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Research Article

Determination of Trace Concentrations of Lead(II) in Environment Samples using Hydroxamic acids: An Important Issue of Public Health

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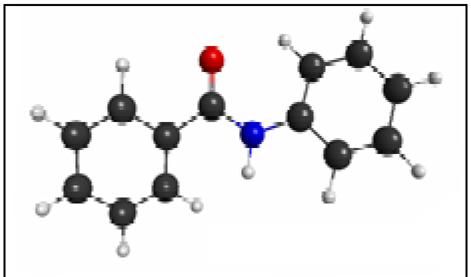
Abstract

N-phenyl-benzo hydroxamic acid (*N-PBHA*), N-phenyl-p-chloro-benzo hydroxamic acid (*N-p-ClPBHA*) and N-phenyl- p-chloro-cinnamohydroxamic acids (*N-p-ClPCHA*) used as analytical reagent for the spectrophotometric determination of Lead (II). Lead (II) reacts with different hydroxamic acids and forms light yellow to orange colored complex in alkaline medium which were extracted in n- hexane. The calibration graph was linear over the concentration range of 0.000999-0.013986, 0.000999-0.01198 and 0.0004995-0.007992 $\mu g ml^{-1}$ for N-Phenyl-benzo-hydroxamic acid (N-PBHA), N-p- Chloro-phenyl- benzo-hydroxamic acid (N-p-ClPBHA) and N-p- Chloro-phenyl-cinnamohydroxamic acid (N-p-ClPCHA), respectively. The molar absorptivities were found to be 2.4×10^5, 8.8×10^4 and 1.2×10^5 L mol^{-1} cm^{-1} for the three hydroxamic acids. The optimum reaction condition and other analytical parameter were evaluated.

Keywords: Lead, Environmental samples, N-PBHA, N-p-ClPBHA and N-p-ClPCHA



Parent Compound (N-PBHA)

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Introduction

Trace metal ions have important roles in our life functioning in a wide spectrum. Thus, the determination of trace metal ions is becoming increasingly important because of the increased interest in environmental samples including water, soil and plant, etc. Lead is a cumulative poison that enters the body from lead water pipes, lead-based paints and leaded petrol [1]. The determination of trace amount of lead is very important in the context of environmental monitoring. Many analytical techniques based on differential pulse polarographic [2], potentiometric stripping [3], colorimetric [4], flame atomic absorption spectrophotometry [5], flame atomic absorption spectrometry after pre-concentration with ammonium pyrrolidinedithiocarbamate immobilized on surfactant-coated alumina [6], automated voltammetric [7],anodic stripping differential pulse voltammetric [8],polymeric electrochemical sensors [9], optical sensor based on 2-amino-cyclopentene-1-dithiocarboxylic acid [10], high performance liquid chromatography [11], electrochemical determination [12] have also been described for determination of lead. A flow injection system for the spectrophotometric determination of lead after preconcentration by solid phase extraction onto Amberlite XAD-4 [13] has also been described. Extraction of lead (II) by sorption on grinded eucalyptus stem and determination with flame atomic absorption spectrometry has been reported [14]. Removal of lead by swine bone adsorbents has also been reviewed [15]. Therefore, there is a continued interest in the synthesis of new organic reagents that could be able to be used for direct and rapid spectrophotometric determination of trace level of lead, especially in aqueous solutions.

In this work, the exploration about the potential of hydroxamic acid as chromogenic agent for determination of Pb from aqueous solution has been made. Several parameters influencing the recoveries of analytes, including pH of sample, sample volume and effect of divers ions have been investigated in detail. An optimized procedure has been applied to the determination of trace metals in water samples. Though many methods for determination of lead by hydroxamic acids are already repoted, the method describe in this paper is better than the earlier as it is much sensitive comparatively. Lead is very harmful even if present in very small concentration. This method can be used not only for determination of lead but also for its recovery from water due to which water may be made free from lead.

Experimental

"Shimadzu spectrophotomter 1700" was used for electronic spectral measurements with 10 mm matched quartz cells. A Hanna 8521 model pH meter was used for pH measurements. All the chemicals were of analytical grade or chemically pure grade. Double distilled de-ionized water was used for preparation of standard solutions, dilution and washing vessels.

