



Spectrophotometric Determination of Phenol in Micellar Medium

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Available online at: www.isca.in

Received 4th May 2012, revised 26th May 2012, accepted 14th September 2012

Abstract

A simple and sensitive spectrophotometric method for the determination of Phenol based on its oxidation by *N*-bromophthalimide (NBP) is proposed. The resulting bromoderivative of phenol oxidizes leucocrystal violet to crystal violet in aqueous medium, the absorbance of which is measured at 595 nm. The colour intensifies with the addition of surfactant, cetyltrimethyl ammonium bromide (CTAB). Beer's law is obeyed in the range of 0.02 – 0.22 $\mu\text{g mL}^{-1}$ of phenol. The molar absorptivity of the dye is found to be $3.13 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and sandell's sensitivity as calculated from the slope is found to be $3 \times 10^{-4} \mu\text{g cm}^{-2}$. The method has been successfully applied for the determination of phenol in coke oven effluents and the result obtained, compares well with other reported methods.

Keywords: Non extractive spectrophotometric, Phenol, NBP, LCV.

Introduction

Phenols are toxic substances, widely used in the manufacture of synthetic phenolic resins, dyes, plastics, lamp black paints, air fresheners, paper soaps, paint removers etc. It is introduced into the environment through industrial discharges from coke oven plants, petroleum refineries, drug manufacturing units, antioxidants and dye industries¹⁻². Phenol traces are also found in automobile exhaust, tobacco smoke and occasionally in hospital air³. Exposure to high concentration of phenol in air for long duration is reported to cause paralysis and severe injury to heart, liver, kidney and lungs and in some cases may cause death also⁴⁻⁵. OSHA (occupational safety and health administration) has set a limit of 5 ppm in air, for workers during 8 hour work shifts⁶. The US Environmental Protection Agency recommends rejection of water for drinking purpose which contains more than 1 μg of phenol/litre.

Wide applicability and toxicity of phenol has resulted in many methods for their detection and determination. The methods used for the determination of phenol include flow injection⁷, GC-FID with SPME⁸, chemiluminescence⁹, HPLC¹⁰, electrochemical methods¹¹, GC-MS¹², solvent extraction¹³, X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) nitrogen-gas adsorption method¹⁴, granular activated carbon¹⁵. Several spectrophotometric methods involving reagents like *p*-aminophenol¹⁶, 4-aminoantipyrine¹⁷, *N*-hydroxyl-*N*, *N*-diphenylbenzamidine¹⁸, sodium nitro-prusside¹⁹, have also been reported for its determination.

In the present communication a spectrophotometric method for determination of phenol is elaborated. The method is based on oxidation of phenol²⁰ by NBP to form a bromo derivative which is subsequently reacted with LCV in micellar medium. The

method has been successfully applied for the determination of phenol in real samples.

Material and Methods

Apparatus: A Systronics Spectrophotometer 106 was used for spectral measurements. Systronics pH meter, model 331 was used for pH measurements. All chemicals used were of analytical reagent grade and double distilled water was used for dilution.

Reagents: Phenol Stock (Merck): 1 mg mL^{-1} stock solution of phenol is prepared in 5% ethanolic solution. Working standards were prepared by the appropriate dilution of the stock.

Leucocrystal violet (LCV) [Eastman Kodak Co.]: 250 mg of Leucocrystal Violet (4,4',4'' methyl-dynetrin (N, N'-Dimethylaniline) was dissolved in 200 mL of distilled water containing 3 mL 85% phosphoric acid (Merck) and the volume was made up to 1 litre with distilled water and was stored in amber coloured bottle away from sunlight.

N-Bromophthalimide (NBP) [Loba chemie]: 0.04 g NBP was dissolved in 8 mL acetic acid and the volume was made up to 25 mL with double distilled water and was stored in amber coloured bottle.

0.5% Sodium hydroxide: 2 g sodium hydroxide in 100 mL distilled water.

Buffer solution: Buffer solution of pH 4 ± 0.1 was prepared by dissolving 17.01 g potassium hydrogen phosphate in 490 mL water followed by drop wise addition of 85% phosphoric acid until the pH becomes 4 ± 0.1 and volume was made up to the mark in 500 mL standard flask.

CTAB Surfactant (Loba Chemie): 10^{-2} M solution was prepared by dissolving 0.3644 g CTAB in 100 mL distilled water.

Procedure: Preparation of calibration curve: To aliquots of working standards containing 0.5 – 5.0 μg of phenol, 1 mL of NBP was added and warmed slightly. After 2 minutes, 1 mL of buffer was added and stirred gently. To this 1 mL of LCV followed by 0.5 mL of 0.5% NaOH and 1 mL of CTAB was added and mixed. The solution was diluted up to 25 mL and kept at 30°C for full colour development. An intense violet coloured dye having maximum absorption at 595 nm was obtained at $\sim 4\text{pH}$.

