Experimental Studies to Determine the Chemical Species Prevalent in the Plasma of an Air Arc and the Boundary Layers Adjacent to Ablating Materials

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FOREWORD

This report was prepared by the Armour Research Foundation of Illinois Institute of Technology under USAF Contract No. AF 33(616)-6686. This contract was initiated under project No. 7364, "Experimental Techniques for Materials Research", Task No. 73652, "Intense Thermal Energy Transfer into Materials". The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. P. W. Dimiduk acting as project engineer.

This report covers work conducted from June 1, 1959 to May 31, 1960.

Major contributions to the work under this contract were made by R. Carrigan, E. Raisen, and K. Schmude with S. Liebson acting as project scientist.
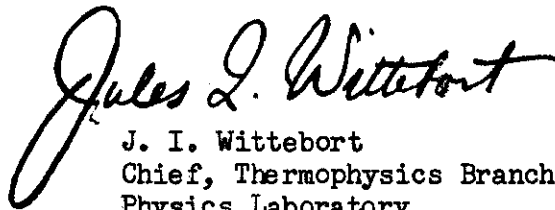
WADD TR 60-359

ABSTRACT

The objective of this work is to obtain an increased understanding of plasma jet processes as related to the use of the plasma jet arc to test ablating systems. Plasma jets were constructed and operated as sources for optical and time-of-flight mass spectrometry. Optical spectroscopic methods were used to identify chemical species and state of excitation when inert gas or air was used as the plasma arc working medium. Time-of flight mass spectrometry was not developed to the point where species could be identified.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

J. I. Wittebort
Chief, Thermophysics Branch
Physics Laboratory
Materials Central

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INTRODUCTION

The objective of this program is to obtain qualitative knowledge of the processes which occur in plasmas and ablating systems. In particular, an evaluation is to be made of the utility of spectroscopic tools such as optical and time of flight mass spectrometry in obtaining information about chemical species in arcs and ablating boundary layers and the states of excitation, dissociation and ionization of such species. To proceed toward this objective, plasma jet arcs were constructed and operated with different gases. These arcs were then used as sources for optical and time-of-flight mass spectrometry. In the course of this work an attempt was made to characterize these arcs in an effort to standardize or render reproducible the measurements made with them.

It is generally recognized that a complete understanding of the detailed processes involved in systems ablating in plasmas will require considerable effort and significant advances in high temperature plasma technology. This report describes the results of a first year effort in contributing to this understanding.

SECTION II

PHYSICAL CHARACTERISTICS OF THE PLASMA JET

DESIGN

The plasma jet has been utilized as a tool for the study of missile re-entry phenomena, an application for which it is especially adapted because of its high operating temperatures, the high gas enthalpies and the high gas velocities it produces. Because of the unusual requirements of the present program, a versatile plasma jet has been designed to allow study of either the arc process or the field free plasma. In addition, the electrodes are readily interchangeable so that the effect of different electrode designs and materials may be examined. Also an environmental chamber has been provided to establish a controlled atmosphere. A diagram of this device is shown in Fig. 1. Essentially, the plasma jet consists of a water cooled cylindrical cathode, a water cooled annular anode, and a transparent vortex chamber. This device has been run with argon, nitrogen and air as the stabilizing fluids. When argon or nitrogen is used, the anode material may be graphite or copper, and the cathode may be graphite or tungsten. When the copper anode is used, the copper spacer A and anode (Fig. 1) are replaced by the annular copper anode (Fig. 2). When air is used, a tungsten electrode is not suitable because of the high volatility of its oxide, unless it is protected from the oxidizing atmosphere.

PLASMA CONTAMINATION

The plasma is relatively uncontaminated when argon is used with the tungsten and copper electrodes. When graphite is used the electrodes erode and contaminate the plasma. This is illustrated in Table 1 and in Fig. 3. Figure 3 shows a mass of carbon vapor deposited from the vapor phase in the orifice of the annular electrode.

Referring to Table 1, it is of interest to note that at the lower gas flow rates the annular electrode imparts approximately six times more contamination to the plasma than the cylindrical electrode. At the higher flow rate, however, the situation is reversed, and the cylindrical electrode wears away approximately four times faster than the annular electrode. At the higher flow rate the plasma seems to be pinched more and apparently makes less contact with the walls of the annular orifice than at the low flow rates. Thus, even when the polarity was reversed (see run 6), the cylindrical electrode eroded more rapidly than the annular one, indicating that the phenomenon is due to the mechanical, rather than electrical, properties of the plasma. Also at the higher flow rates and electrical energy inputs, the total erosion is appreciably enhanced. The similarity of contamination in experiments 2, 3, and 4 indicates that increasing the length of the arc does not appreciably affect the purity of the plasma. Similar studies have not been made with air,

ENVIRONMENTAL
CHAMBER

ENVIRONMENTAL
GAS INLET

ANODE
INSERT

WATER
OUTLET

ANODE

WATER
INLET

COPPER SPACER 'A'
WATER COOLED

+

COPPER PLATE

TRANSPARENT
VORTEX
CHAMBER

−

WATER OUTLET

INSULATED BOLTS

STABILIZING
GAS INLET

COPPER SPACER 'B'
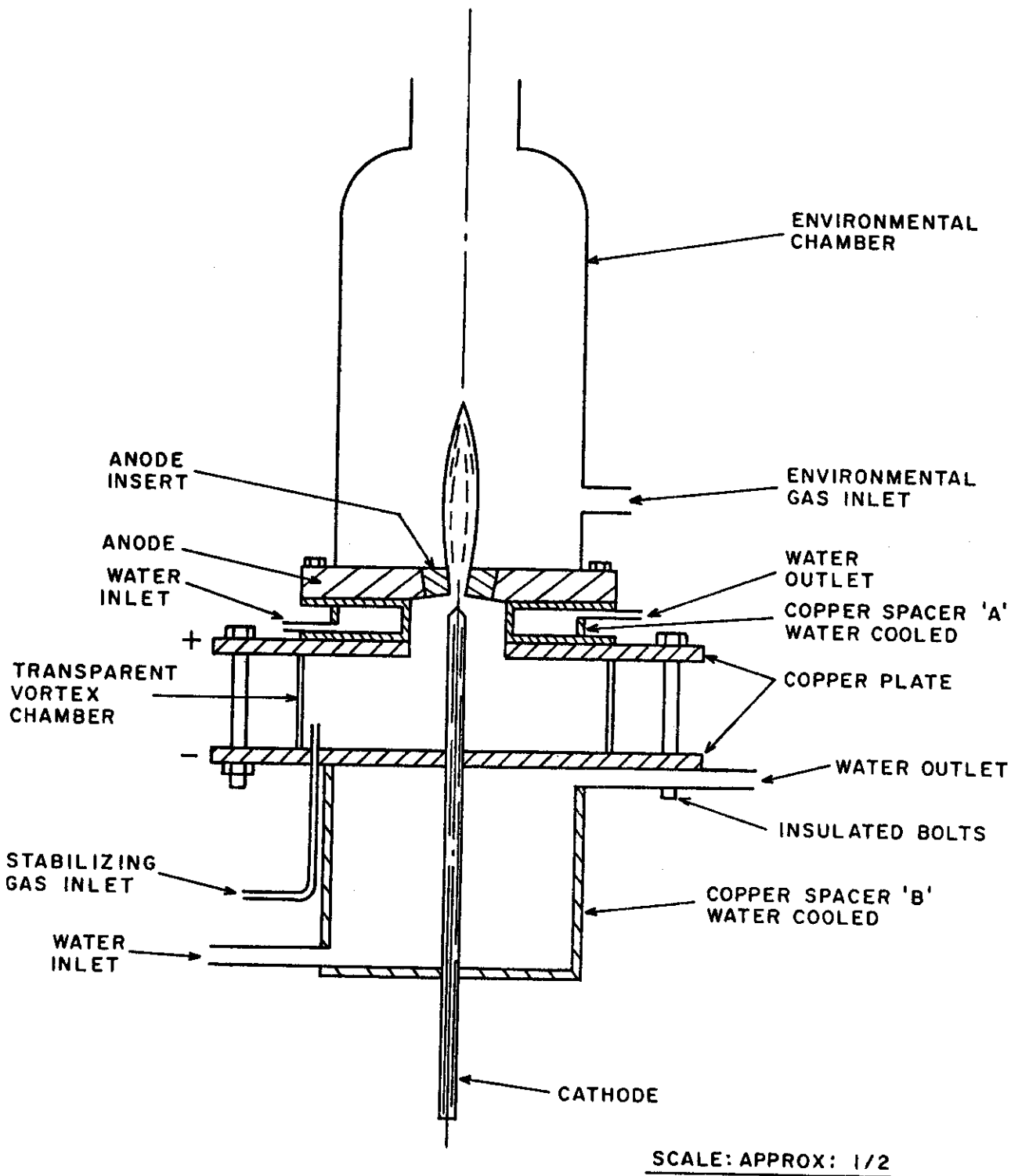WATER COOLED

WATER
INLET

CATHODE

SCALE: APPROX: 1/2

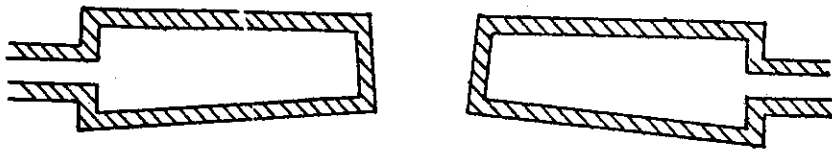FIG. I SCHEMATIC DIAGRAM OF PLASMA JET

Fig. 2. COPPER ANNULAR ANODE
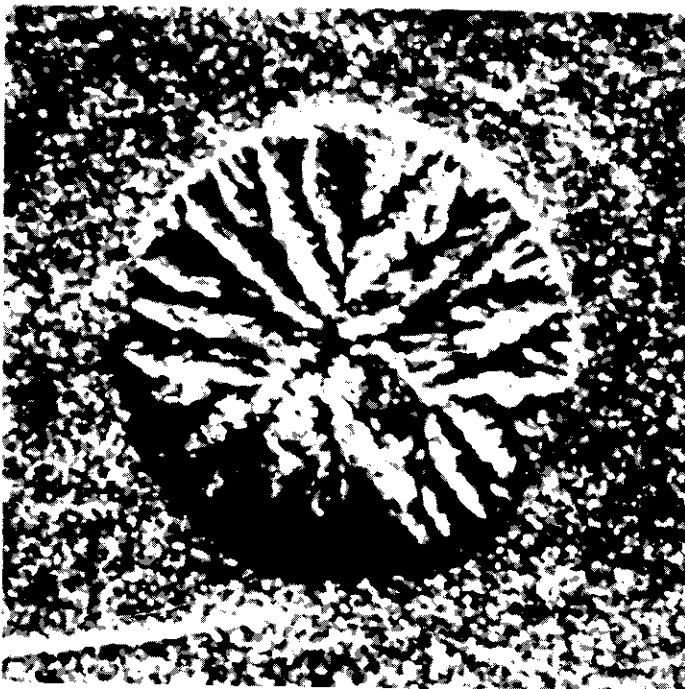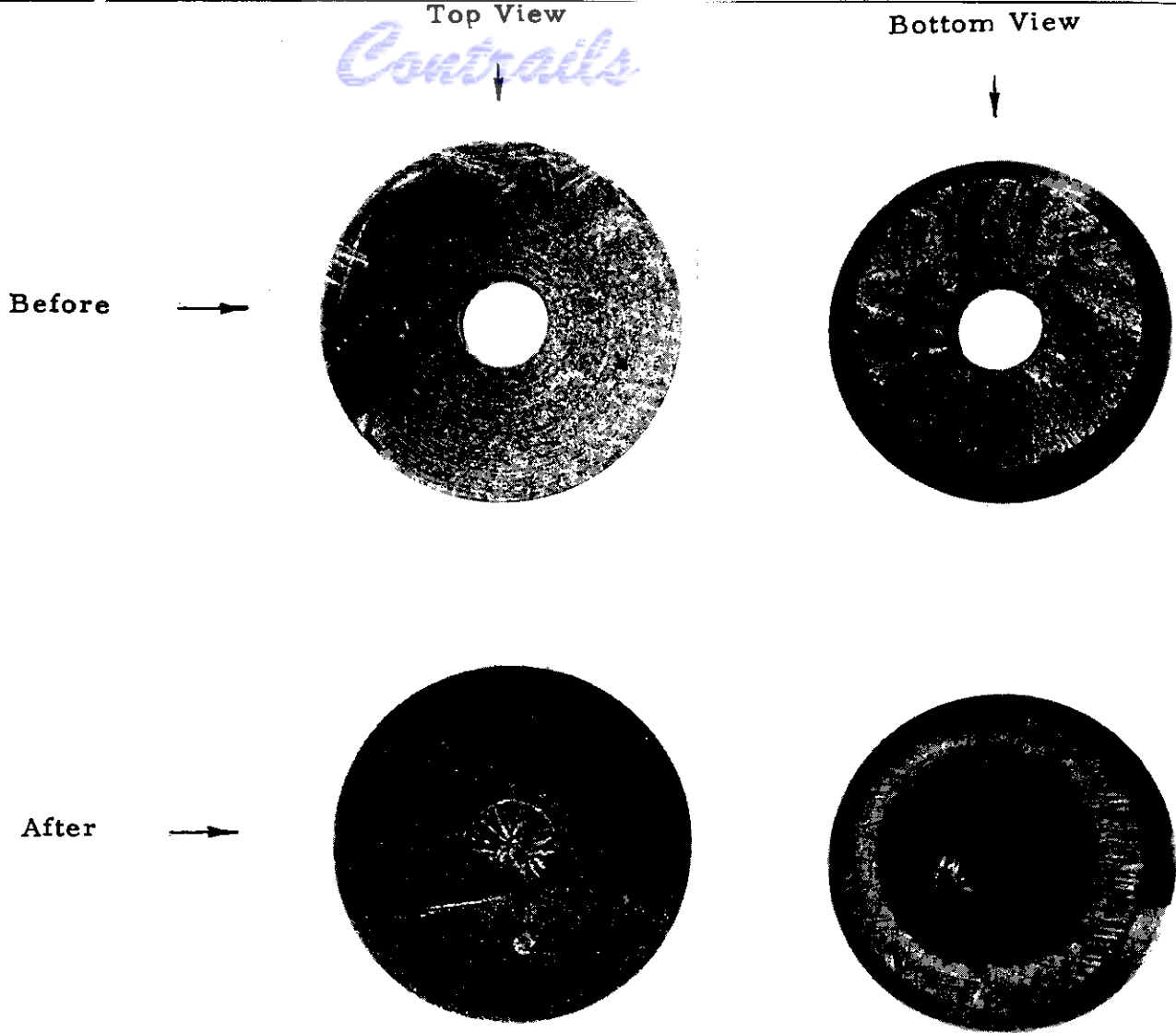(approximately 2:1 scale)

Before →

After →

Fig. 3. GRAPHITE INSERT
FOR THE PLASMA JET CATHODE
BEFORE AND AFTER OPERATION

TABLE 1

PLASMA CONTAMINATION DUE TO GRAPHITE ELECTRODES IN AN ARGON-STABILIZED ARC

	1	2	3	4	5	6
Gas Flow Rate, CFH	15	30	30	30	60	60
Arc Power, KW	2.4	6.5	6.9	7.6	11	9.9
Electrode Gap, in.	-	0.27	0.28	0.78	0.38	0.47
Contamination due to annular anode, atom %**	1.50	1.73	2.14	1.81	2.23	1.2[a]
Contamination due to cylindrical cathode, atom %	.29	.23	.30	.27	9.7	4.9[b]
Contamination due to both electrodes, atom %	1.79	2.05	2.44	2.08	11.93	6.1

* The atom % refers to the g-atoms of carbon per g-atom of argon in the plasma.

** Reverse polarity - "a" annular cathode, "b" cylindrical anode.

but qualitative evidence indicates that the contamination is even greater than with the argon. Therefore, during the latter stages of this program the air plasma was formed using a cylindrical graphite cathode and an annular water cooled copper anode at the higher flow rates.

A summary of the different conditions under which the plasma jet has been operated is shown in Table 2. Many of the experiments in Table 2 were exploratory and only the data shown was recorded. Thus, many of these experiments are not discussed in the subsequent studies.

In general, it was observed that the plasma jet was most stable and easiest to operate with argon as the stabilizing gas. The arc was more difficult to initiate and maintain when nitrogen or air was used. In fact, the arc was usually initiated with argon and then gradually converted to nitrogen or air.

The spectroscopic contamination of the plasma was appreciably reduced by using spectroscopically pure graphite electrodes instead of a standard grade. By this procedure the spectra of Mg I, Mg II, Si I, Ca I, Ca II, Al I, Ti I, Ti II, Fe I, and Fe II, were essentially removed from the plasma.

TABLE 2

PLASMA JET OPERATING CONDITIONS

Stabilizing Gas	Flow Rate ft^3/hr	Voltage	Amperage	Cathode Material (cylindrical)	Anode Material (annular)
Argon	15 to 60 30 10 to 60	12 to 27 22 to 29 26 to 39	250 to 800 380 to 480 240 to 800	Tungsten Tungsten Graphite	Copper Graphite Graphite
Nitrogen	2 to 15	44 to 46	160 to 225	Graphite	Graphite
Air	7 to 35 28 to 59	40 to 46 30 to 42	165 to 340 245 to 400	Graphite Graphite	Graphite Copper

ELECTRICAL CHARACTERISTICS

In order to further characterize the plasma jet the electrical characteristics of an argon plasma were examined as a function of the electrode gap with graphite electrodes. The results are shown in Fig. 4. It is seen that the arc characteristics are positive but non-ohmic.

