NASA TECHNICAL NOTE

NASA TN D-4236

$c, 1$

STABILIZATION OF DC ARCS IN STATIC ARGON ATMOSPHERES FOR USE IN SPECTROCHEMICAL ANALYSIS

by William A. Gordon

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1967

NASA TN D-4236

STABILIZATION OF DC ARCS IN STATIC ARGON ATMOSPHERES

FOR USE IN SPECTROCHEMICAL ANALYSIS

By William A. Gordon

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

STABILIZATION OF DC ARCS IN STATIC ARGON ATMOSPHERES

FOR USE IN SPECTROCHEMICAL ANALYSIS

by William A. Gordon

Lewis Research Center

SUMMARY

The use of metal cathodes in an argon atmosphere was investigated and found to be highly effective in achieving a positionally stable arc column. Visual and spectral evaluations of refractory metal cathodes, including graphite, thoriated tungsten, rhenium, tantalum, molybdenum, niobium, and platinum, were made to ascertain the most suitable cathode material for this application. From these studies a combination tantalum-graphite cathode was developed. This special cathode produced arcs characterized by a diffuse cathode emission, which resulted in a stable arc column. A simple model of the arc column, based on the mechanisms of cathodic gas streaming and thermionic emission, was used to explain experimental observations relevent to stability of arcs in argon.

The emission spectrum of stabilized arcs was evaluated for use in spectrochemical analysis. It was found that, under the specified conditions, the excitation characteristics of the stabilized arc were essentially the same as when conventional graphite cathodes were used. It was therefore possible to integrate the special cathode into analytical procedures by substituting for graphite cathodes. Moreover, each special cathode was used for 100 to 200 analyses with no intervening treatment.

The effect of arc stabilization on analytical precision was determined for seven elements using a procedure for microanalysis in the argon arc. The average relative standard deviations of total integrated intensities were 11.5 percent for the graphite cathode and 8.6 percent for the tantalum-tipped graphite cathode. This improvement in repeatability was presumed to be due to the elimination of errors caused by arc wander.

The advantages of the stable arc for further improving sample vaporization and for arc diagnostics are suggested. The photometric traces of sample vaporization that were obtained when using the stabilized arc are smoother because of the absence of arc wander. These traces are therefore more useful for studying factors other than arc wander which may affect the repeatability of sample vaporization in dc arc analysis. Similarly, studies of excitation phenomena in various regions of the arc column may be more reliably made with the stable arc.

INTRODUCTION

The dc arc is one of the most useful sources for exciting atomic spectra for spectrochemical analysis. It is also one of the most crude, unrefined, and therefore least precise of the many sources available to the analyst. The reason for this apparent incongruity is that analyses can be made at very low concentrations with the dc arc. This makes the source especially valuable for trace and microanalysis even though the analytical precision is poorer than with most other sources. However, the poor precision associated with dc arc analysis limits its usefulness for many analytical problems.

This limitation of the arc is, in part, caused by the lack of positional stability of the arc column. The characteristic wandering of the arc column causes variations in such factors as, illumination of the spectrographic slit, vaporization of samples into the interelectrode space, and excitation of atomic emission, as discussed in references 1 and 2. This problem of positional stability has, more than any other factor, prevented the refinement of the dc arc for spectrochemical analysis.

The work reported herein is an extension of work reported previously (ref. 3). In the previous work nanogram amounts of metals were determined using arc excitation in static argon atmospheres rather than in air. This system was advantageous for both trace and microanalysis compared with arcs in air. Unfortunately, the arc wander is even more pronounced in the argon atmosphere than in air.

A diversity of experimental approaches for minimizing arc wander have been reported. One of the most effective methods of arc stabilization is the use of rapidly flowing gases around the arc column. Several forms of these gas stabilized arcs have been used sucessfully in chemical analysis (refs. 4 to 6). However, gas stabilization could not be applied to the existing analytical procedures which are based on arcing in static argon atmospheres. Other methods which are applicable to arcs in static atmospheres include the use of rotating magnets (ref. 7), rotation of sample electrodes (ref. 8), devices to minimize condensation of sample vapor on electrodes (ref. 9), heat exchangers to minimize temperature gradients in the sample electrode (ref. 10), the use of metal salts contained in cored cathodes (ref. 11), and optical compensation methods for eliminating spurious illumination of the spectrographic slit (ref. 12). Although these methods provide varying degrees of improvement in arc stability, they do not eliminate arc wander. Furthermore, they are difficult to use in gas-tight excitation chambers. The new method reported herein, however, effectively eliminates arc wander in static argon atmospheres.

The elimination of arc wander was achieved in this work by using a Ta-tipped graphite cathode in place of the conventional graphite cathode. Although metal cathode

materials cannot be used in air, because of their rapid destruction by oxidation, they can be used in pure argon atmospheres. The new cathode was developed from a study of arc stability using cathodes made of tungsten (W), thoriated tungsten (W-ThO_2), rhenium (Re), tantalum (Ta), molybdenum (Mo), niobium (Nb), platinum (Pt), and graphite. The best cathode material and cathode geometry were determined from the results of this study.

A discussion of some causes of arc instabilities is also included in this report. In particular, the mechanisms of cathodic gas streaming and thermionic emission are used to correlate the experimental results.

Finally, the experimental conditions are described for adapting the Ta-tipped graphite cathode to trace and microanalysis in argon.

APPARATUS AND MATERIALS

The instruments used in this work consisted of (1) a controlled atmosphere arc chamber, (2) an emission spectrograph, and (3) a source unit for generating the dc arc current. The characteristics of these units are not critical for the description of the procedure for producing stable arc discharges in argon. Only a brief description of these units will, therefore, be given herein.

Atmosphere Arc Chamber

The controlled atmosphere chamber shown in figure 1, was described previously in reference 3. Using this chamber, a dc arc was operated at currents between 2 and 60 amperes with controlled gas composition and gas pressure. All tests were made in static atmospheres of argon at a current of 30 amperes and at a pressure of 46 kilonewtons per square meter (~350 torr), unless otherwise stated. The argon gas used was commercial welding grade, nominally 99.995 percent pure, according to manufacturer's specifications. After each arcing cycle, the chamber was evacuated to about 0.13 newtons per square meter (~10^{-3} torr), and then refilled with argon for subsequent arcing.

