results of analysis of environmental water samples from various sources for chromium are given in Table 6.

Determination of chromium (VI) and chromium (III) speciation in mixture: Suitable aliquots (1-2

mL) of Chromium(VI+III) mixtures (preferably, 1:1, 1:2, 1:3) were taken in a 25-mL conical flask. A few drops of 1 molar sulfuric acid and 1-2 mL of 1% (w/v) potassium permanganate solution were added to oxidize the divalent chromium. A 5 ml of water was added to the mixtures and heated on a steam bath for 10-15 minutes, with occasional gentle shaking, and then cooled to room temperature. Then, 3-4 drops of freshly prepared sodium azide solution (2.5% w/v) were added and gently heated with a further addition of 2-3 mL of water if necessary, for 5 minutes to drive off the azide and cooled to room temperature. The reaction mixture was neutralized with dilute ammonia and transferred quantitatively into a 10-mL volumetric flask. Then total chromium (VI+III) content was determined according to the general procedure with the help of calibration graph. An equal aliquot of the above chromium (VI+III) mixtures (preferably, 1:1, 1:2, 1:3) were taken in a 25-ml beaker and 1 mL of 0.1% (w/v) EDTA solution was added to mask chromium (III) and then neutralized with dilute ammonia. After, the content of the beaker was transferred into a 10-mL volumetric flask and its chromium (VI) was determined according to the general procedure. The value of chromium (III) concentration was calculated by subtracting the concentration of chromium (VI) from the corresponding total chromium concentration. These values were found to be highly reproducible. The results of a set of determination are given in Table 7.

Conclusions

In this paper, a new simple, sensitive, selective and inexpensive method with the Cr(VI)-BSOPD complex developed for the determination of chromium in industrial, environmental, biological and soil samples, for continuous monitoring to establish the trace levels of chromium in different samples matrices. It offers also a very efficient procedure for speciation analysis. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES and ICP-MS, are available for the determination of chromium at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories in developing countries with limited budgets. The

sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method are very reliable for the determination of chromium in real samples down to ngg^{-1} levels in aqueous medium at room temperature ($25 \pm 5^\circ\text{C}$).

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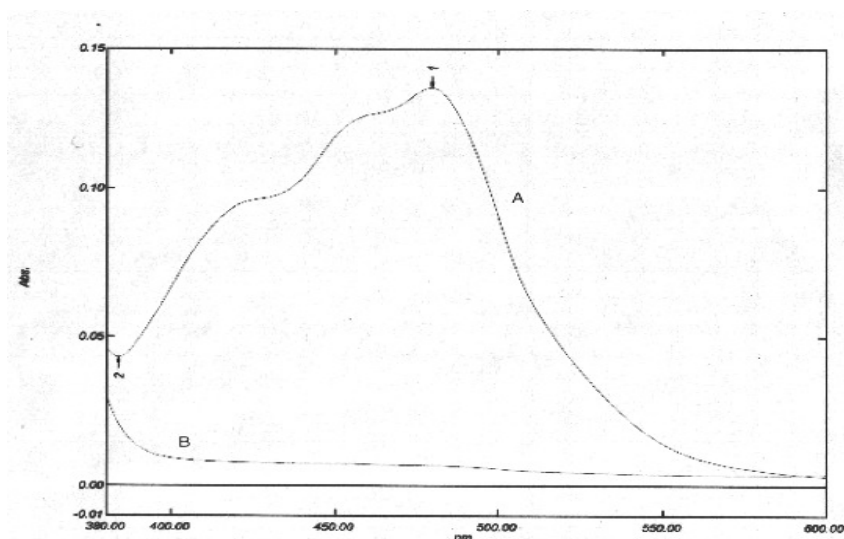


Figure2: A and B absorption spectra of Chromium-BSOPD and the reagent blank ($\lambda_{\max} = 478$ nm) in aqueous solutions.

