

# MICRO-DETERMINATION OF SOME HYDRAZINE DERIVATIVES WITH N-BROMOSACCHARIN

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A quick and convenient method has been developed for the microdetermination of few hydrazine derivatives. Milligram amount of the sample is allowed to react with excess of N-bromosaccharin at room temperature for 5–10 minutes. After the reaction is over, the unconsumed reagent is back titrated iodometrically. The accuracy of the method is within  $\pm 0.5$  per cent.

## INTRODUCTION

HYDRAZINE and its derivatives are quantitatively oxidised with organic and inorganic reagents. Depending upon this property a large number of procedures have been developed for the small scale determination of hydrazine compounds (Barakat & Shaker, 1963; Berka & Busev, 1962; Singh & Siefker, 1966). Taking advantage of the oxidising capacity of N-bromosaccharin (Mathur & Bacchawat 1971) the present authors have developed a method for the small scale analysis of hydrazine derivatives. The hydrazine sample was allowed to react with excess of N-bromosaccharin reagent in a stoppered conical flask for about 10 minutes at room temperature (25 °C). The unconsumed N-bromosaccharin solution was determined by iodometric titration and the recovery of the sample was calculated. The present reagent is highly stable at room temperature and gives precise and reproducible results on micro scale within the accuracy of  $\pm 0.5$  per cent. The present method is superior to existing methods i.e., oxidation with  $\text{KIO}_3$  (Muller & Furman, 1937),  $\text{KMnO}_4$  (Brown & Shetterly, 1909) and ceric sulphate (Dernback & Mehlig, 1942) in the sense that it does not need high reaction temperature and catalyst, operates at milligram sample size and is of general applicability.

## MATERIALS AND METHODS

### Reagents

*N-Bromosaccharin 0.02M Solution* — 1.3116 gm of the synthesised N-bromosaccharin (Mathur & Bachhawat, 1971) was dissolved in 100 ml glacial acetic acid in a 250 ml volumetric flask and made up to the mark with distilled water. The solution was standardised against standard solution (0.01M) of sodium thiosulphate (Barakat *et al.*, 1954).

*Stock Solution* — A stock solution of hydrazine sulphate, hydrazine dihydrochloride, semicarbazide, phenyl hydrazine hydrochloride was prepared by dissolving 50–100 mg of the sample in distilled water, phenyl semicarbazide in hot distilled water and 2,4-dinitrophenyl hydrazine in 50 per cent glacial acetic acid in a 100 ml

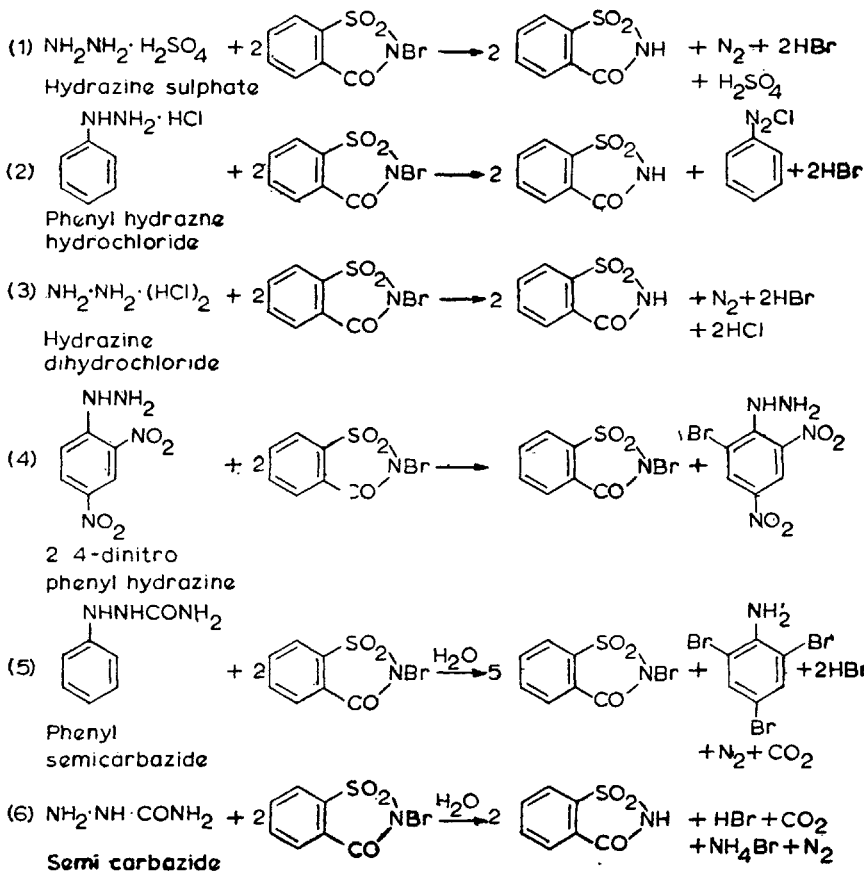
volumetric-flask. All the samples were either A. R., B. D. H. grade or purified by recrystallisation.