Emission Spectrograph

The instrument used for spectral evaluations was a 3.4-meter, focal length, Ebert type (ref. 13), stigmatic spectrograph. Photographic recordings were made on Kodak, type SA#3 emulsion on 101.6- by 254-millimeter glass plates. The spectral region photographed was 250.0 to 420.0 nanometers (2500 Å to 4200 Å). Studies of line and back-
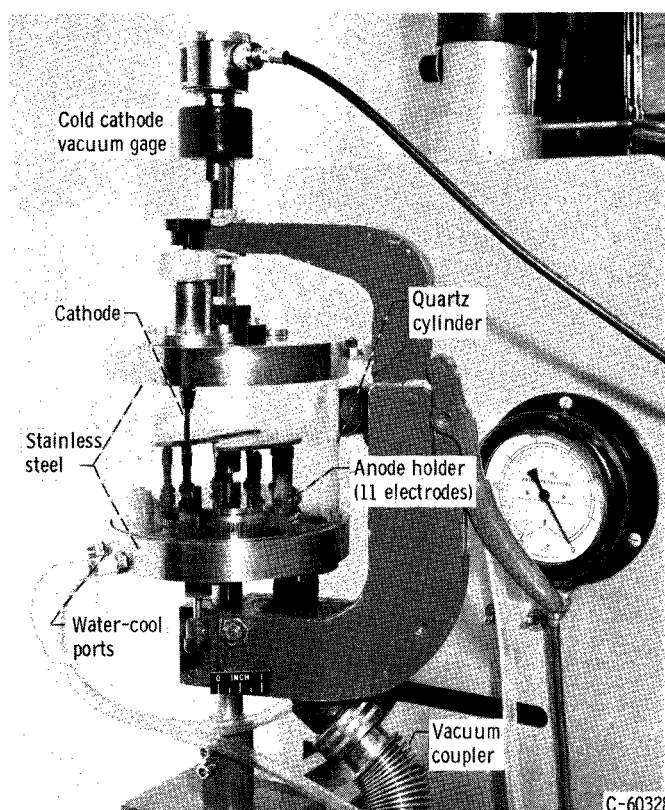
Figure 1. - Controlled atmosphere arc chamber.

ground intensity gradients in the interelectrode axis were made by imaging the arc axis on the spectrographic slit.

Arc Source Unit

The dc arc source was full-wave rectified using mercury rectifiers and inductive smoothing. Open circuit voltage was 250 volts and the current range available was 2 to 60 amperes, controlled by a moving core inductance. The arc voltage, at the current and argon pressure stated, was 18 to 20 volts. The percentage ripple at 30 amperes, the current level most used, was about 3 percent rms.

Materials

Cathodes. - The materials that were evaluated for use as cathodes are listed in table I. The metals were of typical metallurgical grade and were obtained from commercial sources. The graphite cathodes were of spectrographic grade.

4

Cathode material	Related carbides and eutectics	Melting point, °K (a)	Initial cathode wire diameter, mm	Emitting area, mm² (b)	Maximum cathode temperature, °K	Work function, φ, V (c)	Visual evaluation of arc stability	Evaluation of spectral characteristics
W	W_2C $W-W_2C$	3683 3140 2963	0.3	$^c3$	3510	4.5 3.6	Forms diffuse cathode emission but also tends to form small cathode emission with cathodic gas streaming. Forms lower melting carbides. Will not spark ignite. In combination with graphite, cathode spot stays on graphite preferentially.	No atomic lines detected between 300.0 to 400.0 nm (3000-4000 A). One line at 400.9 nm
Thoriated tungsten	--------	----	2.5 (tapered to a 10° point)	$^e3$	2800	Variable 2.6 to 3.4	Will spark ignite. Consistently stable but shows cathodic gas streaming with small cathode spot.	Many faint lines of Th between 250.0 nm to 400.0 nm
Re	--------	3453	1.75 (bundles of 0.38-mm-diam wire)	$^{d,f}40$	3350	5.1	Forms relatively large liquid sphere due to high work function. With much larger cathode diameter, may form even larger emitting areas with reduced cathode temperature.	Re lines detected at 346.5, 346.0, 345.2, and 342.5 nm
Ta	TaC Ta_2C $Ta-Ta_2C$	3269 4150 3673 3175	0.75	$^d7.8$	3130	4.2 3.4	Cathode emission consistently diffuse and stable. Functions as cathode preferentially to graphite. Slowly forms higher melting carbides upon prolonged arcing.	Ta 331.1 nm faintly visible
Mo	MoC Mo_2C $Mo-Mo_2C$	2883 2965 2960 2483	1.0	$^{d,f}71$	2960	4.3	Inconsistently stable. Will not spark ignite. In combination with graphite, cathode spot stays on graphite preferentially. Instabilities due to large fluid sphere.	------------------------
Nb	NbC Nb-NbC	2741 4173 2608	1.0	$^{d,f}67$	2835	4.0	Inconsistently stable. Will not spark ignite. In combination with graphite, cathode spot stays on graphite preferentially. Instabilities due to large fluid sphere.	------------------------
Pt	--------	2046	2.0	$^d\!\gg\!200$	----	5.3	Mechanical strength insufficient to support large cathode sphere. Much cathode vaporization and sputtering even at currents of a few amperes.	------------------------
Graphite	--------	3923 (sublimes)	1.0 3.2	$^e1$ $^e1$ to 2	3560 3640	4.4	Forms small cathode spot with high current density and much gas streaming. Cathode spot not positionally stable.	------------------------

[a] Metals, ref. 14; carbides, ref. 15; eutectics, ref. 16.
[b] Current, 30 A; argon pressure, 46 kN/m².
[c] Ref. 17.
[d] From measured sphere diameter.
[e] Visual estimate.
[f] Temperature gradients in sphere as described in text.

Anodes. - Anodes of graphite and tungsten, 6 millimeters in diameter, were used in this work and were also of commercial grades.

Silver Chloride. - Spectrographic grade silver chloride, available from several commercial sources, was used.

PROCEDURE

Arcing Procedure

The cathode materials listed in table I, were fitted into a 3.2-millimeter-diameter hole in the cathode holder. Electrical contact to the holder was made by bending or folding the wires, as necessary, to approximately match the hole diameter. The arc was started by contacting the electrodes and then separating them to a spacing of about 15 millimeters.

Arcs were formed with the cathode materials at currents between 2 and 60 amperes, and at an argon pressure of 46 kilonewtons per square meter. The arcing was continued until the cathode tip reached an equilibrium diameter (approximately hemispherical or spherical for metal cathodes) and an equilibrium temperature.

The anode material used in these experiments was either graphite or tungsten as will be discussed.

Procedure for Evaluating Cathode Materials

The materials listed in table I were evaluated by comparison of arc stability and emission spectra. These comparisons were made from visual observations, and photographic and photoelectric recordings of the arc spectrum.

Three basic criteria were used in making this evaluation. First, from visual observations and the photoelectric recordings, the arc stability was judged to be satisfactory or unsatisfactory. Second, the spectrograms obtained using cathodes that gave satisfactory stability were evaluated with respect to some spectral characteristics. These included the background intensity relative to conventional graphite cathodes and the number of atomic lines emitted from the cathodes. Third, the analytical detection limits were estimated using the procedure for microanalysis in the argon chamber (ref. 3). These detection limits were estimated from line-to-background intensity ratios obtained for typical elements and compared with those obtained using graphite cathodes. This third criterion was applied only to the final cathode design because it was the most satisfactory cathode in all other respects.

Measurement of Area of Emission and Cathode Temperature

The area of electron emission from the metal cathodes was estimated from the fused area formed on the cathode tip after completion of arcing. The emitting area of the graphite cathodes was estimated visually from the dimensions of the bright cathode spot.

Unless otherwise noted, the cathode temperatures were measured as near to the cathode tip as was allowed by the optical pyrometer. This resulted in a temperature reading on the cathode in an area about 0.5 millimeter from the cathode tip. This was the maximum temperature that could be read on the metal cathodes.

