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# The Routine Determination of Nitrogen in Cast Iron by the Chemical Distillation and Inert Gas Fusion Methods

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Although the chemical distillation method is generally employed for the determination of nitrogen in metals, it has been found that this method involves some difficulties in cast iron and pig iron samples. This paper will, therefore, describe new, repreoducible methods for the determination of nitrogen in chilled cast iron. They are the inert gas fusion and the chemical distillation methods. The most suitable sample for obtaining almost the same results with regard to ordinary cast iron by both methods was found to be a thin plate chilled by a copper mold. The accuracy of both methods was ±0.0004% when thin-plate samples containing from 0.0030 to 0.010% nitrogen were used.

The determination of nitrogen in cast iron and pig iron has acquired increasing importance in recent metallurgy. Nitrogen—one of the slightly-alloying elements in these metals—affects their mechanical properties. Therefore, it is necessary that the nitrogen contents of 0.001 to 0.01% in commercial cast irons be determined accurately by using the adequate analytical methods.

The standard method for the determination of nitrogen in metals is the chemical distillation method. This method is described in JIS G 1228 for the determination of nitrogen in steels and cast irons. The vacuum fusion method may also be used in the determination of hydrogen, oxygen and nitrogen in metals. However, in this method, the residual gas is assumed to be all the nitrogen contained in the metals, and it cannot be utilized as a standard method, for the nitrogen is not completely evolved. Therefore, the vacuum fusion and chemical distillation methods of obtaining the nitrogen contents have previously been described[1-2]; these methods involve the simultaneous determination of hydrogen, oxygen and nitrogen, as well as the determination of nitrogen alone.

Recently, in order to measure the evolved nitrogen in the vacuum fusion and the inert gas fusion methods, gas chromatography was attempted,[3-5] and some authors have described[6-8] how colorimetry can be used to find a trace of nitrogen in metals.

With regard to low carbon steels and alloy steels (with the exception of chromium and manganese steels), investigators have different opinions; one of them[9,10] considers that lower nitrogen value would be obtained in the vacuum fusion method, while others[1,2] consider that the same results would be obtained in both methods. In order to determine accurately the amount of nitrogen, the stable nitrides (e. g., CrN, $Si_3N_4$ and TiN) must be decomposed before analysis by suitable methods (for instance, solidifying the liquid metals quickly).

With regard to stainless steels, carbon steels and some cast irons, the results obtained by these methods have been discussed in a recent paper.[5] The nitrogen in cast iron is determined accurately in two ways. One of them is the use of a thin plate chilled from liquid metal by a copper mold in the inert gas fusion method; the other is the use of a powder prepared by crushing the chilled sample in the chemical distillation method.

## Experimental

**Materials.**—All the cast iron samples, whose chemical compositions are shown in Table I, were prepared by means of several kinds of molds (shown in Table II). The samples were prepared as follows: (1) preparing a specimen 100 mm. in height from a chilled ingot 120 mm. in height, (2) abrasing its surface, (3) washing it in carbon tetrachloride, (4) crushing it in 9—64 mesh (until each sample is about 0.3—1.0 g.) for the inert gas fusion method, and crushing it in 100—200 mesh for the chemical distillation method, by using a mortar and a pestle of high-manganese cast steel.

*Standard Sodium Hydroxide Solution.*—Granular sodium

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[1] Third Report of the Oxygen Sub-Committee, *J. Iron and Steel Inst.*, **143**, 295 (1941).

[2] Fourth Report of the Oxygen Sub-Committee, ibid., **148**. 302 (1943).

[3] A. Fuchs, H. Reinhard, J. Niebuhr and R. Beck, *Arch Eisenhuttenw.*, **34**, 361 (1963).

[4] F. M. Evens and V. A. Fassel, *Anal. Chem.*, **35**, 1444 (1963).

[5] J. Kashima and T. Yamazaki, *Rept. Castings Research Lab., Waseda Univ.* (*Tokyo*), **14**, 33 (1963).

