# QUANTITATIVE DETERMINATION OF THIOUREA & SOME OF ITS DERIVATIVES WITH NBSA REAGENT

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**Abstract**
**An accurate method has been described for determination of thiourea & some of its derivative at micro scale using N-bromosaccharin as brominating & oxidizing agent. A known volume of sample solution of thiourea & some of its derivative 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 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 condition without using any sophisticated instruments. The precision & accuracy was within ±1%**
**Keywords: Analytical studies, Thiourea ,Determination, NBSA**

## I. INTRODUCTION

Thiourea and its derivatives are generally used as preservatives, insecticides, rodenticides and pharmaceuticals; and possess anesthetic, antibacterial and antipyretic properties. They are also used in dye, photographic film, plastic and textile industries and for the manufacture of chemically deposited radiation detectors and sulphide phosphorus materials. They are of great value in the characterisation of organic compounds. A number of methods have been proposed from time to time for determination of thiourea[1-11]. In the present paper we describe a method for determination of thiourea & some of its derivative at the mg level using N-bromosaccharin reagent. 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 the sample and recovery of Thiourea and its derivatives sample was calculated. The method is convenient and performed in ordinary laboratory condition. It does not involve sophisticated instruments and rigrous reaction conditions. The precision and accuracy are within ±1%

## II. EXPERIMENTAL

### REAGENTS AND SOLUTION

### N-BROMOSACCIIARIN : . 0.02 M

1.3116 g of N-bromosaccharin was accurately weighed and dissolved in 100 ml of glacial acetic acid by shaking thoroughly in a 250 ml volumetric flask. The solution was made upto the mark with distilled water and standardised iodometrically.

### SAMPLE SOLUTION

A stock solution of each sample (thioureas) was prepared by dissolving an accurately weighed amount (20-50 mg) of sample in distilled water in a 50 ml standard volumetric flask & made upto the mark. Phenyl and allyl thioureas were dissolved in minimum amount of hot distilled water while thiourea and amino thiourea in cold distilled water and made upto the mark. Aliquots containing 1-4 mg of sample from stock solution were used for each determination.

### GLACIAL ACETIC ACID (A.R., B.D.H.)

### 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 percent (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. 20 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 10ml 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**

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

Determinations of thiourea, allyl thiourea, phenyl thiourea and amino thiourea on small scale have been successfully carried out by the general procedure (table I). The relative errors do not exceed ±2%. Before, applying the reaction for quantitative determination of thiourea and its derivatives, stoichiometry of the reaction has to be determined in each case.

**TABLE-I -** DETERMINATION OF THIOUREAS USING NBSA WITH RECOMMENDED PROCEDURE

| Sample | Aliquots | Amount Present (mg) | Reaction Time (min) | Amount Recovered (mg) | Stoichiometry | Relative error (%) |
|---|---|---|---|---|---|---|
| Thiourea | 1 | 1.0000 | 10 | 1.0038 | 4 | +0.38 |
| | 3 | 3.0000 | | 3.0067 | | +0.22 |
| | 5 | 5.0000 | | 5.0096 | | +0.19 |
| Allyl thiourea | 1 | 1.0200 | 10 | 1.0179 | 4 | -0.20 |
| | 3 | 3.0600 | | 3.0824 | | +0.73 |
| | 5 | 5.1000 | | 5.1279 | | +0.54 |
| Phenyl thiourea | 1 | 1.0100 | 10 | 1.0095 | 7 | -0.05 |
| | 3 | 3.0300 | | 3.0427 | | +0.41 |
| | 5 | 5.0500 | | 5.0833 | | +0.65 |
| Amino thiourea | 1 | 1.0000 | 10 | 1.0084 | 7 | +0.04 |
| | 3 | 3.0000 | | 3.0094 | | +0.31 |
| | 5 | 5.0000 | | 4.9863 | | -0.27 |

