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Floyd Monte Evens
Iowa State University

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A NEW TECHNIQUE FOR THE DETERMINATION OF OXYGEN AND NITROGEN IN STEEL

by

Floyd Monte Evens

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Ames, Iowa

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TABLE OF CONTENTS

I. INTRODUCTION

The presence of oxygen and nitrogen impurities is known to exert pronounced effects upon the mechanical and physical properties of steel (23,33,72). These elements occur as a residual impurity in blast furnace pig iron and are frequently introduced as contamination during oxidation, deoxidation, and recarburization steel refining procedures. The use of high purity oxygen for steel refining operations has made it possible to reduce the nitrogen concentration level to the 0.001 to 0.01 weight % range (8,10,23). However, even this quantity of nitrogen can be troublesome for certain metal forming operations. Procedures can be employed during steel refining which will regulate the oxygen and nitrogen content in the final product. It is therefore desirable to possess suitable analytical procedures for the determination of oxygen and nitrogen in order that their magnitude can be carefully controlled. A rapid analysis is also of importance since it is highly economical to modify or correct the composition of the melt, when necessary, during conventional bessemer and open-hearth steel production techniques.

For the determination of oxygen in steel, the vacuum fusion (1,2,24,28,33,52,66,67,71,72) and inert gas fusion (44, 55,68) procedures have been the most useful techniques.

Kjeldahl chemical procedures (32,33,72) have been the accepted methods for nitrogen analysis, but recently vacuum fusion procedures have become useful for certain types of steel (24, 32,46,51). In spite of the enormous effort that has been devoted to developing these analytical procedures, the determination of the combined oxygen and nitrogen content of a single sample remains a difficult task, requiring from 30 minutes to several hours for completion. Such an extensive analysis period is frequently equal to or greater than the time required for steel refining and casting operations and is therefore inadequate for economical quality control of the product.

In view of the above considerations, it is evident that an analytical procedure capable of measuring the oxygen and nitrogen content of a single steel sample in a minimal time period would not only be useful for industrial applications, but would also be of academic interest. This thesis describes the development of a procedure which makes it possible to determine oxygen and nitrogen simultaneously, with an elapsed time requirement of only five minutes.

II. EXISTING METHODS FOR THE DETERMINATION OF OXYGEN AND NITROGEN IN STEEL

A. Oxygen

Numerous reviews have been written concerning the determination of oxygen in steel and other metals (2,28,33, 66,67,72). Of the various procedures described, the vacuum fusion (1,2,24,28,33,52,66,67,71,72), inert or carrier gas fusion (44,55,68), and emission spectrometric (15,18-21) techniques have been the most acceptable methods of analysis. For this reason, it was deemed appropriate to discuss only these techniques and their relation to the determination of oxygen in steel. Although other chemical techniques have been suggested which may be applicable to the analysis in question, the very nature of their operation and frequently a lack of sensitivity at low concentration preclude their use as a routine, production control procedure.

1. Vacuum fusion

The technique now known as vacuum fusion analysis is a result of pioneering experiments devoted to the determination of oxygen in steel (1,12,66,67,71). In the basic procedure, a metal specimen weighing 0.5 gram or more is fused, under vacuum, in a graphite crucible. The carbon dissolved by the molten sample serves to reduce the oxides present and to liberate carbon monoxide as a reduction product. Sloman (66) has shown from thermodynamic considerations that the most probable reaction is:

$$M_xO + C = xM + CO \quad .$$

Nitrogen and hydrogen accompany the carbon monoxide evolution since the temperatures employed for sample fusion produce thermal decomposition of the dissolved nitrides and hydrides. All of the liberated gases are continuously removed from the reaction zone and transferred to a separate analytical system by high vacuum techniques. Analytical measurement of the individual components is achieved by oxidation of hydrogen to water and carbon monoxide to carbon dioxide in conjunction with fractional freezing and differential pressure measurements.

The vacuum fusion technique provides an absolute measurement of the gases evolved from a metal sample. These measurements are thoroughly satisfactory and possess sensitivity in the part per million range. There are, however, several difficulties associated with the extraction of gases from the metal sample. Firstly, it has been found necessary to "condition" a newly assembled and outgassed furnace-crucible combination by melting a few grams of steel in the graphite crucible (1,33,52). These operations serve to saturate all active gas adsorption sites, which otherwise might lead to low values for the first sample analyzed. Secondly, it has been shown that volatile alloying elements such as manganese, aluminum, and silicon produce low results since they are deposited on the furnace walls and react with the gases evolved from the sample (4,31,33,61,62). The addition of 0.5 to 1.0 gram of tin with each steel sample analyzed has been observed to reduce the "gettering" of the gases to a minimal value (2,52,75). However, a correction for the oxygen contributed by the tin is necessarily required. Solidification of the molten iron that accumulates in the graphite crucible during consecutive sample determinations is another problem and probably the most serious in nature (12, 33,52,69). Excessive dissolution of carbon in the melt is responsible for this solidification, forming what is known as "kish" graphite (69). As a result, the rate and degree of gas evolution decreases for each successive sample added to the graphite crucible and eventually leads to incomplete recovery of the gases to be measured. Frequently, this factor limits the number of samples that can be analyzed in a single crucible to less than five.

Oxygen values obtained by the vacuum fusion technique are considered to be the basic standard with which data obtained by other analytical methods are compared. When vacuum fusion determinations are obtained by an experienced operator and under carefully controlled conditions, a high degree of reliability can be attached to the results. One to two hours is required for outgassing each new furnace and crucible assembly before any analyses are performed. The outgassing period and the time required for analytical measurements lead to an average analysis time of 20 to 30 minutes for consecutive sample fusions in a single crucible. A single sample analysis requires approximately 90 minutes for completion. Attempts to increase the speed of these measurements has resulted in the application of gas chromatography (3,22,46,63), mass spectrometry (50), and emission spectroscopy (42) for the analysis of the gases evolved in the vacuum fusion procedure. For instance, the gas chromatographic approach has been reported to yield a completed measurement in less than 10 minutes (22). Similar claims have also been made for specially designed gas adsorption measuring systems (9). However, the basic difficulties previously described for gas extraction from metal samples are present with all of the above procedures and, as will be described later, there is an uncertainty in the ability of these techniques to provide a satisfactory determination of the nitrogen content of the metal sample. As a result, the vacuum fusion procedure and its modifications do not appear to be applicable for production control operation.

2. Inert gas fusion

The inert gas fusion procedure as described by Smiley (68) has become a useful tool for rapid, routine oxygen determinations (44,55). In principle, this technique is similar to the vacuum fusion procedure since sample fusion in a graphite crucible is employed to liberate the oxygen from a metal sample as carbon monoxide. However, for the inert gas procedure, the fusion operation is conducted under a positive pressure of flowing argon or helium, which eliminates the necessity for a high vacuum system. The inert gas stream also serves to sweep the evolved carbon monoxide from the furnace section, through a suitable oxidizing agent for conversion to carbon dioxide, and subsequently into the analytical system. The carbon dioxide determination is concluded by either manometric (68) or conductimetric (44,55) techniques. Appropriate corrections are required for a 0.001 to 0.002% operating blank.

The inert gas fusion procedure possesses the same bath solidification and gas "gettering" difficulties described above for vacuum fusion analysis. It does, however, offer the ability to conclude an oxygen determination in less than 10 minutes when operated under carefully controlled conditions. Simplicity of construction and ease of operation are additional characteristics which render such a technique quite useful for production quality control.

3. Emission spectroscopy

The application of emission spectrometric measurements to the determination of oxygen in steel has been another area of investigation (16,21,57). Of the procedures reported, the techniques developed by Fassel and Tabeling (21) appear to be the more satisfactory for routine measurements. Their procedure utilized a d.c. carbon-arc discharge in argon to melt the sample, to extract the oxygen as carbon monoxide, and to excite the oxygen emission lines at 7772 Å. An argon emission line at 7891 Å was employed as an internal standard. Quantitative measurements were obtained by correlating the intensity ratio, $O_{7772\ \text{Å}}/Ar_{7891\ \text{Å}}$, with the oxygen concentration of a series of analyzed steel samples. The concentration range of 0.002 to 0.10 weight % oxygen was covered with a relative standard deviation less than ± 10%. Approximately 30 minutes were required for a single determination, but the average time required for each sample could be reduced to less than 15 minutes when several sample exposures were made on a single photographic plate. The lack of photomultiplier tubes with sufficient sensitivity in the 7800 Å region prevented the use of electronic, direct-reading measurements which would have decreased the analysis time to less than five minutes.

Rosen (57) determined oxygen in steel by employing a hollow cathode discharge tube for spectral excitation. The sample was placed in a graphite crucible which served as the cathode in the discharge tube. Argon at a few millimeters pressure was employed as a supporting inert atmosphere. The discharge melted the metal sample, which in turn dissolved sufficient carbon from the crucible to liberate the oxygen content from the melt. An intensity ratio of a carbon monoxide band with respect to an argon line was correlated with oxygen concentration. This procedure retained many of the difficulties associated with a vacuum fusion analysis and required at least one hour for a completed determination.

Fal'kova (16) used a high voltage, high power impulse discharge in a hydrogen atmosphere to determine oxygen in steel. The sample under investigation served as a self-electrode and was opposed by an auxiliary carbon electrode. Twenty consecutive impulses were used to vaporize the sample and the included oxygen impurity. The intensity ratio of the O^{II} 4641.6 Å line with respect to the background was correlated with concentration. This procedure possessed an experimental error of ± 15 to ± 25% and occasionally yielded values which differed considerably from corresponding vacuum fusion data.

B. Nitrogen

Kjeldahl chemical (32,33,72), vacuum fusion (24,32, 46,51), and emission spectrometric (20,37,49,58,59) techniques have been successfully employed for the determination of nitrogen in steel. Neutron activation (33) and isotope dilution (33,70) techniques have also been reported for nitrogen determinations but in general have not possessed the speed, simplicity, or precision necessary for routine operation. As a result, the latter procedures have been omitted from the following discussion.

1. Kjeldahl chemical procedure

Kjeldahl chemical procedures are based upon the conversion of nitrogen to ammonia, distillation of the ammonia from an alkaline solution, and subsequent determination of the ammonia by either volumetric or colorimetric techniques (32,33,72). Sulfuric, hydrochloric, or less frequently perchloric acid is employed for sample dissolution. The solution is treated with excess alkali and the ammonia steam distilled into a suitable receiver. A volumetric acid-base titration of the distillate is satisfactory for the determination of fractional percentage concentrations of nitrogen. Part per million concentrations are measured with greater precision by a colorimetric technique (33,72). Both procedures require careful operation and appropriate blank correction for ammonia contributed by the reagents and introduced during the distillation procedure.

Sample dissolution is the most time-consuming step and greatest source of uncertainty in the Kjeldahl procedure. For instance, high-alloy corrosion-resistant steels frequently require several days for dissolution of the sample. Difficulty is also encountered with alloy nitrides such as aluminum, boron, chromium, niobium, silicon, titanium, vanadium, and zirconium which are resistant towards decomposition (33,72). Chromium, for example, forms an acid-resistant nitride when present in less than 6% composition whereas above 6% the nitride becomes acid-soluble (33). Another example is 3 1/4% silicon steel which consistently yields low nitrogen results by the Kjeldahl technique. A recent report has described a special procedure for silicon steels, where the sample is fused in a hydrogen atmosphere with a mixture of sodium hydroxide and sodium carbonate (39). The evolved ammonia is absorbed and measured colorimetrically. In view of the above considerations, it is readily evident that the Kjeldahl procedure is not applicable for all types of steel samples and, because of the extensive period required for sample dissolution, is not satisfactory for a rapid, single sample analysis.

2. Vacuum fusion

The discussion previously presented for the vacuum fusion determination of oxygen in steel is similarly applicable to the determination of nitrogen. According to Sloman (67), fusion of the sample in a graphite crucible leads to the evolution of molecular nitrogen, primarily through thermal decomposition of the nitride. An operating temperature of 1650 °C is sufficient to decompose iron nitrides but is insufficient for the decomposition of many alloy-nitrides present in steel samples (32,33,51,67,72). The Iron and Steel Institute (32) has conducted an extensive investigation of the vacuum fusion technique and its validity for the determination of nitrogen in a variety of steel samples. The evidence presented by this study indicated that each type of sample and apparatus requires a specific operating temperature for maximal recovery of nitrogen. In general, good agreement between the vacuum fusion and chemical data was achieved when the analyses were completed under optimal conditions.