THERMAL CHARACTERISTICS

In the latter stages of the program, thermometers were inserted into the cooling water inlet and outlet streams, and from the temperature differential and the gas and water flow rates, the enthalpy of the plasma was determined. The results of several representative runs are shown in Table 3.

These enthalpies represent the maximum values, since corrections for conduction losses to materials other than the cooling water have not been attempted.

Comparison of the data in these tables is difficult, because, in most instances, it was not possible to record all the data (thermal, electrical, physical, and spectroscopic) within one experiment, and many of the runs in which different data were recorded were under different conditions. However, wherever possible, the experiments have been cross-referenced. This will be apparent in the tables in the next section.
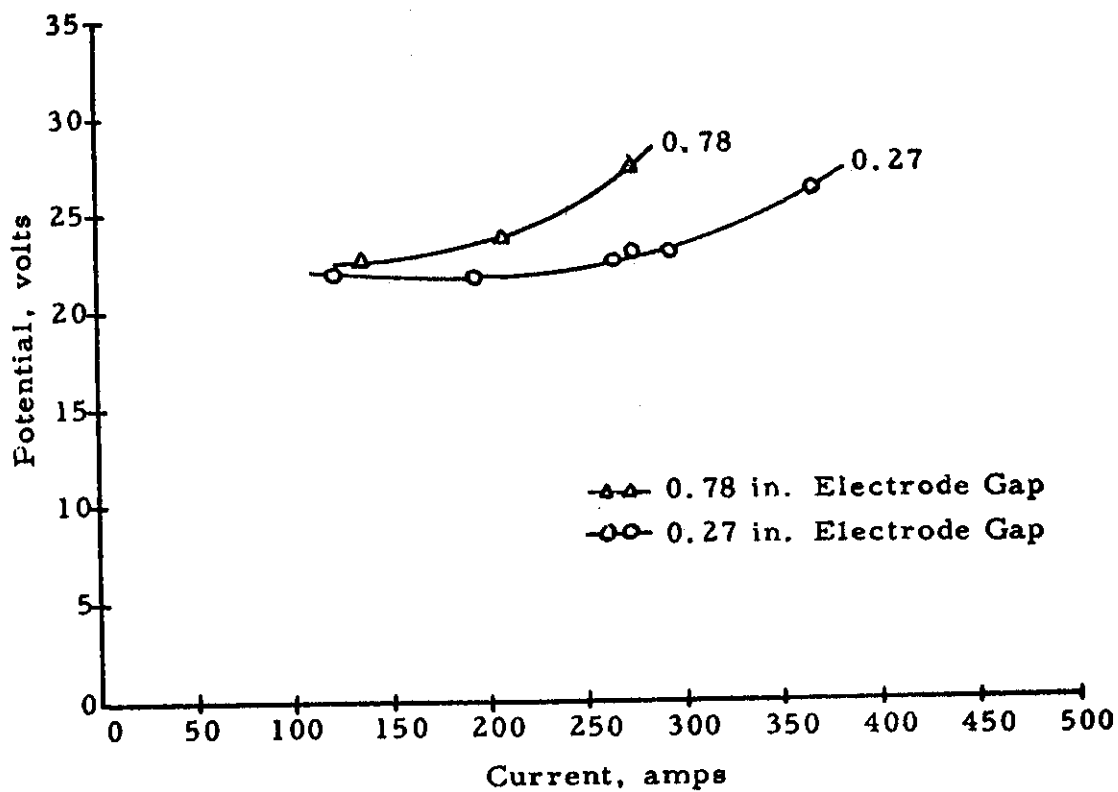
Fig. 4. ELECTRICAL CHARACTERISTICS
OF THE ARGON STABILIZED PLASMA JET
WITH GRAPHITE ELECTRODES

TABLE 3

DETERMINATION OF PLASMA ENTHALPY

	1	2	3	4
Electrical Power Input, BTU/sec	5.93	7.82	9.30	13.2
KW	6.25	8.25	9.80	13.9
Cooling Water Temperature Differential, °C	6.1	5.5	11	11.5
Cooling Water Flow Rate, gal/min	2.3	2.4	2.6	2.4
Power Lost to Cooling Water, BTU/sec	3.54	3.32	7.25	6.95
Stabilizing Gas Flow Rate x 10^3, lbs/sec	1.86 Argon	1.86 Argon	1.32 Air	0.735 Air
Plasma Enthalpy, BTU/lb	1290	2420	1520	8350

SECTION III

OPTICAL SPECTROSCOPY

GENERAL

The optical spectroscopic studies were concerned with the identification of species by observations of emission spectra in the photographically accessible wavelength range. It was desired to correlate these observations, if possible, with thermodynamically predicted species abundances and to evaluate the usefulness of optical spectroscopy as a tool for studying plasma composition. Some spectroscopic temperature measurements were made to provide background information for interpreting the observations on species.

EXPERIMENTAL

The spectrograph used was a 3.4 meter instrument with a 15,000 line-per-inch plane grating in the Ebert mounting. Spectrograms were made in the first and second orders.

Many spectrograms were made by focusing an image of the plasma on an external limiting diaphragm which, in turn, was imaged onto the collimating mirror of the spectrograph so as to obtain spectral lines representing essentially the whole jet. More detailed studies of light distribution from different parts of the jet were made by imaging the jet on the slit of the spectrograph. Axial distributions were investigated by casting an image of the vertical jet directly along the vertical extent of the slit. When transverse distributions were sought, the image on the slit was rotated through 90° by interposing a suitably disposed pair of front-surface mirrors in the external beam between the jet and the slit. The first mirror, facing the jet, was rotated about a horizontal axis through a 45° angle from a vertical plane so as to turn the beam vertically downward. The second mirror, also in a plane 45° from vertical, faced upward toward the first one and reflected the beam horizontally in a direction perpendicular to its original direction in leaving the jet. With the addition of image-forming lenses, this system produced an image of the jet oriented sideways across the slit. Since the spectrograph is itself stigmatic, either of the preceding arrangements produces spectra that display variations of emission from different parts of the jet.

MAJOR SPECIES IDENTIFIED

Of greatest potential interest were the spectra of those molecular, atomic and ionic species that were expected to make up the bulk of the plasma composition. Minor components are interesting because they may supply clues to the role of reaction intermediates in plasma processes, because they may

yield spectra useful for temperature measurements, or for their own intrinsic value in other ways. However, the interest of the current program centered on the major components. Hence, special efforts were made to seek these components either in the light from the whole jet or in isolated regions.

Under our conditions, with rare exceptions, enhancement of spectrum lines or bands was not noted in any region of the jet but the central core. In one or two exceptional cases, with an argon jet, the 7771 Å oxygen triplet appeared near the tip of the jet, but not at its base. Entrainment of air could have been responsible for this effect. The experimental results are presented in the following sections and are summarized in Table 4.

Wavelengths used for identification are recorded to allow comparison with other data and to facilitate additional interpretation. The recorded wavelengths have all been taken directly from the literature. They represent lines and bands that were found particularly convenient for identification purposes under our conditions, either because of their intensities, or because they occur in wavelength regions that were not obscured by interfering spectra.

Standard sources were in most cases adequate for wavelength reference purposes [1-7]. Several representative spectrograms are illustrated and discussed in Appendix 1.

Molecular Nitrogen, N_2. plasmas stabilized with air, nitrogen, and argon showed definite, though not intense, spectra of the first positive system of N_2. Identification of these bands was facilitated by comparison with spectrograms made with a nitrogen-filled Geissler tube. Only those air plasmas generated with a copper anode showed the N_2 bands. Band heads used in the identification were at 5653.5 Å (possibly overlapped by a band head of N_2^+), 5660.8 Å,

[1] G. R. Harrison, M. I. T. Wavelength Tables, Wiley, (1939).

[2] C. E. Moore, A Multiplet Table of Astrophysical Interest, Revised Ed., Contributions from the Princeton University Observatory, No. 20 (1945).

[3] C. E. Moore, An Ultraviolet Multiplet Table, U. S. Nat. Bur. Stds., Circular 488.

[4] R. W. Pearse, and A. G. Gaydon, The Identification of Molecular Spectra, 2nd Ed., Wiley, (1950).

[5] R. F. Barrow, et al., Tables de Constantes et Donnees Numeriques, Vol. 4, Donnees Spectroscopiques Concernant les Molecules Diatomiques. Hermann et Cie. (1951).

[6] R. F. Barrow, et al., Tables de Constantes et Donnee Numeriques, Vol. 5, Atlas Des Longueurs D'Onde Caracteristiques des Bandes D'Emission et D'Absorption Des Molecules Diatomiqeues. Hermann et Cie (1952).

[7] A. Gatterer, Grating Spectrum of Iron, Specola Vaticana, (1951).

TABLE 4

SUMMARY OF OPTICAL SPECTROSCOPIC OBSERVATIONS OF THE PLASMA JET

Gas	Flow Rate (cu. ft./hr.)	Potential volts	Current amps.	Species Observed	Species Sought but not found	Comments
Ar	10 to 40	12 to 30	430 to 800	Ar, Ar^+, N, N_2, N_2^+, O, C, C_2, CN	Ar^{++}, N^+, O^+, O_2^+, C^+, C^{++}, C_3, CO_2, NO, NH, NH^+, OH, OH^+, CN^+	1. Four spectra were made with tungsten cathode and copper anode. The rest were with spectroscopic grade graphite electrodes. 2. All spectra were with environmental chamber in place.
Air	7.6 to 20	42 to 56	160 to 210	N, O, C, C_2, CN	C^+, N^+, O^+, CN^+, C_3, N_2	With spectroscopic grade graphite electrodes
Air	7.6 to 20	42 to 56	160 to 210	C, N, O, C_2, CN, N_2, N_2^+, Ar, Cu, Cu^+	C^+, C_3, CN^+, N^+, O^+, O_2, O_2^+, CO, CO^+, NO, Ar^+	Rod cathode of spectroscopic grade graphite. Copper plug anode supported in copper plate.
N_2	6 to 10	44 to 46	160 to 190	C, N, O, C_2, CN, N_2, N_2^+,	C^+, C_3, CN^+, N^+, O^+, O^+, CO^+, Ar, Ar^+	With spectroscopic grade graphite electrodes

TABLE 4 (Continued)

Notes: 1. When no plus sign (+) is used, the neutral species is meant.

2. In Table 1 of Quarterly Report No. 2, C II (here designated as C^+) was reported as detected in argon plasmas. Re-examination of the plates indicates that the identification should be regarded as doubtful; hence C^+ is reported as non-detected.

3. In the same table in Quarterly Report No. 2, NO^+ was reported as sought, but not found, in argon plasmas. It has since come to our attention that the spectrum earlier attributed to NO^+ (R. W. B. Pearse and A. G. Gaydon: The Identification of Molecular Spectra. Wiley. (1950). Page 184.) has since been attributed to the neutral, NO molecule (R. F. Barrow et al: Tables de Constantes et Donnees Numeriques. Vol. 4. Donnees Spectroscopiques Concernant les Molecules Diatomiques. Hermann et Cie. Paris. 1951. Page 213.)

4. Spectra were examined in the wavelength range 2400 Å to 8800 Å

5. Certain minor species, such as metallic impurities, are omitted in the table, but are discussed in the text.

5733.6 Å, 5748.1 Å, and 5755.2 Å. In two instances the 3894.6 Å band head of the second positive system of N_2 was seen. The presence of N_2 bands in the spectrum of the argon plasma may be explained by air contamination or by the release of absorbed nitrogen from the electrodes.

Molecular Nitrogen Ion, N_2^+. This species was easily detected in argon-, nitrogen-, and air-stabilized plasmas. Identification was made with the aid of the well-resolved band with head at 3914.4 Å in cases when CN bands were not too intense. Weak heads at 3308.0 Å and 3532.6 Å provided confirmation.

Atomic Nitrogen, N. In the air, nitrogen, and argon plasmas, the neutral nitrogen atom was readily found by a spectrum rich in lines, of which the following were observed:

4109.98 Å	4935.03 Å	7442.56 Å	8216.46 Å	8656.32 Å	8718.99 Å
4151.46	5281.18	7468.79	8223.28	8680.35	8729.07
4223.04	5310.52	8185.05	8242.47	8683.61	8747.35
4254.75	5356.77	8188.16	8568.04	8686.38	
4914.90	6708.81	8200.59	8594.34	8703.42	
	7423.88	8210.94	8629.61	8711.78	

Ionized Nitrogen, N^+. Ionized nitrogen was not detected under any conditions.

Molecular Oxygen, O_2. Repeated attempts to obtain spectra of O_2 in the air plasmas were unsuccessful, even when longer exposures were used and the envelope of cooler gases adjacent to the jet were examined. The possible significance of these negative results for such a prominent species as O_2 will be discussed in a later section.

Molecular Oxygen Ion, O_2^+. This species was not found in the jet under any conditions.

Atomic Oxygen, O. Atomic oxygen was easily detected in the argon, air, and nitrogen plasmas by means of the well-known triplet; 7775.43 Å, 7774.14 Å and 7771.93 Å. Other usable lines were the following:

4368.30 Å	5330.66 Å	7479.15 Å	7950.82 Å	8235.41 Å
5299.00	7157.36	7480.65	7952.18	8446.38
5328.98	7476.47	7943.18	8230.02	8820.45
5329.59	7477.26	7947.57	8233.08	

Ionized Oxygen, O^+. Ionic oxygen was not detectable under any conditions.

Nitric Oxide, NO. Plates made under a variety of conditions were examined for spectra of NO. Evidence of its presence was never obtained, despite the high equilibrium concentrations predicted thermodynamically for this species

in the temperature range of our jets.

Diatomic Carbon, C_2. With the exception of a small number of unsuccessful runs in which metallic electrodes were destroyed in air arcs, all experiments with air-stabilized jets were done with graphite electrodes. Carbon-containing species were therefore potentially important as constitutents of the plasma. Among these, the C_2 molecule is well known for the intensity with which its bands are excited in carbon arcs and many carbon-containing flames. These bands, together with those of CN, were the dominating features in practically all spectrograms made with graphite electrodes in either air or nitrogen. In the argon plasmas, C_2 was also very strong when graphite electrodes were used. Following is a list of band heads that served to identify this species.

3398.1 Å	4365.2 Å	4697.6 Å	4770.1 Å	5165.2 Å	5635.5 Å
3399.8	4371.4	4715.2	5097.7	5585.5	6191.2
3607.3	4382.1	4737.1	5129.3		

Triatomic Carbon, C_3. A reported spectrum earlier attributed to other species has more recently been identified as arising from the molecule, C_3. This is the well-known "comet-head" group with its most prominent head at 4051.5 Å. No evidence for this species could be found on our plates.

Atomic Carbon, C. Atomic carbon gave strong spectra in jets from graphite electrodes in atmospheres of air, nitrogen and argon. Most prominent, of course, was the strong line at 2478.57 Å. The following additional lines were also observed:

4762.41 Å	4771.72 Å	5380.24 Å
4766.62	4775.87	8335.19

Ionized Carbon, C^+. C^+ was not detected under any conditions.

"Cyanogen", CN. As mentioned earlier, the spectra of CN and C_2 were the dominant features of spectrograms made with graphite electrodes in air or nitrogen. The CN bands were intense under these conditions, completely obscuring certain spectral regions, and rendering other regions unavailable for the identification of species that might have been detectable had longer exposure been possible in the absence of the CN spectrum. Even in the argon jets made with graphite electrodes, weak, but quite distinct CN bands were observed. Nitrogen, in this case, probably was drawn into the jet from the surrounding air, though the possibility was not excluded that it might have been absorbed in the graphite or have been present as an impurity in the argon.

The following well-known CN band heads of the violet system were used for identification:

3433.0 Å	3603.0 Å	3861.9 Å	3944.7 Å	4167.8 Å	4512.2 Å
3583.9	3628.9	3871.4	3984.6	4181.0	4514.8
3585.9	3658.1	3883.4	4152.4	4197.2	4531.9
3590.4	3854.7	3909.5	4158.1	4216.0	4553.1

The air and nitrogen plasmas from graphite electrodes have been observed to produce distinct red-degraded bands with heads at 7872.7 Å and 7894.7 Å. These bands appeared faintly in an argon plasma when graphite electrodes were used. They are evidently the bands tentatively attributed to MgCl in the Barrow Table.[6] These bands had been observed by J. Querbach[8] in an arc to which magnesium chloride had been added. More recent workers[9] have identified them as CN bands.

Another rather conspicuous group of band heads in our plasmas was identified only after recourse to original literature.[10,11] These bands did not match any plausible species in the Barrow Table,[6] but were suspected of being weak members of a CN system since their intensities paralleled those of known CN spectra in a series of spectrograms. This suspicion has been confirmed in the case of prominent heads at the following wavelengths, recalculated by Johnson and Jenkins[10] from data of King.[11]

3127.9 Å	3160.2 Å	3203.7 Å	3322.3 Å	3380.4 Å	3433.0 Å
3142.9	3180.4	3296.3	3360.1	3404.9	3465.5

Molecular Cyanogen Ion, CN^+. A. E. Douglas and P. M. Routly[12] reported spectral data for this species. A careful search of spectrograms from the air, nitrogen and argon plasmas failed to reveal evidence of it.

