A UNITED STATES DEPARTMENT OF COMMERCE PUBLICATION

NBS SPECIAL PUBLICATION 260-26

Standard Reference Materials:

NATIONAL BUREAU OF STANDARDS-U.S. STEEL CORPORATION JOINT PROGRAM FOR DETERMINING OXYGEN AND NITROGEN IN STEEL

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

UNITED STATES DEPARTMENT OF COMMERCE • Maurice H. Stans, *Secretary*
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, *Director*

Standard Reference Materials:

National Bureau of Standards-U. S. Steel Corporation Joint Program for Determining Oxygen and Nitrogen in Steel

J. F. Martin

Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

National Bureau of Standards Special Publication 260-26

Nat. Bur. Stand. (U.S.), Spec. Publ. 260-26, 40 pages, (February 1971)
CODEN: XNBSA

Issued February 1971

Library of Congress Catalog Card Number: 79-610184

PREFACE

Standard Reference Materials (SRMs) as defined by the National Bureau of Standards are "well-characterized materials, produced in quantity, that calibrate a measurement system to assure compatability of measurement in the nation." SRMs are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. In many industries traceability of their quality control process to the national measurement system is carried out through the mechanism and use of SRMs. For many of the nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRMs produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on all phases of the preparation, measurement, and certification of NBS-SRMs. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. It is also hoped that these papers will provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

Office of Standard Reference Materials
National Bureau of Standards
Washington, D. C. 20234

J. Paul Cali, Chief
Office of Standard Reference Materials

OTHER NBS PUBLICATIONS IN THIS SERIES

NBS Spec. Publ. 260, Catalog of Standard Reference Materials, July 1970. 75 cents.* (Supersedes NBS Misc. Publ. 260, January 1968 and NBS Misc. Publ. 241, March 1962.)

NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, June 1964. 30 cents.*

NBS Misc. Publ. 260-2, Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards, October 1964. 35 cents.*

NBS Misc. Publ. 260-3, Standard Reference Materials: Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard, October 1964. 20 cents.*

NBS Misc. Publ. 260-4, Standard Reference Materials: Sources of Information on Standard Reference Materials, February 1965. 20 cents.*

NBS Misc. Publ. 260-5, Standard Reference Materials: Accuracy of Solution X-Ray Spectrometric Analysis of Copper-Base Alloys, March 1965. 25 cents.*

NBS Misc. Publ. 260-6, Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, July 1965. 45 cents.*

NBS Misc. Publ. 260-7, Standard Reference Materials: Methods for the Chemical Analysis of NBS Copper-Base Spectrochemical Standards, October 1965. 60 cents.*

NBS Misc. Publ. 260-8, Standard Reference Materials: Analysis of Uranium Concentrates at the National Bureau of Standards, December 1965. 60 cents.*

NBS Misc. Publ. 260-9, Standard Reference Materials: Half Lives of Materials Used in the Preparation of Standard Reference Materials of Nineteen Radioactive Nuclides Issued by the National Bureau of Standards, November 1965. 15 cents.*

NBS Misc. Publ. 260-10, Standard Reference Materials: Homogeneity Characterization on NBS Spectrometric Standards II: Cartridge Brass and Low-Alloy Steel, December 1965. 30 cents.*

NBS Misc. Publ. 260-11, Standard Reference Materials: Viscosity of a Standard Lead-Silica Glass, November 1966. 25 cents.*

NBS Misc. Publ. 260-12, Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards III: White Cast Iron and Stainless Steel Powder Compact, September 1966. 20 cents.*

NBS Misc. Publ. 260-13, Standard Reference Materials: Mössbauer Spectroscopy Standard for the Chemical Shift of Iron Compounds, July 1967. 40 cents.*

NBS Misc. Publ. 260-14, Standard Reference Materials: Determination of Oxygen in Ferrous Materials -- SRM 1090, 1091, and 1092, September 1966. 30 cents.*

NBS Misc. Publ. 260-15, Standard Reference Materials: Recommended Method of Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, June 1967. 20 cents.*

NBS Spec. Publ. 260-16, Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards IV: Preparation and Microprobe Characterization of W-20% Mo Alloy Fabricated by Powder Metallurgical Methods, January 1969. 35 cents.*

NBS Spec. Publ. 260-17, Standard Reference Materials: Boric Acid; Isotopic and Assay Standard Reference Materials, February 1970. 65 cents.*

NBS Spec. Publ. 260-18, Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A", November 1969. 50 cents.*

NBS Spec. Publ. 260-19, Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressure of Gold (Certification of Standard Reference Material 745), January 1970. 30 cents.*

NBS Spec. Publ. 260-20, Standard Reference Materials: Preparation and Analysis of Trace Element Glass Standards. (In preparation)

NBS Spec. Publ. 260-21, Standard Reference Materials: Vapor Pressure, Silver and Cadmium. (In preparation)

NBS Spec. Publ. 260-22, Standard Reference Materials: Homogeneity Characterization of Fe-3Si Alloy. (In press)

NBS Spec. Publ. 260-23, Standard Reference Materials: Viscosity of a Standard Borosilicate Glass. December 1970. 25 cents.*

NBS Spec. Publ. 260-24, Standard Reference Materials: Comparison of Redox Standards. (In preparation)

NBS Spec. Publ. 260-25, Standard Reference Materials: A Standard Reference Material Containing Nominally Four Percent Austenite. (In press)

*Send orders with remittance to: Superintendent of Documents, U. S. Government Printing Office, Washington, D.C. 20402. Remittance from foreign countries should include an additional one-fourth of the purchase price for postage.

TABLE OF CONTENTS

		PAGE
1.	INTRODUCTION	2
2.	MATERIALS AND EXPERIMENTAL WORK	3
	A. Analyzers	3
	1. Vacuum-Fusion Analyzer	3
	2. Single-Crucible, Helium-Fusion Analyzer	4
	3. Nitrogen Analyzer	5
	4. Experimental IGF-GC Analyzer	5
	B. Analytical Standards	9
3.	RESULTS AND DISCUSSION	11
	A. Analyzers	11
	1. Vacuum-Fusion Analyzer	11
	2. Single-Crucible, Helium-Fusion Analyzer	11
	3. Nitrogen Analyzer	16
	4. Inert Gas Fusion - Gas Chromatographic Apparatus	16
	B. Standard Reference Material Analysis	20
4.	SUMMARY	25
5.	ACKNOWLEDGMENT	26
6.	REFERENCES	27
	APPENDIX I	29
	APPENDIX II	31

LIST OF TABLES

Table No.		
1.	Operating conditions for inert gas fusion - gas chromatographic system	7
2.	Nitrogen by single-crucible, helium-fusion technique	10
3.	Effect of sample weight on nitrogen recovery (single-crucible, helium-fusion)	13

LIST OF TABLES (con't)

Table No.		PAGE
4.	Effect of various bath materials on nitrogen recovery (single-crucible, helium-fusion) . . .	14
5.	Comparison of nitrogen values obtained with Pt bath and Pt-Sn Bath (single crucible, helium-fusion)	15
6.	Nitrogen values obtained with the single-crucible, helium-fusion technique	16
7.	Nitrogen values on NBS samples obtained with IGF-GC (no bath used)	19
8.	Homogeneity analysis of NBS 1094 (maraging steel) for Oxygen and Nitrogen (single-crucible, helium-fusion)	22
9.	Oxygen values on SRM 1094 obtained with IGF-GC (no bath used)	23