Masson and Pearce (51) have recently shown that an operating temperature between 2100 and 2240 °C is required for obtaining the most accurate nitrogen data. Even at these temperatures, several steel samples yielded low nitrogen recoveries. The low values were attributed, in part, to insufficient stirring of the melt. However, incomplete nitride decomposition was not entirely eliminated as a source for the low recoveries. Data have also been reported for the vacuum fusion analysis of nitrogen in 3 1/4% silicon steel which indicate incomplete nitrogen recovery (39). The low values were explained by the thermal stability of silicon nitride and the inability of conventional vacuum furnace systems to obtain the high temperature required for total nitride decomposition. As a result, considerable disagreement has prevailed as to the validity of vacuum fusion nitrogen determination for various types of steel.

The investigation described in the text of this thesis made it necessary to procure a group of steel samples whose oxygen and nitrogen content had been thoroughly evaluated. Vacuum fusion data were obtained for this purpose. Many of the difficulties described above were encountered when samples were analyzed under operating conditions recommended by other investigators. In order to circumvent these problems, a modified platinum-bath vacuum fusion procedure was developed for the determination of oxygen and nitrogen in steel. This procedure and the data obtained for samples of variable alloying composition are presented later in the thesis.

3. Emission spectroscopy

Spectrographic methods have been devised for the determination of nitrogen in steel. All of these procedures require the use of an inert, nitrogen-free atmosphere. Mandel'shtam and Fal'kova (49) employed a high voltage, high power spark discharge directed to a sample self-electrode to vaporize the sample and to excite the N^{II} line at 3995.0 Å. Carbon dioxide at near atmospheric pressure was used as a nitrogen free atmosphere. Each discharge employed for excitation was directed to a separate area of the sample in order to achieve a reasonable degree of sampling. Analytical calibration was accomplished by correlating the measured line to background ratio with known nitrogen concentrations. A detection limit of 0.003% nitrogen was reported. Frequent discrepancies were observed between nitrogen values determined by this procedure as compared to chemical analysis. Furthermore, a reported experimental error between ± 15 and ± 40% is unacceptably large.

Runge and Bryan (58) modified the above procedure by employing the 3961.2 Å iron line for an internal standard rather than the originally described background radiation. Their investigations were restricted to Austenitic steels and inferred a limit of detection of 0.20% nitrogen. A reported experimental error of ± 17%, however, was undesirable for analytical measurements. The same authors have also approached the determination in Austenitic steels by d.c.arc excitation (59). The metal sample, in the shape of a disk, served as the anode and a graphite rod of appropriate dimension served as the cathode. The emission spectrum of the cyanogen molecule (CN 3883.4 Å), produced by the combination of nitrogen with vaporized carbon, was employed for analytical measurement. Argon, helium, and carbon dioxide were investigated as inert atmospheres in which to conduct the sample excitation. Carbon dioxide provided the most intense cyanogen spectrum. A 0.10% limit of detection was reported with an experimental error of ± 10%. However, such a high limit of detection was insufficient for the analysis of other types of steel samples.

The spectrographic procedure described by Fassel, Gordon, and Jasinski (20) and recently improved by Kamada and Fassel (37) provides a satisfactory analysis for the determination of nitrogen in a variety of steels. The procedure employed is similar to the previously described method developed for the determination of oxygen in steels. A d.c. carbon-arc discharge in an argon atmosphere was used to extract the gas from the sample and to excite the atomic emission spectrum of nitrogen. Quantitative measurements were achieved by correlating the intensity ratio, N_{8216} Å/Ar_{8053} Å, with the nitrogen concentration associated with samples of known composition. A concentration range of 0.01 to 0.20% was measured with an experimental error of ± 5 to ± 10%. The speed of analysis was limited by the time required for photographic photometry, thus precluding the use of this technique for a rapid, single sample analysis. The average time required for each analysis could, however, be reduced to less than 15 minutes when several sample exposures were made on a single photographic plate. As in the case for the spectrographic oxygen procedure, the lack of a photomultiplier detector of sufficient sensitivity in the 8000 Å region prevented the use of electronic, direct-reading techniques which would have decreased the analysis time to less than five minutes.

C. Summary

The various analytical methods described in the preceding pages indicate the magnitude of the effort that has been devoted to the determination of oxygen and nitrogen in steel. Of the procedures described, only the vacuum fusion and spectrographic methods provide a possible simultaneous measurement for these components. The vacuum fusion technique is very useful for research investigations, but lacks the speed and ease of operation necessary for production quality control. The spectrographic approach offers an increase in the speed of analysis, but possesses inadequate sensitivity and reproducibility for concentrations below 0.01 weight %. As a result, there exists a need for an analytical technique which can provide a rapid simultaneous determination of oxygen and nitrogen in steel.

The analytical procedure described in the remainder of this thesis was designed to provide a rapid and precise measurement of oxygen and nitrogen in steel. A sensitivity of measurement at a 0.001 weight % concentration level was considered to be a fundamental requirement. The Laboratory Equipment Corporation has recently reported[1] a similar

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[1] Schultz, Frederick C., Laboratory Equipment Corp., St. Joseph, Michigan. A new rapid method for the determination of nitrogen in metals. Private communication. 1962.

investigation which uses the inert gas fusion technique to extract the gases from a steel sample. The evolved carbon monoxide and nitrogen are concentrated on a molecular sieve trap immersed in liquid nitrogen. The analysis is concluded by desorbing the condensed gases from the molecular sieve trap and transferring the mixture to a gas chromatograph for a separation and measurement of the carbon monoxide and nitrogen. At present, insufficient data have been reported for evaluating the analytical performance of their procedure.

III. PRELIMINARY CONSIDERATIONS IN THE DEVELOPMENT OF A SIMULTANEOUS ANALYTICAL MEASUREMENT FOR OXYGEN AND NITROGEN IN STEEL

A. Extraction of Oxygen and Nitrogen from a Metal Sample

Fusion of a metal sample in a graphite container is in principle the simplest and most direct technique for the extraction of its oxygen and nitrogen content. A thermal source capable of elevating the temperature of the sample above its melting point is necessarily required for such an operation. Frequently, metal nitrides are present which require even higher temperatures for thermal decomposition (33,67,72). Resistance furnaces and high frequency induction heating units have generally been employed for this purpose. Resistance furnaces require elaborate design and expensive components in order to achieve a homogeneous temperature zone when operated above 1000 °C. The material employed to house the metal sample and graphite container must also be elevated to the required operating temperature and can thus contribute a significant "blank" as adsorbed gases are continuously evolved from its surfaces. Induction heating techniques minimize the "blank" contribution from the crucible container since heating can be confined to substances of high electrical conductivity. For instance, a glass envelope surrounding the fusion assembly would only be heated by thermal radiation emitted from the graphite crucible and sample. It is quite expensive to design induction heating units for vacuum fusion operations which will generate temperatures greater than 2500 °C. Many metal nitrides may require a greater temperature for thermal decomposition (33,67,72). In addition, induction heating units frequently fail to generate sufficient stirring of the molten sample so as to provide intimate contact with the graphite container. A maximal contact between the melt and graphite crucible assists the reduction of oxides and subsequent oxygen evolution as carbon monoxide from the sample. The absence of adequate stirring in the molten sample has also been considered as a factor leading to low nitrogen recovery from steel samples (51). Therefore, in addition to the large expense required for their construction, resistance furnace and induction heating techniques may fail to provide a complete evolution of gaseous impurities from many molten samples.

A d.c. carbon-arc discharge operated in an argon atmosphere appeared to offer a solution to the above difficulties. Fassel and co-workers (15,18-21,37) have shown that the extraction of oxygen from a variety of metals and nitrogen from steels can be completed in less than two minutes when an arc source is operated under the proper environmental conditions. In their procedure, a specially designed graphite electrode was employed as a sample container and was opposed by a cylindrical graphite cathode. A 15 to 30 ampere arc initiated between the resulting electrode assembly rapidly melted the sample. A precipitous temperature gradient was established in the molten sample which gave rise to a vigorous stirring of the melt and subsequent intimate contact with the graphite electrode walls. The maximum temperature obtained during the arcing period was considered to be the boiling point of the molten metal and for steels was estimated to exceed 3000 °C. Each sample to be analyzed was seated in an individual outgassed graphite electrode, which provided a completely new reaction environment for gas evolution. The use of a d.c. arc as a thermal source appeared to possess the following advantages over and above other thermal sources:

1. Low cost and ease of construction and maintenance.
2. Ability to achieve temperatures that are required for metal nitride decomposition without elaborate design and operation.
3. Capable of providing a more rapid extraction of the oxygen and nitrogen content of a metal sample.

Therefore, the d.c. carbon-arc was chosen as a thermal source for the establishment of a rapid, routine, analytical extraction of oxygen and nitrogen from the samples to be analyzed.

B. Analytical Measurement

The extraction of oxygen and nitrogen from a steel sample by a d.c. carbon-arc fusion in an argon atmosphere is believed to be a result of the following reactions:

1. $M_xO_y + zC = M_xC_{(z-y)} + yCO$
2. $M_xN_y + zC = M_xC_z + y/2\ N_2$

These equations are similar to those described by Sloman (66,67) and previously illustrated in this thesis. Thermal gradients established during arc extraction produce convection mixing of the evolved gases with the argon atmosphere. A determination of the molecular nitrogen and carbon monoxide content in the argon matrix is therefore required for concluding the analysis.

A rapid and precise determination of the components in the above mixture is desirable for analytical measurement. Of the applicable physical or chemical procedures, gas chromatographic analysis appeared to offer the greatest speed and simplicity of operation (13,14,36,40,56). An analysis by this technique depends upon the ability to introduce a gaseous sample into a carrier gas stream at the front of a suitable partitioning column. The carrier gas serves to move the sample through the partitioning agent and to elute the separated components. For an optimal separation, it is desirable to have the entire sample transferred to the column as a compact unit or "plug" of gas. Sample size is generally limited to less than 10 milliliters in order to achieve maximal resolution and satisfactory shape of elution bands.

Numerous data have been reported for the separation of carbon monoxide and molecular nitrogen by gas chromatography. Greene and co-workers (25) employed a nine-foot, charcoal column with a continuous increase in column temperature from ambient to 170 °C over a 45 minute interval to achieve this separation. Helium was used as the carrier gas at a flow rate of 100 ml/min. Similar data has been reported by other workers (34,48). Silica gel and alumina columns have also been used for the same type of separation (26,64). Column temperatures ranging from -72 to 150 °C were necessary to achieve the desired results. The use of Linde Molecular Sieve 5A as a column material for the separation of carbon monoxide and nitrogen has by far received the most attention (7,35,43,45,54,63,74). Satisfactory separations were obtained for isothermal operation ranging from 0 to 100 °C depending upon the chromatographic variables. Helium was employed as the carrier gas at flow rates ranging from 25 to 100 ml/min. Complete separations were achieved in less than 12 minutes. The only difficulty encountered was poisoning of the column material by an irreversible adsorption of carbon dioxide and water. This situation was eliminated by a preliminary purification of the carrier gas.

The preceding data illustrated that a suitable separation of carbon monoxide and nitrogen could be achieved by gas chromatographic techniques. The use of a molecular sieve column for obtaining this separation appeared to be the most suitable arrangement for an analysis of the gas mixture generated by a d.c. carbon-arc fusion extraction of oxygen and nitrogen in steels. There was, however, a difficulty presented by the argon matrix of the gas mixture. For instance, if helium were employed as a carrier gas, as recommended by previous investigators, argon would elute from the column as a broad band which could not be readily resolved from the nitrogen band. The use of argon as a carrier gas would eliminate such an interference since an argon elution band would not occur. However, as discussed below, a loss in sensitivity of measurement would accompany the use of argon as a carrier gas. These factors therefore led to the decision to employ helium as both an inert atmosphere during d.c. arc fusion extraction and as a carrier gas during gas chromatographic separation and measurement.

When a gas chromatographic separation is conducted under optimal conditions, the individual components appear as an impurity zone in the carrier gas emerging from the column exit. Any method for measuring a physical or chemical property of the minor constituent in the binary mixture can, in principle, be used for analytical evaluation. Several types of differential detecting systems have been developed, which will measure nitrogen and carbon monoxide (47,65). The first criterion that a detector must fulfill is sufficient sensitivity for the analysis in question. For the current investigation, it was of interest to be able to measure a concentration level of 0.001% nitrogen and oxygen as present in steel samples. A review of published data indicated that thermal conductivity (36,54,63,74), radio-frequency discharge (38,41), β-ionization (11,13), and thermionic ionization (17, 27,60) techniques appeared to possess the necessary sensitivity of measurement. An evaluation of the characteristics reported for each of these systems led to the selection of a highly sensitive thermal conductivity cell for analytical measurements. A choice of this particular detecting unit was based upon its simplicity and ruggedness of construction, a proven performance for day-to-day operation, a high signal to noise ratio, ease and minimal cost associated with its replacement or repair when necessary, and adequate sensitivity.