Carbon Monoxide, CO. Spectrograms from air plasmas generated with graphite cathodes and copper anodes were examined for carbon monoxide. Despite the existence of widespread band systems of CO, no evidence for it was found.

Neutral Argon, Ar. Argon plasmas gave intense spectra of the neutral argon atom. This species was also detectable in air plasmas. A list of observed Ar lines follows.

3554.31 Å	4158.59 Å	4266.29 Å	4596.10 Å	5606.73 Å	6052.72 Å
3567.66	4164.18	4300.10	4628.44	5650.70	6059.37
3606.52	4181.88	4333.56	4702.32	5739.52	6105.64
3632.68	4191.03	4335.34	5048.81	5860.32	6145.43
3649.83	4198.32	4345.17	5054.18	5882.63	6155.23
3947.50	4200.67	4510.73	5056.53	5912.08	6170.18
3948.98	4251.19	4522.32	5558.70	6032.12	6173.11
4044.42	4259.36	4587.21	5572.55	6043.23	6215.94

[8] J. Querbach, Z. physik 60, 109-24 (1930).

[9] L. H. Allen and P. C. Keenan, Astrophys. J. 113, 73 (1951).

[10] R. C. Johnson, and H. G. Jenkins, Phil. Mag. 2, 621 (1926).

[11] A. S. King, Astrophys. J. 14, 323 (1901).

[12] A. E. Douglas and P. M. Routly, Astrophys. J. 119, 303 (1954).

6369.58 Å	6677.28 Å	7147.04 Å	7383.98 Å	7723.76 Å	8264.52 Å
6384.72	6937.67	7206.99	7392.97	7724.21	8408.21
6416.32	6965.43	7272.94	7503.87	8006.16	8424.65
6466.56	7030.26	7311.71	7510.42	8014.79	8521.44
6604.85	7067.22	7353.32	7514.65	8103.69	8667.94
6664.02	7107.50	7372.12	7635.11	8115.31	8678.43

Ionized Argon, Ar^+. The Ar^+ spectrum was emitted strongly by the argon plasmas, both with graphite electrodes and with the tungsten-copper system (tungsten cathode, copper anode). Ar^+ was not detected in the air or nitrogen plasmas. The following Ar^+ lines were identified.

4277.55 Å	4430.18 Å	4589.93 Å	4762.89 Å	4933.24 Å
4379.74	4431.02	4609.60	4806.07	4965.12
4401.02	4545.08	4657.94	4847.90	5009.35
4426.01	4579.39	4726.91	4879.90	5062.07

Miscellaneous Observations. Several other gaseous species were sought but not found. These cases are summarized in Table 4. No doubly charged species were found.

The OH band at 3063.6 Å was found in a pilot experiment with an ordinary carbon arc running in air. This experiment was performed to see if the Schumann-Runge bands of O_2 would be emitted from the heated layer of air surrounding a low-amperage arc. The possibility of running such an arc for long periods of time seemed to offer a chance of testing whether it would be worthwhile to try to get long exposures from the nonluminous region around an air plasma jet, in the hope of photographing the oxygen bands. The OH band showed clearly, but no oxygen bands appeared.

In some cases the hydrogen alpha line of the Balmer series appeared. The hydrogen beta line never appeared.

A number of metallic impurity lines were present in most spectra, especially those made with metallic electrodes (tungsten, copper) or with ordinary graphite not of spectroscopic quality. Especially noticeable were lines of Mg, Mg^+, Si, Ca, Ca^+, Al, Ti, Ti^+, Fe, and Fe^+. Vanadium appeared occasionally, probably originating in the graphite where it is often recognized as a "latent" impurity.

From about 5000 Å to 7000 Å, heavily exposed spectra sometimes gave indications of superposition of absorption spectra on the emission spectrum. Both in the continuum and in the band structures there were appearances that suggested absorption edges degraded oppositely from the emission bands. While such effects are sometimes traceable to rapid fluctuations in emulsion sensitivity with wavelength, there were indications that some of the apparent edges may have coincided with absorption band heads of CO, NO, N_2, and O_2.

Spectroscopic Temperature Measurements. Two methods were used to determine the plasma temperatures: (a) relative intensity of atomic lines was used in the argon plasma, and (b) relative intensities of P and R branches of the 0-1 vibrational band of the $^2\Sigma^+ \to {}^2\Sigma^+$ electronic transition of the CN molecule. The theoretical and practical qualifications of both methods are extensively covered in the original literature and a detailed discussion shall not be presented here.

Assuming local thermodynamic equilibrium and considering the analysis by Pearce[13] and Greenshields[14], the experimental error in the temperature measurements is probably ± 200°K. The method utilizing the CN bands is somewhat more precise because experimental variations tend to effect the measured quantities equally.

(a) Temperature determination from relative intensities of atomic lines. Spectroscopic measurement of arc temperatures from the relative intensities of atomic or ionic lines was applied to plasma jets by W. J. Pearce[13], who also compiled some of the available transition probabilities and other physical constants necessary for measurements.

We used Ar I lines at 8424.65 Å, 8408.21 Å, 8264.52 Å, 8103.69 Å, 8014.79 Å, 7514.65 Å, 7503.87 Å to measure the temperature of the argon plasma. The results are given in Table 5.

A considerable broadening of the Ar I lines given above was observed; therefore, the intensities of the lines were obtained from the areas under microphotometer tracings of the line profiles. This broadening is mainly collisional and Stark broadening -- a Doppler half-width calculation yields a temperature value about a hundred times too high.

(b) Temperature determinations from the relative intensities of P and R branches of the 0-1 (4216 Å) vibrational band of the $^2\Sigma^+ \to {}^2\Sigma^+$ electronic transition in the CN molecule. This method for obtaining rotational temperature has been used by D. H. Greenshields.[14] The temperature is determined from the position of the isointensity point of the P and R branches of the 4216 Å CN band. The graph relating the temperature to the position of the iso-intensity point and pertinent calculations are given in detail in Greenshields' paper.

At temperatures higher than 5700°K the isointensity point is obscured by the 4197 Å band head and cannot be obtained directly. Temperatures higher than 5700°K may be measured from intensity ratios of individual lines in P

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[13] W. J. Pearse , Plasma Jet Temperature Study. WADC Tech. Rept. 59-346 (1959).

[14] D. H. Greenshields , Spectrographic Temperature Measurements in Carbon-Arc-Powered Air Jet. NASA Tech. Note D-169 (1959).

and R branches; also, the observed branch profiles may be compared to calculated profiles for various temperatures.

The results of our measurements are summarized in Table 5.

This table is included to illustrate the jet parameters used and the temperatures and enthalpies obtained in argon and air plasmas. The enthalpies were obtained by determining the power lost to the cooling water. Since other losses e.g., radiation and conduction to the plasma jet frame were neglected,* these measurements are less accurate than the temperature determinations, which were done by the spectroscopic methods indicated. It is seen that the argon plasmas ranged from 4200 to 5820°K. Different spectra taken during the same experimental run yielded similar temperatures, e.g., 5820 and 5670°K in the argon plasma and 4200 and 4650°K in the air plasma. The argon plasmas were produced using a tungsten and copper electrode combination, and using graphite electrodes with electrical power inputs of 8.3 to 14.5 KW. The air plasma temperature ranged from 4650 to 6500°K when electrical power inputs of 6.8 to 14.0 KW were used. Graphite electrodes were used in three of the runs cited, and a graphite cathode and copper annular anode was used in the other runs cited. The graphite electrodes contribute CN species to the plasma, and the copper anode introduces copper into the plasma. (Representative spectra are illustrated in the appendix.)

DISCUSSION

Spectroscopic observations on the occurrences of major atomic and molecular species in an air plasma may be compared with the theoretically predicted abundances. A recent report by Hilsenrath, Klein and Woolley[15] gives the results of theoretical calculations for the equilibrium concentrations of atomic and molecular species in air over the range 1500°K to 15000°K. References to earlier work may be found in this paper. No one of Hilsenrath's charts applies to a condition of normal atmospheric pressure over the whole temperature range. The latter condition is represented by a chart prepared by R. E. Otto and Paul Dimiduk of Wright Air Development Division, reproduced herewith as Fig. 6. The curves of this chart are based on some approximate recalculations of the data of Moeckel and Weston.[16]

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* Because of these losses the enthalpy values may be high by a factor of 2, as indicated by the temperature calculations

[15] J. Hilsenrath, M. Klein, and H. W. Woolley, Tables of Thermodynamic Properties of Air Including Dissociation and Ionization from 1500°K to 15000°K. AEDC-TR-59-20. 1959. Page 32 ff.

[16] W. E. Moeckel and K. C. Weston, Composition and Thermodynamic Properties of Air in Chemical Equilibrium. NACA Tech. Note 4265, April, 1958.

TABLE 5

TEMPERATURE MEASUREMENT

	Stabilizing Gas and Electrode Materials	Potential Drop, Volts	Current, Amps.	Gas Flow Rate cu ft/hour	Enthalpy B.T.U./lb	Point of Measurement	Temp. Mode	Temperature, °F *
1	Argon Tungsten rod cathode Copper plate annular anode	25	330	60	2330	On axis of jet, about 1.2 cm from its base	Electronic levels of Ar I	4200
2	Argon Graphite rod cathode Graphite plug annular anode	29	500	30	Not Measured	Integrated light from whole field-free plasma	Rotational levels of CN 4216 A	5820** 5670
3	Ditto	26	480	30		Ditto	Ditto	5300
4	Air Graphite rod cathode	42-45	160-210	10.5-16.3	Not Measured	Ditto	Ditto	4820
5	Ditto	46-48	130-160	12.6	Not Measured	Ditto	Ditto	4650** 4200
6	Air Graphite rod cathode Copper plate annular anode	33	400	34	4900	Stigmatic spectra See Fig. 5	Stigmatic spectra Ditto	See Fig. 5
7	Ditto	30	380	28.2	1910	Stigmatic spectra on axis of jet, about 1.2 cm from its base	Ditto	5450
8	Ditto	41	340	35.2	6100	Ditto	Ditto	6200
9	Ditto	41	280	39.9	2780	Ditto	Ditto	6500

* Temperatures are not corrected for radical intensity distribution

** Different spectra exposures during same run.

20 mm

15 mm.

a. 5250°K
b. 5100°K
c. 5020°K

a b c

7 mm.

a b c d
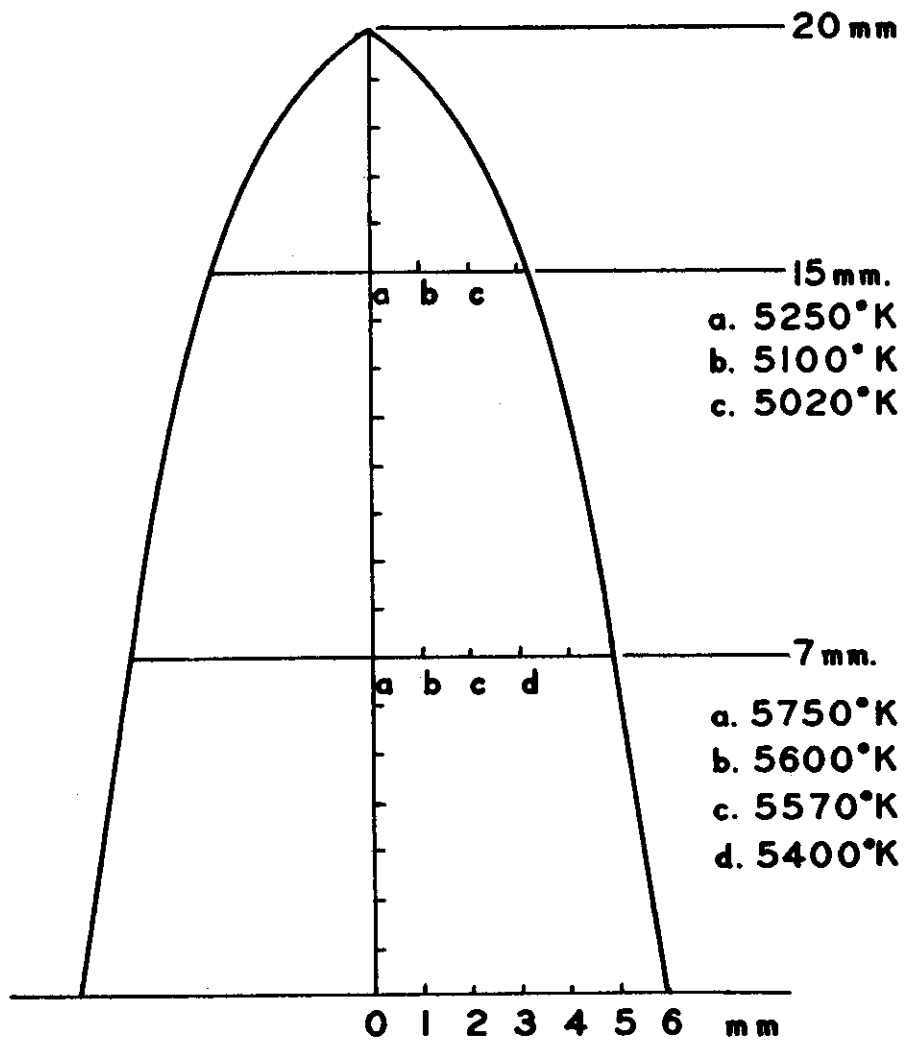
a. 5750°K
b. 5600°K
c. 5570°K
d. 5400°K

0 1 2 3 4 5 6 mm

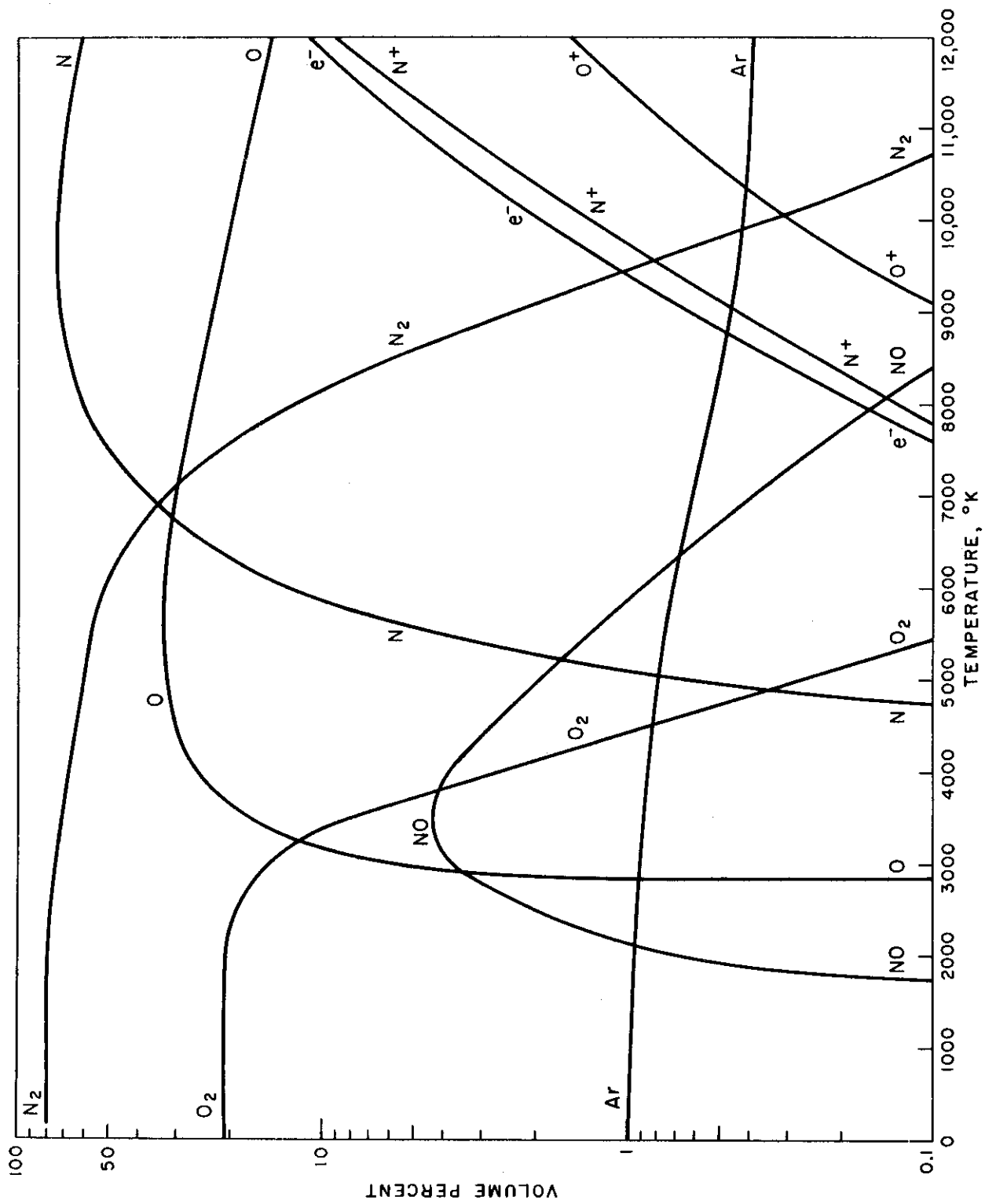FIG. 5. TEMPERATURE DISTRIBUTION IN A REPRESENTATIVE
AIR PLASMA. (SEE TABLE V)

FIG. 6 COMPOSITION OF AIR AT ATMOSPHERIC PRESSURE.