RESULTS OF CATHODE MATERIALS EVALUATION

Visual Observations

All the metals tested, with the exception of Pt, formed arcs with improved stability compared with arcs with graphite cathodes. With Pt wire cathodes the cathode emission was very erratic, even at a few amperes. The fusion of the Pt wire was accompanied by boiling and sputtering of the cathode tip. With the other metals the arc column was more symmetrical around the electrode axis with less tendency to wander. The improved stability was noted for the cathode emission and also for the arc column proper.

In these experiments it was observed that the shape and stability of the arc columns was affected by the area of electron emission on the cathode. The area of emission was sometimes highly localized (cathode spot) and sometimes spread over a relatively large area of the cathode tip. Two features of the arc, in particular, were affected by the cathode emission area: the bright cone of light concentrated near the cathode and the axial symmetry of the arc column. When the bright cathode light was constricted, as was the case with small cathode spots, the arc column was not axially symmetrical but was distorted. (This distortion of the arc column took the form of the familiar arc-flame, for arcs having very small cathode spots.) Arc columns showing an asymmetry, due to the distortion, were also less stable than symmetrical arc columns. Conversely, with larger emitting areas the light in the cathode region was more diffuse. And arcs of this type were more symmetrical and more stable.

Cathode Emitting Area and Temperature

The importance of controlling the cathode spot was indicated by the observed depend-
The

ence of arc shape and stability on the area of cathode emission. Experiments were, therefore, conducted to determine the effect of cathode material on the emission area. It was presumed that this relation involved the thermionic properties of the cathode materials.

Using cathodes of varying diameters, no simple relation was found between emitting area and the thermionic properties of the cathode material. The emitting area for a given cathode material was partly determined by the cathode diameter. For large diameter cathodes the heat conduction through the cathode was an important factor in the heat balance at the cathode. However, for small diameter cathode wires about 1 millimeter diameter, the equilibrium cathode dimensions were rather reproducible for each cathode metal. The arc was drawn to small diameter wires by contact ignition to the anode. The cathode spot that formed on the cathode wire melted the wire tip forming a nearly spherical emitting surface. As reported above, cathodes of this shape also produced the most stable arcs. Further experiments were therefore, done on wires which formed such spherical emitting surfaces.

Each metal wire tested, with the exception of thoriated tungsten, formed a characteristic sphere diameter at a given current. The temperature of the cathode spheres was about the melting point of the cathode material. The fused area of the thoriated tungsten cathode was more hemispherical th. pherical due to its relatively large diameter. The estimated emitting areas and the cathode temperatures for each cathode material are reported in table I.

The repeatability of cathode shape and emitting surface for each material was also dependent on the anode material that was used. When graphite anodes were used in these experiments, the emitting area of the cathode gradually changed in composition. The pure metal cathodes were changed to metal carbides or eutectics on prolonged arcing. This change in cathode composition was sometimes accompanied by an increase in the equilibrium diameter of the spherical cathodes. This occurred when the melting point of the new composition was much lower than that of the pure metal. In the contemplated analytical procedure, carbon in the form of graphite anodes will invariably be present in the system. Some carbon containing compounds that can be formed with the metals tested, are included in table I. The use of these properties aided in the interpretation of experiments when graphite anodes were used.

In experiments where the cathode emitting area was measured and reported, as in table I, tungsten metal anodes were used. With tungsten anodes the equilibrium cathode sphere diameters were more repeatable because no carbon compounds were formed. This procedure improved the correlation of emitting areas with the thermionic properties of the cathode materials.

8

Evaluation of Arc Performance Using Graphite and Metal Cathodes

A summary of results of the evaluation of arc performance using various cathode materials is given in table I. All the results reported in the table were obtained on small diameter cathode wires at 30 amperes current and an argon pressure of 46 kilonewtons per square meter. Arcs at this current and pressure were known to be analytically useful when using graphite cathodes.

Graphite, tungsten, thoriated tungsten. - Cathodes of graphite, W, and thoriated tungsten formed small cathode emitting areas. These cathodes did not give maximum arc stability because the arc columns were not always symmetrical, but showed the distortion characteristic of small emitting areas. Arcs formed with conventional graphite electrodes were marked by the formation of an arc flame, 5 to 6 centimeters in length for a 30 ampere arc. This arc flame revolved around the electrode axis. Similar arc flames were formed with W and thoriated tungsten, but these had little tendency to revolve around the electrode axis.

Another disadvantage was found when using thoriated tungsten cathodes. As noted in table I, the thoriated tungsten cathode emitted many atomic lines of thorium. These lines, although weak in intensity, might cause spectral interferences in analytical applications, particularly when using photoelectric detection.

Tantalum. - Tantalum cathodes produced equilibrium spheres having a larger emitting area than graphite, W, or thoriated tungsten cathodes. For Ta wires, 0.76 millimeter in diameter, the emitting area was 7.8 square millimeters for a 30 ampere arc, and the arc column was symmetrical. In addition, the emission at the cathode was more diffuse with Ta cathodes as compared with W and thoriated tungsten cathodes. The spheres were rigidly attached to the wire; that is, they did not move physically during arcing. Tantalum spheres also showed a relatively uniform temperature distribution over the area of the sphere. The temperature measured at the cathode tip was, therefore, in agreement with the literature value for melting point of Ta.

Tantalum cathodes gave the best overall arc performance including reliability, stability, and freedom from interfering atomic lines. The line intensity of one of the more sensitive lines of Ta at 331.1 nanometers, was very faint in the spectrum when Ta cathodes were used. In addition, the carbides and eutectics formed with Ta had melting points near, or above, that of the metal. After the Ta sphere was formed, therefore, no change in its diameter was seen when arcing with graphite anodes.

Because of its desirable properties and its good performance, Ta was selected as the cathode material for use in chemical analysis in argon atmospheres. The further development of the Ta cathode for this application is given in the section Final Cathode Design.

Niobium, molybdenum, rhenium. - The formation of emitting areas even larger than

those obtained for Ta might appear to favor the use of niobium (Nb), molybdenum (Mo), and rhenium (Re) in producing stable arcs. However, with these larger cathode spheres another form of arc instability was noted. These larger cathode spheres were undesirable because of their tendency to move physically during arcing. This movement, often in the form of low period axial rotations, caused similar motion in the arc column. This form of arc instability was caused by the combined effects of large sphere volume and increased fluidity of the spheres. Because they were highly fluid, these spheres were not rigidly attached to the cathode wire.

The increased degree of fluidity of the large spheres was a result of large temperature gradients in the spheres. Temperatures measured at the tips of Nb, Mo, and Re spheres, formed at 30 amperes, are reported in table I. These temperatures are significantly higher than the melting points of the metals. Temperature measured at points removed from the tip were lower, and approached the melting point of the metal at the interface of the fluid sphere and the solid cathode wire. Temperatures in the spheres, which were higher than the melting point of the cathode metal, promoted the increased fluidity.

When graphite anodes were used with Nb and Mo cathodes, lower melting compounds were formed, as indicated previously. When this occurred, the equilibrium cathode diameters were larger and less reproducible than those reported for the pure metal. The undesirable movement of the large cathode spheres was then intensified. Because of these difficulties with large cathode spheres, Nb, Mo, and Re were judged to be less satisfactory than Ta for 30 ampere arcs.

