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Rapid Differential Determination of Mixtures of Hydrazine and Hydroxylamine by Potentiometric Titration with an Iodide Ion-selective Electrode**

Junko Motonaka,* Sanae Ikeda,[†] and Nobuyuki Tanaka[††]
Technical College of Tokushima University, Minamijosanjima, Tokushima 770
[†]*Faculty of Engineering, Tokushima University, Minamijosanjima, Tokushima 770*
[††]*Faculty of Science, Tohoku University, Sendai 980*

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A rapid method has been established for determination of mixtures of hydrazine and hydroxylamine by potentiometric titration using an iodide ion-selective electrode. Accurate values are obtainable when nitric acid is added to the sample solution. A recommended procedure is proposed in which the sum of hydrazine and hydroxylamine is titrated with an aliquot of sample solution and another aliquot is titrated to the end point for hydrazine after hydroxylamine has been decomposed with nitric acid. Hydrazine and hydroxylamine in mixture can be determined in the concentration range of 0.01—0.5 mmol/dm^3. The best result, with relative error and relative standard deviation both of less than 0.7%, may be obtained on 0.5 mmol/dm^3 hydrazine and hydroxylamine.

Hydrazine and hydroxylamine are widely used in chemical analysis as reducing agents. These two toxic substances have very similar chemical properties and therefore, it is very difficult to determine their respective concentrations in their mixtures.

Rapid methods for determination of each of hydrazine and hydroxylamine were previously reported.[1)] The present paper describes a continuation of that work, in which concentrations of hydrazine and hydroxylamine in mixtures were measured.

Experimental

Apparatus. An automatic potentiometric titrator equipped with an iodide ion-selective indicator electrode and a pH meter were used; they were the same apparatus as described in the previous paper.[1)]

Reagents. All reagents were of analytical-reagent grade (Wako Pure Chemical Industries, Ltd.). Redistilled water was used. For experimental runs, the following stock solutions were diluted as needed: 10 mmol/dm^3 hydrazine sulfate (standardized by the JIS method[2)]); 10 mmol/dm^3 hydroxylamine sulfate (standardized by the JIS method[3)]); 50 mmol/dm^3 iodine–methanol solution (prepared by dissolving *ca.* 12.7 g of pure iodine in 1000 cm^3 of pure methanol, stored in an amber bottle, and standardized by the indicator titration method); 100 mmol/dm^3 silver nitrate solution (standardized by the amperometric titration[4)]).

Recommended Procedure. Into one of two titration cells is measured exactly 5 cm^3 of each of 0.2—10 mmol/dm^3 hydrazine sulfate and hydroxylamine sulfate, and added 15 cm^3 of 50 mmol/dm^3 iodine–methanol solution. The volume is adjusted to 100 cm^3 with redistilled water. The resulting solution is titrated potentiometrically with 10—100 mmol/dm^3 standard silver nitrate solution.

Into the other cell is measured exactly 5 cm^3 of each of 0.2—10 mmol/dm^3 hydrazine sulfate and hydroxylamine sulfate, added 20 cm^3 of 16 mol/dm^3 nitric acid which will decompose hydroxylamine and 10 cm^3 of 50 mmol/dm^3 iodine–methanol solution, and finally added redistilled water to 100 cm^3. The resulting solution is titrated in the same way as above.

Results and Discussion

Potentiometric Titration Curves. Potentiometric titration curves are shown in Fig. 1. The end point of curve (A) corresponds to the equivalence point for hydrazine, and that of curve (B) corresponds to the equivalence point for the sum of hydrazine and hydroxylamine. The amount of hydroxylamine in the mixture is determined from the difference between these two end points. The procedure requires about 5 min for curve (A) and 15 min for curve (B).

Effect of the Amount of Nitric Acid. When the nitric acid is added, hydroxylamine tends to decompose immediately. Therefore, stabilities of hydrazine and hydroxylamine in nitric acid were examined. As shown in Fig. 2, measurement of hydrazine is not affected by the addition of 16 mol/dm^3 nitric acid (0—30 cm^3), but analytical values for hydroxylamine decrease with increase in the volume of nitric acid added, reaching zero at 15 cm^3 of 16 mol/dm^3 nitric acid. Similar results were obtained with a mixture of hydrazine and

