



A contained arc column for emission spectroscopy
by Christopher John Evoniuk

A thesis submitted in partial fulfillment of the requirements for the degree. of MASTER OF SCIENCE
in Chemistry

Montana State University

© Copyright by Christopher John Evoniuk (1976)

Abstract:

Several designs were tested for containing an arc plasma column. Optimum geometries were determined for the cathode, anode and plasma tubes. The effect of flow rates on plasma parameters was investigated. Peak profiles and retention times for Pb, Cu, B, and Zn are reported.

Increased stability of the arc discharge was accomplished by containing the electrodes and plasma tubes inside an airtight, thermally insulated chamber. Tubular graphite electrodes enabled the axial region of the discharge to be used as the spectral volume source. Diffusion losses were limited to the area between the anode and entrance to the plasma tube.

The success of this work in containing an arc discharge suggests that further investigation be carried out. A graphite housing should be constructed so that all of the sample introduced inside of the housing must pass through the plasma tube. This would effectively reduce diffusion losses and maximize detection capability.

STATEMENT OF PERMISSION TO COPY

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication on this thesis for financial gain shall not be allowed without my written permission.

Signature Christopher John Cronick

Date February 6, 1976

A CONTAINED ARC COLUMN FOR
EMISSION SPECTROSCOPY

by

CHRISTOPHER JOHN EVONIUK

A thesis submitted in partial fulfillment
of the requirements for the degree.

of

MASTER OF SCIENCE

in

Chemistry

Approved:

Ray Woodruff
Chairman, Examining Committee

E. W. Gnacker
Head, Major Department

Henry L. Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1976

ACKNOWLEDGEMENTS

The author would like to especially thank Dr. Ray Woodriff, who served as advisor, for his assistance and guidance throughout the project. Special thanks is extended to the author's wife, Marian, for her invaluable help in running samples and typing this thesis.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
INTRODUCTION	1
THEORETICAL CONSIDERATION	5
Arc Length and Equilibrium	5
Factors Governing Line Intensity	6
Temperature Effects on Intensity	7
Spatial Temperature Changes	9
Self Absorption	9
Summary of Design Criteria	10
EXPERIMENTAL	12
Instrumentation	12
RESULTS AND DISCUSSION	18
Design Criteria	18
Plasma Properties and Sample Effects	21
CONCLUSIONS	34
RECOMMENDATIONS	35
LITERATURE CITED	37

LIST OF TABLES

Table	Page
I. Effect of Argon Flow on the Intensity of the 360 Nanometer Line of Argon	19
II. Comparison of Retention Time and Peak Area for Lead Samples	30
III. Effect of Rate of Cup Heating on Peak Heights	32

LIST OF FIGURES

Figure	Page
1. DESIGN I	13
2. DESIGN II	15
3. DESIGN III	17
4. ANODE DESIGNS	20
5. PLASMA HOLDER AND PLASMA TUBES	22
6. ENCLOSED DESIGN	23
7. CATHODE DESIGNS	23
8. EFFECT OF FLOW ON PLASMA DIAMETER	24
9. EFFECT OF CATHODE SPACING ON VOLTAGE DROP AT A FLOW RATE OF 15 ML/SEC.....	26
10. EFFECT OF FLOW RATE ON VOLTAGE DROP AND CURRENT AT A CATHODE SPACING OF 0.25 INCHES	27
11. EFFECT OF FLOW ON VOLTAGE DROP AND CURRENT AT A CATHODE SPACING OF 1 INCH	28
12. CHART RECORDING FOR Pb SIGNAL AT 283.3 NANOMETERS	29
13. PEAK PROFILES FOR BORON, COPPER AND ZINC.....	31
14. STANDARD CURVE FOR COPPER	33
15. SUGGESTED GRAPHITE HOUSINGS	36

ABSTRACT

Several designs were tested for containing an arc plasma column. Optimum geometries were determined for the cathode, anode and plasma tubes. The effect of flow rates on plasma parameters was investigated. Peak profiles and retention times for Pb, Cu, B, and Zn are reported.

Increased stability of the arc discharge was accomplished by containing the electrodes and plasma tubes inside an airtight, thermally insulated chamber. Tubular graphite electrodes enabled the axial region of the discharge to be used as the spectral volume source. Diffusion losses were limited to the area between the anode and entrance to the plasma tube.