Results and Discussion

Spectral characteristics: The absorption spectra of the coloured product formed in the proposed reaction shows maximum absorbance at 595 nm against reagent blank, which gave negligible absorbance at this wavelength.

Adherence to Beer's law Molar absorptivity and Sandell's sensitivity: Beer's law is obeyed over the concentration in the range of 0.02 - 0.22 $\mu\text{g mL}^{-1}$ of phenol. Molar absorptivity and Sandell's sensitivity for the aqueous solution were found to be $3.13 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $3 \times 10^{-4} \mu\text{g cm}^{-2}$ respectively.

Effect of Reagent concentration: Best results were obtained while using 1 mL each of NBP and buffer. It was observed that for maximum absorbance 1 mL of LCV was sufficient. There was no change at higher concentration, whereas at lower concentration there was decrease in absorbance values.

Effect of surfactant: Addition of surfactant increased the intensity of violet coloured dye for which 1 mL of 10^{-2} M CTAB solution was necessary. Sensitivity was affected below and above this concentration.

Order of addition of reagents: The order of addition of reagents is crucial. Addition of reagents in the order NBP, buffer solution, NaOH, LCV and then CTAB gave constant and maximum absorbance. If surfactant is added before addition of sodium hydroxide, sensitivity was affected.

Effect of Time and Temperature: Temperature between $35\text{-}45^{\circ}\text{C}$ was found to be the most suitable for obtaining maximum absorbance values. Above and below this range, absorbance was markedly affected. It was found that 10 minutes time was sufficient for complete colour development and the colour was stable for several days.

Effect of pH: The most suitable range of pH was found to be between 4 to 4.5 for the formation of crystal violet from LCV. This was maintained by using phosphate buffer and sodium hydroxide. It was found that 1 mL of phosphate buffer and 0.5 mL of 0.1 M sodium hydroxide solution was required for maximum colour development. Increase of pH above 5.0 caused turbidity while below 3.5, no colour was observed.

Reproducibility: The reproducibility of the method was checked by six replicate analysis of the solution containing 3 μg per 25 mL of phenol. The standard deviation and relative standard deviation data are summarized in table 1.

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

Optical characteristics	Results
λ_{max} (nm)	595
Limit of Beer's Law ($\mu\text{g mL}^{-1}$)	0.02 – 0.2
Molar absorptivity ($\text{L mol}^{-1} \text{ cm}^{-1}$)	3.13×10^5
Sandell's sensitivity	3×10^{-4}
Standard deviation \pm	0.0063
Relative standard deviation	1.21

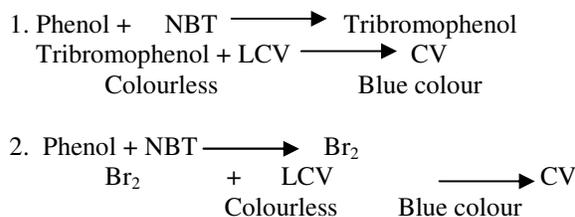
Effect of Foreign species: To check the validity of the method, effects of several species commonly found along with phenol, on the reaction were studied. This was done by addition of known amount of these species to 3 μg phenol prior to its analysis by the proposed method. The tolerance limits for various interfering species are shown in table 2.

Table-2
Effect of diverse ions

Foreign Species	Tolerance level* ($\mu\text{g mL}^{-1}$)
Methanol, Ethanol, Benzene	1000
Toluene	300
Formaldehyde, aniline	300
o-nitrophenol	70
o-cresol, p-cresol, m-cresol	800
Hg^{2+} , Ca^{2+} , Pb^{2+}	850
Al^{3+} , Fe^{3+}	1200
PO_4^{3-} , SO_4^{2-} , CH_3COO^-	1400
S^{2-}	100

*causing an error of $\pm 2\%$ in absorbance value

Reaction mechanism: Reaction mechanisms suggested for the proposed system are as follows:



If the reaction were to proceed by the liberation of bromine, then addition of mercury acetate would have resulted in a change in absorbance values as mercury acetate is known to destroy bromine²¹. However no change in the absorbance values has been observed upon addition mercury acetate thus confirming that the reaction proceeds by formation of tribromophenol.

Application: To check the validity of the method, it was applied for the determination of phenol in real samples like polluted water and coke oven effluents.

Determination of phenol in polluted water: Coke oven effluents and samples from river water, which receives these effluents were collected and analysed by the proposed method. Since these samples contain oil, tar, and other organic compounds, alkaline hydrolysis was done at pH 11-12 and then extracted with carbon tetrachloride in 2x5 mL portion. The organic layer containing tar and oil was discarded. Aqueous portion was warmed briefly on a water bath to remove excess of carbon tetrachloride. After cooling, it was filtered through Whatman no-41 and analyzed by the proposed and reported method²².