LIST OF FIGURES

Figure No.		
1.	Schematic diagram of single-crucible, helium fusion instrument	4
2.	Flow diagram of inert gas fusion-gas chromatographic apparatus	6
3.	Six-way gas sampling valve	8
4.	The new design of sample changer	18
5.	Sampling scheme for homogeneity testing of SRM 1094	21

STANDARD REFERENCE MATERIALS: NATIONAL BUREAU OF STANDARDS-U. S. STEEL CORPORATION JOINT PROGRAM FOR DETERMINING OXYGEN AND NITROGEN IN STEEL

J. F. Martin*

Because of a need for a method for the rapid, simultaneous determination of small concentrations of oxygen and nitrogen in steel, a joint project under the Industrial Fellowship Program of U. S. Steel and the Research Associate Program of the National Bureau of Standards (NBS) was established. After investigation of various techniques, and analytical apparatus was constructed with excellent sensitivity for both elements. This apparatus consists of an inert gas fusion system coupled to a gas chromatograph. Recommended modifications have been completed on this equipment, and simultaneous determinations of oxygen and nitrogen in steel are presently being made. The detection limit is <1 ppm for both oxygen and nitrogen, and the analysis time is about 5 minutes.

A direct result of this program has been the issuance by NBS of a new Standard Reference Material (SRM), a maraging steel, for oxygen. This SRM has the lowest oxygen concentration (4.5 ppm) of any steel standard yet issued by NBS.

Key words: Inert gas fusion; one ppm of oxygen and nitrogen in steel; Research Associate Program; simultaneous determination of oxygen and nitrogen; Standard Reference Material for oxygen.

* Industrial Fellow, 1968-69. Research Associate Program, National Bureau of Standards. Present address: Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania 14156.

1. INTRODUCTION

Under the Industrial Fellowship Program of U. S. Steel and the Research Associate Program of the National Bureau of Standards (NBS), a joint research project was conducted to develop a rapid instrumental technique for the simultaneous determination of trace amounts (<0.005 percent) of oxygen and nitrogen in all grades of steel. This work was conducted at the Gaithersburg, Maryland, laboratory of the NBS by personnel from U. S. Steel and NBS. In this program the USS Industrial Fellow worked at the laboratories of the NBS from August 15, 1967, through September 30, 1968, on a full-time basis. NBS provided technical supervision and assistance, research instruments, and general supplies. In addition, two manufacturers of gas-analysis equipment provided their analyzers for a limited time.

Although commercial equipment has long been advertised as being applicable to the simultaneous determination of oxygen and nitrogen in steel, non proved adequate. One instrument, reportedly applicable to the simultaneous determination of nitrogen and oxygen, an attachment for another instrument for nitrogen only, and another nitrogen analyzer, however, have recently appeared on the market, and these were evaluated as part of the joint project.

In addition to these three instruments, to obtain more versatility and better sensitivity than are available with commercial systems, an inert carrier gas fusion apparatus was designed and coupled to a gas chromatograph (IGF-GC) for the determination of oxygen (as carbon monoxide) and nitrogen. This apparatus was based in part on those of Dallmann and Fassel [1] and one constructed earlier in the U. S. Steel Applied Research Laboratory. Furnace designs and the single crucible technique were investigated with this equipment. The following is a report of this work.

2. MATERIALS AND EXPERIMENTAL WORK

A. Analyzers

Following are brief descriptions of the various analyzers used.

1. Vacuum-Fusion Analyzer. Gerhardt, et al. [2] developed a technique for the determination of nitrogen in steel with a commercial vacuum-fusion unit. During the analysis of successive steel samples by vacuum fusion, graphite is eroded from the crucible walls. Some of this graphite floats on the surface of the molten bath with the result that the evolution of nitrogen is impeded. In this new technique, a crucible is employed that can be spun and emptied between analyses without breaking the vacuum; thus each sample is analyzed in a clean out-gassed crucible. This method is referred to as the spinning-crucible technique. To increase the fluidity of the melt, a small amount of nickel-cerium alloy is added for each analysis so that the eroded graphite that does form appears as nodules and not as flakes.

The apparatus is equipped with a nondispersive infrared system for measuring oxygen as carbon monoxide and a thermal conductivity cell for measuring nitrogen plus carbon monoxide. Nitrogen is determined by difference. Because cerium reacts strongly with oxygen, only nitrogen can be determined conventionally by this technique. When oxygen is to be determined, cerium, which forms a stable oxide, is not added to the crucible. Successive analyses for nitrogen and then oxygen are not practicable because once cerium is added to the crucible, a small amount is retained after emptying the crucible. An advantage of this instrument is that each analysis may be simulated by use of a variable volume, gas dosing system.

2. Single-Crucible, Helium-Fusion Analyzer. An apparatus developed by Lemm and Koch [3,4] employs fusion in helium rather than in vacuum. The unique feature of this equipment is the use of a new crucible for each determination (single-crucible technique). The basic operation of this analyzer provides for the measurement of oxygen as CO by infrared absorption and nitrogen by gas chromatography, with the output integrated in a continuous flow, Figure 1. The Co is measured first and then oxidized by Schutze reagent to CO_2, which is removed on a molecular sieve column; nitrogen and hydrogen are separated on this column. The latter two gases are determined by thermal conductivity. Results for H_2, CO, and N_2 are displayed on a strip-chart recorder and are presented in digital form. Analysis time for oxygen and nitrogen determined simultaneously is about 3 minutes.

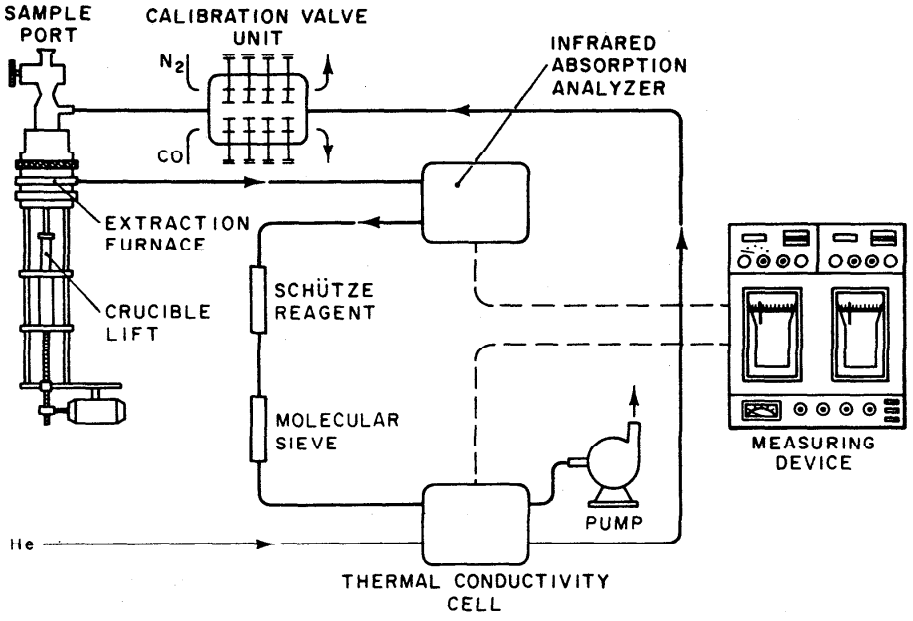

Figure 1. Schematic diagram of single-crucible, helium fusion instrument.