The success of this work in containing an arc discharge suggests that further investigation be carried out. A graphite housing should be constructed so that all of the sample introduced inside of the housing must pass through the plasma tube. This would effectively reduce diffusion losses and maximize detection capability.

INTRODUCTION

Spectral chemical analysis using emission spectroscopy is a well known technique and has been used since the nineteenth century. The existence of cesium was established in 1861 by Bunsen and Kirchoff using a simple spectroscope and Bunsen burner. Since then the Bunsen burner has been replaced by more sophisticated excitation sources.

Emission analysis is based on the principle that if an atom is excited to a high energy state, emission of light will occur when the atom returns to its original state. If a sample is vaporized and the vapor sufficiently heated so excitation occurs, the wavelengths of light emitted are characteristic of the elements in the vapor, and the spectral line intensities are proportional to the concentrations of the elements in the vapor.

Samples may be excited by hot gaseous flames, electric sparks, and electric arcs. The electric arc differs from the electric spark in that the former is a continuous electrical discharge and the latter is a series of electrical discharges i.e. sparks. An electric arc is initiated between the gap separating two electrodes which are connected to an electrical power supply. After electrical breakdown of the gap occurs, a current of electrons flows from the negative to the positive electrode. These electrons ionize and heat the vapor between the gap. The hot ionized gaseous material between the gap is referred to as a plasma.

Convective currents of gas in a horizontal arc cause the plasma (or arc discharge) to bend upwards in an arch-like fashion. The term "arc" originated from this observation. In a vertical arc, the convective currents cause gaseous material to flow upward from the lower electrode.

The capability of doing multielement analysis is the major factor which makes emission spectroscopy a valuable analytical method. Characteristics of analytical emission spectroscopy utilizing electric arcs are high sensitivity and poor reproducibility. High sensitivity is inherent in the excitation process since the high temperature produces a large population of excited atoms. Poor reproducibility is caused by erratic movement of the plasma between the electrodes and selective volatilization of the sample. Movement of the plasma creates a fluctuating light source and selective volatilization causes a changing composition of the plasma which is not representative of the sample composition.

Movement of the plasma is caused by convective air currents and variations of the electrical contact point of the plasma on the surface of the electrodes. The following methods have been used to limit these two types of movement:

- 1) Containing the plasma inside of a rotating tube (18, 20).
- 2) Containing the plasma inside of a tube with an air stream directed tangent to the plasma column (27, 31, 32).

- 3) Applying magnetic fields to the electrodes which cause the plasma contact point to rotate around in a circle on the electrode surface at a fixed frequency (17, 23, 33, 34, 36).
- 4) Using carbon as the upper electrode instead of graphite, since the tendency for the arc to wander is less on carbon (1, 6).
- 5) Electrodes having a core of material with greater electrical conductivity than graphite limits the contact point to the surface of the core material (21).
- 6) Tantalum-tipped graphite electrodes in which the contact point is on the molten tantalum surface.
- 7) Stallwood jet, in which an axial gas stream emerges from a narrow opening concentric with the lower electrode stabilizes the position of the arc (15, 24, 25, 30).

The most popular of these is the axial gas flow stabilization system.

Sample volatilization and rate of sample entry have been investigated and the following techniques are found to be useful:

- 1) Having powdered samples continually sifted into the plasma (26, 28).
- 2) Having the sample deposited on a moving tape to continually renew the original surface (7, 37).
- 3) Injecting samples in the form of aerosols and sprays for constant composition (3, 38).
- 4) Adding a large quantity of material that is easily ionized

and volatilized to a solid sample. The plasma composition is then predominately determined by the added material (2, 4, 8, 9, 10, 13).

The volatilization rate will determine the sample introduction rate. Only a portion of this vaporized material enters the plasma, while the rest is lost by diffusion. A technique devised by Vukanovic, Simiu and Vukanovic (35) to reduce diffusion losses and improve detection limits involves the placement of a short graphite cylinder around the arc gap. Radial diffusion rates were reduced as were plasma temperature gradients.

