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CONTROLLED ATMOSPHERES FOR
SPECTROCHEMICAL ANALYSIS

By C. S. Ansell

Trace Elements Investigations Report 653

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY



UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

April 18, 1957

AEC-446/7

Mr. Robert D. Nininger
Assistant Director for Exploration
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-653, "Controlled atmospheres for spectrochemical analysis," by C. S. Annell, June 1956.

We plan to submit this report for publication in Applied Spectroscopy.

Sincerely yours,

John H. Eric
for W. H. Bradley
Chief Geologist

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Chemistry

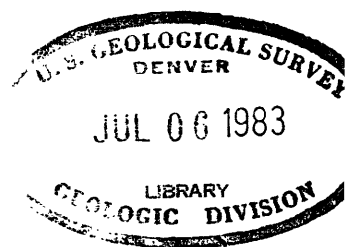
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

CONTROLLED ATMOSPHERES FOR SPECTROCHEMICAL ANALYSIS*

By

C. S. Annell

June 1956



Trace Elements Investigations Report 653

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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CONTROLLED ATMOSPHERES FOR SPECTROCHEMICAL ANALYSIS

By C. S. Annell

ABSTRACT

A review of the literature revealed many designs of electrode chambers which confined various gas atmospheres. The gases He, A, O₂, CO₂, steam, or certain mixtures thereof were preferred in certain chamber designs, samples analyzed, elements determined, and excitation requirements. However, CO₂ was found satisfactory when applied to one method of semiquantitative spectrographic analysis and used in conjunction with the final gas jet design described.

Experiments with the gas jet and CO₂ gas demonstrated that a relatively simple and reproducible method is available for the analysis of sample spectra in the intense CN band region from approximately 3500 to 4200 Å. This part of the spectrum contains many sensitive atomic and ionic excitation lines that can supplement other sensitive lines which may be obscured through interference.

INTRODUCTION

In many spectrochemical procedures the sample is burned in a carbon or graphite arc. One or both of the electrodes may be carbon or graphite and frequently the sample is mixed with carbon or graphite powder. The carbon promotes very desirable burning and excitation without introducing significant quantities of other elements which then would be eliminated from the analytical scheme. In the presence of air, the carbon arc produces intense cyanogen band spectra in the wavelength region from 3500 to 4200 Å. where many sensitive lines are made useless for analytical purposes. A list of some sensitive atom lines (U_1 , U_2 , etc.) and ion lines (V_1 , V_2 , etc.) emitted in the wavelength region from 3500 to 4200 Å is given in table 1. This report concerns a study to find the minimum experimental requirements for the suppression of the CN bands while maintaining spectral sensitivity in other regions of the spectrum. This would permit the use of a greater wavelength region for routine semiquantitative spectrochemical analyses.

Burning the arc in a nitrogen-free atmosphere has been investigated by numerous workers--not only for the purpose of eliminating the CN bands but also for producing specific excitation and burning characteristics. Paschen (1932) used He, Ne, and Ne-H₂ mixtures to excite lines of several metals for the purpose of term analyses. Steadman (1943) suppressed CN bands for the determination of potassium by using O₂ which flowed into a brass tube arranged coaxially about the sample electrode. The brass tube was open at the top and extended 5 mm above the crater tip. A small rectangular notch was cut out of the tube to permit the light to reach the spectrograph.

Table 1.--Sensitive atomic and ionic lines in the wavelength region
from 3500 to 4200 A.1/

Element	Wavelength (A)	Sensitivity	Arc intensity
Al	3961.527	U ₁	3000
	3944.032	U ₂	2000
Ca	3968.468	V ₂	500 R
	3933.666	V ₁	600 R
Cd	3610.510	--	1000
Ce	4186.599	--	80
	4165.606	--	40
	4040.762	--	70
	4012.388	--	60
Co	3529.813	--	1000 R
Dy	4167.966	--	50
	4077.974	--	150 r
	4045.983	--	150
	4000.454	--	400
Er	3906.316	--	25
	3692.652	--	20
Eu	4129.737	--	150 R
Fe	3748.264	U ₄	500
	3745.903	U ₅	150
	3745.564	U ₃	500
	3737.133	U ₂	1000 r
	3719.935	U ₁	1000 R
Ga	4172.056	U ₁	2000 R
	4032.982	U ₂	1000 R
Gd	3768.405	--	20
	3646.196	--	200 w
Hf	4093.161	--	25
Hg	4046.561	--	200
	3663.276	U ₅	500
	3650.146	U ₃	200
Ho	3891.02	--	200
	3748.17	--	60

Table 1.--Sensitive atomic and ionic lines in the wavelength region
from 3500 to 4200 Å--Continued.

