

# Quantification of Aniline with Bleaching Powder via Indophenol Reaction and Its Residual Determination in Lubricating Oils

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**Abstract:** A rapid and one step condensation method for trace level determination of aniline is developed in environmental and real sample i.e., lubricating oil. The method involves the use of oxidative coupling reaction for aniline and phenol using bleaching powder as an oxidizing agent in alkaline medium. The dye has a maximum absorption at 640 nm. Beer's law is obeyed in the range of 0.125 to 0.75 µg/ml and its detection limit is 0.025 µg. Molar Absorptivity and Sandell's Sensitivity were found to be  $4.4 \times 10^3$  litres/mol/cm ( $\pm 100$ ) and  $0.021 \mu\text{g cm}^{-2}$ , respectively. Standard Deviation and Relative Standard Deviation were found to be  $\pm 0.0074$  and 3.12% respectively, for 5 µg of aniline in 10 ml of the final volume. All important parameters have been optimized for complete colour reaction and applied for the analysis of aniline in environmental samples i.e. water and air. It is also applied for the residual aniline determination in lubricating oils.

**Key words:** Spectrophotometer, aniline, phenol, bleaching powder, indophenol dye.

## Introduction

Aniline is a colourless to brown, oily liquid, which darkens on exposure to air and light. It has a characteristic amine odour (detectable at 0.6 to 10 µg/ml) and burning taste. Aniline is hygroscopic and moderately soluble in water and is miscible with most organic solvents (www.npi, Environmental Defense, 1999).

Aniline and its derivatives are highly toxic and suspected carcinogenic agents. Aniline is predominantly used as a chemical intermediate for the dye, ink, agricultural, polymer, and rubber industries. It is also used as a solvent, and has been used as an antiknock compound for gasoline. It is a starting product for the manufacture of many drugs such as Paracetamol (Acetaminophen, Tylenol). Currently the largest market

for aniline is preparation of methylene diphenyl diisocyanate (MDI); some 85% of aniline is serving this market (Sax, 1981; www.epa, U.S. Environmental, 1985; The Merck, 1989; Patty, 1962; en.wikipedia, Aniline Producers, 2002).

Aniline is toxic by inhalation of the vapour, absorption through the skin or swallowing. It causes nausea, vomiting, liver and kidney damage, headache, drowsiness, mental confusion and in severe cases can cause convulsion. The chief symptom of aniline intoxication is cyanosis resulting from the formation of methemoglobin in the blood (Muir, 1971; Kolthoff et al., 1971). The threshold limit value given for aniline is  $7.6 \text{ mg/m}^3$  by ACGIH TLV (American Conference, 1999). Acute exposure to high amounts of aniline may lead to coma and death. Aniline has been found in at

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least 59 of the 1585 National Priorities List sites identified by the Environmental Protection Agency (EPA). The Occupational Safety and Health Administration (OSHA) sets a limit of 5 ppm aniline in workplace air in any 8-hour shift, 40-hour workweek (www.atsdr, Agency for Toxic, 2002).

Various methods including spectrophotometric methods are reported for the determination of aniline and other primary aromatic amines (Deniel, 1961; Steward et al., 1969; Kramer and Hackley, 1971; Krishna and Sastry, 1979; Levin et al., 1967; Kramer and Tolentino, 1979; Rawat and Singh, 1971; Norwitz and Keliher, 1981; Norwitz and Keliher, 1982; Ruch, 1970; Snell and Snell, 1967; Paul and Gupta, 1983; Lugg, 1963; Hanson et al., 1965). Some of them are based on diazotization coupling reaction (Deniel, 1961; Norwitz and Keliher, 1981; Norwitz and Keliher, 1982; Ruch, 1970; Snell and Snell, 1967; Paul and Gupta, 1983; Lugg, 1963; Hanson et al., 1965; Verma and Gupta, 1983) while a few colorimetric methods are based on an oxidative coupling reaction using 9-chloroacridine (Steward et al., 1969), thiotriethiazyl chloride (Levin et al., 1967) and guaiacol (Amlathe and Gupta, 1991).