By controlling diffusion losses and plasma movement, one can improve the detection limits and reproducibility of samples analysed by arc emission. The purpose of this study was to test several apparatus designs to limit plasma movement by containing the arc discharge inside of a tube.

THEORETICAL CONSIDERATIONS

Arc Length and Equilibrium

The total voltage drop across an arc is given by the equation (12, 14, 22):

$$V = EL + V_a + V_c$$

where

$E = dV/dL$, field strength

L = length of arc discharge where the voltage drop is linear.

V_a = anode voltage drop or fall

V_c = cathode voltage drop or fall

Cathode and anode falls are strongly dependent on gas vapor composition. Voltage drops are reduced as extra charge carriers enter the plasma, i.e., as sample evaporates. The anode is heated when electrons impinge upon it. A reduction in the anode voltage drop will cause a reduction in the evaporation rate of material on the anode.

Excitation of gaseous material in the column is due to thermal processes. Local thermal equilibrium in the arc exists when the field strength is approximately 4 volts/mm. (12). For a total voltage drop of 50 V, and anode and cathode drops totalling 26 V, the arc gap should be greater than $(50 - 26)/4 = 6$ mm. Hence, local thermal equilibrium should exist in a column longer than 6 mm.

Factors Governing Line Intensity

Emission originates from a transition of an electron from a higher to a lower energy state. The energy of a light photon is expressed by the formula (5, 6, 12):

$$h\nu = E_q - E_p$$

where

ν = frequency

h = Planck's constant

E_q = energy of state q

E_p = energy of state p

The rate of atoms leaving state q per second by spontaneous emission $((dN_q/dt)_{\text{emission}})$ is proportional to the number of atoms in state q .

$$(dN_q/dt)_{\text{emission}} = A_{qp} N_q$$

where

A_{qp} = transition probability or Einstein's coefficient.

N_q = concentration of atoms per unit volume in state q .

The radiant flux per unit volume of a source is given by:

$$I_{qp} = A_{qp} N_q h\nu_{qp}$$

Dividing I_{qp} by 4π gives the total flux J_{qp} per unit volume, per unit solid angle. This quantity is termed the "spectral emittance", J_{qp} ,

$$J_{qp} = (A_{qp} N_q h\nu_{qp})/4\pi$$

N_q usually varies within the light source. Therefore, J_{qp} is a function of the spatial coordinate X , Y , and Z . The integral of J_{qp} over the portion of the source within the solid angle ω subtended by the effective opening of the spectrograph is termed the spectral intensity (Φ_{qp}):

$$\Phi_{qp} = \iiint J_{qp}(X,Y,Z) dX dY dZ d\omega$$

In utilizing this equation to maximize the intensity from a light source, the investigator should maximize N_q in the volume observed. An ideal volume would correspond to a flat rectangular area the size of the slit, in which all the sample is concentrated.

Temperature Effects on Intensity

Concentration of a substance in a gas phase is given approximately by the gas equation:

$$N_i = P_i/RT$$

where

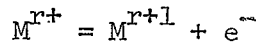
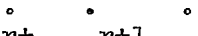
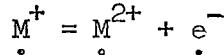
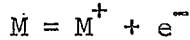
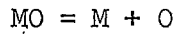
N_i = concentration of i^{th} species

P_i = partial pressure of i^{th} species

R = gas constant

T = temperature ($^{\circ}\text{K}$)

The concentration N_i is also dependent upon dissociation and ionization equilibria which are dependent upon temperature (6, 12). The following equilibria exist in a plasma:



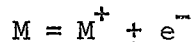
where

MO = metal oxide

M = metal

$M^+, M^{2+}, \dots, M^{r+1}$ = ionized species

For a plasma in an argon atmosphere the metal oxide equilibrium can be neglected due to the absence of oxygen. Also, in the temperature range of the graphite arc, the formation of doubly or higher ionized species can be ignored. Therefore the equilibrium equations reduce to:



From Boltzmann's distribution law, the concentration N_q is given by:

$$N_q = (N_a g_q / Z_a) 10^{-(5040 V_q) / T}$$

where

$$N_a = (1 - \alpha)N$$

g_q = statistical weight of q state

Z_a = partition function

V_q = excitation energy in eV

T = temperature ($^{\circ}$ K)

N = total concentration of ionized and neutral atoms

α = degree of ionization

The spectral emittance equation is now expressed by:

$$J_{qp} = (1/4\pi) g_q A_{qp} h\nu_{qp} N(1-\alpha)(1/Z_a) 10^{-5040} v_q/T$$

The temperature at which the spectral emittance will be highest, can be calculated by taking the partial derivative of J_{qp} with respect to T at constant N .