A thermal conductivity detector has a maximal sensitivity when a maximal conductivity difference exists between the gas mixture being measured and a constant reference. Normal gas chromatographic techniques employ the carrier gas as the reference. A comparison of thermal conductivity values indicates that a maximal sensitivity for nitrogen and carbon monoxide is achieved with hydrogen or helium as a carrier gas.

The former of these gases was eliminated purely from safety considerations. Therefore, helium was chosen as the carrier gas for chromatographic operation and, as was discussed previously, as the inert atmosphere in which to conduct the d.c. arc fusion extraction of oxygen and nitrogen from steel samples.

IV. APPARATUS

A. Arc Extraction Chamber

A high-vacuum chamber, illustrated in Figure 1, was employed for the d.c. carbon-arc extraction of oxygen and nitrogen from metal samples. The National Research Corporation originally constructed the chamber, but it was extensively modified. The body of the chamber and the horizontal extension ports were constructed from 2 mm. thick, 123 mm. and 33 mm. i.d. tubing. The bottom of the chamber was a disk 4 mm. thick and 127 mm. in diameter. A 9.5 mm. thick, 152 mm. o.d., 120 mm. i.d. ring with a recessed 5 mm. O-ring groove was attached to the top of the chamber body. A 32 mm. i.d. vacuum pumping port was inserted into the wall of the chamber. The above components were of 316L stainless-steel composition and were connected by electric welding.

The top of the chamber consisted of a 9.5 mm. thick, 152 mm. diameter stainless steel plate with an internal, water-cooling cavity. A 2 mm. thick, 47 mm. i.d. stainless-steel, vertical port was welded into the top plate to accomodate an insulated electrical terminal (Carborundum Co., Model 95.0056), held in position by a solder joint. A vacuum seal between the top and bottom of the chamber was achieved by compressing a neoprene O-ring between the two surfaces and

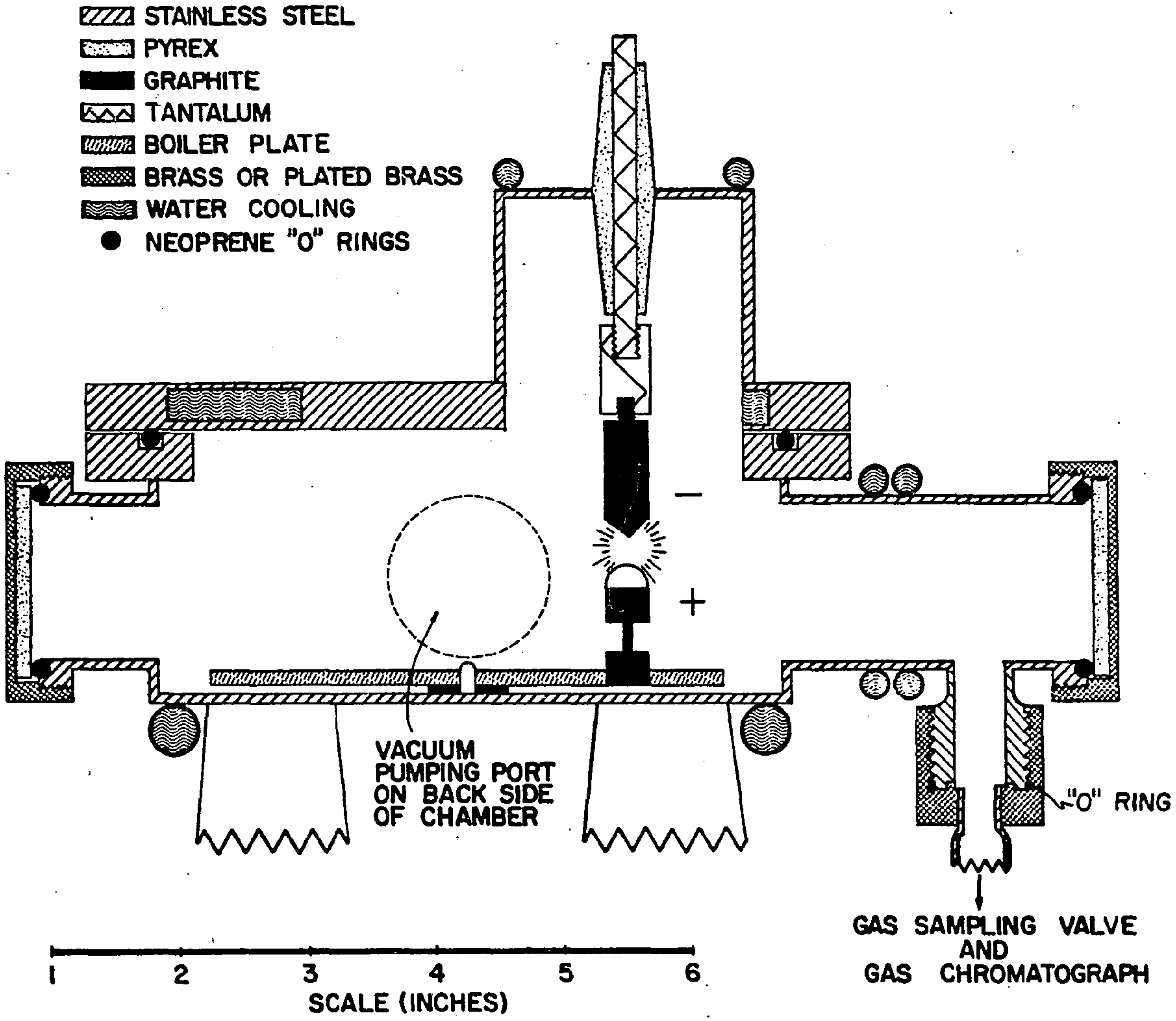


Figure 1. Arc extraction chamber

in the 5 mm. recessed groove. Four equally spaced and removable clamps, which are not shown in Figure 1, held the two sections firmly together. The horizontal ports employed glass windows compressed against neoprene 0-rings by threaded brass sleeves. A high-vacuum coupling (Central Scientific Co., Model 94235-3), inserted into and sealed to one of the horizontal ports by a silver-solder connection, provided a gas-sampling exit to the chamber. Copper coils of appropriate diameter were soldered to the chamber surfaces to provide additional water cooling. The assembled unit was mounted on metal legs and attached to an electrically grounded, metal bar.

A 6 mm. thick, 102 mm. diameter piece of cold-rolled steel served as a rotary electrode holder. Nine holes 8 mm. in diameter and 22 mm. apart were drilled into this disk to accomodate graphite electrodes. Wedges of metal were removed between successive electrode positions in order to obtain a minimal surface area and mass. The final assembly rotated freely on a graphite washer and around a peg projecting from the chamber floor.

Positioning of electrodes was performed with an external magnet. Three crescent-chaped wedges of cold-rolled steel were welded to the exterior rim of the electrode holder to increase magnetic control. A pointed graphite counter electrode, 8 mm. in diameter and 22 mm. in length, was threaded into a tantalum rod which in turn was attached to the insulated electrical terminal. A single electrode of this type could be employed for a complete series of sample arcings.

Electrical connection to the chamber was made with the illustrated insulated terminal. The chamber and the positive terminal of a d.c. source unit (National Spectrographic Laboratories "Spec Power", Model 110-2-S) were placed at ground potential, which permitted the sample electrode to serve as the anode during operation of the arc. The counter electrode thereby served as the cathode without the application of an electrical potential to the remaining equipment.

B. High Vacuum and Gas Handling System

A conventional high vacuum and gas handling system, similar to the apparatus described for spectroscopic investigations (15,18-21), was used for evacuating and introducing helium into the arc extraction chamber. An oil diffusion pump (National Research Corporation, No. H-2-P), backed by a mechanical vacuum pump (Welch Manufacturing Co., Duo-Seal No. 1402) made it possible to evacuate the system to less than 10^{-4} Torr. A high vacuum gate valve (Vacuum Research Co., Model VG-1N5) served to isolate the evacuated chamber from the oil diffusion pump. Helium, purified by passage through a combined Anhydrone-Ascarite column, was added to the system through toggle valves (Hoke, Inc., Series No. 450), which were permanently attached to the vacuum pumping port (Figure 1). An absolute pressure gage (Arthur F. Smith Co., Type 0-760 mm.) and a mercury manometer were used to measure the final helium pressure.

C. Combination of the Arc Extraction Chamber with a Gas Chromatograph

The combination of the extraction chamber with a gas chromatograph (Beckman Instruments, Inc., Model GC-2a) is illustrated in Figure 2. A high-vacuum connection between the two components was accomplished through appropriate combination of a high-vacuum coupling (Central Scientific Co., Model 94235-3), Swagelok tube fittings (Crawford Fitting Co., Models 400-6-3-316 and 400-7-2-316), a toggle valve (Hoke Inc., Model 450), and 1/4" o.d. annealed copper tubing. A 3/16" stainless-steel inlet tube extending from the rear of the chromatograph to the gas-sampling valve is standard equipment for the commercial instrument and is indicated by the shaded tubing shown in Figure 2. For operation, the chromatograph was stabilized with helium flowing through Valve 1 into the internal components and exhausted to the atmosphere at the thermal conductivity cell exits. Valve 2 was closed during this operation. The internal helium supply

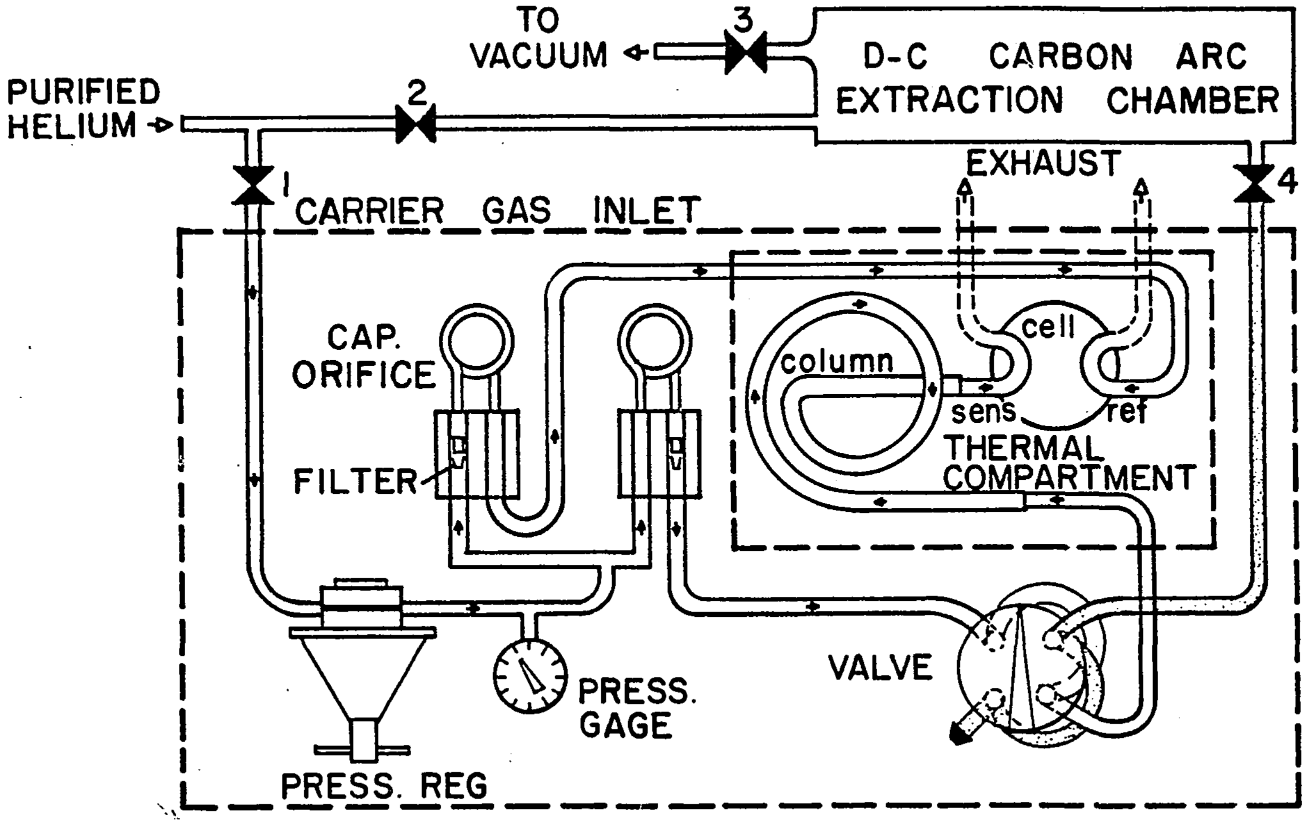


Figure 2. Combined arc extraction chamber and gas chromatograph

is divided into two independent streams by the paralleled capillary orifices. These orifices also serve to produce a constant flow rate of helium for any established forepressure. One of the helium streams proceeds directly to the detection cell and serves as the reference signal for final measurement. The other helium stream flows through a gas sampling valve and the partitioning column before entering the sensing portion of the detecting cell.