This apparatus has several unique features. A gas dosing valve has been incorporated into the system so that pure CO and N_2 can be admitted to the system both for calibration and for checking the response of the gas analyzers. Further, the furnace section includes certain details not found in other commercial analyzers. These include:

1. An electric elevator for raising and lowering the crucible to facilitate changing of crucibles and to exactly locate the crucible during heating,

2. An electroprogrammer to vary the temperature while the gases are extracted from the sample,

3. A flow controller for directing the carrier gas through the sample entry port, and through the furnace section so that air does not enter the system when crucibles are changed, and

4. Plug-in graphite heating elements.

3. Nitrogen Analyzer. Equipment based on the pulse heating method described by Vasserman and Turovsteva [5] and later used by Goldbeck, et al. [6] is now commercially available. In this equipment a high current (between 300 and 400 amp) is pulsed through the graphite crucible so that temperatures in excess of 2800 °C are attained. The H_2 and CO extracted from the steel in a dynamic stream of helium are oxidized to water and carbon dioxide, respectively, and removed in absorption traps. The nitrogen is then measured by thermal conductivity, and the concentration is presented on a digital voltmeter. A new crucible is used for every determination, and each determination requires 2-1/2 minutes.

4. Experimental IGF-GC Analyzer. The fourth apparatus evaluated was an inert gas (helium) fusion - gas chromatographic (IGF-GC) system designed and constructed at NBS, Figure 2. In this apparatus the sample is fused in a graphite

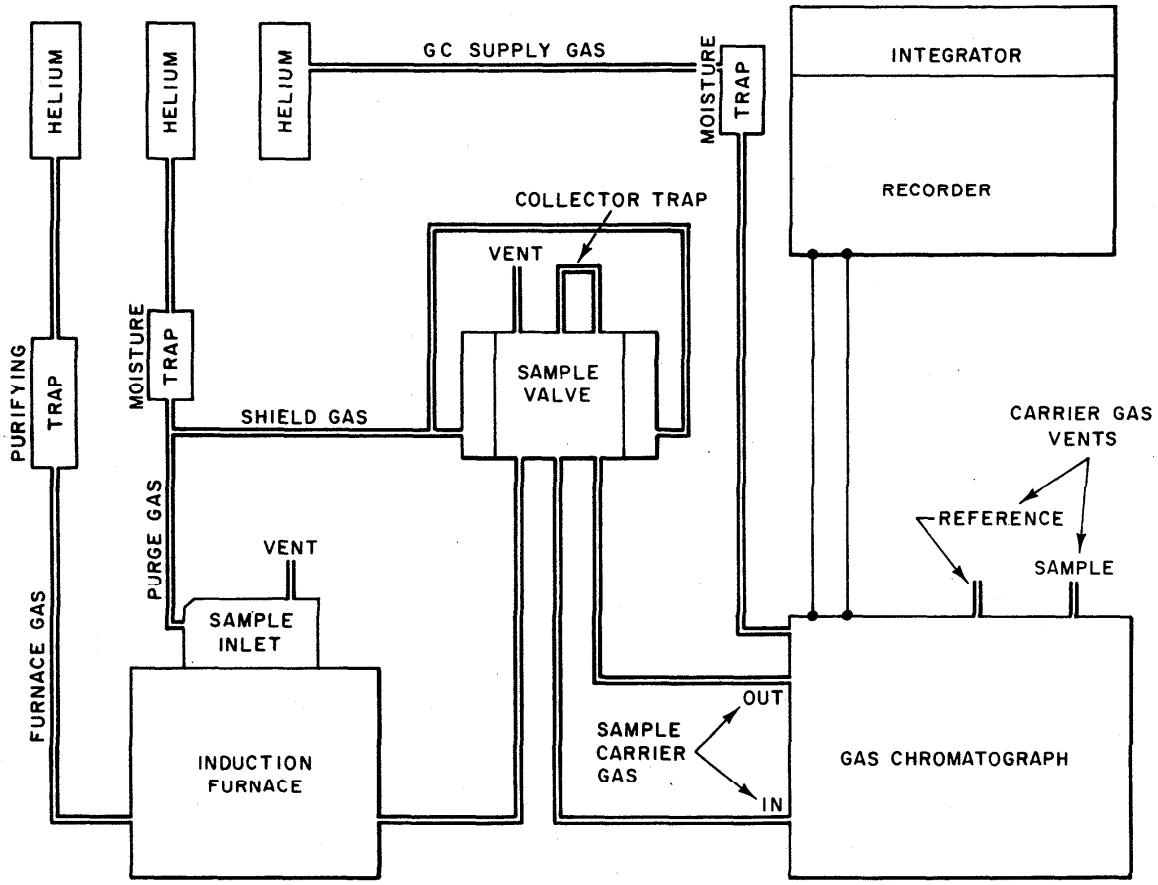

Figure 2. Flow diagram of inert gas fusion-gas chromatographic apparatus.

crucible insulated with graphite powder, both of which are contained in a quartz thimble. Purified helium is passed over the crucible and through the system at a rate of 1.5 liters per minute, Table 1. The crucible assembly is heated inductively, and an operating temperature of 1900 °C is easily maintained. (Toward the end of the program a 10 kw, 450 kHz generator was installed to provide higher temperatures because poor accuracy was obtained for nitrogen due presumably to insufficient power to obtain the high temperatures necessary for the complete decomposition of metal nitrides.)

Table 1. Operating conditions for inert gas fusion - gas chromatographic system.

Inert carrier gas	Helium, 1.5 l/minute
Purification system	1/4-inch-diameter by 20-foot-long copper tube packed with molecular sieve 5A, column temperature -196 °C
Furnace heater	Water-cooled, induction 2.5 kw, 450 kHz
Outgassing temperature	2100 °C
Analysis temperature	1850 to 1950 °C
Collecting loop	Molecular sieve 5A at -196 °C
Chromatograph	Constant temperature, thermistor detector
Chromatographic carrier gas	Helium, tank gage set at 60 psi
Separating column	1/8-inch-diameter by 6-foot-long copper packed with molecular sieve 5A at 50 °C
Detector	Thermal conductivity
Recorder	0 to 1 millivolt, variable chart speed, and response time of 0.75 to 1 second full scale
Integrator	Counting rate 6000/minute full scale

The helium sweeps out the CO, N_2, and H_2 evolved from the molten specimen during fusion. The gas mixture is passed through a special valve (designed and built at NBS and shown schematically in Figure 3) into a collecting loop cooled to -196 °C with liquid nitrogen. The collecting loop or trap is made of stainless steel and is filled with about 5 grams of molecular sieve 5A. The CO and N_2 are adsorbed here during a 3-minute collection period, after