Spatial Temperature Changes

The spectral intensity which reaches the slit opening is (6, 12):

$$\Phi_{qp} = \Delta X \Delta Z \omega \int J_{qp}(X, Y, Z) dY$$

where

$\Delta X \Delta Z$ = cross-sectional area of observation
projected onto slit

ω = solid angle from source to slit

Y = depth of source

In most cases, temperature and concentration will vary along the depth of the source. This is especially true of vertical arcs. One would expect a fairly constant temperature profile along the axis in a horizontal arc in which approximate radial symmetry is imposed by a cylindrical housing.

Self Absorption

Radiation emitted from the interior of the plasma can be absorbed by ground state atoms in the cooler fringes of the plasma. The relation-

ship between the intensity of the radiation before and after absorption is given by:

$$I_v = I_{v0} e^{-k_v l}$$

where

I_v = intensity after absorption

I_{v0} = intensity before absorption

k_v = absorption coefficient

l = absorption path length

To maximize I_v , the depth of the absorbing medium must be minimized (assuming a constant absorption coefficient). For the geometry under consideration in this thesis, a horizontal cylindrical arc viewed along the axis, a non-absorbing gas flowing against the terminal point of the arc can be used to decrease the depth of the absorbing medium.

Summary of Design Criteria

From the previous discussion of the factors affecting intensity, the following design criteria should be implemented for maximum intensity of a transition (q-p):

- 1) Field strength less than 4 V/mm.
- 2) Cross-sectional area of source to approximate that of slit opening.
- 3) Minimum plasma movement.
- 4) Temperature corresponding to maximum concentration of excited atoms of the type with the desired transition level.

- 5) Longitudinal arc for uniform temperature distribution along observation path.
- 6) Flushing gas to minimize self-absorption.
- 7) Uniform sample volatilization.
- 8) Minimum temperature fluctuation.

EXPERIMENTAL

Instrumentation

Spectrophotometer

Beckman Ratio Recording spectrophotometer; Model 1414.

Power Supplies

Electro Matic Control Model PLK; output 130 V.D.C.; 5-15 Amps.

Voltage Monitor

Weston Analyzer Model 980 Mark II.

Recorder

Honeywell Electronic 19.

Optical Pyrometer

Pyro Optical Pyrometer Model 87C.

Arc Housings

Model I

Figure 1 is a schematic drawing of the first model constructed. Its purpose was for preliminary experimentation and visual observation. Components consisted of a 2.5 inch diameter pyrex tube, 4 inches long, fitted with a small graphite cylinder. End plates were made from asbestos sheets and perforated so two pyrex tubes could be inserted. The center of the graphite cylinder was fitted with a quartz tube and a graphite tube for testing. Electrodes were fashioned from tungsten wire and inserted by perforating the tygon tubing. A stream of argon