Table-3

Determination of phenol in water samples

Samples	Amount of phenol found in ($\mu\text{g mL}^{-1}$)		
		Proposed Method	Reported Method
Polluted river water	W1	0.780	0.750
	W2	1.02	1.00
	W3	1.08	1.01
Coke oven effluent	W4	2.12	2.08
	W5	3.14	3.11
	W6	3.75	3.71

Conclusion

The present method for the determination of phenol is simple, sensitive and avoids the use of hazardous chemicals. This method can be compared favorably with other reported methods in table-4. The method can be successfully applied to the trace determination of phenol in polluted water.

Table-4

Comparison with other spectrophotometric methods

Method	λ_{max} (nm)	Beer's law range ($\mu\text{g mL}^{-1}$)	Remarks
4- amino antipyrine ²³	510	0.2 – 2	Metal ion interfere, long Waiting time.
p-nitroaniline ²⁴	530	0.1 – 0.4	Reagent is carcinogenic
p – anisidine, NCS ²⁵	650	0.05 – 0.4	Colored reagent blank, higher temp. required
Sodium nitropruside, hydroxylamine hydrochloride ¹⁹	700	0.05 – 5.0	Interference of metal ions, less sensitive
NCS – Ammonia ²⁶	670	0.3 – 2.04	Less sensitive, metal ion interfere
Vanadium , N-hydroxyl- N,N'-diphenylbenzamidine ¹⁸	600	0.03	Extractive method
NBT, LCV (proposed method)	595	0.02 – 0.22	Non extractive, less time taking, non toxic reagent used, higher colour stability

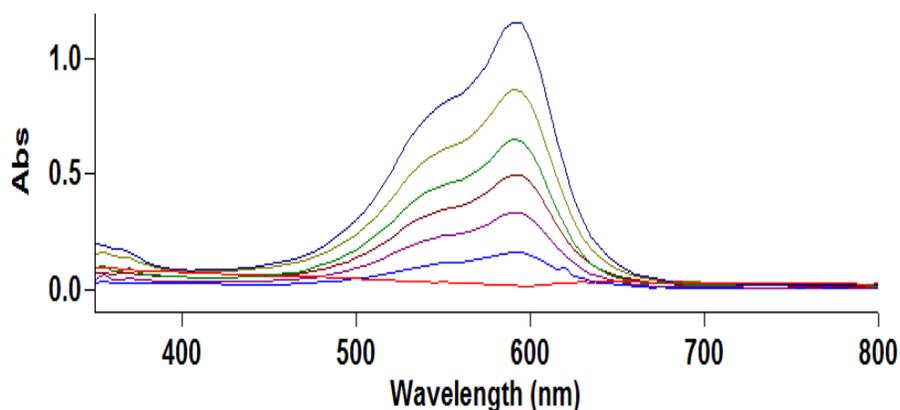


Figure-1
Absorption spectra of colour compound

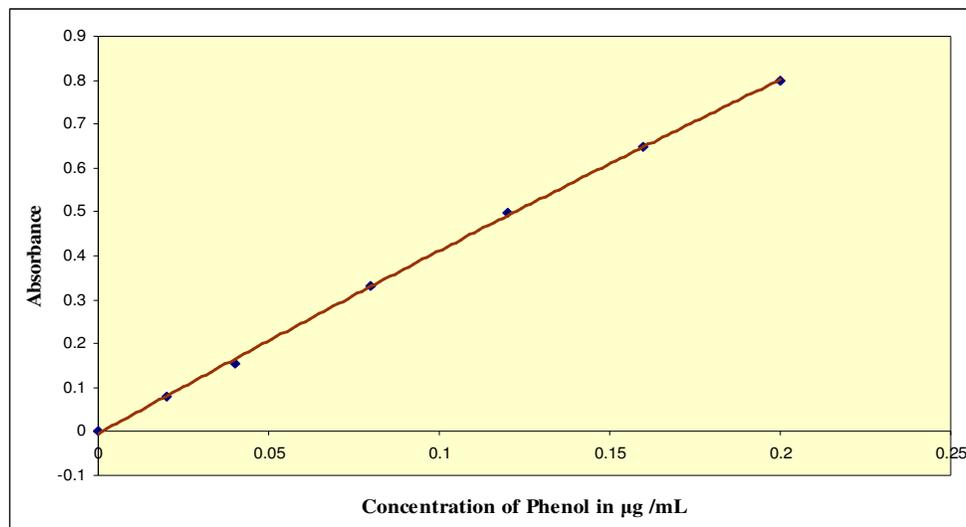


Figure-2
Calibration curve for the determination of Phenol

Acknowledgement

The authors are thankful to DST-FIST for instrumental support and Department of Chemistry, Govt V.Y.T. P G Autonomous College Durg, for providing laboratory facilities.

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