Element	Wavelength (Å)	Sensitivity	Arc intensity
In	4101.773	U ₂	2000 R
Ir	3513.645	U ₂	100 h
K	4047.201	U ₄	400
	4044.140	U ₃	800
La	4123.228	V ₄	500
	4077.340	V ₃	400
	3949.106	V ₂	1000
Lu	3554.43	--	50
Mg	3838.258	U ₂	300
	3832.306	U ₃	250
	3829.350	U ₄	100 w
Mn	4034.490	U ₃	250 r
	4033.073	U ₂	400 r
	4030.755	U ₁	500 r
Mo	3902.963	U ₃	1000 R
	3864.110	U ₂	1000 R
	3798.252	U ₁	1000 R
Nb	4137.095	U ₅	100
	4123.810	U ₄	200
	4100.923	U ₃	300 w
	4079.729	U ₂	500 w
	4058.938	U ₁	1000 w
Nd	4177.321	--	15
	3951.154	--	40
Ni	3524.541	--	1000 R
	3515.054	--	1000 R
Pb	4057.820	U ₁	2000 R
	3683.471	U ₂	300
	3639.580	--	300
Pd	3634.695	U ₃	2000 R
	3609.548	--	1000 R
	3516.943	--	1000 R

Table 1.--Sensitive atomic and ionic lines in the wavelength region
from 3500 to 4200 Å--Continued.

Element	Wavelength (Å)	Sensitivity	Arc intensity
Pr	4189.518	--	100
	4179.422	--	200
	4062.817	--	150
Rh	3692.357	--	500 hd
	3657.987	--	500 W
Ru	3596.179	U ₃	30
Sc	4023.688	U ₃	100
	4020.399	U ₄	50
	3911.810	U ₁	150
	3907.476	U ₂	125
	3642.785	V ₃	60
	3630.740	V ₂	50
	3613.836	V ₁	40
Sr	4077.714	V ₁	400 r
Tb	3874.18	--	200
	3848.75	--	100
	3561.74	--	200
	3509.17	--	200
Th	4019.137	--	8
	3601.040	--	8
Ti	3653.496	U ₂	500
	3642.675	--	300
	3635.463	--	200
Tl	3775.72	U ₂	3000 R
	3519.24	U ₃	2000 R
Tm	3761.917	--	200
	3761.333	--	250
U	3672.579	--	8
	3552.172	--	8
W	4008.753	U ₃	45
	3613.790	--	10
Yb	3987.994	--	1000 R
	3694.203	--	500 R

Table 1.--Sensitive atomic and ionic lines in the wavelength region
from 3500 to 4200 Å--Continued.

Element	Wavelength (Å)	Sensitivity	Arc intensity
Y	3788.697	--	30
	3774.332	--	12
	3710.290	--	80
	3633.123	--	50
	3600.734	--	100
Zr	3601.193	U ₁	400
	3572.473	V ₄	60
	3547.682	U ₂	200
	3519.605	U ₃	100

1/ M. I. T. wavelength tables, 1939, G. R. Harrison, editor, New York,
John Wiley and Sons, Inc.

Johnson and Norman (1943) used CO_2 flowing through a Pyrex tube when determining Cl_2 and Br_2 with a high-voltage spark. This eliminated interference by air lines with the most sensitive Cl_2 and Br_2 lines.

Marks and Gardner (1947) described a water-cooled brass chamber with openings facing the spectrograph and electrode alignment target. These openings were covered with thin microscope cover glasses. This chamber was used with a 10 to 1 He to O_2 mixture flowing at approximately $3 \frac{1}{2}$ cfh.^{1/} Wiggins (1949) devised a chamber for the determination of rare earths. It consisted of a small aluminum can with electrode openings at both ends and a quartz window facing the spectrograph. A flask of boiling water generated steam that was introduced at the base of the chamber and escaped around the electrodes. Later the quartz window was eliminated when it was found that, by generating sufficient steam, air was occluded from the chamber and CN band formation was effectively suppressed. Vallee and others (1950) in a study of ashed biological specimens, described the use of a chamber that enclosed the electrode holders and contained a door for introduction of the electrodes. There was a gas inlet at the base and an outlet at the top. A lens holder was attached on the front of the chamber. Argon, He, CO_2 , and mixtures of O_2 or CO_2 with He or A were used at a flow of 60 chf.

Ellenberg and Owen (1951) developed a method of semiquantitative analysis patterned after that of Harvey (1947). They used a 4 to 1 He to O_2 mixture at a flow of 15 cfh through a fused silica chamber that had been described earlier by Owen (1951). The chamber consisted of a fused silica body with a quartz optical window at one end. A gas inlet was provided at

^{1/} Cubic feet per hour.

the base near the optical window, and an exit was provided at the other end. Electrodes projected through openings in the top and bottom of the chamber. As substitution of A for He greatly suppressed many lines and as less than 5 percent O_2 prolonged the arcing time and over 25 percent O_2 consumed the sample too rapidly, the gas mixture of 4 to 1 He to O_2 was used.

