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THE EMISSION SPECTROGRAPHIC DETERMINATION OF NITROGEN IN STEELS

by

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Major Subject: Analytical Chemistry

Approved:

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In Charge of Major Work

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Signature was redacted for privacy.
Dean of Graduate College

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1958

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I. INTRODUCTION

Techniques have been developed in these laboratories for the spectrographic determination of oxygen in metals. An eventual goal of these studies is a general spectrographic technique which will permit the simultaneous determination of not only the oxygen but also the nitrogen and hydrogen content of metals and alloys. In this thesis the problems encountered in determining the nitrogen content of low and high alloy steels are examined. Solutions to these problems are described and details are presented for the determination of nitrogen in these metals.

II. EFFECT OF NITROGEN ON STEEL

It is now well established that the quantity of nitrogen present in steel, interstitial or bonded as a nitride (37, 38, 39), exerts a significant effect on the physical properties of the finished metal. Gaseous nitrogen dissolves interstitially in both alpha and gamma iron, the low alloy phases stable at room temperature. The maximum solubility of nitrogen (9) in alpha iron is 0.11-0.12% nitrogen; the maximum solubility of nitrogen in gamma iron is 6.14% nitrogen. Effects of this solid solution are important, influencing phenomena associated with plastic flow (7). Small amounts of nitrogen will render steel harder and more brittle. Magnetic, strain and hardness aging phenomena have also been correlated with nitrogen concentration. Oxygen, which also dissolves interstitially in alpha and gamma iron, is of interest mainly in relation to the effects of non-metallic inclusions (7).

Some of the alloying constituents of steel, such as vanadium, manganese and chromium will themselves form stable nitrides, increasing the nitrogen uptake of a steel over and above the amount pure iron would take up under identical conditions. These nitrides will also affect the overall properties of the steel (22, 29, 56). It has been found possible to reduce the nitrogen content of a steel by the addition of aluminum to the melt, since insoluble aluminum nitride separates as a part of the slag. (Titanium and zirconium have been used for the same purpose.) (8). This procedure then results in a steel with low nitrogen content and with the nitrogen primarily in the form of aluminum nitride.

In special cases the presence of nitrogen in steel may be desirable. Austenitic steels are particularly noted for their heat and corrosion resistance. Austenite is a non-magnetic solid solution of carbon and ferric carbide in gamma iron. This solid solution is unstable below its critical temperature separating into two phases. However the addition of manganese and nickel lowers the critical transition temperature so that austenite may be obtained stable at room temperature (41). Recently nitrogen has been found to be an adequate substitute for nickel. For example, 0.2% nitrogen substitutes for 4% nickel in a steel originally containing 18% chromium and 8% nickel (47). A nitrogen to chromium ratio of at least 1:60 is necessary to obtain austenite, rather than a mixture of austenite and ferrite (46). (Ferrite is a low carbon iron phase.) The high temperature strength of steel also improves with increasing nitrogen content.

III. PRESENT METHODS FOR THE DETERMINATION OF NITROGEN IN STEEL

Generally, the nitrogen content of an iron or steel sample is determined by the familiar micro-Kjeldahl method. Mineral acid is used to dissolve the sample, alkali added and the resulting ammonia steam distilled into a receiver. This method is rapid and simple, even on a micro scale. In favorable cases, the entire determination may be carried out in a few minutes (3).

This procedure, like any other analytical method, is subject to certain restrictions. With the present day emphasis on corrosion resistant steels, such as the austenitic steels, application of the Kjeldahl method on a routine control basis has become questionable on two counts. First, difficulty is found in the dissolution of the matrix itself. Secondly, difficulty arises in attempting the dissolution of the stable alloy-nitrides such as the nitrides of aluminum, titanium, zirconium, vanadium, tungsten, niobium and silicon (3).

Both problems are sometimes solved by extensive digestion periods in sulfuric, phosphoric, or perchloric acid (3, 16). Heating the steel sample to sulfur trioxide fumes in a mixture of potassium bisulfate, sulfuric acid and cupric sulfate has also been employed (32). The use of hydrofluoric acid and hydrogen peroxide has been found effective in the decomposition of the nitrides of titanium and zirconium (4, 25).

Various special steels give rise to particular difficulties with the Kjeldahl procedure. Certain samples of ferromanganese (16-44% manganese) contain nitrogen compounds which, upon dissolving in hydrochloric acid, are not converted to ammonium chloride and cannot be determined. There is some correlation between silica content and low nitrogen values. When sulfuric acid is substituted for hydrochloric acid this effect is not present (27). More nitrogen is found in cast iron, if the residue, insoluble in dilute acid, is oxidized with sodium peroxide. This is also explained by the presence of a compound of nitrogen with carbon and silicon (19). High results are obtained by the Kjeldahl method if the mineral acid used in dissolving the sample contains impurities such as nitrates and if the metal being analyzed contains ordinarily negligible amounts of molybdenum (13).

The determination of the resulting ammonia can be carried out by any one of a variety of techniques. Most obvious is that of collecting the ammonia in standard acid and titrating. Alternatively, the distillate can be collected in a Nessler tube, the Nessler reagent added, and the determination completed spectrophotometrically (3). Other workers have employed the Nessler reagent without the ammonia distillation. The iron is either removed by electrodeposition (30) or by precipitation (28) before the addition of the reagent. A polarographic method is also available. This technique is based on the reduction product of ammonia plus phthalaldehyde (36). Another spectrophotometric method is based on the distillation of ammonia into a mixture of sodium hypochlorite and sodium phenolate to form a blue colored indophenolate (11).

A mass spectrometric isotope dilution technique has been developed by H. Svec and G. Staley (52). The nitrogen in the sample is converted to NH_4^+, a known quantity of $N^{15}H_4^+$ is added, the mixture converted to ammonia and the $N^{15}H_3/N^{14}H_3$ ratio measured. The nitrogen content of the steel sample is inferred. Account must be taken of the natural abundance ratio of N^{15}/N^{14}.

An interesting scheme has been devised to determine the amount of Kjeldahl "insoluble nitride" in steel. Bromine and methyl acetate are added to a steel sample (5). A violent reaction takes place with the dissolution of all the sample but the nitride. This residue is filtered off and determined by a modified Kjeldahl method. The nitrides of silicon, zirconium, aluminum, niobium, tantalum, titanium and vanadium can be determined by this method. Some of these nitrides are partially soluble in the unmodified Kjeldahl method.

Nitrogen may also be determined in iron and steel by the vacuum fusion method (33). The metal is brought into contact with carbon in vacuo at a suitable high temperature so that the hydride, oxide and nitride are converted to the carbide with the evolution of hydrogen, carbon monoxide and nitrogen. These gases are then pumped into a collecting vessel and analyzed. The measuring device is usually a McLeod gauge. Carbon monoxide is oxidized to carbon dioxide and frozen out; hydrogen may be removed by a heated palladium filament or may be converted to water and frozen out; nitrogen is usually determined by difference. The analysis may be carried out on a micro (12) or macro scale.

Some difficulty is found in the vacuum fusion analysis of steels containing volatile elements such as manganese. A film of active metal is deposited on the cooler portions of the apparatus. Nitrogen is particularly subjected to "gettering" by these freshly vaporized metal films. This effect can be minimized by the addition of tin with each sample and also between samples. The walls of the furnace will thus be coated with a non-reactive tin film. Using this technique, iron alloys of both aluminum and manganese have been analyzed for nitrogen (33).

Many nitrides are quite thermally stable and require fairly high temperatures for decomposition. Increasing the temperature in the furnace to that required for decomposition often cannot be done. In many cases an increase in temperature also intensifies the gettering aspects of the problem. This consideration is particularly important when analyzing steels containing titanium, zirconium, chromium and aluminum.

As a result nitrogen values obtained by the vacuum fusion method are open to question in some cases. Although this method has merit as a research tool for nitrogen determinations, it is much too slow to be carried out on a process control basis.

Some work has been reported on the application of activation analysis to the problem of determining nitrogen. Use has been made of the following reactions:

$N^{14}(d,n)O^{15}$; $N^{15}(p,n)O^{14}$; $N^{14}(p,\alpha)C^{14}$ (10, 51)

These techniques are, at present slow and undeveloped, but they do have the possibility of extending the limit of detection.

IV. POSSIBILITIES OF DETERMINING NITROGEN 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 nitrogen is excited together with all of the other constituents of the sample. It is, therefore, appropriate to inquire whether nitrogen can be determined in this manner.

B. Basic Problems in the Development of a Spectrographic Method for Nitrogen

There are several basic problems involved in the spectrographic determination of nitrogen which no doubt have discouraged previous studies on this problem. The first is the necessity of excluding atmospheric nitrogen 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 a nitrogen free atmosphere, each of which presents its own difficulties.

If spark excitation is used in a vacuum, voltages on the order of 100,000 volts are required to break down the analytical gap. Commercial spark sources 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 would be volatilized by a vacuum spark. Low sensitivity would be expected, and any effect of surface nitride formation would be greatly magnified. Because of these difficulties and the failure of Sterner (49) in successfully applying this technique, further experimental investigation was postponed in favor of other approaches with greater promise of success.

Direct current arcs can be maintained successfully between carbon electrodes in vacuums down to approximately 10^{-4} to 10^{-2} mm Hg, with electrode gaps of one to four mm (34). 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 should attain a sufficiently high temperature to cause the reduction of the nitrides. The evolved nitrogen could then be determined spectrographically.

This approach was explored by Tabeling (53) in the determination of oxygen in steel. 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 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.

The use of the high frequency spark in nitrogen free, static argon was also investigated under the following excitation conditions: Source parameters: $C = 0.0075$ µF, $L = 0$ µH, $R = 0$ ohms, breaks per half cycle = 4, (Source unit given in Table 1). The data indicated that very little of the sample was volatilized. Approximately one milligram was vaporized during a three minute exposure period. No reaction was observed between the sample and the graphite electrode. The observed intensities for the standard containing 0.25% nitrogen were no greater than the carbon electrode "blank".

C. Previous Spectrographic Work on the Determination of Nitrogen

A few spectrographic methods have been devised which involve the use of an inert, nitrogen free, atmosphere.

S. L. Mandel'shtam and O. B. Fal'kova have described a spectrographic method for determining nitrogen in steel, employing a high voltage, high power spark discharge (31).

The condensed-spark circuit was a modification of the common, series "tank circuit". The input was across the condenser; the output, (analytical gap in series with a resistor) was in parallel with the components of the "tank circuit". A high-voltage transformer charged the 4.5 microfarad capacitor through a kenotron (a high current rectifier tube) and an approximately 50,000 ohm resistor. The kenotron was added to the circuit because the capacitor, owing to its high capacitance, was otherwise unable to accept a sufficient charge during a half-cycle of the line current. The capacitor discharged at a voltage of about 16 kv across a fixed gap (d_2 = 4 mm) plus a resistor (15,000 ohms) which blocked the operating gap. After sparking over this gap the discharge passed through the operating gap (d_1 = 0.3 mm).

The discharge had the character of separate powerful impulses. The diameter of the fused pit left behind by an individual impulse was about 2 mm. Each separate discharge impulse fused an area of the surface of the electrodes so strongly that this area remained considerably poorer in nitrogen. For this reason, following each impulse, the sample under analysis was moved in such a manner as to direct the next impulse onto a fresh area of the electrode surface.

The discharge vessel consisted of the metal plate with attached electrode holders, covered by a glass bell ground to make a tight fit with the plate. The bell was equipped with two side arms, which were closed by plane-parallel glass plates. The side arms were directed along the axis of the spectrum apparatus. One of them served for observation, while the other served to project the shadow of the electrodes for alignment. The sample under analysis was used as one electrode, a 4 mm diameter tungsten rod, ground to terminate on a hemisphere, was used as the counter electrode. The discharge vessel was connected to the vacuum unit and was evacuated to a pressure $P = 10^{-3}$ atmospheres, with an aspirator pump, whereupon it was filled with carbon dioxide to support the discharge.

The N^{II} line at 3995.0A (21.5 e.v.) was the most sensitive line under these discharge conditions; the strong "background" radiation was used as a "comparison line". The limit of detection of the nitrogen line was dependent upon the carbon dioxide pressure, the discharge source parameters and the electrode spacing.

Maximum analytical sensitivity was attained by producing ten spark impulses for each exposure, each impulse affecting an area of the electrode previously untouched by a spark. As indicated above, this was accomplished without removing the bell, but by moving the electrode under analysis with the aid of the ground joint installed in the bottom of the discharge vessel.

Although the technique was sufficiently sensitive (the limit of detection was 0.003% nitrogen), it was not particularly precise. Multiplicate runs on a number of samples gave rise to a standard deviation of approximately ± 20%; the average standard deviation was ± 16%. Some of the major sources of error involved in such an approach were discussed above. The method as described possessed the added disadvantage of not being readily adapted to the simultaneous determination of oxygen in steel, although the use of an inert gas would be the obvious solution of this difficulty. No provision was made for running more than one sample at a time. After each sample, the vacuum system was opened and a new sample inserted. There was however the following advantage. The discharge apparently did not heat the excitation chamber, decreasing the problem of blank (contamination) due to desorption of the atmospheric gases from the chamber walls. Working at atmospheric pressure also favored a low blank.

A modification of this technique was applied by Runge and Bryan (42) to the determination of nitrogen in austenitic steels. A line arising from the iron spectrum (3961.15A) was employed as a reference line rather than the background radiation employed by the authors of the original paper. It was possible to obtain an emission spectrum of nitrogen in steel, in the amount of 0.20% nitrogen, using this high energy, single-discharge spark source. The coefficient of variation, based on a single sample excited twenty times by this technique was ± 17% of the amount reported.

E. F. Runge and F. R. Bryan (43) have also approached the problem of determining nitrogen in austenitic steels from a slightly different point of view. They employed D.C. arc excitation of the cyanogen molecule (CN 3883.4A) resulting from the combination of nitrogen contained in the sample with carbon from the electrode or surrounding gas. The authors constructed a simple chamber consisting of two brass electrode holders which threaded into opposite ends of a methyl methacrylate cylinder. Each of the electrode holders was hollow, allowing the displacement gas to be admitted and exhausted at a flow rate of 20 cu. ft./hr. The sample and counter electrode material were held in place by spring clips on the ends of the brass holders. The lower electrode (anode) consisted of the steel sample in the form of a metal disk, 1 cm diameter and 4 mm thick. A graphite rod, 3.5 mm diameter and 1 cm long served as counter electrode. The transparent cylinder was rotated with respect to the holders to provide an arc gap of 2 mm.

