

## Analytical Studies for the Determination of Some Aromatic Amines with N-Bromo Saccharin at Micro Scale

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**Abstract:** An accurate method has been described for determination of aromatic amines at micro scale using N-bromosaccharin as brominating agent in acetic acid medium. A known volume of sample solution of aromatic amines was treated with excess of N-bromosaccharin. After the reaction was completed the unreacted N-bromosaccharin was determined by titrating against standard sodium thiosulphate solution using starch as indicator. A blank Experiment was also run under identical condition without the sample. The method is simple quick, convenient and accurate and performed in an ordinary laboratory conditions without using any sophisticated instruments. The precision and accuracy are within  $\pm 2\%$ .

**Keywords:** Analytical studies, Aromatic Amines, Determination, N-bromosaccharin

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### I. Introduction

Aromatic amines are of great industrial importance. They are used in manufacture of dyes, drugs, explosives, printing material, plasticizer and accelerator etc. Because of their great chemical importance, a large no of procedures have been developed for determination of aromatic amines<sup>1-10</sup>. In the present paper we describe a method for determination of Aromatic amines at the mg level using N-bromo saccharin as brominating and 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 completed, 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 amines 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  $\pm 2\%$ .

### II. Experimental

#### Reagents And Solution

##### N-Bromosaccharin : . 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 up to the mark with distilled water and standardized 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 up to 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 up to mark and standardized against 0.01 N copper sulphate solution.

##### Potassium Iodide

15 percent (w/v) aqueous solution was employed (Baker analysed reagent).

##### Starch Indicator

1percent (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 standard sodium thiosulphate solution using starch as indicator. A blank experiment was also run under identical experimental conditions, but without the samples.

### Formula For Calculation

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

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.

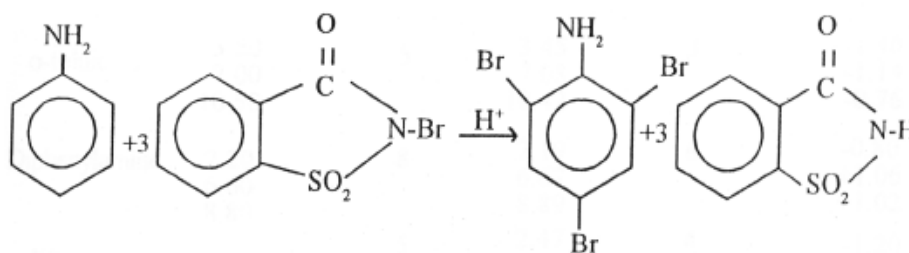
### III. Results And Discussion

Determination of a number of aromatic amino compounds on small scale have been carried out by the general procedure (table-1). The relative errors do not exceed  $\pm 2.0\%$ . Before, applying the reaction for the determination of any amino compound 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. Aromatic amines are known to undergo nuclear bromination reactions by using bromination methods.

The presence of amino groups in aromatic compounds considerably activates ortho para positions of the benzene ring and allows bromine to enter simultaneously into all these positions. The mechanism of reactions in case of aniline was verified by separating tribromo aniline from the reaction mixture. The compound were identified by their m.p.tribromoaniline (m.p. 117°C).