A complex gas chamber for use with arc or spark excitation was described by Hugo and others (1951). This chamber could operate at pressures greater or less than the atmosphere. The chamber could be rotated to permit horizontal or vertical alignment of the electrodes. Kingsbury and Temple (1952) described two gas chambers. The first chamber, type A, contained a brass- or nickel-plated steel body with two side arms. One side arm, facing the spectrograph, was fitted with a quartz window for transmission of the light; the other arm had a glass window for electrode alignment. The gas entered the chamber through two vents in the side arms and escaped around the electrode in the top of the chamber. The second chamber, type B, had the side arms and windows replaced by open vents. The gas entered the chamber through a hollow electrode holder in the base and escaped through the open vents. Either O_2 or CO_2 eliminated CN bands satisfactorily, but CO_2 with a flow rate of approximately 15 cfh was selected because with O_2 there was rapid consumption of the sample and electrode together with possible premature loss of sample. When type A chamber was used, the authors found complete CN band suppression.

However, as the windows of the chamber tended to become obscured with sputtered material, it was found more convenient to use type B chamber for routine analysis whenever a slightly greater background could be tolerated.

A heavy molded glass chamber that contained a sealed quartz window facing the spectrograph was described by Emery (1952). The vents for introduction of electrodes were reinforced with a brass ring to prevent chipping of the glass and were especially fitted for use with the De Gramont spark stand. The fittings were made gas tight and permitted dismantling and reassembling in 3 to 4 minutes during which time the sample was changed and the counter electrode cleaned. This apparatus was designed for quantitative work and could also be used with gases at reduced pressures.

Thiers (1953) gave an excellent review of controlled atmosphere work with the d-c arc. In addition, he investigated the possibilities of stabilizing the arc by using a direct flow of the gas around the electrodes. This was accomplished by using a cylindrical chamber with electrodes aligned on its axis and directing CO₂ into the chamber through four jets arranged horizontally and tangentially to the cylinder. No conclusive results concerning the advantages of a directed flow of gas were reached, however.

Schöntag (1955) used cylindrical quartz chambers for his work with various controlled atmospheres. The cylinder is closed at one end and is capped by a loose-fitting circular quartz cover. The electrodes are inserted in the chamber through holes in the base and cover. In one chamber, a gas inlet was made tangential to the base of the cylinder. The other chamber contained a gas inlet directed radially into its lower side.

The previous work with controlled atmospheres was carried out, for the most part, in chambers that enclosed both electrodes. Some apparatus for containing the special atmospheres (Steadman, 1943; Wiggins, 1949; and Kingsbury and Temple, 1952) had open vents for passage of light from the source to the spectrograph, eliminating the necessity for cleaning and caring for an optical window. This type of chamber for controlled atmosphere work seemed desirable for routine semiquantitative analyses where a large number of samples having various compositions are handled in relatively short periods of time.

ACKNOWLEDGMENTS

The author expresses appreciation to his associates of the U. S. Geological Survey for their help and advice, and especially to A. W. Helz who designed the three gas jets used in this work. He devoted much time assisting and guiding the performance of experiments and offered valuable advice and criticism during the preparation of this report. This work is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

EXPERIMENTAL

Preliminary experiments

A preliminary investigation into the use of controlled atmospheres was undertaken in the Geological Survey laboratory by J. N. Stich. Specifically, the problem concerned the determination of low concentrations of thorium in samples containing major amounts of uranium. Numerous tests were made with

an Owen-type chamber using O_2 , CO_2 , $He-O_2$, and $He-CO_2$ atmospheres. No conclusive results were reported.

An article by Stallwood (1954) concerning the use of an air jet for minimizing selective volatilization and matrix effects in quantitative spectrochemical analyses suggested an application with controlled atmospheres. An assembly diagram of the air jet and insulated holder was obtained from F. A. Lang (Spectrographic Laboratory, Division of Mineral Dressing and Process Metallurgy, Department of Mines and Technical Surveys, Ottawa, Ontario), and a modified form of this jet was made of brass (fig. 1).

The use of pure He, $He-O_2$ mixtures, and CO_2 at various flow rates indicated on the spectrograms that the CN background would be too heavy for general analytical work. The source of the N_2 was probably an impurity in the CO_2 ; also air had entered the gas stream due to turbulence.

A second gas jet was designed to lessen this amount of turbulence. It consisted of a cylindrical tube with a gas inlet near the base and a spring-clip electrode holder coaxially attached to the base. All these components were made of brass. The spectrograms made when using this jet indicated a great diminution in CN background. The main objection to this jet was difficulty in inserting electrodes in the spring-clip holder.