[6] H. F. Beeghly, *Ind. Eng. Chem., Anal. Ed.*, **14**, 137 (1962).

[7] J. Epotein, *Anal. Chem.*, **19**, 272 (1947).

[8] J. P. Riley, *Anal. Chim. Acta.*, **9**, 575 (1953).

[9] M. Ihida, *Japan Analyst*, **8**, 786 (1959).

[10] K. Furuya and H. Kamada, ibid., **14**, 336 (1965).

TABLE I. CHEMICAL COMPOSITION OF WHITE CAST IRON

| Designation | Element, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Al | Cr |
| A01, 02, 05, 08, 10 | 3.04—3.64 | 1.60—1.94 | 0.41—0.95 | 0.045—0.052 | 0.025—0.090 | 0.03—0.04 | 0.03—0.04 |
| A03, 04, 06, 09 | 2.94—3.24 | 2.20—3.52 | 0.27—1.20 | 0.041—0.048 | 0.041—0.080 | 0.03—0.05 | 0.01—0.15 0.15 |
| A07 | 0.66 | 13.72 | 0.43 | 0.029 | 0.034 | | |

TABLE II. PREPARATION OF CHILLED SAMPLE

| Sample designation | Form | Size | Mold |
|---|---|---|---|
| A01, 02 | bar | 0.7 cm. in dia. × 12 cm. length | cast iron |
| A05 | bar | 1.0 cm. in dia. × 12 cm. length | cast iron |
| A06 | bar | 0.6 sq. cm. × 60 cm. length | $CO_2$-process |
| A09 | plate | 1.0 cm. thick. × 5 cm. width × 10 cm. length | cast iron |
| A08 | plate | 0.2 cm. thick. × 2+3 cm. wid. × 10 cm. length | copper |
| A03, 04, 07, 10 | sheet | 0.14 cm. thick. × 4 cm. wid. × 10 cm. length | direct rolling |

hydroxide of analytical grade was dissolved in pure water obtained by passing water through an ion-exchange resin column; it was diluted to a concentration of 1/400 N. This solution was stored in a 1000-ml. polyethylene vessel connected to a Metrohm piston burette, Model E 274. The concentration of this solution was accurately determined by titrating it with benzoic acid. To reduce the nitrogen blank value, sulfuric acid and potassium sulfate of analytical grade were used; the other reagents, of the first grade, were used without purification.

**Apparatus.**—A Shimadzu high-frequency titrator, Model HF-1, was employed to determine the end-point. For the determination of the amount of nitrogen gas, a Yanagimoto Model GCG-100 gas chromatograph, an Ohkura Model AM 101 d. c. amplifier, and a Minneapolis-Honeywell (U. S. A.) Model SY-153 recorder were used. As the furnace used in the inert gas fusion, a Kokusai Denki Model HFT-7a high-frequency combustion furnace was adopted.

**Procedure.**—*The Chemical Distillation Method.*—The apparatus was that of JIS G 1228, the measurements were carried out conductometrically by means of a commercially-available H-F titrator.

The sample, approximately 5.0 g., was slowly dissolved in 100 ml. of dilute hydrochloric acid (1 : 1) in a 500 ml. round-bottom flask with a condenser, while the solution was being heated by an electric heater for at least 60 min. To determine the acid-soluble nitrogen, the solution was separated from the residue by means of a centrifuger (at 2500 r.p.m.).

The solution was then transferred to a distillating flask containing 75 ml. of a 12 N sodium hydroxide solution and 200 ml. of pure water; steam distillation was then carried out. The distillate was collected in a 100 ml. receiving flask containing 10 ml. of 1/10 N sulfuric acid. The distillation was continued until the distillate reached about 95 ml.; this process took about 20 min. The distillate was then transferred to a 100 ml. measuring flask and diluted to the mark with pure water. The amount of acid-soluble nitrogen was obtained by titrating the excess sulfuric acid with a 1/400 N standard sodium hydroxide solution; the total nitrogen content was also calculated. Actually, a 20 ml. portion of this solution was transferred to the cell of a commercially-available high-frequency titrator and was titrated with the standard sodium hydroxide solution. The residue separated by a centrifuger was treated with a mixture of 10 ml. of concentrated sulfuric acid and 5 g. of potassium sulfate at 350°C for about 2 hr., in order to decompose the acid-insoluble nitrides completely. In this way, the acid-soluble and the acid-insoluble nitrogen contents were determined.