The sensing and reference elements of the detecting cell form individual legs of a Wheatstone bridge circuit, which is not shown in Figure 2. The output of the bridge circuit is fed to a series of fixed resistors, which allows the signal to be attenuated to a maximum of one thousandth of the original value in eight individual steps. The desired potential is finally applied to a suitable measuring component, which in this investigation was a one millivolt, one-second response, potentiometric recorder (E. H. Sargent Co., Model SR). Variable resistors in series with the thermal conductivity cell filaments permit balancing of the output signal so as to produce a constant recorder trace of zero potential when thermal and gas flow equilibrium is achieved. The time required to stabilize the instrument after extended shut down is 15 to 30 minutes when the thermal compartment is operated between 0 and 100 °C.

A single gas cylinder filled with compressed helium was employed to supply both the chromatograph and the arc extraction chamber. Valves 3 and 4 were opened to evacuate the chamber and one loop of the gas sampling valve. Valve 2 was closed during the evacuation operation. When the internal pressure of the chamber and sampling loop was reduced to less than 10^{-4} Torr, Valves 3 and 4 were closed and Valve 2 was opened to admit a measured quantity of helium into the chamber. A variable restriction, placed adjacent to Valve 2 and on the helium supply side, controlled the rate of gas flow into the evacuated chamber. This arrangement prevented chromatogram baseline shift, which was otherwise observed as a result of an instantaneous decrease in helium forepressure at the front of the capillary orifices. After the arc extraction operation, Valve 4 was opened to expand an aliquot of the gas into the evacuated sampling loop. A rapid 90^{o} rotation of the sampling valve handle made it possible for the carrier gas stream to sweep the sample onto the partitioning column as a compact unit or "plug". After rotation of the gas sampling valve handle, the alternate sample loop was placed in position for a repetition of the evacuation sequence described above. Within experimental error, both of the sampling loops were identical in volume, thus allowing equivalent quantities of gas to be transferred from the extraction chamber. A typical analysis was completed by observing potentiometric recorder deflections as the individual sample components passed through the thermal conductivity detecting cell.

In addition to concentration, the magnitude of the recorder deflection was a direct function of the column temperature and length, the carrier gas flow rate, and the current applied to the detector filaments (14,36,46). Therefore, it was necessary to employ an optimal and reproducible value for each of these parameters.

V. EXPERIMENTAL

A. Sources of Oxygen and Nitrogen Blank and Control of Their Magnitude

Oxygen and nitrogen originating from impurities in the helium supply, graphite electrodes, or from outgassing of the chamber surfaces can cause an appreciable contamination, or blank, during sample fusion. In order to evaluate the nature and magnitude of the blank associated with the present investigation, the following studies were made:

1. The clean excitation chamber was loaded with eight, graphite sample electrodes plus one 8 mm. diameter x 19 mm. auxiliary electrode (anode) and one 8 mm. diameter x 22 mm. pointed counter electrode (cathode). The chamber was evacuated and recharged with helium to a final pressure of 250 Torr. A 60 second arcing period at 25 amperes current was used to desorb gases from the auxiliary electrode and the chamber surfaces. The resulting gas mixture was exhausted from the chamber without measuring its composition.
2. The chamber was recharged with helium to a final pressure of 250 Torr. A 25 ampere arc was ignited between the counter electrode and one of the sample electrodes and was sustained for 20 seconds. An identical arcing

procedure was repeated for each of the remaining sample electrodes, allowing the gases liberated to accumulate in the initial helium charge. A portion of the resulting gas mixture was transferred to and measured by the gas chromatograph.

3. The excitation chamber was evacuated and Step 2 was repeated.
4. The chamber was filled to atmospheric pressure with helium and opened for 90 to 120 seconds, which simulated a sample loading procedure. At the end of this period, the chamber was closed and evacuated.
5. The excitation chamber was charged with helium to a final pressure of 250 Torr and a 25 ampere arc was ignited between the auxiliary and counter electrodes. The discharge was sustained for 120 seconds. The resulting gas mixture represented the original helium charge plus desorbed portions of gases which were adsorbed on the chamber and electrode surfaces during the sample loading interval. An aliquot of this mixture was transferred to and analyzed by the gas chromatograph.
6. Step 5 was repeated using a 25 ampere arcing period for 60 seconds followed by a 15 ampere arcing period for 60 seconds.
7. A single outgassed sample electrode was arced at 15 amperes for 60 seconds at a helium pressure of 680 Torr.

An aliquot of the resulting gas mixture was transferred to and analyzed by the gas chromatograph.

Table 1 illustrates the data obtained for the blank control studies. Each value shown is the average of ten or more individual measurements obtained over a period of several weeks. The numerical values shown for Steps 2 and 3 represent one-eighth of the measured peak height value in order to normalize the data to a single electrode basis. It is evident from the data in Table 1 that nitrogen either does not occur as a significant impurity or that it is rapidly desorbed from the electrode and chamber surfaces by high vacuum evacuation. Conversely, oxygen occurs as a significant impurity, but is effectively reduced to a constant value by a single electrode and chamber outgassing.

Table 1. Evaluation of blank control procedure

Origin	Relative peak height (mm.)	
	N_2	CO
2[a]	--	32.0 ± 10.0
3	--	2.5 ± 1.0
5	--	30.0 ± 10.0
6	--	3.0 ± 2.0
7	--	2.0 ± 1.0

[a] Numbers correspond to the operational steps used for blank control studies.

The constant value obtained for the oxygen blank level could be caused by an impurity in the helium atmosphere or a slow desorption rate for the final traces of gases adsorbed on the electrode or chamber surfaces. It was not readily possible to distinguish which of these two was responsible for the contamination. However, as shown later during analytical calibration, the magnitude of the oxygen blank was less than 0.0005% and was therefore tolerable for sample measurements. Consequently, operating steps 1, 2, 4, and 5 were routinely employed for blank control during the analysis of steel samples. The total time required for this procedure was approximately 10 minutes.

B. The Extraction and Measurement of the Oxygen and Nitrogen Content of Steel Samples

1. Extraction

A d.c. arc initiated between a steel sample supported by a graphite electrode of suitable geometry and a graphite cathode serves to melt the sample, extract the oxygen and nitrogen impurities as carbon monoxide and molecular nitrogen, and to equilibrate the liberated gases with the surrounding inert gas atmosphere by convection stirring (20, 21). For a given sample size, the rate and degree of gas evolution is critically dependent upon the supporting electrode geometry

(15,18). A one gram sample of steel provides sufficient gas evolution for analytical measurement. Figure 3 illustrates an electrode geometry which was found to provide rapid melting of the sample and maximal gas evolution for a one gram sample. After the discharge was initiated, the arc column rested directly on the metal sample during melting and after it had become entirely molten. A temperature gradient throughout the molten globule induced a rapid stirring of the melt, providing intimate contact with the graphite surfaces for carbon solvation.

During a sample arcing, the average temperature of the molten globule is related to the arcing current. Similarly, the rate and degree of oxygen and nitrogen evolution from the melt is related to temperature. Therefore, it was necessary to establish a value for the arcing current which would yield an optimal evolution of oxygen and nitrogen from a one gram steel sample. A 60 second arcing period at a helium pressure of 680 Torr was used for these studies. Figure 4 illustrates the data obtained for a low alloy steel sample. Each value shown is the average of three or more independent measurements. The maximal response obtained at 15 amperes indicated that this value should be employed for analytical measurements. The lower value shown for 12 amperes was considered to be the result of incomplete gas evolution during the 60 second arcing interval. It was observed that

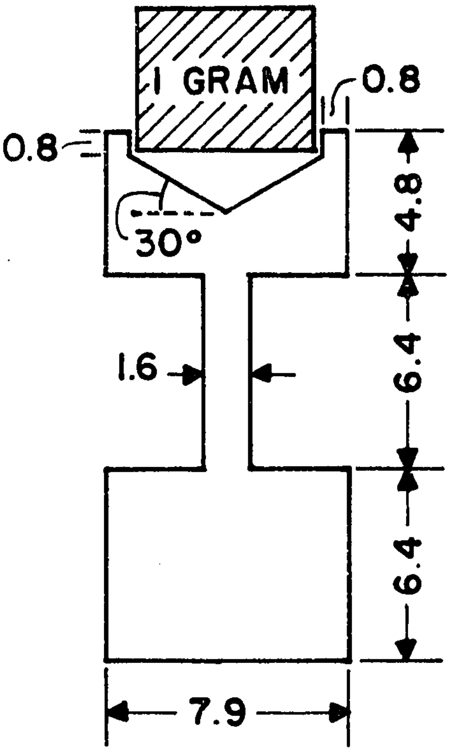


Figure 3. Electrode geometry (dimensions in millimeters)

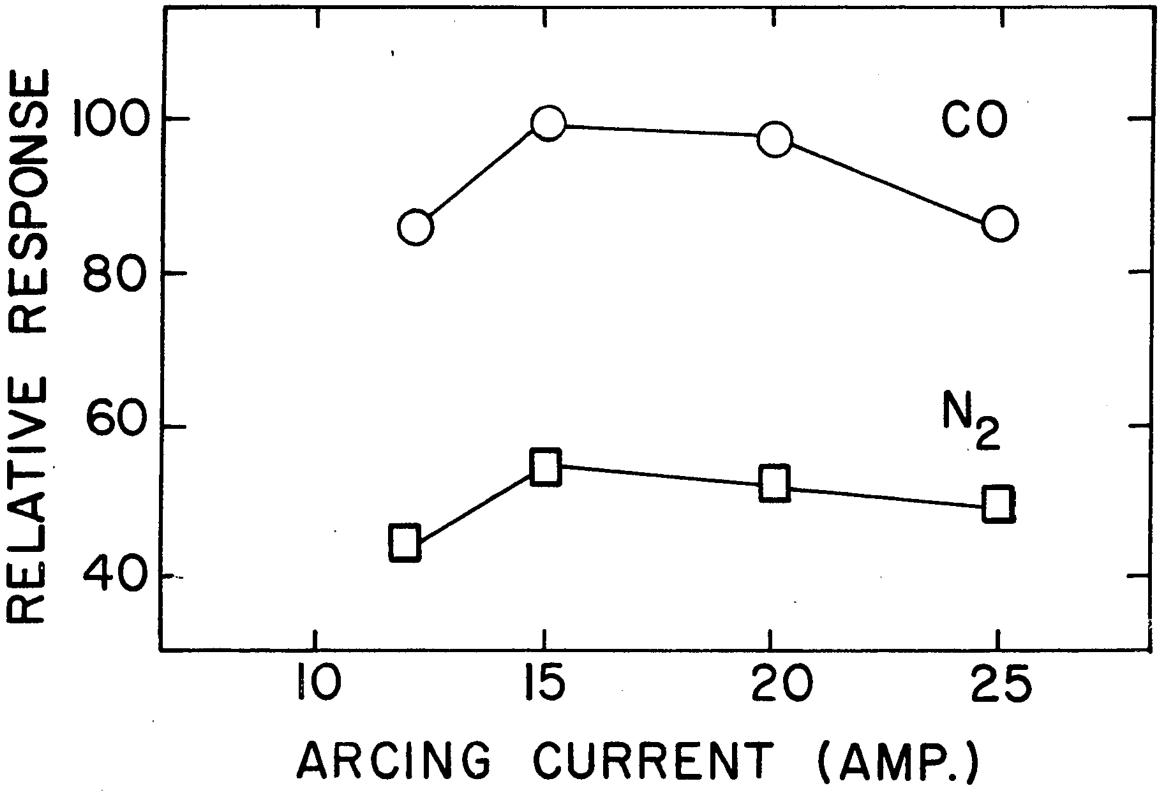


Figure 4. Measured response as a function of arcing current

excessive metal vaporization accompanies the use of 20 and 25 amperes current. Therefore, the decreasing response observed at these values of current was considered to be a result of a chemical recombination of carbon monoxide and nitrogen with the high concentration of metal vapors present in the arc plasma.