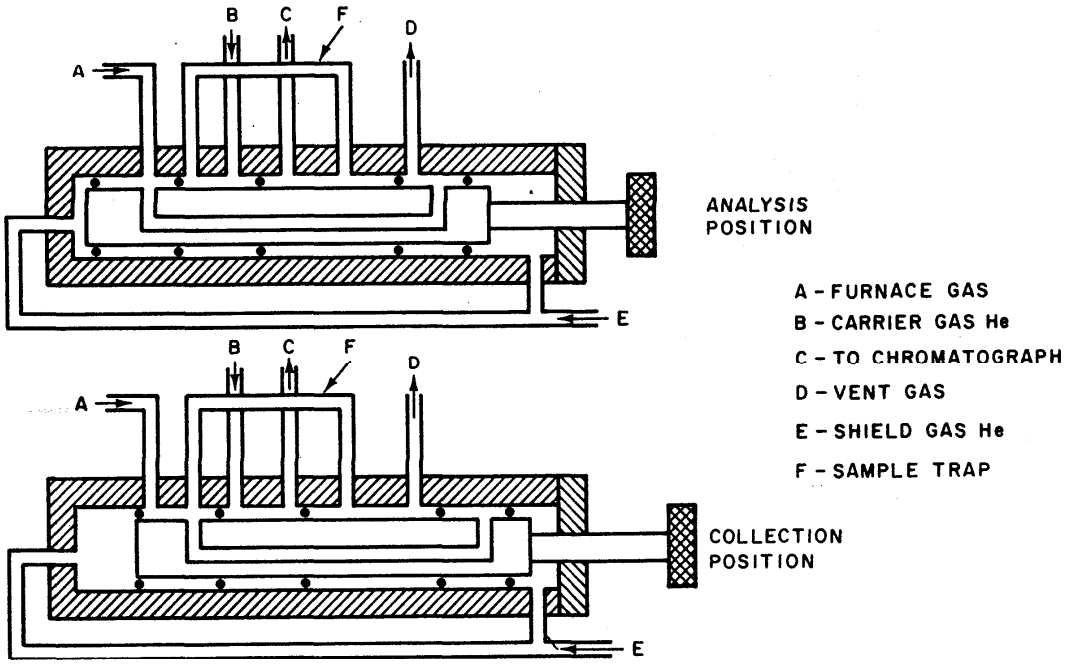

Figure 3. Six-way gas sampling valve.

which a valve is rotated to vent the furnace carrier gas (helium) to the atmosphere and to permit the chromatographic carrier gas (helium) to pass through the collecting loop. Simultaneously, this loop is electrically heated. The CO and N_2 are then desorbed and injected into the chromatograph as a concentrated slug where they are separated on a molecular sieve (5A) column and detected by thermal conductivity.

The output from the cell is recorded on a 1-mv strip-chart recorder. The latter is also connected to an integrator which measures and prints the area under the peaks due to the CO and N_2. The chromatographic apparatus is calibrated by addition of known amounts of pure nitrogen or carbon monoxide either through the furnace section or directly into the collecting loop. No significant difference between the two methods of calibration was obtained.

B. Analytical Standards

To conduct this development work, National Bureau of Standards Standard Reference Materials (SRMs) were used. The oxygen standards, representing iron and two types of steel, are listed in the Certificate of Analysis (Appendix I); these were available in the form of rods. The SRMs for nitrogen, representing a number of different types of iron and steel, are listed in Table 2. Most of these were available only in milled form. For the milled standards, the oxygen values were not recorded because surface cleaning was not practicable. It will be noted that nitrogen values are given in percent and parts per million (ppm). The former has been used for many years because nitrogen values for low-alloy steels usually ranged between 0.005 and 0.02 percent with an estimated precision of 0.001 or 0.002 percent and a similar detection limit. Recently, methods have been developed with a detection limit of 0.0001 percent or 1 ppm and with a precision considerably better than obtainable earlier. For simplicity the ppm unit is now used for steel almost exclusively. Oxygen in steel results are also now expressed in ppm for the same reasons.

Table 2. Nitrogen by single-crucible, helium-fusion technique.

NBS-SRM	Nitrogen					
	Analytical value, ppm			Average ppm	Recommended,[a] ppm	Certified %
3a	84.4	79.4	82.9	82.2	86	
3b	81.1	81.7	90.4	84.0	84	
3b	83.3	83.5	84.3			
3c	45.8	42.5	47.5	45.3	46	
4i	70.7	69.1	71.2	70.3	70	
4j	41.1	41.3	41.3	41.2	37	
5j	79.4	80.1	78.3	78.5		
5j	78.8	76.6	77.8			0.009
5k	111.0	108.0	86.3	102	90	
5L	55.7	58.4	56.8	58.2	58	
5L	54.7	62.4	61.3			
6f	38.4	32.8	32.1	34.4	50	
8i	187.0	176.0	177.0	180		
10g	146.0	142.0	145.0	147		0.018
10g	154.4					0.015
30f	76.1	78.9	75.1	76.7	75	
32e	85.0	88.2	87.2	86.8		0.009
55e	42.5	42.1	43.3	42.6		0.004
72f	102.0	100.0	100.0	101		0.009
101d	222.0	224.0	223.0	223		0.024
125a	42.6	38.2	36.8	38.7		0.002
125a	39.0	38.0	37.9			
129b	132.0	126.0	128.0	129		0.014
163	93.9	77.1	73.1	81.4	91	
343[c]	737.0	732.0	733.0	734.0		0.074
346[c]	4490	4530	4550	4520	4410	

[a]Recommended values form NBS Technical Note 454, July 1968.

[b]This has been shown to be incorrect. A recent recommended value is 0.004 percent.

[c]These samples were available in both chunk and milled form. All other samples were available in milled form only.

3. RESULTS AND DISCUSSION

A. Analyzers

1. Vacuum-Fusion Analyzer. With the vacuum-fusion instrument no method could be developed for determining nitrogen and oxygen simultaneously. Determination of one precluded determination of the other. The instrument also has a rather poor detection limit for nitrogen (10 ppm), and this element must be determined by difference. However, certain analyses for nitrogen in steel were later performed by using the spinning crucible on this instrument.

2. Single-Crucible, Helium-Fusion Analyzer. Although the single-crucible, helium-fusion instrument includes a number of novel features, it has several shortcomings. With analysis for oxygen and nitrogen being performed in the flowing gas stream, the integrator is zeroed immediately be ore adding the sample to the crucible and the signal from the blank is not recorded. Therefore, the magnitude of the blank is not determined. If it becomes a significant fraction of the gas from the sample, the accuracy of the analytical results for both oxygen and nitrogen can be deleteriously affected. Further, results below 10 ppm may be in error because of drift in the digital integrator. In the analysis of samples containing more than 4 ppm hydrogen, there is poor resolution between hydrogen and nitrogen. This could lead to erroneous results for the latter, but could be overcome by using a longer molecular sieve column to effect adequate resolution. Finally, although the dosing valve system facilitates calibration and checking of the apparatus, it is not possible to reproduce each analysis because only fixed calibration volumes are used.

Evaluation of the single-crucible, helium-fusion instrument was limited because NBS personnel also used it and because the instrument was on loan from the manufacturer.

To analyze as many samples as possible, the equipment was first evaluated with solid samples, NBS SRMs 1090, 1091, and 1092. Nominal standard operating conditions were established and results for both oxygen and nitrogen were obtained. After these parameters were fixed, many of the NBS milled steel SRMs were analyzed for nitrogen. The SRMs ranged in nitrogen content from 40 to 4550 ppm, and the results are listed in Table 2.

After the above nitrogen values were obtained, certain standard operating conditions were fixed. Temperature programming for the fusion of the sample was investigated because this is recommended by the manufacturer and must be determined for each type of material analyzed. With NBS SRM 5L, which has a nominal nitrogen content of 58 ppm, samples were analyzed while the temperature at which the samples were introduced into the graphite crucible was varied from 1400 to 1850 °C.

In addition, the normal heating cycle was programmed for a temperature increase of about 100 °C during the last 10 to 20 seconds for the fusion and extraction period. This cycle was varied with respect to both time and temperature to minimize saturation of the metal bath with carbon and to effect complete recovery of nitrogen. This study indicated that some benefits were obtained with temperature cycling if a final temperature of 1900 °C was attained and held for a minimum of 15 seconds. With an initial temperature of 1400 °C, it was not possible to reach 1900 °C in less than two minutes. The best temperature program applicable to steels in general seemed to be to introduce the sample at 1850 °C, fuse at this temperature for 20 to 30 seconds, and then raise the temperature to 1950 °C for at least 15 seconds. However, optimum conditions for the extraction of oxygen and nitrogen from various metals and alloys should be determined for each type of sample.