*The Inert Gas Fusion Method.*—This method has been described in recent papers.[5,12] It is capable of measuring immediately the nitrogen content from the chromatogram obtained by the gas chromatographic separation in the gases evolved by the inert gas fusion. The experiments were carried out in the following ways: (1) the argon gas flow was at a rate of 50 ml./min.; (2) in the gas chromatograph experiment, the bridge current of the thermal conductivity cell was 150 mamp., the potential at the full scale of the recorder was 0.5 mV., and the temperature of the thermostat chamber was 115°C; (3) the gas chromatographic column was a copper tube (1.5 m. long and 4 mm. in dia) packed with Molecular Sieve 5A, and (4) the capacity of the gas sampling cell was 1.0 ml.

Many data concerning nitrogen were obtained from the observations based on the time-concentration curve described in a previous paper.[5] This curve was obtained by introducing 1.0 ml. portions of the argon stream into the gas chromatograph at intervals of 0.6 to 1.0 min.

## Results and Discussion

The nitrogen contents of many chilled cast iron samples were determined. The plate samples prepared by the copper-chilled method, shown in Fig. 1, are suitable for the nitrogen analysis of ordinary cast iron; when they are used, the results obtained by the fusion method are almost exactly

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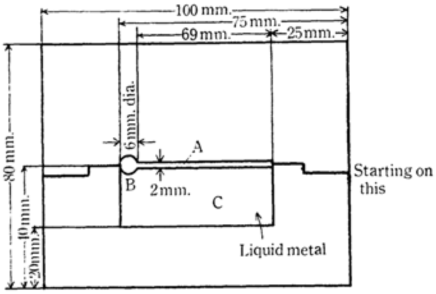
11) J. Kashima and M. Kubota, *J. Spectro. Soc. Japan* (*Bunko Kenkyu*), **13**, 83 (1965).

12) J. Kashima and T. Yamazaki, *Japan Analyst*, **12**, 347 (1962).

Table III. Nitrogen contents in cast iron

| Designation | Inert gas fusion method: No. of determinations | Nitrogen % | Deviation from mean % | Chemical distillation method: No. of determinations | Nitrogen, % sol. | Nitrogen, % insol. | Nitrogen, % total | Deviation from mean % | Sample size |
|---|---|---|---|---|---|---|---|---|---|
| A01 | 5 | 0.0081 | ±0.0006 | 3 | 0.0086 | 0.0002 ~ 0.0003 | 0.0088 | ±0.0002 | bar |
| A02 | 4 | 0.0042 | 0.0005 | 3 | 0.0070 |  | 0.0072 | 0.0004 |  |
| A05 | 4 | 0.0058 | 0.0005 | 3 | 0.0073 |  | 0.0076 | 0.0003 |  |
| A06 | 3 | 0.0016 | 0.0001 | 3 | 0.0018 |  | 0.0020 | 0.0003 |  |
| A03 | 4 | 0.0030 | 0.0003 | 3 | 0.0033 |  | 0.0035 | 0.0002 | plate |
| A04 | 4 | 0.0030 | 0.0004 | 4 | 0.0034 |  | 0.0036 | 0.0001 |  |
| A07 | 2 | 0.0086 | 0.0004 | 2 | 0.0075 | 0.0010 | 0.0085 | 0.0002 |  |
| A08* | 4 | 0.0100 | 0.0003 | 3 | 0.0100 | 0.0002 ~ 0.0003 | 0.0102 | 0.0005 |  |
| A09 | 4 | 0.0085 | 0.0003 | 3 | 0.0083 |  | 0.0085 | 0.0002 |  |
| A10 | 4 | 0.0051 | 0.0003 | 3 | 0.0056 |  | 0.0059 | 0.0003 |  |

* The portion of plate chill sample obtained by split copper mold.