Gas jet III

A third gas jet (fig. 2) was designed which remedied the objection to the second jet. It consists of two parts: a brass base containing a spring-clip electrode holder made from a mild steel. This does not lose its resilience because of heat fatigue as the brass holder did. A cylindrical brass chamber with a tubular opening in its base that can accommodate the

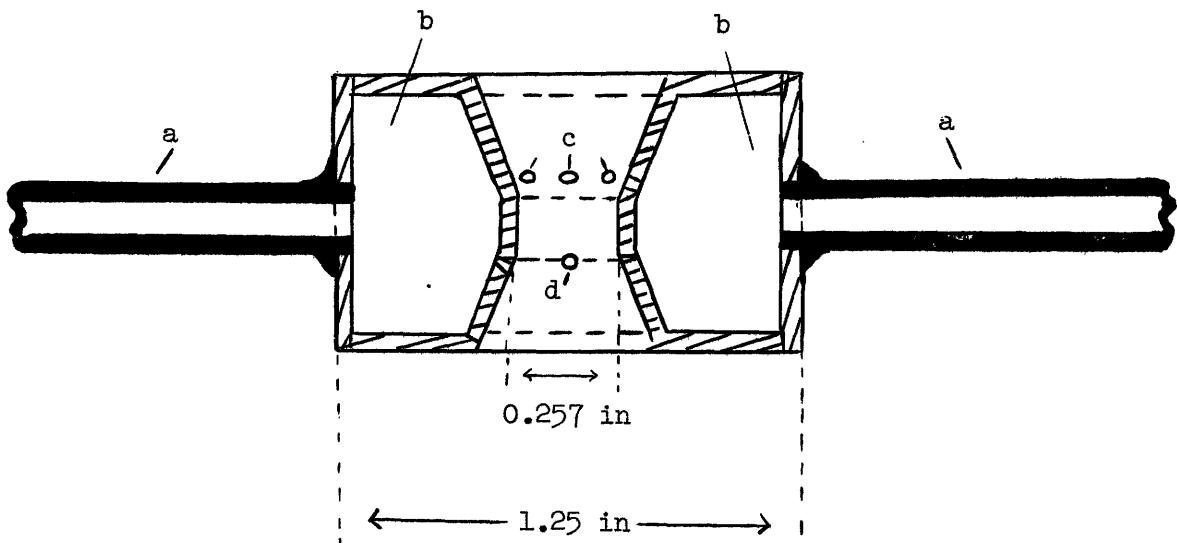


Figure 1.--Gas jet I.

- a) Two 3/16-inch gas inlets.
- b) Hollow cylindrical chamber that encircles sample electrode.
- c) Eight 0.04-inch gas outlets directed upward.
- d) Four 0.04-inch gas outlets directed downward.

