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Raymond William Tabeling
Iowa State College

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SPECTROGRAPHIC DETERMINATION OF OXYGEN IN METALS

by

Raymond W. Tabeling

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

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I. INTRODUCTION

For many years the determination of oxygen has been a difficult task for analytical chemists, and reliable methods for this determination have become available only within the last decade. Several problems are encountered in any method for the determination of oxygen. The foremost problem is the presence of atmospheric oxygen. This necessitates a closed reaction system, most frequently of the high vacuum type.

The second difficulty centers around the fact that oxygen is so abundant and reactive that it is usually found even in the purest materials. This fact makes it necessary to take extreme care in order to keep the residual, or blank, oxygen within tolerable levels.

Of particular importance is the determination of oxygen in metals. The presence of 0.001% to 0.1% of oxygen will drastically affect the physical properties of most metals. For example the presence of oxygen has a marked effect on zirconium, titanium, and alloys of these metals, causing loss of ductility, increased hardness, and grain refinement.

Since the development of the atomic energy program, metals such as zirconium, titanium, uranium, thorium, and the rare earths have become very important. These metals have such a high affinity for oxygen at the temperatures required for their casting, that they must be cast either in a vacuum or in a rare gas atmosphere. Since oxygen affects the physical properties of these metals markedly, and since the oxygen content of these metals can vary greatly depending upon the care taken in their manufacture, it is highly desirable to have a simple routine method for this determination.

This thesis describes a new method for the determination of oxygen in metals.

II. PRESENT METHODS OF DETERMINING OXYGEN IN METALS

The procedures employed for the determination of oxygen and oxides in metals may roughly be classified into residual and reduction methods. The residual methods are based on the separation of the metallic portions of the sample from the oxygen containing constituents. The reduction methods depend upon the reducing action of carbon or hydrogen at elevated temperatures to form either carbon monoxide or water vapor, which is then determined quantitatively.

A. Residual Methods

One of the simplest methods for determining oxygen in metals involves the use of a solvent which selectively attacks the metal, but leaves the insoluble metal oxide behind. Short (1) has recommended this technique for the determination of oxygen in chromium. In this procedure the selective solvent was 1.2 N hydrochloric acid. Rodden (2) has recommended a similar procedure for thorium.

A method similar to the above consisted of fusing the steel sample with aluminum (3). The aluminum reduced the iron oxides and formed aluminum oxide which was insoluble in hydrochloric acid. An adaptation of this technique permitted the determination of the oxygen content of steel while it was still molten (4). The molten metal was sampled in an iron vessel containing an aluminum wire spiral. The aluminum oxide thus formed was determined in the residue after dissolution of the sample in hydrochloric acid.

Electrolysis has been used to dissolve selectively the metallic constituents in an iron sample, the insoluble oxides thereby falling to the bottom of the electrolysis vessel (5). The iron sample was made the anode of an electrolytic cell containing a suitable electrolyte. After electrolysis the loss in weight of the anode was determined, and the insoluble residue assumed to be oxide. The individual metallic oxides were then determined.

Chlorination techniques have been used for the determination of oxygen in titanium (6). Dry chlorine was passed over the sample at 400° C, and the titanium volatilized as titanium tetrachloride. The titanium in the residue was then determined colorimetrically. The oxygen content was calculated by assuming that all of the titanium remaining was titanium dioxide. A correction must be made for the carbon present in the sample, and if molybdenum, tungsten, or vanadium are present, some oxygen will be lost as their oxychlorides. A similar procedure is also applicable to the determination of oxygen in zirconium (7).

Dry hydrogen chloride has been suggested as a reagent for zirconium. The zirconium was volatilized as the tetrachloride leaving the oxide residue behind (8).

An alcoholic iodine solution has been used as a selective solvent for iron. In this method the iron sample was dissolved by the iodine solution and converted to a soluble compound (5). Any oxides in the same were insoluble and were filtered off for further analysis of the individual compounds.

All of the above procedures suffer from several limitations. All require at least two hours or more per determination. The purity of the residue is assumed in these techniques; however, the analytical results can be greatly influenced by the presence of carbides, nitrides or metals of different atomic weight. A complete analysis of the residue should be made in order to be certain of the analytical results.

B. Reduction Methods

The most popular procedure for determining oxygen at the present time is by vacuum fusion. In this method the metal sample is melted <u>in vacuo</u> in a graphite crucible. The oxygen and combined oxides in the sample react with the crucible to form carbon monoxide. The nitrides or hydrides are simultaneously decomposed to liberate nitrogen and hydrogen. Since carbon is soluble to some extent in most molten metals, there is intimate contact between the carbon and the oxides, and the reaction to produce carbon monoxide proceeds smoothly. Typical reactions in the case of iron are:

$$H_2 \text{ (dissolved)} \longrightarrow H_2 \text{ (gas)}$$

$$FeO + C \longrightarrow Fe + CO$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$2Fe_2N \longrightarrow 4Fe + N_2$$

The combined gases are exhausted into a calibrated volume, and their total pressure is measured with a McLeod gauge.

The techniques for analyzing this gas mixture vary from author to author. The two most popular methods are: (1) the use of a mass spectrometer; and (2) selective freezing.

The use of a mass spectrometer for this analysis has the advantages of speed, convenience, and great sensitivity with an accuracy of about 10% of the amount present for a complete analysis. The main disadvantage of this technique is the difficulty in differentiation of the two major components, carbon monoxide and nitrogen, both of which have 28 as their mass number. This can be overcome with considerable loss of accuracy, by determining the mass 29 fraction, which is principally the monoxide of C^{13}, and multiplying by the C^{12}/C^{13} abundance ratio 88.5, to get the total carbon monoxide in the mass 28 fraction. However, as the mass 29 fraction is so small, considerable errors arise if any impurity of mass 29 is present in the gas. The probability that such impurities will be present is quite high since traces of hydrocarbons frequently occur in the graphite blank.

In the selective freezing method, the combined gases are pumped over heated copper oxide which oxidizes the carbon monoxide to carbon dioxide and the hydrogen to water. These are removed by a liquid nitrogen trap, and the residual nitrogen pressure is read on a McLeod gauge. The trap is then warmed from -178° C to -78° C by substituting a dry ice bath for the liquid nitrogen bath. At this temperature only the water remains frozen, and the pressure of the system is now due to the combined carbon dioxide and nitrogen. Knowing these pressures, the original amounts of hydrogen, oxygen, and nitrogen can be calculated by the application of Dalton's law of partial pressures.

In the case of most metals, however, it is found that reduction of the metallic oxides to carbon monoxide does not occur, if the metal is fused directly in the graphite crucible. Possible reasons for this are: (1) the melting point of the metal may be too high; (2) the metal may be largely converted to a high melting point carbide; (3) the dissolution of carbon in the metal may be so slow that an adequate excess of carbon is not available in the short time desired; or (4) the temperature required for the rapid reduction of the oxide may be too far above the melting point of the metal, causing excessive volatilization of the metal. These difficulties may be largely circumvented by the use of a metallic bath in the reduction crucible. Iron and tin are the most popular. Since the metallic bath generally alloys with the metal being determined, the effective melting point of the sample is lowered, thus making a homogenous fusion easier. The tendency for carbide formation is also reduced because of the competition of the alloying agent in forming a stable compound. Since carbon is soluble in the bath material, the bath facilitates an immediate contact between the metal and the reducing medium. The alloying action of the bath material also serves to reduce the vapor pressure of low melting point metals, thus reducing the evaporation of the metal to a cooler part of the apparatus, where the metal may condense and "getter" the gases liberated from the sample.

Data on typical analysis carried out by this method are listed in Table 1.

Some disadvantages of the vacuum fusion method, which have somewhat limited its use, are the complicated apparatus, the necessity for a specially trained operator, and the tedious procedure. It has been difficult to adapt this method to routine work, because each sample requires one to two hours for analysis, and the preliminary outgassing to reduce the blank commonly requires eight hours or more. Various methods have been devised to allow the operator to introduce more than one sample for analysis without opening the vacuum system for each sample. Even so, only four to eight analyses can be carried out in one working day. The number of determinations per experiment is also limited by the maximum concentration of the sample allowable in the bath for optimum reduction.

An important consideration in vacuum fusion techniques

Table 1. Typical data for the vacuum fusion method of determining oxygen in metals.

Metal	Reference	Reduction temperature (°C)	Oxygen recovery	Bath material	Maximum concentration of metal in bath
Fe	9	1650	100%	Fe	
Mo	10	1560	100%	Fe	40%
Mo	11	1800	100%	Fe	5% *
Th	10	1900	100%	Fe	20%
Cr	12	1600	85%	75% Fe 25% Sm	5%
Cr	13	1500	100%	Fe	40%
Cu	13	1100	100%	None	
Ti	14	1900	100%	Sn	*
Ti	10	1750	100%	Fe	20%
Ti	15	1900	97%	Sn	35%
Ti	11	1800	100%	Fe	5% *
U	16	1700	100%	Fe	20%
U	10	1800	100%	None	
Al	13	1550	100%	Fe	10%
Si	13	1500	100%	None	
Zr	17	1950	100%	75% Fe 25% Sn	40%
Zr	10	1625	100%	Fe	30%
Zr	11	1800	100%	Fe	5% *
V	10	1560	100%	Fe	20%
Ni	13	1550	100%	Fe	50%
Mn	13	1550	100%	Fe	10%
Co	13	1550	100%	Fe	50%
W	13	1600	100%	Fe	70%
Mg	13	1600 to 1900	None	Fe	

*New bath material must be added with each sample.

is the relative volatilities of different metals under high temperature and high vacuum conditions. For example, after a normal experiment in which six to eight specimens of steel have been analyzed, the cold walls of the quartz furnace tube above the crucible arecoated with a metallic film consisting of manganese, aluminum, magnesium copper, and other alloying or residual impurities. If this film is allowed to reach an appreciable thickness, it may absorb a considerable portion of any gas subsequently evolved and lead to low analytical results. Magnesium as an impurity in steel presents a great deal of difficulty. The high vapor pressure of magnesium leads to rapid volatilization and condensation upon a cooler portion of the furnace, where it acts as a very efficient "getter".

Smiley (18) has described a modification of the vacuum fusion procedure which eliminates the high vacuum apparatus. The sample was dropped into a molten platinum bath in a graphite crucible. A stream of highly pure argon at atmospheric pressure removed the carbon monoxide and carried it through a modified form of Schutze's reagent which converted it to carbon dioxide. The carbon dioxide was condensed in a capillary trap. After the reaction was complete and the capillary trap evacuated, the refrigerant was removed from the trap, and the pressure of the evolved carbon dioxide was measured with a capillary manometer. The desired sensitivity was achieved by using a small volume rather than measuring low pressures. Approximately twelve minutes were required per determination and the blank could be restored to operating level in an hour or two.

Smiley obtained good results on iron, copper, aluminum, and thorium, but was not successful with titanium. This procedure is applicable only to oxygen, and can not be modified for the determination of hydrogen or nitrogen.

Another modification of the vacuum fusion procedure is due to Kershenbaum (19). A known weight of the metal to be analyzed together with a known weight of the metal containing a known O^{18} concentration was placed in a graphite crucible and heated in a vacuum. At a temperature above the melting point of the metal, the O^{18} will equilibrate between the metal and the gases, and thus the ratio of O^{18}/O^{16} will be the same in the metal as it is in the gases evolved. The carbon monoxide was then drawn off, and the O^{18}/O^{16} ratio determined with a mass spectrometer. Knowing the amounts of O^{18} and O^{16} added in the standard, the amount of oxygen present in the sample could then be calculated. The main advantage of this technique is that complete evolution of the oxygen from the sample is not necessary. Disadvantages are that standard materials of known O^{18} content must be available, and equilibration of the O^{18} takes from one to three hours. The equilibration time together with the time required for outgassing the system and the analysis of the equilibrated gas mixture drastically limit the number of analyses that can be performed per day.

Another reduction method for the determination of oxygen depends upon the reducing action of purified hydrogen at elevated temperatures on the oxides in a metallic sample (5). The quantity of water vapor in the hydrogen leaving the furnace indicates the quantity of oxides reduced. Generally, it is thought that easily reducible oxides, such as those of copper, iron, and manganese are completely reduced but that refractory oxides, such as those of aluminum, zirconium and titanium are not reduced. Better results were obtained on samples in the form of millings or powder rather than on bulk samples. Besides being limited to the determination of oxygen in easily reducible oxides, this method requires several hours per determination as well as a preliminary outgassing.

Bromine trifluoride has proved to be a useful reducing agent for the determination of oxygen in titanium (20). The bromine trifluoride reacted with the titanium sample, forming titanium tetrafluoride and liberating molecular oxygen. The pressure of the liberated oxygen in a calibrated volume was a measure of the oxygen content. A single determination requires at least two hours plus the outgassing time. Only antimony, arsenic, bismuth, boron, copper, germanium, selenium, silicon, thallium, titanium and uranium, were found to be completely reduced with this reagent.

A successful method (21) for the determination of oxygen in titanium employed bromine vapor to decompose and volatilize the titanium as titanium tetrabromide. Carbon was then employed to reduce the residual oxides. In this method a mixture of carbon and the titanium sample was heated in a gold boat at 825° C in a stream of purified helium and bromine. The titanium tetrabromide and excess bromine was removed with dry ice traps. The carbon monoxide was oxidized with hot copper oxide, absorbed on Ascarite, and then weighed. This method has been successfully applied in the concentration range from 0.05% to 0.5% oxygen with a standard deviation of 5% to 10% of the amount present. Approximately two hours are required per analysis.

III. POSSIBILITIES OF DETERMINING OXYGEN IN METALS BY SPECTROGRAPHIC TECHNIQUES

A. Introduction

Spectrographic methods for the determination of alloying and residual impurities in metals are now in common use in all of the metal industries. In principle, the atomic spectrum of oxygen is excited together with all of the other constituents of the sample. It is, therefore, appropriate to inquire whether oxygen, too, can be determined in this manner. In addition to potentially adequate sensitivity and accuracy, a spectrographic method should also reduce the time required per analysis.