A limited investigation of arc atmospheres involved argon, helium and carbon dioxide. Of the three gases, carbon dioxide provided the most intense cyanogen spectrum. Experiments were also conducted to determine the optimum D.C. arc current and exposure time. Even with carbon dioxide, however, a relatively high arc current was necessary to produce the cyanogen band system. Observable spectra were formed throughout the current range of 13 to 16 amperes. A current of 16 amperes was selected and ten seconds, without a preburn period, was chosen as exposure time. Chromium and iron produced possible interfering lines, located at 3883.292 and 3883.289A respectively. These interferences were resolved by use of a Bausch and Lomb echelle grating attachment crossed with a large Littrow quartz spectrograph. The limit of detection was 0.1% nitrogen; the "repeatability" was ± 10% of the amount present. The primary difficulty with this technique is that the limit of detection is far above the nitrogen concentration commonly found in steels (except the austenitic steels).

Methods hitherto available for the determination of oxygen in metals similarly suffered from a lack of sensitivity, precision and adequate speed of analysis. A rapid, accurate and precise spectrographic technique for the determination of oxygen in low alloy steels was recently developed at the Ames Laboratory by Fassel and Tabeling (20). This technique was then adapted by Fassel and Gordon (21) to the spectrographic determination of oxygen in titanium and titanium alloy. The method was based upon the liberation of the gas content of metals into a static argon atmosphere by the elevated temperatures attained in a high current D.C. carbon arc discharge.

A metal sample was supported in a graphite receptacle, which served as anode. When a 1.0 gram steel sample was arced in these electrodes at 20 amperes, the specimen quickly melted and dissolved carbon from the retaining wall of the anode. The dissolved carbon came into intimate contact with the combined oxygen of the sample cuasing evolution of the gas by the resulting chemical reduction reactions. If the reactions occurring in the molten globule were the same as those prevailing under vacuum fusion conditions the oxygen was evolved as carbon monoxide. Simultaneously, a saturated solution of carbon in steel was formed which reduced the volatility of the iron.

Since the gas evolution reactions appeared to proceed somewhat erratically, it was desirable to allow the reduction reactions to reach completion before starting the spectroscopic observations. The evolved gases were therefore determined as impurities in the argon atmosphere. The carbon monoxide was dissociated and the atomic emission spectrum of oxygen was excited as the argon atmosphere underwent natural diffusion through the arc column. Under these conditions, selected argon lines served as virtually ideal internal standards for the determination of oxygen. The oxygen and argon internal standard lines underwent rather large intensity changes during the arcing cycle, but since the lines behaved in consort, the intensity ratios remained virtually constant. At the end of the exposure period, the chamber was evacuated to a pressure of 10^{-4} mm Hg, a new charge of purified argon was admitted, the next sample was rotated into position, and the procedure repeated. The analytical curve for the determination of oxygen in steel covered the concentration range 0.1% to 0.002% oxygen.

A rapid, simultaneous determination of oxygen and nitrogen possesses significant advantages in time-of-analysis for the routine, control determination of gases in steels. It is also of academic interest to determine whether nitrogen, a non-metal, can be determined by emission spectrographic techniques. Thus, the purpose of this investigation was:

1. To determine whether nitrogen is evolved under conditions similar to those employed by Fassel and Tabeling.
2. To determine whether the evolved nitrogen can be detected with adequate sensitivity and precision.
3. To establish whether evolution can be made reproducible and quantitative.

V. EXPERIMENTAL

A. Apparatus

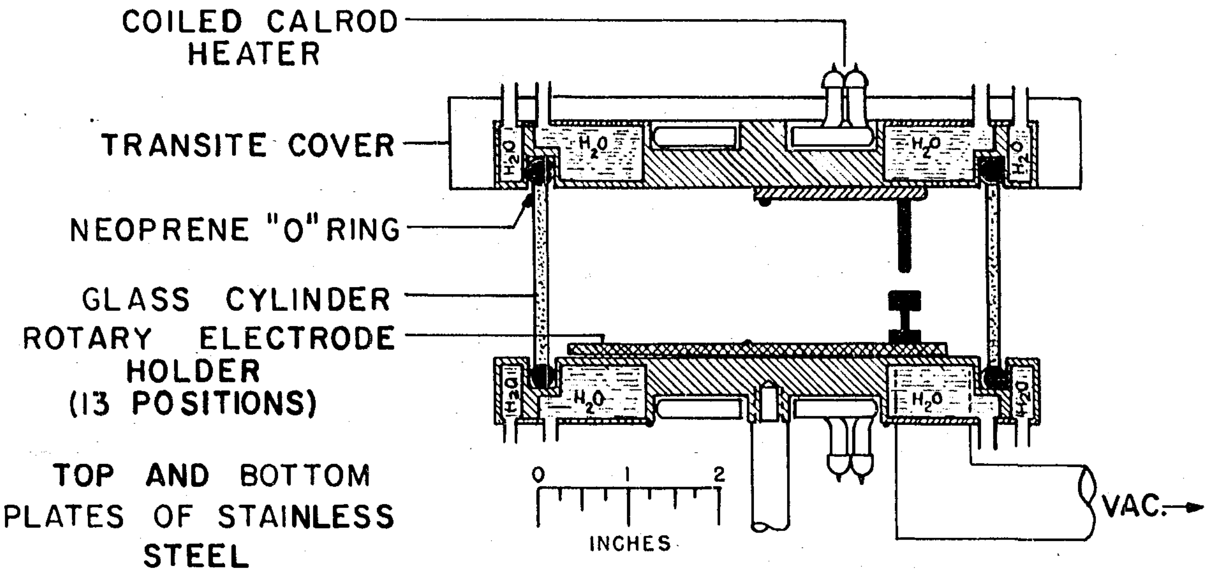
1. Excitation chamber

The excitation chamber was a modification of the chamber described by Fassel, Tabeling and Gordon (20, 21), (Figure 1), designed such that it was readily constructed, easily cleaned and rapidly outgassed.

Six inch diameter stainless steel which was about 3/4" thick after machining was used in forming the top and base plate. These plates with a Pyrex glass cylinder measuring 5" in diameter and 2" in height formed the body of the chamber. The glass cylinder fitted into grooves which were cut in the steel plates and which contained Neoprene "O" rings to provide the vacuum seal. In addition to the large water tight compartment used to cool the body of the chamber, there was provided a smaller, outer compartment in both the top and base plates. Water flowed through these compartments during the outgassing cycles to protect the "O" rings from thermal decomposition.

The rotary electrode holder accepted 13 electrodes spaced 3/4" apart on a 4" diameter circle and rotated on a graphite spacer. Because of the large quantity of iron vaporized during analysis it was impractical to run more than five or six samples without opening the chamber to

Figure 1. Schematic diagram of the excitation chamber


COILED CALROD HEATER
TRANSITE COVER
NEOPRENE "O" RING
GLASS CYLINDER
ROTARY ELECTRODE HOLDER (13 POSITIONS)
TOP AND BOTTOM PLATES OF STAINLESS STEEL
H₂O
0
1
2
INCHES
VAC.

remove the deposited metal from the optical path. Blocking of the light by the electrodes between the source and the spectrograph was avoided by tilting the chamber forward a few degrees. Since the rotation of the electrode holder was accomplished by means of a magnet from outside the chamber, the electrode holder was constructed of 1/4" cold rolled steel rather than non-magnetic stainless steel. By removing the pivot screw the electrode holder was easily removed for cleaning and disposing of electrodes. The counter electrode was a 1/8" diameter graphite rod, 3/4" in length. This rod was threaded and screwed into a steel bar attached to the top plate of the chamber. It was not necessary to provide a new counter electrode between samples, i.e. one electrode was sufficient for a chamber load of samples.

Electrical connections were made by mounting the base plate directly to the accessory bar by means of a conventional lens mount. The accessory bar was at ground potential. The lead from the source unit was connected to the top plate through one of the stainless steel water inlets. This placed the entire top plate at a negative potential with respect to ground (the positive side of the source unit was grounded). A Transite cover provided protection against the danger of electrical shock. Since the assembly was operated under atmospheric pressure, it was necessary to place four "C" clamps symmetrically around the chamber to insure air tightness.

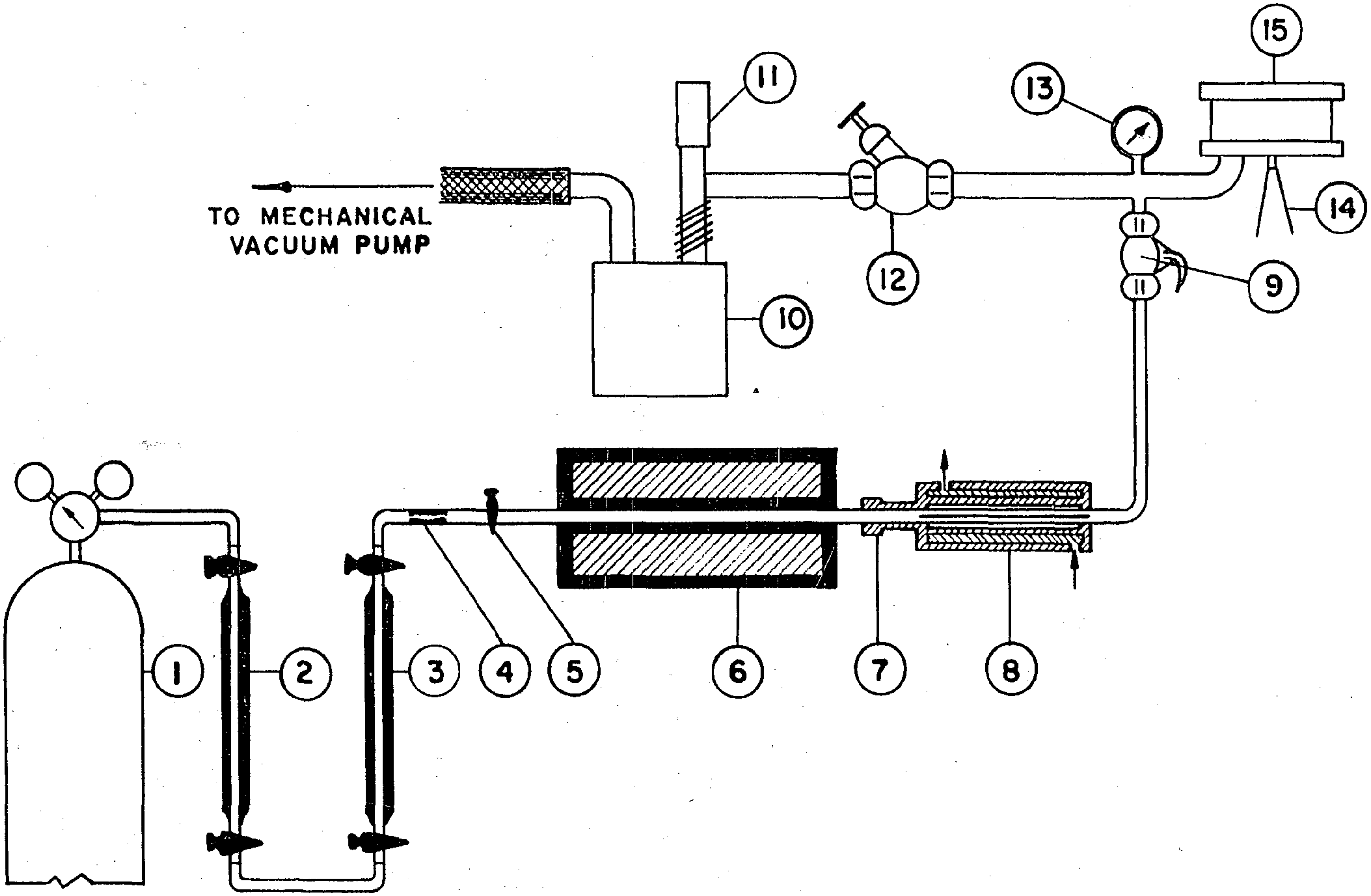
2. Vacuum system

The vacuum system (Figure 2) consisted of an oil diffusion pump, 10, (Consolidated Vacuum Corp. VMF 20-01) with a liquid nitrogen trap, constructed of stainless steel, attached directly to the diffusion pump stack, 11. A one inch diameter high-vacuum valve (Vacuum Research Co. VG-101), 12, with "O" ring grooves in each flange was joined to the system by 4" diameter brass flanges. This valve was considered to be simpler than the one inch diameter bellows type valve employed in earlier work. A mechanical pump (Welch #1405) was used as the forepump in series with the oil diffusion pump. The pressure in the system was monitored with a Philips Gauge (Consolidated Vacuum Corp.) which covered a pressure range from 25 to 0.01 microns (2.5×10^{-2} mm to 1×10^{-5} mm Hg).

3. Gas purification

Atmospheric impurities were removed from the commercial argon by passage over active metal filings at elevated temperatures (Figure 2). The metal was contained in a 1/4" diameter combustion tube (90% silica). An 18" split tube furnace (Hevi Duty Electric Co.) was used to maintain the proper temperature, 6. Two furnaces were employed in series. The argon tank, 1, was followed by an absorption tube containing sodium hydroxide on asbestos (Ascarite) for the absorption of carbon dioxide, 2. This was followed by an absorption tube containing anhydrous magnesium perchlorate

Figure 2. Schematic diagram of the high vacuum system and the gas purification system


TO MECHANICAL VACUUM PUMP
1
2
3
4
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7
8
9
10
11
12
13
14
15

(Anhydrone), 3, for the removal of water vapor. A 0.7 mm capillary, 4, was placed in the system to throttle the flow of gas through the train. A high vacuum stopcock, 5, permitted the outgassing of the combustion furnace after recharging the combustion tube.

The heat exchanger, 8, aided in maintaining a constant temperature of the gas entering the chamber. This consisted of seven copper tubes 1 1/6" i.d. and six inches long, enclosed in a water tight jacket. The unit was coupled to the system by a commercial vacuum coupling, 7, employing a rubber "O" ring (Central Scientific Co. Cat. No. 94230).