In this paper a new spectrophotometric method based on the oxidative coupling reaction is described. Aniline is oxidized by bleaching powder and subsequently coupled with phenol in strong alkaline medium. The blue colour dye is formed which has maximum absorption at 640 nm. The colourless reagent blank has negligible absorbance at this wavelength.

The reaction conditions i.e. time, temperature and alkalinity have been optimized and applied for the determination of aniline in polluted water (Amlathe and Gupta, 1991; U.S. Environmental, 1985; Zhao et al., 2001), laboratory air and residual aniline determination in lubricating oil.

## Experimental

**Apparatus:** A systronics spectrophotometer 166 with matched 1 cm cells and systronics digital spectrophotometer model BSM-13 was used for all spectral measurements.

**Reagents:** All chemicals used were of analytical reagent grade and all solutions were prepared in demineralized water.

**Standard aniline solution:** A stock solution of 1 mg/ml (v/v) was prepared in 10% ethanol. A working standard of 5 µg/ml was prepared fresh daily by the appropriate dilution of the stock.

**Bleaching powder:** A 1.0% (w/v) was prepared in distilled water in 1.0% (v/v) in dil. HCl.

**Phenol:** A 1.0 % (v/v) solution was prepared in 10% ethanol.

**Sodium hydroxide:** A 0.6 M aqueous solution was prepared fresh daily by appropriate dilution of stock sodium hydroxide and standardized by standard procedure (Jeffery et al., 1999).

**Hydrochloric acid:** A 0.18 M hydrochloric acid was used as an absorbing solution.

## Procedure

An aliquot of solution containing 5 µg of aniline was taken in a 10 ml volumetric flask. To it 1 ml of bleaching powder followed by 1 ml phenol solution was added. The flask was then stoppered, shaken well, and kept for 30 minutes for complete colour reaction. The blue colour develops and changes to intense blue after the addition of 1 ml sodium hydroxide. The volume was brought up to the mark with distilled water. A reagent blank was prepared in the same manner. The colour of the dye formed was measured at 640 nm against a reagent blank.

## Result and Discussion

### Spectral Characteristics

The dye formed shows maximum absorbance at 640 nm (Figure 1). The reagent blank has negligible absorbance in this range (Table 1).