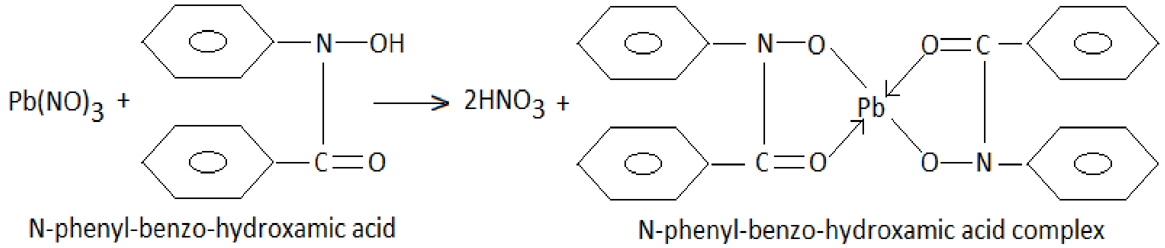
Reagents and Chemicals

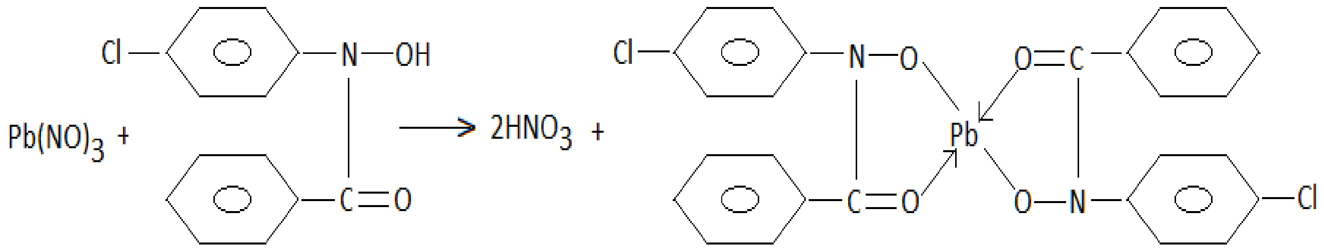
- Pb (II) stock standard solution: It was prepared by dissolving 0.1598 g of $Pb(NO_3)_2$ in 100 ml of water. 1 ml of nitric acid was added to prevent hydrolysis [16].Working standard was prepared by appropriate dilution of stock solution.
- Stock solution of hydroxamic acids: N-PBHA, N-p-ClPBHA and N-p-ClPCHA stock solutions were prepared by dissolving 0.1g of respective hydroxamic acid in 100 ml n-hexane and diluted upto the limit where they give maximum absorbance (0.0001%).
- Buffer solutions: These were prepared by 1M hydrochloric acid – 1M sodium acetate (pH 0.5-3.5); 0.2 M acetic acid - 0.2 M sodium acetate (pH 4.0 -7.0); 2M ammonium chloride - 2M ammonium hydroxide (pH 7.5-12.0).
- Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively.
- EDTA and Thiourea solutions are also used.

Procedure

Expected Reactions an aliquot of the sample solution containing 0.000999-0.013986, 0.000999-0.01198 and 0.0004995-0.007992 µgml^{-1} of lead for N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively was transferred to a series of 25 ml calibrating flask. In this solution, 7.5, 8, 8.8 ml of 2M ammonium chloride - 2M ammonium hydroxide solution was added to maintain the pH at 9, 9.5 and 10 for determination of lead with N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively. Finally, 1 ml, 1.5ml and 1.8 ml of 0.0001% of N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively were added. The colour reaction of lead with reagents is instantaneous even at room temperature (28 ± 2^0C), N-PBHA gives light yellow, N-p-ClPBHA gives bright yellow while N-p-ClPCHA gives orange colour complex immediately. The solution was kept for 2 minutes and the coloured complex was made up to the mark with n-hexane. A blank solution was prepared exactly in the same manner as test solution but without addition of lead. The organic phase containing only the lead hydroxamic acids complex were separated and the absorbance of the coloured solutions were determined against the blank at 470 nm, 455 nm and 510 nm, respectively with three hydroxamic acids. The absorbance of the colored complexes remains stable for several days. The amount of the lead present in the volume taken was computed from the calibration graph.