A plane figure

Fig. 1. Copper chill for sampling liquid metal.
A Plate sample with 2 mm. thickness × 44 mm. width × 10 cm. length
B Bar sample
C Pouring basin with 20 mm. curvature

Table IV. Nitrogen content obtained by the concentration—injection method*

| Designation | No. of determinations | Nitrogen % | Deviation from mean % |
|---|---|---|---|
| A02 | 6 | 0.0043 | 0.0006 |
| A08 | 5 | 0.0102 | 0.0003 |
| A09 | 3 | 0.0087 | 0.0001 |

* Application of this method does pricisely proved on the analytical method for oxygen in metals.

the same as those obtained by the solution method. The data are shown in Tables III and IV. The nitrogen contents obtained by the inert gas fusion method are somewhat lower, as is also shown in the tables. The plate samples, which show a deviation from the average value of below ±0.0004%, were preferable to the bar samples, which show a deviation from the average value of ±0.0004% in the chemical distillation method and a deviation from the average value of ±0.0006% in the inert gas fusion method. Therefore, the sample which can be used for both the methods is the plate form of the A08 sample, which is prepared by the split copper mold shown in Fig. 1.

The cast iron samples generally used for the chemical distillation method were of gray cast iron with a matrix of eutectic graphite cells growing about a cluster of kish graphite, for this sample can easily be treated by the machinery and dissolved in acid. The nitride contents in a sample are determined separately, an acid-soluble nitrogen and an acid-insoluble nitrogen. Some remarks on the determination of the acid-insoluble nitrogen demonstrated in a recent paper[5] are given below:

1) The blank value for nitrogen found in the decomposition of insoluble nitride is very high, about 50 $\mu$g., while the nitrogen contained in the sample is 50—200 $\mu$g.

2) The nitrogen contents of the sample containing insoluble nitrides show a deviation from the average value of ±0.0009%; this value is 2—9 times that found in the case of soluble nitrides obtained by the chemical distillation method.

3) It is necessary to separate graphite from the solution before steam distillation, because the graphite residue prevents the evolution of ammonia to some extent.

4) Some investigators[13,14] have had the opinion that the amount of acid-insoluble nitrogen is

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[13] Y. Ueda, *J. Japan Foundrymens Soc.* (*Imono*), **33**, 776 (1961).

[14] B. B. Bach, J. V. Dawson and I. W. L. Smith, *J. Iron and Steel Inst.*, **176**, 257 (1954).

changed by the sampling methods or by the annealing treatment.

This must be taken into account before executing the conventional chemical distillation. However, if the total nitrogen content of the cast iron can be established by the simple chemical distillation procedure, without treating the acid-insoluble residue, this procedure may be most desirable. For this reason, the authors have studied this problem, particularly in connection with white cast irons.

The acid-soluble powdered samples were prepared by crushing solid white cast iron (acid-proof), but their acid-dissolution-time was not short, even though the nitrides included were almost acid-soluble compared with those of the gray cast iron. However, the deviation of the nitrogen content of each sample is small in white cast iron, as Table III shows.

In this experiment, the calibration for the nitrogen content was performed by the following procedure: the relation between the concentration and the chromatogram area was obtained by introducing into the 1.0-ml. samping cell of the gas chromatograph manometrically-measured standard nitrogen in liter glass container.

The sample chilled by the copper mold is suitable for nitrogen analysis or for spectroscopic analysis.[11) This may be due to the fact that nitrogen is dissolved in cast iron. If refractory nitrides are included in the sample, it seems impossible to decompose the nitrides perfectly by the inert gas fusion method, by which the sample is quickly heated to 2000°C. Although it may be difficult to decompose the refractory nitrides formed in some cast iron by ordinary methods, they may be decomposed by the inert gas fusion method using a platinum bath.