The latter chart extends only down to 0.1 volume-percent. Since spectro-
scopic observations may reveal much lower concentrations of some species, it
is of interest to make comparisons with Hilsenrath's data extending down to
0.01 mole-percent.

Broadly speaking, the equilibrium calculations show that rising temperature
is accompanied by falling concentrations of the initial low-temperature molecular
species, O_2 and N_2, and corresponding increases in the concentrations of their
dissociation products, atomic oxygen and nitrogen (Fig. 6). At atmospheric
pressure, nitric oxide, NO, rises to a maximum of about four volume percent in
the neighborhood of $3500^{\circ}K$, falling again at higher temperatures. Neutral
argon, Ar, has decreased by less than an order of magnitude at $12,000^{\circ}K$.

The charts of Hilsenrath et al. show the progressive dissociation of CO_2
at relatively low temperatures, say below $3000-4000^{\circ}K$. It is replaced by
its dissociation product, CO, which displays a broad concentration maximum
roughly in the $3000-8000^{\circ}K$ region. Beyond the carbon monoxide maximum, neutral
atomic carbon rises to a more or less broad maximum, to be replaced in turn
by the carbon ion, C^+.

At higher temperatures, ionized species assume greater importance, though
they contribute only minor fractions to the total composition of the heated
air even up to $16000^{\circ}K$, except at very low densities.

The foregoing body of conclusions derived from equilibrium calculations
provides a background in the light of which the spectroscopic observations may
be discussed. Intensity maxima in the emission spectra of molecular and atomic
species have been observed within favored temperature ranges in gaseous systems
by other workers.

A species may emit its spectrum most strongly over a preferred temperature
range simply because it is more abundant within this range. For example, the
chemical stability of NO in air at normal pressure near $3500^{\circ}K$ is such that a
concentration of about four mole per cent can exist in equilibrium, though
higher temperatures lead to dissociation. On the other hand, intensity maxima
of species on the temperature axis are highly dependent on conditions affecting
excitation and de-excitation. Consequently, spectral intensities will not
necessarily bear a simple relationship to species concentrations.

An additional complication arises from variations in the efficiencies of
various excited species as emitters of radiation in the accessible wavelength
range. Minute traces of extremely efficient emitters, such as C_2, can produce
intense spectra that are out of all proportion to the importance of these
species as components of the emitting gas. Thus Gaydon and Wolfhard[17], in
estimating spectroscopically the actual concentration of C_2 radicals in a

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[17] A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. 201, 570, (1950).

stoichiometric oxy-acetylene flame, found a partial pressure of C_2 equal to 1.1×10^{-6} atmosphere in a flame at 5.5 mm total pressure. The concentration of <u>excited</u> C_2 radicals was thus only 4×10^{-11} atmosphere.

Unless the temperature is so high that molecular species are virtually nonexistent, the optical spectrum of an air plasma from a graphite arc is likely to be characterized by extensive, and intense band systems from the efficient emitters C_2 and CN which, however, may be quantitatively insignificant as contributors to the total species composition.

Intense spectra from such species as C_2 and CN tend to cover wide ranges of wavelength with bands that obscure weaker spectral features of other species. This type of interference is hard to deal with, since the longer photographic exposures that could bring out weaker bands and lines only serve to overexpose the interfering bands. Some experimental techniques are available for minimizing the difficulty, such as working with the highest possible dispersion or using high contrast photographic conditions. These expedients are not ordinarily of much help when heavy interfering bands are present. Of more help is the spatial resolution of spectral features obtained by imaging the plasma jet on the slit of a stigmatic spectrograph, when it may be possible to separate bands that are emitted in only a single region of the jet. In general, however, the existence of a strong interfering spectrum is likely to mean that weaker spectral emitters must be sought in interference-free wavelength regions.

The efficiency of a species as an emitter depends upon the properties of the species and upon factors influencing its excitation and deactivation. The free radicals, C_2 and CN, can be expected to produce the strongest and most easily observable band systems since their resonance transitions involve relatively low excited states leading to intense spectra in the visible or near ultraviolet. The more stable gases, e.g., N_2, O_2, and CO have resonance transitions arising from higher electronic energy levels. Hence, their spectra are harder to excite thermally and, moreover, the most intense bands tend to occur so far in the ultraviolet that they cannot be observed with ordinary spectrographs.

Aside from the effects of variable excitation conditions as they affect different species, spectral intensities are also strongly influenced by the interrelation between transition probabilities and deactivation processes. The inverse of the transition probability, the mean radiative lifetime of the excited state, is to be compared with the collision lifetime predicted from the kinetic theory. Intensity of emission is reduced under conditions leading to collision deactivation of the excited state. Failure to attain desired sensitivity may at times stem from this cause.

Measured temperatures did not exceed $6500^\circ K$ in these experiments. Consequently with the type of plasma jet used, it was not possible to explore the growth and decline of various species over a wide temperature range, as illustrated in the paper by Hilsenrath et al.[15] This explains, for example, why our stigmatic spectrograms did not reveal concentration maxima for low temperature species in the relatively cooler regions of the outer layers of the jet.

In comparing the optical spectrographic results with the predicted equilibrium values, it must be recognized that the spectrographic sensitivity is such that some species (e.g., C_2 and CN) can be detected at concentrations orders of magnitude below the lower limit of 0.01 mole per cent plotted by Hilsenrath et al, while other species (e.g., O_2, N_2, NO) were detectable with only moderate sensitivity, or not at all, even though probably present in major proportions. Thus, species like N_2^+ and Ar^+, which, below $6000^\circ K$, fall far below the 0.01 mole per cent lower limit of the equilibrium diagram, were easily detected. Others, like O_2 or CO, at least one of which presumably must have constituted a significant proportion of the gas of the air jets from graphite electrodes[18] were not detected. An attempt will be made in the following sections to evaluate the meaning of the optical spectroscopic observations, in the light of factors affecting the appearance or nonappearance of the spectrum of a given species.

Molecular Nitrogen, N_2. Equilibrium calculations predict that, within the temperature range of our jet, N_2 should be the chief component in uncontaminated air. In these experiments, portions of the first and second positive systems of the N_2 spectrum were observable when copper anodes were used. Even so, the N_2 spectra were never strong, and the likelihood of being able to detect minor concentrations of N_2 under our conditions is regarded as slight. Moreover, substitution of a graphite anode for one made of copper seemed to increase the intensity of C_2 bands in the region where the first positive system of N_2 could be observed. The result was that N_2 could not be detected under these conditions, probably because of spectral interference rather than because of any reduction in content of N_2. It appears, therefore, that only marginal feasibility exists for detecting N_2 in carbon-contaminated plasmas of this type.

Molecular Nitrogen Ion, N_2^+. The spectrum of N_2^+ was observed in a wavelength region ordinarily heavy with CN bands in the presence of much carbon and nitrogen. It is not surprising, then, that this species was found only when a copper anode was used. According to the thermodynamic calculations, the equilibrium concentration of N_2^+ in air uncontaminated with excess carbon vapor (as from the graphite cathode) should lie well below 0.01 mole per cent in our temperature range. This would indicate that the spectroscopic method

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[18] H. Y. Wachman, M. J. Linevsky and J. H. McGinn, The Effects of Electrode Contamination on the Properties of Air-Arc Plasmas, General Electric Co., Missile and Space Vehicle Dept., Tech. Info. Series No. R59SD427 (1959).

is highly sensitive for this species, a conclusion that is supported by the easy detection of N_2^+ in the argon plasma. Unfortunately, it was not possible to estimate the extent of entrainment of air by the argon jet.

Another possibility is that N_2^+ may have been present at concentrations exceeding those predicted for equilibrium. This question could be studied if transition probability data could be applied to the determination of actual number densities of N_2^+.

Atomic Nitrogen, N. The observation of strong spectra of neutral atomic nitrogen is in agreement with the thermodynamic predictions. Optical spectroscopy is ideal for studying this species; numerous strong lines, free of interfering spectra, are available.

Of all the species observable by optical spectroscopy, and for which thermodynamically predicted concentrations are available, this one displays the widest gamut of concentration changes over the temperature range of these experiments i.e. from $4200°K$ to $6500°K$. It would be interesting, therefore, to attempt a correlation between temperature and the intensity of the N spectrum if sufficiently well controlled experiments could be carried out. Such experiments might confirm that the concentration of atomic oxygen is higher than that of atomic nitrogen below approximately $6500°K$ (cf. Figure 6).

Ionized Nitrogen, N^+. Numerous intense spectral lines of N^+ occur in the accessible wavelength region. The fact that N^+ was not detected is probably a result of too low temperature for extensive dissociation of N_2; undoubtedly N^+ can be studied spectrographically when the temperature is high enough to produce the species and to excite it.

Molecular Oxygen, O_2. The feasibility of detecting molecular oxygen, O_2, by optical spectroscopy has been tested by looking for the Schumann-Rounge bands which, in emission, are usually strongest in the region 2440 Å to 4375 Å. They are favored by thermal excitation at ordinary pressures, and they have been observed in a "high-tension" oxygen arc and in $CO-O_2$ and H_2-O_2 flames (Ref. 4, page 193).

Nondetection of the Schumann-Runge bands raises the question whether O_2 was virtually absent or whether conditions were unfavorable for its excitation. Chemical reactions must have accounted for some reduction in O_2 content of the plasma, e.g., dissociation under the influence of high temperature, or reaction with carbon vapor to form carbon monoxide. The thermodynamic data indicate a rapid drop in the O_2 concentration of uncontaminated air above $3000°K$, though even at $6000°K$ its concentration should be appreciable. Nondetection of the O_2 bands is probably a result of weak emission rather than the absence of molecular oxygen. Unfortunately, intense CN spectra interfered with the possibility of compensating for weak O_2 emission by increasing the exposure time.

The Schumann-Runge bands are known to be difficult to excite. In this respect O_2 falls in the category of those permanent gases like N_2 and CO that have resonance transitions arising from relatively high electronic energy levels. These gases are characteristically among the less sensitive emitters and hence, under many conditions, are not as amenable to detection by emission spectroscopy as the diatomic radicals, such as C_2 and CN, or many atomic species. Other conceivable reasons for weak emission of the Schumann-Runge bands might be the existence of an effective deactivation process or of the failure to meet some special requirement for production of the excited state. The latter possibility is suggested by the fact that the excitation potential for the Schumann-Runge bands (6.1 ev) lies above the dissociation potential (5.08 ev).

In view of the extensive dissociation of O_2 predicted thermodynamically, it was felt that ultraviolet emission might occur in the relatively cooler envelope of gases surrounding the luminous portion of the jet. Some encouragement for such a search was found in a paper by Herman et al.[19], who found O_2 bands in emission with the equivalent of a 10-second exposure from a series of explosions of CO and O_2 in 7-liter spherical bomb. The bands were those of the "atmospheric absorption" system between 7200 Å and 8800 Å. In order to have longer exposure times than would be possible with the plasma jet, a pilot experiment was carried out in our laboratory by stigmatically imaging an ordinary carbon arc onto the spectrograph slit. The Schumann-Runge bands were sought, but the only new feature observed was the well-known OH band at 3063.6 Å.

The tentative conclusion must be that O_2 is not detectable by the Schumann-Runge bands under our conditions. Time did not permit an examination for the "atmospheric absorption" bands found by Herman et al., but their work strongly suggests that such experiments should be done with the plasma jet.

Molecular Oxygen Ion, O_2^+. This ion was never detected by us either in air or argon plasmas. Hilsehrath et al[15] give no data on its abundance in high-temperature air. The existence of O_2^+ in discharge tubes, especially near the cathode, has been demonstrated by others. Citations to the literature are given by Pearse and Gaydon.[4]

Atomic Oxygen, O. The excitation of the spectrum of atomic oxygen in a carbon arc is known to be strongly influenced by the surrounding atmosphere.[20]

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[19] R. C. Herman, H. S. Hopfield, and S. J. Silverman, J.Chem. Phys. 17, 220 (1949).

[20] V. A. Fassel, W. A. Gordon and R. W. Tabeling, Emission Spectrometric Determination of Oxygen in Metals. Syposium on Spectrochemical Analysis for Trace Elements. A.S.T.M. Special Technical Publication No. 221, p. 3, (1958).

In general, the oxygen triplet at 7771 $\overset{\circ}{A}$ is close to the threshold of detection in ordinary exposures of metal d.c. arcs in air. With carbon arcs, the level of excitation is not depressed by the presence of large quantities of metal atoms of low ionization potential, and the oxygen spectrum is then more intense. When the effective temperature of the arc is increased by surrounding it with an inert gas, even traces of oxygen are detectable by the 7771 $\overset{\circ}{A}$ triplet. In the plasma jet in air or argon, higher temperatures are encountered than in ordinary low-current arcs. Accordingly, the oxygen spectrum is easily excited even in the air plasma. The equilibrium calculations show that most of the oxygen should be in the atomic form in the applicable temperature range.

Ionized Oxygen, O^+. This species should exist only in trace quantities within our temperature range at ordinary pressures. No lines of O^+ were found in any of our plasmas, though many lines of the ion are available in the accessible wavelength region. Almost surely, its detection would be feasible if significant quantities were present.

Nitric Oxide, NO. In pure air at equilibrium, NO rises to a sharp concentration maximum at about four mole per cent near $3500°K$, yet its spectrum was not recorded on any of our plates. Even if the predicted equilibrium levels of NO were not fully realized, it seems doubtful that quite significant proportions of NO would not have been formed. In all likelihood, the non-detection of NO stems from failure of excitation, or from deactivating collisions that prevented radiation by excited particles.

The gamma bands of NO are rather widely distributed over a wavelength range from 3459 $\overset{\circ}{A}$ to beyond the ultraviolet limit of our instrument. If they were emitted strongly by the jet, there should be no difficulty in finding them in regions where the CN and C_2 bands would not interfere. Other workers have found these bands in arcs running in air, e.g., Guillery[21], who stated that the gamma bands of NO occur regularly in many types of metal arcs, especially between copper electrodes. However, even with the most favorable combination of arc length and voltage, Guillery had to expose for four hours to get a high dispersion spectrogram of air at atmospheric pressure. It seems highly probable that the inability to observe NO in the jet was a result of the short exposure times (usually less than one minute). On the other hand, with longer exposure, the presence of carbon vapor in the air arcs would probably result in serious interference from C_2 and CN bands, even in relatively clear spectral regions.

Diatomic Carbon, C_2. As indicated in an earlier section, the very intense C_2 bands are probably emitted by a quantitatively insignificant concentration of C_2 molecules. These bands illustrate Gaydon's remark[22] that, in ordinary

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[21] M. Guillery, Z. Phys. 42, 121 (1927).

[22] A. G. Gaydon, The Spectroscopy of Flames, Wiley (1959).

flames, the spectroscopic method tends to throw undue emphasis on a small number of electronically excited radicals. Evidently the same comment applies to carbon arcs in air under $6000°K$.

Triatomic Carbon, C_3. This species is not included in the available equilibrium calculations, but its presence has been recognized in the spectra of discharges, furnace atmospheres, comet heads, flames, and in flash photolysis experiments. Kiess and Broida[23] observed the C_3 spectrum in strong emission from an acetylene-oxygen flame when the acetylene/oxygen ratio was slightly greater than unity. Short exposures sufficed to produce a spectrogram. Non-detection of C_3 in the jet from graphite electrodes may indicate that the species is unimportant under these conditions, but interference from CN near the C_3 bands around 4050 Å could have prevented detection. Further experiments in a nitrogen-free system might reveal the presence of this interesting species.

Atomic Carbon, C. Optical spectroscopy is well suited to the detection of neutral carbon atoms. A number of easily identified lines are available. The line at 2478.57 Å is especially strong.

Ionized Carbon, C^+. There appears to be no reason why C^+ could not be easily studied spectrographically in systems hot enough to produce it in quantity, though it was not found in these experiments.

Cyanogen, CN. As mentioned earlier, the CN spectrum is one of the most easily observed in our jets. Bands of this radical are so intense and so widespread that they constitute a major interference with the detection of other species.

Carbon Monoxide, Co. The equilibrium calculations for pure air show that most of the carbon content of the original CO_2 goes over to CO in the temperature range of our jets.[4] When graphite electrodes are used, even higher concentrations of CO should exist in the air plasmas.

It is perhaps not surprising that CO bands were not found in the plasma jet, in view of their usual absence in flame spectra except when long exposures are made.[22] The literature is replete with studies of CO band spectra but most of this work is done in vacuum systems, and long exposures are common. It appears at this time that optical spectroscopy is probably relatively insensitive for detecting CO in arcs and jets at atmospheric pressure.

Argon, Ar and Ar^+. The feasibility of detecting Ar and Ar^+ was amply demonstrated. Equilibrium calculations indicate that Ar^+ must exist at very low concentrations below $6000°K$ in air.

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[23]
    N. H. Kiess, and H. P. Broida, Can. J. Phys. 34, 1471 (1956).