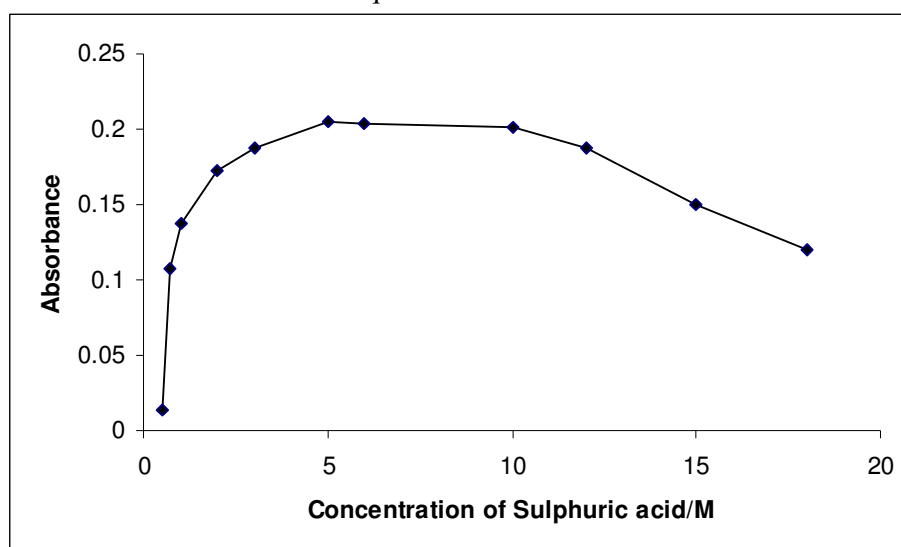


Figure3: Effect of acidity on the absorbance of the Cr^{VI}-BSOPD system

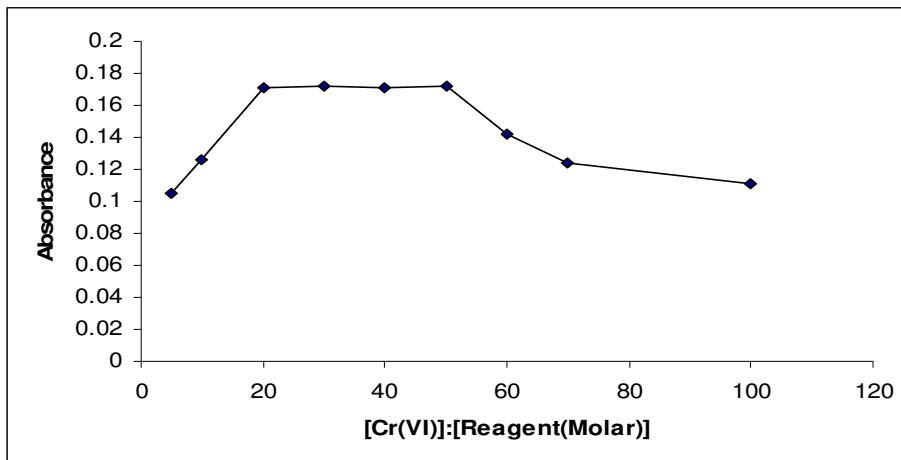


Figure 4: Effect of the reagent (BSOPD:Cr^{VI} molar concentration ratio) on the absorbance of the Cr^{VI}-BSOPD system