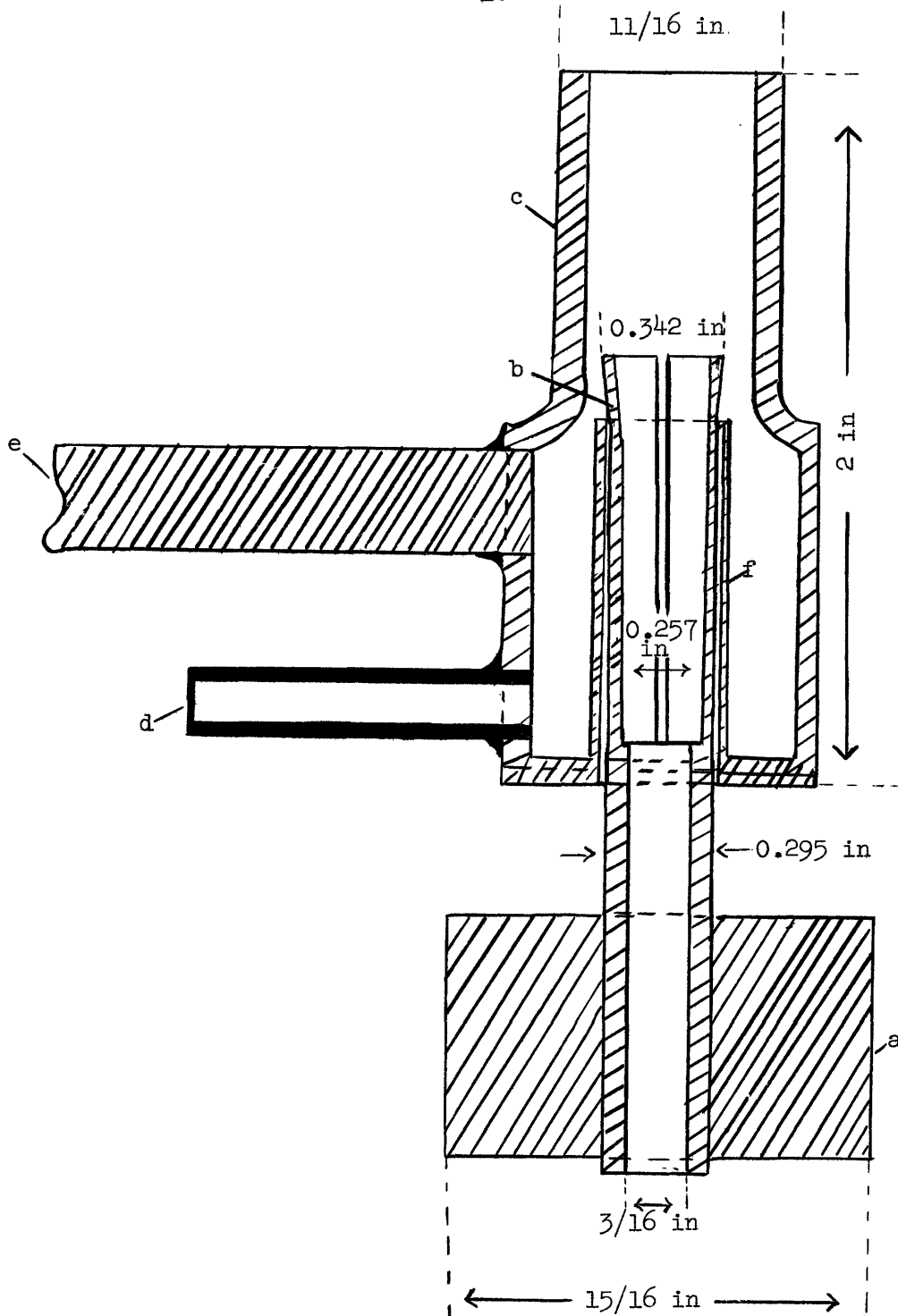


Figure 2.--Gas jet III.

- a) Cylindrical brass base.
- b) Steel electrode holder, flared at top and fastened to brass base with set screw.
- c) Brass cylindrical body, open at top.
- d) Gas inlet.
- e) Brass rod attached to arc stand. A wire braid is fastened between (a) and (e) to insure good electrical contact.
- f) Brass sleeve for inserting electrode holder.

electrode holder. The large brass base supplies the necessary force to hold the electrode in the spring clips. This gas jet combines simplicity of design and satisfactory performance.

Controlled atmosphere tests with gas jet III

Preliminary tests with controlled atmospheres were made with 10-mg silicate rock samples that were mixed with 20 mg of pure graphite and placed in a 1/4-inch carbon electrode. The dimensions of the anode cup and counter electrode have been described by Waring and Annell (1953). A d-c arc source of 9 to 10 amp was used with the arcing periods varying from 60 to 120 seconds depending upon the rates of sample consumption in the different atmospheres.

Further tests were made with He, O₂, He-O₂ mixtures, and CO₂ atmospheres. The d-c arc in a pure He atmosphere with a flow of 26 cfh prolonged the arcing time relative to an air atmosphere and produced an extremely weak spectrum with very little sample consumption. The use of pure O₂ as the arcing atmosphere at a flow of 32 cfh engendered such rapid sample consumption that possible sample loss might occur. However, further tests at different current strengths might be warranted because the line intensities for the O₂ arcings were much more intense than the corresponding line intensities produced in pure He or a mixture of 26 parts He and 4 parts O₂.