B. Basic Problems in the Development of Spectrographic Method for Oxygen

There are several basic problems involved in the spectrographic determination of oxygen which no doubt have discouraged previous studies on this problem. The first basic problem is that it is necessary to exclude atmospheric oxygen during the excitation of the sample. This problem can be met in one of two ways. Excitation can be carried out in a vacuum or in an oxygen free atmosphere, each of which present their own problems.

Excitation in a vacuum can be accomplished with either a high voltage spark or with a d.c. arc. The vacuum spark has the disadvantage of requiring a special high voltage source unit with sufficient electrical insulation to handle the 100,000 volts needed to initiate the spark in a vacuum. A vacuum arc has the disadvantage of being highly unstable and erratic and thus not conducive to precise results.

Excitation in an oxygen-free atmosphere also presents some difficulties. First, is the problem of preparing the oxygen free gas. The second disadvantage is that little is known about the behavior of electrical discharges in atmospheres other than air. The work that has been done in rare gas atmospheres (22) indicates that entirely different rates of volatilization, levels of excitation, and other excitation properties prevail in discharges in inert atmospheres.

The second basic problem encountered in the development of the spectrographic method for oxygen is that the resonance line, together with the other most sensitive lines of oxygen, fall in the vacuum ultraviolet region of the spectrum, and are thus unavailable with the ordinary spectrograph. The oxygen lines that are in the more readily photographed region are much weaker and also require a relatively high energy for excitation (10-13 electron volts).

The third basic problem is that spark discharges which are normally found best for the analyses of metallic samples actually only vaporize about a milligram of sample from the surface. In effect the specimen is sampled to a depth of only 0.1 mm to 0.01 mm. With metallic impurities this is sufficient, but for oxygen the extent of surface oxidation could be the major factor, thereby overshadowing the true concentration of oxygen in the sample. Moreover, when only a few milligrams are vaporized, low sensitivity would be expected, particularly if an insensitive line must be used for the analysis.

C. Previous Spectrographic Work on the Determination of Oxygen

Because of the obstacles encountered in the development of the spectrographic method for the determination of oxygen, few investigators have worked on this problem.

Sterner (23) in 1939 first approached the problem of the spectrographic determination of oxygen in steel using a vacuum spark. Steel samples were used as the electrodes and sealed in a quartz tube which served as the vacuum spark chamber. After the vacuum system was thoroughly outgassed, a 100,000 volt condensed spark was passed between the electrodes. Any gases that were liberated were pumped by an auxiliary Toepler pump into a small Geissler discharge tube. The spark was continued until the pressure in the discharge tube reached about 0.1 mm. The gas was then analysed spectrographically. Since no standards were run and no quantitative data were obtained with this method, it is difficult to fully evaluate Sterner's work.

Yudowitch (24) noticed that very strong titanium oxide bands are emitted when titanium was arced in air, and suggested a method based on measuring the intensities of these bands. The titanium metal sample was arced in a purified rare gas atmosphere, and the spectrum was recorded. However, work on this technique was abondoned when the sensitivity was found to be only 2-3% oxygen in titanium, and the usual concentration range to be covered in commercial titanium metals and its alloys is from 0.01% to 0.5% oxygen.

While this thesis investigation was in progress, Rosen (25, 26) published a procedure for the determination of oxygen in steel using a hollow cathode discharge tube. The steel sample was placed in a graphite crucible which acts as the cathode, and the discharge, which takes place in argon at a few mm. pressure, heats the crucible. Substantially the same reactions take place as those in the vacuum fusion method. The oxygen from the sample was liberated as carbon monoxide into the discharge tube, and its spectrum is recorded. The intensity ratio of one of the Angstrom carbon monoxide band heads to an argon line was then measured.

Rosen's procedure appears to have little advantage over vacuum fusion methods. The time per analysis is at least one hour and the apparatus blank appears to be considerably larger than in vacuum fusion procedures. In addition this technique retains the disadvantage of fusing the sample at a low pressure, where sputtering is more apt to take place. A special power supply for the hollow cathode is required, and the method utilizes a spectroscopic source with which very few analytical spectroscopists are familiar.

The most objectionable point in Rosen's procedure from a spectrographic viewpoint is this method of standardization. The hollow cathode tube used has provision for the excitation or more than one sample without opening the tube to the atmosphere. The carbon monoxide liberated from each sample accumulates in the excitation chamber, and intensity differences must be obtained in order to calculate the intensity contributed by a particular sample. In addition, the standards must be run on each plate along with the samples. This is necessary, according to Rosen, because of variables such as argon pressure, spectrographic slit settings, photometry, and excitation.

Rosen reported an error of approximately 10% of the amount present for triplicate analyses on two separate steel samples containing about 0.03% oxygen.

D. Possibilities for Further Spectrographic Work

The spectrographic determination of oxygen by conventional arc or spark discharges either in rare gases or in other oxygen-free gases has not been investigated. Data on the sensitivity of these excitation techniques should be obtained to indicate the feasibility of determining oxygen in this manner.

The possibility of using atomic oxygen lines rather than band emission has not been explored. In general, the atomic line spectra of the elements are usually much more intense than emission spectra of molecular combinations, hence considerably higher sensitivity seems probable. If argon were used as an internal standard as was done in Rosen's work, better internal standardization would result by using the atomic emission lines of oxygen because of the close match in excitation potentials.

In addition the excitation of metal samples in oxygen-free atmospheres by the carbon d.c. arc method should be studied. The high temperature of the supporting carbon electrode should cause reduction of the metallic oxides just as in vacuum fusion methods. The liberated carbon monoxide would be dissociated in passing through the arc and the atomic spectrum of oxygen would be excited.

IV. APPARATUS

A. Vacuum System and Vacuum Arc Stand

The vacuum system shown in Figure 1 consisted of an oil diffusion pump (No. 2) (Consolidated Vacuum Corp. VMF 20-01), a liquid nitrogen trap (No. 3) constructed of stainless steel and attached directly to the diffusion pump stack, and a one inch vacuum valve (No. 5) (Distillation Products Inc. KV-1). A mechanical pump (No. 1) (Welch #1305H) was used as the forepump in series with the oil diffusion pump. The connecting tubing (No. 4) was fabricated from 1" stainless steel pipe. The pressure of the system was monitored with a Phillip's gauge (Distillation Products Inc., model PHG01) which covers a pressure range from 25 to .01 microns (2.5×10^{-2} mm to 1×10^{-5} mm*).

The vacuum arc stand is shown in Figure 2. The design was such that it was readily constructed, easily cleaned, and capable of evacuation to at least 1×10^{-5} mm. It consisted essentially of two brass plates, one-half inch thick and six inches in diameter, and a cylindrical glass separator. A groove of suitable dimensions to accept a 4 3/4" X ¼" neoprene "O" ring was machined in one side of each of the brass plates. On the outer side of each plate a water tight compartment was fabricated to provide cooling. One plate (No. 7, Figure 1) was secured to the optical bench

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*Pressures given in this thesis are expressed in millimeters of mercury.

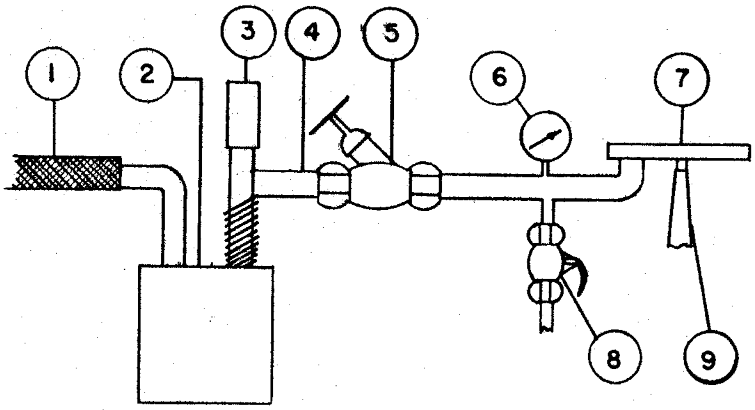

Figure 1. Vacuum System

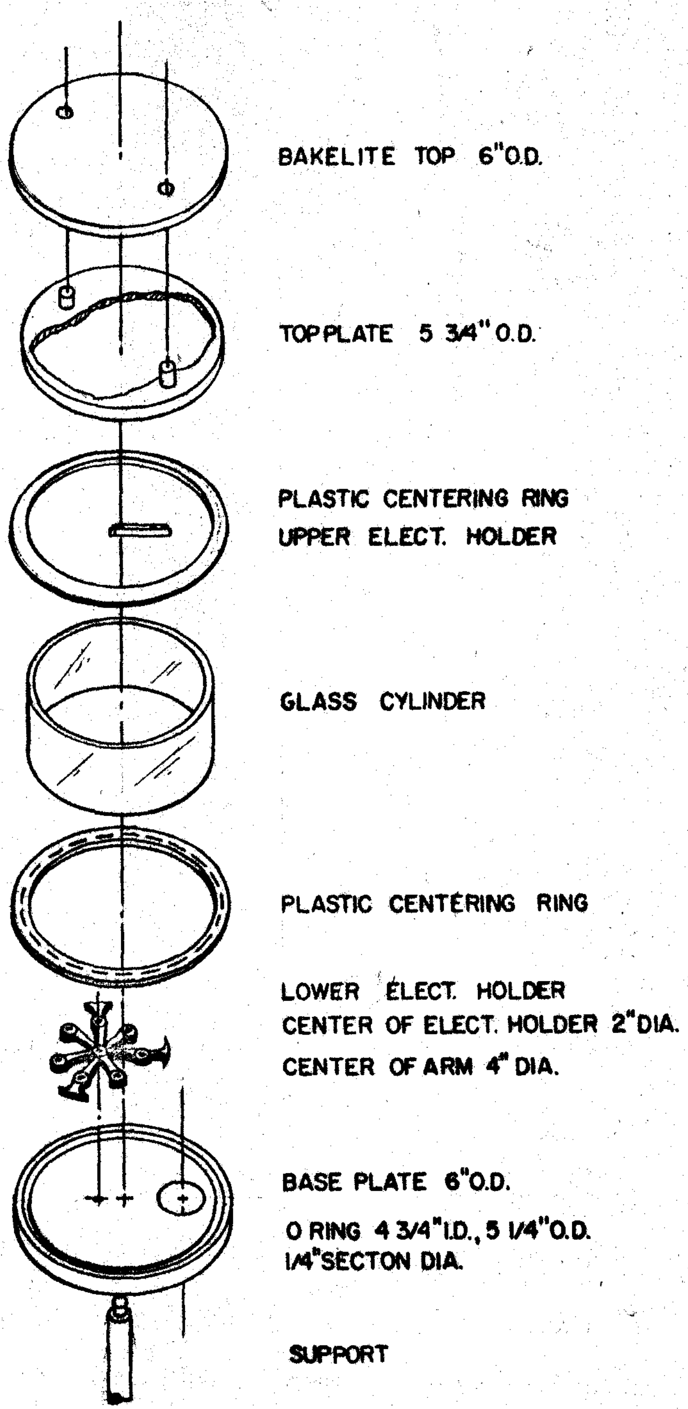

Figure 2. Excitation Chamber

by means of a suitable clamp (No. 9), and the vacuum connection was made to this plate. A two inch cylinder of 5" diameter glass (pyrex) tube was placed between the brass plates and acted as the electrical insulator and optical window. Vacuum grease was not used in the "O" ring metal to glass joint, because of the high temperatures generated during long arc exposures. For exposures near atmospheric pressure in oxygen free atmospheres, the tightness of the chamber was assured by applying pressure to the top plate of the chamber with three 5 inch "C" clamps, symmetrically spaced around the chamber. A bakelite cover was placed over the top plate of the chamber to provide electrical insulation when the clamps were used. Proper design of this cover will completely eliminate danger of electrical shock. A Bourdon dial (30 inches of Hg) vacuum gauge (No. 6, Figure 1) (Welch Scientific Co. #1431A) was installed to measure the pressure of gases introduced into the chamber. Small spring clip electrode holders served to hold the samples for excitation.

B. Gas Purification

Preliminary spectrographic examination of commercial argon, helium and hydrogen indicated the presence of considerable oxygen. Mass spectrographic analyses showed that helium was the purest of the three, containing only traces of oxygen, carbon monoxide, carbon dioxide, and water vapor, or a total oxygen content of about 0.01%. Argon had a total oxygen content of about 0.03%; and hydrogen about 0.2%.

Since the vacuum arc chamber contained about one liter of argon, or approximately two grams of argon, the presence of 0.01% oxygen in the argon would introduce 0.2 mgs. of oxygen into the chamber. If a one gram metallic sample were used for the determination of 0.1% of oxygen, this sample would contain only 0.1 mg. of oxygen. The argon atmosphere would thus contribute twice the oxygen content of the sample. For a sample containing 0.002% oxygen the argon atmosphere would contribute one hundred times the oxygen contributed by the sample. Clearly this is more oxygen than can be tolerated in the atmosphere, consequently the gases used had to be purified.

Relatively little quantitative work has been done in the ultra-purification of gases. The preferred method among workers in this field has been the use of hot metals to chemically combine with the oxygen and nitrogen impurities. Gibbs, Svec, and Harrington (27), and Newton (28) have recommended uranium turnings at a temperature of 600° C or greater for the complete removal of oxygen and nitrogen from the rare gases. Since all oxygen containing compounds are dissociated in the high energy arc or spark, thereby becoming a source of atomic oxygen line emission, provision had to be made for the removal of water vapor and carbon dioxide from the gases used.