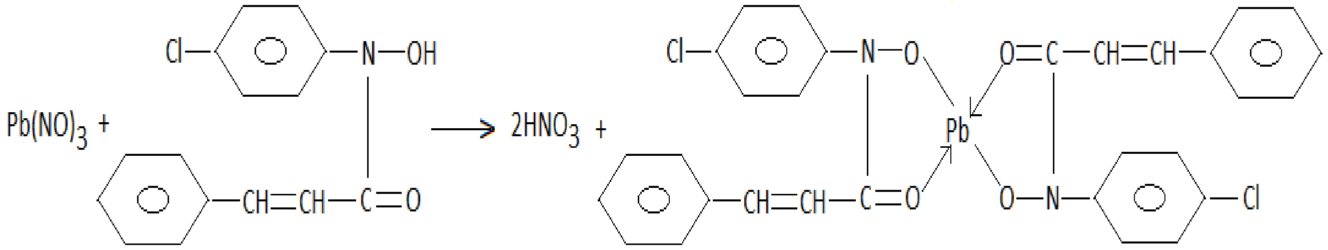
Involved Reaction





N-p-Cl- phenyl-benzo-hydroxamic acid

N-p-Cl- phenyl-benzo-hydroxamic acid complex



N-p-Cl-phenyl-cinnamohydroxamic acid

N-p-Cl-phenyl-cinnamohydroxamic acid compex

Results and Discussion

Absorption spectrum and calibration curve

After reaction, complex present in organic phase was separated from aqueous layer and scanned from 400 nm to 600 nm against reagent blank (**Figure 1**). Maximum absorption values were observed at 470 nm, 455 nm and 510 nm for lead complex with N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively. Therefore, 470 nm, 455 nm and 510 nm were selected for N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively for the absorbance measurement throughout the experiments.

A calibration plot of absorbance against concentration of N-PBHA, N-p-ClPBHA and N-p-ClPCHA complexes at the absorption maxima gave a linear and reproducible graph in the concentration range of 0.000999-0.013986, 0.000999-0.01198 and 0.0004995-0.007992 µgml^{-1}, respectively (**Figure 2**). The Beer's law is obeyed in this range. Optical characteristics, precision and accuracy of the proposed method are summarized in **Table 1**.

Effect of different solvent

Different organic solvents like ethanol, n-butanol, diethyl ether, ethyl-methyl ketone, ethyl acetate, chloroform, toluene, n- hexane and carbon tetrachloride were used for determination. n- hexane was found to be most suitable solvent as it gave better and quick phase separation. Therefore, n- hexane was selected.

Effect of temperature

The effect of temperature on absorbance of the complex was studied over the temperature range of 1°C – 40°C. It was observed that reaction becomes very fast at the room temperature and formed complexes gives maximum and stable absorption at the temperature of 22°C, 25°C and 20°C for N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively. Therefore, all experiments were performed at the above temperature (**Figure 3**).

Effect of pH

Hydroxmic acids react with Pb (II) in alkaline medium to give yellow to orange coloured complexes with various hydroxamic acids. The colour reaction between Pb (II) and various hydroxamic acids are instantaneous even at room temperature in the pH range 8.0- 12.0. The absorbance of the coloured species remains constant for more than 24 hours. The maximum colour intensity was observed at pH 9.8, 10.2 and 9.5 for N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively. Therefore, all experiments were performed at the above pH (**Figure 4**).