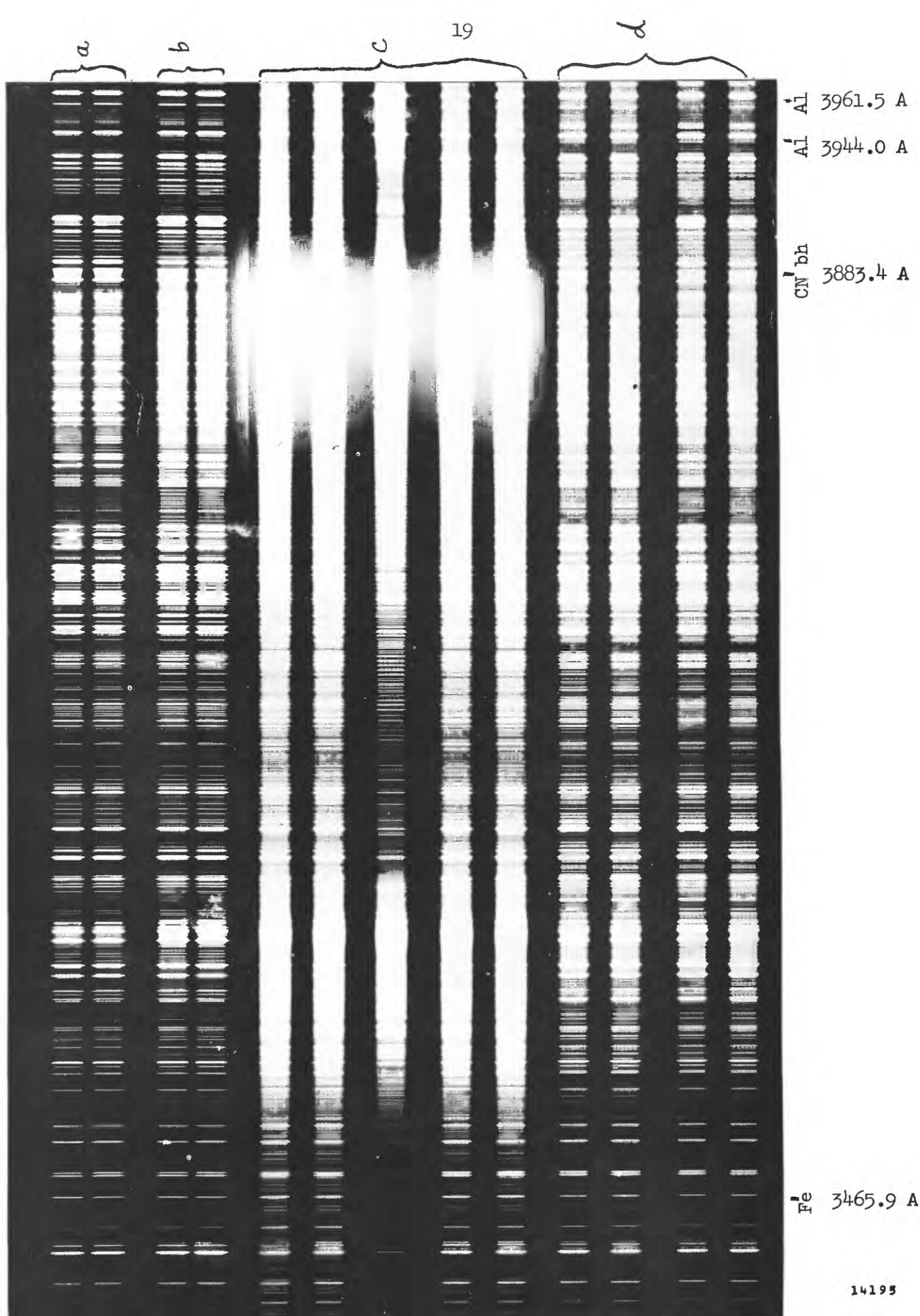
Mixtures of He and O₂ were used at He flow rates of 13 and 26 cfh and an O₂ flow rate of 4 cfh (fig. 3a,b). The spectra produced in these two atmospheres were considerably enhanced compared to the arcing in pure He and were accompanied by faster sample consumption. Suppression of CN bands was satisfactory for a semiquantitative analysis when using a mixed flow of 26 cfh He and 4 cfh O₂.

Figure 3.---Spectra in wavelength region from 3525 to 4000 A. Silicate rock samples arced to completion in various gas atmospheres with gas jet III, using 25 percent light transmission and SA-1 emulsion.

a)	Arcing atmosphere:	26 cfh He and 4 cfh O ₂	Exposure:	120 seconds
b)	Arcing atmosphere:	13 cfh He and 4 cfh O ₂	Exposure:	120 seconds
c)	Arcing atmosphere:	3 cfh CO ₂	Exposure:	120 seconds
d)	Arcing atmosphere:	24 cfh CO ₂	Exposure:	90 seconds

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Photograph by Malcolm Ross, U. S. Geological Survey.



The use of CO_2 as the ambient atmosphere was tested using flows of 3 cfh and 24 cfh (fig. 3c,d). The slower flow failed to exclude the surrounding air and the CN background was prohibitive. However, the faster flow of CO_2 satisfactorily suppressed CN formation and resulted in greater line intensities than were realized with either He or He- O_2 mixtures.

In examining the possible source of N_2 responsible for the residual CN emission, moving plate spectrograms were made while arcing both pure graphite and regular carbon electrodes, with and without samples. No attenuation of CN bands was noted during prolonged arcings using gas jet III with either CO_2 or various He- O_2 mixtures. To determine whether the N_2 came from admixed air or was an impurity in the gases used for the arcing atmospheres, the experiments were repeated using a fused silica gas chamber patterned after one designed by Owen (1951). The CN bands were not detected when an atmosphere of 26 cfh He and 4 cfh O_2 was used, but they were noted when 24 cfh CO_2 was used. On the basis of these tests it was concluded that there was a certain amount of N_2 impurity in the CO_2 gas as well as some air entering the arc stream when the gas jet was used. When duplicate exposures were made using gas jet III and different He- O_2 mixtures, the CN band emission decreased as greater proportions of O_2 were mixed with a constant flow of He. The CN bands were not apparent when pure O_2 was used.

On the basis of the above tests, it was decided that gas jet III offered greater simplicity of operation than the fused silica gas chamber without the necessity for periodic cleaning of any optical window. These advantages compensated for the increased CN-band emission which caused no excessive interference for the analytical method used.

