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EDGEWOOD ARSENAL TECHNICAL REPORT

ED-TR-76048

A DIRECT METHOD FOR THE DETERMINATION OF PHENOL IN NATURAL WATERS

by

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October 1976

DEPARTMENT OF THE ARMY
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Present methods for the determination of phenols in water require a two-step procedure: separation of phenol by steam distillation or extraction with solvent; determination of phenol colorimetrically. The need to find a simple analytical method applicable to field situations led to the investigation of the Berthelot reaction. It was found that:

1. Phenol is detectable to 1 μg/ml in water solutions using a modification of the Berthelot reaction.

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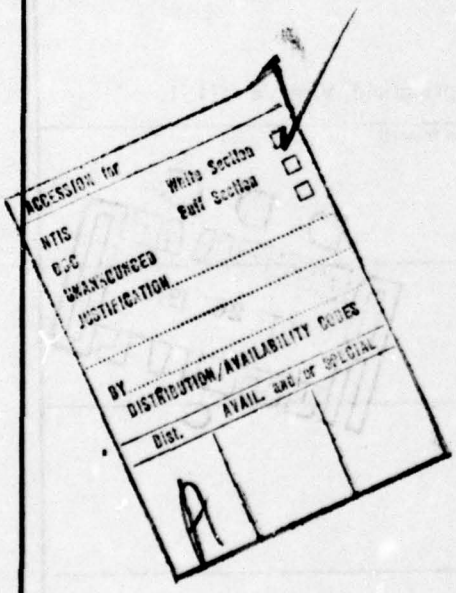
20. ABSTRACT (contd)

2. Linearity of the method is good from 1 to 5 μg/ml of phenol, with a range of up to 15 μg/ml with some loss of linearity.

3. When tested against 33 potential pollutants, the method showed good specificity for phenols.

4. This method is adequate for laboratory determination of phenol; however, the requirements for addition of several reagents and heating makes field use impractical.



PREFACE

The work described in this technical report was authorized under an agreement with the Environmental Protection Agency, EPA-1AG 0546, 2 May 1974. This work was started in June 1974 and completed in October 1974. Experimental data are recorded in notebooks 9169 and 8685.

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SUMMARY

A rapid, direct procedure for the determination of phenol, sensitive in the microgram range, has been devised utilizing a modification of the Berthelot reaction. The method is especially applicable to water samples and requires no extraction or distillation. Phenol, as the limiting factor, produces a strong indophenol blue color, which is linear in the range of 1 to 5 μg/ml. Challenge of the method with 33 potential water pollutants shows good specificity for phenols.

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A DIRECT METHOD FOR THE DETERMINATION OF PHENOL IN NATURAL WATERS

I. INTRODUCTION.

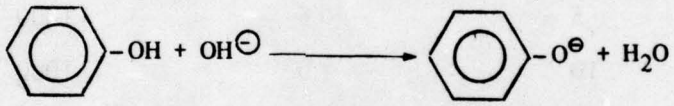
Present methods for the determination of phenols in water require a two-step procedure:

1. Separation of the phenol from the solution by steam distillation[1,3] or extraction with solvent.[2]

2. Determination of phenol is then accomplished colorimetrically by reaction with 4-aminoantipyrine[1] or 3-methyl-2-benzathiazolinone.[3] Analysis can also be accomplished by various elaborate instrumental methods,[4] as was reviewed by Minear and Pagoria.[5]

The requirement for a simple analytical method applicable to field situations, involving spills of toxic materials in waterways, led to the investigation of the Berthelot reaction.[6] This well-known method is used for determining blood urea nitrogen in serum,[7,8] for the direct estimation of ammonia in biological fluids,[9] and, more recently, for the determination of ammonia in natural water.[10,11]

The classical Berthelot reaction utilizes phenol, ammonia, and alkaline hypochorite to form indophenol blue in the presence of a suitable catalyst:



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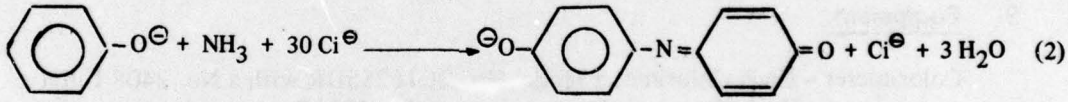

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II. EXPERIMENTATION.

Analytical grade chemicals were used for all of the following preparations:

A. Reagents.

1. NaOCl/NaOH.

Add 10 ml of commercial bleach (5% NaOCl) to 60 ml of 10% aqueous NaOH and dilute to 1 liter with distilled water.

2. Ammonia Reagent.

Dilute 10 ml of concentrated ammonium hydroxide to 100 ml with distilled water.

3. Sodium Nitroprusside.

a. Stock Solution.

Dissolve 6.0 grams of sodium nitroprusside in 100 ml distilled wtaer.

b. Working Solution.

Dilute 12.5 ml of stock solution to 500 ml with distilled water.

4. Phenol Standards.

a. Stock Solution (10 mg/ml Phenol).

Place 5.0 grams of melted phenol in a 500-ml volumetric flask and dilute to volume.

b. Working Standards.