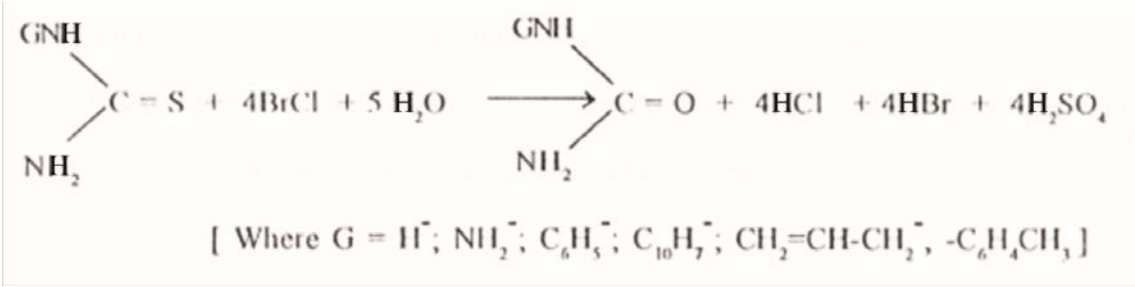
The observed stoichiometry of 4 in case of thiourea, aJIyl thiourea, amino thiourea, and of 7 in case of phenyl thiourea may only be explained by assuming oxidation of sulphur function in these compounds giving rise to formation of sulphate ions.

Serwer et al. have studied oxidation of thiourea and thioncetamide in detail and reported similar observations i.e. formation of sulphate ions.

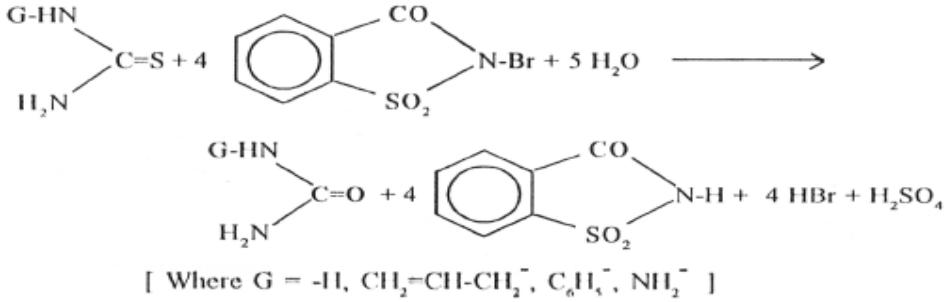
Skramovsky et al. have also studied oxidation of thiourea into urea and sulphate ions with iodine in alkaline sloution as :

$$NH_2CS\,NH_2 + 4OI^- + H_2O \longrightarrow NH_2CONH_2 + H_2SO_4 + 4I^-$$

The oxidation of thiourea using bromine monochloride in acetic acid medium have also been studied in our laboratories by Prakash and the following mechanism has been suggested :




On the basis of observed stoichiomctry, overall reaction between thiourea, allyl thiourea, phenyl thiourea, amino thiourea and N-bromosaccharin may be represented as




In case of phenyl thiourea observed stoichiometry of 7 may be explained by assuming that 4 equivalents of N-bromosaccharin are being utilized for oxidation while 3 equivalents for bromination of phenyl ring at two ortho and one para positions.

The above course of reaction was also verified by the fact that reaction mixture of thiourea and N-bromosaccharin gave white precipitate of barium sulphate on treatment with hydrochloric acid and barium chloride solution.

The reaction as proposed above finds support from previous works using hypoiodide, N-bromosuccinimide or bromine monochloride as oxidants for determination of thioureas.

## ADVANTAGES

The procedure gives accurate results with all the thioureas studied. Any drastic reaction condition is not required. The results obtained are comparable with those obtained earlier using N-bromosuccinimide or bromine monochloride. Therefore, N-bromosaccharin is a suitable substitute for N-bromosuccinimide for oxidation of thioureas.

## INTERFERING FACTORS

Presence of organic compounds or group susceptible to oxidation or brominaion such as phenols and aromatic amines interfere with determinations.

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