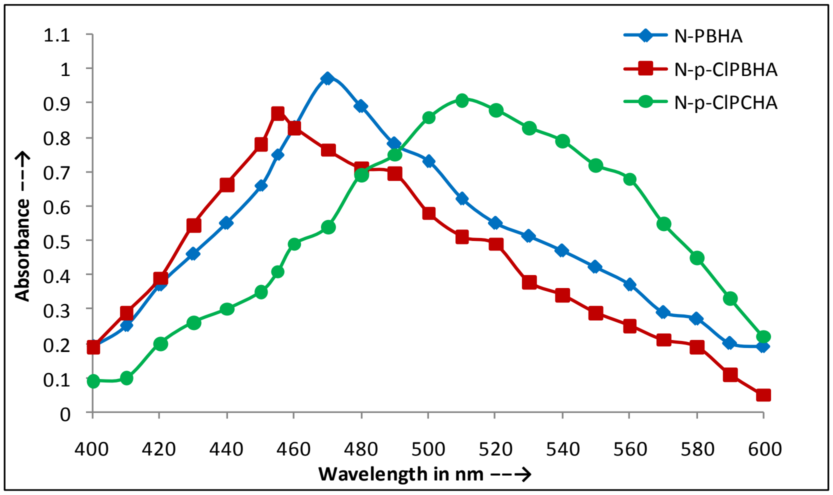


Figure 1 Absorption spectra of lead complexes with hydroxamic acids

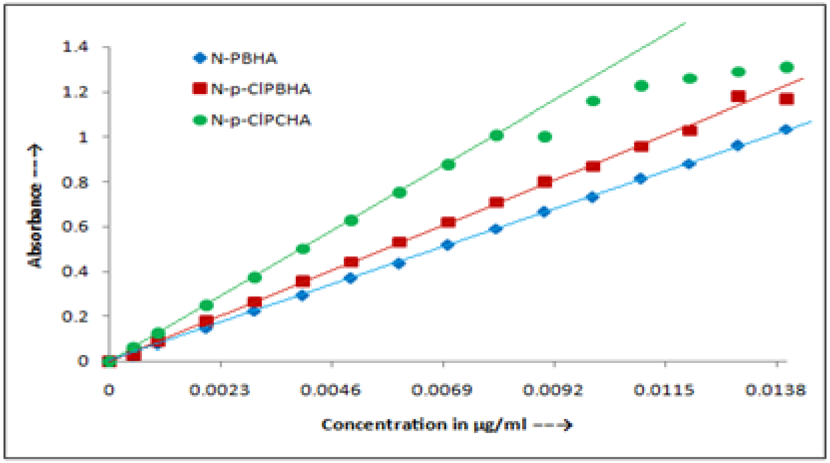


Figure 2 Calibration plot for lead complexes with hydroxamic acids

Table 1 Optical characteristics, precision and accuracy of the proposed method

Characteristics	**N-PBHA**	**N-p-ClPBHA**	**N-p-ClPCHA**
λmax, nm	470	455	510
Beer's law limits in concentration range μg ml^{-1}	0.000999-0.013986	0.000999-0.01198	0.0004995-0.007992
Molar absorptivity, L mol^{-1} cm^{-1}	2.4 x 10^{5},	8.8 x 10^{4}	1.2 x 10^{5}
Sandell's sensitivity, μg cm^{-2} per 0.001 absorbance unit	1.381 x 10^{-5}	1.126 x 10^{-5}	7.96 x 10^{-6}
Limit of detection, μg ml^{-1}	2.308 x 10^{-4}	2.003 x 10^{-4}	1.707 x 10^{-4}
Relative standard deviation %	1.04	1.01	1.34
Quantitation limit μg ml^{-1}	6.99 x 10^{-4}	6.07 x 10^{-4}	5.17 x 10^{-4}

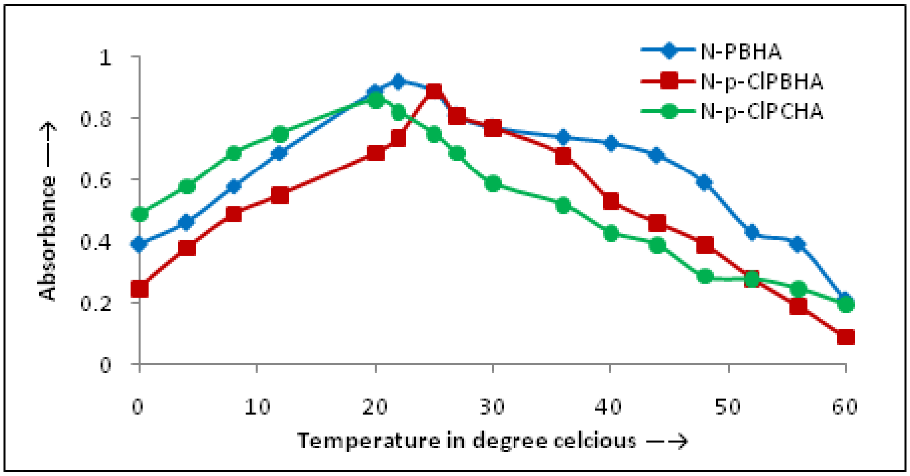


Figure 3 Effect of temperature on absorbance of lead complex with hydroxamic acids