To ascertain the effect of sample weight on nitrogen recovery, a series of samples containing about 150 ppm nitrogen was analyzed by using samples weights from 0.05 to 1.0 gram. All but one of the results obtained (rounded off to the nearest 10 ppm), Table 3, agreed within 10 ppm of the certified value obtained chemically.

Because complete nitrogen recovery from some steels is difficult or presently impossible by conventional fusion, the effect of bath material was also investigated. Copper, nickel, and platinum were used as a bath in the ratio of 10 parts bath material to 1 part sample, and the results were compared with those obtained by the single crucible technique.

Table 3. Effect of sample weight on nitrogen recovery (single-crucible, helium-fusion).

NBS-SRM 10g (Low alloy)[a]	
Nominal weight, g	Nitrogen, ppm
0.05	145
0.06	173
0.07	163
0.08	150
0.09	147
0.1	149
0.2	154
0.3	158
0.4	159
0.5	143
0.5	145
0.5	141
0.5	147
1.0	143
1.0	141
1.0	144

[a]NBS certified value 0.015 percent nitrogen.
NBS certificate range 0.014 to 0.015 percent nitrogen.

NBS SRM 10g, from which nitrogen is easily recovered, was used for this part of the investigation. These results are shown in Table 4. Only the platinum bath technique yielded results in agreement with the 140 to 150 ppm expected range. For reasons unknwon, values with the copper and nickel baths were low by 11 percent and 18 percent, respectively.

Table 4. Effect of various bath materials on nitrogen recovery (single-crucible, helium-fusion).

NBS-SRM 10g (Low alloy)[a]	
Bath	Nitrogen, ppm
None	146, 146
Copper	129, 128, 124, 129
Nickel	115, 120
Platinum	145, 144

[a]NBS certified value 0.015 percent nitrogen. NBS certificate range 0.014 to 0.015 percent.

In addition to the straight platinum bath, a technique proposed by Dallmann and Fassel [1] using 18 percent platinum-20 percent tin with a minimum ratio of 3(Pt•Sn):1Fe was investigated. Results were obtained for both oxygen and nigrogen on SRM 1091, and AISI Type 431 stainless steel, with this technique and also with the platinum bath technique. Results are listed in Table 5. With the platinum bath the oxygen values obtained agreed with the certified result; the nitrogen results were low by comparison with the NBS pressure bomb result which is preferred to that obtained by vacuum fusion. The oxygen values obtained with the platinum-tin bath were often high and low nitrogen values were again obtained.

Table 5. Comparison of nitrogen values obtained with Pt bath and Pt-Sn bath (single-crucible, helium-fusion).

NBS-SRM 1091 (AISI Type 431)

Platinum Bath	
Oxygen, ppm	Nitrogen, ppm
140	873
137	850
133	858
141	869
133	860
132	851

80% Platinum - 20% Tin Bath	
Oxygen, ppm	Nitrogen, ppm
153	819
157	836
183	843
140	833
147	815
139	827
NBS Certified value 131	945[a]
	861[b]

[a] Pressure bomb - not certified.

[b] Vacuum fusion - not certified.

Table 6 is a listing of nitrogen values obtained for solid samples by using various metals as a flux in the ratio of 1 part flux to 1 part sample. Experimental values for SRM 1091 and 1092 were lower than the recommended values for undetermined reasons, with the value of 1091 falling between that obtained by the pressure bomb and Kjeldahl or vacuum-fusion methods. For SRM 1093 the average nitrogen value with the platinum flux lies between the values obtained by the Kjeldahl and pressure-bomb techniques. Use of platinum flux material for SRM 1092 had no apparent effect on the nitrogen recovery as compared with no flux at all.

Table 6. Nitrogen values obtained with the single-crucible, helium-fusion technique.

NBS-SRM sample	Flux	Nitrogen, ppm Experimental			Average	Recommended or other
1091[a] (AISI Type 431)	None	920	917	911		945[b]
		927	926	921		865[c]
		903	922	906		861[d]
		913	911	901	915	
1092 (Vacuum Melted Steel)	Platinum	1.4	2.3	1.5		3.6[b]
		1.2	1.2	1.2		10.0[c]
		2.1	1.9		1.6	4.0
	None	1.1	1.5	2.6		
		3.6	2.7	2.0	2.3	
1093 (Valve Steel)	Cobalt	4540	4350	4420	4440	4940[a]
	Nickel	4440	4540	4440	4470	
	Platinum	4510	4570	4580	4550	3640[d]

[a] See also Table 6.

[b] Pressure bomb.

[c] Kjeldahl.

[d] Vacuum fusion.

3. Nitrogen Analyzer. The nitrogen analyzer based on the pulse-heating method was used for nitrogen analyses. Because of the very good agreement obtained between this analyzer and NBS certified values, a recommendation was made to both the Laboratory and NBS that this apparatus be investigated further. Subsequently, equipment of this type was purchased and evaluated by the Applied Research Laboratory and is presently being used routinely.

4. Inert Gas Fusion - Gas Chromatographic Apparatus. The apparatus that was designed and built at NBS had a sufficiently good detection limit for both oxygen and nitrogen, as noted earlier. As originally designed, however, the apparatus did not have sufficient power to

attain the high temperature needed to extract the nitrogen, but when a 10 kw power unit was installed, temperatures in excess of 2300 °C were attained. Various modification of crucibles were tested to ascertain the practical number of samples that could be analyzed before a crucible change.

This experimental apparatus was found to have a sensitivity of 120 counts/µl for carbon monoxide and 122 counts/µl for nitrogen or 168 counts/µg oxygen and 98 counts/µg nitrogen. (A count is an arbitrary unit of area printed by an electronic peak-area integrator.) The results are estimated to have a reproducibility of about 20 counts; therefore, a detection limit of 0.2 µg for both oxygen and nitrogen can be conservatively attained. If necessary, this sensitivity can be increased by increasing the bridge current on the thermal conductivity cell.

It was found that increasing the temperature and using a large crucible and a platinum bath resulted in lower nitrogen values than were obtained by the Kjeldahl or pressure-bomb dissolution techniques. This is evidenced by values of 124 ppm that were obtained on samples of SRM 10g certified at 0.015 percent nitrogen. Because of this low nitrogen recovery with the multiple-sample technique, it was decided to modify the apparatus.