The purification train is shown in Figure 3. It

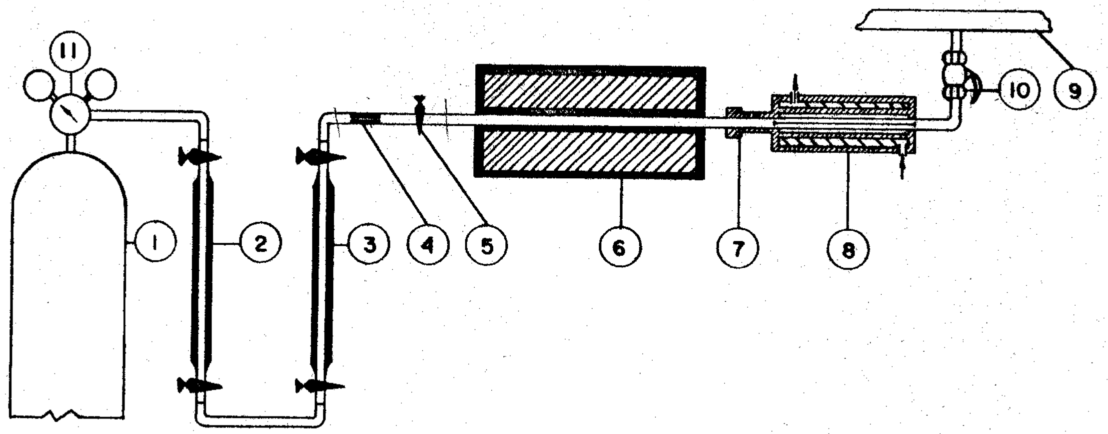

Figure 3. Gas Purification Train

consisted of a cylinder of gas (No. 1), an absorption tube containing sodium hydroxide on asbestos (Ascarite) for the absorption of carbon dioxide (No. 2), an absorption tube containing magnesium perchlorate (Anhydrone) for the removal of water vapor (No. 3), a 0.2 mm capillary to reduce the flow rate of the gas through the purification system (No. 4), a combustion tube (98% silica) packed with uranium turnings to remove molecular oxygen and nitrogen, heated by a 18" X 1 1/8" split tube furnace (Hevi Duty Electric Co.) (No. 6), a metal to glass coupler (Central Scientific Co. Cat. No. 94230) (No. 7), a water-jacketed gas cooling chamber (No. 8), and a 1/8" toggle vacuum valve (Hoke, Inc., No. 450) (No. 10, also No. 8 in Figure 1). The flow rate of the gas through the purification train was adjusted by the pressure regulator (No. 11), and was set for a flow rate of approximately two liters per minute. A high vacuum stop cock (No. 5) permitted vacuum outgassing of the uranium after recharging the combustion tube.

The water-jacketed gas cooling chamber (No. 8) permitted rapid cooling of the gas, before it passed into the arc chamber. This greatly shortened the waiting period before accurate pressure measurements could be made. This cooling chamber consisted of seven copper tubes 1/16" I.D. and six inches long, surrounded by a water tight jacket.

It will be shown later that purification by means of this system was capable of reducing the total oxygen content

Table 2. Spectrographic Equipment .

Spectrograph	Jarrell-Ash Co., 3.4 meter plane grating spectrograph Ebert mounting, using a 6 inch 15,000 line per inch grating blazed for approximately 12,000 A first order (29).
Microphotometer	Jarrell-Ash Co., Console Microphotometer, Model JA-2100.
D. C. Arc and high frequency spark source	National Spectrographic Laboratories "Spec-Power" unit, Model 22.
Over-damped 60 cycle condenser discharge	Applied Research Laboratories-Dietert Multisource (30).
Developing machine	Applied Research Laboratories-Dietert (31).

of argon to less than 0.001%.

C. Spectrographic Apparatus

The spectrographic equipment used in this investigation is summarized in Table 2.

The external optical system used to illuminate the spectrograph was designed to provide not only uniform illumination over the entire length of the spectrograph slit, but also permitted the full utilization of the spectrograph aperture even with narrow electrode gaps. A quartz cylindrical lens, 350 mm. focal length, with its axis horizontal was placed immediately over the spectrograph slit, and a 10 cm. focal length quartz cylindrical lens with its axis vertical was placed 47.2 cm. from the slit could then be projected on the collimating aperture of the spectrograph. An aperture was then made in the screen of such dimensions that if this aperture were considered a luminous source, it would completely fill the spectrograph collimating aperture with radiation. The electrodes were placed 90 cm. from the slit, and were focused on this screen with a 10 cm. focal length spherical quartz lens. This lens was placed 73.8 cm. from the slit.

This optical system permitted the external diaphragming of the continuous radiation from the incandescent electrodes, thus reducing the amount of stray light inside the spectrograph. The spherical lens and screen also served as a very convenient projection system for the alignment of the electrodes. An electric light bulb behind the electrodes was sufficient to image them upon the screen for alignment.

V. EXPERIMENTAL

A. Determination of Oxygen in Steel

1. Standard samples

Steel samples of known oxygen content were available from the National Bureau of Standards. These standards were carefully prepared and checked for uniformity by the National Bureau of Standards. The oxygen content was determined in thirty-five separate laboratories using eight different methods. The results obtained have been tabulated and carefully evaluated (5). The results for oxygen in the standards used are given in Table 3.

Table 3. Oxygen content of the National Bureau of Standards cooperative steel samples.

Standard	Oxygen Content (%)
#1	.018
#4	.002
#6	.007
#7	.106

2. Excitation of samples with a vacuum spark

In principle, the excitation of samples in a vacuum provides the simplest means of eliminating interference from atmospheric oxygen. Unfortunately, this approach is seriously hampered by experimental limitations. If spark excitation is used, voltages on the order of 100,000 volts are required to break down the analytical gap. Commercial spark sources only provide a maximum of 30,000 volts. The construction of a unit providing the required voltage presents serious insulation problems for all components of the source. Even if such a unit were available, only minute amounts of sample are volatilized by a vacuum spark. Low sensitivity would be expected, and the effect of surface oxidation would be greatly magnified.

Because of the difficulties outlined above and the failure of Sterner (23) in successfully applying this technique, further experimental investigation was postponed in favor of other approaches with greater promise of success.

3. Excitation with a vacuum arc

Direct current arcs can be maintained successfully between carbon electrodes in a vacuum of approximately 10^{-4} to 10^{-2} mm. with electrode gaps of one to four mm. (32). The arc must be struck by bringing the two electrodes together until they touch, and then slowly separating them until the required gap width is obtained. An arc of this type has the potential advantage that conditions similar to those employed in vacuum fusion are obtained. A metal sample placed in the cavity of the carbon anode attains a sufficiently high temperature to cause the reduction of the oxides by the carbon dissolved from the electrode walls. The evolved carbon monoxide can then be determined spectrographically.

To explore the possibilities of this excitation technique, the excitation chamber was modified. The upper electrode holder of the excitation chamber was attached to a vacuum bellows which was, in turn, sealed to the brass cover plate. Compression or extension of the bellows by a screw adjustment made it possible to strike the arc and adjust the electrode spacing inside the vacuum chamber.

Although vacuum d.c. arcs could be maintained, metallic samples supported in the carbon anode sputtered violently, and in a few seconds the entire inside portion of the arc chamber was coated with an evaporated metal film. The transmission of the optical window was reduced to zero in only a few seconds. The problem of observing the arc discharge in a vacuum was insurmountable, because no method was available to reduce the extremely long mean free path of the metal vapor sufficiently to keep the optical window clean. Since no data could be recorded, work on this approach was stopped.

4. High frequency spark excitation in oxygen-free atmospheres

Examination of the spectra of arc and spark discharges in air revealed that the most intense oxygen line is found at 7771.93 A. Even though the atmosphere surrounding the discharge contained 21% oxygen, the oxygen line was weak. It was, therefore, evident that every effort should be made to introduce as much sample as possible into the discharge in order to achieve sufficient intensity to detect oxygen in the lower concentrations encountered in metals.

Since little was known about the vaporization of samples by spark discharges in atmospheres other than air, exposures of steel samples were made in air, argon, helium, hydrogen, oxygen, and nitrogen. These steel samples were weighed before and after the exposure so that a comparison of the amount of sample vaporized could be made. Source conditions were: C = 0.015 uF., L = 0uH., R = 0 ohms, breaks per half cycle = 4, and secondary peak voltage = 30,000 volts.

The data in Table 4 show that approximately one milligram of sample was vaporized during a three minute exposure in argon, helium or hydrogen atmospheres compared to approximately 5.4 milligrams in air. A three minute exposure was sufficient time for the continuous background to be recorded under the line spectra, and thus was the maximum practical exposure time for ultimate sensitivity.

In order to definitely establish whether this method

Table 4. Amount of sample vaporized in various atmospheres with a high frequency spark discharge.

Atmosphere	Amount of sample vaporized per minute	Approximate relative iron line intensity
H_2	0.3 mg	1 (lowest)
He	0.3 mg	2
A	0.4 mg	5
O_2	1.9 mg	9
N_2	1.8 mg	10 (highest)
air	1.8 mg	9

of excitation provided sufficient sensitivity, the series of oxygen in steel standards were run in argon, helium and hydrogen atmospheres. For this investigation it was found necessary to carefully clean the surface of the standard, since surface oxidation resulting from the exposure of the sample to the atmosphere was readily detected. Surface preparation consisted of abrading the sample surface with a clean file followed by immersion in carbon tetrachloride. When this treatment was used, the observed oxygen intensities for even the highest available standard were no greater than the carbon electrode "blank".

5. Overdamped condenser discharge excitation in argon and hydrogen

In an effort to vaporize more sample and thus obtain better sensitivity, an overdamped condenser discharge from the Multisource unit was tried. In this unit a bank of condensers are charged to a fixed voltage, and then discharged through a series of variable inductances and resistances. The result is a unidirectional discharge that is highly reproducible.

In unidirectional discharges the question arises: which electrode polarity will provide maximum sample volatilization? Several investigators have shown from high speed photography (33) that volatilization occurs almost entirely from the negative electrode in spark-like discharges. It is postulated that sample volatilization takes place through positive ion bombardment causing intense localized heating of the electrode surface. This suggests that maximum volatilization with a spark-like discharge should occur when the sample specimen serves as the cathode. To confirm this prediction, steel samples were excited in air, argon, and hydrogen, and the change in weight was observed. The discharge conditions were; V = 940 volts, C = 60 ufd., L = 400 uH., R = 5 ohms, T = 2 minutes. The results are summarized in Table 5.

The gain in weight of the anode in the case of air was attributed to the formation of Fe_2O_3. The presence of Fe_2O_3 was apparent from the bright red color of the oxide.

The overdamped condenser discharge in an atmosphere of argon covers a relatively large area without deep penetration of the specimen. In hydrogen, however, a localized

Table 5. Amount of sample vaporized as anode and cathode with a unidirectional discharge.

Atmosphere	Weight Change Anode (mg.)	 Cathode (mg.)
air	+2.9	- 8.1
A	0.0	-25.4
H_2	0.0	-28.4

crater approximately 2 mm. deep was formed. This surface penetration should help to minimize the effect of surface oxidation on analytical results. The crater formation in hydrogen was possibly due to a chemical reaction between the iron and hydrogen. An attempt to verify this hypothesis was made by examination of the emission spectrum for Fe-H bands in the region of 4288 A, but no band system could be found.

Table 6 summarizes the results of extended determinations of the amount of sample vaporized from steel cathodes in various atmospheres. The discharge conditions were the same as those used in the previous study. The data in Table 6 show that relatively large amounts of sample were volatilized in hydrogen and argon atmospheres. However, line to background measurements obtained from duplicate exposures of the standard samples showed that the sensitivity of detecting oxygen was approximately 0.06% for argon and 0.02% for hydrogen atmospheres. When oxygen concentrations above

Table 6. Amount of sample vaporized with an overdamped condenser discharge in various atmospheres.

Atmosphere	Sample vaporized (mg.)	Approximate relative intensity of iron lines
H_2	28.4	5
A	25.4	10
O_2	17.2	10
N_2	1.1	9
air	8.1	8

this figure are encountered, this excitation technique should prove useful. However, a sensitivity of 0.002% was sought for the determination of oxygen in steel.

It was impossible to use a helium atmosphere as the supporting atmosphere in the experiments, because the excitation unit overloaded the protective circuit breaker. Stone (34) had a similar experience and postulated that the overloading of the unit was due to:

> ...the comparatively large energies (ca. 20 electron volts) of the ionized helium in the spark. Theory predicts that if the energy of an ion is greater than twice the work function of the electrode surface, when a collision between an ion and the surface takes place, two electrons may be liberated from the cathode. The high currents produced by this effect cause the automatic circuit breaker in the power source to turn the power off. The addition of a few per cent of oxygen to the helium stabilizes the spark, probably quenching the ionization chains formed.

This explanation does not seem plausible when one examines the electrical circuit of the Multisource unit. In this unit the charge and discharge phases of the power condensers are electrically isolated. The protective circuit breaker is in the charging circuit, hence it can only be overloaded in charging these condensers, not in discharging them as Stone postulates. It is more probable that the charging circuit is overloaded because of the slower decay of the ionization in the analytical gap. Should the gap remain conductive for longer than approximately 5×10^{-2} seconds, a direct path is provided to ground for the charging current. Since the gap then has a low resistance, large currents will be drawn causing the circuit breaker to overload. One would expect a slower decay of ionization in helium than in other gases, because of the metastable triplet state, which is approximately 17 e.v. above the ground state. Helium in this metastable state could supply energy through collisions of the second kind for ionization after the condenser has discharged.

6. Direct current arc in helium

When the intensities of the oxygen lines were observed in the spectra of d.c. arc discharges in air, argon, helium, and hydrogen atmospheres anomalous results were obtained. Exposures of an iron arc discharge in air produced no oxygen lines, and in a carbon arc discharge only very faint oxygen lines were detected, even though the atmosphere surrounding the arc contained 21% oxygen. In contrast, d.c. carbon arc exposures in helium containing less than 0.05% oxygen produced very intense oxygen lines. Similarly d.c. arc exposures in argon and hydrogen containing comparable amounts of oxygen produced strong oxygen lines, though not so intense as in helium.

In order to even partially explain such seemingly inconsistent results, it must be realized that the d.c. arc is a thermal source. That is, the excitation energy is primarily derived from the kinetic energy or temperature of the particles in the arc gap.

The relationship between a given spectral line intensity and the kinetic temperature of the particles in the gap is given by the equation:

$$I \propto N P \varepsilon^{-\frac{\Delta E}{kT}}$$

where:

I = is the intensity of the spectral line.

N = is the number of atoms per unit volume.

P = is the transition probability of the transition giving rise to the spectral line.

E = is the energy above the ground state of the transition giving rise to the spectral line.

K = Boltzmann's constant.

T = is the absolute temperature.