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

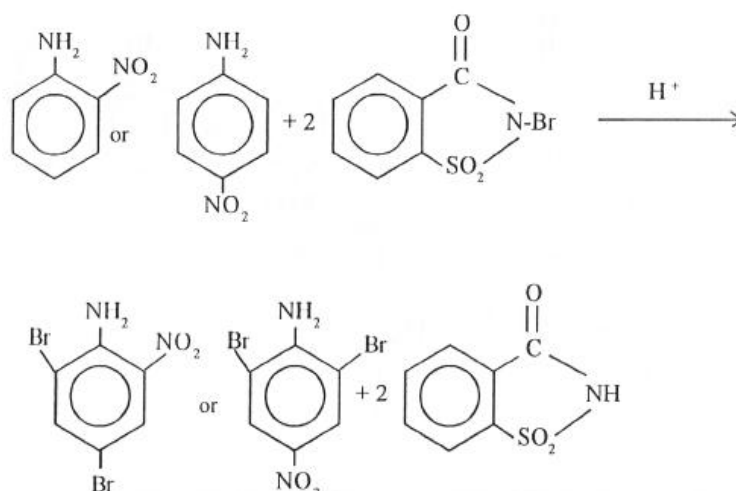


**Table – 1** Small Scale Determination Of Aromatic Amino Compounds With The Recommended Procedure

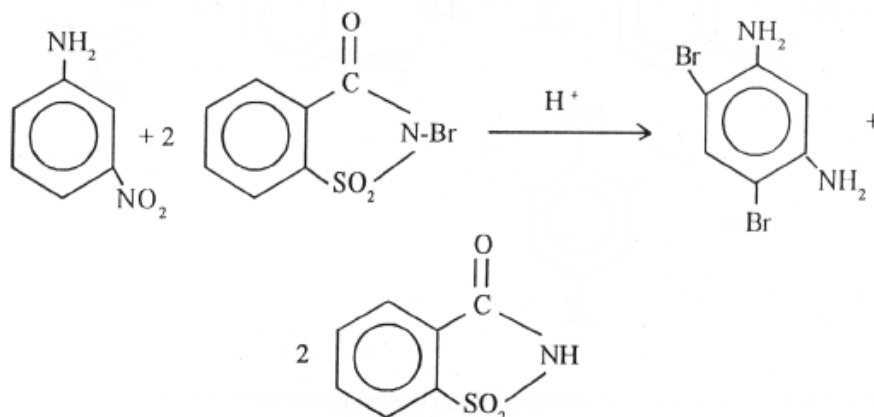
Sample	Amount Present (mg)	Reaction time (min)	Amount Recover (mg)	Stoichiometry	Relative error (%)
Aniline	2.50	5	2.52	3	+0.08
	5.00		5.04		+0.08
	10.00		10.1		+1.00
o-nitro aniline	2.20	5	2.22	2	+0.90
	6.60		6.67		+1.06
	8.80		8.89		+1.02
m-nitro aniline	2.50	5	2.52	2	+0.80
	7.50		7.56		-0.80
	10.00		10.08		+0.80
p-nitro aniline	2.50	5	2.47	2	+1.20
	7.50		7.57		+0.93
	10.00		10.1		+1.00

o-amino benzoic acid	2.50 7.50 10.00	3	2.49 7.42 10.09	3	-0.40 -1.06 +0.90
m-amino benzoic acid	2.50 7.50 10.00	6	2.46 7.43 10.08	3	-1.60 -0.93 +0.80
p-amino benzoic acid	7.00 10.50 3.50	6	3.44 7.06 10.59	3	-1.70 +0.85 +0.85
o-toluidine	3.50 7.00 10.50	5	3.45 7.08 10.42	3	-1.40 -1.14 -0.76
Diphenylamine	2.20 6.60 8.80	8	2.19 6.67 8.89	6	-0.80 +1.06 +1.02
Benzidine	2.50 5.00 7.50	5	2.47 5.05 7.43	4	-1.20 -1.00 -0.93
Sulphanilic acid	2.50 7.50 10.50	3	2.48 7.43 10.42	3	-0.80 -0.93 -0.76

Aniline 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 :