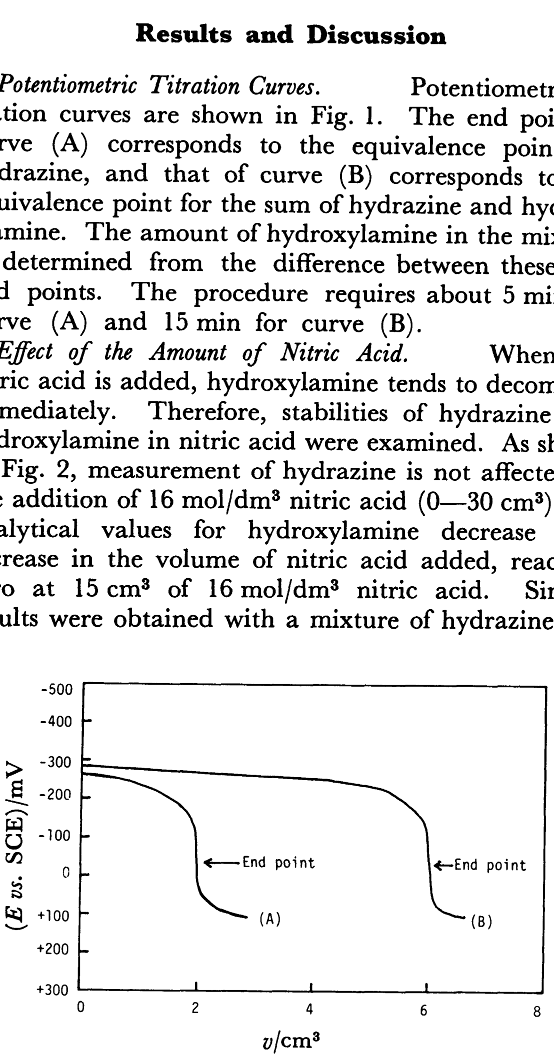

Fig. 1. Potentiometric titration curves for hydrazine and hydroxylamine mixtures.
v=Volume of 100 mmol dm^{-3} AgNO$_3$ solution added. (A): Solution: 100 cm^3, containing hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid (16 mol dm^{-3}, 20 cm^3) and iodine–methanol (50 mmol dm^{-3}, 10 cm^3), (B): Solution: 100 cm^3, containing hydrazine sulfate (10 mmol cm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}) and iodine–methanol (50 mmol dm^{-3}, 15 cm^3).

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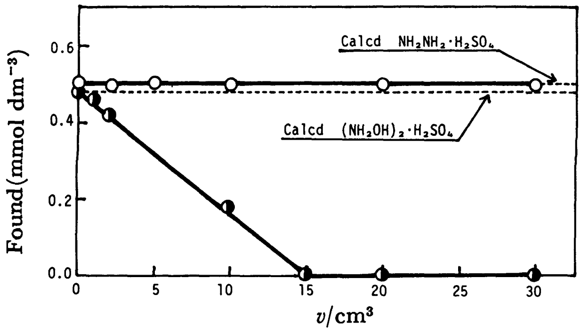

Fig. 2. Effect of nitric acid on determinations of hydrazine and hydroxylamine.
v= Volume of 16 mol dm^{-3} HNO_3 solution added. —○—: Solution: 100 cm^3, containing hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid and iodine–methanol (50 mmol dm^{-3}, 5 cm^3), —◐—: solution: 100 cm^3, containing hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid and iodine–methanol (50 mmol dm^{-3}, 10 cm^3).

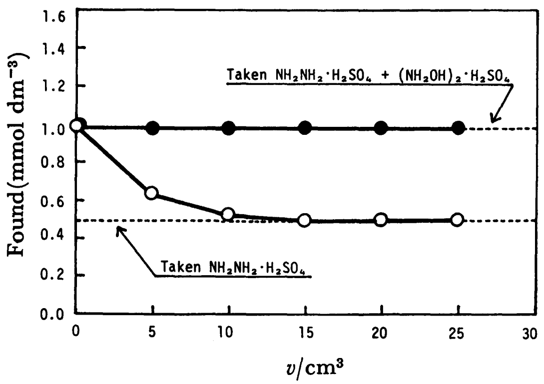

Fig. 3. Effect of nitric acid on the determinations of hydrazine and hydroxylamine in mixtures.
v= Volume of 16 mol dm^{-3} HNO_3 solution added. —○—: Solution: 100 cm^3, containing hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid and iodine–methanol (50 mmol dm^{-3}, 10 cm^3), —●—: solution: 100 cm^3, contining hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid and iodine–methanol (50 mmol dm^{-3}, 10 cm^3).

hydroxylamine (Fig. 3). All subsequent titrations of hydrazine were carried out in the presence of 20 cm^3 of 16 mol/dm^3 nitric acid.

Effect of the Amount of Iodine–Methanol. A mixture of hydrazine and hydroxylamine was titrated in the presence of various amounts of iodine–methanol (Fig. 4). Analytical values for hydrazine are in good agreement with those obtained by the JIS method provided that iodine is added in excess. Values for hydroxylamine are also in good agreement with those obtained by the JIS method provided that iodine is added in more than 1.7 times the equivalent amount.