The purified argon was introduced into the chamber through a 1/8" toggle vacuum valve (Hoke Inc. No. 450), 8. A compound gauge, 13, calibrated from 0-30" mercury and from 0-15 psi was used to monitor the pressure in the reaction chamber. Control of the volume and temperature of argon introduced into the chamber was necessary to achieve good internal standardization. The volume of gas was determined primarily by the dimensions of the Pyrex separator. Since no provision was made on the present apparatus to measure the gas temperature directly, the temperature was reproduced by maintaining a constant flow rate through the furnace tube and heat exchanger.

4. Spectrographic apparatus

The spectrographic equipment used in this investigation is summarized in Table 1.

The external optical system used to illuminate the spectrograph had been designed to provide uniform illumination over the entire length of the spectrograph slit, and to permit the full utilization of the spectrographic aperture defined by the rectangular surface of the collimator.

A 10 cm focal length spherical quartz lens, placed 73.8 cm from the slit, focused the electrodes about an aperture cut into a screen. This secondary source was projected over the width of the collimator by a quartz cylindrical lens with its axis vertical (10 cm focal length) placed 47.2 cm from the slit. A second quartz cylindrical lens (35 cm focal length), with its axis horizontal, was placed over the spectrograph slit. This lens focused the light over the height of the collimator.

Such an optical system permitted the external diaphragming of the continuous radiation from the incandescent electrodes, 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.

Table 1. Spectrographic facilities

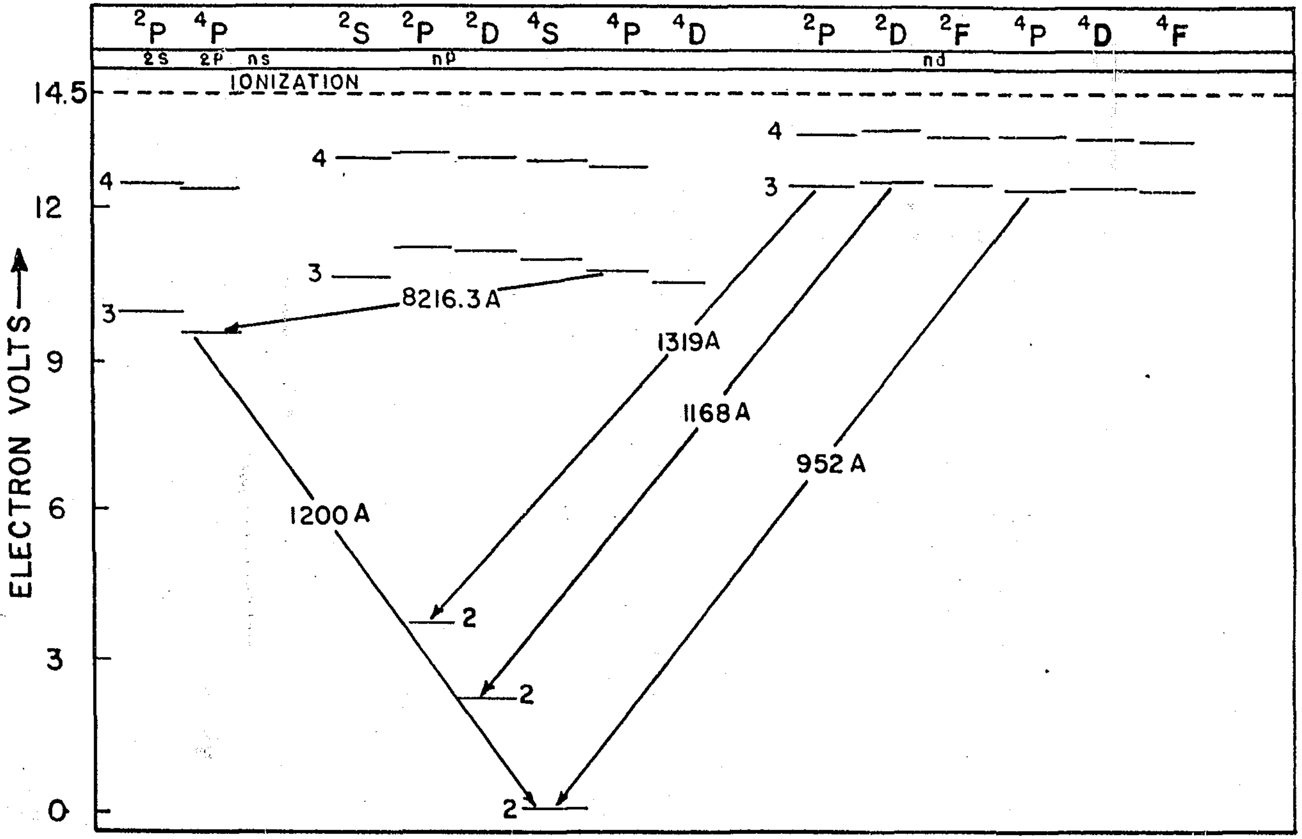
Spectrograph	Jarrell-Ash Company, 3.4 meter Ebert mounting plane grating spectrograph, 5900 rulings/cm grating blazed for 13,000A, first order.
Source Unit	National Spectrographic Laboratories, "Spec Power" Model 110-25, 250 volts, 35 amperes capacity.
Densitometer	Applied Research Laboratories Comparitor Densitometer.
Wavelength	a) 3700 - 4300 3rd order b) 7100 - 8400 1st order.
Emulsion	Eastman Type M in wavelength region a Eastman Type IN in wavelength region b.
Filter	Corning 2-63 in region b.
Slit	0.05 mm.
Development	4 minutes at 21°C in Eastman Kodak D-19 with continuous agitation in an Applied Research Laboratory developing machine.
Emulsion Calibration	Two-step sector, preliminary curve method (15).

B. Emission Spectra of Nitrogen-Containing-Species

The analytical technique developed by Fassel and Tabeling (20) for the determination of oxygen in steel was based on the extraction of the gas out of the metal into a static argon atmosphere by a D.C. carbon arc discharge. Since some nitrogen was probably evolved under these conditions, it was of first interest to establish which nitrogen-containing-specie could be detected by a D.C. arc discharge in an argon atmosphere containing traces of nitrogen.

To detect traces of nitrogen in an argon atmosphere it is theoretically possible to use radiation arising from nitrogen and cyanogen molecules or from atomic nitrogen. The sensitive resonance lines of atomic nitrogen occur in the vacuum ultraviolet; the energy level diagram of atomic nitrogen is shown in Figure 3. Although progress is being made in observing spectra in this wavelength region, quantitative intensity measurements in the 200-1300A region are still in their infancy. The lines in the more readily accessible regions of the spectrum are considerably weaker in intensity and require relatively high energies (11-15 e.v.) for excitation. Experimentally, the most sensitive available nitrogen line (8216A) is not detectable in the spectrum of a 25 ampere D.C. arc discharge in air carried out between a carbon cathode and an iron anode. In D.C. carbon arc discharges in air, this line is detected with moderate

Figure 3. Partial energy level diagram of atomic nitrogen


2P 4P 2S 2P 2D 4S 4P 4D 2P 2D 2F 4P 4D 4F
2s 2p ns
np
nd
IONIZATION
14.5
12
9
6
3
0
ELECTRON VOLTS
4
3
8216.3 A
1319A
1168 A
952 A
1200 A
2

intensity. But in D.C. arcs in rare gas atmospheres, several hundred ppm nitrogen are readily detectable.

Most of the energy available in a high current arc carried out between an iron anode and a carbon cathode is dissipated by the volatilization, excitation and ionization of iron. The iron atom possesses a multitude of energy levels requiring 3 e.v. or less for excitation. The D.C. carbon-iron arc and D.C. carbon-carbon arc in air readily dissociates nitrogen and oxygen molecules and excites cyanogen, nitrogen, oxygen and nitrous oxide molecules. These processes generally require 3 to 8 e.v. Thus little energy remains available to excite the nitrogen or oxygen atom, processes requiring in excess of 10 e.v. The lowest excited state of argon lies 11.5 e.v. over the ground state. In a pure argon atmosphere containing only traces of nitrogen and oxygen there are no low energy (<8 e.v.) processes available to dissipate the energy of the arc. Thus the nitrogen line at 8216A, requiring 11.79 e.v. for excitation is more readily produced.

Experimentally it did not appear possible to detect molecular nitrogen radiation for nitrogen concentrations much less than 0.05% nitrogen, at one atmosphere of argon. Low gas pressures are apparently necessary for the efficient excitation of the nitrogen band systems. The effect of argon pressure on the band spectrum of nitrogen has been discussed in the literature (54). Upon increasing the argon content of a gas discharge tube containing a small amount of nitrogen, the "first positive system" of nitrogen (ultraviolet bands) is suppressed relative to the "second positive system" (red nitrogen bands). In the "second positive system", there is a shift of intensity from the higher vibrational states ($v^1 = 3,4$) to the lower states ($v^1 = 0,1$). As the argon pressure approaches one atmosphere, the excitation of even the lower states of the "second positive system" evidently becomes more difficult.

The ultraviolet cyanogen band systems are readily excited by the D.C. carbon arc in an argon atmosphere. At a pressure of one atmosphere, the cyanogen band head at 3883A is particularly sensitive, detecting as little as 0.003% nitrogen in a gram of argon. A second cyanogen band head at 3871A is slightly less intense, with a limit of detection of about 0.005% nitrogen.

Energies of excitation found in a high frequency spark discharge are considered higher than those found in a D.C. arc, generally producing ion lines and high energy atom lines. Since only a small amount of a specimen is sampled by a spark discharge, it was thought to be worth while to employ a D.C. arc to melt the sample, and release the gases into the static argon atmosphere. The arc would then be discontinued and an empty electrode moved into position for sparking. It was hoped that the high frequency spark would favor the excitation of the high energy atom lines of nitrogen.

However it was found that the use of a high voltage spark in argon at one atmosphere pressure does not increase the efficiency of excitation of N8216A. This line was barely detected in an argon atmosphere containing 0.035% nitrogen. A D.C. arc, 25 amperes, in the same atmosphere gave rise to a line possessing a signal to noise ratio of approximately 4.0. The spark did not at all excite the cyanogen bands at 3883A, 3871A.

Although a helium atmosphere was not used in the Fassel and Tabeling technique, helium was investigated here for use in place of argon as a supporting atmosphere. The lowest lying excited state of helium lies 17 e.v. over the ground state. Such an atmosphere should favor excitation of high energy lines. D.C. arcs in helium excited cyanogen 3883A; the high voltage spark did not excite cyanogen 3883A, but nitrogen 8216A was detected. These discharges in helium were no more efficient than the arc and spark in argon containing an identical nitrogen concentration. The use of helium presented the added difficulty of having only one line available for use as an internal standard line. The large difference in energy between helium lines (approximately 23 e.v.) and nitrogen 8216A (11.5 e.v.) rendered this use of helium unadvisable. The excessive volatilization of carbon was also unfavorable.

C. Blank Control

It was of course necessary to conduct the discharge in an argon atmosphere which was nitrogen free. The possible sources of nitrogen contamination were the following: 1) a leak in the vacuum system; 2) ineffective purification of the argon; 3) incomplete outgassing of the electrodes and excitation system.

Because of the greater nitrogen content of the atmosphere, the problem of a vacuum leak was more serious when analyzing for nitrogen than when determining the oxygen content of a sample. The care which had to be taken to afford a nitrogen-tight system is illustrated by the following. All joints, other than metal-metal seals were coated with glyptal or with sealing wax (Apiezon W). This was particularly necessary at the joint of the heat exchanger and the silica furnace tube. The fourth C clamp was necessary to render a leak proof seal between the glass separator and the "O" rings of the excitation chamber. Only after the "O" rings softened upon repeated use was this seal impervious to nitrogen. Small cuts across the ground glass rim of the glass separator afforded significant nitrogen contamination through leakage.

1. Argon purification

Since it appeared to be difficult to obtain commercially argon which was free of the last traces of nitrogen, a scheme had to be devised to remove the nitrogen impurity. This problem was complicated by the low chemical reactivity of the nitrogen molecule. Although nitrogen is a very inert gas at room temperature, its reactivity is considerably augmented by raising the temperature. Particularly stable nitrides are formed by reaction of the gas at elevated temperatures with titanium (ΔH_f = -73.0 kcal/mole) and with zirconium (ΔH_f = -82.2 kcal/mole). To make use of this property, a cylinder of "crystal bar" titanium was placed in the excitation chamber and arced at a high current while the argon was being admitted. The molten titanium metal and the titanium vapor were expected to "getter" the oxygen and nitrogen impurities. However this experiment was only partially successful, reducing the nitrogen content from 0.005% to 0.003% nitrogen. An identical experiment carried out on a zirconium block was less successful.

Another technique which made use of nitride formation at elevated temperatures involved passage of the impure gas over heated metal filings or metal sponge contained in a silica tube. Nitride formation took place on the surface of the metal; the argon passed through unaffected.

Titanium sponge, heated to 900° - 1000°C has been previously thus employed for the quantitative removal of nitrogen and oxygen from argon (18), and from hydrogen (2). At a temperature of 1000°C or higher the film of Ti + O_2 flakes off (17), exposing reactive metal. Although this is not the case with the reaction product of titanium and nitrogen, the entire charge of titanium can be considered available for reaction with nitrogen. As anticipated the rate of reaction is lower with nitrogen than with oxygen.

It has been reported (23, 35) that uranium and thorium filings are similarly successful in removing the nitrogen from argon at temperatures lower than employed with titanium. These metals were investigated and were found to be effective, under working conditions, at temperatures of about 900°C. The applicability of thorium filings to this purpose was however questionable because of its limited availability and limited capacity. A tenacious yellow film of nitride formed on the surface of the filings, inhibiting further reaction. The progression of the film along the filings did provide a visible indication of the amount of furnace charge still available. Uranium filings were more readily available and no less effective than thorium in purifying argon.

The purification system finally employed in this investigation consisted of two silica furnace tubes. The first tube contained uranium (or thorium) filings, the second titanium sponge. Both tubes were heated to 1000°C; the proximity of a wax seal prevented the use of higher temperatures for extended periods of time.

The rate of flow of the argon through the purification tubes was expected to exert an effect on the efficacy of the "gettering" process. A long contact time between the gas and the active metal should favor the clean-up of the argon. Such an effect was indeed observed. Flow rate was varied by adjusting the argon tank pressure; relative flow rate was inferred from the maximum deflection attainable on the compound-gauge at the manifold. Variations in flow rate exerted only a second order effect within the limits of flow rate possible with the available apparatus. For more accurate control, measurement and investigation of the flow rate, a bleeder valve should be inserted at the argon inlet on the manifold.