Optical spectroscopy is undoubtedly a necessary tool in any study of conditions in high temperature gaseous systems. Like any observational method, however, it has its own particular set of advantages and limitations. These will be discussed with reference to the results of the program.

The most basic type of information obtainable by emission spectroscopy relates to the composition of the emitting medium. Qualitative identifications are possible for many species with great sensitivity. Other species, presumably present in major concentrations, are not detectable readily, if at all.

In comparing the optical spectroscopic method with the thermodynamically calculated species abundances, the limitations of both methods must be taken into consideration. The thermodynamic calculations apply only to equilibrium conditions and they are available only for restricted ranges of ultimate elemental composition. On the other hand, only a beginning has been made in applying emission spectroscopic methods to fully quantitative analyses of high temperature gases under laboratory conditions. Quantitative emission spectrographic analysis for individual dissociation or ionization products of atomic and molecular species is not possible in the same sense that such analyses are made in the routine spectrographic analysis for chemical elements in metals and alloys, for example. In the latter case, what is wanted is a measurement of the entire amount of a given element in the alloy; it is immaterial how the element is distributed among its ionization states in the emitting gas of the spark or arc. It is only necessary that this distribution be reproducible in both the standardization experiments and the analytical discharges. On the other hand, the measurement of the populations of individual ionization states or dissociation fragments in a plasma cannot be standardized by reference to synthetic preparations, since the distribution of any added substance among its own ionization and dissociation fragments depends on pressure, temperature, and the presence of other species. It is just this distribution which must be measured, and this can only be done by absolute measurements of the spectrum emitted by each species.

Quantitative analyses can be made only when actual quantum yields are known through absolute intensity measurements, and when the quantum yields can be translated into number densities of particles in the excited state of the transition involved. Such a calculation is possible only when the appropriate transition probability is known. In general, transition probabilities are known for relatively few species. This is a serious limitation on the feasibility of quantitative emission studies of plasmas at present. Research on transition probabilities is progressing, however, and further advances can be expected. After the population of an excited state is calculated, as indicated above, the Boltzmann factor can be used to arrive at the concentration of particles of the given species in the ground state, which is the desired analytical result unless the temperature is so high that particles in excited states constitute an appreciable fraction of the whole. In either case, use of the Boltzmann distribution implies an assumption of thermodynamic equilibrium. Departures from equilibrium can invalidate the results, but their

existence can be studied spectroscopically.

An example of a favorable case for a quantitative analysis is discussed by Gaydon (Ref. 22 page 192), who shows how the particle density (in particles per cubic centimeter) could be calculated for C_2 molecules in an acetylene-oxygen flame by the above procedure. In this case, the transition probability was known approximately, and the order of magnitude could be calculated for the abundance of C_2. The calculated partial pressure of normal C_2 molecules was of the order of magnitude of 10^{-6} atmosphere.

The preceding discussion leads to the conclusion that, until more comprehensive information is available on transition probabilities of various atomic and molecular species, the best guide to the quantitative abundances of the major species in air will be the thermodynamic predictions. This is not to say that the equilibrium calculations can be applied literally to the plasma, since it is not in complete equilibrium. Nevertheless, the thermodynamic calculations should at least be useful for setting limits on the probable abundances, and even for estimating orders of magnitude.

The fact that the plasma jet is not an equilibrium system is in itself an important reason for further developing the spectroscopic method. To this end, more research needs to be done on transition probabilities and on the refinement of applicable spectroscopic techniques. In the latter category, it will be important to study the effects of self-absorption in reducing the emission line intensities. The elimination or evaluation of absorption effects could play a significant role in advancing the development of quantitative procedures, since proportionality between the density of an emitting species and the spectral intensity will not hold when absorption is significant. With further advances along these lines, optical spectroscopy will play an increasingly important role in plasma research.

On the purely qualitative side, optical spectroscopy suffers from its inability to detect certain important species, at least under the conditions of our experiments. This failure is not believed to be due to the absence (relatively speaking) of the species themselves, but to the lack of conditions favorable to emission, or to masking by more intense spectra of other species. Possibly the only real limitation in the ability to detect such species as O_2, CO and NO lies in a need for much longer exposure times than were tried. Much of the classical work in the spectroscopy of gases has had to be done with very long exposure times. To be sure, longer exposures result in the obscuring of wide wavelength ranges by sensitive band systems, but completely negative conclusions cannot be drawn until more experiments are performed. For example, the "atmospheric absorption" bands of O_2 should be investigated in this fashion.

Unless the plasma has an unusually low temperature, some species, of which O_2 and NO would be typical examples, would be more stable in the relatively cooler regions surrounding the hotter central core of the jet. Carefully done experiments with stigmatic imaging on the slit might permit long exposures in such regions if special precautions were taken to avoid halation and emulsion turbidity effects.

Both qualitative and quantitative studies tend to become less complicated in some respects as temperatures increase. At sufficiently high temperatures (above about $8000^{\circ}K$) the spectra of CN and other diatomic and polyatomic species disappear, owing to virtually complete dissociation of the emitting molecules. There remain only the much simpler spectra of monatomic species, free of the often extremely complex molecular bands. Interferences are greatly reduced and smaller (and faster) spectrographs can be used. In the temperature region just above $8000^{\circ}K$, the spectra of most species likely to occur are well known and identifications by optical spectroscopy should be fairly straightforward, though forbidden transitions may come into play.

The optical spectroscopic method also enjoys another advantage when applied to systems at higher temperatures -- self-absorption introduces less interference with the interpretation of quantitative emission measurements under certain conditions. Stated differently, thin layers of emitting gas tend to become more transparent with increasing temperature. This is because the black-body curve of maximum possible emission under equilibrium conditions falls at higher values. Correspondingly, any given actual emission may be only a small fraction of the maximum possible emission, which implies that self-absorption accounts for a smaller fraction of the emission. These remarks apply to a body of gas of limited thickness and at uniform temperature -- no reference is made to an envelope of cooler gas.[24]

Species undetectable by direct spectroscopy may ultimately be measured by applying the thermodynamic equations of chemical equilibrium to relations involving species that can be quantitatively measured by spectroscopy. This amounts to the same thing as is done by Hilsenrath et al[15] in the purely thermodynamic calculation of species abundances, except that known values for spectroscopically measurable species would serve as starting points for the non-equilibrium cases, definite conclusions on the abundance of a spectroscopically unobservable species would have to depend on obtaining consistent quantitative results from at least two independent measurements based on different observable species. An example of this type of calculation is given by Gaydon,[22] (page 192).

In addition to direct observations on major species, optical spectroscopy can give crucial information about processes going on in the plasma. The observation of reaction intermediates is a case in point. Some species of

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[24] W. Lochte-Holtgreven, Production and Measurement of High Temperatures Repts. on Progress in Physics 21, 312 (1958), Cf. page 317.

short lifetime, e.g., CN and C_2, are extremely efficient emitters. These can exist neither in the initial nor in the final products. Hence spectroscopic studies of their conditions of occurrence may yield clues to the roles they play as intermediates in the various plasma processes.

Finally, the origins of excited species can be studied spectroscopically by observing departures from normal Boltzmann distributions of the populations of energy levels. Important information about plasma processes can thus be obtained by way of distinguishing between thermal excitation and the direct chemical formation of excited species.

SECTION IV

TIME-OF-FLIGHT MASS SPECTROMETRY

EXPERIMENTAL

One of the major problems encountered in attempting to study plasma jet species with a mass spectrometer was the design of a suitable "probe". This must be capable of transferring ions and excited species from the jet, operating at atmospheric pressure, into the evacuated mass spectrometer with a minimum probability of charge exchange, de-excitation, etc. Since most of these undesirable effects result from collisions of the species of interest with other molecules, it is a necessary condition that the probe be operated at a low enough pressure that the path length of the species be short compared with their mean-free-path.

Originally a probe was designed that would produce the required low pressure with a single stage of pumping before the mass spectrometer. This is shown schematically in Figure 7. For this system to be successful it would be necessary for the entrance pinhole to be of the order of 0.1 mil diameter. In addition to the difficulty in obtaining such a small opening, it was soon learned that an orifice of this size would be extremely susceptible to plugging by atmospheric dust. Hence this design was abandoned.

A new design for an inlet system which utilized differential pumping was prepared. This was adapted from a similar system used by M. K. Testerman for the study of combustion processes.[25] Drawings of the assembled probe and of the components are shown in Figures 8 through 12.

Of the common materials of construction, stainless steel, type 304, was chosen for the probe system because of its relatively high melting point, durability, and resistance to corrosion.

The choice of diameter for the orifice in the probe tip was governed by the desire to obtain a high intensity of species through the tip while maintaining the pressure between the tip and the fore-orifice low enough that the mean-free-path of the species would be greater than the distance between the tip and the fore-orifice. Some work of S. N. Foner has indicated that maximum intensity through the orifice in the probe tip would be obtained when the diameter of the orifice is approximately seventy times the mean-free-path in

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[25] M. K. Testerman, "The Development of an RF Mass Spectrometer for the study of Combustion Processes" WADC Technical Report 58-429, July, 1958.
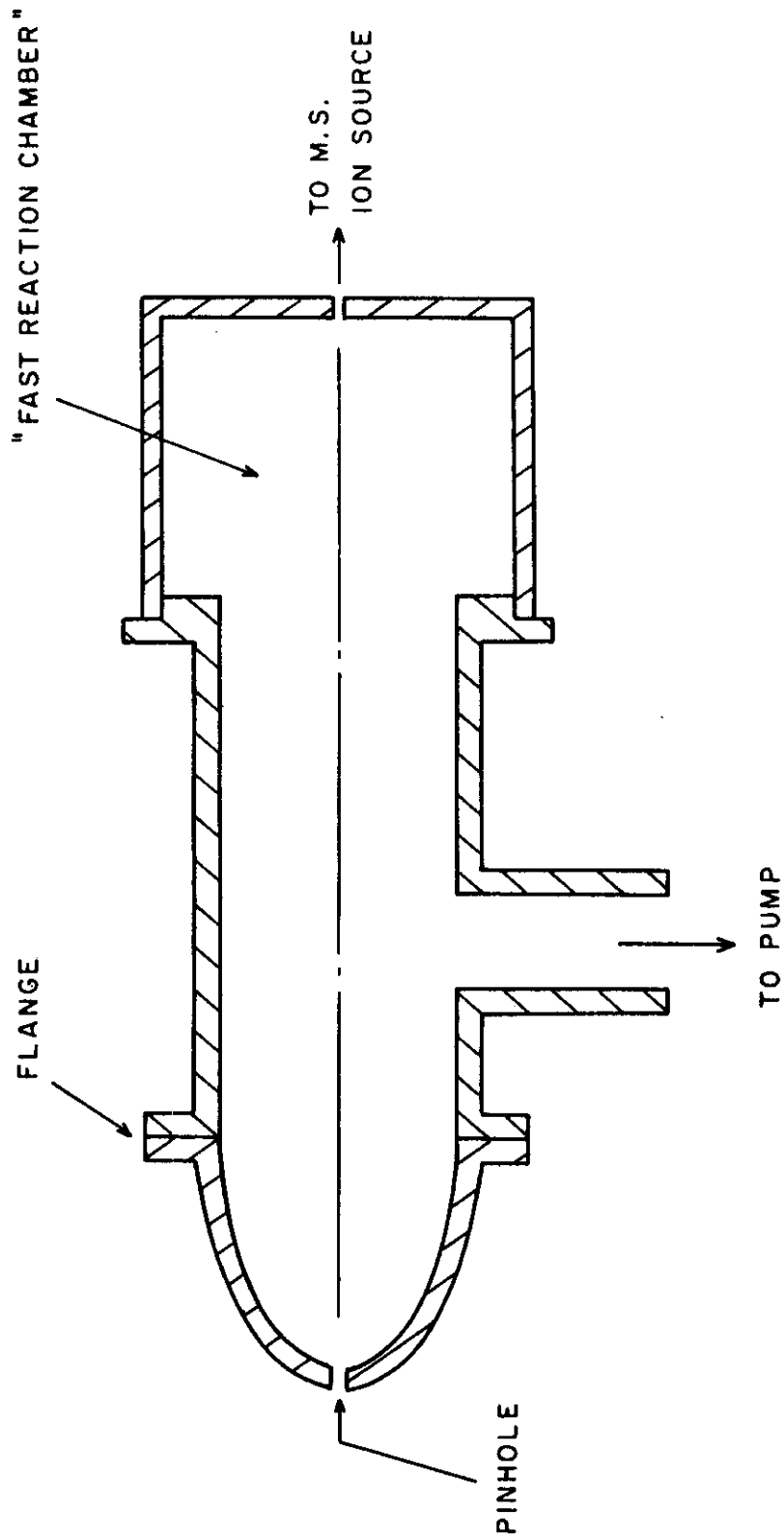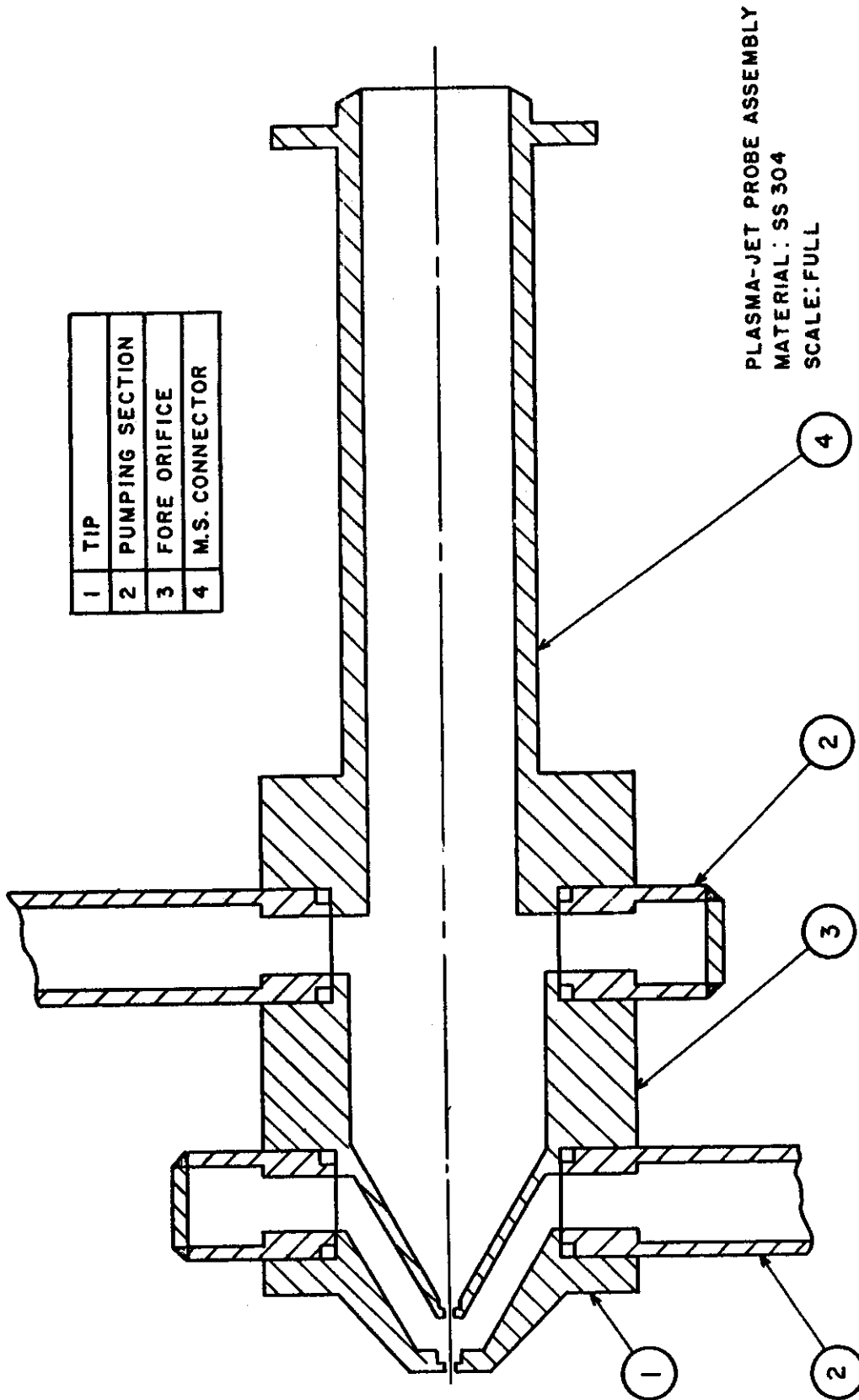
FIG. 7   SINGLE STATE PROBE SYSTEM

1	TIP
2	PUMPING SECTION
3	FORE ORIFICE
4	M.S. CONNECTOR

PLASMA-JET PROBE ASSEMBLY
MATERIAL: SS 304
SCALE: FULL

FIG. 8 -- PLASMA-JET PROBE ASSEMBLY

TOLERANCES FOR ALL DRAWINGS:
±0.003 THREE PLACE DECIMALS
±0.02 TWO PLACE DECIMALS

PLASMA-JET PROBE ASSEMBLY
PART I - TIP
MATERIAL: SS 304
SCALE: FULL
NO REQ'D:

DETAIL B

DETAIL A
(FOR ALL RINGS)
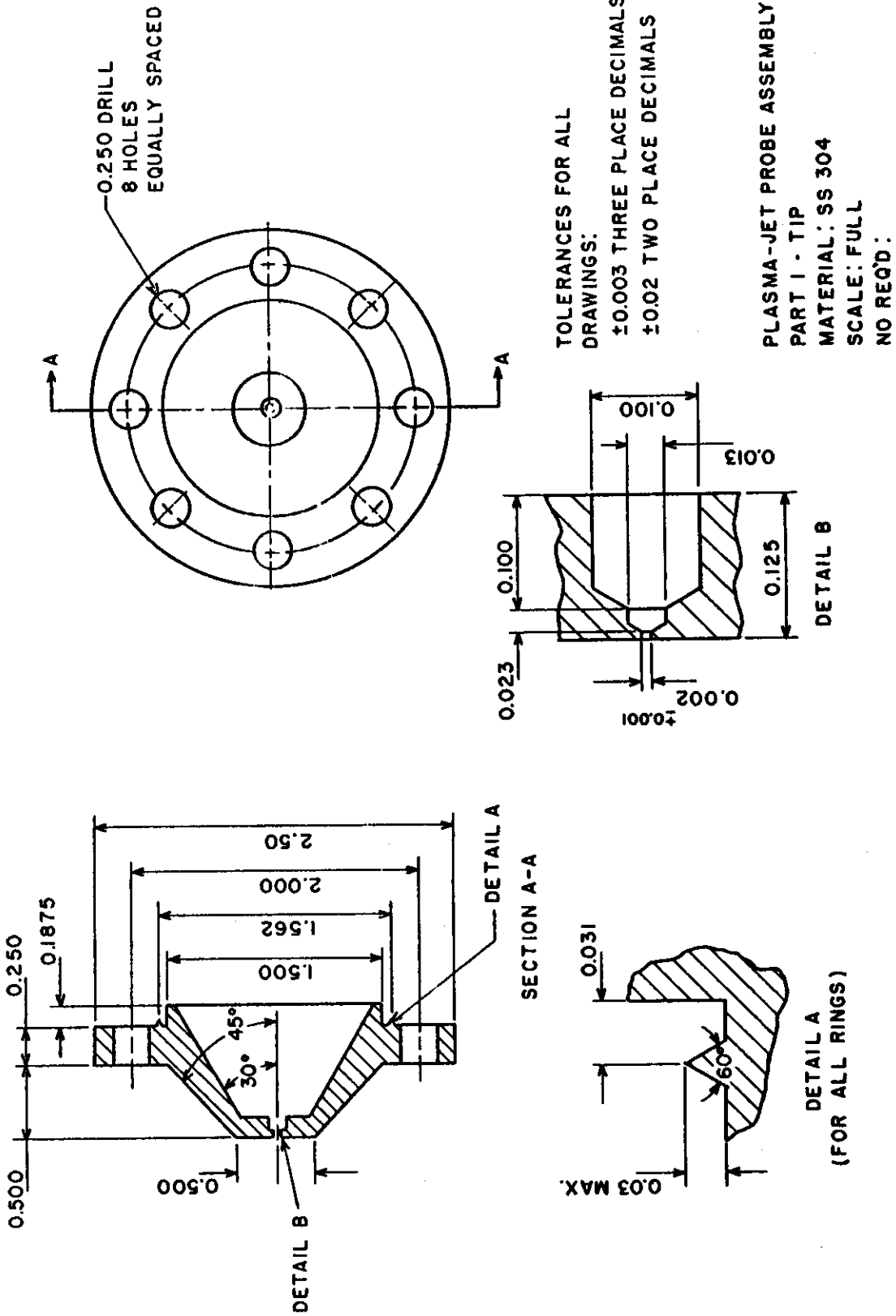
SECTION A-A

FIG. 9 -PLASMA-JET PROBE TIP

0.250 DRILL
8 HOLES
EQUALLY SPACED

0.250 DRILL, 8 HOLES
EQUALLY SPACED
ON 2.000 B.C.

PLASMA-JET PROBE ASSEMBLY
PART 2 – PUMPING SECTION
MATERIAL: SS 304
SCALE: FULL
NO. REQ'D: TWO

FILLET WELD

1.38

1.12

0.750

0.50

1.75R

FILLET
WELD

3.75

3.50

2.50

1.625

1.562

1.500

0.562

0.375
REAM

0.092

DETAIL A

0.50

0.750

SECTION B-B

2.200

DETAIL C
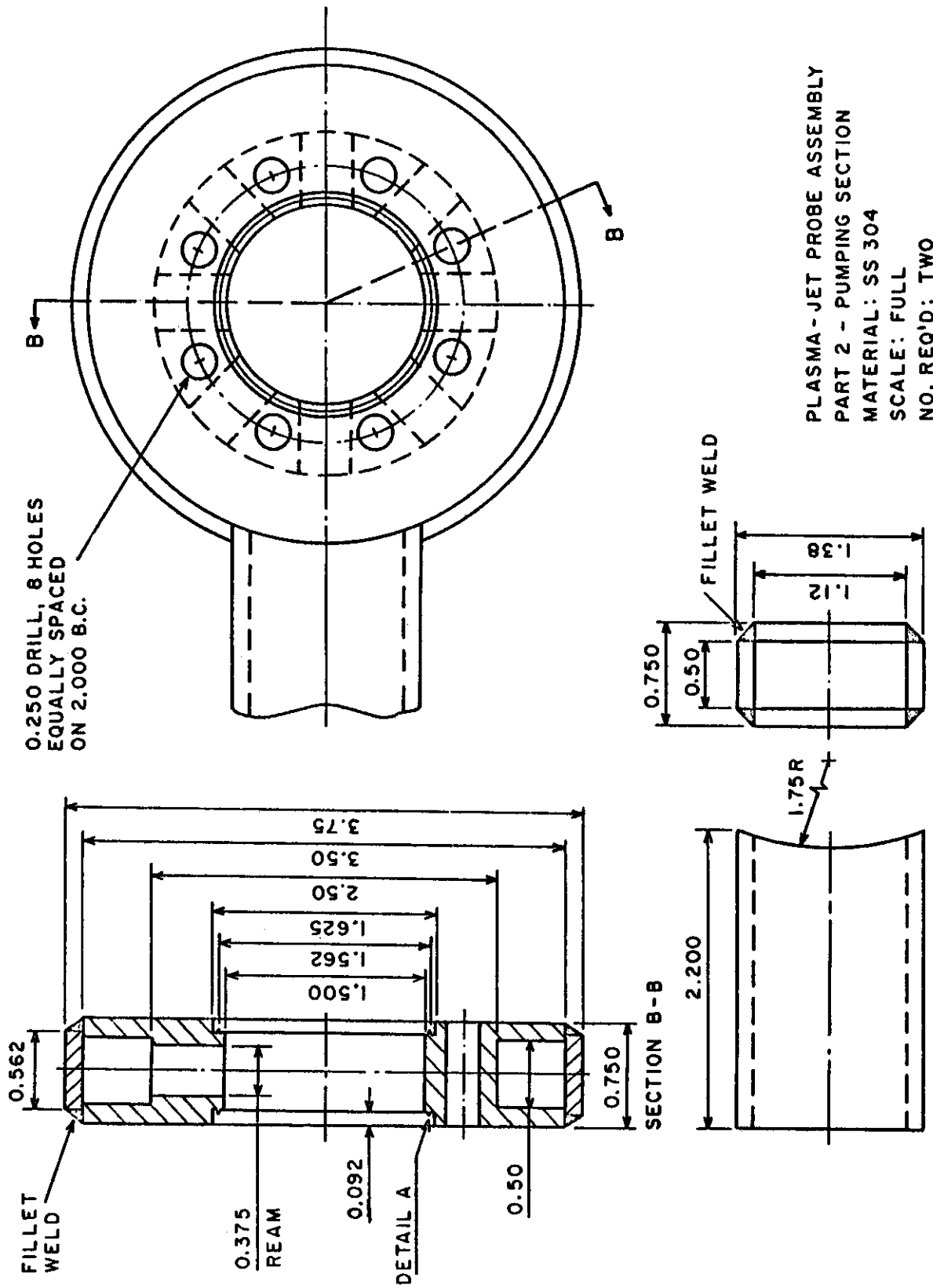
FIG. 10 PLASMA JET PROBE PUMPING SECTION.

0.250 DRILL
8 HOLES
EQUALLY SPACED

C
C

PLASMA-JET PROBE ASSEMBLY
PART 3 - FORE ORIFICE
MATERIAL: SS 304
SCALE: FULL
NO. REQ'D: ONE

FIG. 11 PLASMA-JET PROBE FORE ORIFICE

2.50

2.000

1.562

1.500

1.212

0.1875

1.000

1.255
1.282

2.343

0.1875

30°

0.125

SECTION C-C

DETAIL A

DETAIL D

0.125

0.04

0.06

0.020

#80 DRILL

#54 DRILL

DETAIL D

WADD TR 60- 359

39

PLASMA-JET PROBE ASSEMBLY
PART 4 - M.S. CONNECTOR
MATERIAL: SS 304
SCALE: FULL
NO. REQ'D: ONE

4 SLOTTED HOLES ON 2.071 B.C. TO BE
WITHIN 0.010 OF TRUE POSITION

DETAIL E

1/4-20 TAP, 0.50 DEEP, 8 HOLES
EQUALLY SPACED ON 2.000 B.C.

DETAIL A

DETAIL E
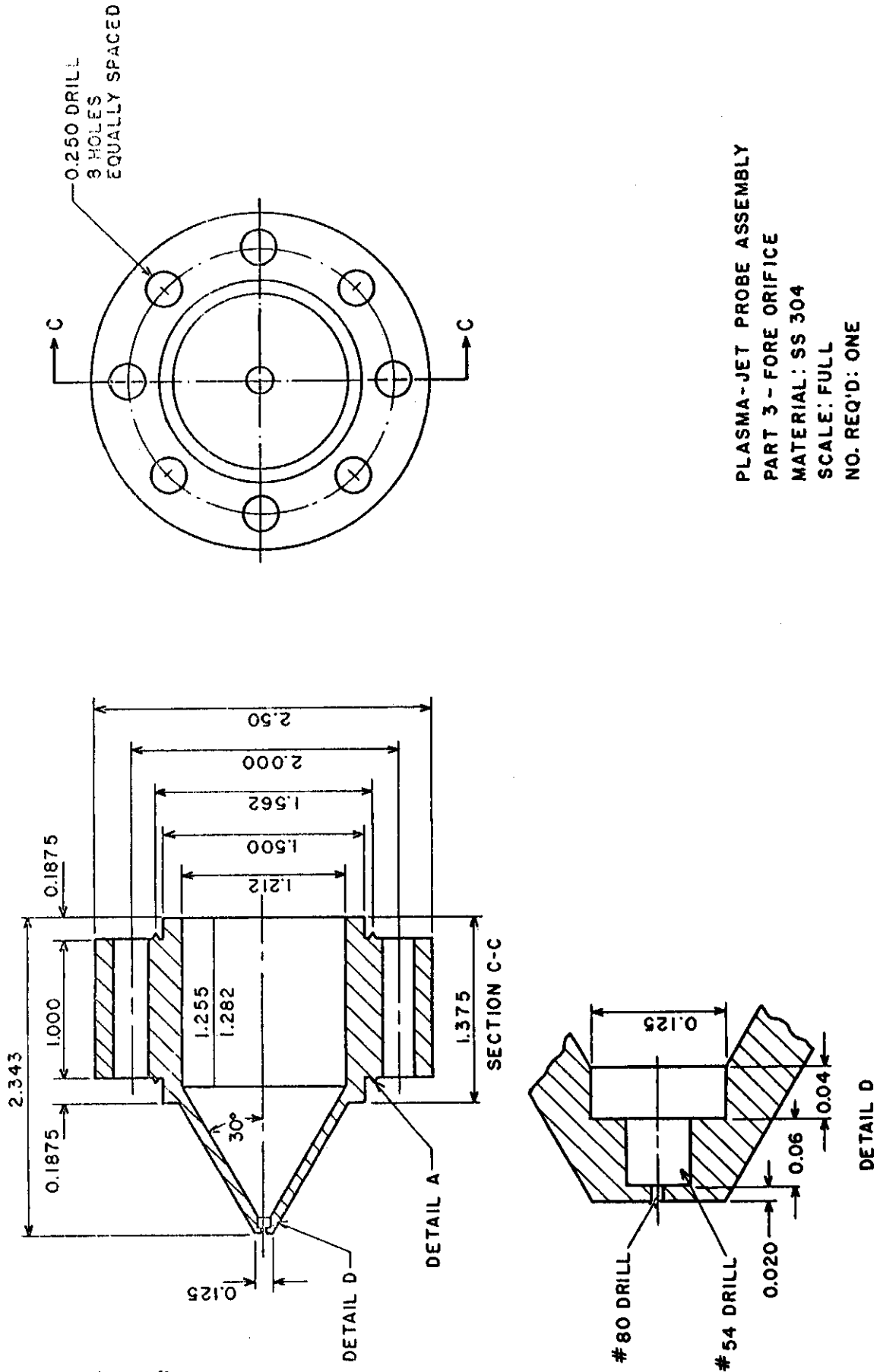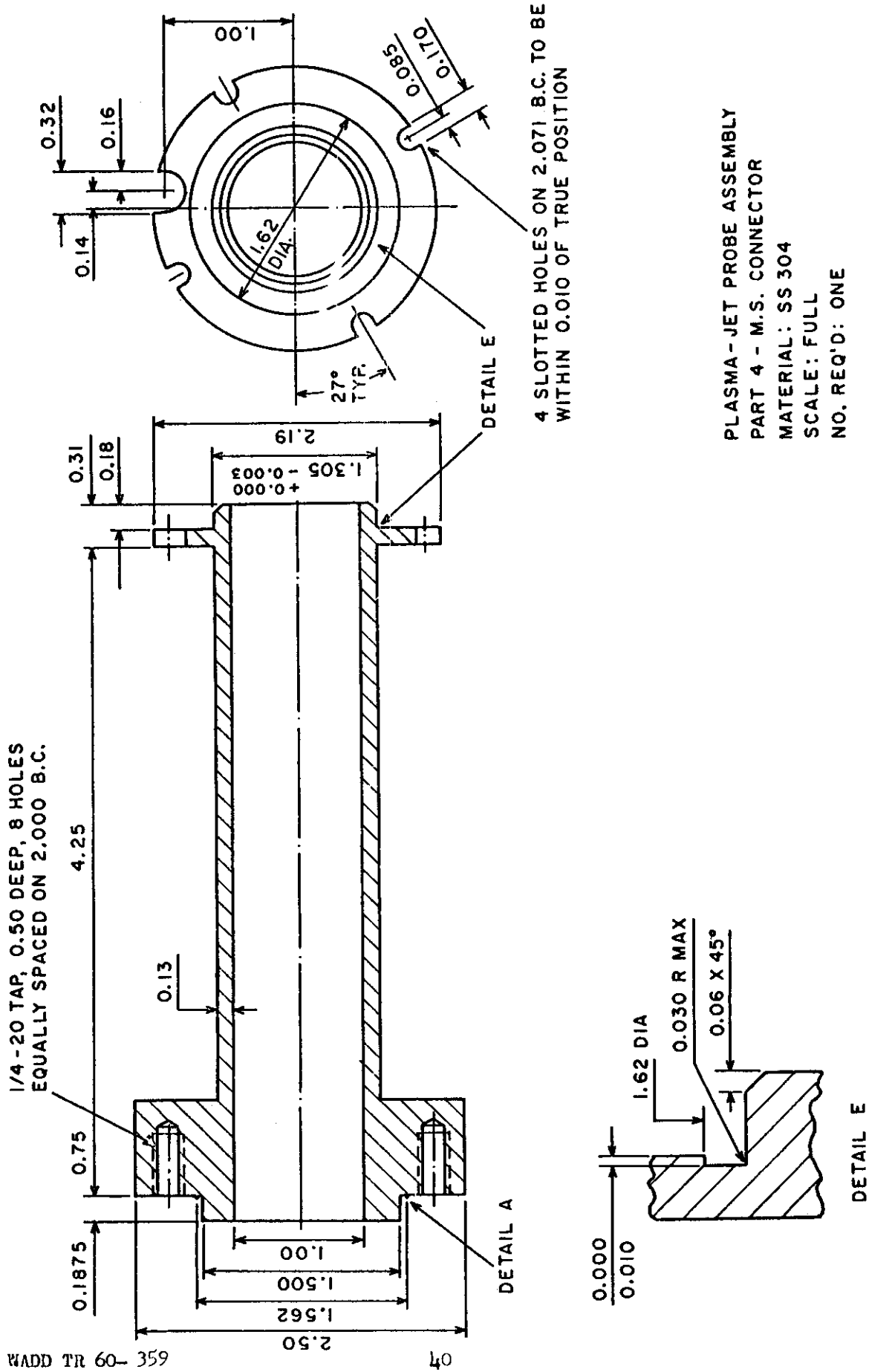
FIG. 12 PLASMA JET PROBE MASS SPECTROMETER CONNECTOR.

the source[26] (i.e., plasma jet). This suggests that a 2-mil diameter orifice would be about the optimum from the standpoint of intensity. An orifice of this size is also desirable because of its relative ease of fabrication and freedom from fouling. The work of Testerman[25] indicates that a pressure in the range 10^{-1} - 10^{-2} mm Hg should be obtained under these conditions when using a Welch 1402B mechanical pump. This corresponds to mean-free-paths of the order of 0.1 - 1 inch. Since the distance between the pinhole and the fore-orifice is approximately 0.35 in., it is possible for the path length to be about three mean-free-paths under certain conditions. Although some ninety percent of the primary species would undergo at least one collision in a flight path three times as long as the mean-free-path, it should be possible to obtain some idea of the nature and abundance of primary species by examining the changes in the mass spectrum with changing hole size. Two different tips were used in this work. The orifice diameter of one was originally about 3.5 mil and the diameter of the other was about 3 mil. For reasons to be discussed later no differences were seen in the spectra obtained with these tips.