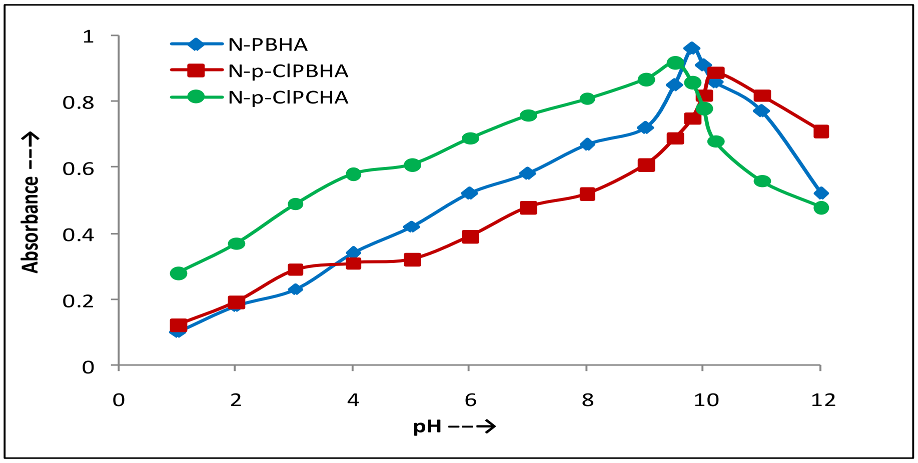


Figure 4 Effect of pH on absorbance of complexes

Effect of foreign ions

In order to evaluate the suitability of the proposed method for the determination of Pb(II) species in environmental samples, the interference study was carried out. The interfering ions were added in the form of their respective salts to find the interference. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ±1.2% in absorbance values for lead (II) at 0.013986, 0.01198 and 0.007992 µgml^{-1} for N-PBHA, N-p-ClPBHA and N-p-ClPCHA, respectively. The interference of associated metal ions such as Fe (III) and Cu (II) is decreased with masking agent thiourea respectively. The results indicated that most of the common ions did not interfere.

Applications of the method

The proposed method was applied for the quantitative determination of lead (II) in various environmental samples.

Determination of lead in Polluted Water Samples

Environmental contamination with lead has been a potential threat to humans and animals because it does not undergo biodegradation. Removal of lead from waste streams employs various technologies, which are often either expensive or inefficient, especially when very low residual concentrations in the wastewater. Available data on lead from environmental samples of Bhopal city is very less therefore to investigate the applicability of this procedure to water and soil samples, the recoveries of known amounts of lead by adding to water samples were examined by the proposed procedure.

The analyzed water samples were collected from different areas of Bhopal district in polyethylene bottles, which were filtered through whatmann 42 filter paper. The lead levels found 0.12-1.23 μgL^{-1} in water samples showed that high concentration (more than permissible limit) of lead is not present in the investigated areas. Lead recovery was measured using a standard addition method. The results are given in Table 2; EDTA and Thiourea were used to eliminate the interferences. Recovery of lead varied from 98.4- 100%. These results summarized in **Table 2** demonstrats that the current procedure is applicable for lead analysis in different water samples with a satisfactory recovery.

