

RAPID VOLUMETRIC METHOD FOR THE DETERMINATION OF NITROGEN IN NITRIDIZED STEELS

By

L. ERDEY and L. KÁPLÁR

Department for General and Analytical Chemistry, Technical University, Budapest

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Nitridizing, the enrichment of the surface of steels with nitrogen is widely used to increase the resistance of workpieces to abrasion and seizing, and to increase the fatigue limit thereof. Nitridizing can be performed by heating in ammonia atmosphere. Heat-treated and surface-finished pieces are heated in a closed electric furnace to 500—600°C in ammonia atmosphere and maintained at this temperature for a period of time necessary to obtain the required layer thickness. Since 1960 also the salt-bath method has been used. This procedure was developed by the firm Degussa (GFR) in the fifties under the name "Soft-Nitridizing Procedure" (Weichnitrier-Verfahren).

The process-control of nitridizing is made in most cases by mechanical methods and only partly by chemical methods. First of all surface hardness and thickness of the nitridized layer are determined. The latter can be estimated on the basis of studying the microstructure or the change of hardness with the distance from the surface. Finally, also the nitride-nitrogen is determined in industrial laboratories. For this determination Kjeldahl's method is specified in the Hungarian Standard MNOSZ 19840—54.

According to this standard metal chips are dissolved in sulphuric acid, while nitride nitrogen is transformed quantitatively into ammonium sulphate. Ammonia is liberated with alkali in a Kjeldahl flask, distilled off, and absorbed in a known excess of acid standard solution. Excess acid is then back-titrated with alkali standard solution. The nitrogen content of the steel can be calculated from the difference. A blank test is also made in order to correct for the possible ammonia content of the chemicals used.

Owing to the known drawbacks of the Kjeldahl method (fragile equipment, high time consumption, several sources of error etc.) it is not favoured in the case of industrial serial analyses.

There arose a reasonable demand on behalf of industrial chemists for a reliable, simple and rapid method to the determination of nitride nitrogen in steels without distillation, which also enables the surface of steels to be analysed within 0.1—0.01 mm layers at an adequate accuracy with the purpose of following and controlling the nitridizing process by chemical means.

The authors of the present paper found the volumetric method developed earlier for the determination of ammonia with sodium tetraphenyl borate to be best for performing the above task [1]. Sodium tetraphenyl borate is readily soluble in water while its potassium and ammonium analogues form precipitates in water or alcohol. Sodium tetraphenyl borate is a very sensitive and selective reagent for ammonium and potassium ions [2, 3].

The basis for the quantitative determination is that ammonium and potassium tetraphenyl borate precipitated in water are soluble in acetone while silver tetraphenyl borate is insoluble both in water and acetone. Hence in the solution of potassium or ammonium tetraphenyl borate in acetone the tetraphenyl borate anion can be titrated with silver nitrate standard solution. The redox indicator Variamine Blue (4-amino-4'-methoxy diphenylamino-hydrochloride) can be used for the sensitive detection of the end-point of titration [4]. No expensive and special glass equipment and no distillation is needed to the determinations. The method is rapid, satisfactorily accurate and suited to routine analyses. The volumetric determination of ammonia with tetraphenyl borate is disturbed by potassium, rubidium, cesium, silver and mercury(II) ions which also form precipitate with the reagent. Working in solutions of dilute mineral acids, cobalt, nickel, manganese, copper(II), aluminium, iron(III), sulphate and phosphate ions do not interfere with the determination. The precipitate is readily filterable. A further advantage of this method is that it is not sensitive to small changes in the pH. The determinations are best made at pH 3—4.

Experimental

Reagents

1. 1 : 4 diluted sulphuric acid solution.
2. 20% sodium hydroxide solution.
3. 20% acetic acid solution.
4. Acetone.
5. 0.6% sodium tetraphenyl borate solution.

Preparation: Dissolve 0.6 g of the solid reagent in 60 ml distilled water, shake the solution with some (5—6 g) a.g. water-free aluminium oxide and filtrate after a short time of standing. Fill up the filtrate to 100 ml with water. The solution stored in a dark bottle at 19—25°C remains unchanged for about 2 months.

6. 1% Variamine Blue indicator solution. For its preparation see reference [5].
7. 0.05 M silver nitrate standard solution.
8. Wash liquor: water saturated with ammonium tetraphenyl borate.

