

Simple Spectrophotometric Determination of Phenol in Industrial Waste Water

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A new simple, selective and rapid spectrophotometric method for the determination of phenol in trace amounts has been described. The method is based on the colour reaction of phenol with 1,2-naphthaquinone-4-sulphonic acid (NS) in alkaline medium at pH 8.7-9.3, to give bluish-green indophenol dye. The dye produced has a maximum absorbance at 650 nm. The method obeys Beer's law up to $6.0 \mu\text{g phenol ml}^{-1}$ in aqueous phase. The molar absorptivity of the method is $1.4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The detection limit of the method is $0.05 \mu\text{g phenol ml}^{-1}$. The method is reproducible and the relative standard deviation of the method for 10 replicate measurements is 0.97%. Various analytical parameters have been studied to find the optimum condition for determining trace amounts of phenol in the industrial waste water.

INTRODUCTION

Phenols are highly toxic and are chiefly derived from industrial waste water, effluents, municipal sewage and coking plant effluents.¹ Phenol is used in the production of a large variety of aromatic compounds, *e.g.*, explosives, pharmaceuticals, fertilizers, paint, paint removers, textiles, drugs, bakelite and plastics.^{2,3} Exposure to phenol occurs during its use as a disinfectant and as an insecticide.² The iron and steel-making industry is one of the major sources of its release into the environment.⁴

Phenol is readily absorbed by ingestion, inhalation and the skin.⁵ Prolonged oral or subcutaneous exposure causes damage to the lungs, liver, kidneys and genitourinary tract.⁶ The US Environmental Protection Agency recommends a maximum of 10 mg l^{-1} of total phenolic compounds in domestic water and 5 mg l^{-1} for other waters.⁷

Various spectrophotometric methods have been reported⁸⁻¹¹ for the determination of phenol. The most common reagents for the determination of phenol are 4-aminoantipyrine,¹² Gibb's reagent,¹³ Millon's reagent¹⁴ and Folin and Ciocalten's phenol reagent.¹⁵

In this investigation, we report a new simple and rapid spectrophotometric determination of phenol at trace amount. The present method involves the formation of bluish-green indophenol dye,¹⁶ when phenol is reacted with

1,2-naphthaquinone-4-sulphonic acid (NS) in ammoniacal medium. The molar absorptivity of the method is $1.4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 650 nm. Beer's law is obeyed upto $6.0 \mu\text{g ml}^{-1}$ phenol in the aqueous solution. The method is less time consuming and independent of interfering foreign species. The method has been successfully applied to the determination of phenol in industrial waste waters.

EXPERIMENTAL

Apparatus

A Carl Zeiss Jena Spekol spectrophotometer with two matched glass cuvettes of 1-cm path length was used for all spectral studies. A Systronic pH-meter type-335 was used for all pH measurements. Calibrated glass apparatus was used for all volumetric work.

Reagents

Standard phenol solution: Standard phenol solution of 1 mg ml^{-1} strength was prepared in glass distilled water. A working standard of $25 \mu\text{g ml}^{-1}$ was prepared freshly daily by appropriate dilution of the standard stock solution.

1,2-Naphthaquinone-4-sulphonic acid (NS): 0.1% (m/v) or $3.8 \times 10^{-3} \text{ M}$ solution of this reagent was prepared in glass distilled water.

Dilute ammonia and hydrochloric acid were used for pH adjustment. All chemicals used were of analytical reagent grade (BDH).

Procedure

An aliquot of the standard test solution containing up to $60 \mu\text{g}$ phenol is taken in a 10-ml Nessler's tube. To this 2 ml of 0.1% NS is added. The pH of the solution is adjusted to *ca.* 9.0 using dilute ammonia water in a final volume of 10 ml solution. After 5 min the absorbance of the bluish-green indophenol dye is measured at its λ_{max} against distilled water as blank. A reagent blank was also prepared in a similar way.

RESULTS AND DISCUSSION

Absorption Spectra of the Dye

The dye produced by the reaction of phenol with 1,2-naphthaquinone-4-sulphonic acid in ammoniacal medium had a maximum absorbance at 650 nm. The reagent blank, prepared in a similar fashion, had negligible absorbance in this region. Hence, in all spectral studies water was used as reference.

Effect of pH

The pH of the reaction mixture was studied and it was observed that the colour of the bluish-green dye started to develop at a pH around 7.8 and the colour development was completed at a final pH of 8.7. The colour of the dye remained unchanged upto pH 9.3.