The proposed method is compared with other spectrophotometric methods in **Table 3**

Table 2 Determination and recovery of lead in water and soil samples

S No.	Locations in Bhopal	Lead added (μg L^{-1})	Lead found			Recovery %		
			N-PBHA	N-p-ClPBHA	N-p-ClPCHA	N-PBHA	N-p-ClPBHA	N-p-ClPCHA
1	GI	0.00	1.2	0.9	0.75	–	–	–
		2.00	3.18	2.86	2.71	99.3	98.6	98.5
2	MI	0.00	0.99	1.02	1.0	–	–	–
		2.00	2.98	3.019	2.98	99.6	99.9	99.3
3	SL	0.00	0.56	0.35	0.27	–	–	–
		2.00	2.56	2.32	2.25	100	98.8	99.2
4	UL	0.00	0.93	0.76	0.87	–	–	–
		2.00	2.91	2.74	2.86	99.3	99.2	99.6
5	LL	0.00	0.78	0.65	0.88	–	–	–
		2.00	2.75	2.62	2.84	98.9	98.8	98.6
6	ANUC	0.00	1.2	1.02	1.23	–	–	–
		2.00	3.15	2.98	3.22	98.4	98.6	99.6
7	KD	0.00	0.12	0.16	0.13	–	–	–
		2.00	2.12	2.15	2.11	100	99.5	99

GI = Govindpura industrial area, MI = Mandideep industrial area, SL = Shahpura Lake, UL = Upper Lake, LL = Lower Lake, ANUC = Area Near Union Carbide, KD = Kolar Dam

Conclusion

The proposed procedure provides a selective, accurate and precise method for the determination of lead in environmental samples. Common metal ion such as Fe^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, Ca^{2+} do not interfere. Chloride, sulphate, phosphate and other anions also do not interfere. This suggested method could be used for rapid and simple determination of Pb(II) in various water and other environmental samples. The results of analysis of samples are very close to those obtained by the other common methods. Our method has enormous practical potential for simple detection of lead, including field conditions which require no complex equipment or skilled laboratory support. As seen in Figures this method based on using various hydroxamic acids are very suitable for the analysis of natural samples. These chelating agents have been used before to determine other metals with different methods but this is its first application to the determination of lead in environment of Bhopal district.

Table 3 Comparison of determinatiom of lead with other spectrophotometric methods

S. no	Reagents/reference	λ_{max}, nm	Range of determination, mgl^{-1}	Remarks
1	3,5-Dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazone (DMHBIH) [18]	430	0.414-10.360	Stability of reagent is only 48 hrs
2	Benzil α- monoxime isonicotinoyl hydrazone [19]	405	0.41- 13.26	Interference ion change absorbance by ± 2
3	2,5-Dimercapto-1,3,4-thiadiazole (DMTD) [20]	375	0.1–40	In the study of interfering ions, concentration of interfering ions in not clear.
4	2-(2-Thiazolylazo)-p-cresol(TAC) [21]	650	up to 6.0	Less sensitive
5	Pyridine-2-acetaldehyde salicyloylhydrazone (PASH) [22]	380	1.5–6.2	Less sensitive
6	Benzoic Acid Azo PhenylCalix[4]arene (BAPC) [23]	440	2.0×10-6 − 2.4×10-5	Toxic solvent(MeCN) is used
7	Dithizone [24]	750	0.2-14	Extraction required, more chemicals are used
8	1,5-Diphenylthiocarbazone [25]	500	0.06–60	surfactants are used
9	Carboxylic carbon nanotubes (CNTs) and cetyltrimethyl ammoniumbromide (CTMAB) [26]	600.4	0.02–0.44	Indirect, tedious method
10	Alizarin yellow [27]	364	0.008- 0.17	Less sensitive
11	4-(2-Pyridylazo) resorcinol (PAR) [28]	508	0 - 9.81	Less sensitive
12	7-(6-Methoxy 2-benzothiazolyl azo)-8-hydroxyquinoline [7-(6MBTA8HQ)] [29]	524	0.005-0.1	Extraction and surfactants required, Tedious and indirect method
13	2,5-Thiophene dicarboxaldehyde, thiosemicarbazone(TDATSC) [30]	442	2.0− 2.4	Stability of reagent solution is less
14	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) [31]	575	0.760 ± 0.0012	Reagent solution is prepared in highly acidic medium
15	Different hydroxamic acids: N-PBHA, N-PClPBHA and N-PClPCHA (Proposed method)	470 nm, 455 nm 510 nm	0.000999-0.013986, 0.000999-0.01198 0.0004995-0.007992	Sensitive, simple, rapid; free from common interference, colour is stable for several days.

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