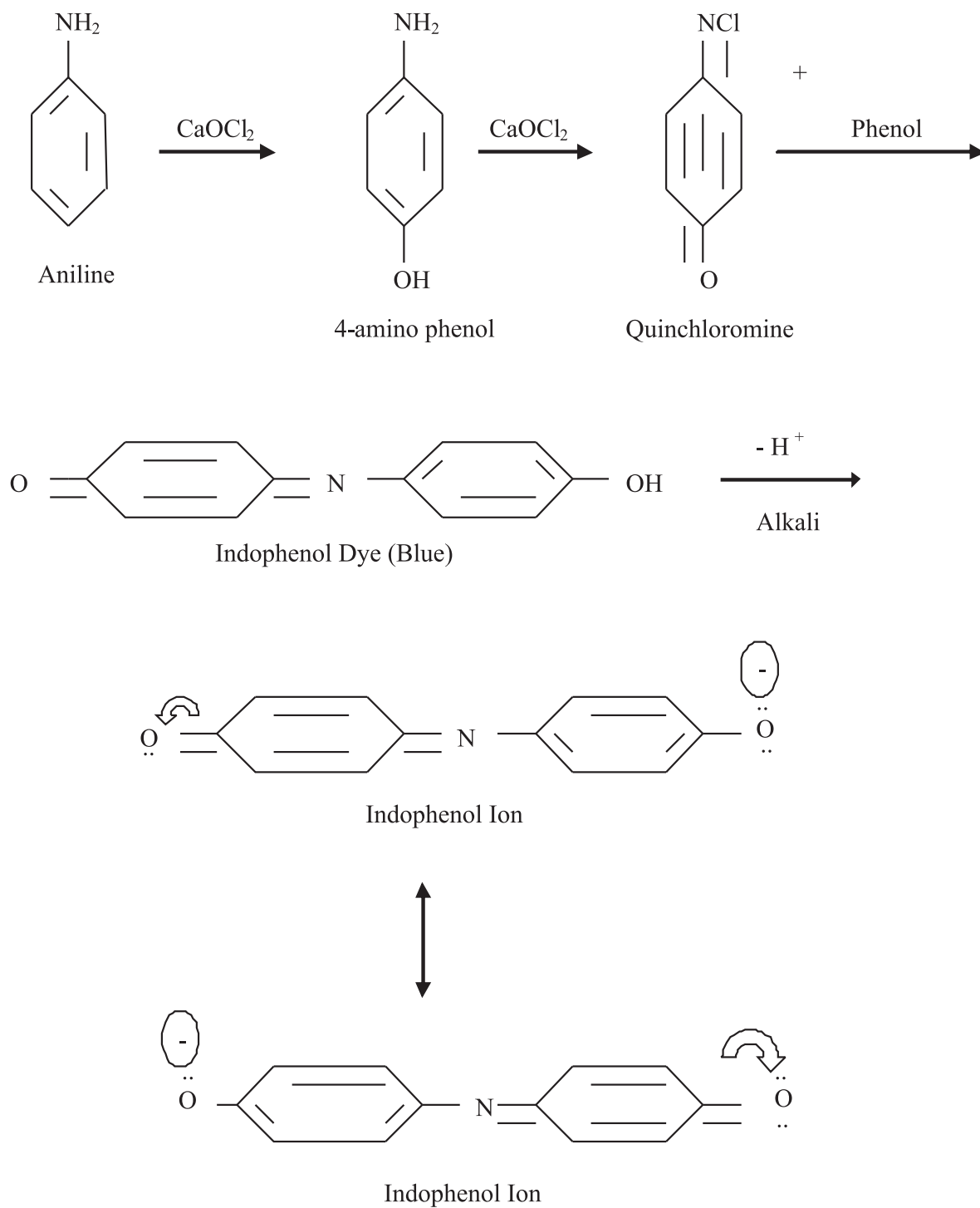
### Effect of Varying Reaction Conditions

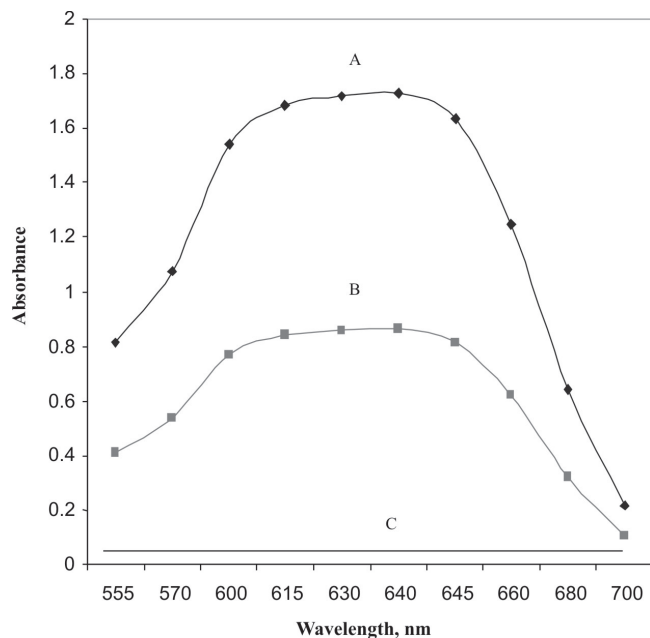
The blue colour of the dye appeared immediately after addition of phenol but it reached the maximum after addition of sodium hydroxide at room temperature, i.e., 25°C. The stability of the dye formed was also checked and it is found that below 10°C the colour development is incomplete but above 40°C the dye becomes unstable. The dye formed shows maximum absorbance in the temperature range of 25-40°C (Figure 2).