The mass spectrometer connector was designed to attach to the mass spectrometer "fast reaction chamber" in place of the chamber sealing flange. The over-all length was chosen to clear the leads to the mass spectrometer ion source and to allow the attachment of a support for the probe. Since the pressure behind the fore-orifice can be maintained about 10^{-4} mm Hg or less, the mean-free-path of the plasma jet species does not impose any severe restrictions on the length of this region.

Soft copper gaskets were used between the components of the probe system. A Teflon gasket was used between the probe and the mass spectrometer in place of the rubber O-ring supplied with the instrument.

The region between the tip and the fore-orifice was evacuated with a Welch 1402B mechanical pump in the first half of these experiments. This was later replaced with a Welch 1397B mechanical pump since some question had developed about the ability of the 1402B to maintain an adequately low pressure in this region. A CEC type MCF-60 oil diffusion pump was used to evacuate the region between the fore-orifice and the mass spectrometer.

The pinhole in the tip, the opening in the fore-orifice, and the 0.0135 in. opening between the fast reaction chamber and the source region of the mass spectrometer serve to define a beam of plasma jet species. This beam is in optical alignment with the detector at the end of the mass spectrometer drift tube. Hence only those species which have traveled an essentially straight path from the plasma jet should have an appreciable probability of entering the source region of the mass spectrometer.

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[26] S. N. Foner and R. L. Hudson, J. Chem. Phys. **21**, 1374 (1953).

Because of the high temperature of the plasma jet, some means is needed to protect the probe tip from undue deterioration. The work of Bonin and Price[27] serves to illustrate what might be expected from prolonged exposure of the tip to the plasma jet. Using a 1000-KW plasma jet and cone-shaped samples having a length of 3 3/8 in. and a base diameter of 3 1/2 in., they obtained the following values for the time required for surface melting to occur: aluminum, 0.38 sec.; and copper, 1.72 sec. For stainless steel, which has a higher melting point than copper but a lower thermal conductivity, one second probably represents a reasonable upper limit to exposure time under these conditions.

Since the Bendix Time-of-Flight Mass Spectrometer produces ten thousand complete spectra per second, it is possible to use sampling times of less than one second and still obtain a reasonable statistical sampling for all but very low intensity species. Therefore a mechanical shutter was designed to be placed between the plasma jet and the probe. The shutter consists of a plate of a suitable material having a rectangular opening cut near its center. The plate is supported vertically in front of the probe and secured with a latch so that the slot is above the pinhole. To make an exposure the latch is released and the slot passes in front of the probe, allowing the plasma jet to impinge upon the pinhole for a time determined by the width of the slot and the friction between the plate and the guideways. Some of the early runs were made with a slot 3/8 in. wide. This was later increased to 5/8 in. In the absence of frictional forces this latter width would give an exposure time of roughly 0.06 sec.; the true time of exposure is probably closer to 0.1 sec. Two shutters are available for use: one of high density graphite, and the other of water-cooled copper. The shutters are 3/8 in. thick.

A Bendix Model 14-107 Time-of-Flight Mass Spectrometer was used in this work. The output from the mass spectrometer was displayed on a Tektronix Type 545 oscilloscope having a Type 53/54 K preamplifier. A DuMont oscilloscope camera loaded with Polaroid Type 47 film was used to record the scope display.

In practice the maximum gain obtainable from the mass spectrometer is limited by broadening of the scope trace by noise from the amplifier. For the majority of this work the mass spectrometer controls were set to give the maximum gain subject to this restriction with the oscilloscope set for maximum sensitivity (vertical deflection 0.05 volts/cm). If a lower gain was desired, the sensitivity of the oscilloscope was decreased.

To obtain a plasma jet spectrum, the jet was ignited and allowed a few seconds to stabilize. A time exposure of the oscilloscope trace was taken as

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[27] J. H. Bonin and C. F. Price in "Conference on Extremely High Temperatures", Boston, Mass., March, 1958, page 237 (John Wiley and Sons, Inc., 1958).

the opening in the shutter passed in front of the pinhole. A calibration spectrum and a picture of the undisturbed trace were usually recorded on the same photograph. Some two hundred plasma jet spectra have been obtained in this manner. Most of these spectra are of a nitrogen-stabilized jet although some runs have also been made with an argon-stabilized jet. Because of the problems which arose in the resolution of the spectra, the use of an air-stabilized jet with a corresponding increase in the variety of ions present was considered to be inadvisable until such a time as adequate resolution could be effected.

The probe tips hold up quite well under the conditions used in this work. After about forty exposures to the plasma jet the diameter of the orifice in one of the tips had increased to slightly over 4 mil. After several runs a dark deposit begins to build up on the tip. This is thought to be copper oxide which is formed by the action of the jet on the copper anode of the plasma jet assembly. Some of this material has also been found to deposit on the fore-orifice. There has been no difficulty with this material clogging the orifices.

RESULTS AND DISCUSSION

A plasma jet spectrum typical of those obtained with nitrogen as the stabilizing gas is shown in Figure 13B. A calibration spectrum is shown in Figure 13A, and Figure 13C shows the undisturbed oscilloscope trace. The vertical deflection for Figure 13B is 0.1 volt/cm., and the spectrum covers a mass region bounded approximately by mass 12 on the left and mass 44 on the right. The power input to the jet was approximately twenty kilowatts.

It is readily seen by comparing Figure 13B with Figure 13A that if the spectrum in Figure 13B does indeed arise from ionic species removed from the plasma jet, then mass resolution is not being effected. In view of this, the experimental work has proceeded along two general lines: attempts to determine the origin of the plasma jet spectrum and attempts to obtain mass resolution.

There are a number of factors which might possibly give rise to a spectrum of the nature of the one shown in Figure 13B. At the first Annual Bendix Mass Spectrometer Users Symposium held in October, 1959 it was pointed out by several people that the detector is quite sensitive to radio frequency fields. Since the plasma jet might be expected to radiate rf noise, several photographs were made of the scope trace while the jet was running but was not in contact with the probe. No disturbing effect was noted.

A better test of the existence of a possible disturbing effect of the plasma jet on the operation of the mass spectrometer is the simultaneous determination of a plasma jet spectrum and the mass spectrum of the background gases in the mass spectrometer. To obtain the background spectrum the mass spectrometer electron gun, which was normally not in operation when plasma jet spectra were sought, was turned on and adjusted to give ion peaks of a convenient magnitude. The spectrum in Figure 13A is an example of this back-
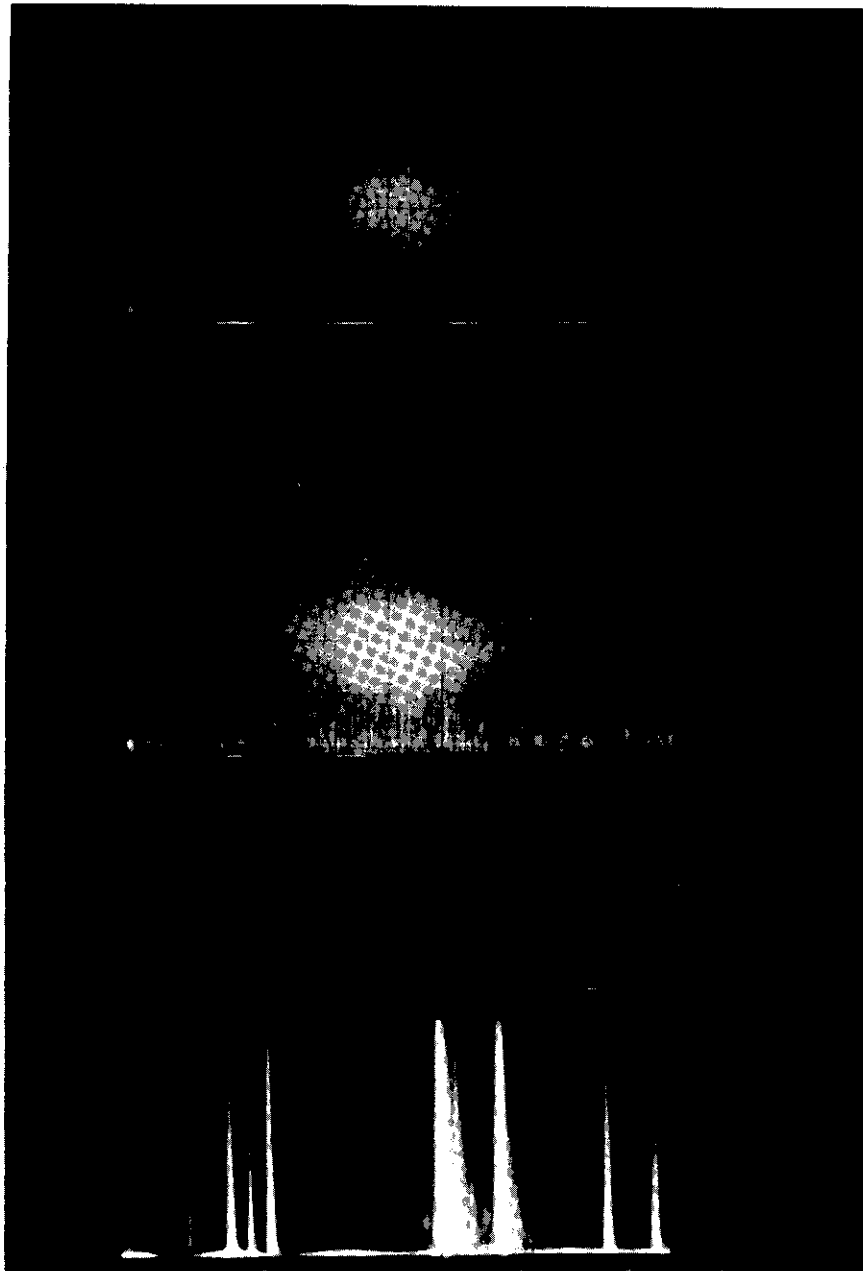
C. BLANK SPEC[T]

B. PLASMA JET
SPECTRUM

A. CALIBRATION
SPECTRUM

FIG. 13 TYPICAL OSCILLOSCOPE DISPLAYS

ground spectrum. Plasma jet spectra were then obtained while ions of the background gases were being generated in the mass spectrometer. The result was a superposition of the two spectra with no apparent distortion of the background spectrum. This leads to the conclusion that the plasma jet is not affecting the normal operation of the mass spectrometer.

Since the plasma jet is in optical alignment with the mass spectrometer's electron multiplier detector, there is the possibility of photoelectron emission from the cathode of the multiplier. To test this a quartz window was placed in front of the pinhole in the probe. No peaks were observed when the jet was allowed to impinge on the quartz window. As a further test of photoelectron emission, the quartz window was removed and the mass spectrometer was adjusted to detect negative ions. Since the occurence of negatively charged species other than electrons in the plasma jet is relatively unlikely, any indication of a mass spectrum could be reasonably attributed to photons. No indication of a spectrum was observed.

By removing the accelerating potential from the mass spectrometer ion source it should be possible to eliminate the plasma jet spectrum if it is due to ions. No spectrum was observed when the accelerating potential was removed. This is also added evidence for the lack of photoelectron emission.

The plasma jet spectra have been observed to change in the manner expected for plasma jet ions for certain changes in operating conditions. When the Welch 1402B pump in the first probe section was replaced by the Welch 1397B pump, the average peak height was observed to increase by about a factor of two. Such an increase would be expected as a consequence of the reduced pressure in the first section and the corresponding increase in the mean-free-path of the entrant ions. A similar increase in peak height was noted when the probe tip was replaced with one having a smaller orifice. This would also be due to a decrease in pressure in the first section.

A decrease in power input to the arc in general results in a decrease in the average peak height of the spectra. However, the length of the jet also decreases with decreasing power input and there is some difficulty in assuring that equivalent portions of the jet are being sampled.

Because the first photographs of plasma jet spectra were indistinct and tended to show discrete peaks, the possibility of inadequate mass resolution was not suspected until clearer photographs showed spectra of the nature illustrated in Figure 13B. Since the available evidence indicates that the plasma jet spectra are indeed due to positively charged species entering the mass spectrometer from the jet, then mass resolution has not been effected.

The arrangement of elements in the mass spectrometer ion source pertinent to the problem of plasma jet ion resolution is shown in Figure 14 along with representative bias potentials and waveforms for both the so-called "pulsed"

and "continuous" modes of operation for the detection of positive ions. The elements are identified as follows: EG, ion energy grid; FG, ion focus grid; TG, trapping grid; BP, backing plate. The ions from the plasma jet enter the ion source perpendicular to the planes of these elements.

From a consideration of Figure 14 it is seen that in the pulsed mode of operation ions from the plasma jet would be continually accelerated down the drift tube to the detector with perhaps some modulation due to the negative-going pulse that appears every 100 microseconds on the trapping grid. Hence this mode of operation cannot be used for the present work.

In the continuous mode of operation ions entering the source region are repelled by the positive bias on the focus grid and should then oscillate back and forth through the trapping grid until they are pulsed out of the source by the negative-going pulse on the focus grid. Since resolution depends to some extent upon the position of an ion in the source before the ion is accelerated, the negative pulse on the backing plate serves to limit the source volume from which ions are accelerated to the region between the trapping grid and the focus grid. Hence, in principle, to obtain mass resolution of plasma jet ions, it is necessary only to apply the appropriate potentials to the ion source elements.

The mass spectrometer controls allow the following variations in bias potentials: FG 0 to +20 volts; TG 0 to -2 volts; BP 0 to +5 volts. The depth of the pulses can also be varied somewhat with the maximum values being -290 volts on the focus grid and -40 volts on the backing plate. No combination of these variables has been found experimentally which will provide resolution of the plasma jet spectrum, or, indeed, which has a significant effect on the appearance of the spectrum.

By the use of an external source of potential it has been possible to vary the bias potential on the focus grid from 0 to +60 volts and on the backing plate from 0 to +40 volts. While the higher potentials cause a decrease in the average peak height of the spectra, there has been no improvement in resolution. In addition, a constant negative bias on the backing plate of up to 30 volts seems to have no effect on the plasma jet spectrum.

It has not been possible to provide any additional variation in the depth of the pulsing waveforms, so that the effect of a deeper pulse has not been tested.

It is interesting to note that when the controls are set such that leakage of internally generated ions through the focus grid can occur, the spectrum is similar to those obtained from the plasma jet with the exception that the peaks of the more abundant ions can still be detected above the unresolved background. That such peaks cannot be seen in the plasma jet spectra may be due to their smaller intensity.
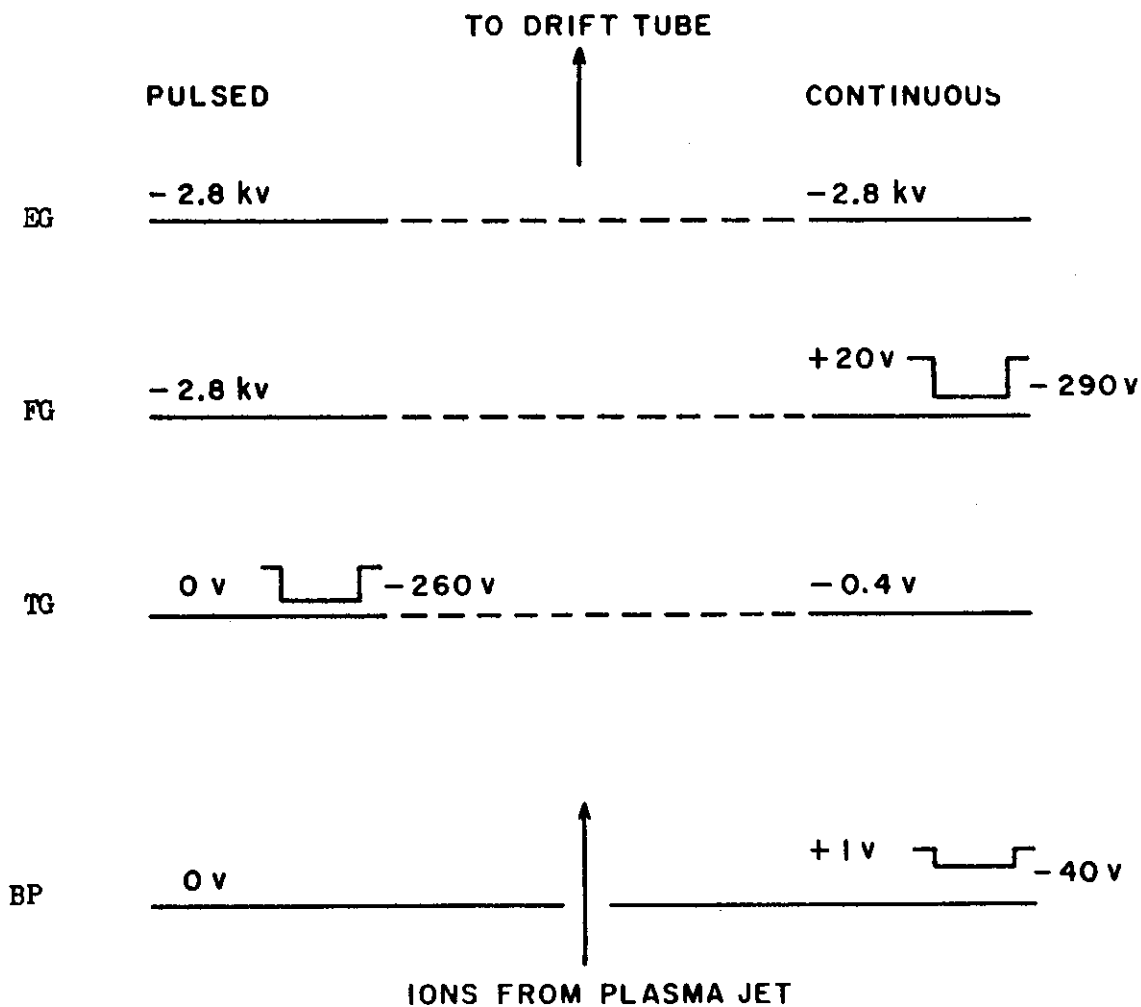
TO DRIFT TUBE

PULSED   CONTINUOUS

EG   − 2.8 kv   −2.8 kv

FG   − 2.8 kv   +20v ⎍ −290 v

TG   0 v ⎍ −260 v   − 0.4 v

BP   0 v   +1 v ⎍ −40 v

IONS FROM PLASMA JET

FIG. 14 MASS SPECTROMETER ION SOURCE ELEMENTS

The problem of resolution has been discussed with a representative of Bendix. A solution to the problem has not yet been realized.