Platinum. - Platinum cathodes are an example of the limitations of forming even larger cathode spheres. The surface tension of the fused metal was not sufficient to support the large spheres formed at 30 amperes. The emitting area for Pt spheres is reported in table I as greater than 200 square millimeters. This was the maximum diameter obtained before the sphere was detached from the Pt wire. Because equilibrium diameters could not be achieved, temperature measurements were not made on the Pt spheres.

DISCUSSION OF RESULTS

The use of metal cathodes improved the stability of the arc in argon by eliminating the cathode spot wander and by forming more symmetrical arc columns. The results of the experiments using metal cathodes can be explained by considering the mechanism of cathode emission and also the forces which act to shape the arc column. These phenomena are intimately related to the causes of arc instabilities. Furthermore, an understanding of the interaction of these phenomena was useful in designing a cathode which

10

minimized instabilities of arcs operated in argon.

In the next section a cause of asymmetry in the arc column, cathodic gas streaming, will be described. Later, the thermionic mechanism of cathode emission will be discussed. In this discussion the relations between the arc column shape, the area of cathode emission, and the thermionic work function of cathodes will be clarified.

Physical Appearance of Arc Column and Origin of Arc Flame

The physical features of the typical arc column used in spectrochemical analysis, can be described using the three forces in the arc column listed as follows:

(1) Evaporation of the anode causes a gas flow in the direction of the cathode.

(2) Cathodic gas streaming in the direction of the anode. This force explains the origin of the flame-like projection from arcs in static atmospheres. It is caused by compression of the gas ions by the magnetic fields associated with the high current density in the region near the cathode. Reference 18 contains a good discussion of this effect and also some experimental demonstrations of the effect.

(3) Convection and buoyancy arising from the thermal gradient between the hot arc column and the cooler surrounding atmosphere.

The main features of the arc column in static atmospheres can be described in terms of the relative actions of these three forces. For a 30 ampere arc in air, between graphite electrodes, the anode vaporization is usually the dominant effect on the physical appearance of the arc column. In pure argon, however, the evaporation of the graphite anodes is a small fraction of that in air and effect (1) is, therefore, negligible. But the influence of effects (2) and (3) are readily observed in argon arcs. The arc flame formed in argon when graphite cathodes were used has been described. Figure 2 illustrates the
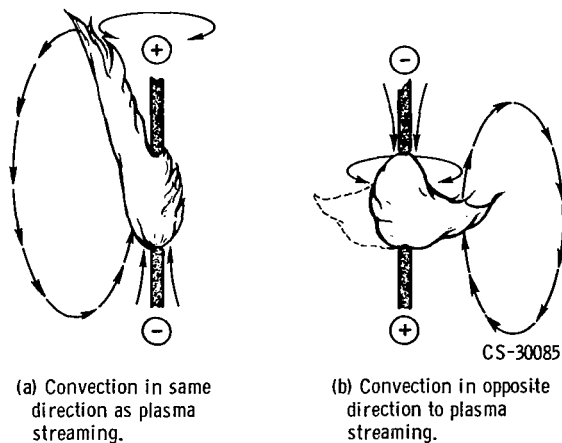

(a) Convection in same direction as plasma streaming.

(b) Convection in opposite direction to plasma streaming.

CS-30085

Figure 2. - Physical features of 30-ampere argon arc at atmospheric pressure (100 kN/m^2).

shape of the arc column when these forces are, (a) in the same direction, and (b) in opposite directions.

From this simple model of the arc column, it may be concluded that the blowing force due to cathodic gas streaming can be reduced by decreasing the current density at the cathode. The arc will then tend to be more symmetrical and, therefore, more stable. This effect was achieved by the relatively large spherical surfaces of the metal cathodes formed from wires. The increased cathode surface effectively reduced current density at the cathode tip by increasing the area of electron emission. Furthermore, for spherical cathodes formed with Ta wires, the emitting area was sufficiently large that the effects of cathodic gas streaming on the arc column were virtually eliminated.

The effect of cathodic gas streaming on arc-column shape was also observed at operating conditions other than those reported for table I. For example, stable arcs of the diffuse cathode type were formed even with graphite cathodes by reducing the argon pressure. At pressures below about 7 kilonewtons per square meter these arcs were highly stable. But they were of limited use in spectrochemical analysis because of poor detectability. Another method of forming stable diffuse arcs was to use large diameter cathodes so that the heat conduction through the metal prevented fusion of the cathode tip. For example, a 3.0-millimeter-diameter tungsten rod with hemispherical tip formed a diffuse arc with a larger emitting area and lower temperature than that reported for tungsten in table I. However, the diffuse emitting areas of arcs of this type had a tendency to change abruptly to a smaller cathode spot with a simultaneous increase in emitting temperature. This change in emitting area and temperature was accompanied by a change in the arc column from symmetrical to distorted. The cause of this erratic movement of the cathode spot is discussed in the next section.

Thermionic Emission and Cathode Spot Wander

In addition to asymmetry of the arc column, a second source of arc instability with graphite cathodes was the wandering of the cathode spot over the face of the cathode. The causes of cathode spot movement observed with both graphite and metal cathodes can be understood by considering the mechanism of electron emission from the cathode surface. In arcs of the type considered it is generally accepted that the electron emission is controlled by thermal energy at the cathode. Equation (1) is the Richardson-Dushman relation which describes the thermionic balance among the work function, the current density, and the cathode temperature. The equation is valid when electrons are removed from the cathode at the same rate that they are emitted from the cathode surface.

$$i/a = A_o T^2 (\exp) - e\varphi/kT \tag{1}$$

where

i   arc current, A

a   emitting area, cm^2

A_o 120 $A(cm^{-2})(^oK^{-2})$

e   elementary charge $(1.602 \times 10^{-19}$ C$)$

φ work function, V

T   cathode temperature, ^oK

k   Boltzmann constant $(1.38 \times 10^{-23}$ J$/^oK)$

Other energy balance relations such as for radiation emission, thermal conduction, cathode evaporation, arc voltage, and space charge effects will be ignored in this discussion.

The most stable cathode emission can be achieved by maintaining constant the values of φ, T, and a of equation (1). Small variations of φ, in particular, can cause much larger changes in emission area, due to the dominance of the exponential term in equation (1). For example, a relative variation of only 1 percent in the φ/T term of equation (1) requires a compensating adjustment of about 37 percent in emission area. This was calculated for a 30 ampere arc operating at the temperature measured for graphite cathodes (about 3560° K).

The cathode spot wander observed with graphite cathodes is believed to be caused by the variability of the work function φ of graphite. Work functions, in general, are critically dependent on crystalline structure and smoothness of the cathode surface. Graphite cathodes continuously undergo changes in the degree of graphitization in the arc. In addition to these changes in crystalline structure, graphite has naturally a rougher surface than the fused metal spheres. Both of these effects make graphite an unsuitable cathode material for forming stable arcs in argon.

In contrast to graphite, the spherical emitting surfaces formed by fusing metal wires, were highly uniform and mirror smooth. The area of electron emission was also well defined by the surface of the sphere. Consequently, the emission from these spherical metal cathodes did not move over the cathode surface.