Figure 5 illustrates time resolved data for a 15 ampere arcing current and a helium pressure of 680 Torr. Each value shown is the average of three or more independent sample arcings and were obtained as individual 30, 60, 90, and 120 second intervals rather than as consecutive 30 second measurements. Experimentally, equivalent points were obtained for carbon monoxide at 30, 60, and 90 second arcing intervals. A maximal response for nitrogen was not obtained until a 60 second period had elapsed, thus indicating a slower evolution rate for nitrogen than for carbon monoxide. The rapid decrease illustrated for both carbon monoxide and nitrogen during the 90 to 120 second interval was considered to be the result of a chemical recombination of these gases with metal vapors, whose concentration in the arc plasma increased with time. For nitrogen, a chemical combination with carbon vapor to form cyanogen was an additional factor for the decreased response with arcing time.

The steady state condition obtained for both carbon monoxide and nitrogen at 60 and 90 second arcing intervals

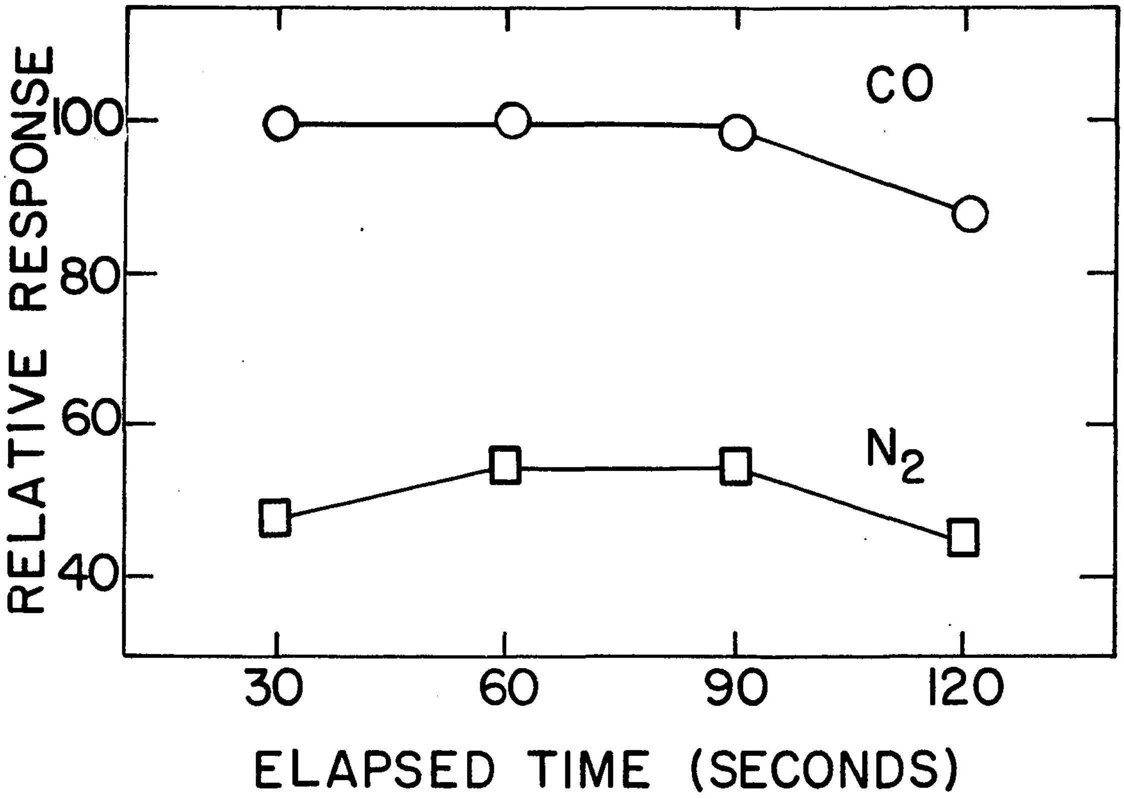


Figure 5. Measured response as a function of arcing time

made either of these periods suitable for analytical measurement. Since several high alloy steels yielded a slightly greater nitrogen value for a 90 second arcing, this period was selected for analytical measurement so as to insure a maximal nitrogen evolution for all types of steel. Precise timing of the arcing period was also considered to be essential in order to reproduce any loss of the evolved gases through chemical interactions in the arc plasma. Visual observations disclosed that the 15 ampere arcing current, used with the electrode geometry illustrated in Figure 3, completely melted the metal sample in less than 15 seconds.

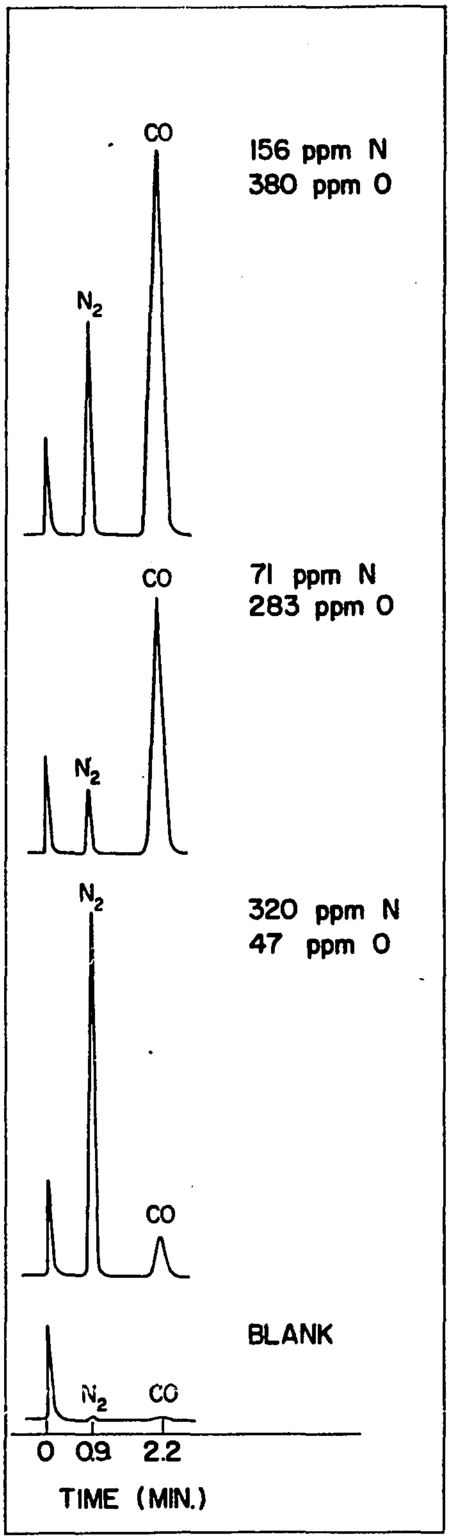
2. Measurement

The carbon monoxide, nitrogen, and helium mixture obtained by the arc extraction procedure was analyzed by the gas chromatograph associated with the extraction chamber. Table 2 illustrates the final parameters selected for analytical measurement. Included in the table are the arc extraction parameters so as to illustrate the combined operating conditions developed for the determination of oxygen and nitrogen in steel. Typical chromatograms obtained under these conditions are illustrated in Figure 6. The deflection shown at zero time is a false peak which is produced by an interruption of the carrier gas flow rate when the gas sampling valve is rotated. This initial deflection served as a time reference point for the chromatographic recordings.

Table 2. Combined arc extraction and gas chromatographic operating parameters

A. Gas extraction	
1. Sample size	1.0 ± 0.1 g. (Measured concentrations were normalized to a 1.0 gram basis by multiplication with the appropriate conversion factor.)
2. Type of electrodes	(United Carbon Co. Spectro-Tech)
a. Anode	Undercut graphite electrode as shown in Figure 3.
b. Cathode	8 mm. diameter pointed graphite rod, 22 mm. long.
3. Helium pressure	680 Torr, reproduced to ± 1%.
4. Arcing current	15 amp.
5. Arcing interval	90 sec.
6. Gas cooling period	60 sec.
7. Volume of gas aliquot transferred to chromatograph	5 cc., reproduced to ± 1%.
B. Gas chromatograph	
1. Helium forepressure	25 lb./in.^{2}
2. Carrier gas flow rate at column exit	72 cc./min.
3. Column packing	Molecular sieve 5A
4. Column length	3 ft.
5. Column temperature	70 °C
6. Detector output attenuation	5x (1/5 of the total output)
7. Recorder chart	1/2" / min.
8. Recorder span	1 mv. (full scale)
9. Recorder response	1 sec. (full scale)

Figure 6. Gas chromatograms of the nitrogen and carbon monoxide extracted from steel samples


CO
N_2
156 ppm N
380 ppm O
CO
N_2
71 ppm N
283 ppm O
N_2
320 ppm N
47 ppm O
CO
BLANK
N_2
CO
0
0.9
2.2
TIME (MIN.)

The absence of a molecular oxygen peak, which would precede the molecular nitrogen peak, showed that any oxygen evolved was converted to carbon monoxide during the arcing interval.

The variation in peak height measurements, for gas samples which were immediately transferred to the chromatograph at the end of the arc extraction procedure, was found to be greater than ± 5%. This variation was decreased to less than ± 2% by allowing the gases to cool to a reproducible temperature after termination of the arc. A 60 second period was adequate for this purpose.

C. Analytical Calibration

Quantitative data are obtained for gas chromatographic techniques by relating peak heights or peak areas in the chromatograms to the concentration for each component of interest. Precise regulation of column temperature and carrier gas flow rate is essential for reproducible peak height measurements (14, 36). In general, peak heights are directly proportional to concentration for symmetrical elution bands. Peak areas are less sensitive to column temperature and carrier gas flow rate and are equally useful for both symmetrical and unsymmetrical elution bands (14,36). In the present investigation, reproducible and symmetrical elution bands were obtained. Therefore, peak heights were measured.

Quantitative measurements require a correlation of the observed carbon monoxide and nitrogen peak heights with the absolute amounts of oxygen and nitrogen in a steel sample. A logical method for concluding these correlations is to measure the peak heights produced by analyzing steel samples of known oxygen and nitrogen content. Another approach to the calibration experiments is the addition of known quantities of carbon monoxide and nitrogen to the arc extraction chamber followed by an observation of peak heights when an aliquot of these mixtures passes through the chromatograph. Both of these procedures were investigated.

1. D.C. arc, gas chromatographic investigations with synthetic gas mixtures

Synthetic gas mixtures of 0.05% carbon monoxide in helium and 0.05% nitrogen in helium (The Matheson Company, Inc.) were used for calibration investigations. The volume of the arc extraction chamber was measured by pressure-volume expansions of helium from a standard volume into the evacuated chamber. For analytical measurements, a specified pressure of the gas mixtures was added to the chamber. The resulting quantity of carbon monoxide and nitrogen present in the chamber was determined from the ideal gas law. The total pressure in the chamber was adjusted to 680 Torr by the addition of tank helium.

A gas mixture introduced into the arc extraction chamber was subjected to the arcing and chromatographic procedures established for the extraction and measurement of oxygen and nitrogen in steel. The arcing period was essential for several reasons. Firstly, there are many appendages associated with the arc extraction chamber (Figure 1) which may retard a rapid mixing of the carbon monoxide or nitrogen with the helium diluent added to the chamber. The thermal gradients established during the arcing period provide a convection stirring of the gases which yields a reproducible, steady state mixing of the components. Secondly, chemical reactions are induced by the violent arc plasma during the extraction of oxygen and nitrogen from steel samples. For example:

a. $CO \longrightarrow C + O$

$O + \Delta E \longrightarrow O^* \longrightarrow O + h\nu$

$O + CO \longrightarrow CO_2$

$O + O \longrightarrow O_2$

$O + N \longrightarrow NO$

b. $N_2 \longrightarrow N + N$

$N + \Delta E \longrightarrow N^* \longrightarrow N + h\nu$

$N + O \longrightarrow NO$

$$N_2 + 2C_{(g)} \longrightarrow (CN)_2$$

$$(CN)_2 \longrightarrow CN + CN$$

$$CN + \Delta E \longrightarrow CN^* \longrightarrow CN + h\nu$$

If metal vapors are present, which is the case when steel samples are arced,

c. $$xM + y/2\ N_2 \longrightarrow M_xN_y$$

$$xM + y/2\ O_2 \longrightarrow M_xO_y$$

Therefore, the quantity of carbon monoxide and nitrogen converted to other chemical forms during the arcing period must be constant and reproducible in order to achieve a satisfactory calibration.