2. Outgassing of the excitation chamber

Some provision must also be made for the removal of the nitrogen and oxygen adsorbed on the surface of the structure. The most common technique is to subject a system to a high vacuum for an extended period of time. This time necessary to "outgas" the system can usually be shortened by heating the apparatus while it is under vacuum. However, such a procedure, as described by Fassel and Tabeling, did not provide for sufficient decontamination of adsorbed nitrogen.

Nitrogen may be dissociated into atoms to an appreciable extent by the action of an electrical glow discharge at low pressures. Since atomic nitrogen is very reactive chemically, it is not unreasonable to expect atomic nitrogen to be irreversibly adsorbed by the surface of the chamber. The thermal desorption of nitrogen and oxygen molecules from the chamber surfaces by the action of the glow discharge was also anticipated.

These outgassing properties of a glow discharge were investigated as follows. A high frequency spark was discharged to a block electrode. The chamber was slowly evacuated until the discharge was no longer confined to the analytical gap and until the pitting of the spark upon the chamber floor was no longer visible. This argon pressure and the discharge were then maintained for 10 minutes. After discontinuing the discharge, the chamber was evacuated (p = 0.02 microns Hg). A high current D.C. arc was run to the block electrode to aid in removing the "loosened" gases. The resulting blank was lower than would have been obtained by employing only the D.C. arc. However, the overall improvement in blank was at most 15 ppm nitrogen. Increased time of analysis and the excessive volatilization of carbon by the glow discharge outweighed the advantage of the small improvement in blank.

A more rigorous version of the procedure described by Fassel, Tabeling and Gordon (20, 21) was successful in removing the gases adsorbed on the surfaces of the glass separator, on the steel plates and on the electrodes. The most critical step of the outgassing procedure was the decontamination of the sample electrodes. Rather stringent conditions were found necessary to insure complete removal of the last traces of nitrogen. The following procedure, although tedious was chosen to insure complete outgassing. A 30 ampere D.C. arc was run to each electrode for 30 seconds at an argon pressure of 10" mercury. Evacuation of the chamber was then initiated. The arc was maintained for seven seconds after violent eruption of carbon particles from the electrode was noticed. At this point the entire electrode was a bright orange, having attained a temperature of approximately 800°C. This procedure was carried out twice on each electrode. The large amount of carbon deposited on the glass separator was removed by wiping the glass with a pad of absorbant tissue after the samples were loaded.

Provision was made to restrict adsorption of nitrogen from the atmosphere while loading samples into the chamber. A Teflon cover was quickly placed on the glass separator after the top of the chamber was removed. Grooves were cut into the Teflon to match the diameter of the glass separator. A 1/2" hole was cut into the cover over the sample electrodes to permit the loading of samples. An outward flow of argon through this hole and around the grooves, restricted the readsorption of the atmospheric gases.

The principle followed in removing the gases adsorbed on the chamber was to subject all inside surfaces of the chamber to stronger outgassing influences than were attained when samples were excited. This objective was achieved by arcing an auxiliary, cylindrical electrode at a high current (35 amperes) for a relatively long time (3 minutes) under a reduced argon pressure (15" Hg).

The heat generated by the discharge "loosened" the adsorbed gases for removal upon evacuation of the chamber. During these chamber outgassing arcings, only the "O" ring cavity was water cooled. A simple cylindrical anode was used in place of the undercut variation for the outgassing arcings so that the heat generated in the electrode was conducted more efficiently to the rotary electrode platform and to the chamber. It was necessary to direct a blast of air onto the external surface of the glass separator nearest the arc discharge to prevent overheating and cracking of the separator. Three outgassing arcings were made with intervening evacuation and replenishing with pure argon. Evacuation of the chamber was carried out as quickly as possible after the 30 ampere arc was terminated. When samples were excited, lower arc currents and shorter arcing periods reduced heat flow to the chamber; higher argon pressures and additional cooling provided by the flow of water through the inner cavity reduced the chamber blank to negligible proportions. As a precautionary measure, a monitoring blank exposure was made at the beginning and at the end of a series of exposures. When operating conditions permit, the chamber may be outgassed while evacuating and heating externally. This alternative method was effective only if the heating and evacuation were applied for three or four hours.

D. Standard Samples and Sample Preparation

Table 2 contains a list of samples of known nitrogen content used in this investigation.

Table 2. Nitrogen standards

No.	Sample designation	Nitrogen conc. wt. %	General composition (Note that remainder is iron)
1.	NBS 122c	0.004	3% C, 0.5% Mn
2.	NBS 111b	0.009	0.7% Mn, 1.8% Ni, 0.25% Mo
3.	NBS 8h	0.017	0.45% Mn, 0.12% C, low alloy
4.	NBS 101c	0.035	low alloy
5.	J and L 87997	0.017	0.33% Mn, 0.05% C
6.	J and L 92171	0.025	0.4% Mn, low alloy
7.	410A	0.035	13% Cr, 1% Ni, 0.15%, C
8.	304A	0.060	18% Cr, 8% Ni
9.	347A	0.083	18% Cr, 7% Ni, 2% Mn, 1% Nb
10.	Nichrome	0.039	60% Ni, 16% Cr
11.	A9	0.240	10.5% Mn, 12.2% Cr
12.	84	0.023	15% Cr, 24% Ni

Samples 1, 3, 5, 6, 10, 11, were analyzed by both the Kjeldahl and isotope dilution techniques (52) to establish the nitrogen concentration. Sample no. 12 was particularly difficult to analyze by wet chemical means. The value quoted in the table is the result of a vacuum fusion analysis performed at the Ames Laboratory. Samples 7, 8 and 9 were analyzed by both the Kjeldahl and the vacuum fusion techniques. The values obtained by the two methods agree within experimental error. The Kjeldahl values are quoted in the table. Samples 1, 2, 3 and 4 were obtained as filings from the National Bureau of Standards. Samples 5 and 6 were obtained from the Jones and Laughlin Steel Co.; samples 7, 8 and 9 from Republic Steel Co.; samples 11, 12 from the Ford Motor Co.

E. Nitrogen Evolution from Steel Samples

Low alloy steel samples, differing in nitrogen content were arced under the experimental conditions developed by Fassel and Tabeling (20) for the determination of oxygen in steel. The nitrogen line at 8216A and the cyanogen band head at 3883A were detected. The signal-to-noise ratio of the line and of the band head increased roughly with increasing nitrogen concentration.

It was then necessary to investigate the effect of the high current D.C. arc on the evolution of the nitrogen contained in the sample and the effect of iron vapor in the arc column on the subsequent excitation and measurement of N 8216A and CN 3883A. Determination of the short term properties of each of the lines and of the line pair during a discharge was accomplished by moving the photographic plate at definite, short intervals while the discharge was being carried out. Thus the exposure on the plate consisted of a sequence of intensities, each arising from a five or ten second interval of the discharge. A plot of the relative line intensities and of the intensity ratio against time gave some idea of the processes taking place in the arc and the response of the lines to these processes.

Figures 4 and 5 are examples of such plots. CN 3871.4A was measured because of an iron interference at 3883.4A. The discharge was carried out in an argon atmosphere between a carbon rod and a low alloy steel sample-graphite electrode assembly. In the first ten seconds the iron sample melted; the electrode cup reached a red heat during the next ten seconds interval. The sample then underwent violent agitation, slowly sinking into the electrode to occupy about half the space above the electrode originally occupied by the unfused sample. Iron vapor, of low excitation energy, flooded the analytical gap for about 130 seconds, when arcing at 20 amperes. This period was shortened to 90 seconds by employing a 25 ampere arc. Throughout the arcing process small particles of molten metal were discharged from the

Figure 4. Variation of cyanogen, argon and iron intensities with time

Arcing current - 25 amperes

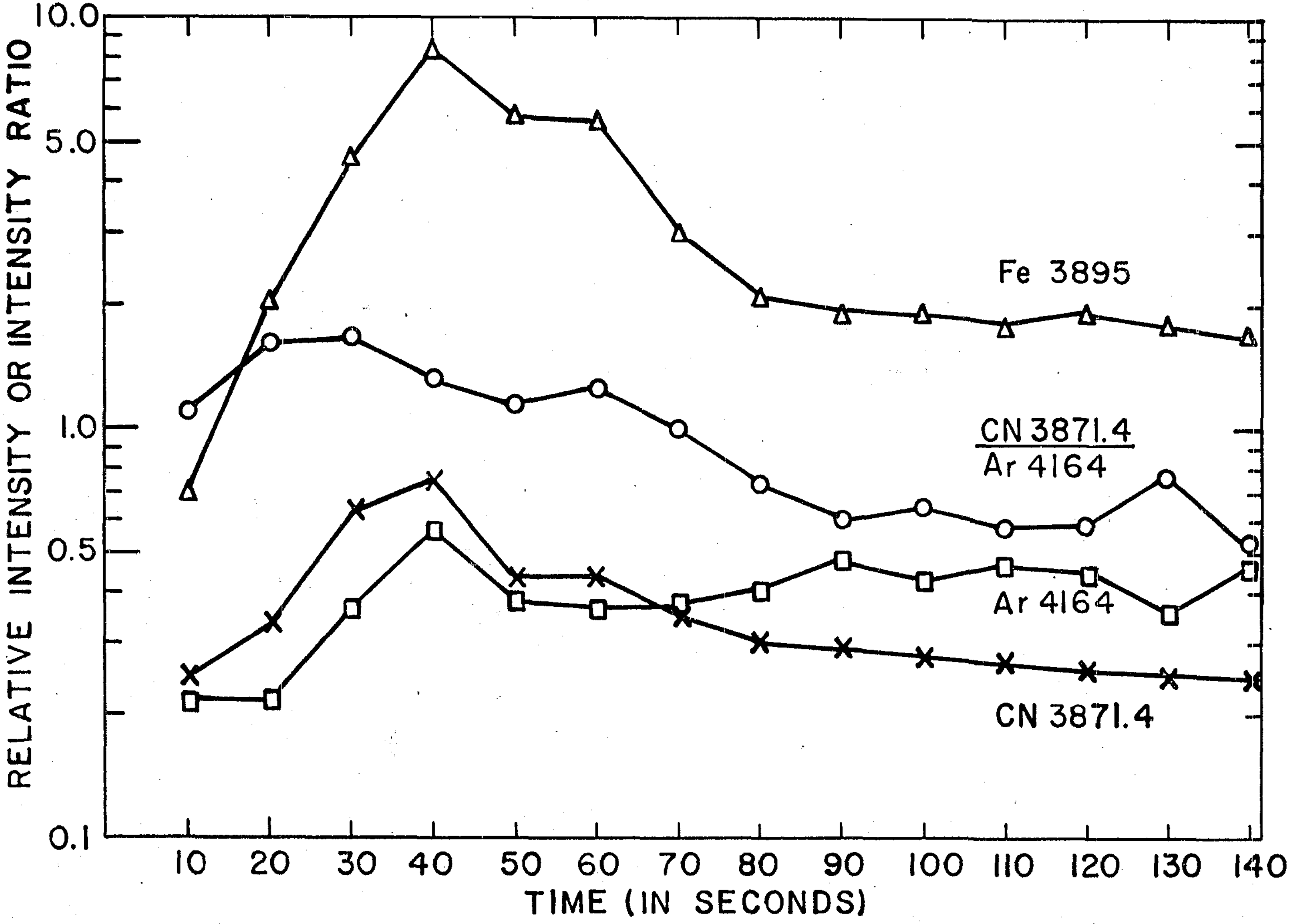
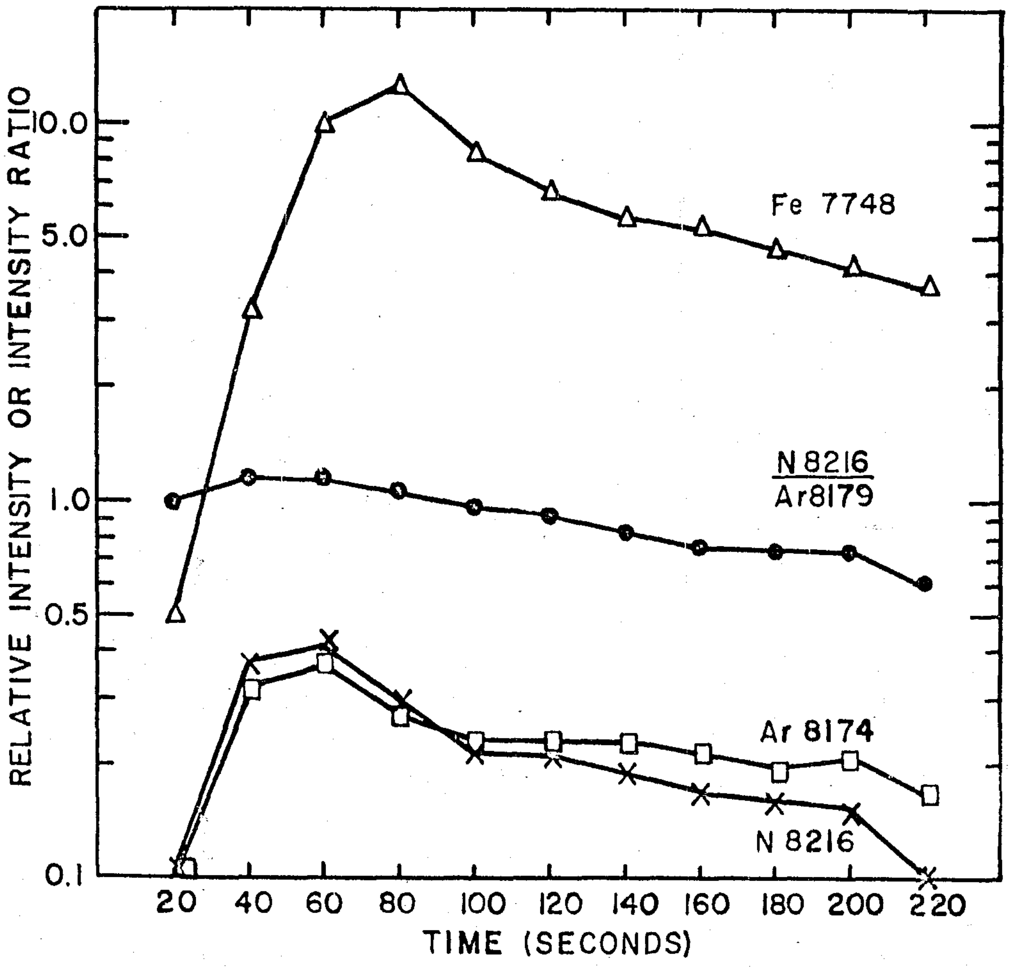

RELATIVE INTENSITY OR INTENSITY RATIO
10.0
5.0
1.0
0.5
0.1
10
20
30
40
50
60
70
80
90
100
110
120
130
140
TIME (IN SECONDS)
Fe 3895
CN 3871.4 / Ar 4164
Ar 4164
CN 3871.4

Figure 5. Variation of nitrogen, argon and iron intensities with time

25 amperes arcing current


RELATIVE INTENSITY OR INTENSITY RATIO
10.0
5.0
1.0
0.5
0.1
20
40
60
80
100
120
140
160
180
200
220
TIME (SECONDS)
Fe 7748
N 8216 / Ar8179
Ar 8174
N 8216

electrode. When dealing with samples containing more than 0.03% nitrogen, an expansion and contraction of the molten metal was apparent. At an arcing current of 20 amperes this expansion takes 45 to 60 seconds while arcing at 25 amperes shortened this by about a factor of two.