Procedure

Weigh 0.2—0.5 g of the chips of the nitridized steel, transfer into a 200 ml beaker and pour 25 ml 1 : 4 diluted sulphuric acid on it. Warm the beaker covered with a watch-glass on a steam bath until the steel is dissolved. Fuse the undissolved residue after filtration, washing and drying, dissolve it in water acidified with sulphuric acid and add to the original solution. Adjust the pH to about 3.6 with 20% sodium hydroxide or acetic acid solution using methyl orange as indicator. Precipitate ammonium tetraphenyl borate with 20 ml 0.6% solution of sodium tetraphenyl borate. Filtrate the precipitate on a 9 cm diameter analytical filter paper and wash with 2 × 5 ml saturated ammonium tetraphenyl borate wash liquor. Place the filter paper with the precipitate into the beaker in which the precipitation was effected. Pour onto the precipitate 10 ml acetone so that it flows down the side of the beaker in small portions in order to dissolve adhering precipitate particles. After adding 2 ml 20% acetic acid solution open the filter paper and shake it to promote complete dissolution of the precipitate. After adding 3 drops of 1% solution of Variamine Blue acetate titrate with 0.05 M (if necessary, 0.1 M) silver nitrate standard solution until the appearance of violet colour, under vigorous stirring, adding the titrant in small portions. Take care not to pour the titrant on the filter paper.

Carry out a blank test with the reagents and take this into account in calculating the results.

1 ml of 0.05 M silver nitrate solution corresponds to 0.7004 mg nitrogen.

Results

The method described has first been tried on a known ammonium compound, and the official MNOSZ method was used for checking. The results are given in Tables 1 and 2. Then the nitrogen content of nitridized steels was

Table 1

Determination of the nitrogen content of analytical grade iron(III) ammonium sulphate according to the MNOSZ specification

$\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ taken, mg	0.01 N H_2SO_4 in receiver, ml	Consumed 0.01 M NaOH, ml	N content found, mg	Mean mg	Calculated N content, mg	Deviation mg resp. %
278.4	10.26	4.77	7.69	7.66	8.08	-0.42 mg
		4.90	7.50			
		4.71	7.77			
		4.83	7.60			
		4.80	7.64			
		4.73	7.74			
						-5.2%

Table 2

Determination of the nitrogen content of analytical grade iron(III) ammonium sulphate by the method using tetraphenyl borate

$\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ taken, mg	Consumed 0.05 M AgNO_3 , ml	N content found mg	Mean mg	N content calculated	Deviation
278.4	11.53	8.07	8.29	8.08	+0.21 mg +2.5%
	12.20	8.54			
	11.31	7.92			
	11.90	8.33			
	12.30	8.51			
	11.84	8.29			

Table 3

Determination of the nitrogen content of DAMW-steel according to the MNOSZ specification

Weight of sample, mg	0.01 N H_2SO_4 in receiver ml	Consumed 0.01 NaOH, ml	M N content found %	Mean %	N content given, %	Deviation %
193.9	10.26	9.96	0.011	0.010	0.011	-9.0
211.1	10.26	9.81	0.010			
277.4	10.26	9.78	0.009			

Table 4

Determination of the nitrogen content of DAMW-steel by the method using sodium tetraphenyl borate

Weight of sample, mg	Consumed 0.05 M AgNO_3 , ml	N content found %	Mean %	N content given %	Deviation %
183.0	2.60	0.010	0.012	0.011	+9.0
194.8	3.34	0.012			
203.7	4.20	0.014			

determined according to the MNOSZ specifications (see Table 3) and by the method using tetraphenyl borate (Table 4). Table 5 compiles the results of the parallel analysis of various steel samples.

A series of measurements were made on six samples taken from every 0.1 mm layer of the workpiece, going from the surface inwards. The nitrogen

Table 5

Results of analysis of industrial nitridized steel samples

Symbol of sample	Nitrogen content, %	
	by MNOSZ method	by NaTFB method
1	0.34	0.36
2	0.06	0.08
51/1	0.44	0.48
51/2	0.045	0.048
Cone 1	0.81	0.83
Cone 2	0.40	0.41
Cone 3	0.31	0.34

content could be estimated only in the case of the three upper layers, although nitrogen could be detected in the lower layers by means of sodium tetraphenyl borate reagent.

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Summary

A rapid volumetric method has been elaborated for the determination of nitrogen in nitridized steels by means of tetraphenyl borate. Ammonium tetraphenyl borate precipitated in weakly acid medium was dissolved in acetone after washing and filtration and titrated with silver nitrate standard solution at a pH of about 3.6, in the presence of Variamine Blue as indicator. The method proved to be applicable to rapid analyses in industrial control laboratories.

References

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Prof. Dr. László ERDEY }
 Dr. László KÁPLÁR } Budapest XI., Gellért tér 4, Hungary