Table 3 shows data obtained for carbon monoxide gas mixture studies. Each value shown is the average of three or more independent measurements and represents the net value obtained by subtracting the average peak height, produced by arcing a graphite electrode or steel sample in pure helium, from the experimentally measured peak heights. Similar data are shown for nitrogen in Table 4. A graphical correlation of peak height versus concentration disclosed that each set of data yielded linear relationships that were not superposable.

The observed differences between the graphite electrode

Table 3. Comparison of carbon monoxide peak heights for empty electrode and steel sample arcings

Carbon monoxide added to chamber (μg.)	Peak height (mm.)	
	Empty electrode arcing	Steel sample arcing
40	10.5	8.1
81	20.7	17.3
162	42.1	34.4
324	83.0	72.8
490	121.8	109.2

Table 4. Comparison of nitrogen peak heights for empty electrode and steel sample arcings

Nitrogen added to chamber (μg.)	Peak height (mm.)	
	Empty electrode arcing	Steel sample arcing
40	15.0	32.0
81	35.0	62.0
162	85.0	113.0
324	177.0	219.0
490	275.0	325.0

and metal sample arcing experiments indicated that the metal sample has a definite influence upon the final peak height measurements. In view of this condition, additional experiments were completed to evaluate the magnitude of the peak height change caused by the arcing period. For these studies, either the carbon monoxide-helium or the nitrogen-helium gas mixture was added to the evacuated chamber until a final pressure of 680 Torr was obtained. Chromatographic measurements were completed for these mixtures before and after the arcing period. At the end of the arcing period, the gases were cooled to their starting temperature before completing the chromatographic measurement. Table 5 illustrates the results obtained for these studies. Each value shown is the average of two or more individual measurements, and is corrected for any blank contributed by the arcing operation. The experimental facilities available for the gas mixture calibration studies were inadequate for identifying the true chemical reaction or reactions responsible for the loss of carbon monoxide and nitrogen during the arcing period. However, the data illustrated in Tables 3, 4, and 5 definitely show that arcing to a steel sample has an influence upon peak height measurements.

During the arc extraction of oxygen and nitrogen from steel samples, there is a higher concentration of carbon monoxide and nitrogen passing through the arc plasma than is represented by an equilibrium mixture of carbon monoxide, nitrogen, and helium. Chemical reactions occurring during these conditions cannot be reproduced with gaseous blends.

Table 5. Comparison of carbon monoxide and nitrogen peak heights before and after arcing period

Before arcing	After arcing	
	Graphite electrode	Steel sample
	Carbon monoxide	
114.0	106.0	92.0
	Nitrogen	
329.0	264.0	308.0

Therefore, the use of synthetic gas mixtures for correlating carbon monoxide and nitrogen peak heights with the absolute oxygen and nitrogen content of steel samples was considered to be an unsatisfactory technique.

2. Steel samples of known oxygen and nitrogen content

A limited number of steel samples with a certified composition were available from the National Bureau of Standards. However, several of these samples possessed a random variation in their oxygen content because of inhomogeneity (2,53). Steel manufacturers and other laboratories provided an additional source of samples whose oxygen and/or nitrogen content had either been determined by their existing analytical procedures or was an unknown quantity. Therefore, it was necessary to establish the exact oxygen and nitrogen concentration of many of the steel samples employed for chromatographic calibration experiments.

The vacuum fusion technique used for the determination of oxygen and nitrogen in metals can, in principle, provide a simultaneous determination of these constituents. An attempt was therefore made to use this technique for validating the oxygen and nitrogen content in the steel samples of interest. A commercial vacuum-fusion, gas analysis unit (National Research Corporation, Model 912D) was employed for this investigation. The basic construction and operating principles developed for this equipment have been described (53,76). The original apparatus was modified by connecting an ionization type pressure gage (National Research Corporation, Type 710) to the furnace, through a liquid nitrogen trap. This gage was used to monitor the furnace pressure during gas extraction so as to determine the rate and degree of gas evolution from metal samples.

A typical analysis involved the fusion of a metal sample, under vacuum, in an outgassed carbon crucible according to specified operating conditions. Gases evolved by the sample fusion were transferred to a gas analysis unit where they were compressed into a calibrated McLeod gage. The total gas pressure was measured and corresponded to a summation of the partial pressures of nitrogen, carbon monoxide, and hydrogen.

$$p_1 = p_{N_2} + p_{CO} + p_{H_2}$$

The gas mixture was then circulated over a copper and cerium oxide reagent, heated to 325 °C, which oxidized carbon monoxide to carbon dioxide and hydrogen to water. An activated Anhydrone trap removed the water from the system and the carbon dioxide was solidified in a liquid nitrogen trap. The remaining gas, which was the nitrogen, was returned to the McLeod gage for a pressure measurement, P_2. The liquid nitrogen trap was warmed to room temperature in order to sublime the carbon dioxide, which in turn was transferred to the McLeod gage. The pressure measured corresponded to the sum of the partial pressures of nitrogen and carbon dioxide.

$$P_3 = p_{N_2} + p_{CO_2}$$

An algebraic solution of P_1, P_2, and P_3 yielded the partial pressures of the individual components. The weight of gas associated with each of the determined pressures was calculated from the ideal gas law and was related to the original sample composition as follows:

$$\%\ \text{Nitrogen} = \frac{\text{wt. nitrogen} \times 100}{\text{wt. sample}}$$

$$\%\ \text{Oxygen} = \frac{\text{wt. carbon dioxide} \times 0.364 \times 100}{\text{wt. sample}}$$

$$\%\ \text{Hydrogen} = \frac{\text{wt. hydrogen} \times 100}{\text{wt. sample}}$$

A value for the blank associated with the analysis system was determined in a similar manner and was subtracted from the corresponding concentration obtained for a sample analysis.

The initial operating conditions used for the determination of oxygen and nitrogen in steel were adapted from procedures developed by other investigators (1,52,71). Solid samples were cut into cubes of appropriate dimensions so as to yield a sample weight of 0.5 to 1.0 gram. The surface of these samples was cleaned by dry abrasion with a fine steel file. Samples in the form of metal chips were pressed into a 6.4 mm. diameter cylinder by means of a briquetting press (Applied Research Laboratory model No. 52) operated at 8000 psi. The resulting specimens and the crucible assembly (53, 76) were loaded into a borosilicate glass furnace (29) and the entire furnace and gas analysis system was evacuated to a pressure of 10^{-6} Torr. The furnace temperature was gradually elevated to 2400 °C and maintained at this value for several hours. At the end of this period, the crucible and furnace assembly was satisfactorily outgassed. The temperature was reduced to 1650 °C and five grams of iron were melted in the carbon crucible in order to have a fluid bath for sample fusions. The gases evolved from the iron bath served to saturate any active gas adsorption sites on the furnace walls so that the subsequent sample measurement would not exhibit a loss of evolved gases (33,52). As soon as the iron bath was completely degassed, a sample was added to the molten bath and the evolved gases were transferred to the analysis unit for measurement. The time required for total gas extraction was measured as the time interval required for the furnace pressure to return to its starting value. For the operating conditions used, this period varied from 45 to 60 minutes. The gases transferred to the analysis unit were measured by the described procedure.

In general, the average oxygen values obtained by the above procedure agreed, within experimental error, with corresponding values reported by other sources. However, considerable variation existed for repeated sample measurements and frequently the data were significantly low. The simultaneously determined nitrogen values were consistently lower than corresponding values reported by other methods of analysis. Furthermore, the molten iron bath began to solidify (12,33,52,69) after several hours of operation, producing a decreased rate of gas evolution during sample fusion and frequently limited the number of consecutive samples that could be quantitatively measured in a single crucible to less than five.

The iron bath procedure was repeated at a furnace temperature of 2150 °C in an attempt to obtain an increased recovery of nitrogen during sample fusion (51). A definite increase was observed for nitrogen data at this temperature, but simultaneous oxygen measurements were significantly low in comparison to equivalent data obtained at 1650 °C. An increased bath solidification rate and a decreased precision of analysis were also associated with the higher temperature. As a result, the iron bath procedure did not appear to be satisfactory for the simultaneous determination of oxygen and nitrogen in steel.

Success has been reported for the vacuum fusion analysis of many metals through the use of a platinum bath procedure (5,6,30,73). Several investigators have implied the use of this technique for the determination of oxygen in steel (9,33), but supporting evidence for a simultaneous nitrogen analysis has not been described. In view of the unsatisfactory results described above for the iron bath investigations, the use of a platinum bath technique as a possible method for the simultaneous determination of oxygen and nitrogen in steel was evaluated. Operating conditions employed for this investigation were similar to those described by Wilkens and Fleischer (73). The sample preparation and furnace-crucible outgassing operations were identical to those described above for the iron bath procedure.

Upon completion of the furnace and crucible outgassing period, the furnace temperature was decreased to 1850 °C and a minimum of 35 grams of platinum was added to the graphite crucible, melted, and degassed so as to form a molten bath in which to conduct sample fusion. A modification was introduced into the original procedure of Wilkens and Fleischer (73) which consisted of a simultaneous addition of a 0.5 gram platinum rod with each sample admitted to the crucible assembly. This operation served to continuously renew the molten bath as sample analyses proceeded. An appropriate blank correction was required for the gases evolved from the platinum rod. Total gas extraction from a 0.5 to 1.0 gram steel sample, as measured by a return of the furnace pressure to its starting value, was completed in 15 to 30 minutes, depending upon the quantity of gas evolved from the sample. An analysis of the extracted gases was completed by the described gas analysis unit.

Table 6 illustrates a comparison of the data obtained by the platinum bath procedure at 1850 °C, with corresponding data obtained by the iron bath procedure at both 1650 and 2150 °C. It is evident from the values shown that the platinum bath technique yielded oxygen values equivalent to or greater than the iron bath procedure at 1650 °C. The lower oxygen values obtained at 2150 °C were indicative of gas gettering by the excessive metal vaporized and deposited on the furnace walls during sample analysis (4,31,61,62). The data shown for nitrogen tend to confirm the work of Masson and Pearce (51) since an improved nitrogen recovery was obtained by increasing the iron bath temperature to 2150 °C.

Table 6. Comparison of vacuum fusion data for the iron bath and platinum bath procedures

Sample[a]	Iron bath 1650 °C	Iron bath 2150 °C	Platinum bath 1850 °C
		Oxygen	
8h	0.036	0.031	0.038
101d	0.027	0.020	0.027
461	0.025	0.025	0.028
462	0.0056	0.0048	0.0082
		Nitrogen	
8h	0.013	0.016	0.016
101d	0.018	0.020	0.024
461	0.0053	0.0053	0.0071
462	0.0062	0.0078	0.0092

[a] Chemical composition of the samples can be found in Table 7.

However, the significantly higher nitrogen values obtained by the platinum bath procedure, for three of the samples, indicated an incomplete recovery of this component during the iron bath analyses, even at the higher temperature.

Table 7 is a comparison of the oxygen and nitrogen values obtained by the platinum bath procedure with corresponding data reported by other sources. Of particular interest is the nitrogen comparisons for samples 22 and 23 which have been reported to yield low nitrogen values when analyzed by the vacuum fusion technique (39).

Table 7. Comparative oxygen and nitrogen data for various steel samples

Sample	Description	Concentration (wt %)		Method of analysis
		Nitrogen	Oxygen	
1. 8h	Bessemer steel	0.016	0.038	Av. of 13 vacuum fusion values[a]
	(Chips) 0.5% Mn	0.017		NBS certified
		0.016		Kjeldahl[a]
		0.016	0.032	Spectrographic[a]
		0.019		Isotope dilution (70)[b]
2. 152	B.O.H. 0.8% Mn	0.0036	0.031	Av. of 3 vacuum fusion values[a]
	(Chips) 0.2% Si	0.004		NBS certified
		0.0033	0.032	Spectrographic[a]
3. 111b	SAE(4620) 1.8% Ni	0.0048	0.030	Av. of 3 vacuum fusion values[a]
	(Chips) 0.3% Mo	0.0051		Av. of 3 Kjeldahl values[a]
	0.3% Si	0.0045		Spectrographic[a]
	0.7% Mn			

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[a] Iowa State University.

[b] Numbers shown in parentheses refer to bibliography.