Effect of Reagents

The effect of 1,2-naphthaquinone-4-sulphonic acid (NS) concentration on the formation of bluish-green indophenol dye was studied. At least 3.8×10^{-5} M NS was required to initiate the colour formation. On subsequent addition of NS the colour intensity of the dye increased simultaneously. An addition of NS more than 9.5×10^{-4} M results in increased blank absorbance. Hence, an optimum reagent concentration of 7.6×10^{-4} M NS was kept constant throughout the experiment.

Effect of Time and Temperature

The effect of standing time and the temperature of the reaction mixture were studied for complete colour formation of the dye. It was found that 5 min were sufficient for full colour development and the colour of the dye remained stable for at least 4 h in the room temperature (30°C).

Beer's Law, Molar Absorptivity and Detection Limit

The method obeyed Beer's law upto $6 \mu\text{g phenol ml}^{-1}$ aqueous solution (6 ppm) at 650 nm with a correlation coefficient value of 0.98 at 95% confidence level. The molar absorptivity of the method is $1.4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The detection limit of this method is $0.06 \mu\text{g phenol ml}^{-1}$ aqueous solution. For samples those containing very low amounts of phenol solvent-extraction with n-butanol can be used ($\lambda_{\text{max}} = 650 \text{ nm}$).

Precision of the Method

The precision of the method was checked by taking absorbance measurement of 10 repetitive analyses of phenol at a level of 25 μg per 10 ml final solution. The relative standard deviation of the method is 0.97%.

Effect of Foreign Species

The effect of various foreign species which are generally found associated with phenol in industrial waste waters have been studied. The tolerable amounts of some foreign species were investigated by adding different known concentrations to phenol and then measuring the absorbance at 650 nm. Table 1 shows the tolerable amounts of some foreign interferences in the determination of 25 μg phenol.

Application of the Method

The effluents collected from coke-oven, by-product plant and waste waters from different industries were separately preconcentrated to a known volume (25 ml) by evaporation. These samples were extracted with carbon tetrachloride at pH 12.0–12.5 in order to remove other substituted phenols and oils.¹⁷ The organic phase containing unwanted species was discarded and the traces of carbon tetrachloride in the aqueous layer were removed by warming in a water bath. The aqueous phase was diluted to a desired volume.

TABLE 1
EFFECT OF FOREIGN SPECIES ON THE DETERMINATION OF 25 µg PHENOL
IN 10 ml FINAL SOLUTION

| Foreign species | Tolerable amounts† µg |
|--|--------------------------|
| 2-Nitrophenol, 4-nitrophenol, 2, 4-dinitrophenol | 75 |
| 2-Cresol, 3-cresol, 4-cresol, xylene | 80 |
| 3-Nitrophenol, aniline, phenylhydrazine | 100 |
| Benzene, pyridine, methanol, ethanol | 200 |
| Formaldehyde, benzaldehyde, hydroxylamine | 280 |
| 3-Aminophenol, 4-aminophenol | 300 |
| Fe ³⁺ (masked with 2 ml, 10% trisodium phosphate) | 100 |
| Ca ²⁺ , Pb ²⁺ , Sn ²⁺ (each masked with 1 ml, 5% EDTA) | 150 |
| Mg ²⁺ , Hg ²⁺ , Cu ²⁺ , Sr ²⁺ (each masked with 1 ml, 5% EDTA) | 200 |
| Acetate, nitrite | 350 |
| Nitrate | 400 |

†Causing error less than ±2%.

Aliquots of these samples were taken and the amount of phenol was determined by the recommended procedure. In each determination 1 ml of 5% EDTA solution was added as masking agent. The phenol content as determined above was checked with the standard 4-aminoantipyrine method.¹⁸ Table 2 shows the determination of phenol in various industrial waste waters.

TABLE 2
DETERMINATION OF PHENOL IN INDUSTRIAL EFFLUENTS

| Effluent samples | Phenol found | | RSD† of the present method (%) |
|---|-----------------------|------------------------------------|--------------------------------------|
| | Present method ppm | 4-Aminoantipyrine method ppm | |
| Coke-oven; Bhilai Steel Plant, Bhilai (M.P.) | 1.88 | 1.84 | 0.96 |
| By-product plant: Bhilai Steel Plant Bhilai (M.P.) | 2.62 | 2.59 | 0.98 |
| BNC Mills: Rajnandgaon (M.P.) | 0.89 | 0.90 | 0.98 |

†Five replicate determinations were made.

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