The recommended modification (put into effect after the writer left NBS and returned to the Laboratory) involved the use of a crucible for a single determination, rather than using the same crucible for successive extractions. (See Figure 4 and Ref. 9.) Thus, the influence of previously analyzed samples is eliminated. In addition, the carbon content of the molten bath arising from erosion of the crucible is minimized and a more fluid bath results. Finally, although it is possible to have a film of deposited metals that volatilized from the bath and that may react with gases evolved from a succeeding sample, it is expected

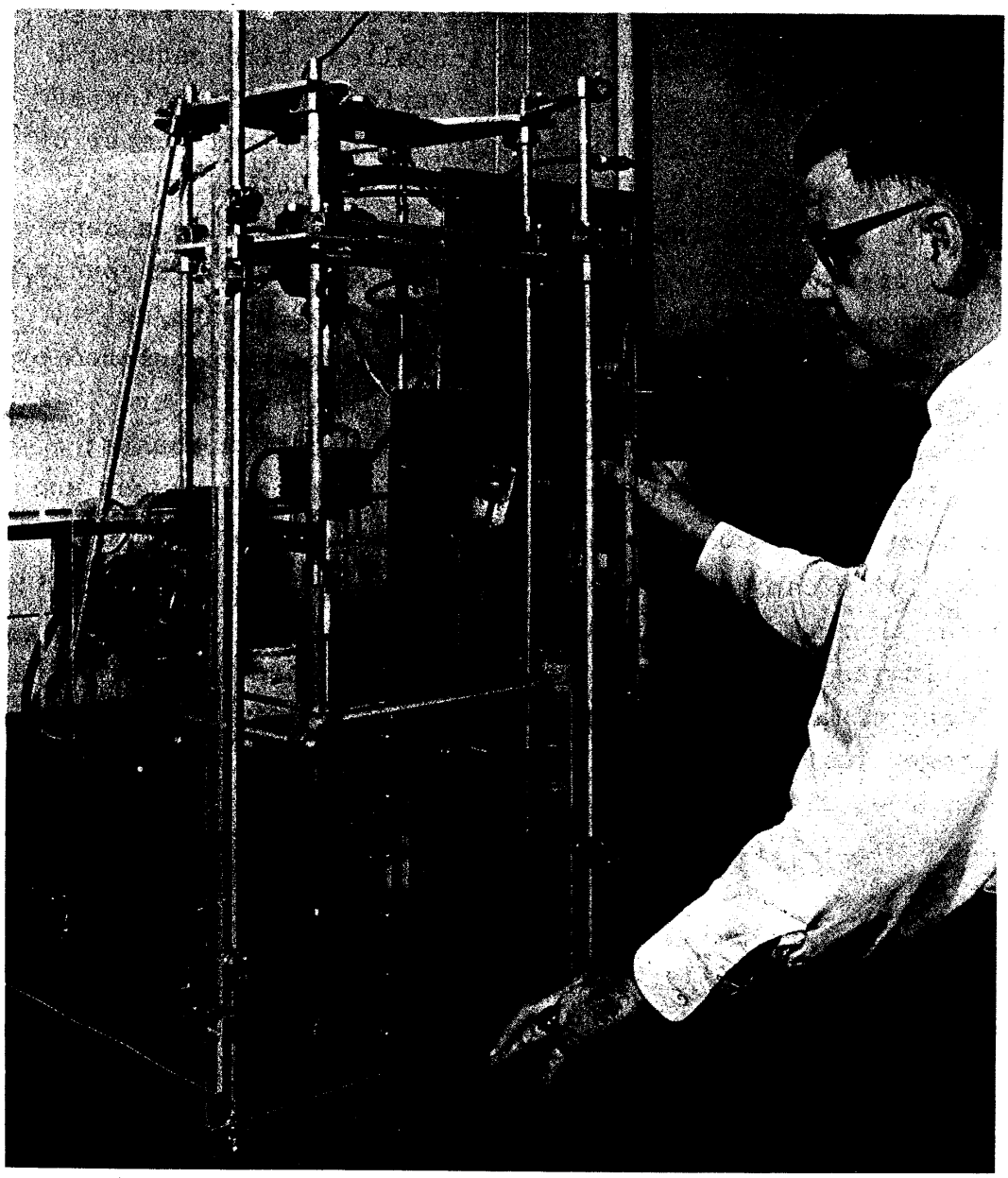

Figure 4. The new design of sample changer.

that this film would be covered by graphite volatilized during bake-out of a succeeding crucible.

The modified graphite crucible was prepared with the following dimensions: 9/16 inch OD, 7/16 inch ID, and 3/8 inch high. A furnace tube, approximately 1 inch ID, was

fabricated of quartz. The crucible was supported from the bottom by a graphite pedestal, the cross section of which was reduced to minimize heat conduction. This pedestal was supported by a boron nitride rod which was held in place by a slip joint fabricated in the ground-glass plug used to close the bottom of the furnace chamber. The closure designed for the bottom of the furnace assembly employs O-ring seals to permit rapid changing of the crucible, during which the flow of helium through the furnace minimizes its contamination with atmospheric gases.

With this equipment, it was possible, after outgassing the crucible for 3 minutes at 2300 °C and by using a cyclic heating technique, to obtain a nitrogen value of 147 ppm for SRM 10g, which compares favorably with the certified value of 0.015 percent. The crucible is changed for each sample. The necessity for this was additionally demonstrated when decreasing nitrogen values were obtained for second and third samples of the same steel added to the crucible. The same experiment was repeated with SRM 1091. A nitrogen value of 950 ppm was obtained for the initial sample, as compared with 945 ppm by the pressure-bomb solution method, Table 7. However, when subsequent samples were added to the preceding melt, the values dropped to 825 ppm. Nitrogen values for

Table 7. Nitrogen values on NBS samples obtained with IGF-GC (no bath used).

NBS-SRM	Nitrogen, ppm	
	This method	Other methods
SRM 1090	60	61.4[a], 49.5[b], 60[c]
SRM 1091	950	945[b]
SRM 1092	4	3.6[b], 4.0[c]

[a] Kjeldahl-distillation-photometry.

[b] Pressure bomb-distillation-photometry.

[c] Vacuum fusion.

SRMs 1090 and 1092 obtained with this equipment are also listed in Table 7.

Oxygen values for these samples obtained with this system and used for certification appear in Appendix I. These values and the representative standard deviations of a single determination agree favorably with the corresponding data obtained by vacuum fusion and neutron activation. Work performed at NBS after conclusion of the USS Industrial Fellowship, but based on recommendations of the Fellow, showed the apparatus to be applicable to the simultaneous determination of nitrogen and oxygen in a number of different grades of steel by using the single crucible technique. The detection limit for both oxygen and nitrogen is <1 ppm, and the analysis time is about 5 minutes.

B. Standard Reference Material Analysis

During the period spent by the author at NBS, various samples were analyzed as part of the NBS Standard Reference Materials Program. Analyses of SRMs 1090, 1091 and 1092 by inert-gas fusion were performed, Appendix I, because when these were first issued results for oxygen by vacuum fusion only were reported and certified. However, the certificate was recently replaced with one on which results by three methods, vacuum fusion, IGF-GC, and activation analyses, are reported. Nitrogen results on these samples were also obtained as noted earlier, Table 7.

In addition, NBS had been requested by various analysts to provide a new SRM for oxygen in steel at a very low level, and the Laboratory furnished a 12Ni-5Cr-3Mo maraging steel for this purpose. This material (later designated SRM 1094) was shipped in the form of a 1/2-inch-thick plate approximately 3 feet by 6 feet and weighing 300 pounds. Preliminary testing was done on this material by analyzing samples from diametrically opposite corners, taking care

to obtain samples at least 1/2 inch from the edges which had been flame cut during the processing of the sheet. Analysis of this material by vacuum fusion indicated an oxygen content of ≤ 5 ppm.

Other samples of this material were then analyzed for both oxygen and nitrogen with the IGF-GC apparatus. The sampling scheme for the homogeneity testing is shown in Figure 5. Strips of the maraging steel, approximately 1/2-inch wide, were cut by sawing from either side of the plate. These strips were then hot-forged and swaged into rods from the left and right sides of the plate, respectively, were assigned the numbers 1 and 2 as the first part of their identifying marks. Each rod was then cut after preparation into specimens as noted.