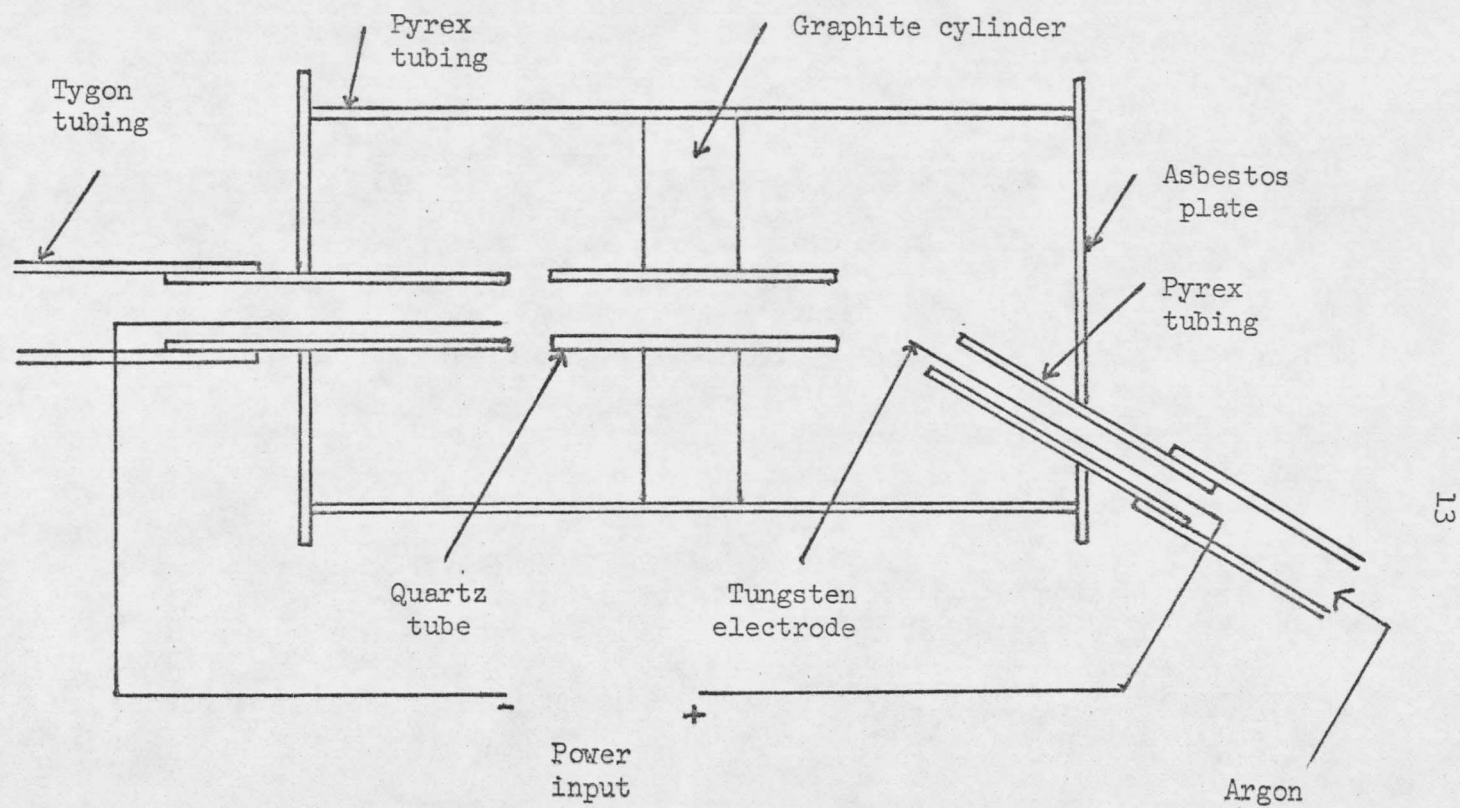


FIGURE 1. DESIGN I

gas was connected to right end of the housing. The argon stream was excited on passing through the center of the graphite cylinder, and then vented out of the left end into the atmosphere.

Model II

Figure 2 is a schematic drawing of the second model. This unit served to test tubes made from zirconium oxide, thorium oxide, and graphite. It consisted of a 2.5 inch diameter metal cylinder, 10 inches long, fitted with end plates. A graphite tube 15 cm. long and 2.54 cm. in diameter, served as the internal housing for the cathode and as a holder for the tubes to be tested. This large tube had a small graphite tube attached to its side to provide an exit for the argon gas.

The cathode consisted of a graphite tube 30 cm. long and 0.91 cm. in diameter. A brass sleeve fitted over the tube provided electrical contact and cooling for the cathode. A porcelain tube served to insulate the cathode from the metal cooling plates and the large graphite tube.

The anode consisted of a graphite tube, 15 cm. long and 0.91 cm. in diameter which entered the metal housing through a porcelain insulator at an angle of 45 degrees. Fitted to the external end of the anode was a graphite cylinder with a 0.34 cm. diameter hole drilled in its center. This hole served as a port to insert samples up to the end of the anode. A 0.16 cm. hole was drilled in the side of the anode to permit argon gas to enter through a brass sleeve fitted over the hole. This brass