In addition to maintaining constant thermionic parameters, it was important to operate the cathode near its melting point. This was indicated by observations made on the spherical emitting surfaces formed by melting wires, and also from observations on larger diameter cathodes. Arcs formed in either case were more stable when the cathode surface was melted. The diffuse arcs formed with large diameter cathodes had emitting temperatures much lower than the cathode melting point. However, the diffuse emission of these arcs often changed abruptly to a smaller cathode spot, as was reported in the previous section. And simultaneously with this decrease in emitting area, the cathode

temperature increased to about its melting point. After the smaller cathode spot was formed, the arc was rarely observed to revert back to the diffuse form.

This special stability with melted cathodes can be explained by the lowering of the work function at increasing temperatures. This effect of temperature on work function has been reported for Ta (ref. 19), and correlates with the increase in lattice parameter for most metals at higher temperatures. It can further be speculated that in the liquidus state some metals have a still lower work function than in the solid state, although this has not been established for Ta. The high stability of melted cathodes, however, is believed to result from the lower thermionic energy of the emitting surface having the lower work function.

Using the thermionic emission model with the simplifying assumptions, it was found that useful calculations could be made. These calculations were sufficiently precise to help confirm the experimental observations. For example, equation (1) was solved for sphere diameter for a current of 30 amperes and a temperature of 3269° K, the melting point of Ta. The calculated emitting area of Ta was 7.0 square millimeters, which compares well with the experimentally determined area of 7.8 square millimeters. Comparable agreement was obtained for Ta at currents between 10 and 60 amperes. A calculation of the emitting area required to support a 30 ampere arc using Pt cathodes gave an area of about 2×10^4 square centimeters - approximately a millionfold greater than calculated for Ta. From these and similar calculations for other metals was concluded that under the conditions reported in table I, the sphere diameters are primarily determined by the value of φ/T for each material.

These calculations also suggest that values of φ/T could be used to estimate the applicability of other materials for forming stable arcs under varying conditions. No further work was done using this method of evaluation because Ta appeared to have all the necessary requisites for producing analytically useful arcs in argon.

FINAL CATHODE DESIGN

A combination Ta-graphite cathode was designed which was substituted for conventional graphite cathodes in the argon arc. No differences in either arc stability or in emission spectrum was found in comparisons of arcs formed with this combination cathode with those formed using pure Ta cathodes.

The preparation of the Ta-graphite cathode is shown in figure 3. A small wire of metallurgical grade Ta was inserted into a hole drilled in a 3.2-millimeter-diameter graphite electrode having a conical tip, as shown. A 30-ampere arc was formed between the wire tip and the anode by contacting the cathode wire to either graphite or tungsten anodes. When graphite anodes were used, the contact time was kept as short as possible
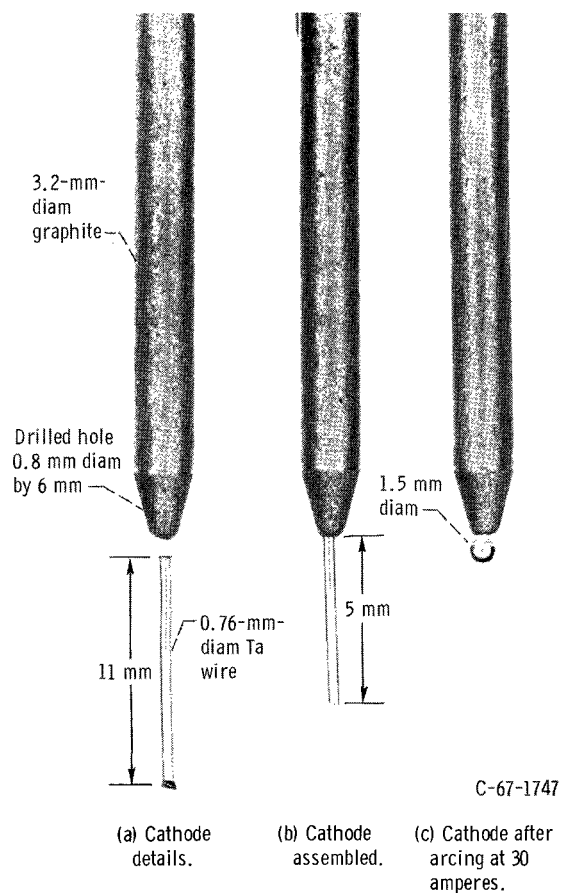
3.2-mm-
diam
graphite

Drilled hole
0.8 mm diam
by 6 mm

1.5 mm
diam

11 mm

0.76-mm-
diam Ta
wire

5 mm

C-67-1747

(a) Cathode
details.

(b) Cathode
assembled.

(c) Cathode after
arcing at 30
amperes.

Figure 3. - Preparation of Ta-tipped cathodes.
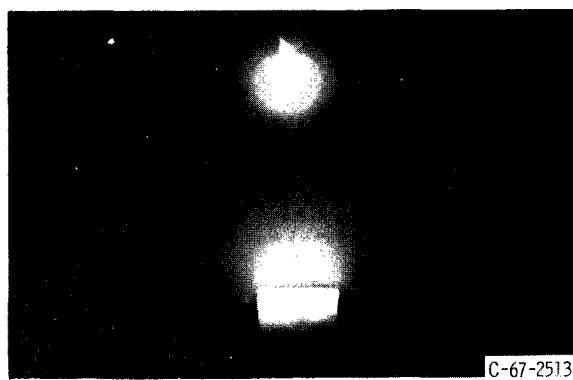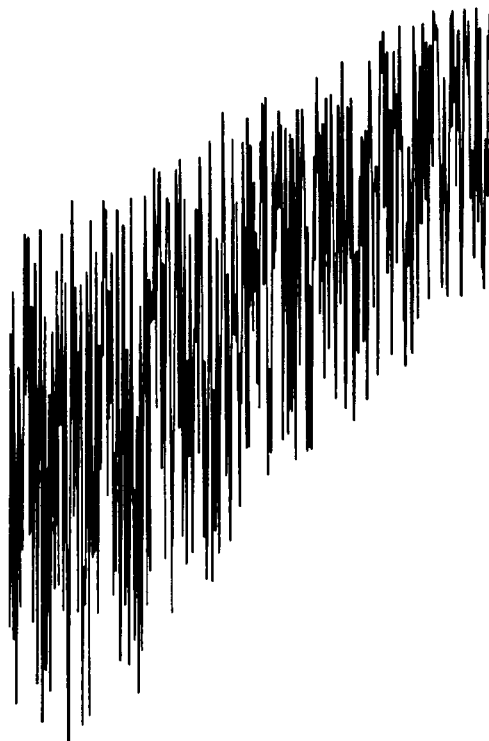

C-67-2513

Figure 4. - Photograph of dc arc using Ta-tipped graphite
cathode. Argon pressure, 46 kN/m^2; current, 30 amperes;
sample, 4 mg AgCl in graphite anode cavity. Note symmetry
of cathode emission and of arc column.

15

to avoid excessive pickup of graphite by the cathode wire. On continued arcing, the wire tip melted and grew to the equilibrium diameter, forming a diffuse cathode emission. At equilibrium the sphere was separated by about 0.5 millimeter from the supporting graphite rod. This small separation was desirable to retard diffusion of carbon and the resulting carburization of the Ta sphere. The cathodes were prepared at a rate of about five cathodes per fifteen minutes.