Reproducibility tests with gas jet III

A series of tests were designed to determine the reproducibility of spectral line intensities when various samples were arced in still air, 30 cfh flowing air, 24 cfh CO₂, and 26 cfh He plus 4 cfh O₂. The arcing and exposure conditions are given below:

Excitation: d-c, 9 to 10 amp
 Electrode gap: 5 to 6 mm, monitored during arcing
 Spectrograph: 3-meter grating, modified Eagle mounting
 Wavelength: 2780 to 3480 A, second order
 Transmission: 4-step rotating sector (25, 12.5, 6.25, 3.13 percent).
 Grating masked 50 percent in some measurements.
 Slit: 25 microns
 Optics: Arc image focused on grating
 Emulsion: SA-1 (Eastman)
 Development: 4 min at $18^{\circ} \pm 1/2^{\circ}$ C, D-19 (Eastman)

To make comparative measurements of line densities it was necessary to mask 50 percent of the grating when samples were arced in air or CO₂. The spectral intensities obtained from identical exposures in the He-O₂ atmospheres were considerably weaker.

Three different rock samples selected for these tests had matrices representing a large part of the samples submitted to this laboratory for analysis: National Bureau of Standards standard samples no. 120 (phosphate rock) and no. 78 (burnt refractory 70 percent Al₂O₃), and the granite standard G-1 (Fairbairn and others, 1951).

The lines selected for density measurements originated in both atomic and ionic states and included elements with a wide volatility range. A list of lines used in the corresponding sample spectra along with any pertinent excitation and ionization potentials (Moore, 1945, 1949, 1950, 1952a,b) are presented in table 2. The average relative logarithmic values of the intensity obtained from triplicate spectra for the lines indicated are listed in table 3. The average difference from these values are recorded to obtain an approximation of the line reproducibility. The average logarithmic I values of the respective lines in the corresponding sample spectra are listed according to the arcing environment. A more concise arrangement that relates the order of spectral line intensity with respect to the arcing atmosphere is shown in table 4.

The ionic lines usually acquired greater intensities in He-O₂. However, CO₂ was also effective, being better generally than air. Flowing air was better for ionic excitation than still air, whereas the opposite condition prevailed in atomic excitation.

On the basis of all tests made with He-O₂, CO₂, flowing air, and still air, it was decided that CO₂ would most efficaciously suppress CN-band formation and permit a high degree of reproducibility. In addition, comparatively good line sensitivities are obtainable for both atomic and ionic spectra with respect to those obtained in air. An additional variable, engendered by possible changes in the ratio of gases mixed in a proportioner, would be eliminated.

Table 2.--Spectral lines used for samples and excitation and ionization potentials of the lines.

Samples	Lines (A)	Excitation potential (electron volts)	Ionization potential (electron volts)
NBS 78	Al II 2816.2	7.39-11.77	5.96
G-1	Al I 3064.3	3.59- 7.62	--
NBS 120	Fe 2957.4	0.11- 4.28	--
NBS 78	Fe 2999.5	0.86- 4.97	--
NBS 78, NBS 120	Fe 3100.67	0.95- 4.93	--
G-1	Fe 3153.2	2.44- 6.35	--
G-1	Fe 3200.5	2.46- 6.31	--
G-1, NBS 78, NBS 120	Mg 2776.9	2.7 - 7.14	--
NBS 120	Mn II 2949.2	1.17- 5.35	7.40
G-1, NBS 78, NBS 120	Pb 2833.1	0.0 - 4.4	--
G-1, NBS 78, NBS 120	Si 2970.3	0.78- 4.93	--
NBS 78	Ti II 3046.7	1.16- 5.21	6.81
NBS 120	Ti II 3088.03	0.05- 4.05	6.81
G-1, NBS 78	Zr II 3273.0	0.16- 3.93	6.92

Table 3.--Average relative logarithmic I values of the intensities in various arc atmospheres and average differences from these values.