If the intensities of the reference line and the analytical line vary drastically but in consort, the intensity ratio of the two lines will remain constant. As shown in Figures 4 and 5, the nitrogen line and cyanogen band head do not vary completely in consort with the iron lines. This is particularly apparent early in the discharge period where the fluctuations of iron intensity are more drastic than the corresponding fluctuation in cyanogen and nitrogen intensity. Thus iron lines are not particularly suitable as internal standard lines.

Previous demonstrations by Fassel and Tabeling (20) have shown that the measurement of oxygen line intensities relative to the intensities of argon lines excited simultaneously, provided a high degree of compensation for the intensity fluctuations of the analytical line. Variations in argon line intensity were however slightly more drastic than the corresponding variations in intensity of the cyanogen band head. As a result of this incomplete compensation, the intensity ratio $I_{CN\ 3871}/I_{Ar\ 4164}$ was not at all constant with time. This effect implied that the eventual precision of analysis of nitrogen in steel through the use of cyanogen radiation would be poor, i.e. a standard deviation greater than ± 10% would probably be obtained.

Good compensation for the fluctuation of intensity of the atomic nitrogen line at 8216A was provided by the argon line at 8179A. Variations in the amount of iron vapor present in the analytical gap exerted almost an identical effect on the intensity of each of the two lines. As a result the intensity ratio $I_{N\ 8216}/\ I_{Ar\ 8179}$ was relatively constant with time (Figure 5). Better precision than possible using cyanogen radiation was anticipated.

Observation of the intensity ratios N 8216/Ar 8179 and CN 3883/Ar 8179, directly proportional to nitrogen concentration in the chamber atmosphere, were expected to provide useful information on the time dependence of the nitrogen evolution process. However the presence of a competing process became apparent from the moving plate studies. The slow decrease of the ratios I_{CN}/I_{Ar} and I_N/I_{Ar} with time (as shown on the moving plate curves) must have been due to a "gettering" process involving the cyanogen molecule and/or atomic nitrogen. This process was evidently more rapid than the slow increase of nitrogen due to the outgassing of the excitation chamber. Such an increase has been noted for oxygen (20) and was expected for nitrogen. Cyanogen is known to be a highly reactive specie, more stable as the dimer in the gaseous state or as the cyanide ion in solution. Similarly atomic nitrogen is chemically a highly reactive specie. It was not unreasonable therefore to expect the cyanogen radical or atomic nitrogen to be irreversibly adsorbed to the chamber walls or to the electrodes. A reasonably accurate (± 10 seconds) reproduction of the length of all arcing steps was necessary because of this effect. Only when the arc was in progress was the cyanogen radical produced and, of course, gettered. The common procedure of extending the arcing times at the end of a chamber load to insure adequate spectral intensity could not be done here because of this gettering phenomenon. Consideration had to be taken of this effect regardless of the specie supplying the radiation which was related to nitrogen concentration.

Because of this gettering process and because of the possible effect of iron vapor on the line intensities, it was not possible to accurately infer the time necessary for complete evolution of nitrogen from the molten steel samples via the moving plate studies.

However, these values were determined in the following manner. A sample-electrode assembly was arced at a chosen current for 60 seconds. An auxiliary electrode was then moved into position for the photographic exposure. After the exposure the chamber was evacuated. This procedure was then repeated twice more, but at 45 second arcing periods. Fifteen seconds of this period was necessary to remelt the sample. Absence of the cyanogen band head (at 3883A) on the plate was taken as an indication of the complete evolution of nitrogen from the sample. Table 3 contains a summary of the data for the various arcing currents investigated. The times quoted are believed to be accurate within ± 15 seconds.

Table 3. Pre-arc periods for nitrogen evolution

Current (amperes)	Time (minutes)
20	1.5
25	1.5
30	1.0

The use of a current of 30 amperes was experimentally impractical. An excessive quantity of iron was volatilized and the problem of increased blank due to heating the chamber was enhanced.

Two factors which most significantly influence the rate of removal of the gas from the sample are the electrode temperature and the rate of solution of carbon in the molten sample. Electrode temperature itself is significant on two counts, i.e. determining the rate of decomposition of the nitrides and the solubility of the available carbon in the melt. The presence of carbon in the iron melt does not appear to be necessary for the reduction of the nitrides (55) although carbon is necessary for the decomposition of oxides. Vacuum fusion work has shown that such a melt will become viscous and even solidify upon excessive dissolution of carbon. Although the molten sample has never been observed to solidify under the D.C. arc, increased viscosity of the melt may prevent evolution of nitrogen from the sample in the time allotted.

The most pertinent dimension of the sample electrode was believed to be that of the 1/16" constriction which restricted heat flow out of the cup into the base of the electrode. Under operating conditions the sample cup became a bright orange, while the electrode base remained black. By keeping the electrode cup only as large as necessary to hold the sample, heat losses through radiation were reduced. Thus heat poured into the electrode from the arc was used in heating the sample, favoring the increase in the rate of decomposition and reduction of the nitrides and oxides.

Dissolution of carbon by the molten sample was investigated for two types of sample electrodes. The first electrode possessed just enough of a retaining wall to prevent the sample from falling off the electrode. In the second case the retaining wall was equal in height to the sample

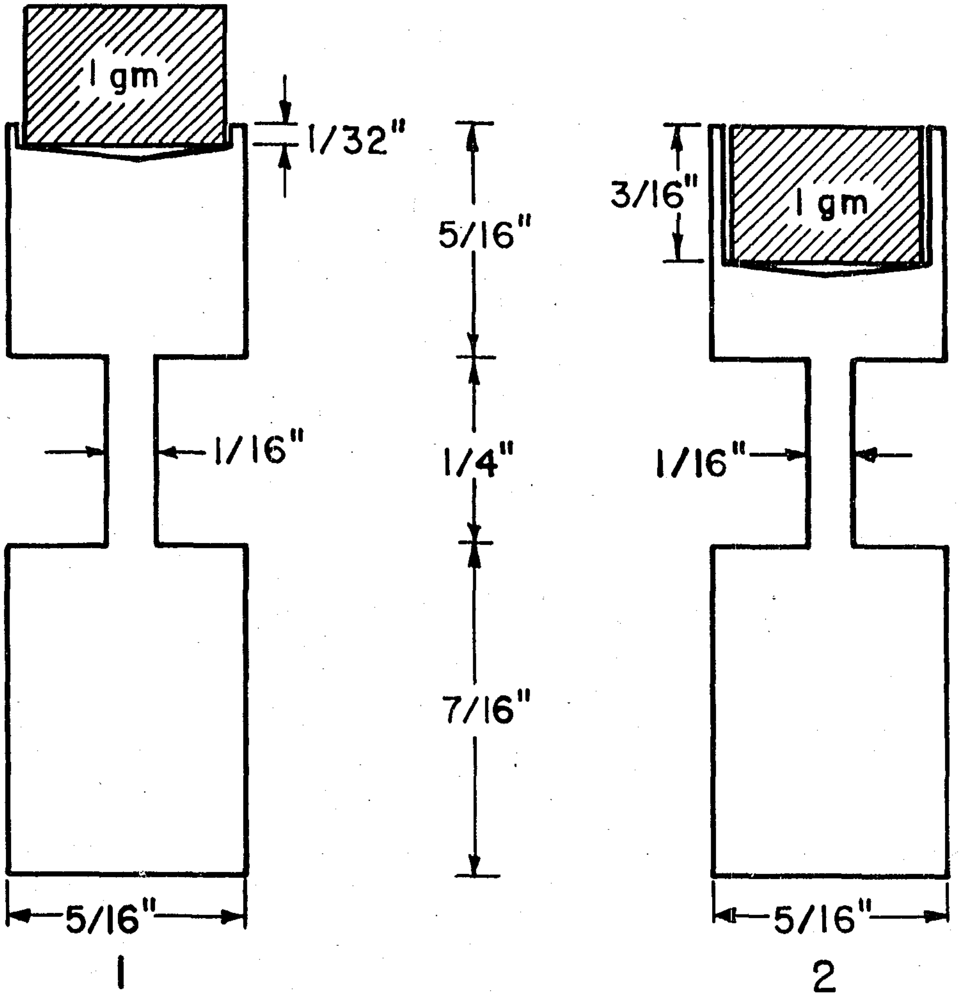
(Figure 6). All dimensions were kept constant except the cup depth and the cup-base thickness. The sum of the two was equal to 5/16". Electrode #1 had a cup depth of 1/32"; electrode #2 had a cup depth of 3/16". The arc was observed to strike both the wall of the 3/16" cup and the sample. Graphite from the heated wall and from the cup base was rapidly dissolved by the molten sample, while the sample contained in the 1/32" cup was able to dissolve a significant amount of carbon only from the base of the cup. The final carbon content of the sample was determined by routine chemical procedures; the 1/32" cup sample contained 4.46%C while the 3/16" cup sample contained 6.76%C. Identical arcing periods at 20 and 25 amperes were investigated. Table 4 summarizes the results.

Table 4. Effect of cup depth on intensity ratio

Intensity ratio	Current (amperes)	Cup depth		Standard
		1/32"	3/16"	
CN 3883A/Ar 4164A	20	0.822	0.702	NBS 111b
	25	0.822	0.711	NBS 111b
N 8216A/Ar 8179A	25	0.590	0.480	NBS 8h

Figure 6. Supporting anodes

1. 1/32" cup depth
2. 3/16" cup depth

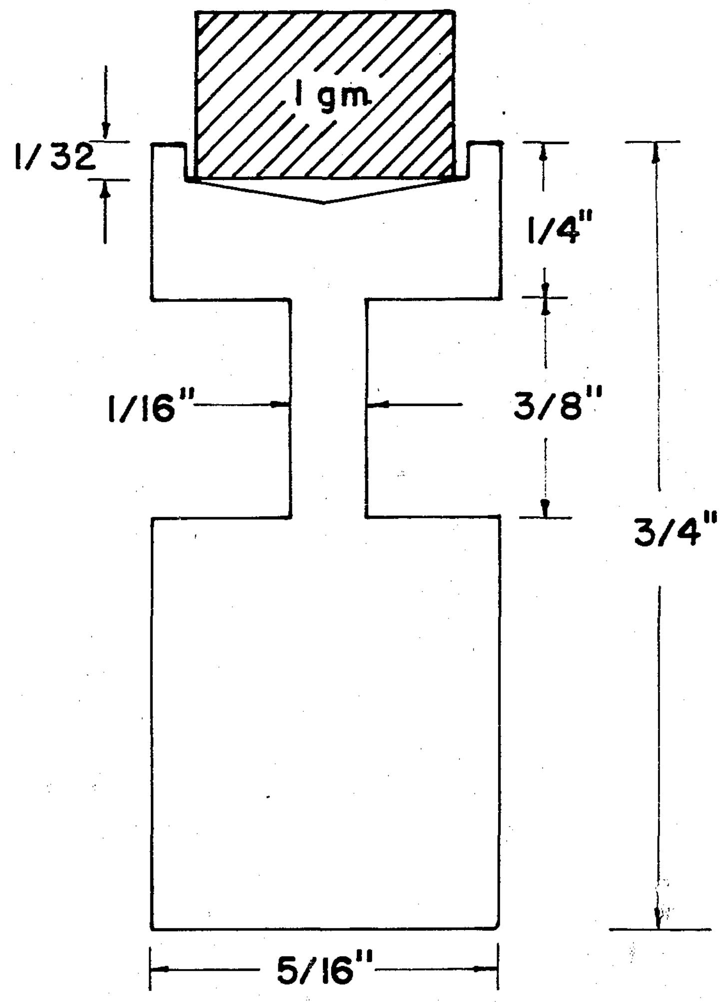

1 gm
1/32"
5/16"
1/16"
1/4"
7/16"
5/16"
1
3/16"
1 gm
1/16"
5/16"
2

The most significant result of the experiment was that the intensity ratio obtained with the 1/32" electrode was in all cases significantly higher than the corresponding value obtained with the 3/16" electrode. More nitrogen was thus extracted from the sample when the shallow cup was used. Apparently the larger amount of carbon introduced into the molten sample was detrimental to the release of nitrogen into the argon atmosphere. Modification of the original electrode design was therefore made; a 1/32" cup depth was substituted for the 1/16" cup depth employed by Fassel and Tabeling (Figure 7). The large electrode cup base of Figure 6 was reduced in size, decreasing the amount of carbon to be outgassed.

Carbon did perform the useful function of "holding" the molten globule to the electrode. The importance of this factor was demonstrated by the following experiment. A 0.2 gram slug of zirconium was placed upon a sample electrode. Upon arcing, the zirconium melted and assumed the shape of the electrode, forming ZrC, which melts at 3540°C. An iron sample was then run on this electrode in the normal manner. Excessive volatilization of iron was observed. The globule rolled out of the cup 60 seconds after the arc was initiated, attaching itself to the underside of the electrode.

Evolution of nitrogen and oxygen, even though complete, could not be observed in the direct analysis of steel samples containing a large percentage of a volatile alloying metal.