Each of the cathodes prepared in this way was used many times. When the arc was reignited using a spark discharge, the cathode was initially formed near the tip of the graphite rod. The temperature of the Ta sphere increased until thermionic emission from the wire surface was sufficient to produce the necessary electron emission. At that time the Ta sphere functioned as the cathode. The time required to form a stable arc on the Ta tip after the arc was ignited was about two seconds. Figure 4 is a photograph showing the symmetry of electron emission from the Ta sphere and of the arc column.

A comparison of arc stability using the Ta-graphite cathode and a conventional graphite cathode, is shown in figure 5. These traces were made using a photoelectric multiplier tube in a direct reading spectrometer and a strip-chart recorder readout. The optical axis of the spectrometer was alined for the same field-of-view in the arc column as was used in spectrochemical analysis. The region of the arc column in which the measurements were made is indicated by the heavy dashed line between the illustration of the electrodes below the coordinates in figure 6. (The additional data plotted in fig. 6 will be discussed later.) The time constant of the measuring system was about 50 milliseconds and the full-scale recorder response was 2 seconds. The traces illustrate the improvement in light stability when using the Ta-tipped graphite cathode. This improvement is due to elimination of the physical movement of the arc column. Also shown in figure 5(b) and (c) is the effect of anode diameter in achieving maximum column stability. This anode effect can be seen in arcs in pure argon but not in atmospheres such as air, where the anode is oxidized. Vaporization of samples from the anode in the argon arc also masks these effects. They were, therefore, only of incidental interest in this work.
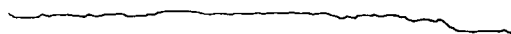
In the design of the Ta-tipped graphite cathode, graphite was used in combination with Ta to facilitate starting the arc. The conventional method of starting the arc, using a high voltage spark, was unworkable with pure metal cathodes. However, this method of starting the arc was a convenient experimental procedure and it was desirable to retain the method using metal cathodes. Unfortunately, using pure metal cathodes and graphite anodes, the spark ignitor caused the arc to form between the graphite anodes and a part of the arc chamber constructed of stainless steel that was also at the cathode potential. This faulty ignition occurred regularly even though the anode-to-cathode distance was often less than 1 millimeter, whereas the distance to the point of ignition was 50 to 60 millimeters. Attempts to vary the spark current and the capacitance, inductance, and resistance of the spark circuit also did not improve the ignition. However, the design of
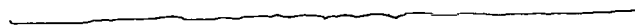
(a) 3.2-Millimeter-diameter graphite cathode.

(b) Ta-tipped graphite cathode with 3.9-millimeter-diameter graphite anode.

(c) Ta-tipped graphite cathode with 4.2-millimeter-diameter graphite anode.

(d) Electronic noise baseline.

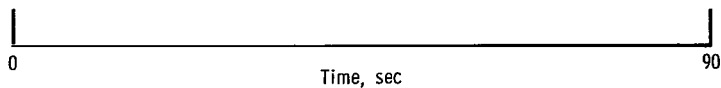0   Time, sec   90

Figure 5. - Comparison of photometric stability of graphite and Ta-tipped graphite cathodes. Atmosphere, argon; current, 30 amperes; pressure, 46 kilonewtons per square meter.
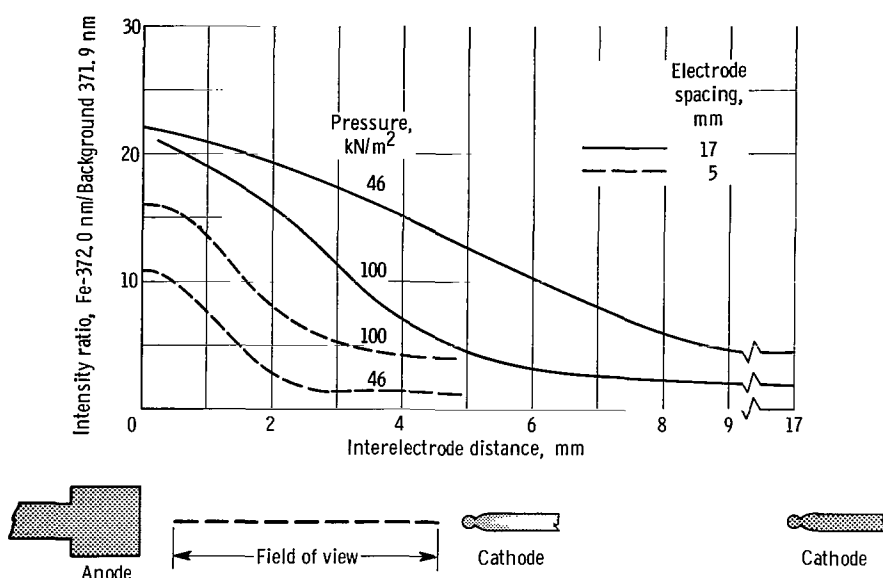
17

Figure 6. – Line-to-background intensity profile between anode and cathode for Fe at 372.0 nanometers. Arc current, 30 amperes (dc); cathode Ta-tipped; sample, 4 milligrams AgCl in anode crater.

the new cathode effectively combines the properties of graphite and Ta to overcome these problems in starting the arc.

In contrast to pure metal cathodes, thoriated tungsten and compounds such as TaC gave consistently reliable spark ignition. This was presumably because of the lower work function of these materials. Tantalum carbides were formed by repeated contact ignition to graphite anodes. After prolonged use, these formerly pure Ta cathodes formed compositions ranging from Ta to TaC on the metal surface. The arc could then be spark ignited using these cathodes. Confirmation of these results was obtained by carburizing the surface of pure Ta cathodes in an induction furnace. The arc could also be spark ignited using these cathodes. This procedure, however, was not acceptable as a solution to the problem of arc ignition because both the thoriated tungsten and the Ta carbides formed arcs with small cathode spots and showed evidence of cathodic gas streaming.

ADAPTION OF TANTALUM-TIPPED GRAPHITE CATHODE

FOR TRACE AND MICROANALYSIS IN ARGON ARC

The Ta-tipped graphite cathode was substituted for the graphite cathode that was formerly used in the argon arc. Arcs were formed between the cathodes and cupped graphite anodes. The graphite anodes contained the sample, generally a residue from evaporation of a few drops of metal salt solution, and 4 milligrams of silver chloride

18

(AgCl). The vaporization of AgCl with the sample residue enhanced line intensities, as described in reference 3. Each Ta-tipped graphite cathode was used for 100 to 200 arcings with no intervening treatment. The cathodes were replaced as a matter of procedure when the Ta sphere began to lose its spherical shape due to the formation of Ta carbides. Furthermore, the spectral intensities of the most sensitive Ta lines were negligible. For example, in an application of the Ta cathode to the determination of Ta in tungsten metal, as little as five ppm Ta, added as Ta_2O_5, could be determined. This exemplified the small amount of cathode vaporized in this procedure.