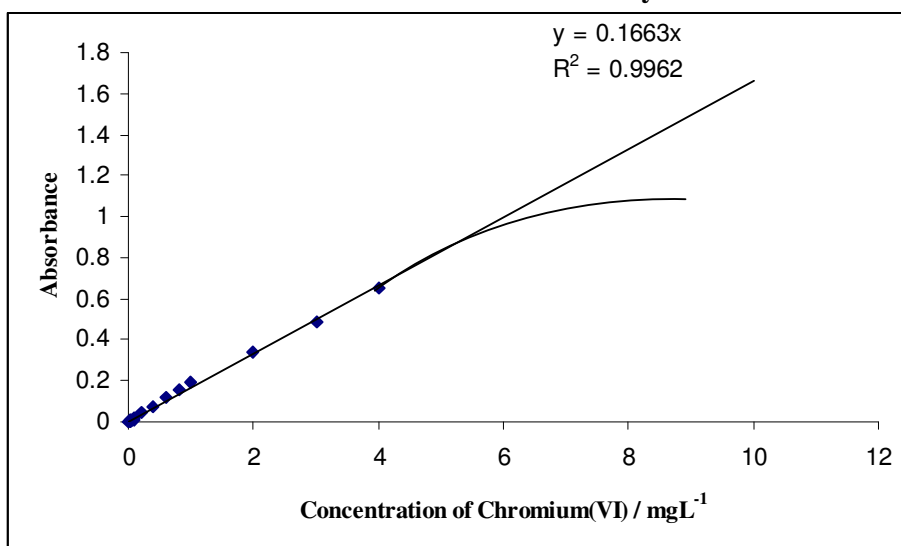


Figure 5: Calibration graph for 0.02 – 10.00 mg L⁻¹ of chromium (VI)

Table-1: Review of existing spectrophotometric methods for the determination of chromium using different reagents

Reagent	λ_{max} (nm)	Molar absorption co-efficient (L mol ⁻¹ cm ⁻¹)	Beer's Law (mgL ⁻¹)	Remarks
Ferron ¹⁴	510	---	5-70	1. Solvent extraction method was used 2. Carcinogenic chloroform solvent was used
Propylene carbonate ¹⁵	362	1.95 × 10 ³	0-100 µg	1. Solid phase extraction was used 2. UV range
Benzyltributylammonium ¹⁶	365	---	0-100 µg	1. Solvent extraction method was used 2. Carcinogenic chloroform solvent was used 3. UV range

Reagent	λ_{\max} (nm)	Molar absorption co-efficient ($L\text{ mol}^{-1}\text{ cm}^{-1}$)	Beer's Law (mgL^{-1})	Remarks
Protriptylinium ¹⁷	365	---	500 μg dichromate	1. Solvent extraction method was used 2. Carcinogenic chloroform solvent was used 3. UV range
Alizarin blue S(ABS) ¹⁸	510 575	7.4×10^4	0.4-1.0	1. Dual wavelength method 2. Time consuming
Tween-80 microemulsion ¹⁹	528		0.0480	1. pH dependent 2. Time consuming
Diphenyl carbazide and 4-methylbenzenesulfonic acid ²⁰	540	5×10^4	0-0.8	1. Liquid-liquid extraction method was used 2. Color stable for 3 h.
1,5-diphenylcarbazine complex on a column of chitin ²¹	541	3.5×10^4	0.05–0.6	1. Time consuming elution method 2. Tolerance limits for Fe(III) is low
Iodonitrotetrazolium chloride and Tetrazolium Violet ²²	---	---	---	1. Extraction method was used
Iodnitrotetrazolium chloride ²³	250	$(3.70 \pm 0.08) \times 10^4$		1. Extraction method was used 2. UV range
Methylene Blue ²⁴	--	--	--	1. Extraction method was used
Diphenylcarbazine ²⁵	--	--	--	1. Micellar media 2. Elution technique
Variamine blue ²⁶	556	0.911×10^4	2-12 mg mL^{-1}	1. Not trace method 2. Cu(II), Fe(III), Ce(IV) interfere severely
Lissamine Turquoise ²⁷	641	---	0.2 - 5	1. Interference from Cr(III), Hg, Sb, Fe and Se 2. pH dependent
Sulfanilic acid and hydrogen peroxide ²⁸	360	---	up to 200 ng mL^{-1}	1. pH dependent 2. Cu^{2+} and Co^{2+} interfere 3. Highly toxic Potassium cyanide used 4. UV range
1,4,8,11-tetraazacyclotetradecane (cyclam) ²⁹	379	1.5×10^4	0.2–20	1. UV range
Diphenylcarbazine ³⁰	540	4×10^4	---	1. Reagent very unstable 2. Mo(VI), Hg(II) and Indium interfere.
bis(salicylaldehyde) orthophenylenediamine ³¹	482	3.5×10^5	0.01-12	1. Micellar media
bis(salicylaldehyde) orthophenylenediamine (Proposed method)	478	1.67×10^4	0-4.0	1. Non-extractive 2. Highly sensitive 3. Fairly selective 4. Aqueous reaction medium 5. Simple and rapid

Table-2: Selected analytical parameters obtained with the optimization experiments.