Figure 7. Supporting anode (dimensions in inches)


1 gm
1/32
1/4"
1/16"
3/8"
3/4"
5/16"

One of the steel standards (A9) contained a large amount of manganese (10%). This metal is quite volatile under the discharge conditions employed, flooding the gap with easily excited manganese atoms, completely suppressing the argon, nitrogen, cyanogen and oxygen spectra. Consequently, nitrogen in high manganese steels could not be determined by exposing while arcing directly to the sample. If, however, the arc was discontinued after two minutes arcing time and an auxiliary electrode moved into position, the subsequent exposure carried out on the auxiliary electrode yielded consistent N/Ar intensity ratios. Manganese deposited on the counter electrode and chamber walls did not apparently result in noticeable "gettering".

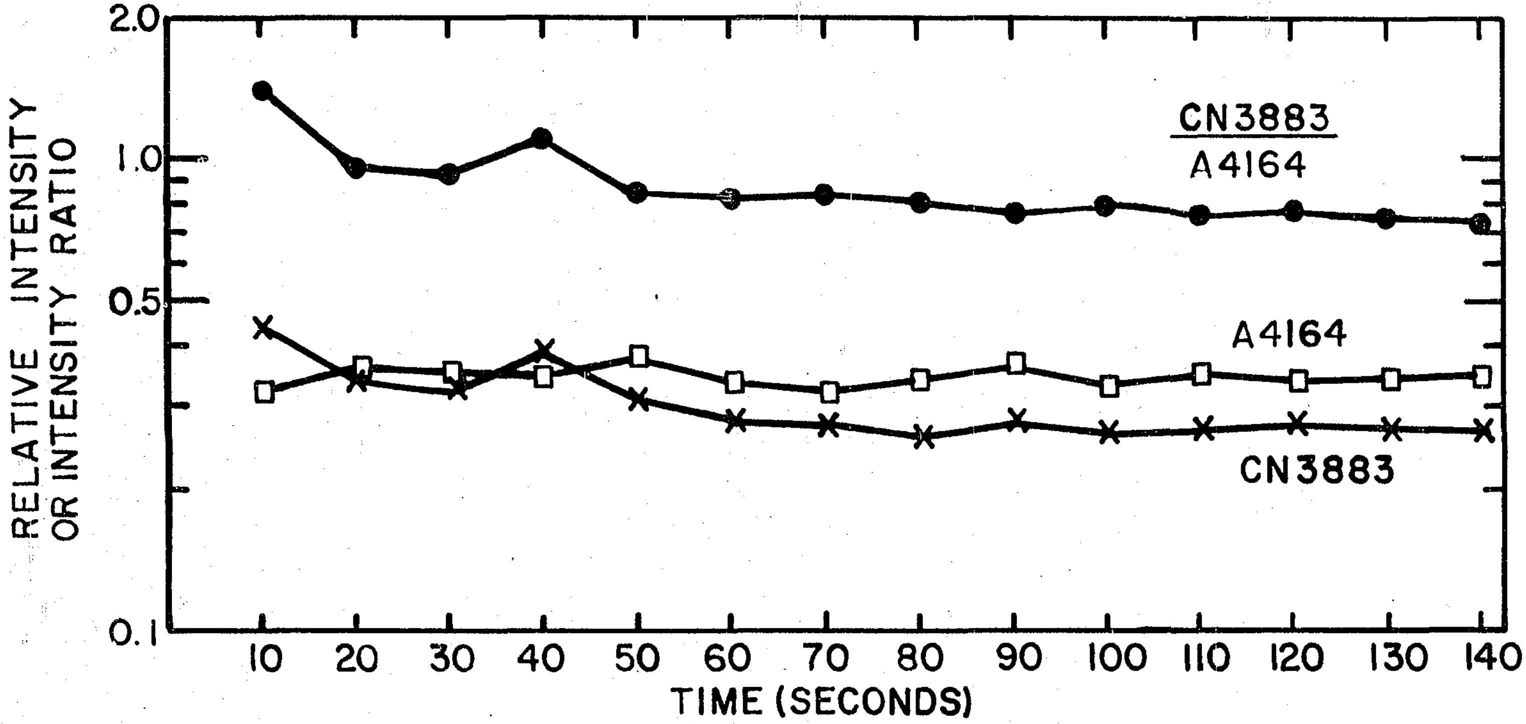
This auxiliary electrode technique also alleviated the problem of poor precision which arose from the non-reproducible volatilization of iron vapor into the analytical gap while photographing the analytical line pairs involving cyanogen band heads. The following two experiments verified this conclusion.

First, a steel sample was arced for two minutes at 25 amperes to insure evolution of nitrogen. The arc was discontinued and an empty sample electrode was moved into arcing position. The arc was re-initiated and a moving plate study was carried out. Large fluctuations in relative intensity and intensity ratio noted earlier were not present here. (Figure 8).

Figure 8. The variation of the cyanogen and argon intensities with time

25 amperes arcing current

graphite electrodes


2.0
1.0
0.5
0.1
RELATIVE INTENSITY
OR INTENSITY RATIO
CN3883
A4164
A4164
CN3883
10
20
30
40
50
60
70
80
90
100
110
120
130
140
TIME (SECONDS)

The second experiment was carried out as follows: Case I. A series of exposures were taken, each while arcing directly to a steel standard. Case II. After the gases were completely evolved from the sample, the arc was discontinued and an auxiliary electrode moved into position. The exposure was then taken. Multiplicate runs were made of Case I and Case II. The intensity ratio CN 3883/Ar 4164 was measured. A standard deviation of ± 22% was obtained in Case I; a standard deviation of ± 14% was obtained in Case II. The auxiliary electrode technique was therefore used in preparing the analytical curve for the determination of nitrogen in steel through use of cyanogen and atomic nitrogen radiation.

VI. CALIBRATION EXPERIMENTS

Argon lines available as reference lines for the cyanogen band head in the wavelength region 3800 - 4300A were not numerous. Ar 4164A and Ar 4200A were reasonably free of interference by strong iron lines and of the proper intensity for use as internal standard lines. However some error in the measurement of the intensity ratios was introduced due to the variation in photographic plate response with wavelength. This effect was manifested in separate plate calibration curves for CN 3883A and Ar 4164A. The separation of these curves was particularly large on some Kodak IN and SAI plates; however the separation was always small with Kodak M plates.

Another technique (50) of converting percent transmission into relative intensity, the "Delta Method", was investigated. This method requires that the separation of the two calibration curves be only constant at 10% or 25% transmission for a given intensity. (The choice of % transmission is somewhat arbitrary). A small improvement in precision was obtained, lowering the standard deviation by about two percent in the case of CN 3883/Ar 4164.

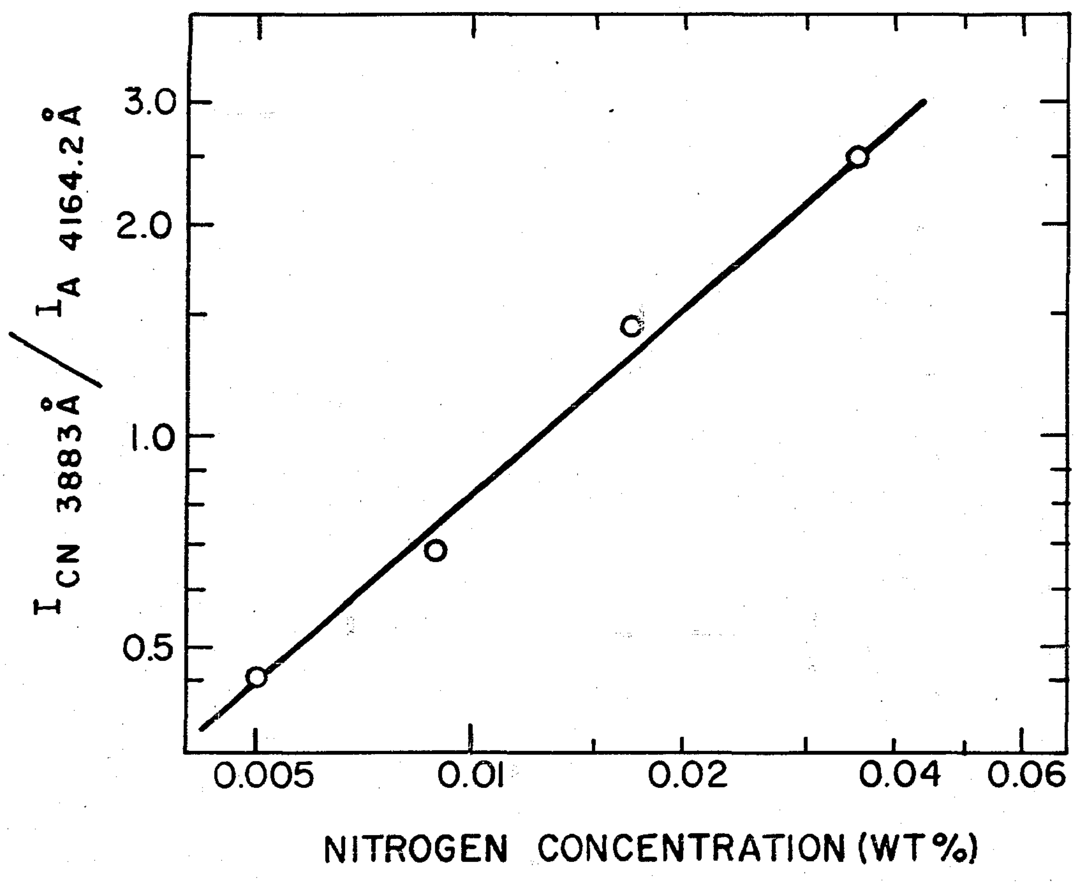
Since the spread of the points used for plate calibrations of the Kodak M plates was seldom greater than commonly obtained in calibrating the less uniform and grainier IN plates employed for oxygen analysis, and since only a small improvement in precision was obtained through use of the more tedious "Delta Method", standard plate calibration procedures were employed (15) to measure the intensity ration $I_{CN\ 3883}/I_{Ar\ 4164}$.

A. Analytical Curve Employing Cyanogen Radiation

National Bureau of Standards low carbon steel samples, listed in Table 2, (no. 1, 2, 3 and 4) were used to develop the analytical curve shown in Figure 9. One gram samples were run; the line pair CN 3883/Ar 4164 was measured. Spectral interferences, Cr 3883.29A and Fe 3883.30A, were rendered inconsequential by application of the auxiliary electrode technique. Argon lines, first and second order, did not interfere with the measurement of CN 3883.4A.

Thirty ppm nitrogen in steel gave rise to a quantitatively measurable intensity ratio. It was for this reason that a good deal of importance was attached to the investigation of cyanogen radiation, despite the anticipated poor internal standardization. Computations of the precision of the technique were carried out on the basis of eight analyses of sample NBS 8h. A standard deviation of ± 14.4% of the amount reported was so obtained. The spread of intensity ratios obtained from quintuplicate analyses of the three remaining standards was essentially the same. It was found

Figure 9. Analytical curve for the determination of nitrogen in steel employing GN 3883A


$I_{CN\ 3883\text{Å}} / I_{A\ 4164.2\text{Å}}$
3.0
2.0
1.0
0.5
0.005
0.01
0.02
0.04
0.06
NITROGEN CONCENTRATION (WT %)

necessary to correct the analytical curve for a "blank" contribution of 0.005% nitrogen.

The cyanogen band head at 3871A was less intense than the 3883A band head by a factor of 1.5, detecting about 0.005% nitrogen. A standard deviation of ± 12.3% was obtained for multiplicate analyses (intensity ratio CN 3871/Ar 4164) on standard sample NBS 8h. A disadvantage in the use of CN 3871, photographed in the second order, arises from an interference due to a first order argon line.

This high standard deviation obtained with the two line pairs involving the cyanogen band heads was essentially a manifestation of one factor. The analysis line and the internal standard line differ greatly in excitation potential (E_{CN} = 3.6 e.v.; E_{Ar} = 14.5 e.v.). The significance of this point lies in the equation correlating the factors which determine the ratio of the intensities of two spectral lines.

$$\frac{I_1}{I_2} = \frac{A_1}{A_2}\,\frac{g_1}{g_2}\,\frac{f_1}{f_2}\ \exp -(E_1 - E_2)kT$$

I = intensity, A = transition probability, g = statistical weight, f = frequency, E = excitation energy, k = Boltzman constant, T = absolute temperature. If $(E_1 - E_2)$ is identically zero, the exponential term vanishes and the intensity ratio is independent of arc temperature. This is desirable since the temperature of the arc column does fluctuate in an erratic manner, as the arc wanders across the sample cavity.

As discussed in section V. B, the materials present in the arc column will influence the quantity of energy (measured by temperature) available for the excitation of a specie. For example, the presence in the arc, of a large amount of iron, with a multitude of excited levels around 3 e.v. would decrease the probability of occurrence of processes requiring 14 e.v. while favoring other processes requiring about 3 e.v. This effect will vary in magnitude, (i.e. the "temperature" will vary) depending on the quantity of iron volatilized.

Similarly, steel samples containing different quantities of alloying constituents and a given amount of nitrogen, may not give rise to the same N/Ar or CN/Ar intensity ratios. Erratic volatilization of iron into the analytical gap would be expected to significantly influence intensity ratios. The quantity of material present in the analytical gap is dependent on the boiling point of the steel. This value may differ between steels due to different pretreatment in the manufacture and the variation in alloying constituents. Such effects are relatively unimportant if the internal standard line is well matched to the analysis line in excitation potential.

The excitation potential of the ultraviolet band system of cyanogen is 3.6 e.v. (v^{1}, $v^{11} = 0$); the excitation potential of the argon internal standard line at 4164A is 14.5 e.v.

Therefore, little internal standardization is to be expected because of the large mismatch of excitation potentials. However, the production of this cyanogen radiation is only the second step of a two-stage process. First, the cyanogen molecule must be formed and only then excited. If the rate controlling step is a high energy process, a higher degree of internal standardization would be obtained than would be anticipated from the excitation potential data alone.