About 25-30 minutes are required for full colour development. Dye formed is stable for 45 minutes at room temperature.

It was found that 1 ml of 0.6 M sodium hydroxide was needed for complete colour reaction (Figure 3). It was found that a minimum of 1 ml of 1% phenol was required to obtain maximum absorbance values (Figure 4). Colour system does not obey Beer's law when sodium

## THE COLOUR REACTION



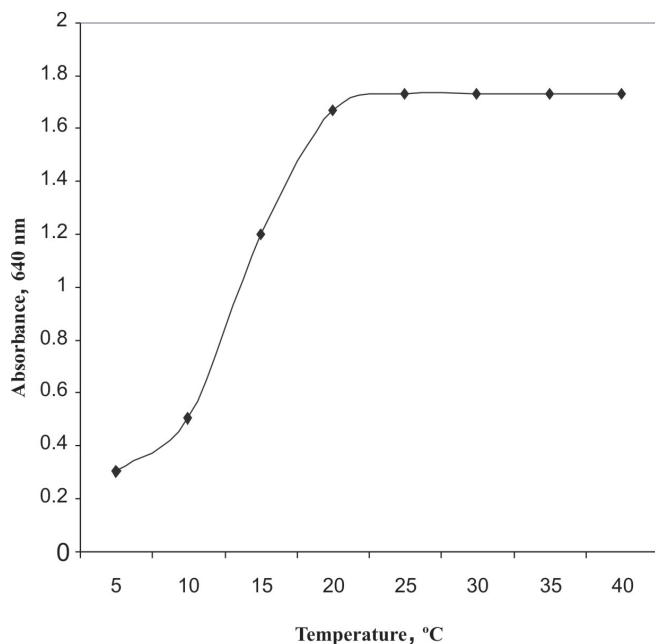


**Figure 1: Absorption spectra of the dye and reagent blank.**

**A.** Concentration of aniline = 40 µg/10 ml.

**B.** Concentration of aniline = 20 µg/10 ml.

**C.** Reagent blank.



**Figure 2: Effect of temperature on the colour reaction.**

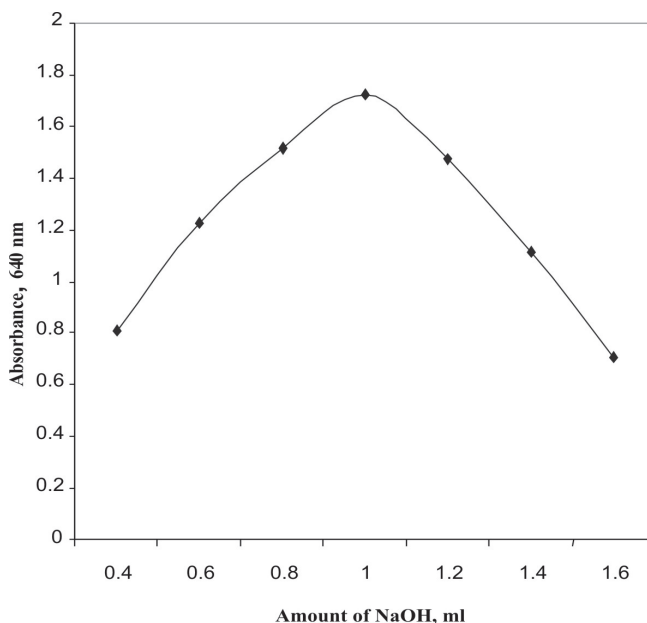
**Concentration of aniline = 10 µg/10 ml**

hydroxide or phenol is added either less or more than 1 ml of 0.6 M.

