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Quantative Determination of Aromatic Phenols with NBSA Reagent

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Abstract: *An accurate method has been described for determination of Aromatic phenols & its derivatives at micro scale using N-bromosaccharin as brominating & oxidizing agent. A known volume of sample solution of Aromatic phenols was treated with excess of N-bromosaccharin. After the reaction was complete the unreacted N- bromosaccharin was determined by titrating against standard sodium thiosulphate solution using starch indicator. A blank Experiment was also run under identical condition without the sample. The method is simple, quick, convenient and accurate and performed in ordinary laboratory condition without using any sophisticated instruments. The precision & accuracy was within ±1%.*

Keywords*: Analytical studies, Aromatic phenols, Determination, NBSA*

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I. Introduction

Aromatic phenols are widely used is the manufacture of dyes, drugs, explosive, resins, plasticizers, printing materials, accelerators etc. A large number of polyphenolic compounds present in nature are responsible for their colour and taste. In view of the fact that a large number of naturally occurring compounds containing phenolic functions are of great practical and industrial importance. Suitable methods for determination of these functions or of the compounds containing these functions would be of special significance to analytical chemists. Large number of procedure for determination of organic compounds containing these functions are available[1-13].These procedures are based on application of important reactions of such functions, like esterification, oxidation, diazotisation, nitrosation and bromination of the phenyl ring. Although some of these methods are gravimetric, it has been found that volumetric or colorimetric methods are better and these frequently forms the basis of specific methods. Methods based on spectrophotometry, mass spectrometry, fluorometry or chromatography have also been proposed from time to time and are frequently employed .In the present paper we describe a method for determination of Aromatic phenols at the mg level using N-bromosaccharin as oxidizing agent. The sample was allowed to react with excess of N-bromosaccharin and reaction was allowed to proceed for 10 minutes at room temperature. After the reaction was complete, the unreacted N-bromosaccharin(NBSA) was back titrated iodometrically using starch as indicator. A blank titration was also run under identical experimental condition using reagent without sample and recovery of Aromatic phenols sample was calculated. The method is convenient and performed in ordinary laboratory condition. It does not involve sophisticated instruments and rigorous reaction conditions. The precision and accuracy are within ±1%.

II. Experimental

REAGENTS AND SOLUTION

N-BROMOSACCIIARIN : 0.02 M

0.5240 g of N-bromosaccharin was accurately weighed and dissolved in 40 ml of glacial acetic acid by shaking thoroughly in a 100 ml volumetric flask. The solution was made upto the mark with distilled water and standardised iodometrically.

SAMPLE SOLUTION

A stock solution of each sample was prepared by dissolving an accurately weighed amount (20-60 mg) of sample in a minimum amount of 4 M sodium hydroxide (for phenols) by shaking thoroughly in a 50 ml standard volumetric flask. The solution was made upto the mark with distilled water. Aliquots containing 1-5 mg of sample from stock solution were used for each determination.

GLACIAL ACETIC ACID (A.R., B.D.II.)
SODIUM THIOSULPHATE (A.R., B.D.H.), 0.01 N
2.4820 g of sodium thiosulphate was accurately weighed and dissolved in distilled water in 1 litre volumetric flask. The solution was made upto mark and standardised against 0.01 N copper sulphate solution.

POTASSIUM IODIDE
15 percent (w/v) aqueous solution was employed (Baker analysed reagent).
STARCH INDICATOR
1% (w/v) aqueous solution was employed .
GENERAL PROCEDURE

An aliquot containing 1-5 mg of sample from the stock solution was transferred to a 100 ml glass stoppered conical flask. 10 ml of N-bromosaccharin solution was added. The flask was stoppered and contents were shaken thoroughly. The reaction was allowed to proceed for 10 minutes at room temperature (25 °c) with occasional shaking. The stopper was washed with 5 ml of distilled water followed by addition of 5ml potassium iodide solution. The contents were shaken thoroughly and liberated iodine was titrated against stan-dard sodium thiosulphate solution using starch as indicator. A blank experiment was also run under identical experimental conditions, but without the samples.

FORMULA FOR CALCULATION

$$\text{Recovery of sample (mg)} = \frac{(V_B - V_S) \times N \times W}{2 \times n}$$

Where

V_B = Volume of sodium thiosulphate solution required to titrate blank (ml).

V_S = Volume of sodium thiosulphate solution required to titrate sample (ml).

N = Normality of sodium thiosulphate solution.