Parameters	Studied range	Selected value
Wavelength / λ_{\max} (nm)	200 – 800	478
Acidity / M H ₂ SO ₄	0.0005 – 18	5.0-10 (preferably 5.0)
pH	0 – 3.25	0.3 - 0.4 (preferably, 0.3)
Time / h	0 – 24	1 min – 6h (preferably 5 min)
Solvent / % DMF	0 – 100	40- 60 (preferably, 50)
Temperature / °C	25 ± 5	25 ± 5
Reagent (fold molar excess, M : R)	1 : 5 – 1: 100	1:20-1:50(preferably 1:40)
Average molar absorptivity / L mol ⁻¹ cm ⁻¹	0.985×10 ⁴ - 2.355×10 ⁴	1.67 ×10 ⁴
Linear range / mg L ⁻¹	0.0-100	0.02 – 4.0
Detection limit / µg L ⁻¹	0.01 – 20	1.0
Sandell's sensitivity / ng cm ⁻²	1.0 – 20	10.0
Reproducibility(% RSD)	0 – 2	0 -2
Regression co-efficient	0.9984 -0.9999	0.9998

Table-3: Table of tolerance limit of foreign ions^a

Species x	Tolerance ratio [Species (x) / Cr (w/w)]	Species x	Tolerance ratio [Species (x) / Cr (w/w)]	Species x	Tolerance ratio [Species (x) / Cr (w/w)]
Acetate	100	Cadmium	100	Potassium	1000
Ammonium (I)	1000	EDTA	100	Selenium (IV)	100
Arsenic (III)	500	Fluoride	1000	Silver	1000
Citrate	1000	Iron (II)	10 ^b	Sodium	1000
Barium	100	Lead (II)	100	Strontium	100
Bismuth(II)	100	Magnesium (II)	100	Tartrate	100
Bromide	1000	Manganese (II)	50	Perchlorate	1000
Cadmium	100	Mercury (II)	100	Nitrate	1000
Calcium(II)	1000	Molybdenum (VI)	100	Tin (II)	100
Chromium (III)	100	Nickel (II)	100	Tungsten (VI)	100
Cerium(II)	100	Nitrate	1000	Zinc(II)	100
Copper (II)	100	Phosphate	100		

^a Tolerance limit defined as ratio that causes less than 5 % interference.

^b With 10 µg mL⁻¹ EDTA

Table-4: Determination of chromium in some synthetic mixtures

	Composition of mixtures / mg L ⁻¹	Chromium (VI)/mg L ⁻¹		
		Added	Found ^a	Recovery \pm s _r ^b (%)
A	Cr(VI)	0.50	0.50	98 \pm 0.8
		1.00	0.99	100 \pm 0.0
B	As in A + Ca ²⁺ + Mg ²⁺	0.50	0.49	100 \pm 0.0
		1.00	1.02	99 \pm 1.0
C	As in B + Mn ²⁺ + Al ³⁺	0.50	0.48	98 \pm 0.6
		1.00	0.98	102 \pm 1.0
D	As in C + Mo(VI) + Hg ²⁺	0.50	0.52	104 \pm 0.8
		1.00	1.03	106 \pm 1.5
E	As in D + Co ²⁺ + Cu ²⁺	0.50	0.54	108 \pm 1.8
		1.00	1.09	109 \pm 2.0

^a Average of five replicate determinations.