It was found that 1 ml of bleaching powder was required for complete colour reaction. Above and

**Table 1: Spectral characteristics**

S.N.	Wavelength (λ) nm	Absorbance
1	500	0.305
2	510	0.340
3	525	0.441
4	540	0.592
5	555	0.817
6	570	1.075
7	600	1.540
8	615	1.682
9	630	1.716
10	640	1.730
11	645	1.634
12	660	1.245
13	680	0.643
14	700	0.216



**Figure 3: Effect of amount of NaOH on the colour reaction.**

**Concentration of aniline = 10 µg/10 ml**

below 1 ml of bleaching powder gives unstable reading (Figure 5).

### Beer's law, Sandell's Sensitivity, Molar Absorptivity and Reproducibility

The colour system was found to obey Beer's law in the range of 0.125 to 0.75 µg/ml (1.25-7.5 µg) of aniline in 10 ml of the final volume (Figure 6). Molar absorptivity and Sandell's sensitivity were found to be  $4.4 \times 10^3$  litres/mol/cm ( $\pm 100$ ) and  $0.021 \mu\text{g cm}^{-2}$ , respectively.

The reproducibility of the method was checked by three replicate analyses over a period of seven days. Standard Deviation and Relative Standard Deviation were found to be  $\pm 0.0074$  and 3.12% respectively, for 5  $\mu\text{g}$  of aniline in 10 ml of the final volume.

### Effect of Interferents

To check the validity of the method the effect of various

possible interferents was studied by adding known amounts of these species prior to the determination of 5  $\mu\text{g}$  of aniline. The tolerance limits for various interfering species are shown in Table 2. The tolerance limits of various interfering species in alkaline medium were improved after masking with EDTA. Primary aromatic amines show positive interference.

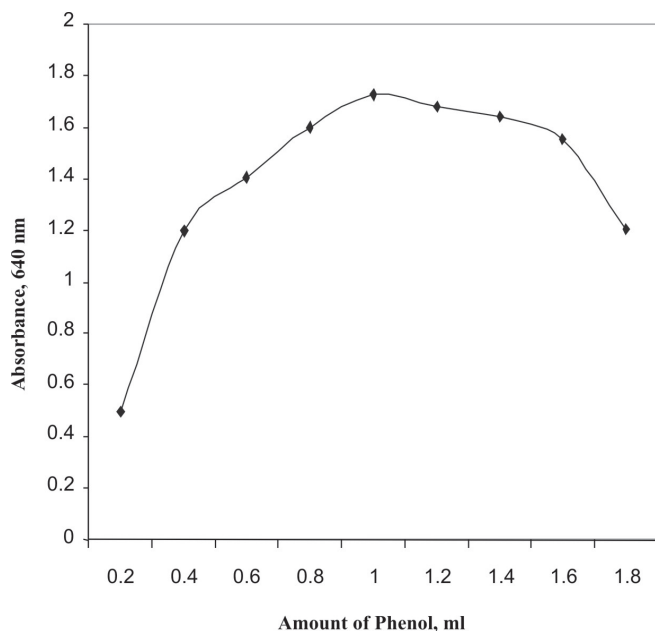


Figure 4: Effect of amount of phenol on the colour reaction.