Table 7 (Continued)

Sample	Description	Concentration (wt %)		Method of analysis
		Nitrogen	Oxygen	
4. 122c	Cast iron 0.6% Mn	0.0050	0.056	Av. of 3 vacuum fusion values[a]
	(Chips) 0.6% Si	0.005		NBS certified
5. 101d	18% Cr, 9% Ni	0.024	0.027	Av. of 14 vacuum fusion values[a]
	(Chips) 0.7% Mn	0.024		NBS certified
	0.5% Si	0.024		Av. of 3 Kjeldahl values[a]
		0.018	0.028	Spectrographic[a]
6. 129a	(SAE X1112) 0.8% Mn	0.013	0.069	Av. of 2 vacuum fusion values[a]
	(Chips) 0.3% S	0.014		Av. of 3 Kjeldahl values[a]
7. 461	Low alloy 0.4% Mn	0.0071	0.028	Av. of 3 vacuum fusion values[a]
	0.3% Mo, 1.7% Ni	0.006	0.020	NBS uncertified
8. 462	Low alloy 0.9% Mn	0.0092	0.0082	Av. of 3 vacuum fusion values[a]
	0.3% Si, 0.7% Ni	0.008	0.006	NBS uncertified
	0.7% Cr			

Table 7 (Continued)

Sample	Description	Concentration (wt %)		Method of analysis
		Nitrogen	Oxygen	
9. 463	Low alloy 1.15% Mn	0.0072	0.0095	Av. of 4 vacuum fusion values[a]
	0.4% Si, 0.4% Ni	0.006	0.007	NBS uncertified
	0.4% Cu, 0.2% Zr			
10. Type 321	18% Cr, 9% Ni	0.0097	<0.001	Av. of 2 vacuum fusion values[a]
	2% Mn, 1.0% Si			
11. Type 347	18% Cr, 7% Ni	0.084	<0.001	Av. of 2 vacuum fusion values[a]
	2% Mn, 1% Nb	0.083		Kjeldahl[c]
		0.072		Spectrographic[a]
12. Type 430	16% Cr, 1.0% Mn	0.032	0.0047	Av. of 3 vacuum fusion values[a]
	1.0% Si		0.0044	Av. of 3 vacuum fusion values[d]
13. 1040	Low carbon 0.3% Mn	0.0037	0.023	Av. of 3 vacuum fusion values[a]
		0.003	0.018	NBS certified
		0.0025		Vacuum fusion (51)[b]
		0.0031	0.018	Vacuum fusion (24)[b]

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[c] Republic Steel.

[d] Allegheny-Lundum.

Table 7 (Continued)

Sample	Description	Concentration (wt %)		Method of analysis
		Nitrogen	Oxygen	
14. 1042	Bessemer 0.7% Mn	0.016	0.011	Av. of 3 vacuum fusion values[a]
		0.014	0.017	NBS certified
		0.015		Vacuum fusion (51)[b]
		0.015	0.018	Vacuum fusion (24)[b]
		0.013	0.019	Vacuum fusion (46)[b]
15. 1043	Low carbon 0.6% Mn	0.0051	0.0036	Av. of 2 vacuum fusion values[a]
		0.005	0.002	NBS certified
		0.0040	0.0031	Vacuum fusion (24)[b]
		0.003	0.002	Vacuum fusion (46)[b]
16. 1045	Medium carbon 0.5% Mn	0.005	0.0068	Av. of 2 vacuum fusion values[a]
		0.004	0.007	NBS certified
		0.0036	0.0074	Vacuum fusion (24)[b]
		0.005	0.007	Vacuum fusion (46)[b]

Table 7 (Continued)

Sample	Description	Concentration (wt %) Nitrogen	Oxygen	Method of analysis
17. 1047	Low carbon 0.4% Mn	0.0041	0.013	Av. of 2 vacuum fusion values[a]
		0.004	0.017	NBS certified
		0.0042	0.018	Vacuum fusion (24)[b]
18. E	Low alloy	0.0043	0.0048	Av. of 4 vacuum fusion values[a]
		0.0039		Vacuum fusion (51)[b]
		0.0052		Isotope dilution (70)[b]
19. Type 302	14.3% Cr, 6.9% Mo 0.7% Mn	0.064	0.027	Av. of 2 vacuum fusion values[a]
			0.028	Av. of 3 vacuum fusion values[d]
20. Nickel steel (X37608)	2.8% Ni, 0.7% Mn 0.3% Si, 0.9% Cr 0.2% V, 0.2% Cu	0.0071	<0.001	Av. of 2 vacuum fusion values[a]
21. Nickel steel (X37610)	3.0% Ni, 0.7% Mn 0.6% Mo, 0.8% Cr 0.2% V	0.0044	0.0050	Av. of 4 vacuum fusion values[a]

Table 7 (Continued)

Sample	Description	Concentration (wt %)		Method of analysis
		Nitrogen	Oxygen	
22. Silicon steel	2.6% Si	0.0092	0.0022	Av. of 3 vacuum fusion values[a]
		0.0089		Av. of 11 coop. laboratories (Kjeldahl)[e]
		0.0060		Av. of 7 coop. laboratories (vacuum fusion)[e]
23. Silicon steel	3.4% Si	0.0045	<0.001	Av. of 4 vacuum fusion values[a]
		0.0047		Av. of 11 coop. laboratories (Kjeldahl)[e]
		0.0029		Av. of 7 coop. laboratories (vacuum fusion)[e]

[e] Karp, Lewis, and Melnick (39).

The platinum bath oxygen values shown for samples 13, 14, 15, 16, and 17 were obtained from one gram samples that were taken from the center of one inch diameter rods issued by the National Bureau of Standards. A large deviation was obtained for repeated analyses of these samples. This variation was considered to be a result of the sample heterogeneity that has been reported for this series of standards (2,53). Large deviations for oxygen measurements below 0.005 weight % indicated an increasing difficulty in obtaining reliable analytical data in this concentration range. These deviations may be related to a deficiency in the analytical method, but sample heterogeneity may also be an important factor.

The agreement illustrated in Table 7 for the platinum bath data and corresponding values reported by other investigators was considered to be a verification of the accuracy of the established vacuum fusion procedure. Table 8 illustrates the reproducibility of the analytical measurements. Each pair of oxygen and nitrogen values shown is the result of a single analysis completed at four week intervals. The accuracy, reproducibility, and increased speed for total gas extraction indicated that the platinum bath procedure is the most satisfactory vacuum fusion technique that has been developed for the determination of oxygen and nitrogen in steel. Furthermore, as illustrated by the data shown in Table 9, as many as 12 one gram samples can be analyzed in a single

Table 8. Reproducibility of single sample measurements for four week intervals

Sample	Nitrogen concentration weight %			Oxygen concentration weight %		
	1	2	3	1	2	3
461[a]	0.0075	0.0072	0.0065	0.029	0.028	0.029
152	0.0036	0.0036	0.0036	0.032	0.030	0.031
Type 302	0.064	0.066	0.062	0.030	0.026	0.027

[a] Chemical composition of the samples can be found in Table 7.

Table 9. Oxygen and nitrogen recovery for consecutive sample analyses

Run no.	Sample 8h[a]		Sample 101d[a]	
	Nitrogen weight %	Oxygen weight %	Nitrogen weight %	Oxygen weight %
1	0.015	0.038	0.024	0.027
2	0.016	0.038	0.024	0.027
3	0.015	0.039	0.024	0.028
4	0.015	0.038	0.024	0.028
5	0.015	0.037	0.023	0.027
6	0.016	0.037	0.023	0.027
7	0.013	0.041	0.023	0.027
8	0.016	0.038	0.023	0.027
9	0.015	0.037	0.022	0.026
10	0.016	0.038	0.023	0.025
11	0.016	0.038	0.024	0.025
12			0.024	0.025

[a] Chemical composition of the samples can be found in Table 7.

crucible without loss of accuracy or precision. This factor, contrasted with a limit of one to five consecutive analyses reported for other procedures (1,52,71), emphasizes the improved performance of the platinum bath technique. The sample-to-bath ratio, at the conclusion of the measurements shown in Table 9, was 22% and 25% for samples 8h and 101d respectively. It was therefore illustrated that the sample-to-bath ratio could be extended to 20% and still possess a safe margin for analytical operation.

The only difficulty encountered during the platinum bath, vacuum fusion determinations of oxygen and nitrogen in steel was a low oxygen recovery for the first steel sample added to a degassed platinum bath. An explanation for this factor has not been determined, but its presence was avoided by the addition of an iron conditioning sample to the molten bath prior to sample analysis. Table 10 illustrates oxygen and nitrogen data obtained for a low alloy steel as related to the quantity of iron conditioning agent added to the molten platinum bath. Each of the evaluations shown corresponds to the addition of one steel sample to an individually preconditioned molten bath. The experimentally equivalent values shown, for an iron to platinum weight ratio of 2.7 or greater, indicate that a one gram iron sample should be added to a 35 gram molten platinum bath before analytical measurements are begun.

Table 10. Oxygen and nitrogen recovery as a function of the quantity of iron conditioning metal added to the platinum bath

Iron conditioner added to bath, grams	Weight ratio Fe/Pt, %	Nitrogen weight %	Oxygen weight %
0.00	0.00	0.0090	0.0004
0.30	0.8	0.0090	0.0003
0.96	2.7	0.0093	0.0080
2.7	7.3	0.0093	0.0082
7.0	9.8	0.0094	0.0084

3. Correlation of chromatographic peak height measurements with oxygen and nitrogen concentration

The steel samples described in Table 7 were analyzed with the d.c. carbon-arc sample fusion and gas chromatographic parameters described in Table 2. Prior to analysis, surface contamination was removed from solid samples by dry abrasion with a fine steel file and samples in the form of metal chips were pressed into a 6.4 mm. diameter cylinder by means of a briquetting press (Applied Research Laboratory model No. 52) operated at 8000 psi. Graphical correlations of the data obtained by these calibration experiments are illustrated in Figures 7 and 8. Each value indicated in these graphs represents the average peak height for three or more individual sample arcings and the average oxygen or nitrogen concentra-