Optimum experimental conditions were estimated for detecting the lowest possible amounts of elements using the new cathode. Specifically, the effects of argon pressure, interelectrode spacing, and the region of the arc column sampled, were adjusted to achieve maximum line-to-background L/B intensities for representative elements. These L/B intensities were used as the criterion for estimation of the best conditions because they are indicative of the detectibility of the elements - a factor of great importance in trace and microanalysis. The region of the arc column yielding the highest L/B intensities was studied by imaging the electrodes on the entrance slit of the spectrograph. From the photographs of the spectrum, L/B intensities were determined at approximately 1 millimeter increments in the interelectrode space. These studies were made for two interelectrode spacings, 5 and 17 millimeters, and for two gas pressures, 46 and 100 kilonewtons per square meter. The results of these experiments are summarized in figures 6 and 7, for a sensitive atomic line of a typical element, iron (Fe)(372.0 nm).

Figure 6 shows the L/B intensity of Fe plotted as a function of position in the interelectrode space for anode-to-cathode spacings of 5 millimeters (dashed lines) a typical spacing used in the arc chamber, and 17 millimeters (solid lines), the largest practicable spacing used in the arc chamber. An illustration of the electrode spacings corresponding to the abscissa scale, is also shown on figure 6. The heavy dashed lines between the electrodes in this illustration represent the optical field-of-view in the arc column.

For each of the two interelectrode spacings the data are shown at two pressures,
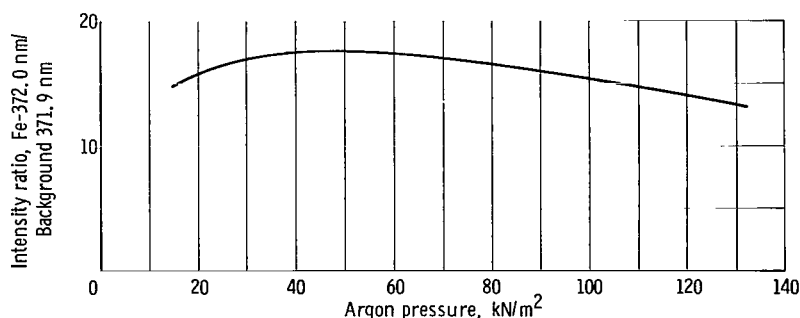

Figure 7. - Effect of argon pressure on line-to-background ratio. Arc current, 30 amperes (dc); sample in anode crater, 4 milligram AgCl; cathode, Ta-tipped interelectrode spacing, 17 millimeter; light sampled in region of arc column shown by heavy dotted line in illustration below figure 6.

46 kilonewtons per square meter, the approximate pressure used with graphite cathodes, and 100 kilonewtons per square meter, about atmospheric pressure. From these data it was concluded that detection of the light from a region near the anode was desirable for achieving high L/B intensities. These data also indicated that higher L/B intensities were achieved with the larger electrode spacing at the lower pressure. A more detailed study of gas pressure for the larger electrode spacing is shown in figure 7. The higher L/B intensities were obtained with the wider spacing at reduced argon pressure, as shown.

The near-optimum conditions adopted at Lewis were (1) an interelectrode spacing of 15 millimeters, (2) an argon pressure of 46 kilonewtons per square meter, and (3) a field-of-view in the arc column, as shown by the dotted line between the electrodes in the illustration below figure 6. The spectrograms of samples arced under these conditions were almost identical with similar spectrograms obtained using graphite cathodes.

Using the conditions reported above, the effect of arc stabilization on analytical precision was determined. This was done by comparing the precision obtained with the Ta-tipped graphite cathode with that obtained with conventional graphite cathodes. In these tests, measured amounts of metal salts were added to a bulk quantity of AgCl which was then mechanically blended. Samples, consisting of 4 milligrams of the batch-doped AgCl, were arced to completion at 30 amperes in argon. The absolute amount of each trace metal in the samples was approximately 1 microgram. The absolute amounts of seven elements were measured in replicate for samples run in sequence on the same day. The

TABLE II. - COMPARISON OF REPEAT-

ABILITY OF LINE-TO-BACKGROUND

INTENSITY RATIOS FOR TANTALUM

AND GRAPHITE CATHODES

[30 Ampere dc arc in argon, at 46 kN/m^2, 1 μg
of each element per 4 mg of AgCl]

Element	Relative standard deviation, percent	
	Ta-tipped cathode	Graphite cathode
Al	13	17
Co	10	12
Cr	5.8	11
Cu	3.4	4.6
Fe	6.0	13
Mg	16	13
Ni	6.0	10
Average	8.6	11.5

repeatability, thus obtained, for the graphite cathode and for the Ta-tipped graphite cathode is tabulated in table II. The data show a significant improvement in repeatability for some elements when using the Ta-tipped graphite cathode. This improved repeatability was presumed to result from the elimination of arc wander.

The conclusion that improved precision can be achieved by reducing arc wander appears to be justified by the data in table II and similar data of others (refs. 7 and 10). However, further generalizations concerning the degree of improvement that may be realized for specific elements or for conditions other than those specified, can not be inferred from these data. In some cases, where other errors predominate, the improvement in analytical precision may not be apparent at all with the elimination of arc wander. Magnesium, for example, showed no improvement in precision with the stable arc. It was later found that $MgCl_2$, one of the more refractory chlorides, was not completely volatized under the conditions used. Incomplete volatilization was the major source of error for magnesium and improvement in precision, therefore, did not result from the elimination of arc wander.

Although arc wander is not always the predominant error in dc arc analysis, the elimination of arc wander is ultimately essential for achieving the highest degree of precision in chemical analysis.