### PROCEDURE

An aliquot of the sample was taken in 100 ml iodine flask and 15 ml of 0.02M solution of N-bromosaccharin was added. The flask was stoppered and allowed to stand for 10 minutes at room temperature (25 °C) with occasional shaking. After the reaction was over the stopper was washed with 5 ml distilled water and 10 ml potassium iodide (10 per cent) was added to it, Contents were shaken thoroughly and kept for one minute. The liberated iodine was titrated with standardised 0.01M sodium thiosulphate solution using starch (1 per cent solution) as indicator. A blank experiment was also run under identical conditions using all the reagents except the sample.

### CALCULATION

$$\text{mg sample} = \frac{(B-A) \times M \times N}{n \times 2}$$



where

$A$  = ml sodium thiosulphate for sample,

$B$  = ml sodium thiosulphate for blank,

$n$  = moles of N-bromosaccharin for the sample,

$M$  = molecular weight of the sample and

$N$  = molarity of sodium thiosulphate solution.

#### RESULTS AND DISCUSSION

It was observed that the recovery of the sample is constant from 1–10 mg of sample size. The effect of concentration of *N*-bromosaccharin reagent and reaction time was studied, and the stoichiometry of the reaction was also established for all the compounds. Table I shows the determination of a few hydrazine compounds with *N*-bromosaccharin.

TABLE I

*Determination of few hydrazine compounds with N-bromosaccharin*

S. No.	Amount taken mg	Sample	Amount recovered mg	Moles of N-bromo-saccharin per mole of compound	Reaction time in minutes	No. of determination	% Deviation
1.	1.050	Hydrazine sulphate	1.058	2	5	3	+0.76
	2.100		2.102				+0.09
	3.150		3.168				+0.57
2.	1.018	Phenyl hydrazine hydrochloride	1.022	2	5	3	+0.39
	2.036		2.042				+0.29
	3.054		3.058				+0.13
3.	1.006	2,4-dinitrophenyl hydrazine	1.012	1	10	3	+0.59
	2.012		2.018				+0.29
	3.018		3.022				+0.13
4.	1.020	Hydrazine dihydrochloride	1.028	2	5	3	+0.78
	2.040		2.048				+0.39
	3.060		3.091				+0.01
5.	1.016	Phenyl semi-carbazide	1.018	5	15	3	+0.19
	2.032		2.034				+0.09
	3.048		3.035				-0.42
6.	1.020	Semicarbazide	1.028	2	10	3	+0.78
	2.040		2.054				+0.68
	3.060		3.070				+0.32

On the basis of the stoichiometry and the literature available on the oxidation (1, 6) of hydrazine compounds a possible course of reaction is also suggested. In case of hydrazine the final oxidation products were identified and confirmed. Phenols and aromatic amines interfere in the determination while urea and its derivatives, Fe(III) and rare earths are non-interfering.

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