Concentration of aniline = 10  $\mu\text{g}/10\text{ ml}$

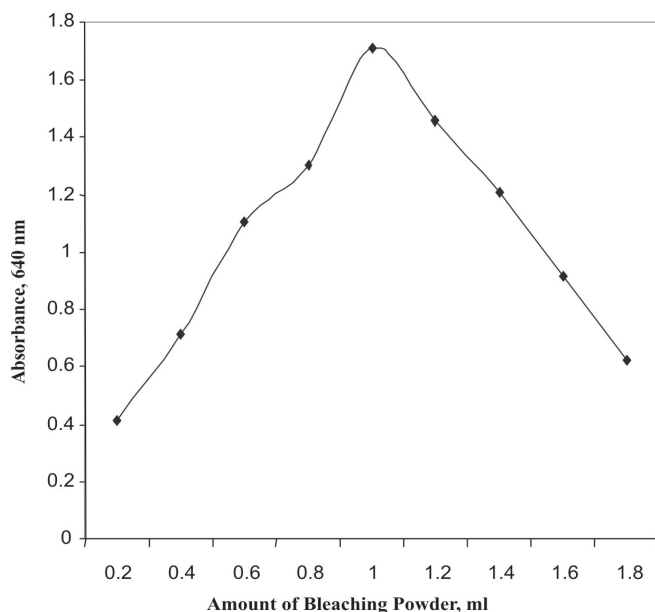


Figure 5: Effect of amount of bleaching powder on the colour reaction.

Concentration of aniline = 10  $\mu\text{g}/10\text{ ml}$

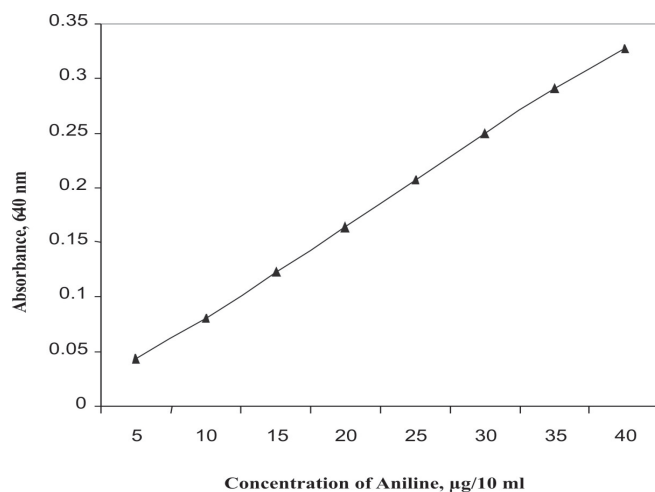


Figure 6: Calibration curve for spectrophotometric determination of aniline with phenol.

Table 2: Effect of foreign species

Foreign species	Tolerance limit <sup>a, b</sup> ( $\mu\text{g}/\text{ml}$ )
<i>p</i> -chlorophenol	600
Acetone	1800
Hydroxylamine	200
Hydrazine	1000
<i>p</i> -nitroaniline	600
Ammonia	200
Acrylonitrile	1800
Methanol	1800
<i>m</i> -Cresol	600
Formaldehyde	200
Benzene	1800
$\text{Ca}^{2+}$	600
$\text{Se}^{4+}$	1600
$\text{Cu}^{2+}$	8000
$\text{Mg}^{2+}$	600
$\text{Br}^-$	1600
$\text{SO}_4^{2-}$	8000
$\text{Ba}^{2+}$	600
$\text{Fe}^{3+}$	1600
$\text{SO}_3^{2-}$	1600
$\text{As}^{3+}$	1600

Note: Concentration of aniline 5  $\mu\text{g}/10\text{ ml}$ .

<sup>a</sup> Causing an error  $\pm 2\%$  or less.

<sup>b</sup> Masked with 1 ml of 10% EDTA.

## Application

To assess the applicability of the method it has been applied for the determination of aniline in environmental sample i.e. polluted water and laboratory air. It has also been applied for the residual aniline determination in lubricating oils.

### Analysis of Aniline in Polluted River Water

Since polluted river water samples were found to be free from aniline, synthetic samples were prepared by spiking the river water with known amounts of aniline prior to analysis. These samples were then analyzed by the proposed method. The results obtained are in good agreement (Table 3).