W = molecular weight of sample.

n = Stoichiometry = number of moles of N-bromosaccharin required per mole of sample for complete reaction.

III. Results And Discussion

Determination of a number of phenolic compounds on small scale have been carried out by the general procedure (table-I). The relative errors do not exceed ±1%. Before , applying the reaction for the determination of any phenolic stoichiometry of the reaction has to be determined in each case.

The number of bromine atoms entering the molecule depends upon the structure of compound, but it must be known for each determination. Phenols are known to undergo nuclear bromination reactions by using bromination methods.

The presence of phenolic groups in aromatic compounds considerably activates orthopara positions of the benzene ring and allows bromine to enter simultaneously into all these positions. The mechanism of reactions in case of phenol was verified by separating tribromophenol from the reaction mixture.The compounds isolated were identified by their m.p. and m.m.p. determinations as tribromophenol (m.p. 94°C).

The overall reaction of N-bromosaccharin with phenol (stoichiometry 3) proceeds in the same way as in the case of N-bromosuccinimide and may be represented as:

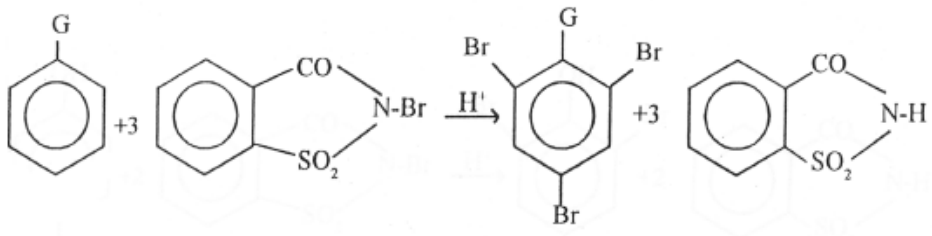
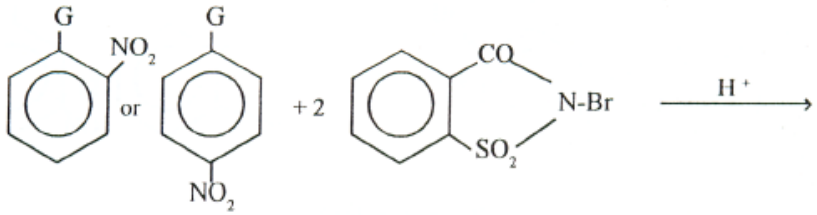
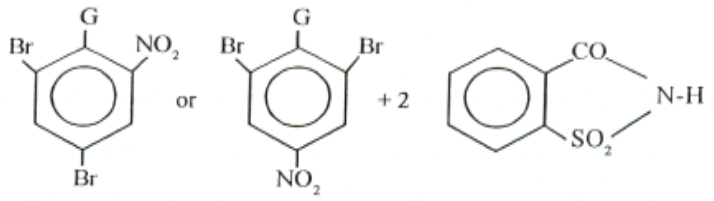


TABLE I : Determination Of Phenolic Compounds Using Nbsa

Sample	Aliquots taken (ml)	Amount taken (mg)	Reaction time (min)	Stoichio-metry (mg)	Stoichio-error (%)	Recover (mg)	Relative error (%)
Phenol	2.00	2.40	5	3		2.36	-1.67
	3.00	3.60				3.54	-1.67
	4.00	4.80				4.84	+0.83
o-nitrophenol	2.00	2.08	5	2		2.07	-0.48
	3.00	3.12				3.10	-0.64
	4.00	4.16				4.17	+0.24
m-Nitro phenol	2.00	2.40	5	2		2.36	-1.67
	3.00	3.60				3.62	+0.56
	4.00	4.80				4.72	-1.67
p-Nitrophenol	2.00	2.20	5	2		2.16	-1.82
	3.00	3.30				3.28	-0.60
	4.00	4.40				4.36	-0.90
p-chlorophenol	4.00	2.80	5	2		2.84	+1.43
	5.00	3.50				3.54	+1.14
	6.00	4.20				4.13	-1.67
o-hydroxy benzoic acid	2.00	1.50	4	3		1.49	-0.67
	4.00	3.00				2.95	-1.67
	6.00	4.50				4.45	-1.11
m-Hydroxy benzoic acid	2.00	2.00	5	3		1.98	-1.00
	3.00	3.00				2.96	-1.33
	4.00	4.00				3.95	-1.25
p-hydroxy benzoic acid	2.00	2.10	5	3		2.13	+1.43
	3.00	3.15				3.12	-0.95
	4.00	4.20				4.18	-0.48
Resorcinol	2.00	2.00	4	3		1.99	-0.50
	3.00	3.00				3.02	+0.67
	4.00	4.00				3.98	-0.50
Pyrogallol	2.00	2.20	3	3		2.18	-0.90
	3.00	3.30				3.32	+0.60
	4.00	4.40				4.38	-0.45
Phloroglucinol	4.00	2.40	4	3		2.36	-1.67
	6.00	3.60				3.64	+1.11
	8.00	4.80				4.75	-1.04
a-Naphthol	2.00	1.50	4	2		1.48	-1.33
	4.00	3.00				2.98	-0.67
	6.00	4.50				4.45	-1.11
b- Naphthol	2.00	1.60	4	2		1.62	+1.25
	4.00	3.20				3.18	-0.63
	6.00	4.80				4.75	-1.04