The probability of excited species reaching the mass spectrometer from the plasma jet is higher than that for ions due to their higher concentration in the jet. Hence a series of experiments was performed to determine if these species could be detected. To enhance the possibility of detection, a mixture of nitrogen and iso-propyl alcohol vapor was used as the stabilizing gas. The iso-propyl alcohol was expected to give a variety of radicals and other excited species some of which would fall in mass regions which would be relatively free of background contaminants.

To detect these excited species it is necessary to ionize them after they enter the source region of the mass spectrometer. To discriminate between excited species and those in the ground state it is necessary to determine the appearance potentials of the product ions. This entails working with low-energy beams of ionizing electrons and consequently low ion intensities.

The plasma jet was operated at as low a power input as was consistent with the maintenance of a stable arc, i.e., approximately ten kilowatts, to reduce the probability of ionization. However, in all trials a spectrum similar to that shown in Figure 13B resulted, obscuring any ions that might be generated within the mass spectrometer. Hence the attempts to measure appearance potentials were abandoned.

In summary, the appearance of a spectrum such as is shown in Figure 13B seems to be dependent upon the admission of material from the plasma jet into the probe. While there is no conclusive evidence that the spectrum represents plasma jet ions, it has not been possible to prove otherwise. Assuming the observed spectra to be due to plasma jet ions, the potentials on the elements of the mass spectrometer ion gun were systematically varied in an unsuccessful attempt to resolve the spectrum. Because of the persistence of this spectrum, even at low power inputs, attempts to study neutrals were also unsuccessful.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

PLASMA JET

Several areas where future work could be applied to enhance the use-
fulness of the plasma jet for these studies are apparent. One of the foremost
areas where improvement is required is in producing an air plasma that is not
contaminated with electrode material. In many instances, it will be impossible
to distinguish between the contaminants and the material being studied, and in
other instances the effects of the contaminants, even though they may be dis-
tinguished, will mask the effects being studied. The latter is especially
significant in the optical spectroscopic studies where it was observed that
species such as O_2, N_2, and NO could not be detected. Attempts to produce an
uncontaminated plasma during the present program were partially successful.
It is believed that a small amount of further effort on the nitrogen sheath[*]
method will allow an uncontaminated air plasma to be produced.

Better methods of stabilizing the plasma would be useful. One might
attempt to adapt the type of plasma jet described by the National Bureau of
Standards.[**] This particular device produces an extremely stable and un-
contaminated plasma, even with pure oxygen.

A refined device in which the enthalpy of the plasma could be accurately
measured, may allow the experimental determination of the "apparent" specific
heats of gases, especially at the lower plasma temperatures where the tempera-
ture measurements are more certain.

OPTICAL SPECTROSCOPY

Most important of the problems to be solved by optical spectroscopy would
appear to be the quantitative estimation of species concentrations. A start
could be made with the C_2 spectrum, and perhaps also with CN using available
data on transition probabilities, and following procedures indicated in the
foregoing text. Atomic species could probably also be studied, such as O, C
and N. If adequate data on transition probabilities cannot be obtained, con-

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[*] This method was indicated to us by Messrs. Dimiduk and Wittebort at WADD.
In this method a blanket of nitrogen is injected around the tungsten
electrode to protect it from the oxidizing atmosphere.

[**] H. Kostkowsky in "The Proceedings of an International Symposium on High
Temperature Technology", McGraw-Hill Book Co., Inc., New York, 1960,
page 42.

sideration should be given to a program of determining the necessary values.

As a part of the quantitative study of species abundances, experiments should be devised to evaluate absorption effects so as to insure that "net emission" is proportional to the concentration of the emitting species. This study can be approached by experiments on "net emission" from variable depths of the plasma.

Some further work on the search for weakly emitting species should be instituted. Suggestions for such work appear in the text.

More detailed spectroscopic temperature measurements are needed in order to recognize separately the different temperature modes, e.g., the so-called electronic, vibrational and rotational temperatures in non-equilibrium cases, where populations of excited states are nevertheless normally distributed with a given degree of freedom. This type of information is required for the characterization of the plasma, both for the full description of its physical and chemical state, as well as to permit recognition of processes taking place in it. In circumstances of still wider departure from equilibrium, as when a non-Boltzmann distribution of the populations of excited states prevails (e.g., within the electronic, vibrational or rotational degree of freedom), one may identify the chemiluminescent production of excited states as a direct result of a chemical reaction, or through an intermediate energy transfer process following a chemical reaction. This type of result is distinguished from excitation by purely thermal processes.

Application of the new infrared scanning spectrophotometer to infrared emissions should be undertaken.

TIME-OF-FLIGHT MASS SPECTROMETRY

Since it has been impossible to either prove or disprove the effectiveness of the mass spectrometer as a tool for the study of plasma jets, it would be desirable to continue the present investigation until definite conclusions can be drawn. The following paragraphs outline some modifications in the experimental set-up that would be tried to this end.

The probe should be modified so that it is possible to ground it separately rather than through the mass spectrometer. This would require that a means be devised for insulating the probe from the mass spectrometer without affecting the ability to maintain a vacuum. This feature is desirable since the effect of currents flowing from the probe to ground is not known.

The possibility of bringing the plasma jet species into the mass spectrometer through a side port should be investigated. This would have the advantage that the entrant species would have only a small component of velocity parallel

to the axis of the drift tube of the mass spectrometer rather than being
directed along this axis as in the present experimental set-up. Hence if
ion leakage into the accelerating region is presently a problem, it would be
greatly reduced by introducing the ions perpendicular to the drift tube. This
method of introducing the sample was not tried originally for several reasons.
It was felt that a greater intensity could be obtained with the present system
since, in principle, all ions entering the source region would be trapped there
until pulsed out by the mass spectrometer. However, in the proposed system
only those ions which happened to be passing through the source region when
the pulse was applied would be detected. Although essentially the same probe
could be used in the proposed system, the difficulties in alignment of the
probe with the ion source are expected to be more severe. In spite of these
difficulties this system should be tried if further work with the present
system does not produce usable spectra.

Although there is no apparent reason to believe that the probe is
faulty, alternate designs should be considered. One such design would utilize
a water-cooled copper probe tip rather than uncooled stainless steel as at
present.

If, as is expected, further work shows that it is possible to identify
plasma jet species with a mass spectrometer, the characterization of the plasma
jet and its environment should be carried out as originally planned.

COMPARISON OF SPECTROMETRIC TECHNIQUES

It is evident from the comparison of the information cited within this
report, that the optical spectrometric techniques can yield information about
species present in the discharge, states of excitation, ionization, and temper-
ature of the jet. Should time-of-flight mass spectrometry be developed to the
point of ion identification, it would supplement the above information especial-
ly for those species for which optical spectroscopy is insensitive. In par-
ticular more information about the role of O_2^+ or CN^+ in the plasma jet might
be obtained.

On the other hand, optical spectroscopy has a decided advantage in
enabling information to be obtained about species in the interior of the arc
whose lifetimes are short compared with times involved in their extraction for
analysis by the mass spectrometer. The problem of sampling species in the
arc for mass spectrometer analysis is rendered more difficult by the necessity
for removing the species from the environment which produced it. In the process
of sampling, thermodynamic conditions are changed drastically such that, at
best, mass spectrometry would yield information which must be extrapolated
back to the initial conditions of the discharge; an extrapolation which would
be difficult and uncertain.

Mass spectrometry may well present an advantage however, when it is
applied to ablating systems whose ablating species may be too complex for

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optical spectroscopic identification. Polyatomic molecules in general have more complex optical spectra with ill-defined band heads and rotational structure. This characteristic of mass spectrometry may well imply that it could be more useful in revealing the actual processes of ablation in terms of the polyatomic fragments released, while optical spectroscopy may have advantages for measuring the environmental conditions for ablation, such as the temperatures and composition of the gaseous medium. In general, it is to be expected that conventional optical spectroscopy will reveal primarily the spectra of atomic and free radical species in ablating layers of carbon-aceous materials. This was, in fact, the result of our preliminary experiments on an ablating graphite body in a plasma generated in argon with a tungsten cathode and a copper anode. The spectra of C, C_2 and CN were observed by optical spectroscopy. Had more complex carbonaceous materials been used, such as plastics, polyatomic fragments may have been present, and these would probably be more readily identified by mass spectroscopy.

APPENDIX I

REPRESENTATIVE PLASMA SPECTRA

Several representative spectra are given in this section for illustrative purposes. An iron reference spectrum is included in each plate for wave length measurements. All plates in this section are stigmatic images representing the radial intensity distribution within the field-free plasma.

Plate I -- Argon Plasma

The spectrum of an argon plasma is presented in this plate. The exposure and excitation conditions were as follows:

Wavelength range -- 3900-5150 Å
Exposure time -- 1 sec (10 seconds with a 10% open reducing sector)
Electrodes -- tungsten rod cathode
            copper plate anode
Argon flow -- 30 cu ft/hr
Potential Drop -- 26 v
Current -- 380 amp.

The plasma jet was imaged horizontally across the slit of the spectrograph. Some of the more prominent Ar I and Ar II lines are indicated by the arrows. Only a very slight contamination with the electrode materials was observed in the argon plasma.

Plate II -- Air Plasma

This plate shows some of the most prominent oxygen and nitrogen lines. Two argon lines that are not apparent in the reproduction were also observed in the original plate at 8103.69 Å and 8115.31 Å.

The exposure and excitation conditions were as follows:

Wavelength range -- 7600-8800 Å
Exposure time -- 30 sec
Electrodes -- graphite rod cathode
            copper plate anode
Air flow -- 32.8 cu ft/hr
Potential Drop -- 42 v
Current -- 360 amp.

The plasma jet was imaged horizontally across the slit of the spectrograph.
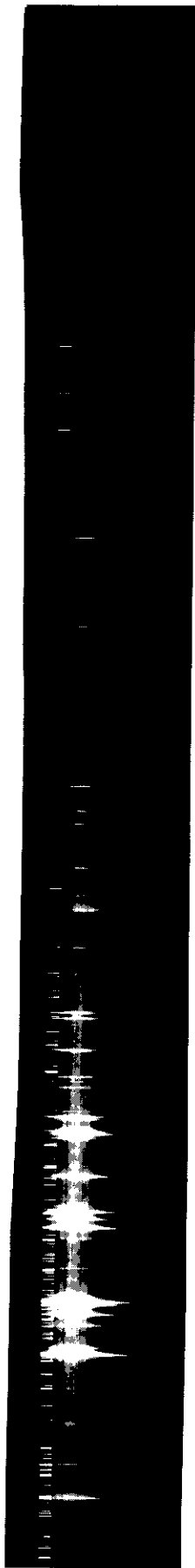
APPENDIX I (Continued)

Plate III -- Air Plasma

This plate represents some of the most intensely emitting molecular species: CN and C_2. The CN band at 4216 Å was used for the determination of rotational temperatures (see the section on temperature measurements). The exposure and excitation conditions were identical to the ones given for plate II. The wavelength range was $3900-5200$ Å. The plasma jet was imaged horizontally across the lower portion of the slit to include the boundary regions of the plasma. A considerable contamination with copper was observed in this plate.

PLATE I - ARGON PLASMA

Wavelength range: 3900-5150 Å

Exposure time: 1 sec (10 sec with a 10% open reducing sector).

Electrodes: tungsten rod cathode, copper plate anode.

— Ar II 4806. 07 Å

— Ar II 4589. 93 Å

— Ar II 4426. 01 Å
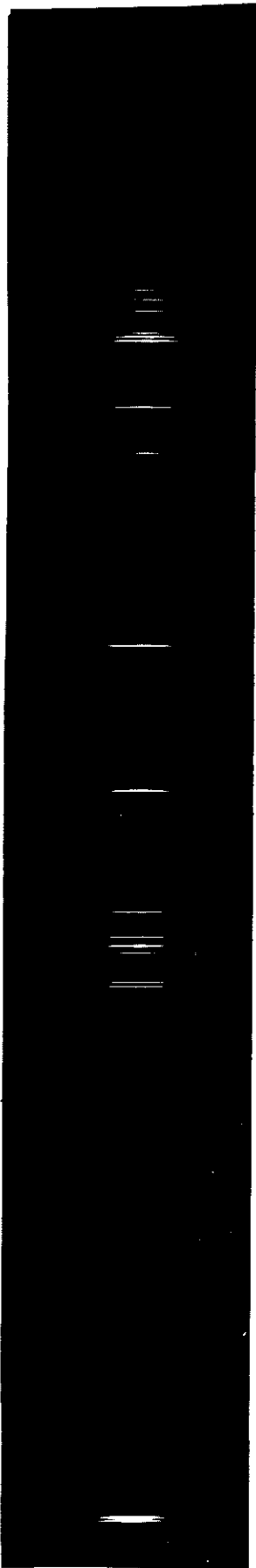
— Ar I 4333. 56 Å

— Ar I 4300. 10 Å

Ar I $\begin{cases} 4200.\ 67\ \text{Å} \\ 4191.\ 03\ \text{Å} \\ 4181.\ 88\ \text{Å} \end{cases}$

PLATE II - AIR PLASMA

Wavelength range: 7600-8800 $\overset{o}{A}$

Exposure time: 30 sec

Electrodes: graphite rod cathode, copper plate anode.

NI 8216.46 $\overset{o}{A}$

NI $\begin{cases} 8188.16 \ \overset{o}{A} \\ 8185.05 \ \overset{o}{A} \end{cases}$

Ar I 8115.31 $\overset{o}{A}$

OI $\begin{cases} 7952.18 \ \overset{o}{A} \\ 7950.82 \ \overset{o}{A} \\ 7947.58 \ \overset{o}{A} \end{cases}$

Cu I 7933.13

OI $\begin{cases} 7775.43 \ \overset{o}{A} \\ 7774.14 \ \overset{o}{A} \\ 7771.93 \ \overset{o}{A} \end{cases}$

C_2 5165.2 Å

PLATE III - AIR PLASMA

Wavelength range: 3900-5200 Å

Exposure time: 30 sec
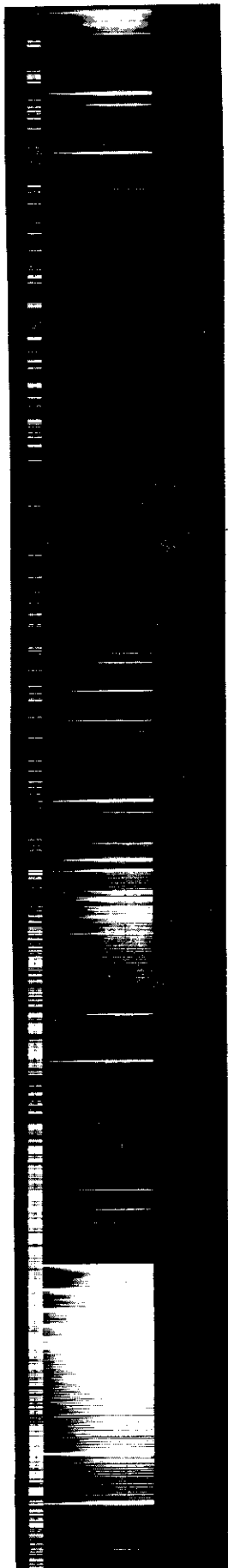
Electrodes: graphite rod cathode, copper plate anode.

CN 4553.1 Å
(bandhead)

Cu I 4253.34 Å
Cu I 4248.96 Å
CN 4216.0 Å
(bandhead)