The energy distribution curve of these particles in the gap closely approximates a Boltzmann distribution curve and the peak of this curve is shifted to higher or lower energies depending upon the nature of the atoms or molecules in the gap. Semenova (35) measured arc temperatures spectrographically for iron and carbon arcs in air and found a temperature of 5500° K and 7700° K respectively. Thus higher energies exist in a carbon arc than in an iron arc. This higher temperature accounts for the increased intensity of the oxygen spectrum in the case of the carbon arc. Since arc temperature measurements are not available for other atmospheres, an adequate explanation of the enhancement of the oxygen spectrum intensity can not be given. However this enhancement seems reasonable when the case of a carbon arc in helium is considered. The ionization potential of the helium is 24.5 e.v., and the first excited state requires 17 e.v. for excitation. Contrasted to this is the case of an iron arc in air. In this instance energy can be dissipated by the excitation and ionization of iron, the dissociation of nitrogen and oxygen, and the excitation of C-N and N-O molecules, all of which require less than 8 e.v. A lower average excitation energy would certainly be expected.

Because maximum oxygen line intensities appeared to be obtained in helium, it was appropriate to investigate the excitation behavior of actual steel samples in a helium atmosphere. If a steel sample were placed in a carbon electrode and arced so that sufficiently high electrode temperatures were obtained, reduction of the oxides in the steel sample should occur. The conditions found successful by vacuum fusion workers would be essentially duplicated. The evolved carbon monoxide would be confined inside the chamber, and it could then be determined by excitation with the same discharge used for the reduction process.

In order to obtain, simultaneously, data on the behavior of the electrode system at various arc currents and the course of events in the discharge, a series of moving plate studies were undertaken. In the moving plate technique the photographic plate is moved at regular intervals, in this case every thirty seconds, so that the variation of the spectrum intensity with time can be observed. The spectrum intensity changes that occur can then be interpreted as a change in the concentration of the radiating species as a function of time, or as changes in the excitation temperature of the discharge as various atomic or molecular species are introduced.

For these studies, one gram specimens of the 0.106% oxygen in steel standard were placed in electrodes of the type shown in Figure 4. At 5 amperes the fusion was not complete; however, the oxygen spectrum obtained persisted for the entire three minute exposure. At 7½ amperes the sample completely fused, but the oxygen spectrum persisted only 30 seconds, after which a strong iron spectrum was obtained. At higher currents a good fusion and a strong iron spectrum

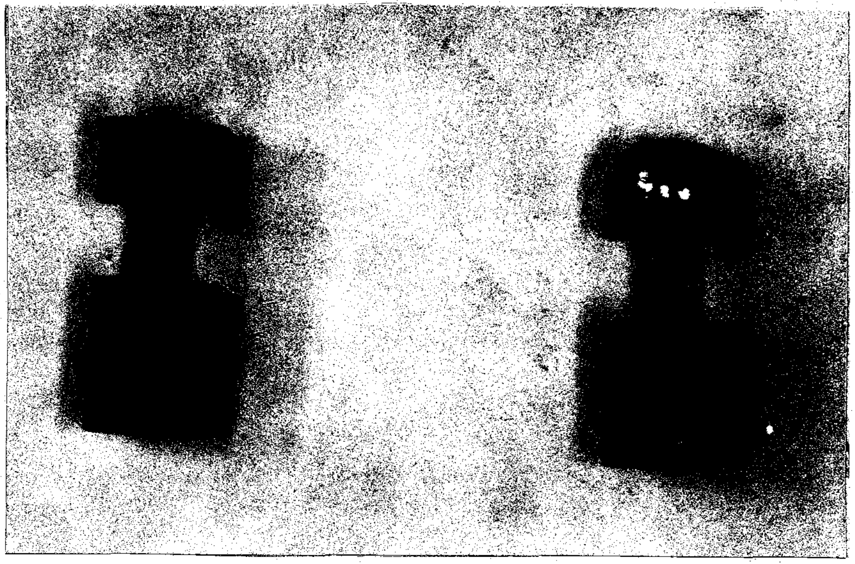

Figure 4A. Empty and Properly Fused Electrode.

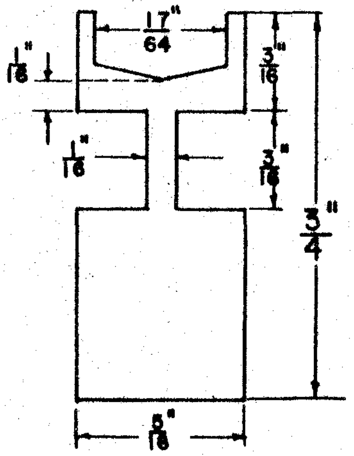

Figure 4B. Lower Electrode Used for the Determination of Oxygen in Steel.

was obtained but little or no oxygen spectrum. A photograph of an empty electrode and of an electrode in which the sample has been properly fused is shown in Figure 4A.

Apparently the intensity of the oxygen spectrum was dependent upon the amount of iron vaporized, either because the iron vapor lowered the excitation level of the arc and thereby reduced the efficiency of the oxygen excitation, or because the finely divided, vaporized iron recombined with (gettered) the oxygen and permanently removed it from the discharge zone. This question was answered by the results of a moving plate study shown in Figure 5C. From this figure it was apparent that the effect of iron on the oxygen intensity was caused primarily by the lowering of the excitation power in the gap. When the iron concentration in the gap increased, the oxygen intensity decreased. "Gettering" action must have played a minor role, because the oxygen intensity was restored to its initial value near the end of the exposure when the iron concentration in the gap was again a minimum.

Data obtained from integrated exposures at 4, 6, 8 and 10 amperes supported these conclusions. As the arcing current was increased, the iron intensity increased, while the oxygen intensity decreased correspondingly. Data from this experiment are shown in Figure 6. Two other significant conclusions can be made from Figure 5. First, iron would be

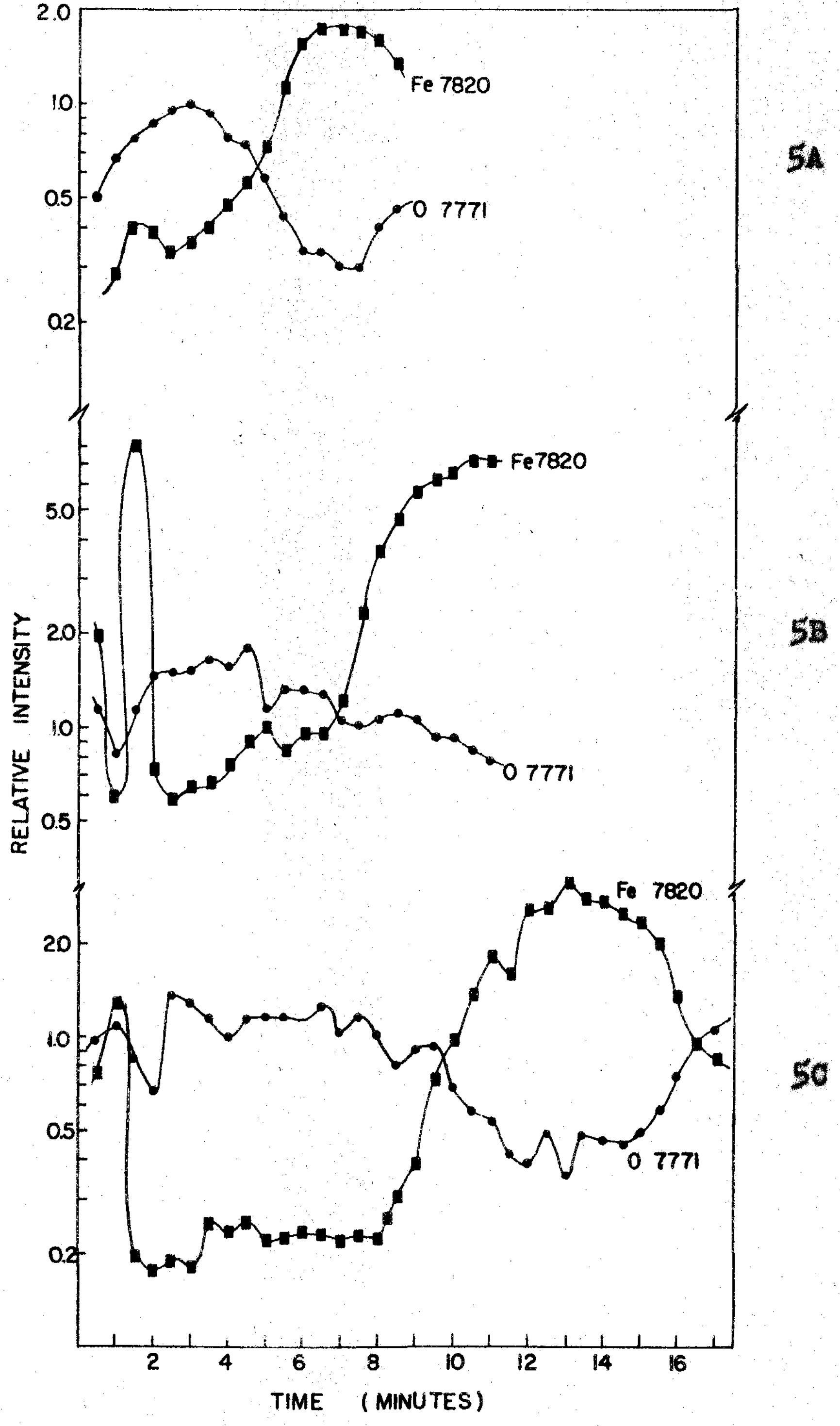

Figure 5. The Variation of the Relative Intensities of O 7771 and Fe 7820 with Time.

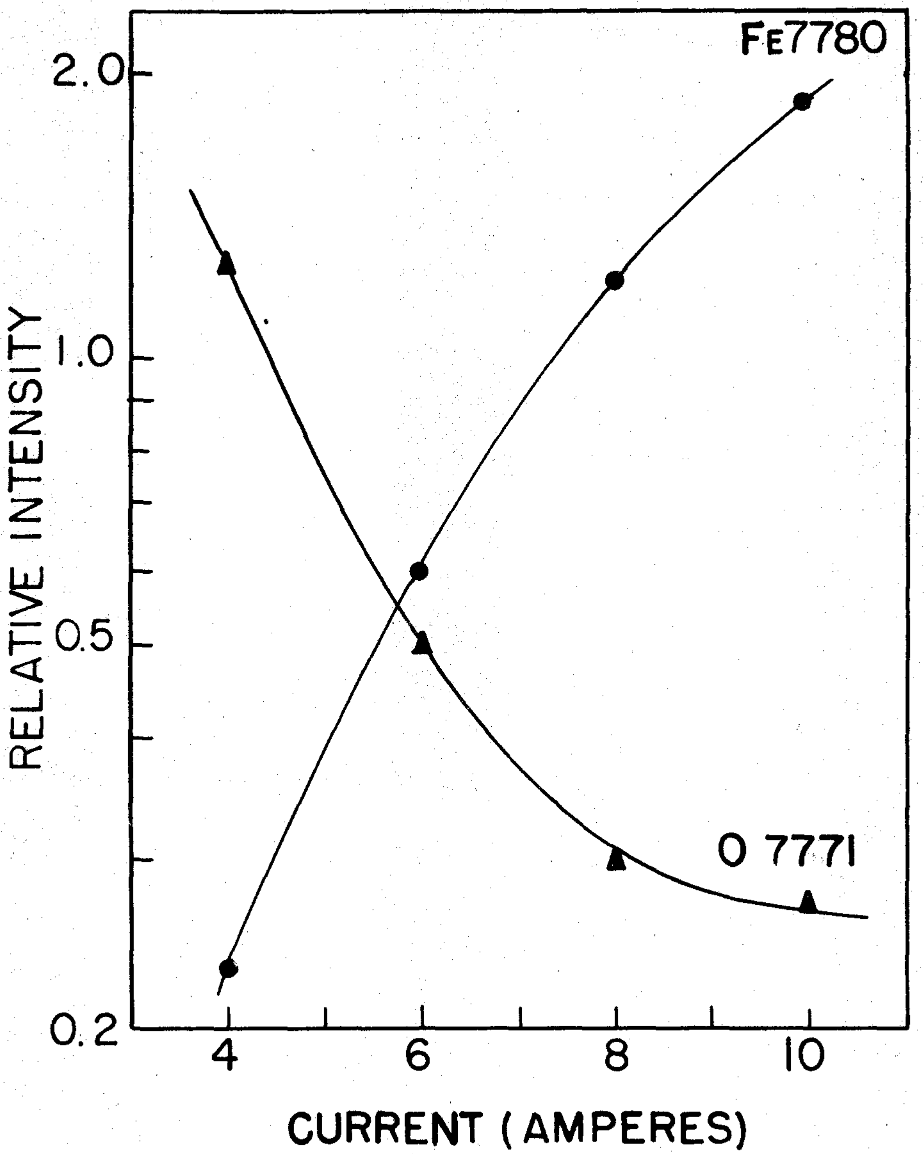

Figure 6. The Variation of the Relative Intensity of O 7771 and Fe 7780 with Arcing Current.

most unacceptable as an internal standard, because the intensity of the iron spectrum does not closely parallel the intensity of the oxygen spectrum with changes in excitation conditions. Instead, there appears to be an inverse relationship.

Second, the three moving plate studies shown in Figure 5, although made under identical exposure conditions, with the exception of overall time, indicated that the widely varying oxygen intensities could not have been integrated into reproducible relative intensities. This point was verified when the standard samples were exposed in triplicate at 7½ amperes. The data were so erratic that quantitative calibration could not be made.

During these experiments severe bubbling of the 0.106% oxygen in steel standard was noticed for the first 30 seconds of an exposure. After the initial "bubbling" period the sample ran very smoothly. A simple calculation for a one gram sample containing 0.1% oxygen showed that 10.3 ml. of carbon monoxide would be released at the electrode temperature (2000° K). Since this amount of gas could account for the violent bubbling action, it was felt that the oxygen was released from the sample within the first 30 seconds under these conditions.

The experimental data summarized above showed rather conclusively that the oxygen intensity was dependent on the amount of iron volatilized. It was impossible to control the amount of iron volatilized even in successive samples under identical conditions. This was indicated in the moving plate studies shown in Figure 5.