Table-5: Determination of Chromium in certified reference materials

Certified Reference Materials (Composition, %)	Chromium / mg L ⁻¹		RSD, %
	Certified Value	Found (n = 5)	
(i) BAS-CRM 69b High-Speed Steel, (Cr=4.55, Mo=4.95, V=1.99 and Te=0.52)	4.55	4.52	1.3
(ii) BCS-CRM-261 Straighe 18/12 Stainless Steel, (C=0.083, Si=0.39, SCr=17.20, Ni=13.08, Mn=0.66, Nb+Ta=0.71)	17.20	17.00	1.00
(iii) GSBH-40101-96a Cr17MoVCo Dies tensile steel (Cr=11.63, Ni=0.095, Cu=0.82, Mo=0.986, V=0.411, Co=0.02)	11.63	11.58	1.5
(iv) SBC -1013-1-95a Cr17MoVCo High tensile steel (C=90, Si=0.44, Mn=0.81, Cr=16.3, Mo=0.52, V=0.24, Co=1.45)	16.3	16.1	2.0

^aThese CRMs were obtained from Beijing NCS Analytical Instruments Co. Ltd., China.

Table 6. Determination of chromium in some environmental water samples

Sample		Chromium / $\mu\text{g L}^{-1}$		Recovery \pm s (%)	S_r^b (%)
		Added	Found ^a		
River water	Sangu (upper)	0	20.0		
		100	120.0	100 ± 0.0	0.00
		500	522.0	100.4 ± 0.5	0.20
	Sangu (lower)	0	22.0		
		100	120.0	98.5 ± 1.2	0.35
		500	525.0	100.6 ± 1.5	0.44
Sea water	Bay of Bengal (upper)	0	8.0		
		100	109.5	100.9 ± 0.5	0.29
		500	510.5	100.4 ± 1.0	0.47
	Bay of Bengal (lower)	0	12.0		
		100	112.0	100 ± 0.0	0.00
		500	516.0	100.8 ± 1.0	0.35
Kaptai lake water		0	20.0		
		100	122.0	101 ± 0.8	0.26
		500	525.0	100.6 ± 1.5	0.45
Tap water		0	16.25		
		100	105.00	98.9 ± 0.2	0.31
		500	516.00	99.9 ± 0.1	0.25
Tube-well water		0	20.00		
		100	119.00	99 ± 0.5	0.19
		500	520.00	100 ± 0.0	0.00
River water	Karnafuli (upper)	0	25.0		
		100	124.0	99 ± 1.0	0.23
		500	525.0	100 ± 0.0	0.00
	Karnafuli (lower)	0	28.0		
		100	129.5	99.6 ± 0.6	0.26
		500	530.0		
	Halda (upper)	0	15.0		
		100	116.0	99.8 ± 0.6	0.16
		500	514.0		
	Halda (lower)	0	18.0		
		100	118.0	100 ± 0.0	0.00
		500	520.0	100.4 ± 1.0	0.18

^aAverage of five replicate determinations.

Table 7. Determination of chromium (III) and chromium (VI) speciation in mixtures

Sl. No.		Cr, taken (mg L ⁻¹)		Cr, found (mg L ⁻¹)		Error (mg L ⁻¹)	
Sl. No.	Cr(VI) : Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
1	1 : 1	1.00	1.00	0.98	0.99	0.02	0.01
2	1 : 1	1.00	1.00	1.00	1.02	0.00	0.02
3	1 : 1	1.00	1.00	0.97	0.99	0.03	0.01
Mean error : Cr (VI) = ± 0.01; Cr (VI) = ± 0.01 Standard deviation : Cr (VI) = ± 0.05; Cr (III) = ± 0.006							
1	1 : 2	1.00	2.00	0.99	1.98	0.02	0.02
2	1 : 2	1.00	2.00	0.98	1.98	0.01	0.01
3	1 : 2	1.00	2.00	0.98	1.98	0.02	0.02
Mean error : Cr (VI)= ± 0.013; Cr (III)= ± 0.01 Standard deviation : Cr (VI)= ± 0.006; Cr (III)= ± 0.006							
1	1 : 3	1.00	3.00	0.99	2.99	0.01	0.01
2	1 : 3	1.00	3.00	0.98	2.98	0.02	0.02
3	1 : 3	1.00	3.00	0.98	2.98	0.02	0.02
Mean error : Cr (VI)= ± 0.016; Cr (VI)= ± 0.016 Standard deviation : Cr (III)= ± 0.058; Cr (VI)= ± 0.058							

