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Micro Estimation of Some Hydrazine Derivatives With Bromamine-T

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A simple, convenient and a method of choice has been developed for the micro estimation of some hydrazine derivatives. Milligram amount (1–5 mg) of the sample is allowed to react with excess of bromamine-T in 2N-sulphuric acid medium at room temp. for 10–15 minutes. After the reaction is over, the unconsumed reagent is back titrated iodometrically. The accuracy of the method is within ± 1%.

INTRODUCTION

Bromamine-T (sodium salt of N-bromo-*p*-toluene sulphonamide has been used as oxidising and brominating agent in kinetic studies[1–3] and estimation[4–6] of some compounds. Hydrazine and its derivatives are an important class of compounds used in plastics, fuel cells, medicinal and biological sciences. Hydrazine is an important material with respect to present day explosives and rocket fuels. Phenyl hydrazine and 2,4-dinitrophenyl hydrazine are valuable analytical reagents for the characterisation of aldehydes and ketones. In the present study we describe the estimation of some hydrazine derivatives with bromamine-T in acidic medium. A number of methods[7–12] have been reported for estimation of hydrazines. The present method gives precise and reproducible results, and is simple and of general applicability. The sensitivity of the method is up to 1 mg as compared to 5 mg by earlier method[12].

EXPERIMENTAL

Bromamine-T was synthesised[13] and its 0.1N solution was made by dissolving accurately weighed 8.105 gm. in distilled water in a 250 ml measuring flask and made up to the mark with the distilled water. Stock solution of sodium thiosulphate (0.05 N) was prepared by dissolving accurately weighed 6.2044 gm. of sodium thiosulphate (BDH) in distilled water in a 500 ml volumetric flask.

The accurately weighed copper sulphate (3.21 gm) (AnalaR, BDH) was dissolved in distilled water in a 250 ml measuring flask for preparation of 0.05N-solution. 2N-sulphuric acid v/v was prepared. 10% w/v aqueous solution. of potassium iodide and 1% w/v aqueous solution of starch was prepared.

Sample solution

Stock solution of hydrazine sulphate, phenylhydrazine hydrochloride and semicarbazide were prepared by dissolving accurately weighed 100 mg of the sample in cold distilled water, while phenyl semicarbazide was dissolved in hot water in 100 ml measuring flask and made up to the mark with distilled water. 2,4-Dinitrophenyl hydrazine (100 mg) was dissolved in minimum amount of 2N-H_2SO_4 in 100 ml measuring flask and made up to the mark with distilled water.

Procedure

Aliquots containing 1–5 mg of the sample were placed in a 100 ml Erlenmeyer flask and 5 ml of 0.1N bromamine-T solution was added followed by the addition of 2 ml of 2N-H_2SO_4. The reaction mixture was shaken thoroughly and the flask was stoppered. Contents were allowed to stand at room temp. for prescribed reaction time. After the completion of reaction 5 ml of potassium iodide (10%) was added to reaction mixture. Contents were shaken thoroughly and kept for one minute. The liberated iodine was titrated with standardised (0.05N) hypo solution using starch as indicator. A blank was also run under identical conditions using all the reagents except the sample. The amount of the sample was calculated by the following expression.

$$\text{mg of the sample} = \frac{(B - A)MN}{2n}$$

where B = Volume of sodium thiosulphate for blank,
A = Volume of sodium thiosulphate for sample,
M = Molecular weight of the sample,
N = Normality of sodium thiosulphate solution,
n = No. of moles of bromamine-T consumed per mole of the sample.

In each case of the sample SD and CV were also calculated; the results obtained are given in Table 1.

TABLE 1
MICRO ESTIMATION OF SOME HYDRAZINE DERIVATIVES WITH BROMAMINE-T
(0.1N) Reagent in Sulphuric Acid (2N-H_2SO_4) medium

Sample	Aliquots taken (ml)	Amount* present (mg)	Reaction time (min)	Molecularity	Amount† obtained by calculation (mg)	S.D.	CV (%)
1. Hydrazine sulphate	1	1.002	10	2	1.003	0.0036	0.3589
	3	3.006			3.022	0.0030	0.0992
	5	5.010			5.020	0.0327	0.6357
2. Phenyl hydrazine hydrochloride	1	1.012	10	2	1.010	0.0093	0.9207
	3	3.036			3.042	0.0131	0.4306
	5	5.060			5.053	0.0323	0.6392

Sample	Aliquots taken (ml)	Amount* present (mg)	Reaction time (min)	Molecularity	Amount† obtained by calculation (mg)	S.D.	CV (%)
3. 2,4-dinitro	1	1.012	10	2	1.010	0.0093	0.9207
phenyl	3	3.003			3.006	0.0194	0.6454
hydrazine	5	5.005			5.016	0.0319	0.6360
4. Semicarbazide	1	1.006	10	2	1.008	0.0026	0.2579
	3	3.018			3.025	0.0132	0.4364
	5	5.030			5.023	0.0346	0.6888
5. Phenyl	1	1.003	15	5	1.004	0.0032	0.3187
semicarbazide	3	3.009			2.998	0.0241	0.8089
	5	5.015			5.026	0.0196	0.5173

*In each sample size nine determination were done.
†Average of nine determinations.