In addition to the improvement in analytical precision, the use of the stable arc was also advantageous in the development of new analytical procedures. Recordings of sample vaporization are smoother with the stable arc; the best experimental conditions can, therefore, be more accurately determined. This point is illustrated in figure 8, which shows comparative traces of the vaporization of 4 milligrams of AgCl from the anode cavity into the arc column. In these traces, the spectral intensity of Ag (350.2 nm) was recorded throughout the vaporization at 30 amperes for (1) a 3.2-millimeter-diameter graphite cathode, and (2) the Ta-tipped graphite cathode. It can be seen that critical studies of the vaporization event using graphite cathodes as in (1) are limited by the overriding effect of arc wander. With the higher stability provided by the Ta-tipped graphite cathode as in (2), such traces are more meaningful.
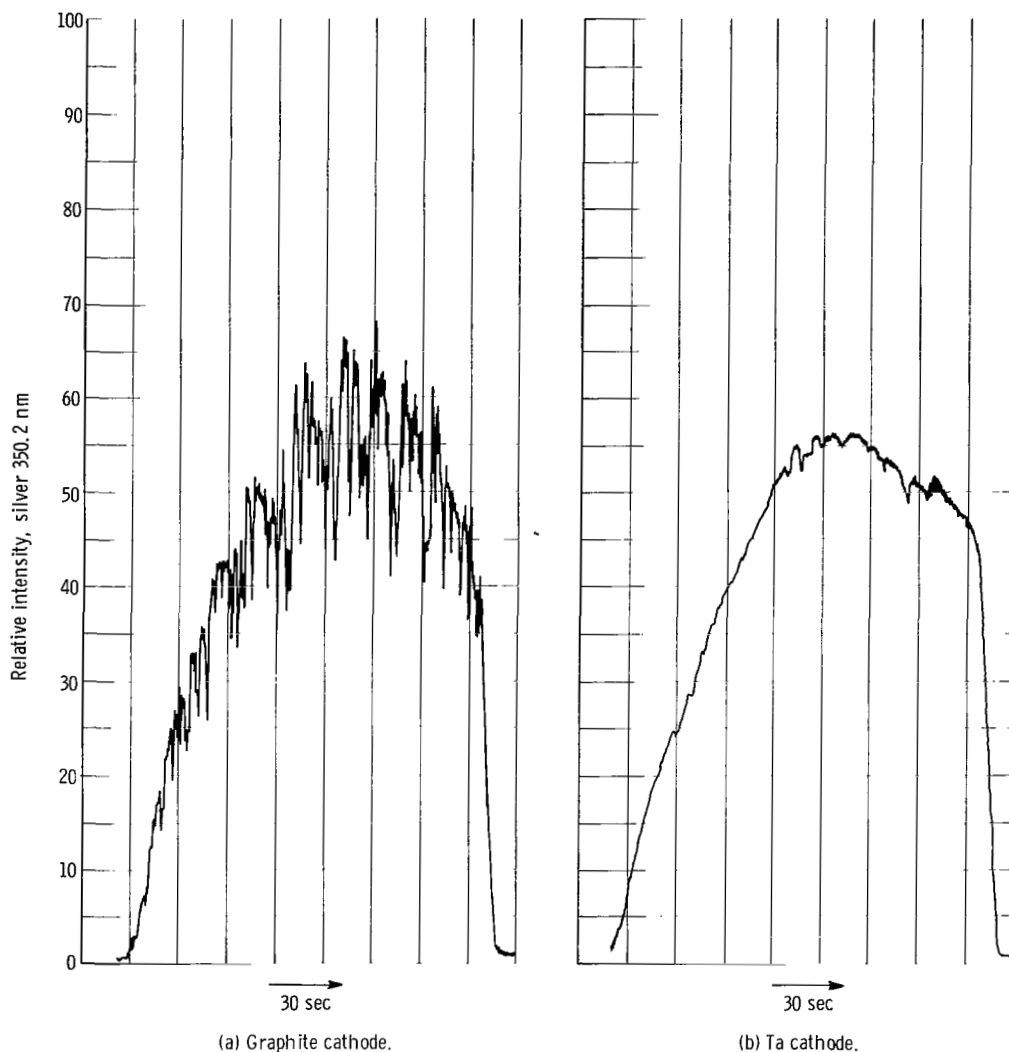
(a) Graphite cathode.   (b) Ta cathode.

Figure 8. – Vaporization profiles of silver. Argon arc, 30 amperes.

CONCLUDING REMARKS

The method of arc stabilization, described herein, has provided a solution to the problem of arc wander for dc arcs operated in static argon atmospheres. The new Ta-tipped graphite cathode can be substituted for the conventional graphite cathode and used for trace and microanalyses in the argon arc chamber. Each new cathode can be used many times and no limitations were encountered in its use. The precision of analysis was improved for some elements using the new cathode in the determination of microgram amounts of metals.

The selection of Ta as the cathode material, and the special geometry of the metal tip, can be explained in terms of the mechanisms of thermionic emission and cathodic

gas streaming. Of the materials evaluated for use as cathodes, Ta had the best combination of work function and melting point for producing stable arcs at 30 amperes. All the other materials formed arcs having electron emitting areas either too large or too small for maximum arc stability.

The author suggests that the method of arc stabilization, described herein, would be useful in studies of spectral excitation mechanisms in the argon arc. Such studies are of fundamental importance in understanding the spectrochemical relations in chemical analysis. The stabilization of the arc column overcomes a limitation imposed by arc wander when these measurements are made in specific locations in the arc column.

REFERENCES

1. Scribner, Bourdon F.: The Present Status of Excitation in Spectrographic Analysis. Spec. Tech. Publ., no 76, ASTM, 1946, pp. 2-11.

2. Margoshes, Marvin: Some Properties of New or Modified Excitation Sources. Symposium on Spectroscopic Excitation. Spec. Tech. Publ., no. 259, ASTM, 1960, pp. 46-58.

3. Gordon, William A.: Use of a Temperature Buffered Argon Arc in Spectrographic Trace Analysis. NASA TND-2598, 1965.

4. Anon.: The Stallwood Jet: Progress Report. The Spex Speaker, vol. 7, no. 3, 1962, pp. 1-5.

5. Margoshes, M.; and Scribner, B. F.: The Plasma Jet as a Spectroscopic Source. Spectrochim. Acta. vol. 15, 1959, pp. 138-45.

6. Margoshes, Marvin; and Scribner, Bourdon F.: Simple Arc Devices for Spectral Excitation in Controlled Atmospheres. Appl. Spectros., vol. 18, no 5, 1964, pp. 154-155.

7. Myers, A. T.; and Brunsteter, B, C.: Magnetic Rotation of the Direct Current Arc in Spectrographic Analysis. Anal. Chem., vol. 19, no. 1, Jan 1947, p. 71.

8. Jaycox, E. K.; and Ruehle, A. E.: Quantitative Spectrochemical Analysis of Alloys, Solutions, and Powders. Proceedings of the Seventh Summer Conference on Spectroscopy and its Applications. John Wiley and Sons, Inc., 1940, pp. 10-15.

9. Boumans, P. W. J. M.: Determination of Concentration of Metal Vapors in an Arc Source. Colloquium Spectroscopicum Internationale, VI. Pergamon Press, 1956, pp. 146-151.

10. Hoens, M. F. A.; and Smit, J. A.: Stabilization of the Vaporization of the Filled Cathode in a D.C. Arc. Colloquium Spectroscopicum Internationale, VI. Pergamon Press, 1956, pp. 192-196.

11. Mellichamp, J. W.: Cored Cathodes for Stabilization of the dc Arc. Appl. Spectros., vol. 21, no. 1, Jan.-Feb. 1967, pp. 23-27.

12. Preuss, Ekkehard: Spectrographic Illumination with Lenticular Screens. Heidelberger Beitr. Mineral. u. Petrog., vol. 4, 1954, pp. 163-171.

13. Jarrell, R. F.: Stigmatic Plane Grating Spectrograph with Order Sorter. J. Opt. Soc. Am., vol. 45, no. 4, Apr. 1955, pp. 259-269.

14. Lyman, Taylor, ed.: Properties and Selection of Metal. Vol. 1 of Metals Handbook. Eighth ed., Am. Soc. Mat., 1961.

15. Shaffer, Peter T. B.: Handbook of High-Temperature Materials. Plenum Press, 1964.

16. Elliot, Rodney P.: Constitution of Binary Alloys (First Supplement). McGraw-Hill Book Co., Inc., 1965.

17. Fomenko, V. S.; and Samsonov, G. V., eds.: Handbook of Thermionic Properties. Plenum Press, 1966.

18. Maecker, H.: Plasma Streams in Electric Arcs as a Result of Eigenmagnetic Compression. Z. Physik, vol. 141, 1955, pp. 198-216. (English Translation No. 07G6G available from Associated Technical Services, Inc., East Orange, N.J.).

19. Bol'shov, V. G.: Electron Emission of Germanium, and Germanium Treated with Cesium. Radiotekh. i Elektron, vol. 5, 1960, pp. 1241-1245.

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546