### Analysis of Aniline in Air

The method has also been applied for the determination of aniline in air. Due to non-availability of standard air samples containing aniline, air samples were prepared synthetically. Purified air was passed through a preheated chamber to which a known amount (50 µg) of aniline was added drop by drop from a micro burette and evaporated in a course of 10 min as reported earlier (Levin et al., 1967). The vapours thus generated were captured in 10 ml of 0.1 M hydrochloric acid taken in two midjet impingers connected in series and attached to an air sampling train at a flow rate of 750 ml/min for 10 min as recommended (American Conference, 1999). Absorption of 96-98% was obtained in first impinger at the flow rate of 750 ml/minute. Above and below this flow rate the absorption value decreased. After sampling, the absorbed aniline was analyzed by the proposed method. The values obtained were almost identical.

### Analysis of Residual Aniline in Lubricating Oil

The aniline point of oil gives an indication of the possible deterioration of rubber sealing, packing etc. in contact with the oil. The aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubber. As the aniline point is a measure of 'Paraffinicity' of oil, the higher the aniline point the lower is the percentage of aromatic hydrocarbons and the higher is the content of paraffin. Since paraffins give easy starting and a minimum of knock in a diesel engine, a high aniline point usually indicates a high cetane number.

The recovery of aniline required 10% alcoholic solution of lubricating oil and the method is compared

with the reported method. The values are given in Table 4.

**Table 3: Analysis of aniline in polluted river water**

<i>Proposed method<sup>1</sup></i> (µg)	<i>Reported method<sup>1</sup></i> (µg) (Amlathe)	<i>Reported method<sup>1</sup></i> (µg) (Hanson)
12.42	12.35	12.40
15.50	15.55	15.49
20.80	20.73	20.77
40.05	40.00	40.01
50.08	50.25	49.99

Samples used were prepared synthetically.

<sup>1</sup>Mean of three repetitive analyses

**Table 4: Recovery of aniline from lubricating oil**

<i>Set No.</i>	<i>Aniline added</i> (µg)	<i>Aniline found</i>			
		<i>by proposed method</i>	<i>Recovery %</i>	<i>by reported method</i>	<i>Recovery %</i>
1	5	4.82	98.40	4.74	94.80
2	10	9.90	99.00	9.28	92.80
3	15	14.94	99.60	14.25	95.00

## Conclusion

The proposed method is simple, highly sensitive and free from most of the interfering species. The method is also compared with other spectrophotometric methods reported for its determination (Table 5). The results are in agreement with them. It can be successfully applied for the analysis of aniline in water, air and lubricating oil.

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**Table 5: Comparison with other spectrophotometric method**

<i>S. No.</i>	<i>Reagent (Ref.)</i>	<i><math>\lambda</math> max (nm)</i>	<i>Range of determination (<math>\mu\text{g/ml}</math>)</i>	<i>Remarks</i>
1	Sodium hypochlorite, Sodium hydroxide (Ruch)	534-540	Above 0.5	Aromatic amines interfere; time for colour reaction, 30 min.
2	9-Chloroacridine hydrochloric acid (Steward)	435	1 to 10	Reagent unstable; time for colour reaction, 15 min.
3	Metol potassium dichromate, sulfanilamide (Krishna)	520	3 to 20	Less sensitive, other amines interfere
4	Sodium nitrite, sodium carbonate, 2-naphthol 3,6- disulfonic acid (Deniel)	485	1 to 10	Reagent unstable; time for colour reaction, 1 h
5	Thiotrithiazyl chloride, hydrochloric acid (Levin)	630	5 to 200	Unstable reagent, difficult to prepare, less sensitive
6	H-acid, hydrochloric acid, sodium nitrite, sodium bicarbonate (Norwitz)	526	0.5 to 2	Time for colour reaction, 15 to 45 min.
7	N-Chlorosuccinimide, guaiacol, sodium hydroxide (Amlathe)	615	1 to 8	Time for colour reaction, 10 min; sensitive; stable dye
8	Bleaching powder, phenol, sodium hydroxide (proposed method)	640	0.125 to 0.75	Time for colour reaction, 30 min; sensitive, low determination/detection limit.

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