An element whose spectrum would behave in a manner very similar to the oxygen spectrum with changes of excitation in the gap was clearly needed for an internal standard. Argon appeared to fill this need, because its spectrum has some lines with excitation potentials similar to the oxygen 7771 A line. Since the oxygen was liberated so swiftly into the chamber atmosphere, the ratio of oxygen to argon rapidly assumes a constant value. A spectrographic determination of the oxygen in the chamber atmosphere should then be a good indication of the original oxygen present in the sample.

7. Direct current arc in argon

Vallee, *et al*. (22, 36), observed that the electrode temperature of a d.c. carbon arc in argon was much lower than in air and helium. This suggests that much higher currents would be required to achieve electrode temperatures sufficiently high to cause reduction of the metallic oxides by the carbon of the electrodes. Confirming data as shown in Table 7 were obtained by measuring electrode temperatures with an optical pyrometer (Leeds and Northrup Cat. No. 8622-C) at various arc currents in both argon and helium. Because of the high electrode temperatures required the undercut electrodes shown in Figure 4 were used. The constricted portion of these electrodes reduced heat conduction

Table 7. Electrode temperatures at various currents in argon and helium.

Arc current (amperes)	Carbon arc in argon (°C)	Carbon arc in helium (°C)
5	838	1375
10	1038	1610
15	1385	2150
20	1650	2310
25	1665	2400
30	1760	2490
35	1827	2590

so that the cavity attained a much higher temperature.

An arc current of twenty amperes was selected for use in the argon atmosphere, since this produced approximately the same temperature (1650° C) which was successful in an atmosphere of helium. A temperature of 1650° C was also recommended by vacuum fusion workers (9) for the determination of oxygen in steel. The actual temperature of a molten steel standard in a carbon electrode at an arc current of twenty amperes was found to vary between a maximum 1700° C at the anode spot and a minimum of 1460° C at the base of the electrode cavity.

A moving plate study of the carbon arc excitation of a sample of the 0.106% steel standard in argon showed the high degree of internal standardization achieved with argon lines. As shown in Figure 7, the relative intensity of the argon and oxygen lines closely parallel one another, even when large changes occur in the amount of iron vaporized. A plot of the oxygen to argon intensity ratio yielded an almost linear curve indicating that the internal standard adequately compensated for variations in excitation conditions within the analytical gap. Consideration of wave length proximity, similarity of excitation potential, and line intensity dictated the choice of the argon 7891.07 A line as the internal standard.

Preliminary calibration experiments revealed an oxygen blank equivalent to about 400 ppm. oxygen in steel. The possible sources of this blank which came to mind were: (a) oxygen or oxygen containing compounds adsorbed on the walls of the excitation chamber (hereafter called "chamber blank"), (b) oxygen content of the argon gas, (c) oxygen content of the graphite electrodes, and (d) surface oxidation of the standards. The relative importance of these possible sources was then evaluated by suitably designed experiments.

The magnitude of the "chamber blank" should be reduced by the outgassing technique commonly used in high vacuum operations, i.e., subjecting the vacuum container to high temperatures while evacuating. This outgassing operation was approximated by arcing a pair of carbon electrodes eight consecutive times at a high current (35 amperes) and immedi-

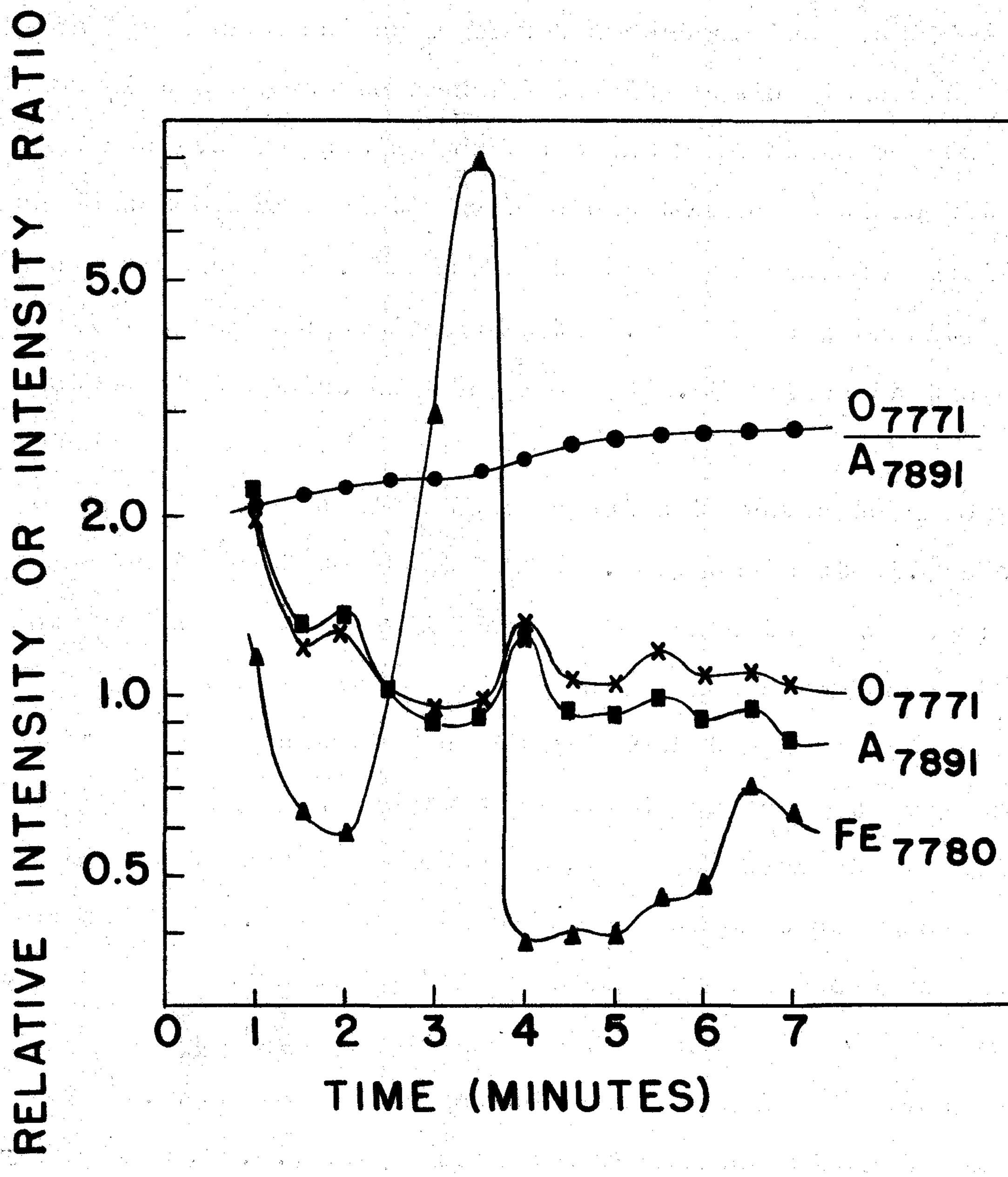

Figure 7. The Variation of the Oxygen, Argon and Iron Intensities with Time.

ately evacuating the chamber after each arcing. The chamber was not watercooled during this operation. The chamber was then refilled with argon and the above operation repeated. Figure 8A shows graphically the results obtained from experiments of this nature. The reduction in blank obtained by successive excitation reflects the reduction of the "chamber blank" plus the probable liberation of any oxygen impurities from the electrodes. The ultimate values obtained (flattening of the curves in Figure 8) was a direct measure of the purity of the argon gas and in the case of Figure 8A, was equivalent to 50 ppm. of oxygen in steel. Smiley (18) recommended the use of Ascarite and Anhydrone absorption tubes in addition to heated uranium turnings for the purification of argon. Since previously only heated uranium turnings were used, this addition was made. Figure 8B shows that this addition reduced the argon blank ten fold, down to a value equivalent to approximately 5 ppm. oxygen in a steel sample.

The results of this experiment suggested that it would be advisable to employ a rotary electrode assembly which could accommodate six sample electrodes and one additional electrode for outgassing purposes. The same counter carbon electrode could be used throughout because of the low carbon consumption in argon. In this way one outgassing would serve for six samples. This rotary electrode holder consisted of a seven spoke disc with each spoke containing a clamp for

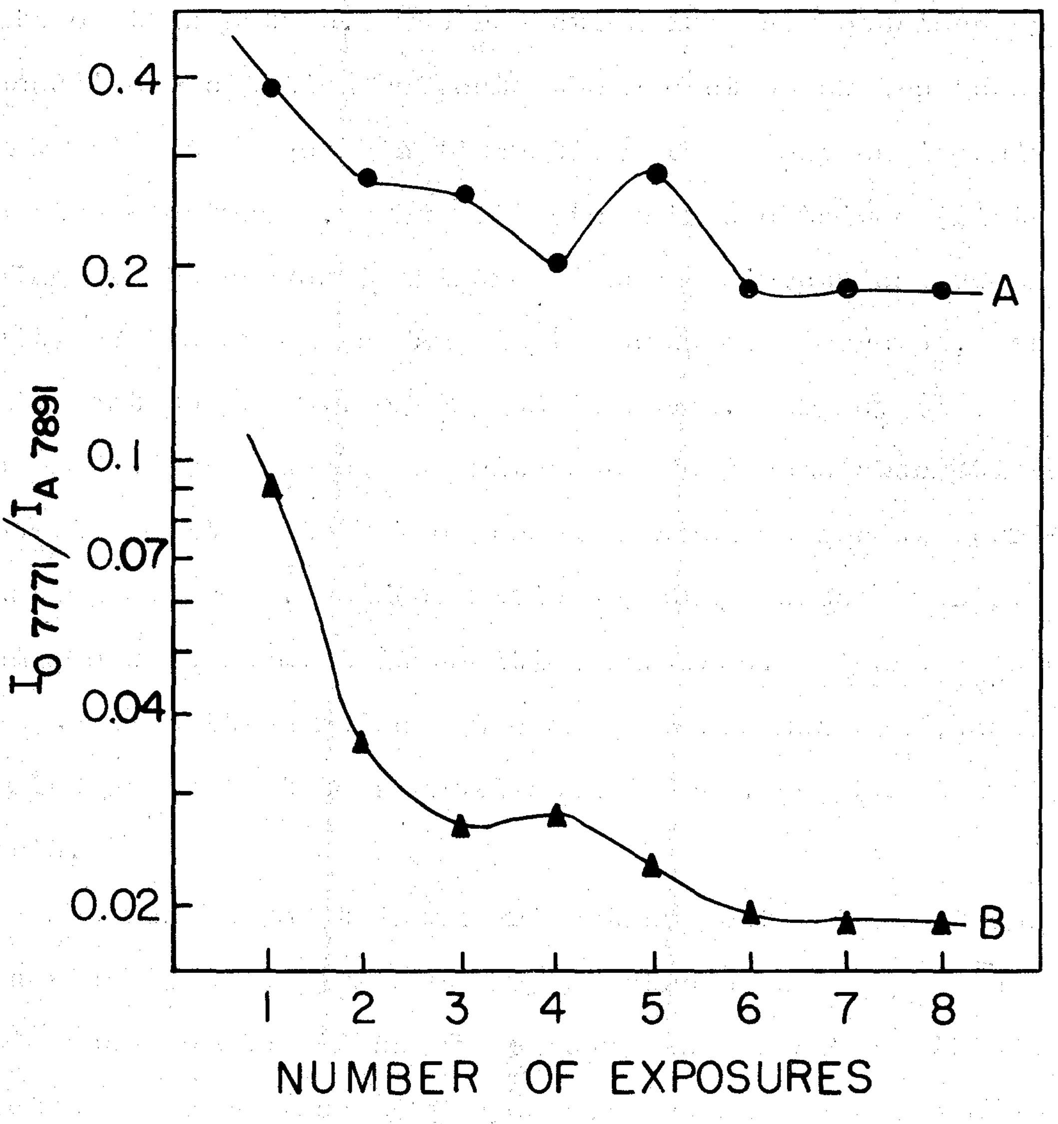

Figure 8. Outgassing of the Excitation Chamber by Consecutive Arcings of Carbon Electrodes.

holding one electrode. Rotation of this disc with the aid of a small magnet made it possible to bring the various electrodes into the optic axis without opening the chamber.

With this multiple electrode system it was now possible to evaluate the oxygen content of the graphite electrodes. After thoroughly outgassing the chamber, the following electrodes were arced; (a) an untreated electrode, (b) an electrode which had been prearced at 35 amperes for 3 minutes, and (c) an electrode which was heated to 1000° C for 4 hours in a vacuum of 1×10^{-6} mm. The average results from six such experiments are summarized in Table 8.

Table 8. Oxygen content of treated electrodes.

Electrodes	Blank (equivalent per cent oxygen in steel samples)
Untreated electrodes	0.0056 *
Prearced electrodes	0.0036 *
Vacuum outgassed electrodes	0.0026 *

*It should be noted that the values quoted included the chamber and argon blank, which were previously shown to be at least 0.0005%.

The data in Table 8 clearly show that the lowest blank was obtained with vacuum outgassed electrodes. Such electrodes can be outgassed in quantity and stored in a vacuum until use.

The blank contributed by surface oxidation of the standards was difficult to evaluate, but judging from the results obtained from other workers (9, 17) using the vacuum fusion technique this value must be negligible. The samples had a low surface to volume ratio and retained their bright surface during their short exposure to air.

Since argon was to be used as the internal standard, it was necessary that: (a) the oxygen in the sample be completely volatilized before the exposure was begun, and (b) that the number of moles of argon admitted into the chamber be reproducible.

Evidence obtained from Figure 7 indicated that substantially all of the oxygen was liberated from the sample within one minute. Further proof of this was obtained by exciting the 0.106% oxygen standard for one minute at twenty amperes, evacuating the gas evolved, refilling the chamber with pure argon, and then rearcing the same sample for three minutes, recording photographically only the last two minutes. A value of 0.0030% was obtained as the amount of oxygen remaining after a one minute arcing. This compared within experimental error with a blank of 0.0026% found when empty electrodes were arced.