It is safe to infer from vacuum fusion analysis that the nitrogen is evolved from the sample as the specie N_2. The overall reaction for the formation of cyanogen then is: $2C(solid + N_2(gas) \rightarrow 2CN(gas)$. The heat of formation is 94 kcal/mole (or 3.63 e.v.). It is not known whether the reaction proceeds directly as written, or proceeds stepwise through the thermal dissociation of nitrogen with the subsequent attack of the nitrogen radical on carbon. Two pieces of information implied the existence of atomic nitrogen in the arc. The most direct indication was the ready observance of the emission spectrum of atomic nitrogen. This in itself was not conclusive since atomic nitrogen may also have been formed through the dissociation of cyanogen before the "gettering" of cyanogen. The second indication of the high energy dissociation of nitrogen was more indirect. Cyanogen radiation is primarily observed in the hotter portions of the arc (1). Many workers have suppressed cyanogen emission by the addition of alkali metal chlorides and carbonates to the arc. These materials are readily excited (2 e.v.) and serve as low energy buffers, preventing higher energy processes from taking place. Thus the excitation of cyanogen would seem to be a high energy process, implying that the dissociation of nitrogen (7-9 e.v.) is the controlling step. However, there is still a significant mismatch in "excitation" potentials to account for the relatively high standard deviation.

B. Analytical Curve Employing Atomic Nitrogen Radiation

The analytical curve for the determination of nitrogen in steel, employing the auxiliary electrode technique and the nitrogen line, is shown in Figure 10. Experimental conditions were identical to those listed in Table 5.

Ar 8179A was employed as an internal standard line for N 8216A. This line was of the proper intensity and of close proximity in wavelength. Plate response to N 8216A and Ar 8179A was identical, within experimental error.

The composition of the various steel samples employed to develop the curve are listed in Table 2. Both high alloy and low alloy steels were investigated since there was no "a priori" reason to expect the high alloy steels to behave in a manner similar to the low alloy steels. The auxiliary electrode technique prevented the alloying constituents from exerting a deleterious effect on the excitation characteristics

Figure 10. Analytical curve for the determination of nitrogen in steel employing N 8216A

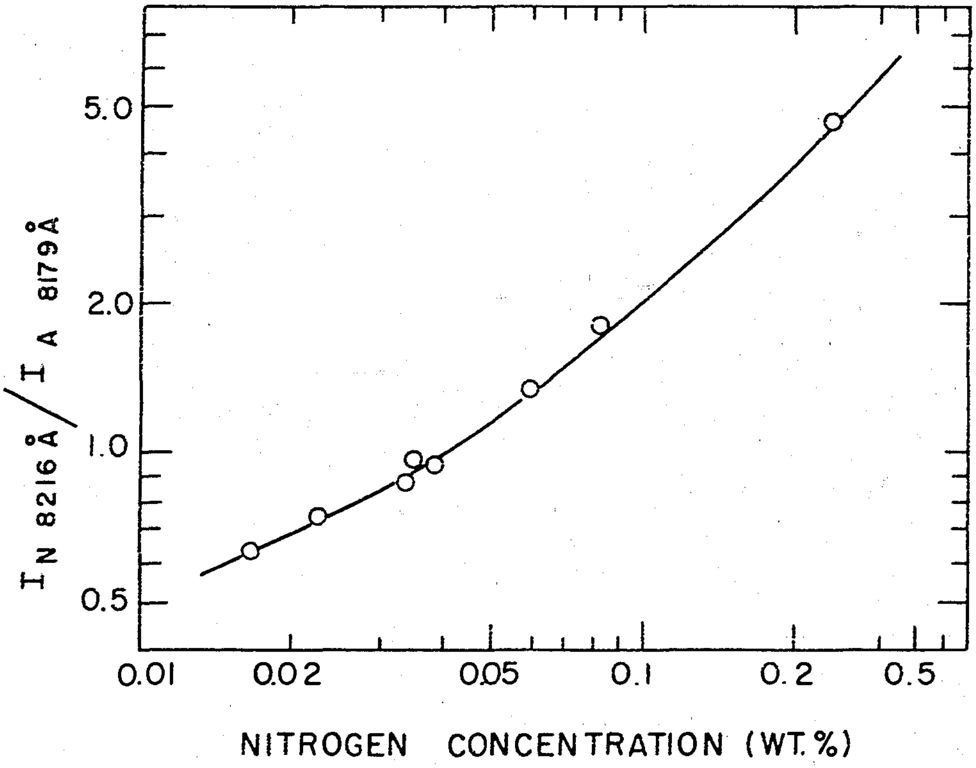

$I_{N\ 8216\ Å} / I_{A\ 8179\ Å}$
5.0
2.0
1.0
0.5
0.01
0.02
0.05
0.1
0.2
0.5
NITROGEN CONCENTRATION (WT.%)

Table 5. Excitation conditions for the determination of nitrogen in steel

Line Pairs (A)	CN 3883.4/ Ar 4164.2 N 8216.5/ Ar 8178.8
Weight Sample	1.0 gram
Anode (graphite supporting electrode)	shown in Figure 7
Cathode (graphite)	1/8" diameter 3/4" long
Argon pressure (mm of Hg)	640 ± 6
Analytical Gap (mm)	6
Arc Current (amperes)	25
Exposure Conditions	
Pre-arc	120 seconds
Exposure	120 seconds

of the arc. However the possibility of gettering of the gases by an active film of one of the alloying constituents could not be discounted. It also was not known beforehand whether, during the prearc period, the alloy would release into the argon atmosphere the same percentage of nitrogen that a low alloy steel sample would release under identical arcing conditions. It can be seen from the analytical curve that the high alloy and low alloy standards did in fact, behave quite similarly. Analytical points arising from both types of samples formed one line, within experimental error. Neither blank nor background corrections were made. Apparently the background produced by the reproducible analytical gap conditions of the auxiliary electrode technique rendered this latter correction unnecessary. The small curvature at low nitrogen concentrations was due to the presence of this continuous background radiation and not to the small blank. Radiation from the 0.003% blank contributed proportionately less to the overall signal at the limit of detection of the nitrogen line than at the limit of detection of the more sensitive cyanogen band head. Hence the analytical curve N/Ar showed less curvature due to the effect of the blank.

The excitation potential of N 8216.5A is 11.79 e.v. This compares favorably with the excitation potential of the Ar 8179A line (15.25 e.v.). Thus this analysis pair should be relatively independent of the effective excitation temperature, more so than CN/Ar. As anticipated, the determination of nitrogen in steel by the measurement of the radiation arising from the spectrum of atomic nitrogen was found to be more precise than the corresponding analysis involving cyanogen radiation. Intensity ratios (N 8216A/Ar 8179A) measured on eleven runs of sample NBS 8h were used for the calculation of the standard deviation. The value obtained in this manner was ± 6.30% of the quantity reported. Nine runs carried out on NBS 101c had a standard deviation of ± 1.8%. NBS 101c was however a special case. The intensity ratio for NBS 101c was almost identically one. There should have been little photometry error since both the internal standard line and the analysis line involved the same portion of the plate calibration curve.

The analytical method appeared to be only slightly dependent upon current employed. Four samples of NBS 8h and NBS 101c and one sample of A9 were run at 20 amperes. The samples were arced for two minutes; one minute exposures were taken on the auxiliary electrode. The analytical curve obtained with these values coincided with the curve obtained at 25 amperes, within experimental error.

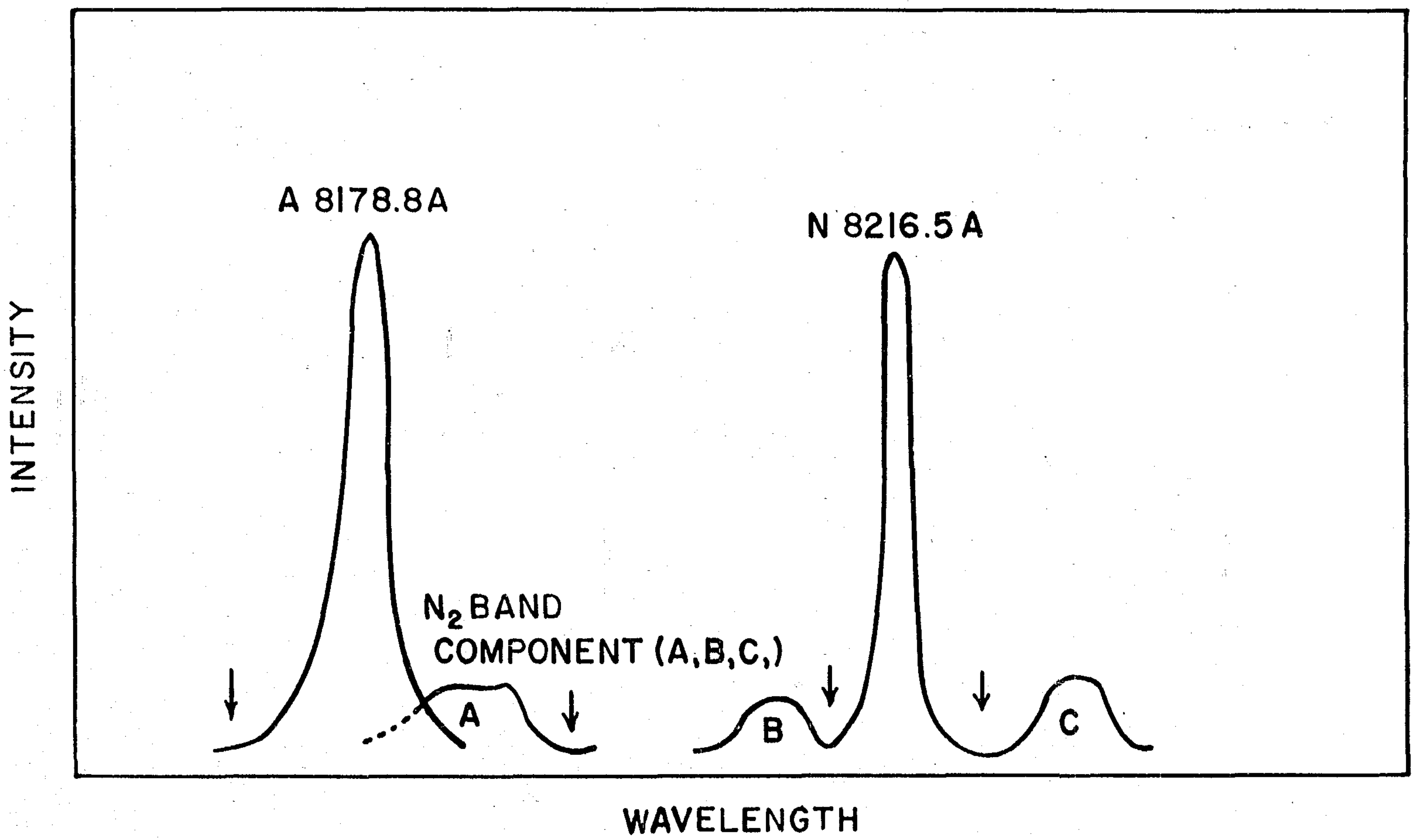
At nitrogen concentrations of 0.03 wt % or greater, a system of diatomic molecular bands arose in the wavelength region above 7800A. The intensity ratio of one of these band components correlated with the known nitrogen content. Cyanogen and N_2 are the only nitrogen containing molecules present in the discharge column in significant concentration. The band head of the cyanogen "red" system, degraded to higher wavelengths, at 7874A was observed; it is also possible that the "open" band structure at 8000A and higher belong to the "second positive" band system of nitrogen. However characteristic band heads were obscured by intense argon lines.

The nitrogen line, 8216A is free of interference from the band components; Ar 8179A possesses a slight interference. A sketch of the line contour and wavelength regions adjacent to the two lines is shown in Figure 11; background was read, when necessary at the positions indicated by arrows. The dotted line under Ar 8179A is an extrapolation of the band component intensity. Fortunately, nitrogen concentrations which would bring about sufficient broadening of the band component and hence a significant contribution of the band component to the intensity of Ar 8179A (due to halation effects on the photographic plate) involved the use of the weaker steps of the argon line for the calculation of intensity ratios. This problem of halation was insignificant in the weaker steps.

C. Simultaneous Determination of Nitrogen and Oxygen

Development of a method for the determination of nitrogen in steel involving the atomic nitrogen line at 8216A permitted the simultaneous determination of nitrogen and oxygen, at least in low alloy steels. It was fortunately possible to record on one photographic plate the line pairs needed for both the oxygen and the nitrogen analyses. Three high alloy steels which served as standards for the determination of

Figure 11. Line contour Ar 8178.8A and N 8216.5A and adjacent wavelength regions

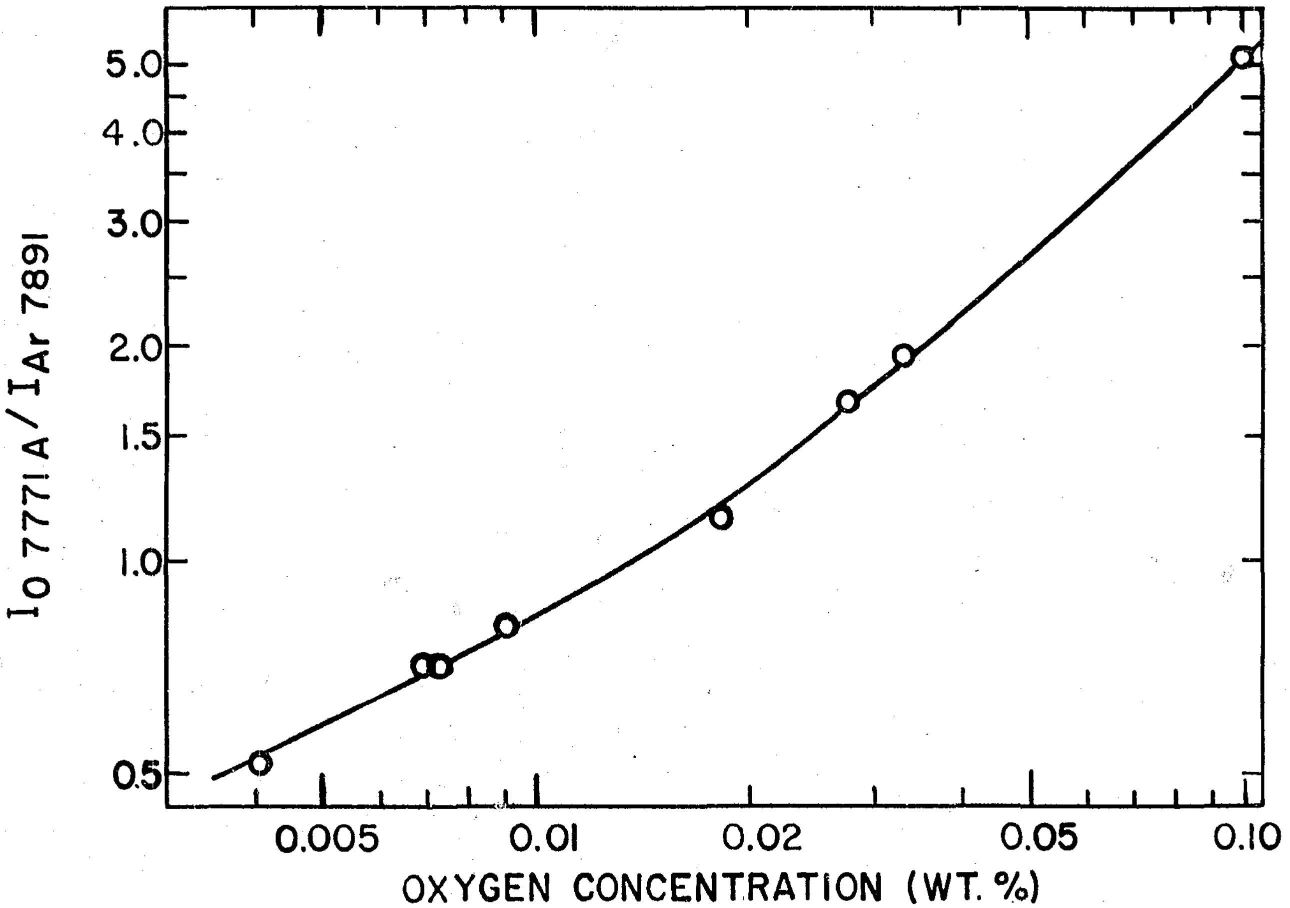

A 8178.8A
N 8216.5 A
INTENSITY
N_2 BAND
COMPONENT (A,B,C,)
A
B
C
WAVELENGTH

nitrogen were also available as standards for the determination of oxygen in steel. The low alloy steel samples analyzed by Fassel and Tabeling were also available. Table 6 contains a complete list of the oxygen-in-steel standards.