In this experiment, in the presence of nitric acid iodine (50 mmol/dm^3, 10 cm^3) was added in 2.5 times the equivalent amount.

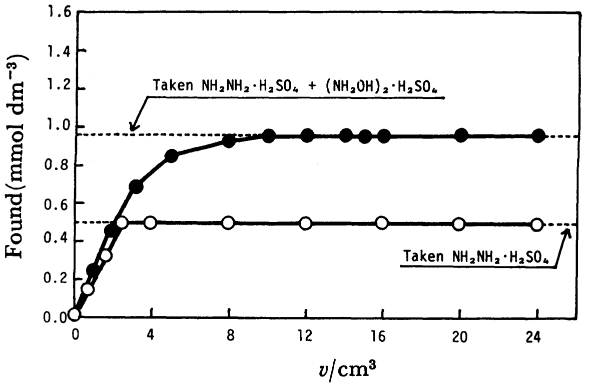

Fig. 4. Effect of the amount of iodine–methanol solution on the determination of hydrazine and hydroxylamine in mixtures.
v=Volume of 0.05 mol dm^{-3} I_2-CH_3OH solution added. —○—: Solution: 100 cm^3, of hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid (16 mol dm^{-3}, 20 cm^3) and iodine–methanol, —●—: solution: 100 cm^3, of hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3) and iodine–methanol.

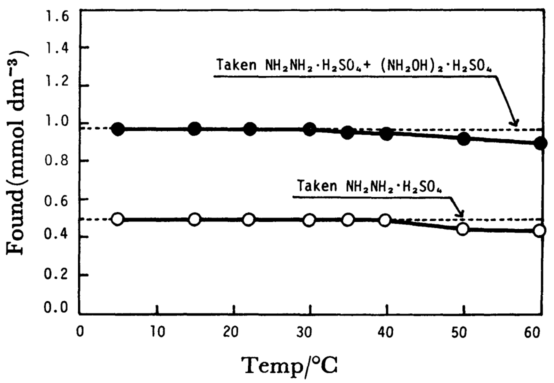

Fig. 5. Effect of temperature on the determination of hydrazine and hydroxylamine in mixtures.
—○—: Solution: 100 cm^3, of hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), nitric acid (16 mol dm^{-3}, 20 cm^3), and iodine–methanol (0.05 mol dm^{-3}, 10 cm^3), —●—: solution: 100 cm^3, of hydrazine sulfate (10 mmol dm^{-3}, 5 cm^3), hydroxylamine sulfate (10 mmol dm^{-3}, 5 cm^3), and iodine–methanol (50 mmol dm^{-3}, 15 cm^3).

Effect of Temperature. Titration of hydrazine and hydroxylamine mixtures is affected by temperature neither in the range of 5—30 °C when no nitric acid is added, in nor the range of 5—40 °C when nitric acid was added (Fig. 5). Hydroxylamine decomposes above 30 °C and hydrazine decomposes above 40 °C.

For convenience all subsequent measurements were conducted at room temperature (20 °C).

Effect of Concomitant Compounds. Mixtures of hydrazine and hydroxylamine were titrated in the presence of each of 15 compounds, the results being shown in Table 1.

The following compounds have little or no effect: sodium or magnesium nitrate in a molar ratio to hydrazine sulfate or hydroxylamine sulfate of 100 : 1,

TABLE 1. EFFECTS OF CONCOMITANT COMPOUNDS ON DETERMINATION OF HYDRAZINE AND HYDROXYLAMINE IN MIXTURE[a)]

Concomitant compound added	Molar ratio (Sample : Compound)	Relative error/%	
		$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$
$NaNO_3$	1 : 100	+0.6	+0.1
$Mg(NO_3)_2$	1 : 100	+0.7	+0.2
$(NH_4)_2SO_4$	1 : 50	+0.9	−0.1
$Ni(NO_3)_2$	1 : 20	+0.1	−0.9
$Cd(NO_3)_2$	1 : 1	+1.0	−0.3
NH_4Cl[b)]	1 : 1	+0.1	+1.3
KCl[b)]	1 : 1	+1.4	-0.0_2
KBr[b)]	1 : 1	−2.9	+0.9
NaF	1 : 1	+0.4	−1.6
$Pb(NO_3)_2$	1 : 1	+1.7	−2.1
$(NH_4)_2CO_3$	1 : 1	+1.3	−1.9
K_2CO_3	1 : 1	+0.2	−2.9
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1 : 1	+0.2	−15
$Fe_2(SO_4)_2(NH_4)_2SO_4 \cdot 24H_2O$	1 : 1	+0.7	−47
$NaNO_2$	1 : 1	−97	+19