RESULTS AND DISCUSSION

The effect of variables such as the volume and concentration of the reagent, sulphuric acid, temperature and reaction time were studied. It was found that 0.05 to 0.10 concentration of bromamine-T reagent was suitable to achieve quantitative reaction. The recommended amount of $2N\text{-}H_2SO_4$ was necessary for better ionisation of bromamine-T which did not change by addition of more volume or more concentrated sulphuric acid. It was also found that a lesser reaction time did not give constant and accurate results. An increase in reaction time did not have any improvement on the accuracy. Heating of the reaction mixture at steam bath gave inaccurate and inconsistent results, because of the decomposition of the reagent at a higher temperature. Therefore the room temp. (27°C) has been recommended for the determination.

On the basis of stoichiometry, liteature available on the oxidation of hydrazine compounds and the isolation of reaction products, a possible course of reaction has been suggested for each compound. While studying the oxidation of hydrazine derivatives it is noticed that hydrazine is completely oxidised to nitrogen and water, the evolution of nitrogen has qualitatively been established.

$$\underset{\text{Hydrazine sulphate}}{H_2N.NH_2.H_2SO_4} + \underset{\text{Bromamine-T}}{2TsN.NaBr} \rightarrow N_2 + 2NaBr + \underset{\text{p-Toluenesulphonamide}}{2TsNH_2} + H_2SO_4$$

(where Ts stands for $p\text{-}CH_3C_6H_4SO_2\text{-}$)

Semicarbazide is oxidised to nitrogen, carbon dioxide and ammonium salt.

$$\underset{\text{Semicarbazide}}{H_2N.NH.CONH_2} + 2TsN.NaBr + 2H_2O \rightarrow N_2 + CO_2 + NH_4Br + 2TsNH_2 + NaBr + NaOH$$

Phenyl hydrazine hydrochloride is oxidised to diazonium salt.

$$C_6H_5NH.NH_2.HCl + 2TsN.NaBr \rightarrow C_6H_5N_2^+ + 2TsNH_2 + 2Na^+ + 2Br^- + Cl^-$$

Phenylhydrazine hydrochloride

Phenyl semicarbazide change to S-tribromoaniline. The overall reaction is as follows:

$$C_6H_5NH.NHCONH_2+2TsNaBr+4H_2O \rightarrow 2,4,6\text{-}Br_3C_6H_2.NH_2+5TsNH_2+N_2 + CO_2+2NaBr+2NaOH$$

Phenylsemicarbazide — S-tribromoaniline

In case of 2,4-dinitrophenyl hydrazine the final product is found to be bromo derivative.

$$2,4\text{-}(NO_2)_2C_6H_3NH.NH_2 + TsN.NaBr + H_2O \rightarrow 2\text{-}Br,4,6\text{-}(NO_2)_2C_6H_2NH{\cdot}NH_2 + NaOH$$

2,4-dinitrophenyl-hydrazine — 2-bromo, 4,6-dinitrophenyl-hydrazine

The effect of interfering substances is also studied. While carrying out the estimation a known amount of phenol, aromatic amine and urea is added and the results are calculated. It is noticed that the experiments containing phenol and aromatic amines give higher recovery and positive error while urea has no effect.

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REFERENCES

1. B. Singh, N.B. Singh and B.B.L. Saxena, *J. Indian Chem. Soc.*, **61**, 319 (1984).
2. B. Singh and A.N. Singh, *J. Indian Chem. Soc.*, **62**, 523 (1985).
3. B. Singh and R. Chand, *Tetrahedron*, **41**, 2871 (1985).
4. D.S. Mahadevappa, K.S. Rangappa, B.T. Gowda and N.M.M. Gowda, *Michrochem. J.*, **26**, 132 (1981).
5. B.N. Usha, Rangaswamy and H.S. Yathirajan, *Analyst*, **109**, 101 (1984).
6. A. Abou-Out, M.I. Walash, and F.B. Salem, *Analyst*, **106** (1266), 949 (1981) (Eng.).
7. B. Singh and A. Singh, *J. Indian Chem. Soc.*, **29**, 34 (1952).
8. A. Berka and A.K. Busev, *Anal. Chim. Acta*, **27**, 493 (1962).
9. M.Z. Barakat, M.F.A. Wahab, and M.M. Elsav, *J. Am. Chem. Soc.*, **77**, 1670 (1955).
10. S. Singh and J.R. Siefker, *Anal. Chim. Acta*, **36**, 449 (1966).
11. E.V. Egginton and M.S. Graham, *Analyst*, **89**, 226 (1964).
12. M.Z. Barakat and M. Shakar, *Analyst*, **88**, 59 (1963).
13. C.G.R. Nair, R. Lalithakumara and R.I. Senan, *Talanta*, **25**, 525 (1978).

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