Concentrated phenol	Stock	Final volume
µg/ml	ml	ml
1	0.1	1000
5	0.5	1000
10	1.0	1000
15	1.5	1000

B. Equipment.

Colorimeter - Hach Colorimeter Model No. DC16255DR with a No. 2408 Filter
Hach Chemical Company, Ames, IA 50010

C. Procedure.

1. In a 25-ml graduated glass-stoppered cylinder place:

	Distilled water	Phenol standard	Caustic/bleach	NH_3 reagent	Catalyst
	ml	ml	ml	ml	ml
Blank	21.0	–	2.0	1.0	1.0
Test	–	21.0	2.0	1.0	1.0

2. Incubate both blank and test in water bath for 5 minutes at 56°±2°C.

3. Cool at room temperature for 5 minutes. Read in colorimeter, setting zero absorbance with blank solution.

III. RESULTS AND DISCUSSION.

After determining, qualitatively, that the reaction did proceed as theorized, a series of studies was carried out to optimize the procedure and determine its linearity.

A. Effect of Catalyst Concentration.

Working concentrations of sodium nitroprusside were prepared and utilized in the procedure described. The results shown in table 1 indicate that acceptable absorbance ranges are attained with a catalyst concentration of 60 μg/ml in the final reaction mixture. Above this level, the deep yellow color produced interfered with the zeroing of the colorimeter, as was found by Chaney and Marbach.[8]

Table 1. Effect of Sodium Nitroprusside Catalyst Concentration on the Reaction Rate

Phenol	Catalyst concentration of final reaction mixture		
μg/ml	μg/ml		
	16	32	60
	Absorbance		
1	0.050	0.098	0.135
5	0.280	0.450	0.690
10	0.435	0.720	1.150

B. Effect of Temperature.

Holding other parameters constant, standard curves were prepared (as shown in table 2) at reaction temperatures of 30°, 40°, and 56°C for 10 minutes. Table 2 shows that at 56°C a maximum absorbance was attained. Although temperatures higher than those recorded here were tried, unreliable results were obtained. The results show a rapid attainment of maximum color development at 56°C; and it was also noted that upon standing the samples processed at lower temperatures approached but did not attain the absorbance of those prepared at 56°C. This temperature was also used by several workers[8,9] with consistent results.

Table 2. Effect of Temperature on the Reaction Rate

Phenol	Temperature, °C ±2		
μg/ml	30°C	40°C	56°C
	Absorbance		
1	0.015	0.088	0.135
5	0.078	0.310	0.680
10	0.082	0.620	1.150

C. Effect of Time.

Standard curves were prepared, as described above, with incubation times of 5 and 10 minutes. The curves that these data produced showed no significant differences; thus the 5-minute time of incubation was adopted.

D. Linearity.

A standard curve was prepared over a working range of phenol (table 3, 1). Due to the high absorbance readings above 1.0, a further curve was constructed (table 3, 2) which showed good linearity in the range of 1 to 5 μg/ml, and this was determined to be the most useful operating range for this method.

Table 3. Phenol Standard Curves

1.	Phenol μg/ml	Absorbance
	1	0.168
	5	0.700
	10	1.180
	15	1.420
2.	Phenol μg/ml	Absorbance
	1	0.150
	3	0.400
	5	0.660

E. Specificity.

The method was challenged with 33 potential industrial pollutants (listed in the appendix) to:

1. Test the specificity of the method

2. Gain some appreciation of the method's usefulness as a field test. To accomplish the latter, the following procedural changes were made:

a. The reagent blank was deleted – the colorimeter was therefore set against distilled water, thus simplifying the procedure since the absorbance of the reagent blank is consistently low.

b. Heating was done with a small portable field stove fired by a concentrated fuel tablet.

Utilizing the modifications, it was found that only four potential pollutants showed any response (table 4). Phenol and nonylphenol reacted as was expected. Also reacting were benzene, probably containing phenol as a contaminant, and technical grade Sevin, a pesticide which contains naphthol from either the hydrolysis of Sevin itself or from its synthesis.

Table 4. Specificity of Response

Compound	μg/ml	Absorbance
Phenol	1	0.162
	10	1.100
	100	1.580
	1000	1.800
Nonylphenol	1.7	0.100
	17	0.296
Benzene	1000	0.088
Sevin	4	0.162
	40	0.202

IV. CONCLUSIONS.

1. Phenol is detectable to 1 μg/ml in water solutions using a modification of the Berthelot reaction.

2. Linearity of the method is good from 1 to 5 μg/ml of phenol, with a range of up to 15 μg/ml with some loss of linearity.

3. When tested against 33 potential pollutants, the method showed good specificity for phenols.

4. This method is adequate for laboratory determination of phenol; however, the requirements for addition of several reagents and heating makes field use impractical.

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APPENDIX

HAZARDOUS MATERIALS

1. Phenol
2. Methyl alcohol
3. Acrylonitrile
4. Chlorosulfonic acid
5. Benzene
6. Ammonium chloride
7. Phosphorous pentasulfide
8. Styrene
9. Acetone cyanohydrin
10. Calcium hypochlorite
11. Nonylphenol
12. Isoprene
13. Xylenes
14. Nitrophenol
15. Ammonium nitrate
16. Aluminum sulfate
17. Aldrin
18. Toxaphene
19. DDT
20. EPN
21. Malathion
22. Parathion
23. Dieldrin
24. Heptachlor
25. Sevin
26. Chlordane
27. Fermate
28. Lead arsenate
29. Disodium methylarsenate
30. Phenylmercuric chloride
31. 2,4-D (Acid)
32. 2,4,5-T (Acid)
33. Ammonium phosphate, dibasic

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