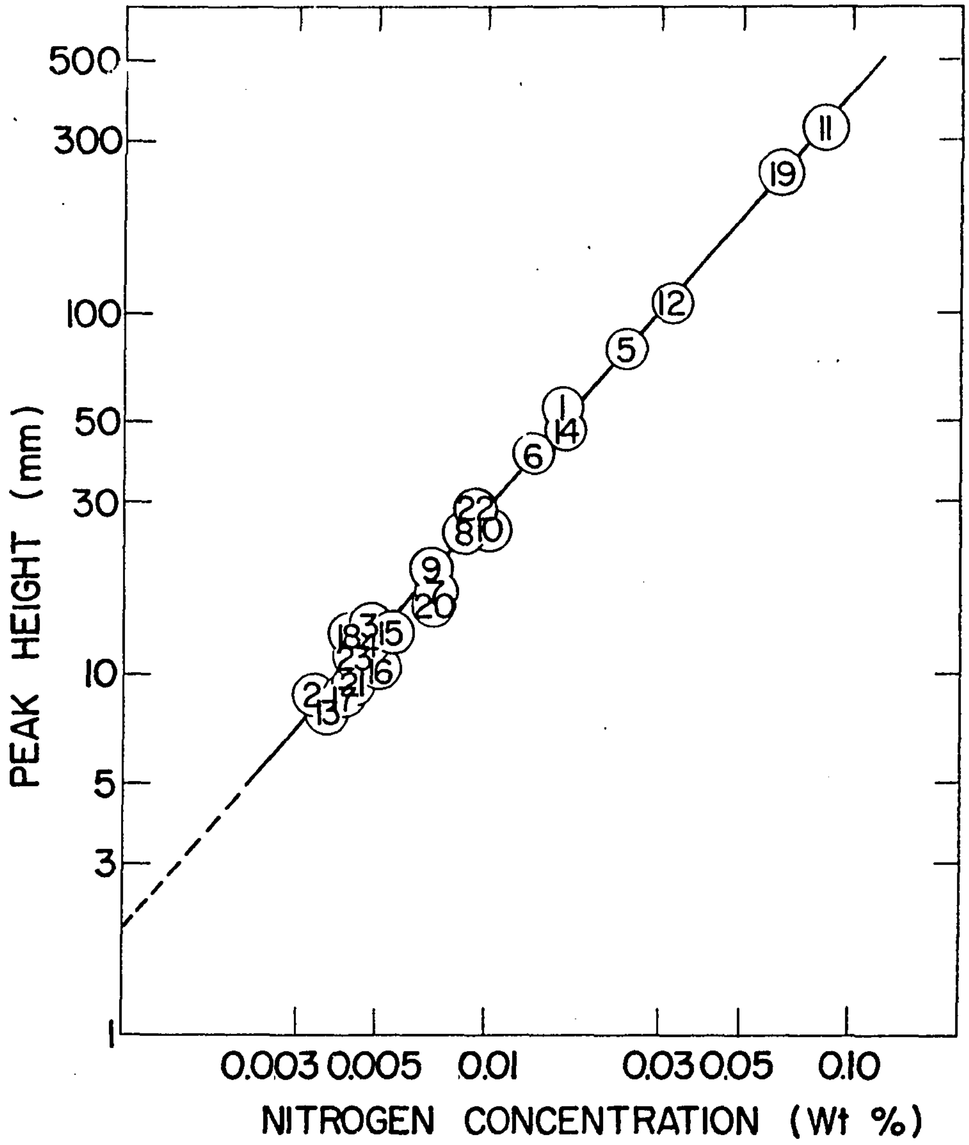

Figure 7. Analytical calibration for the determination of nitrogen in steel

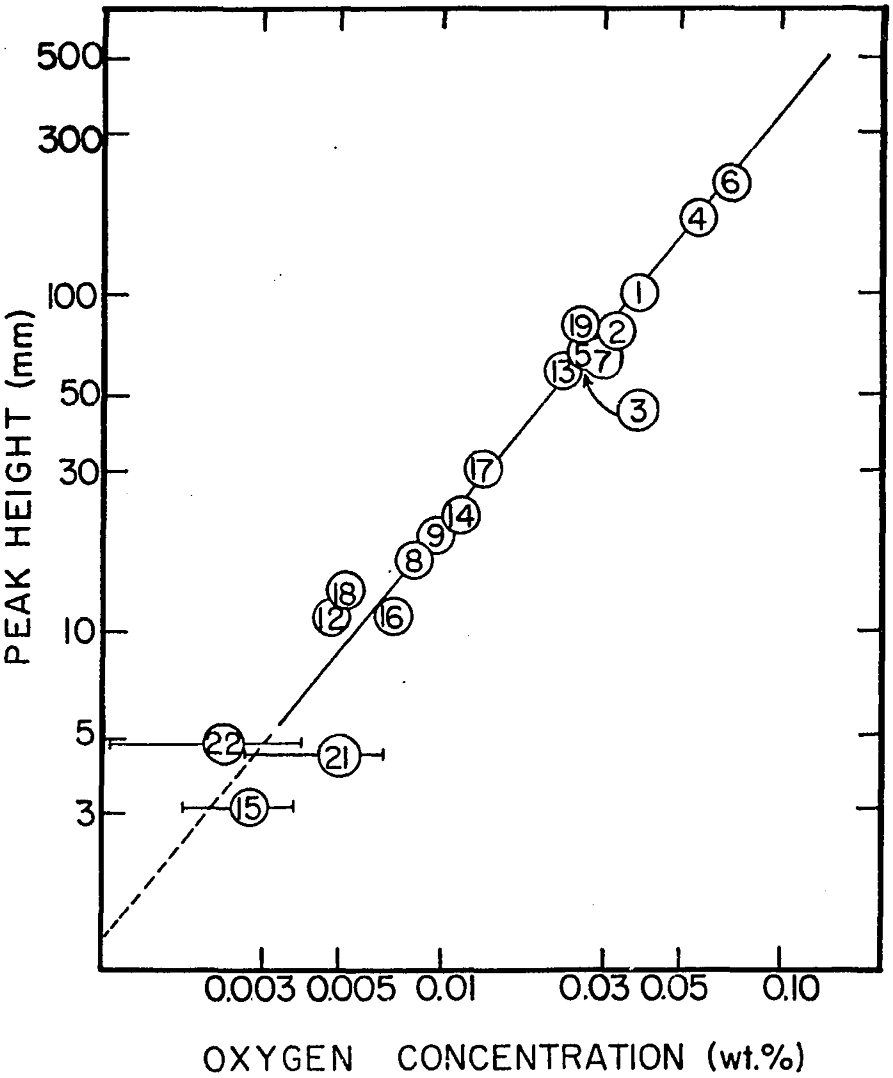

Figure 8. **Analytical calibration for the determination of oxygen in steel**

tion shown in Table 7. A correction for the blank generated during individual sample arcings was not required, since the magnitude of this contamination represented less than a one mm. peak deflection for both nitrogen and carbon monoxide. The lower concentration range of the calibrations was limited by the absence of suitable samples of known oxygen and nitrogen content. The extrapolated portion of the calibrations is included, however, to illustrate that the sensitivity of measurement is sufficient to be analytically useful at the 0.001 weight % level.

All of the steel samples described in Table 7 are indicated in Figure 7. Within experimental error, these samples yielded a single, congruent analytical correlation for the 0.003 to 0.080 weight % concentration range. Samples 10, 11, 20, and 23 were omitted from the calibration in Figure 8 since the validity of their oxygen values was questionable. The carbon monoxide peak heights obtained for samples 11, 20, and 23 corresponded to an equivalent oxygen concentration of 0.002 to 0.003 weight %. For sample 10, a carbon monoxide peak was not detectable. The maximum variation in the known oxygen values for samples 15, 21, and 22 are indicated in Figure 8 to infer that the chromatographic peak heights for these samples corresponded to an oxygen value that falls within an acceptable range. For these samples, the deviation in the measured carbon monoxide peak heights was less than

± 1 mm. Therefore, the indicated 0.003 to 0.080 weight % calibration was considered to be valid.

VI. PRECISION

Table 11 shows precision data obtained by single measurements for individual samples over a period of several weeks. Relative standard deviation is reported on the basis of concentration and was determined as follows:

$$\text{Relative standard deviation, } \% = \sqrt{\frac{\sum_{i}(x_i - \bar{x})^2}{n-1}} \cdot \frac{100}{\bar{x}}$$

where x_i = individual values

$\bar{x}$ = arithmetic mean

n = number of observations

Precision data obtained for synthetic gas mixtures that were admitted to the extraction chamber and analysed in the same manner as steel samples are also included in Table 11. These values indicate that part of the deviation observed for steel samples was related to sample heterogeneity.

Table 11. Precision data

Sample	Average peak height, mm.	Average concentration, weight %	Number of determinations	Relative standard deviation, %
		Nitrogen		
8h[a]	54.0	0.017	10	± 2.7
462	25.0	0.0089	10	± 2.9
He + N_2	228.0	------	9	± 1.5
		Oxygen		
8h	97.0	0.037	10	± 2.6
462	16.0	0.0085	10	± 5.5
He + CO	70.0	------	7	± 2.0

[a] Chemical composition of the samples can be found in Table 7.

VII. DISCUSSION

The d.c. arc extraction, gas chromatographic method developed for the simultaneous determination of oxygen and nitrogen in steel is a rapid and precise instrumental method of analysis which can be readily adapted for a production control procedure. Eight consecutive sample measurements, including electrode and chamber outgassing operations, can be completed in less than 50 minutes. For quality control during production operations, a single sample could be added to a pre-outgassed extraction chamber by loading through one of the chamber extension ports (Figure 1). Flushing the chamber with helium at a flow rate of two to three liters per minute during the loading operation would eliminate a chamber outgassing for blank control. Under these operating conditions, the total time required for a single sample measurement can be reduced to less than five minutes. A further decrease in analysis time could be achieved if the prescribed 60 second gas cooling period were eliminated from the operating procedure. However, a corresponding increase in experimental error would be obtained.

The chemical composition of the samples employed for the calibration experiments illustrates the validity of the established procedure for both high and low alloy steels. The concentration range covered by the established calibrations was chosen according to the existing purity of commercial steel samples. Theoretically, the measurements could be extended into the percentage concentration range since the output of the chromatographic detector can be attenuated as needed. The lower concentration range could also be extended by several methods. Firstly, only one fifth of the signal generated by the chromatographic detector was employed in the calibration measurements. Consequently, a five fold increase in sensitivity is readily available by operating the instrument at its maximum output. The noise level under these conditions is less than ± 0.3 mm. and therefore does not present a serious interference. Secondly, the quantity of nitrogen and carbon monoxide released from a metal sample during the sample fusion operation is a direct function of the sample weight. Therefore, as long as a suitable sample-electrode combination is available for reproducible evolution of the gases from the molten sample, the sensitivity of measurement would increase directly with sample weight. Thirdly, the present analysis procedure uses an aliquot for chromatographic measurements that corresponds to less than 1% of the total oxygen and nitrogen content evolved from a one gram steel sample. A concentration procedure which would provide all of the extracted gases for chromatographic measurement would therefore give a 100 fold increase in sensitivity. Several investigators have described a concentration procedure which might be applicable for this operation (54,74). In their procedure, a molecular sieve trap, at liquid nitrogen temperatures, was used to adsorb the carbon monoxide and nitrogen impurities from a stream of helium. The adsorbed gases were desorbed by heating the trap to approximately 100 °C and were admitted to a gas chromatograph for separation and measurement. If this concentration technique were used for the determination of oxygen and nitrogen in steel, however, the time required for the gas adsorption and desorption operations would significantly increase the time required for completing a single sample measurement. In view of the above discussions, a measurement at the fractional part per million level appears to be possible.

The need for samples of known oxygen and nitrogen content for calibration purposes imposes a restriction on the procedure developed for the determination of oxygen and nitrogen in steels. Complex chemical reactions in the arc plasma and with metal vapors during a sample arcing were responsible for this restriction. Therefore, arcing time, arcing current, and helium pressure must be reproduced in order to obtain satisfactory carbon monoxide and nitrogen peak height measurements.

VIII. SUGGESTIONS FOR FURTHER WORK

The technique and apparatus developed in this thesis provide sufficient opportunity for additional investigations.

The simultaneous determination of oxygen and nitrogen in metals other than steel is certainly of interest. A starting point for this investigation would be to reproduce the arc extraction conditions previously described for the emission spectrometric determination of oxygen in various metals (15,18-21). Modifications of the electrode geometry, sample size combinations may be necessary for obtaining a maximal nitrogen evolution. A brief study of this nature has been conducted for niobium and yttrium metals, and the results have been encouraging.

Associated with the above investigations would be an exploration of the d.c. arc platinum bath technique, developed for the determination of oxygen in titanium metal (20), as a possible procedure for the establishment of a master analytical calibration for the determination of oxygen and nitrogen in a variety of metals. The excess platinum employed for the arc extraction of the gases from the metal sample would have to eliminate sample matrix effects and their influence upon the final measurements. In this event, it may also be worthwhile to reinvestigate the use of synthetic gas mixtures as a method for correlating chromatographic peak height data with concentration, thus eliminating the use of metal samples for calibration experiments.

The basic principles associated with a combined d.c. arc-gas chromatographic apparatus should prove useful for the study of high temperature reaction phenomena. For example, a d.c. carbon-arc operated in an argon or helium atmosphere will convert molecular nitrogen into cyanogen. The rate and degree of cyanogen formation during the arcing period appears to be a complex function of the variables arcing current and time, gas pressure, and nitrogen concentration. A study of this reaction could be conducted by admitting a known quantity of nitrogen into the arc extraction chamber, diluting it with a known volume of helium, and measuring the quantity of cyanogen formed as a function of the associated variables. A gas chromatographic measurement of the final cyanogen and molecular nitrogen concentrations would provide the necessary analytical data.

Another example for high temperature reaction studies would be the use of the d.c. arc as a thermal source for the decomposition of organic compounds. A gas chromatographic determination of the resulting products would provide information that might possibly be used for elemental chemical analysis as well as for kinetic and thermodynamic measurements. A particularly useful technique that might be generated from these investigations would be the development of a quantitative procedure for the determination of oxygen in organic compounds.

In view of the above discussions, it is reasonable to assume that many useful data can be obtained by the d.c. arc, gas chromatographic technique. A wide choice of equipment design and experimental operating conditions are readily available for this purpose.

IX. SUMMARY

A new technique has been developed for the simultaneous determination of oxygen and nitrogen in low and high alloy steels. A d.c. carbon-arc discharge in a static helium atmosphere rapidly extracts the oxygen and nitrogen content of the sample as carbon monoxide and molecular nitrogen. An aliquot of the resulting gas mixture is transferred to a gas chromatograph, where a molecular sieve column separates the individual components. A sensitive thermal conductivity cell detects the carbon monoxide and nitrogen in the effluent stream. For the described operating conditions, a concentration range of 0.003 to 0.008 weight % oxygen or nitrogen can be measured with a relative standard deviation that is less than ± 5%. For production control operations, a single sample analysis can be concluded in less than five minutes.

The need of steel samples of known oxygen and nitrogen content for correlating chromatographic peak heights with concentration led to the development of a platinum bath, vacuum fusion procedure for the determination of oxygen and nitrogen in steel. An analytical evaluation of this technique has shown that it is a more satisfactory vacuum fusion procedure than has previously been described.

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