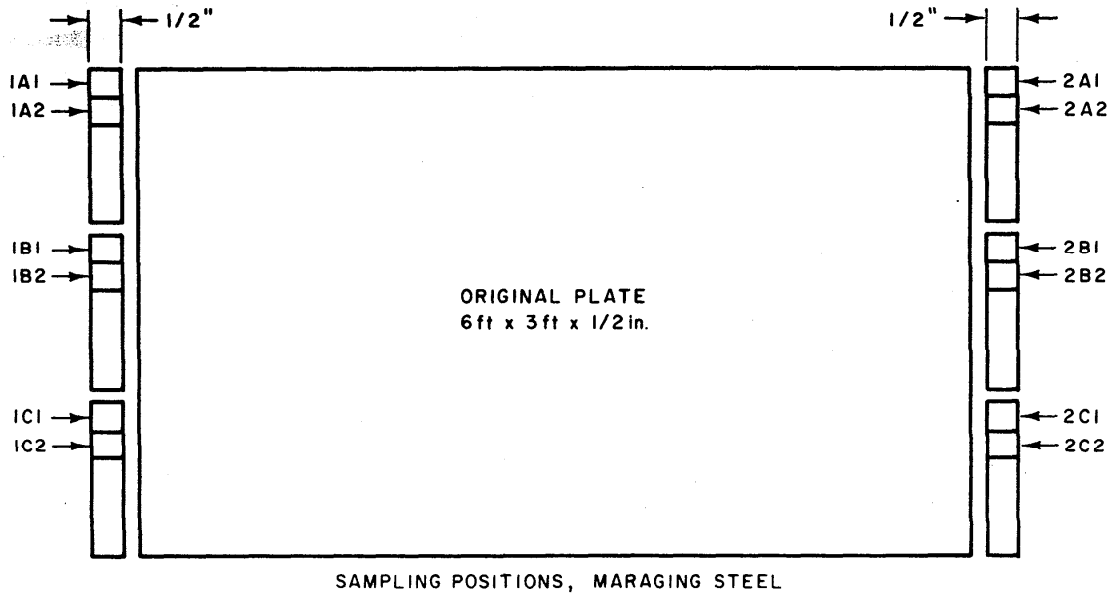

Figure 5. Sampling scheme for homogeneity testing of SRM 1094.

For the homogeneity screening the single-crucible, helium-fusion equipment was used to determine both oxygen and nitrogen, Table 8. As noted earlier, results (oxygen in this case) below 10 ppm were suspect because of the drift

Table 8. Homogeneity analysis of NBS 1094 (maraging steel) for Oxygen and Nitrogen (single-crucible, helium-fusion).

Sample	Oxygen, ppm Single-crucible helium-fusion (no bath)	Nitrogen, ppm Single crucible-helium fusion (no bath)	Nitrogen, ppm Spinning crucible (ni-Ce bath)
1A1	4.3	---[a]	NA[b]
1A2	3.0	58.8	
1B1	4.3	48.5	64.0
1B2	6.0	59.3	
1C1	3.7	61.8	NA
1C2	3.4	59.3	
2A1	3.4	57.9	62.7
2A2	3.9	58.5	
2B1	3.9	48.4	60.7
2B2	3.2	59.0	
2C1	4.3	47.4	58.6
2C2	3.2	59.0	
1A1	3.7	58.3	NA
1B2	3.0	61.3	
Average	3.9	49.0	61.5

[a] Sample lost.

[b] NA = not analyzed.

in the digital readout. Because 71 ppm nitrogen was obtained by the pressure-bomb method [7,8] as compared with 50 ppm with the helium-fusion apparatus, analyses for nitrogen using the vacuum-fusion, spinning-crucible method developed by Gerhardt, et al. [2] were also performed. The results from the latter compared more favorably with those obtained on the helium-fusion instrument than with those by the pressure-bumb method.

Vacuum fusion was the method used to initally certify SRM 1094 for oxygen (provisional certificate, Appendix II). Analysis for oxygen, Table 9, was also performed with the IGF-GC system. The sample numbers 1A1, 1A2, etc., assigned for homogeneity studies, refer to the position in the original plate. The very low oxygen content of this material together with optimum sample size of one gram made it necessary to measure microgram quantities of oxygen. Because it was possible to measure blanks at a level of 1 microgram per minute of collection time with the IGF-GC apparatus, this presented no problem.

Table 9. Oxygen values on SRM 1094[a] obtained with IGF-GC (no bath used).

Sample	Oxygen, ppm	Mean Oxygen, ppm
1A1	6.0, 4.0, 3.8, 4.0, 3.9	4.3
1A2	4.0, 4.6, 4.0, 3.9, 5.6	4.4
1C1	4.1, 3.6, 3.8, 3.9, 3.2	3.7
1C2	4.0, 5.6, 4.2, 3.1, 2.5	3.9
2A1	3.8, 5.4, 4.2, 3.1, 2.7	4.0
2A2	4.0, 3.2, 5.6, 5.4, 4.2	4.5
2C1	3.5, 4.3, 4.0, 6.0, 3.6	4.3
2C2	3.1, 3.0, 5.6, 2.6, 3.2	3.5
1x	5.6, 4.1, 6.2, 3.2, 5.1	4.5
2x	3.0, 3.0, 3.4, 2.6, 2.9	3.0
1y	4.0, 3.2, 4.5, 2.6, 3.3	3.5
2y	4.8, 3.1, 4.5, 3.3, 4.8	4.1

All Values Mean = 4.00
S.D. = 0.96

[a]Certified oxygen content based on 109 determinations by IGF-GC and vacuum fusion = 4.5 ppm.

For certification, samples taken from the original material were analyzed, as were samples selected randomly from the entire portion of material after forging, swaging, and centerless grinding. The random samples are designated x and y. Results based on 109 determinations gave a value of 4.5 ppm with an uncertainty of ±2 ppm that includes the variations due to inhomogeneity as well as to the apparatus and operator biases. This final oxygen value is based on both inert-gas-fusion and vacuum-fusion analyses and will be stated on a new certificate.

In addition to the above-mentioned steel SRM, two platinum SRMs were certified for oxygen content. The first, SRM 680, is a high-purity platinum metal that contains 4 ppm oxygen; the second, SRM 681, platinum metal doped with twelve elements, contains 7 ppm oxygen. Tentative values were established on two high-purity gold SRMs, SRM 685W at 2 ppm oxygen and SRM 685R and <2 ppm oxygen.

4. SUMMARY

U. S. Steel and the National Bureau of Standards have conducted a joint project in which various methods were evaluated for the determination of nitrogen and in particular the simultaneous determination of oxygen and nitrogen in steel. An inert gas fusion-gas chromatographic apparatus with excellent sensitivity for both elements has been constructed. Recommended modifications have been completed on this equipment, and simultaneous determinations of oxygen and nitrogen in steel are presently being made. The detection limit is <1 ppm for both oxygen and nitrogen, and the analysis time is about 5 minutes.

A direct result of this program has been the issuance by NBS of a new Standard Reference Material, a maraging steel, for oxygen. This SRM has the lowest oxygen concentration (4.5 ppm) of any steel yet issued by NBS.