The number of moles of argon admitted into the excitation chamber may be reproduced by maintaining an established pressure, volume and temperature. The volume of the chamber was kept constant by replacing the glass separators, when necessary, with others of identical dimensions. The temperature of the chamber and the gas were kept within narrow limits by watercooling the chamber and passing the hot argon gas from the purification train through a watercooled heat exchanger. Temperature fluctuations of 3° C were permissible, since this introduced an error of only 1% in the quantity of argon present. Pressure measurements with a Bourdon gauge could be readily made to within 1%. A mercury manometer could have been used, but the higher precision obtainable was not necessary and in addition, the manometer lacks the compactness, convenience and ruggedness of the Bourdon gauge.

Sample preparation consisted of sawing strips 3/16 inch X 3/16 inch X 2 inches from each of the National Bureau of Standards standards. Samples weighing approximately one gram were cut from these strips. The samples were cleaned with a small file until smooth and bright. Any grease was removed with carbon tetrachloride. The samples were then accurately weighed and stored in a vacuum until used.

The four National Bureau of Standards oxygen in steel standards were then exposed in sextuplicate under the conditions shown in Table 9. The data obtained are presented in

Table 10, and the background corrected analytical curve is presented in Figure 9. If the data from this analytical curve are plotted on a linear coordinate scale, Figure 10, it is seen that an intensity ratio of 0.155 remains when the curve is extrapolated to zero concentration. This intensity ratio was due to the oxygen contribution of the blank. If another line is drawn parallel to the first, and passing through the origin, a true relationship between oxygen concentration and intensity ratio is obtained. The intensity ratio of 0.155 corresponds to an average oxygen blank of 0.0031% under these conditions. This value compared very favorably with the 0.0026% obtained when empty carbon electrodes were exposed.

The precision of this method for determining oxygen (approximately 6%) is very satisfactory at higher concentrations, but becomes poorer for the 0.007% and 0.002% standards (approximately 12%) because of the comparatively large (0.0032%) and erratic blank. It should be possible to reduce this blank further and recommendations for doing this are given in section VI . However, even with a blank of this magnitude this method appears more precise than any previously reported.

It has been shown that the gases adsorbed on the surfaces of the excitation chamber make the largest contribution to the overall blank. This blank can be minimized by adhering to experimental details. When the chamber is not in use,

Table 9. Operating conditions of obtaining calibration data.

Line pair	O 7771.928 A 7891.075
Weight of sample	Approximately 1 gm. (The measured oxygen concentration may be corrected to a 1.000 gram sample by dividing the measured intensity ratio by the actual sample weight.)
Type of Electrodes Anode	(United Carbon Co. Grade U-2). Undercut 5/16" graphite as shown in Figure 4.
Cathode	1/8" diameter graphite, 1" long with a 120° point.
Argon pressure	640 mm. reproduced to 1%.
Excitation source	300 volts d.c., 20 amperes.
Length of exposure	1 minute prearcing plus 2 minute exposure.
Analytical gap	6 mm.
Emulsion	Eastman 1-N
Wave length photographed	7100-8400 A, 1st order
Filter	Corning 2.63
Slit	0.05 mm.
Development	4 minutes at 21° C in Eastman Kodak D-19 with continuous agitation.
Emulsion calibration	Two step sector, preliminary curve method.

Table 10. Calibration data for the determination of oxygen in steel.

Standard $\%O_2$	Intensity ratio I_O 7771/I_A 7891	Mean I_O 7771/A 7891	Percent deviation from mean
0.106	5.18	4.76	8.8
	4.68		1.7
	4.28		10.0
	4.89		2.7
	4.78		0.4
	4.78		0.4
Average per cent deviation from mean = 4.0			
0.018	0.897	0.877	2.3
	0.923		5.2
	0.837		4.6
	0.797		9.1
	0.823		5.2
	0.984		12.0
Average per cent deviation from mean = 6.4			
0.007	0.479	0.462	3.7
	0.426		7.8
	0.507		9.7
	0.503		8.9
	0.430		6.9
	0.426		7.8
Average per cent deviation from mean = 7.5			
0.002	0.246	0.250	1.6
	0.313		25.0
	0.211		15.0
	0.275		10.0
	0.237		5.2
	0.216		14.0
Average per cent deviation from mean = 12.0			
Overall average percent deviation = 7.5			

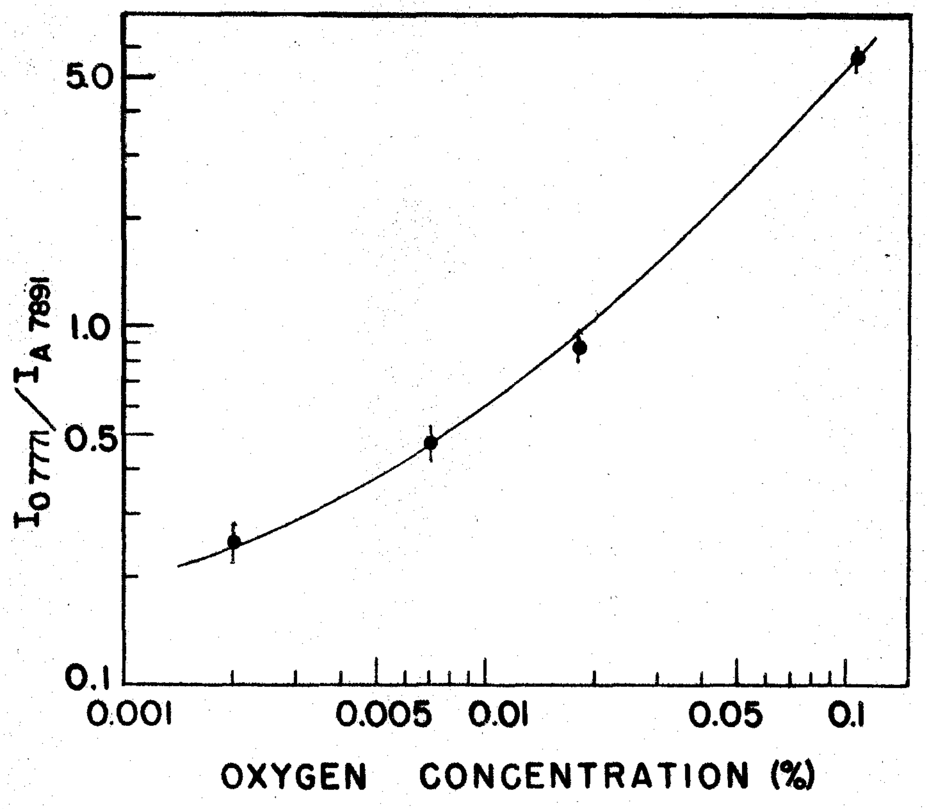

Figure 9. Analytical Curve for the Determination of Oxygen in Steel.

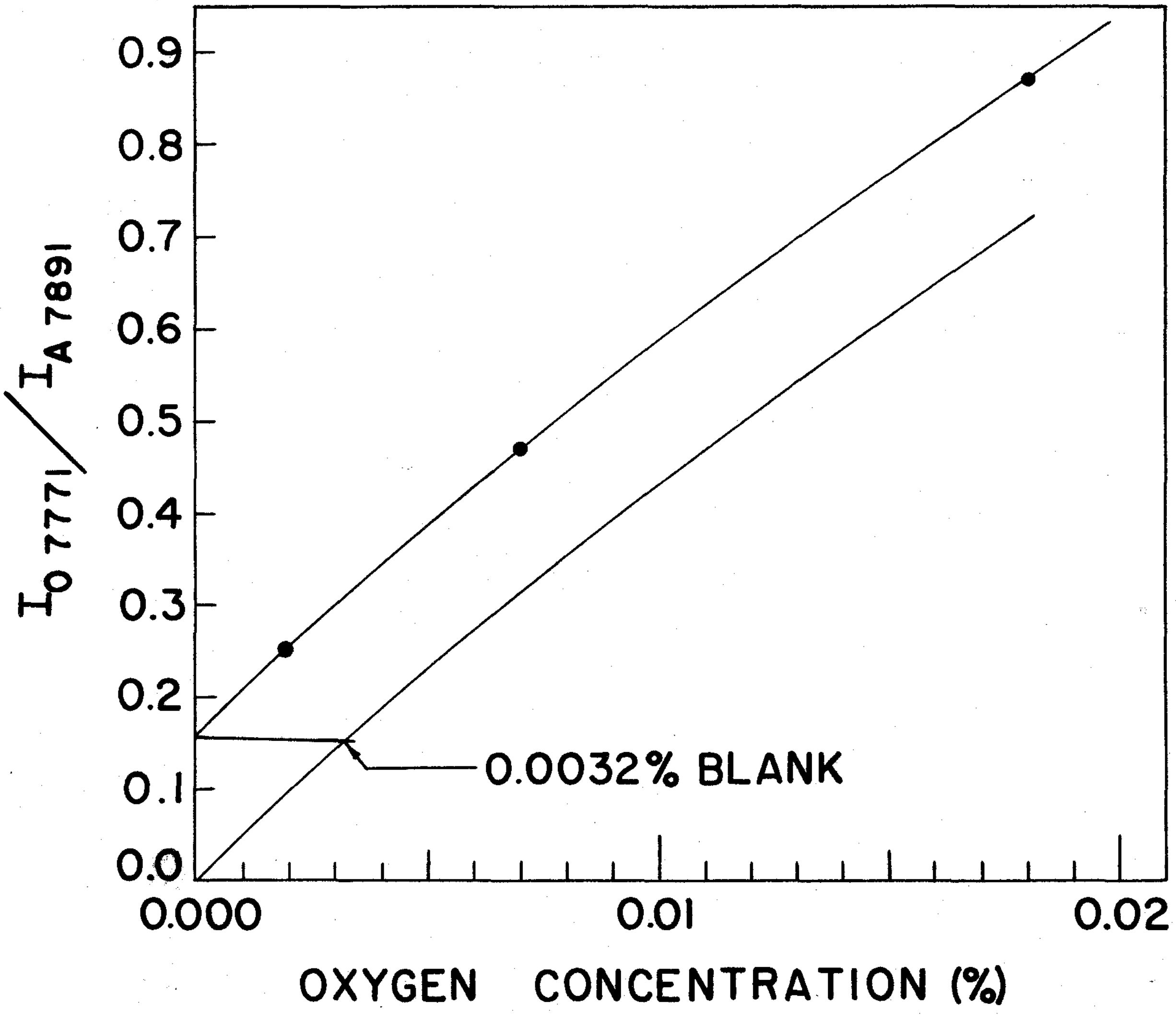

Figure 10. Coordinate Blank Determination Plot for Oxygen in Steel.

it should be evacuated or filled with argon. Before the chamber is opened to the atmosphere, a 35 ampere arc should be operated for about three minutes to heat the chamber surfaces, since smaller quantities of atmospheric gases are adsorbed on hot surfaces. A high degree of chamber outgassing is achieved by simply pulling a high vacuum, hence a vacuum of at least 2 X 10^{-5} mm. is obtained before any outgassing is attempted. Finally, three "outgassing", 35 ampere, d.c. carbon arcs should be run in sequence at reduced pressures (120 mm.) with intervening pumping out of the chamber to further reduce the blank before any exposures are made.

In order to evaluate the blank an exposure recording the blank arising from the chamber and the argon was made at the start and finish of each set of exposures. This was accomplished by arcing the outgassing electrode under the same conditions used for the excitation of the samples.

B. Extension of the Spectrographic Method of Determining Oxygen to Other Metals

1. Preparation of standards of known oxygen content

The extension of this method to the determination of oxygen in other metals required the preparation of standards with known oxygen contents. This same problem has been encountered by vacuum fusion analysts who have employed two different methods: (a) the addition of oxide to a metal sample, and (b) the reaction of molecular oxygen with the metal sample.

The method of adding a known weight of oxide to a metal sample is generally used for the preparation of bulk metal standards and entails insuring sample homogeneity. The sample is usually melted in a vacuum several times but even so comparison of the oxygen content of various portions must be made.

Individual standards of the more reactive metals can usually be prepared conveniently by placing a given weight of gaseous oxygen in a reaction chamber together with a known weight of a metal. At a sufficiently high temperature, the oxygen will react completely with the metal. Samples prepared by this procedure certainly are not homogeneous, and thus can only be used when the oxygen from the entire sample is consumed. Samples of some metals prepared in this fashion can be made homogeneous, however, by prolonged annealing at a temperature slightly below the melting point of the metal.