Phenol having a nitro group at ortho or para positions consumes two moles of N-bromosaccharin and gives dibromo product. The reaction may be represented as :

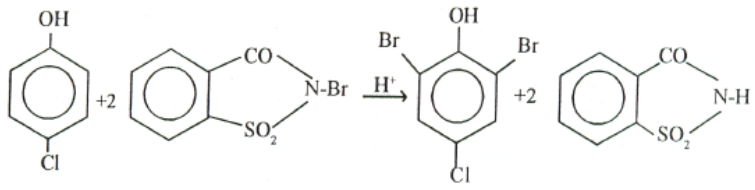




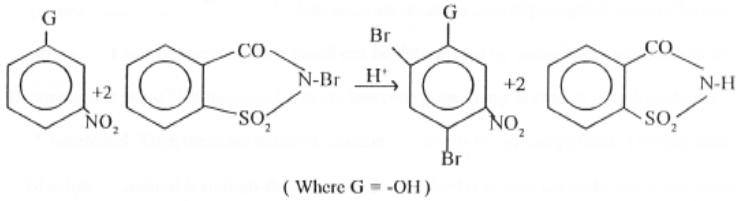
(Where G = -OH)

(Where G = -OH)

Similarly p- chlorophenol consumes two moles of N-bromosoaccharin giving dibromo derivative as:



In case of m-nitrophenol the observed stoichiometry of two be explained by assuming the formation of a dibromo product as:

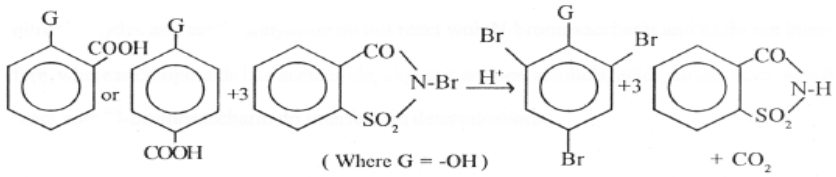


(Where G = -OH)

(Where G = -OH)

One of the ortho positions remains unsubstituted due to steric hindrance.

Phenol having carboxyl group in ortho or para positions (stoichiometry 3) undergo decarboxylation followed by substitution with bromine atoms in the same way as in the case or N-bromosuccinimide and the reaction may be represented as:



(Where G = -OH)

Similarly the observed stoichiometry in all cases may be explained by assuming the formation of corresponding bromoderivatives.

In case of o-hydroxybenzoic acid, hydrogen bonding present between o-hydroxyl and carboxyl groups, whereas in case of resorcinol, pyrogallol, and phloroglucinol steric hin-drance play as important role, responsible for slow reactivity of these compounds.

ADVANTAGES

One advantage of the present procedure using N-bromosaccharin over the other using N-bromosuccinimide is that, it gives accurate results in case of pyrogallol, phioroglucinol, p-nitrophenol and benzidine which could not be determined by using N-bromosuccinimide. Brominations using N-bromosaccharin are less time consuming in case of o-hydroxybenzoic acid, resorcinol. Then there are uniform reaction conditions for all compounds. The only stan-dard solution required is sodium-thiosulphate. The method is simple, accurate and quick, since the complete determination including pipetting and titration can be completed in about 20 minutes.

INTERFERING FACTORS

Determinations can be carried out even in presence of most of the likely impurities. Compounds like nitobenzene, m-dinitrobenzene, naphthalene, aromatic aldehydes, nitroaldehydes and acetic anhydride do not react with N-bromosaccharin and so do not inter-fere, whereas compounds like acetanilide, aliphatic amines, alcohols, acids, amino acids which react with N-bromosaccharin do interfere in determinations.

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