5. ACKNOWLEDGMENT

Appreciation is expressed to the U. S. Steel Corporation for my appointment as an Industrial Fellow at the National Bureau of Standards under their Research Associate Program. I would also like to express my sincere thanks and appreciation to Dr. W. Wayne Meinke, Chief of the Analytical Chemistry Division, NBS, and to Dr. Oscar Menis, J. T. Sterling and other members of the Analytical Coordination Chemistry Section of this NBS division. The work at NBS was carried with assistance of J. T. Sterling. In addition to the above named, I would like to acknowledge the continuing cooperation by Mr. R. E. Michaelis of the Office of Standard Reference Materials and Dr. George Gordon and P. R. deBruyn of the Office of Industrial Liaison, NBS.

6. REFERENCES

[1] Dallman, W. E. and Fassel, V. A., Anal. Chem. 39, 133R (1967).

[2] Gerhardt, A., Kraus, T., and Frohberg, M. G., "Development of a Method for the Rapid Determination of the Nitrogen Content of Steel Based on the Vacuum Fusion Method with Special Consideration of the Degassing of Carbon Saturated Iron Melts", PhD. Dissertation of A. Gerhardt for the Institute of General Metallurgy of the Technische Universitat, Berlin, 1965, Balzers High Vacuum Co., Liechtenstein.

[3] Lemm, H., "A New Instrument for the Rapid Determination of Nitrogen in Steel", presented at the 1967 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

[4] Lemm, H. and Kock, W., "New Apparatus for the Rapid Determination of Oxygen and Nitrogen in Steel by the Fusion Extraction Carrier Gas Method", presented at the 1968 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

[5] Vasserman, A. M. and Turovtseva, Z. M., Zh. Analit. Khim., 20, 1359 (1965).

[6] Goldbeck, C. G., Turel, S. P., and Rodden, C. J., Anal. Chem., 40, 1393-4 (1968).

[7] Menis, O., Editor, Analytical Coordination Chemistry Section: Summary of Activities July 1967 to June 1968, U. S. National Bureau of Standards Technical Note 454, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, 1968.

[8] Sterling, J. T., "Differential Thermal Analysis", 53-66, Analytical Coordination Chemistry Section: Summary of Activities July 1968 to June 1969, U. S. National Bureau of Standards Technical Note 504, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, 1970.

[9] Menis, O. and Schultz, J. I., Editors, Analytical Coordination Chemistry Section: Summary of Activities July 1969 to June 1970, U. S. National Bureau of Standards Technical Note 544, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, 1970.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Materials 1090, 1091, 1092
Oxygen in Ferrous Materials

The oxygen content of these three standards has now been determined by three independent methods of analysis, namely, vacuum fusion, inert gas fusion and fast neutron activation analysis. The results of the vacuum fusion determinations were reported on a Certificate of Analysis dated March 1, 1966. At this time recommended or certified values are not being reported because of small but undetermined systematic biases which exist in one or more of the methods used. For this reason, all the pertinent analytical data are presented in tabular form below.

Oxygen in Ferrous Metals
(ppm by weight)

SRM No.	Material	Vacuum Fusion			Neutron Activation			Inert Gas Fusion		
		$\bar{X}$	s	n	$\bar{X}$	s	n	$\bar{X}$	s	n
1090	Ingot Iron	484	14	216	492	28	6	497	13	12
1091	Stainless Steel (AISI 431)	131	8	286	132	7	6	129	8	11
1092	Vacuum Melted Steel	28	2	105	28	4	5	29	5	20

$\bar{X}$ = mean oxygen value; s = standard deviation of a single determination; n = number of independent determinations.

(Note: the standard deviation includes error due both to the imprecision of the analytical method and to possible heterogeneity of the materials analyzed).

Size: SRM 1090 and 1092 are in the form of rods 1/4 in in diameter and 4 in long. SRM 1091 is 5/16 in in diameter and 4 in long.

The analyses reported herein were performed by staff members of the Analytical Chemistry Division, Institute of Materials Research, National Bureau of Standards.

Additional technical information on this series of standards, including the names of cooperators who participated in the original analyses is to be found in NBS Miscellaneous Publication 260-14, Standard Reference Materials: Determination of Oxygen in Ferrous Materials; SRM 1090, 1091 and 1092, (1966).

Caution: Oxygen determinations should be made on thoroughly and freshly cleaned samples that represent the full cross-section of the rods.

Washington, D. C. 20234
March 1, 1966
April 2, 1969 (Revision)

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

SUPPLEMENTARY INFORMATION

Although not certified at this time, the nitrogen content of these three SRMs has been determined by the analytical methods shown below:

SRM No.	Method of Analysis	Nitrogen (ppm by weight)		
		$\bar{X}$	s	n
1090	Acid digestion – distillation – indophenol – photometry	61.5	3.5	14
	Pressure bomb – distillation – indophenol – photometry	59.4	2.0	4
	Vacuum Fusion	60	1	15
1091	Pressure bomb – distillation – indophenol – photometry and titrimetry	945	20	12
	Vacuum Fusion	861	3	48
1092	Pressure bomb – distillation – indophenol – photometry and titrimetry	3.6	0.7	8
	Vacuum Fusion	4.0	1	6

The symbols $\bar{X}$, s, and n have the same meaning as given for the oxygen determinations and the note appended thereto applies here as well.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 1094

Oxygen in Maraging Steel

This standard is intended primarily for application by vacuum and inert gas fusion methods for the determination of oxygen. The low value of oxygen at 4 ppm in the maraging steel material makes the determination by neutron activation analysis difficult.

SRM No.	Description	Oxygen, ppm (by wt)
1094	Maraging Steel	4.5^{a}

[a] Results determined by vacuum fusion techniques on 1-gram samples. The value given is the grand mean based on 109 determinations on 32 samples. The values found ranged from 2.5 to 7.5 ppm. Determinations made over a period of several months indicate the existence of systemic errors of the order of 2 ppm. Examination of the data indicates that the material is homogeneous relative to the magnitude of the systematic errors in the method.

This standard is supplied in rods ¼ in (0.6 mm) in diameter and 4 in (8.2 cm) long.

The material for this standard was furnished to NBS by the Applied Research Laboratory of the U. S. Steel Corp., Pittsburgh, Pennsylvania.

Analyses were performed by J. T. Sterling, J. F. Martin, and O. Menis.

The overall direction and coordination of technical measurements leading to the certification were under the chairmanship of P. D. LaFleur.

The technical and support aspects concerning the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
March 4, 1969
(Revised June 12, 1969)

W. Wayne Meinke, Chief
Office of Standard Reference Materials

CAUTION: Oxygen determinations should be made on thoroughly and freshly cleaned samples that represent the full cross section of the rods.

(over)

SUPPLEMENTAL INFORMATION

OTHER ELEMENTS: Nitrogen, at 71 ppm, was determined by a pressure bomb-distillation-indophenol-photometric method. The nitrogen value obtained by vacuum fusion was 61 ppm. Work is now underway at NBS to discover and resolve systematic biases existing in either or both of these methods.

PREPARATION FOR THE DETERMINATION OF OXYGEN:

1. Samples should be cut from the original rod in such a manner as to minimize heating of the sample; i.e., by a hand hacksaw.
2. All surfaces of the cut sample should be thoroughly cleaned with a fine file.
3. Samples should be washed with C. P. ether, acetone, or other suitable solvent, dried in a stream of warm clean air and then handled only with clean forceps.
4. Analyses should be made as soon as possible after cleaning the sample.

CONDITIONS FOR ANALYSIS AT NBS:

Method	Vacuum fusion
Furnace temperature	1675 °C
Furnace pressure	$<10^{-5}$ torr
Collection time	4 min
Bath material	High-purity nickel
Carbon monoxide determination	Infrared absorption