This second approach was adopted as the most versatile and convenient. The sample preparation apparatus is shown in Figure 11. It consisted of an oil diffusion pump (B) (National Research Corp. H-2-P) backed by a mechanical vacuum pump (A) (Welsh 1405-H), a 3/4 inch homemade vacuum valve (C), a 3/8 inch vacuum valve (D) (Hoke, Inc. #445), a thermocouple vacuum gauge (E) (Distillation Products TG-02),

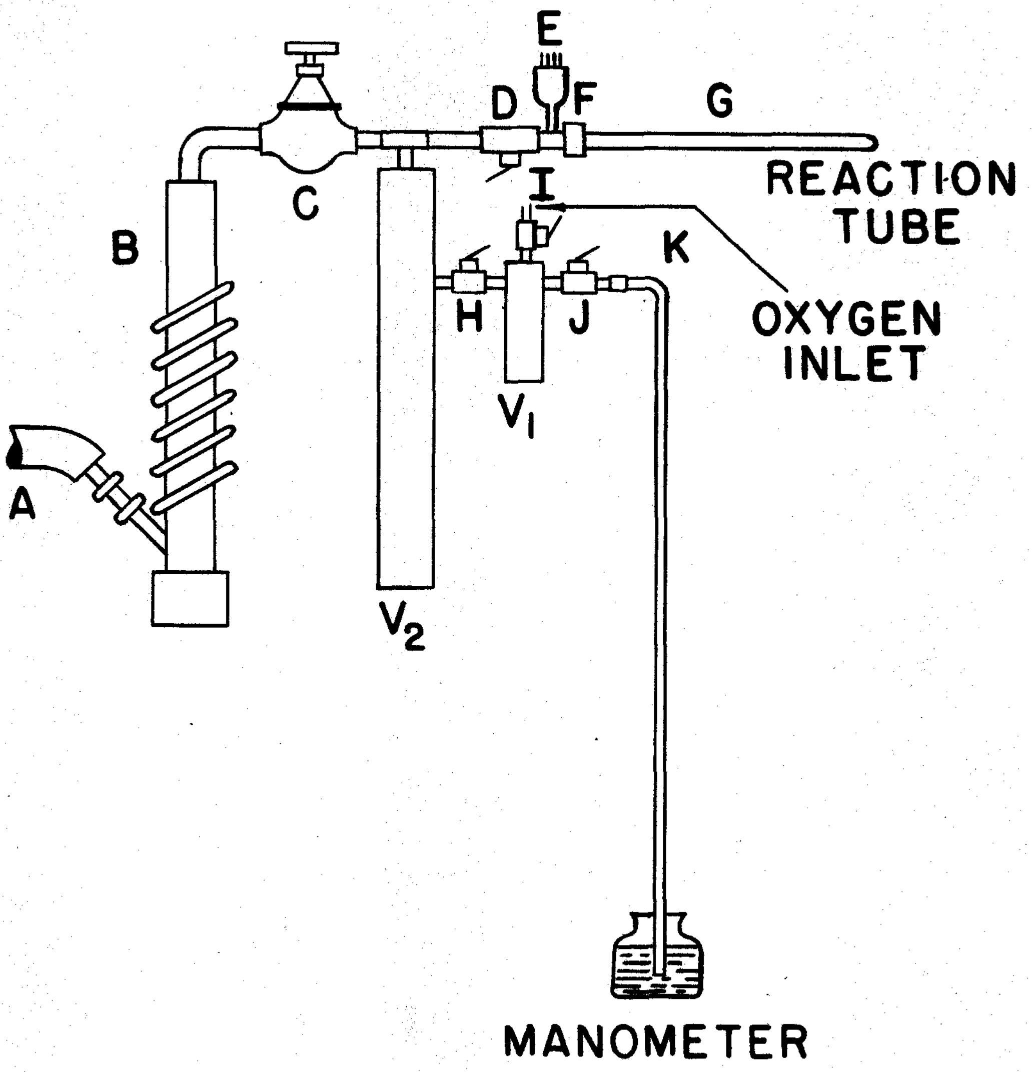

Figure 11. Standard Preparation Apparatus.

a metal to glass coupler (F) (Central Scientific Co. Cat. #94230), a silica reaction tube (G) 13 mm. X 12 inches, volumes V_1 (approximately 900 ml.) and V_2 (approximately 100 ml.), 1/8 inch vacuum valves (H, I, and J) (Hoke, Inc. #450) and a mercury manometer (K) constructed from 1 mm. bore capillary tubing.

Since 100 mm. of pressure can be read with ten times the accuracy of 10 mm. using the same manometer, expansion volume (V_2) was used to permit higher accuracy to be obtained in measuring the low pressures required for the preparation of low oxygen standards. This was accomplished by adding oxygen at a higher pressure to V_1, then expanding the gas into V_2 plus the reaction system (G plus F plus E) to give the lower pressure required.

Calibration of the volumes V_1, the reaction system (G plus F plus E), and V_2 plus the reaction system was accomplished by expanding a known volume of gas into the various components and noting the pressure change. The maximum standard deviation for this calibration was only three parts per thousand, which was well within the needed accuracy.

The operation of this apparatus was very simple. Knowing the volume of the reaction system, (that portion isolated by valve D) the pressure of oxygen to be added was calculated from the ideal gas law. If this pressure was more than 100 mm. (which could be read to 1 mm. or 1%) the oxygen was added directly to the reaction system by closing only valve C and measuring the pressure on the manometer (K). After the gas had been added, the reaction system was isolated by closing valve D. If the pressure required was less than 100 mm. greater accuracy was obtained by using the expansion volume. The required pressure was multiplied by the ratio of the volume V_1 plus V_2 plus the reaction system to the volume of V_1. This pressure of oxygen was added to V_1. When this gas was expanded into V_2 plus the reaction system, the desired pressure of oxygen was obtained. The reaction chamber was then isolated by the valve D.

A small tube furnace was placed around G and heating was continued until the residual pressure, as shown by the thermocouple gauge, was insignificant in comparison to the added oxygen pressure. Typical reaction times were from 5 to 15 minutes for the addition of 0.1% oxygen to a gram of zirconium or lanthanum.

2. Determination of oxygen in lanthanum

Because of their very high affinity for oxygen, all of the rare earth metals must be prepared and handled either in a vacuum or rare gas atmosphere. Even though many precautions are taken in the production of this metal, the oxygen content is commonly greater than 0.03% (37). Standard preparation is readily accomplished with the apparatus described because of the high reactivity of the metal.

All attempts at the direct reduction of a lanthanum metal standard in a carbon electrode failed. However, a successful vacuum fusion approach (37) to this problem involved the use of a nickel bath containing approximately 30 per cent lanthanum and a reduction temperature of 1900° C. These conditions were approximated in the spectrographic method by machining a nickel cup 3/8 inch O.D. by 1/4 inch high and having a 1/4 inch I.D. cavity drilled 1/8 inch deep. The weight of such a cup was approximately 1.8 gm. A 0.5 gm. sample of lanthanum was placed in this cavity, and the whole assembly was placed into the cavity of a 1/2 inch undercut graphite electrode. An arc current of 30 amperes was found to supply the temperature needed for the reduction to take place, and visually the reduction phase appeared to be over in 60 seconds. The emission spectrum of the discharge was then recorded for an additional minute. Otherwise spectrographic conditions were identical to the determination of oxygen in steel.

The concentration of the standards run, and the intensity ratios obtained for separate specimens are given in Table 11.

The average value for each of the above standards was plotted in Figure 12 (curve A). Since an average intensity ratio of 0.215 can be attributed to the blank, this value was subtracted from the intensity ratio of each standard (curve B). The resultant intensity ratio (0.85) for the 0.00% standard indicated that there was considerable residual

Table 11. Calibration data for the determination of oxygen in lanthanum.

Oxygen added (%)	Intensity ratio $\frac{O\ 7771}{A\ 7372}$
0.42	5.40, 5.30
0.18	2.70, 3.1
0.06	1.71, 1.62, 1.67
0.00	1.10, 1.22, 1.03
blank*	0.228, 0.202

*Obtained by arcing nickel cup and electrode minus the lanthanum.

oxygen present in the lanthanum metal used for the preparation of the standards. This residual oxygen was determined by constructing a line through the origin (curve C) parallel to the curve obtained experimentally and applying to it, the intensity ratio obtained for the 0.00% standard. A residual of 0.09% oxygen was found. Correcting the concentration of each of the standards by the residual concentration and replotting the data of Table 11 gave the analytical curve of Figure 13.

If purer lanthanum metal had been available from which to prepare standards, the analytical curve could undoubtedly have been extended to much lower concentrations (approximately 0.002%).

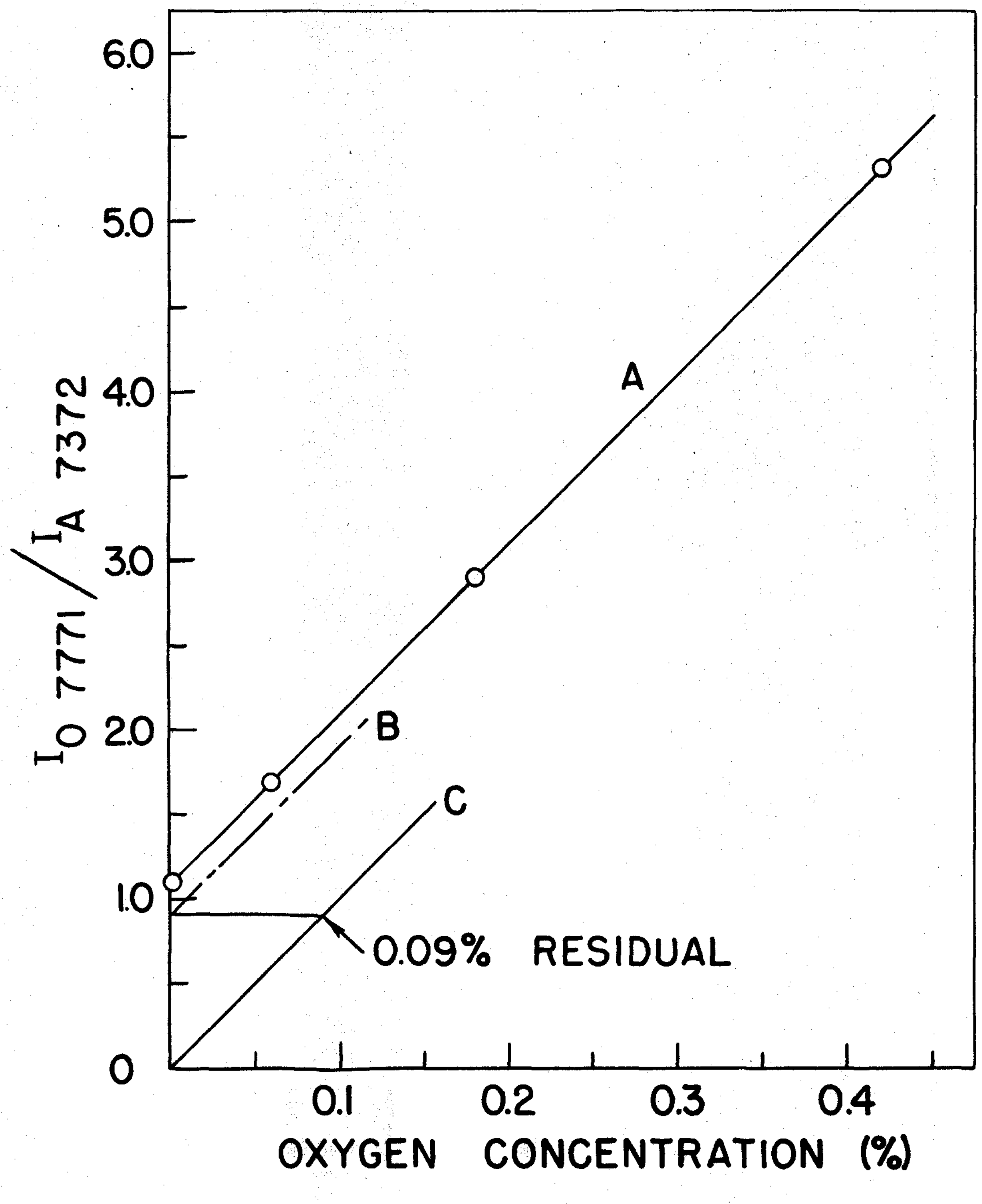

Figure 12. Coordinate Residual Determination Plot for Oxygen in Lanthanum.

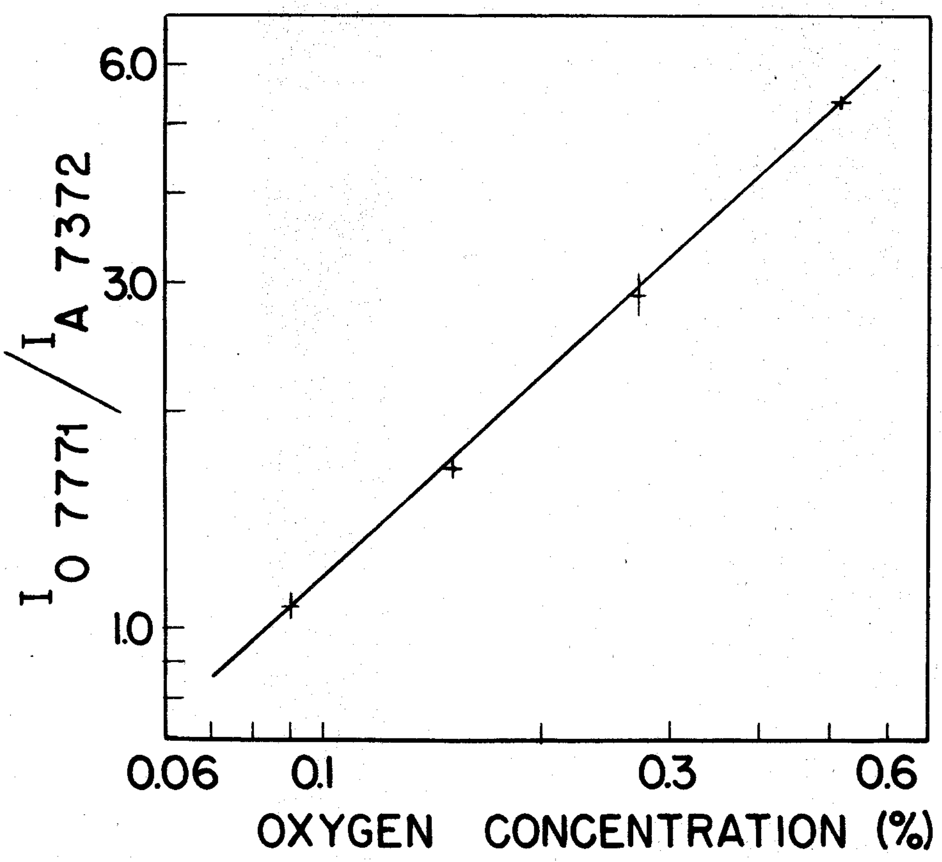

Figure 13. Analytical Curve for the Determination of Oxygen in Lanthanum.

3. Attempts to determine oxygen in zirconium metal

The determination of oxygen in zirconium is a very difficult problem, and at present there is no satisfactory procedure for this analysis. Several investigators have published vacuum fusion data on this determination (10, 17). However, duplication of their results has not generally been possible by other laboratories. The difficulties encountered in this determination center around: (a) the high thermodynamic stability of zirconium oxide, and (b) the relative ease with which the high melting point zirconium carbide is formed. The formation of zirconium carbide impedes the reduction of the oxide by causing the sample to solidify, and occluding unreduced oxide.

a. Overdamped condenser discharge in argon and hydrogen.

Although the sensitivity for the determination of oxygen in steel was judged insufficient with an overdamped condenser discharge, a sensitivity of 0.02% to 0.05% of oxygen in zirconium would be ample because of the relatively high oxygen content of commercial zirconium.