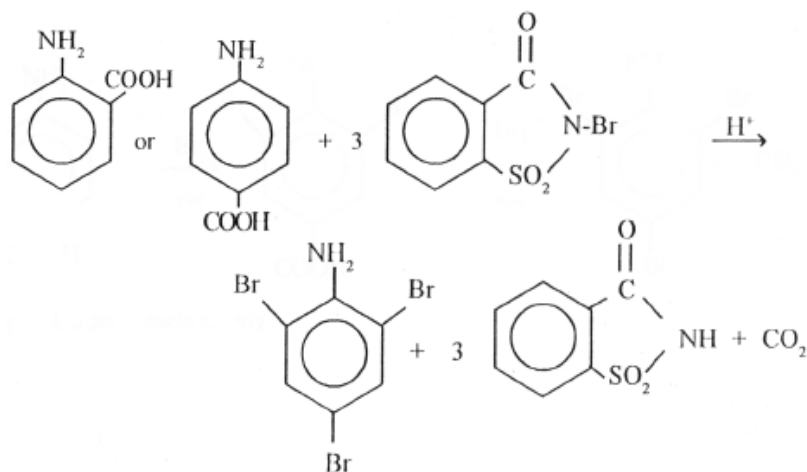


Similarly in the case of m-nitro aniline the observed stoichiometry of two may be explained by assuming the formation of a dibromo product as :

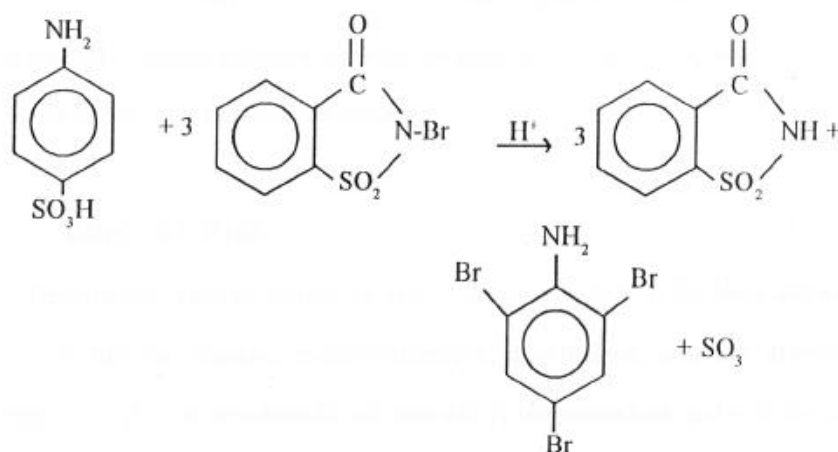


One of the ortho positions remains unsubstituted due to steric hindrance.

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

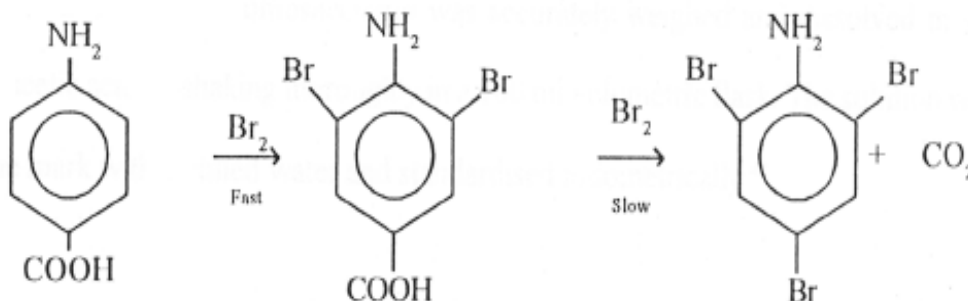


Sulphanilic acid (stoichiometry -3) undergoes disulphonation followed by substitution with bromine atoms giving tribromo aniline as:



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

The slow reactivity of arylamines having carboxylic and sulphonic acid groups in their structures may be due to slow rate of decarboxylation followed by substitution by a bromine atom as :



Diphenylamine also reacts slowly.

### Advantages

One advantage of the present procedure using N-bromosaccharin over the other using N-bromosuccinimide is that, it gives accurate results and less time consuming in case of p-aminobenzoic acids, diphenylamine and sulphanilic acid. Then there are uniform reaction conditions for all compounds. The only standard 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 interfere, whereas compounds like acetaniline, aliphatic amines, alcohols, acids, amino acids which react with N-bromosaccharin do interfere in determinations.

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