**Synthesis and Characterization of the bis (salicylaldehyde)
orthophenylenediamine (BSOPD)**

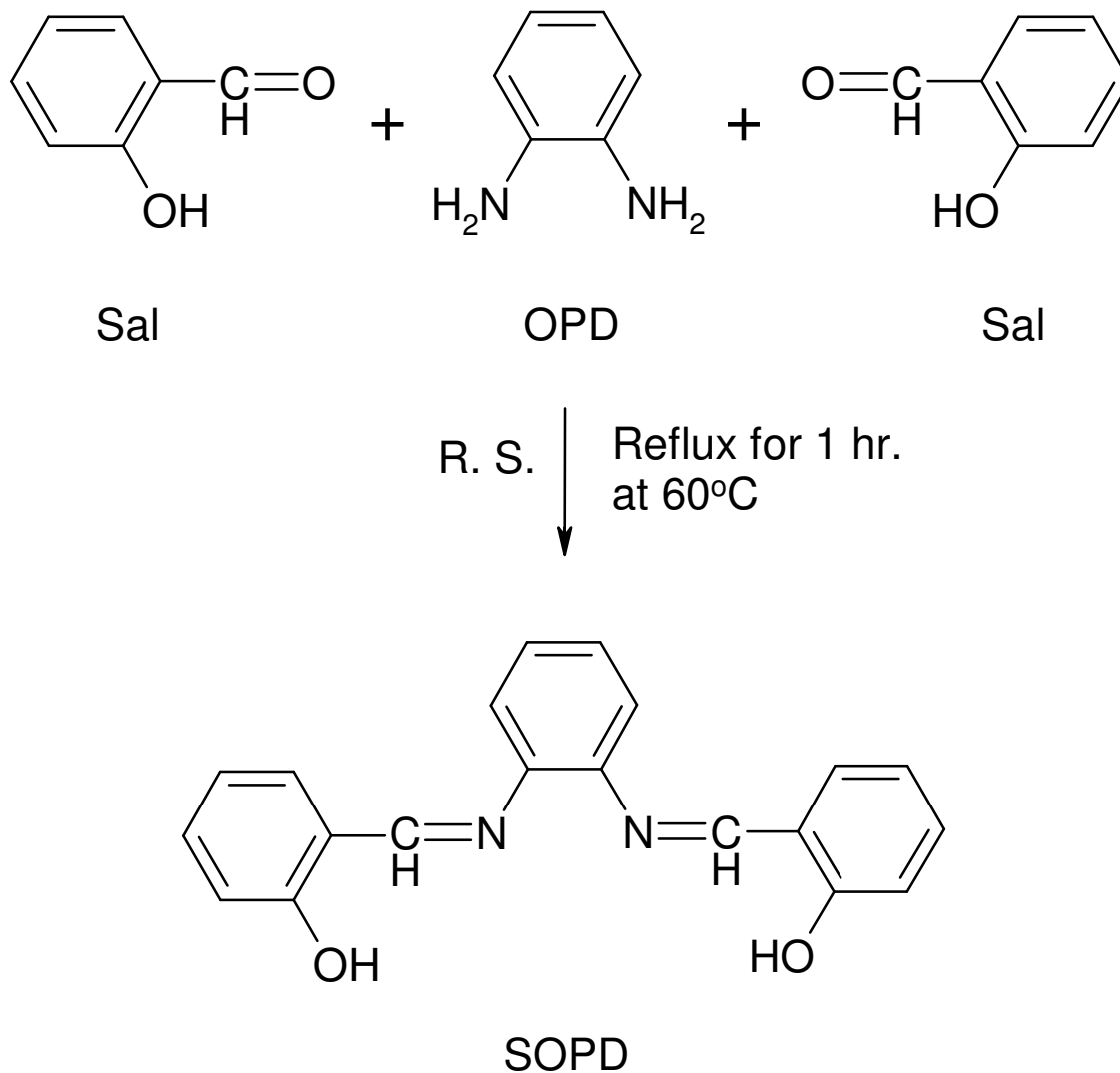


Figure1: Synthesis of bis(salicylaldehyde)orthophenylenediamine (BSOPD)