The procedure employed for the determination of nitrogen in steel was applied directly to the determination of oxygen. There were two principal differences in technique between the method originally developed for the determination of oxygen in steel and the method described here for the simultaneous determination. These involved the use of higher arcing current and the use of the auxiliary electrode procedure for exposure purposes. Outgassing and gas purification steps described in this thesis are more rigorous than those described by Fassel and Tabeling. Use of the auxiliary electrode was justified by the arguments given in the section dealing with the use of the nitrogen line. As mentioned, it was a device for the extension of the scope of the method.

The analytical curve obtained for oxygen in alloy steel is shown in Figure 12. The line pair O 7771/Ar 7891 was employed for analysis. Again the standard deviation of the technique was computed on the basis of multiplicate runs of NBS 8h and NBS 101c. Ten runs of NBS 101c gave rise to a standard deviation of ± 7.0%; nine runs of NBS 8h showed a standard deviation of ± 5.3% of the amount of oxygen reported.

Figure 12. Analytical curve for the simultaneous determination of oxygen in low alloy and high alloy steels


$I_{O\ 7771\ A}/I_{Ar\ 7891}$
5.0
4.0
3.0
2.0
1.5
1.0
0.5
0.005
0.01
0.02
0.05
0.10
OXYGEN CONCENTRATION (WT. %)

Three standards (0.007, 0.018, 0.106 wt. % oxygen) employed by Fassel and Tabeling were run in triplicate. Standards 8h, 101c available in the form of filings were formed into briquettes before analysis. Briquettes of this nature were analyzed for oxygen at the Ames Laboratory by the vacuum fusion technique. The average oxygen concentration of duplicate analyses of sample NBS 8h and NBS 101c are given in Table 6. It is probable that the alloy steel 347 was not homogeneous. A high standard deviation was obtained for both the oxygen and nitrogen analysis of this sample.

Table 6. Oxygen in steel standards

Sample	Oxygen concentration (wt. %)	Description
NBS 8h	0.033	a
NBS 101c	0.028	a
NBS #1	0.018	low alloy
NBS #6	0.007	low alloy
NBS #7	0.106	low alloy
347A	0.008	a
304A	0.009	a
410A	0.007	a

[a] See Table 2.

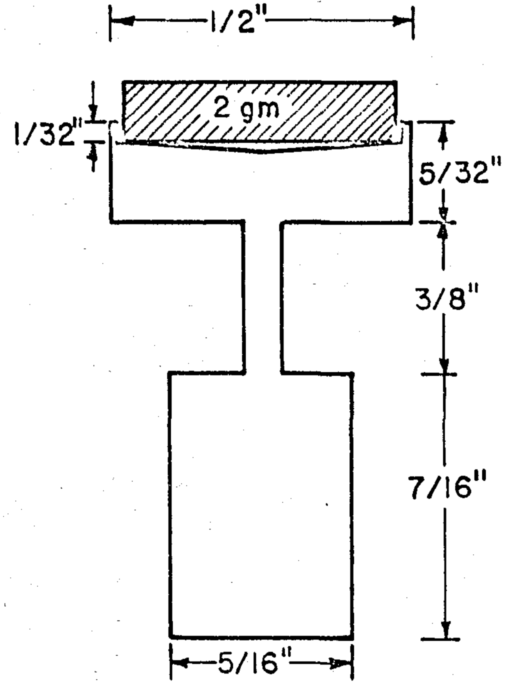
D. Effect of Sample Weight

The quantity of nitrogen evolved from the steel samples appeared to be linearly dependent upon sample weight, in the weight range 0.5 to 1.0 grams. Half gram samples of standard NBS 101c were run under the experimental conditions employed to develop the analytical curve in Figure 10. The intensity ratios for the 0.5 gram and 1 gram samples were plotted against sample weight. A line of unit slope indicated half as much nitrogen was evolved from a 0.5 gram sample as from a 1.0 gram sample. Similar results were obtained with alloy A9. Within these weight limits it was possible to adjust the weight of the high nitrogen concentration steel samples to permit the use of the more accurate portions of the analytical curve. The use of lower weight samples is particularly advantageous when dealing with steels of high manganese content. Although the excessive volatilization of manganese is not particularly detrimental to the N/Ar intensity ratios, the large amount of metal deposited on the glass separator in the light path materially reduces the overall spectral intensity.

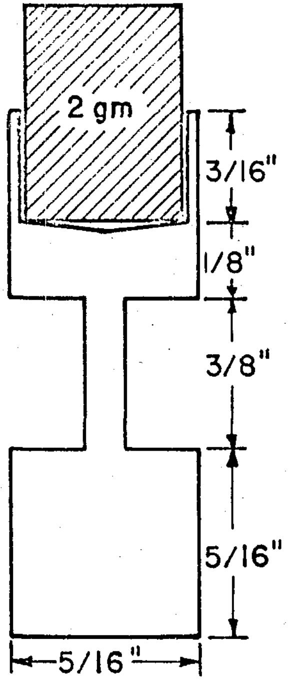
Since the analytical technique described in this thesis actually measured directly the concentration of nitrogen in argon, any device which would increase the quantity of nitrogen in the argon would thereby increase the limit of detection of the method. The simplest such device was the use of heavier samples. Arcing two gram samples of steel (which contained only small amounts of volatile metals such as manganese) was expected to increase the limit of detection of N 8216A to 0.005% nitrogen. Such an expediency of course would reduce the effect of the blank by a factor of two. Three gram samples were experimentally too bulky to use.

Preliminary experiments with two gram samples indicated that the amount of nitrogen evolved from the sample was critically dependent upon the electrode cup dimensions. A similar, though less serious effect was noted in the work with one gram samples. The principles discussed in the section dealing with electrode design for one gram samples applied equally well in dealing with two gram samples. A 2 gram sample of NBS 8h, arced in a graphite sample electrode at 25 amperes, cup 1/2" o.d. (Figure 13.1) yielded the amount of nitrogen usually obtained from a one gram sample. A 2 gram sample of alloy 304A was then arced for two minutes at 25 amperes in an electrode of the dimensions indicated in Figure 13.2. About three fourths of the total amount of nitrogen present in the sample was evolved. Further modification of the electrode design (use of a more shallow cup) was made (Figure 13.3). The cup wall was just sufficient to retain the sample. Nitrogen was evolved from a sample of NBS 8h in the theoretical amount; the data for an alloy sample indicated less than the theoretical amount of the nitrogen was evolved. It is apparent from the appearence of the

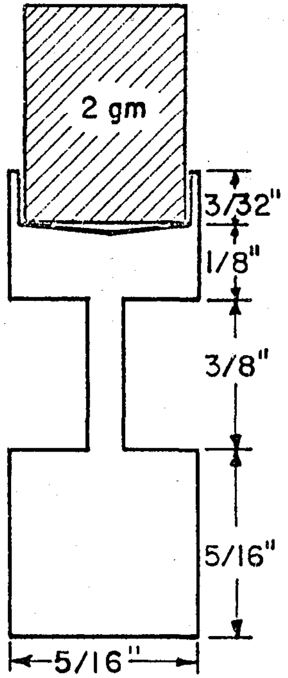
Figure 13. Electrode design for two gram samples


1/2"
2 gm
1/32"
5/32"
3/8"
7/16"
5/16"

1


2 gm
3/16"
1/8"
3/8"
5/16"
5/16"

2


2 gm
3/32"
1/8"
3/8"
5/16"
5/16"

3

arced alloy standards that higher arcing currents and/or longer times would be necessary to effect complete fusion of the sample and thus total evolution of the nitrogen from the sample.

VII. SUGGESTIONS FOR FURTHER WORK

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

Consistent results achieved with the auxiliary electrode technique over a wide range of steel compositions, suggest the possibility of using one master curve for the determination of nitrogen and oxygen in various metals. When arcing to an auxiliary electrode the nitrogen present in the argon atmosphere is independent of the nature of the original sample from which it was evolved, provided complete evolution of the nitrogen from the sample during the pre-exposure arcing step was achieved (or that the same fraction of nitrogen was evolved from all samples). Other than the simplicity involved in using one analytical curve, this idea possesses the added advantage of being applicable to the analysis of non-routine samples, i.e. metals for which a separate analytical curve has not yet been determined.

It should be possible to exploit the good sensitivity of cyanogen radiation by providing for better internal standardization. The results obtained with CN 3883A/Ar 4164A confirms the opinion of many observers that poor precision is to be expected if the intensity ratio of a band head/atom line is measured, despite highly reproducible analytical gap conditions. There is the possibility of measuring the ratio of two band heads, one of which arises from a specie always present in constant amount. This has been the basis of a flame spectroscopic method for the determination of nitrogen in organic compounds (26). A CH band head at 3890A was employed as an internal standard line for CN 3883A. The "standard deviation of the mean" was ± 2.23%. The spectroscopic method described in this thesis could be modified to permit the admission of a small constant amount of a gas such as methane into the excitation chamber, which would produce the CH radical during the excitation step.

A high frequency electrodeless discharge may be useful in extending the limit of detection. A number of workers (6, 14, 45, 48) have described the determination of nitrogen in rare gases by the use of high frequency excitation. Servigne <u>et al</u>. (48) have studied the determination of nitrogen in helium, argon, neon, krypton, and xenon at the 1 ppm level. The sample was at a pressure of a few cm mercury; the spectrum was excited with cm waves from a magnetron with a rectangular waveguide. The N_2 and N_2^+ band systems were detected. A similar system was described by Scribner and Mulligen (45). A glow discharge in a flowing system of argon excited by a microwave field is viewed end on for maximum sensitivity; the spectrum is observed with an automatic scanning photoelectric spectrometer. With this system a detectability of 1 ppm has been attained for nitrogen. Such systems could be adapted for use with the excitation chamber described in this thesis. After the nitrogen was extracted from the sample and the D.C. arc discontinued, an aliquot of the gas mixture would be admitted to a discharge tube for excitation as described. Such a procedure should increase the limit of detection of nitrogen in steel by a factor of 100.

The reduction of the nitrogen blank was the most difficult phase in developing the analytical procedure. Of particular difficulty was the problem of purifying the argon. Different modes of attach on this problem have been described in the literature. Modifications of the "hot metal" technique are common. Typical of these is the following (40). Purified argon is passed through molten magnesium at 900-950°C or through magnesium vapor at 1000°C to remove the nitrogen and oxygen. Schroeter (44) has described the use of an electrical gas discharge for argon purification. A high frequency discharge is superimposed upon a low current D.C. arc, to insure ionization of the nitrogen contained in the argon. The cathode is made out of a liquid potassium amalgam. The argon is purified at a pressure of 5-10 mm and a current of 0.5 to 1 ampere.

An interesting method has been reported recently for the preparation of pure argon (24). After removing oxygen chemically argon is separated from nitrogen by passage through silica gel at 143-90°K. Starting with crude argon containing 5-15% nitrogen, argon spectroscopically pure was obtained. Such a system might readily be adapted to the problem discussed.

VIII. DISCUSSION

The analytical technique described in this thesis is of both academic and practical significance.

A direct quantitative emission spectrographic determination of the non-metals (particularly oxygen, nitrogen, sulfur, phosphorus and the halogens) has always been considered a difficult task. Techniques hitherto available were relatively insensitive, not particularly precise and difficult to execute. If the method described here were modified by the use of a simple three channel direct reading spectrograph, the simultaneous determination of oxygen and nitrogen in steel could be readily accomplished at the rate of ten minutes per sample. The precision of analysis is more than comparable to that obtained by the standard vacuum fusion method.

The principal practical advantage of the method is the speed of analysis, particularly in the determination of nitrogen in the high alloy steels. The nitrogen content of such alloys can be determined only with considerable difficulty and loss in time-of-analysis by the Kjeldahl Method.

Additional sensitivity can be obtained by recourse to the suggestions given in section VII.

IX. SUMMARY

An effective spectrographic method for the determination of nitrogen in low alloy and high alloy steels in the range 0.01% to 0.24% has been developed. The standard deviation of analysis was less than 5% relative, measured in the concentration range 0.02% to 0.04%. An extension of the limit of detection to 0.003% nitrogen was achieved by the use of cyanogen radiation. However the standard deviation of analysis was increased to 14% relative. This method makes possible the simultaneous determination of oxygen and nitrogen in low alloy steels. Further work is necessary to extend this simultaneous determination to high alloy steels.

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