Standards containing 0.03%, 0.1% and 0.3% oxygen were prepared by reacting a known weight of oxygen with a known weight of zirconium. Since excitation with the overdamped condenser discharge does not consume the entire sample used, the standards were heated to 1000° C for 100 hours in a vacuum of 4×10^{-7} mm. to permit the oxygen to diffuse from the surface into the interior of the sample.

Exposures of these standards (as the cathodes) using the Multisource conditions of V = 940, C = 60 ufd., L = 400 uH., R = 5 ohms and T = 3 minutes in both argon and hydrogen atmospheres failed to produce any oxygen lines. This lack of sensitivity can probably be attributed to the relatively large quantities of finely divided and highly reactive zirconium that was volatilized, which recombined with the oxygen to effectively remove it from the discharge zone.

b. Direct current arc in argon. Attempts to reduce a standard of oxygen in zirconium directly in a carbon electrode over a temperature range of 1500° C to 2100° C failed.

Several vacuum fusion workers (10, 17) recommend the use of an iron bath containing approximately 20% zirconium for this determination. This recommendation was carried out in the spectrographic method by fitting an iron cup weighing approximately four grams into the cavity of a 1/2 inch undercut carbon electrode. A one gram sample of zirconium was then placed into the cup. Fusion of the zirconium and iron was readily accomplished to form an iron bath containing 20% zirconium, but no oxygen was liberated from the sample even at a temperature of 2100° C. In fact, the addition of zirconium prevented even the residual oxygen known to be present in the iron cup from being reduced. Similar attempts with a nickel bath also failed.

The difficulty encountered in liberating the oxygen from zirconium seems centered about the fact that it was impossible to keep the various baths molten at the maximum temperatures obtainable with a 35 ampere arc (approximately 2000° C).

Smith (38) suggests that the solidification of the bath in the case of iron is due to the high carbon content of the bath. After micrographic examination of various portions of solidified iron baths from vacuum fusion experiments, he concluded:

> The very heavy concentration of graphite flakes near the top of the melt would cause this region to become very viscous or pasty. Such a condition at the top of the bath would not allow dropped samples to penetrate into the bath...
>
> It is possible to account for this particular distribution of graphite as follows: When the iron is heated in contact with graphite, the bath becomes saturated with carbon. Because of the thermal gradients in the bath, loss of iron by evaporation, and radiation losses, some free graphite is either precipitated or carried to the top of the bath. Once formed, these particles can continue to grow, as thermal gradients will supply more carbon to the growing graphite flakes.

McDonald, et al. (11), was successful in the determination of oxygen in zirconium only after using an iron bath of minimum carbon content and keeping the zirconium content of the bath below five per cent. These conditions were not readily duplicated in the spectrographic method.

4. The determination of oxygen in nickel

The determination of oxygen in nickel has been found relatively easy by vacuum fusion procedures (12) using conditions very similar to those used in the determination of oxygen in steel. No oxygen in nickel standards were available, and they were not readily prepared with the standard preparation apparatus used for zirconium and lanthanum, because of the inertness of the metal.

However, samples of commercial nickel were obtained from two separate sources, and were run in duplicate. The conditions used were identical to the determination of oxygen in steel, using the d.c. arc in argon. The intensity ratios obtained for the nickel from source 1 were 0.261 and 0.260, while those from source 2 were 0.163 and 0.171. Since the oxygen blank as determined by arcing empty carbon electrodes gave an intensity ratio of only 0.039, the increase of intensity ratio must have been due to the reduction and volatilization of the oxygen in the nickel sample.

Because of the lack of nickel standards or conveniently made standards, calibration experiments were impossible. However, it would be expected that the same analytical curve (Figure 9) as obtained for oxygen in steel would also apply to this determination, since the nickel oxides are readily reduced and most probably all of the oxygen from the sample is volatilized as in the case of steel.

C. Determination of Oxygen in Organic Compounds

From the work on determining oxygen in steel, it would seem possible to apply a similar procedure to the determination of oxygen in organic compounds. If the organic compound is volatilized into an arc discharge, it will be dissociated, and any oxygen present probably will be converted to highly stable carbon monoxide. After this takes place the problem of determining the amount of carbon monoxide in the argon is identical to work previously done on oxygen in steel.

Ten milligram samples of various organic compounds were weighed into deep carbon electrodes. These carbon electrodes were cut from 5/16 inch carbon stock and were 3/4 inch long. A cavity 1/8 inch by 1/2 inch deep was drilled into the electrode to accept the sample. The exposure conditions were identical to the determination of oxygen in iron with the exception of the arcing current which was 15 amperes. The data obtained from this experiment are summarized in Table 12.

From Figure 14, it is apparent that there is a good relationship between the intensity ratios obtained for these compounds and their oxygen concentrations.

Two compounds, pentabromophenol, and diacetylmonoxine, gave reproducible results which did not fall near the analytical curve. It was thought that these compounds were probably impure, and for this reason the results were not included in the data presented.

While this method apparently does not have sufficient accuracy to be of use in quantitative organic analysis, it does demonstrate that the same principle used in the determination of oxygen in metals is applicable to other problems

Table 12. Intensity ratios observed for various oxygen containing organic compounds.

	Compound	Oxygen concentration (%)	Intensity ratio $\frac{\text{O } 7771}{\text{A } 7891}$ (individual determinations)	
A.	Triphenylcarbinol	6.2	0.63	0.69
B.	B-naphthol	11.0	0.84	1.05
C.	Anthraquinone	15.4	1.25	1.27
D.	1,4 naphthalene-diol	20.0	1.35	1.52
E.	Benzoic Acid	26.2	1.95	2.02
F.	Salicylic Acid	34.8	2.35	2.49
G.	Adipic Acid	44.0	3.05	3.42
H.	Ascorbic Acid	54.0	3.50	3.82
I.	Tartaric Acid	66.6	4.10	3.52

in which the desired element can be converted to a gaseous form by a suitable reaction.

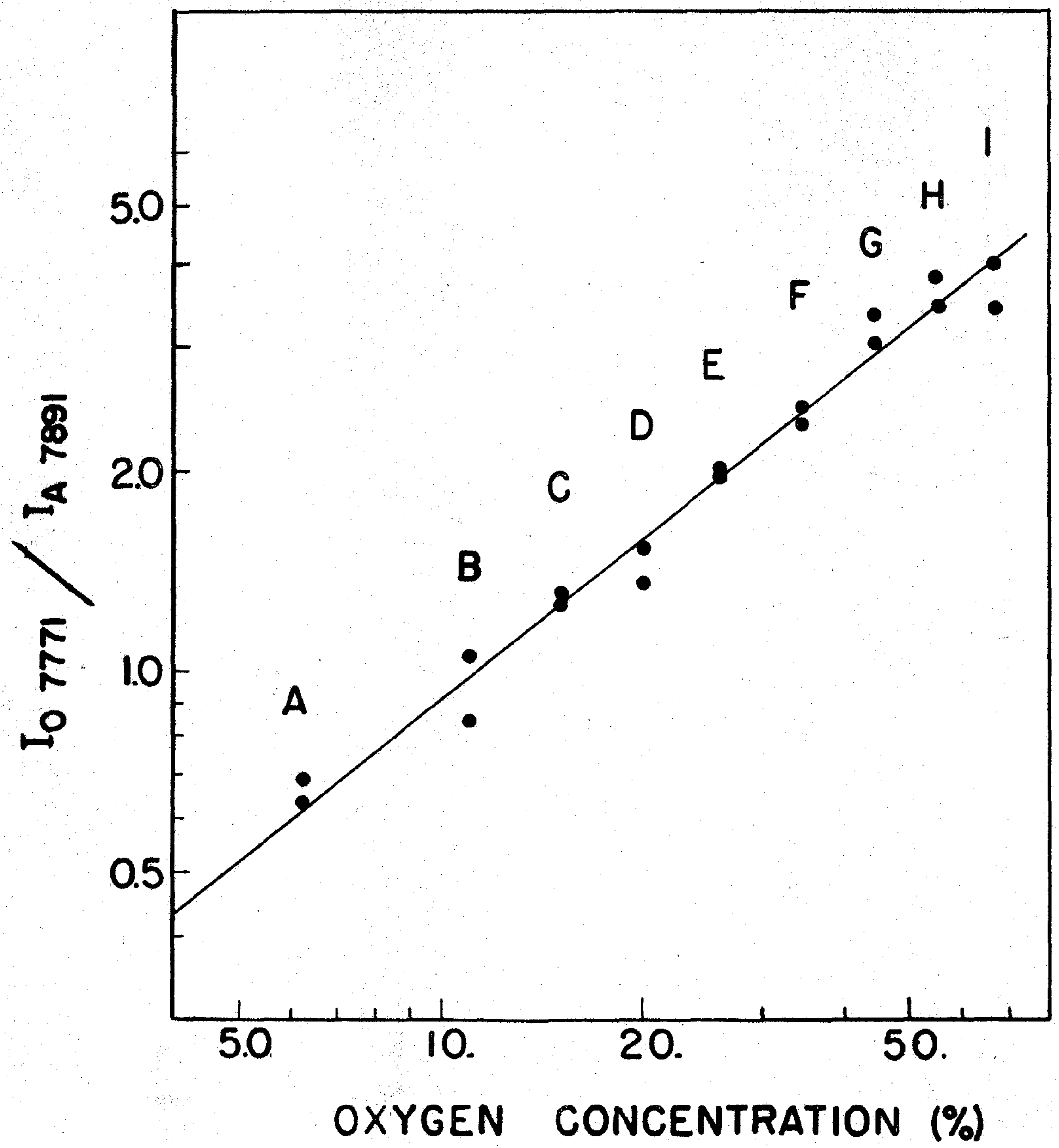

Figure 14. Analytical Curve for the Determination of Oxygen in Organic Compounds.

VI. SUGGESTIONS FOR FURTHER WORK

The technique as developed in this thesis provide ample opportunity for further exploration.

It would be highly desirable to eliminate the blank arising from impurities in the argon, electrodes, and outgassing of the chamber. At present no provision is made for the removal of carbon monoxide which may be present in the argon used. The addition of a copper oxide combustion tube to the purification train would oxidize the carbon monoxide to carbon dioxide, which would then be absorbed with Ascarite. The effectiveness of the purification train could also be improved by increasing the length of the various purifying elements or by reducing the argon flow rate.

Although vacuum outgassing of the carbon electrodes provided a low blank (0.0025%) there was no assurance that this treatment removed all of the blank oxygen from the electrodes. Induction heating would permit temperatures in excess of 2000° C to be obtained to better outgas these electrodes should it prove necessary. The amount of oxygen reabsorbed on transferring these electrodes from the outgassing apparatus to the excitation chamber is also not known. Should the reabsorbed oxygen prove appreciable it might be possible to saturate the electrodes with chlorine or some other gas that is strongly absorbed to eliminate this source of blank oxygen. Studies to determine what measures need to be taken to better outgas the excitation chamber are also needed.

If the blank were eliminated, it is probable that the sensitivity of the determination of oxygen in metals could be extended down to 0.0001%. Methods of increasing the sensitivity would include using a larger sample and reducing the volume of the excitation chamber so that a higher oxygen to argon ratio in the chamber would result.

In order to determine the general applicability of this method, work should be directed to include the determination of oxygen in other metals. It seems certain that oxygen could be readily determined in those metals that do not require the aid of a fluxing bath in vacuum fusion procedures. Some of these metals in addition to iron and nickel are chromium, cobalt, copper, molybdenum, tungsten and vanadium. Metals that require a fluxing bath for a successful oxygen determination could probably be determined spectrographically by providing this bath as was done in this thesis in the case of lanthanum.

In principle the technique developed in this thesis could be extended to include the determination of hydrogen and nitrogen. Hydrogen and nitrogen are liberated simultaneously with the carbon monoxide, and the same principle for their determination should apply.

An interesting problem would be that of developing analytical methods based on the controlled reaction of the sample with the atmosphere to disintegrate the sample and permit the oxygen in the sample to be vaporized. An example of this would be the arcing or sparking of uranium in hydrogen to form uranium hydride. Titanium reacting with chlorine, hydrogen chloride or bromine gas to form the volatile tetra chloride or tetra bromide would be another example. In this way oxides that are very difficult to reduce could be volatilized directly.

This thesis work has also pointed out indirectly the very high sensitivity obtainable spectrographically for the analysis of gaseous impurities in gases, and utilization of this fact could be made.

VII. DISCUSSION

A comparison between the spectrographic and vacuum fusion methods for determining oxygen in metals points out some decided advantages of the spectrographic method.

First is the great advantage of increased speed. As opposed to approximately five samples per day by vacuum fusion methods, twenty per day can be run spectrographically using photographic photometry, or the time of analysis per sample could be reduced to ten minutes using a simple two channel direct reading spectrograph.

The second advantage is precision. In vacuum fusion work, a precision of 5% to 10% is considered excellent for a concentration of oxygen greater than 0.01%. Below this concentration the precision varies between 25% to 200% depending upon the particular apparatus and operator. The precision of the spectrographic procedure at low concentrations is dependent mainly upon the level of the blank. Assuming a suitable low blank the precision should be less than 10% even at 0.001%.

The sensitivity of the spectrographic method as described in this thesis appears to be approximately 0.001%. With the modifications described in Section VI, the sensitivity probable could be extended to at least 0.0001% of oxygen in steel. This sensitivity is considerably higher than can be obtained with vacuum fusion apparatus.

At present the spectrographic method for determining oxygen in metals is readily applicable to metals with easily reduced oxides such as chromium, cobalt, iron, molybdenum, nickel, and tungsten and the rare earths. By exact duplication of vacuum fusion conditions with this apparatus, the oxygen in any metal that can be determined by vacuum fusion techniques should be determinable by the spectrographic method.

VIII. SUMMARY

A successful method for the determination of oxygen in steel in the range of 0.002% to 0.106% with a precision of 10% has been developed. The major problems of apparatus design, reduction of blank oxygen, and vaporization and determination of oxygen have been overcome. Data were also presented to show that this method is also applicable to the determination of oxygen in nickel and lanthanum.

Further work needs to be done on this method to determine the applicability of this procedure to other metals, however, in principle it should have the same wide applicability as vacuum fusion techniques.

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