NOTES

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Gas Chromatographic Determination of Nitrogen in Metals by Means of Inert Gas Fusion Using Silicon

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Nitrogen in metals has been determined by means of chemical distillation which is a modification of the Kjeldahl method.[1,2] A vacuum fusion method and inert gas fusion method each making use of a platinum bath have also recently come into use. The results obtained by these methods agree with those obtained by the Kjeldahl method.[3,4]

This paper deals with the determination of nitrogen by means of inert gas fusion. We found that when a metal or alloy is melted in a graphite crucible in the presence of silicon, nitrogen and oxygen contained in the metal or alloy are completely set free. The molten product passes into the graphite crucible. Utilizing this fact a new method for the determination of nitrogen was worked out. This method is much simpler than the Kjeldahl method.

A tin capsule containing the sample (10—80 mg) and silicon (100—300 mg) was put in a graphite crucible. The graphite crucible was heated in a stream of argon up to 1900°C by means of a high frequency induction furnace. In less than a minute the molten product passed into the crucible. All of the gases contained in the sample were liberated. The gases were then passed through a column (length=70 cm, inner diameter=0.4 cm), filled with activated charcoal and kept at −20°C, for 3 min. The gases absorbed by activated charcoal were liberated by heating the column up to 140°C, and the amount of liberated gases was determined by means of gas chromatography. The amount of nitrogen was calculated by means of the formula

$$m = A\frac{a-b}{w} \times 100,$$

where m=nitrogen in wt %, A=constant, a=chromatographic area in cm^2, b=chromatographic area in blank test in cm^2, w=weight of sample in gram.

The constant A denotes the weight of nitrogen per square centimeter of chromatographic area. It has the value 1.5 μg per cm^2. The results are shown in Fig. 1. For the construction of the figure, the procedure given in a previous paper was used.[5] Linearity holds up to 5 μg of nitrogen. Deviation from linearity takes place for the values of nitrogen higher than this.

Degassed graphite crucibles were used in the experiment. Degassing was carried out by heating

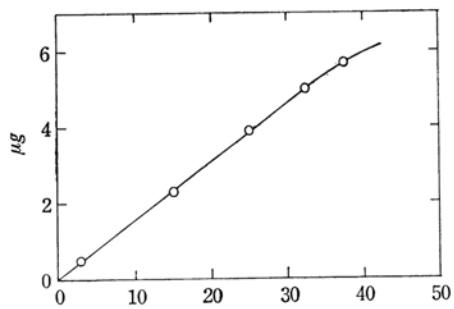

Fig. 1. Relation between the weight of nitrogen and gas chromatographic area.

TABLE 1. BLANK TEST OF GRAPHITE CRUCIBLE

Grade of crucible	Weight in μg	
	Nitrogen	Oxygen
Reactor	0.25	0.14
Spectroscopic	0.80	0.32

1) B. A. Generozov, *Zavodskaya Lab.*, **3**, 314 (1947).

2) National Academy of Sciences, "Report of the Panel on Analytical Problems in Refractory Metals," Rept. MAB-154-M(1), Vol. 11 (1959), p. 17.

3) V. A. Fassel, F. M. Evens and C. C. Hill, *Anal. Chem.*, **36**, 2115 (1964).

4) B. D. Holt and H. T. Goodspeed, *ibid.*, **35**, 1510 (1963).

5) J. Kashima and T. Yamazaki, This Bulletin, **39**, 1448 (1966).

TABLE 2. NITROGEN CONTENT OF PURE IRON PREPARED BY VARIOUS METHODS

Preparation of iron	No. of determinations	Nitrogen, wt%		Standard deviations %
		Inert gas fusion	Kjeldahl method	
Iron, melted by arc, melted for the second time in a vacuum furnace	4	0.0008_8	0.0009	0.0001_0
Iron, melted by arc	4	0.0035_5	0.0035	0.00009_6
Iron, open hearth	5	0.0106_0	0.0106	0.0001_3

a crucible containing 100 mg of silicon at 1900°C for 3 min in a stream of argon. Most of the gases were eliminated by this treatment. The treatment was repeated. The amounts of nitrogen and oxygen liberated by the second treatment were determined by means of gas chromatography and were found to be negligibly small. A degassed graphite crucible could be use three times for the determination of nitrogen. The results are given in Table 1.

As an illustration, the results of the determination of nitrogen in pure iron are given in Table 2. The values obtained coincide with those obtained by means of the Kjeldahl method. The results obtained from other metals are summarized in Table 3.

TABLE 3. NITROGEN CONTENT IN METALS

Metals	No. of determinations	Nitrogen, wt %	Avarage deviation %
Stainless steel (25Cr12Ni)	5	0.0522	±0.003
Nitrogen-doped tungsten (wire)	4	0.0068	0.0008
Nitrogen-doped molybdenum (wire)	3	0.0215	0.002
Pure silicon (on market)	4	0.00043	0.00005
Silicon (on market)	4	0.0010	0.0002