a) Solution: 100 cm^3, containing 5 cm^3 of 10 mmol dm^{-3} hydrazine sulfate, 5 cm^3 of 10 mmol dm^{-3} hydroxylamine sulfate, a concomitant compound, and 10 cm^3 of 50 mmol dm^{-3} iodine–methanol with or without 20 cm^3 of 16 mol dm^{-3} nitric acid. b) With 10 cm^3 of 10 mmol dm^{-3} aluminium nitrate.[5)]

ammonium sulfate in a molar ratio of 50 : 1, nickel nitrate in a molar ratio of 20 : 1, and cadmium nitrate in a molar ratio of 1 : 1. Hydrazine and hydroxylamine can be determined with an error of about ±1% in the presence of any one of these compounds. However, lead nitrate, ammonium carbonate, and nitrous acid cause an interference. Ammonium chloride, sodium fluoride, potassium carbonate, ammonium iron(II) sulfate, and ammonium iron(III) sulfate do not affect the titration of hydrazine, and potassium chloride and potassium bromide do not affect the titration of hydroxylamine when aluminium nitrate is added.[5)]

Effect of the Ratio of Hydrazine to Hydroxylamine. Mixtures of hydrazine and hydroxylamine in various ratios were titrated (Table 2). Mixtures of hydrazine sulfate and hydroxylamine sulfate in ratios of 1 : 1, 5 : 2, and 5 : 1 can be determined with an error of less than ±1% and a relative standard deviation of less than 0.4%. However, with a mixture of hydrazine sulfate and hydroxylamine sulfate in a ratio of 1 : 5, the error is of the order of several percent.

Therefore, the amount of hydroxylamine should not be more than that of hydrazine.

Accuracy and Precision of the Method. Table 3 shows results obtained by the recommended procedure from four repeated titrations on mixtures of hydrazine and hydroxylamine of various concentrations.

Hydrazine and hydroxylamine in mixture can be determined in the concentration range of 0.01—0.5 mmol/dm^3. The best result, with relative error of less than ±0.7% and relative standard deviation of less than 0.4%, is obtained with the concentration of 0.5 mmol/cm.

Conclusion. Rapid and accurate differential determination is possible of hydrazine and hydroxylamine in mixture by potentiometric titration with silver nitrate solution and an iodide ion-selective electrode, if nitric acid is added to the sample solution. When 15 cm^3 or more of 16 mol/dm^3 nitric acid is added to a sample solution, analytical results for 0.05—0.5 mmol/dm^3 hydrazine sulfate in the presence of hydroxylamine sulfate are in good agreement with those obtained by the JIS method. The best result, with relative error and relative standard deviation both of less than 0.7%, is obtained with 0.5 mmol/dm^3 hydrazine sulfate and hydroxylamine sulfate.

By this method both hydrazine and hydroxylamine can be determined accurately at 5—30 °C.

TABLE 2. DETERMINATION OF HYDRAZINE AND HYDROXYLAMINE IN MIXTURE

Sample concentration/mmol dm^{-3} [a)]		Relative error/%[b)]		Sr/%[c)]	
$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$	$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$	$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$
0.5	0.5	−0.2	+0.7	0.2	0.4
0.5	0.2	−0.5	+1.0	0.2	0.2
0.5	0.1	+1.0	+1.0	0.1	0.2
0.1	0.5	+6.0	−2.7	1.1	0.1

a) Solution: 100 cm^3, containing hydrazine sulfate, hydroxylamine sulfate, and 10 cm^3 of 50 mmol dm^{-3} iodine–methanol with or without 20 cm^3 of 16 mol dm^{-3} nitric acid. b) Average of 4 titrations. c) Relative standard deviation.

TABLE 3. ACCURACY AND PRECISION DATA

Sample concentration/mmol dm^{-3}[a)]		Relative error/%[b)]		Sr/%[c)]	
$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$	$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$	$NH_2NH_2 \cdot H_2SO_4$	$(NH_2OH)_2 \cdot H_2SO_4$
0.5	0.5	−0.2	+0.7	0.2	0.4
0.1	0.1	+0.9	+0.6	0.2	0.2
0.05	0.05	+1.4	+1.0	0.2	0.6
0.01	0.01	+6.6	+0.7	1.1	1.6

a) Solution: 100 cm^3, containing hydrazine sulfate, hydroxylamine sulfate, and iodine–methanol with or without nitric acid. b) Average of 4 titrations. c) Relative standard deviation.

The determination is not affected by the presence of sodium nitrate, magnesium nitrate, ammonium sulfate, nickel nitrate, or cadmium nitrate, but is affected by lead nitrate, ammonium carbonate, and nitrous acid.

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