Sample	Lines (A)	He + O ₂		CO ₂		Flowing air		Still air	
		k log I	Diff.	k log I	Diff.	k log I	Diff.	k log I	Diff.
NBS 78	Al II 2816.2	4.85	0.48	3.07	0.003	2.09	0.05	1.88	0.08
G-1	Al I 3064.3	0.32	0.05	2.39	0.02	1.68	0.07	1.70	0.08
NBS 120	Fe 2957.4	1.72	0.02	2.88	0.07	3.25	0.01	3.59	0.03
NBS 78	Fe 2999.5	1.30	0.05	2.38	0.06	3.39	0.02	3.61	0.05
NBS 78	Fe 3100.67	1.15	0.05	2.00	0.04	3.22	0.06	3.52	0.10
NBS 120	Fe 3100.67	1.55	0.03	3.05	0.06	3.34	0.03	3.63	0.06
G-1	Fe 3153.2	0.90	0.03	2.86	0.03	2.30	0.07	2.27	0.04
G-1	Fe 3200.5	1.24	0.01	3.06	0.05	2.66	0.08	2.66	0.03
G-1	Mg 2776.9	0.78	0.003	3.04	0.06	2.63	0.06	2.79	0.04
NBS 78	Mg 2776.9	0.59	0.01	2.37	0.04	3.20	0.02	3.57	0.07
NBS 120	Mg 2776.9	0.92	0.07	3.65	0.06	3.58	0.07	3.86	0.02
NBS 120	Mn II 2949.2	2.54	0.06	3.16	0.03	2.63	0.01	2.32	0.04
G-1	Pb 2833.1	0.65	0.02	2.20	0.03	1.78	0.07	2.22	0.07
NBS 78	Pb 2833.1	0.95	0.01	2.51	0.02	2.88	0.04	3.20	0.03
NBS 120	Pb 2833.1	1.46	0.02	1.77	0.03	1.56	0.09	1.74	0.06
G-1	Si 2970.3	2.16	0.06	---	---	2.97	0.04	2.71	0.03
NBS 78	Si 2970.3	1.79	0.04	2.54	0.03	3.39	0.09	3.62	0.12
NBS 120	Si 2970.3	0.54	0.02	2.33	0.01	2.20	0.04	2.33	0.02
NBS 78	Ti II 3046.7	3.50	0.22	3.70	0.04	3.15	0.15	2.87	0.19
NBS 120	Ti II 3088.03	2.19	0.06	3.34	0.08	3.14	0.02	3.01	0.11
G-1	Zr II 3273.0	1.96	0.06	1.44	0.02	1.71	0.12	1.74	0.12
NBS 78	Zr II 3273.0	2.30	0.07	0.91	0.03	1.90	0.36	2.12	0.39

Table 4.--Order of intensity of spectral lines with respect to arcing environment.

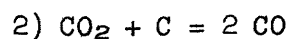
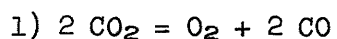
Sample	Line		Order of intensity and atmosphere <u>1/</u>			
			1	2	3	4
G-1	Mg	2776.9	CO ₂	SA	FA	He-O ₂
	Pb	2833.1	SA	CO ₂	FA	He-O ₂
	Al	3064.3	CO ₂	SA	FA	He-O ₂
	Fe	3153.2	CO ₂	FA	SA	He-O ₂
	Fe	3200.5	CO ₂	SA	FA	He-O ₂
	Si	2970.3	CO ₂	He-O ₂	FA	SA
	Zr II	3273.0	He-O ₂	SA	FA	CO ₂
NBS 78	Mg	2776.9	SA	FA	CO ₂	He-O ₂
	Pb	2833.1	SA	FA	CO ₂	He-O ₂
	Fe	2999.5	SA	FA	CO ₂	He-O ₂
	Fe	3100.67	SA	FA	He-O ₂	CO ₂
	Si	2970.3	SA	FA	He-O ₂	CO ₂
	Al II	2816.2	He-O ₂	CO ₂	FA	SA
	Ti II	3046.7	He-O ₂	CO ₂	FA	SA
	Zr II	3273.0	He-O ₂	SA	FA	CO ₂
NBS 120	Mg	2776.9	SA	CO ₂	FA	He-O ₂
	Pb	2833.1	CO ₂	SA	FA	He-O ₂
	Fe	2957.4	SA	FA	CO ₂	He-O ₂
	Fe	3100.67	SA	FA	CO ₂	He-O ₂
	Si	2970.3	CO ₂	SA	FA	He-O ₂
	Ti II	3088.03	CO ₂	He-O ₂	FA	SA
	Mn II	2949.2	He-O ₂	CO ₂	FA	SA

1/ CO₂, 24 cfh; SA, still air; FA, flowing air, 30 cfh;

He-O₂, He, 26 cfh, O₂ 4 cfh.

THE CARBON ARC IN A CO₂ ATMOSPHERE

The use of CO₂ as the ambient gas in a d-c arc provides a source of O₂ to the sample electrode. In this respect the reactions occurring between the arc environment and sample electrode are similar for CO₂ and air. The essential reactions involving CO₂ when it flows past carbon electrodes in a d-c arc can be depicted as follows (Ephraim, 1947):



The kinetics and mechanisms of reaction (2) have been investigated by numerous workers (Gulbrandsen and Andrew, 1952). However, their experiments were conducted in a temperature range of 500° C to 900° C, which is considerably lower than the temperatures of several thousand degrees centigrade prevailing in the d-c carbon arc in air (Ahrens, 1950).

Equilibrium constants (K) for the above reactions have been determined using experimental data and statistical calculations of thermodynamic functions (Wagman and others, 1945). Although equilibrium conditions are not attained in the d-c arc, the free energy values indicate the tendency of both reactions to favor decomposition of CO₂ with increasing temperatures:

Reaction	T(°K)	ΔF^0 (cal/mole)	K
1	1000	46,668	6.321×10^{-11}
	1500	36,338	5.076×10^{-6}
	3000	6,960	3.16×10^{-1}
2	1000	- 1,275	1.900
	1500	- 22,034	1.623×10^3

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