A SPECTROSCOPIC STUDY OF HIGH-POTENTIAL ALTERNATING

CURRENT ARC WITH AUXILIARY HEATER

by

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INTRODUCTION

This is a study of a low-frequency high-potential arc. In the field of spectroscopy such an arc has been finding widespread use as one of the essentials in the analysis of metals, alloys, and materials in general. Prior to the development of the low-frequency high-potential arc, the excitation sources in common use were the flame, the spark, and the low-potential arc.

The flame as an excitation source was originally used by Bunsen in 1859 (9, p. 15). In this method a platinum wire loop covered with the sample was held near the bottom of the blue cone in the Bunsen flame. The resulting spectra were of value principally in identifying a relatively small group of metals, namely, the alkali and the alkaline earth metals. The lines recorded with a flame were mostly in the visible region of the spectrum and not in the more desirable ultraviolet region. While, for a given charge, the spectrum of the sodium flame lasted for considerable time, the spectrum of the other metals showed only for a short time and the observations had to be made the instant the sample was introduced into the flame. An oxyhydrogen flame has also been used, and its more intense heat was found to excite lines for a greater variety of elements. Several rather complicated devices were built to enable the operator to keep the spectrum in the flame long enough to make a permanent record of it on a negative (3, 7, 10). With the

exception of its adoption with these special devices, the
flame spectra have been restricted to use in visual tests.

The spark as an excitation source was employed extensive-
ly by the founders of the spectroscopic method. Hartley in
1882 reported the results of his experiments and was followed
by De Gramont and Pollok (11). Unlike the flame, which was an
oxidation process, the spark was an electrical phenomenon pro-
duced by a high potential from an induction coil or from a
transformer. The standard electrical circuit consisted of a
condenser of the proper capacity placed across the terminals of
the high-potential source in parallel with a coil of self in-
ductance and a spark gap. For most installations at atmospher-
ic pressure the spark gap was about five millimeters. By vary-
ing the capacity of the condenser the intensity of the spark
was changed, the spark intensity increasing as the capacity of
the condenser increased. The self-inductance coil was used to
remove the air lines from the spark spectrum, but unfortunately
it also diminished the intensity of the spark and so was often
omitted in practice. When the samples were in the form of
electrical conductors, they were used directly as the elec-
trodes across which the spark was produced. A certain amount
of noise is always associated with the spark, and the air lines
or bands prevented the production of a clear-cut spectrum. The
spark used a very small amount of the sample and was nearly
constant in position and character so that it gave constant
illumination on the spectrograph slit.

The low-potential arc was the first electrical method used
in exciting spectra, as it was discovered by Davy in 1808 to
1810 (6, p. 605). The arc was easy to produce and was operated
off either d.c. or a.c. source at various voltages. Rods of
pure metal or graphite were used as the electrodes. The arc
was usually only a few millimeters in length. When a carbon
rod was used, a small hole was drilled in the lower electrode
and the sample was placed in this hole. The specimens fre-
quently included were metal particles, powders, filter pre-
cipitates, dry residues from solutions, in fact, almost any-
thing. The energy in the arc was so great that the electrodes
were heated to a red heat in a short time. When the space be-
tween the electrodes was the same distance as from the ends of
flat rods, the arc traveled around over the electrodes, moving
at will but covering all parts of the flat ends so that its
motion made uncertain the amount of illumination on the spec-
trograph slit. When the electrodes were pointed, the arc
stayed at or very near the points; but the points were con-
sumed rather rapidly and the distance between the electrodes
increased. As the distance increased, the intensity of the
spark diminished, again making uncertain the amount of
illumination on the slit.

The Low-Frequency High-Potential Arc

As may be seen from the preceding observations, the ordinary arc, the spark, and the flame as excitation sources possess many inconveniences. Some of these inconveniences have been removed in a type of arc which is relatively new. It is known as the low-frequency high-potential arc and is a combination of arc and spark. While it is difficult to determine just when these arcs were first employed, their adoption on a large scale is rather recent. Duffendack, Wiley, and Owens (1) have described the use of such an arc in the quantitative analysis of solutions. Jaycox and Ruehle (5) reported that it is a very reliable source with dilute solutions dried on electrodes, and Hees, Owens, and Reinhardt (4) stated that the a.c. arc source was superior to the d.c. arc in the analysis of organic materials for traces of metallic impurities. Duffendack and Thompson (2) reported that this method of analyzing solutions could be completed with a smaller amount of the sample than was needed in other methods. Sawyer and Vincent said of the high-voltage a.c. arc:

Each new half cycle starts with a glow, probably with some explosive release of electrode material, as in a spark discharge, followed by a transition to an arc. The wandering of the cathode spot is controlled or regularized in that it is forced to reestablish itself at each half cycle. The result is a form of arc which is considerably more reliable than the simple d.c. arc.
The a.c. arc may be thought of as an uncondensed spark with a sinusoidal current of low frequency and of constant amplitude.

This low-frequency high-potential arc is produced by
connecting two electrodes directly across a high-voltage
transformer operating with the ordinary 60-cycle a.c. current.
The transformer ordinarily used has such a high output that a
high current discharge like that of the arc is produced. On
the other hand, the potential developed is sufficiently high to
give to the discharge those advantages associated with sparks.
The low-frequency high-potential arc is thus a discharge which
is part arc and part spark.

PURPOSE

Because of the importance of the low-frequency high-
potential arc in spectroscopic research and in routine testing,
it was decided to make a systematic study of this arc with the
intention of improving its performance. The well-known disad-
vantages of this source of excitation are the predominance of
the air lines and bands, a disadvantage common to sparks, and
its instability, a disadvantage common to arcs. The air lines
and bands are so close together that many special lines needed
in an analysis are hidden entirely or so masked that their
identity is uncertain. Instability of the arc is caused first,
by its shifting position, and second, by the variation in the
amount of electrode material consumed. This causes it to change
both in position and in intensity.

The purpose of this investigation was to devise a method
for keeping the characteristics of the arc constant while it

operated, and also to find a method of suppressing the air
lines and bands.

DESCRIPTION OF EXCITATION SOURCE

The source of the arc used in this investigation was a
7.5-K.V.A., 60-cycle hi-reactance transformer made by the
American Transformer Company of Newark, New Jersey. The
primary coil had six taps to vary the number of turns in the
primary circuit and thus control the output voltage. In these
investigations only tap number four was used. There were eight
sockets for 600-watt heater element coils, connected in paral-
lel, and the current in the primary was varied by changing the
number of coils used. A sketch of the electric circuit is
shown in Plate I, Figure 1. This variable resistance was
placed in series with the primary coils. An ammeter with
range from 0 to 75 amperes was permanently connected in the
primary circuit. The secondary circuit terminals numbered 8
and 9 produced a current of 0.75 ampere at 4000 volts when
there was no resistance in the primary.

STABILIZING THE ARC

Fluctuations in the performance of an arc are of two
types, those originating in irregularities of the electrical
circuit and those depending upon irregular changes in the
arc itself.

The electrical circuit for this type of arc is by its

Fig. 1. The high-potential transformer.

       This transformer operates from the ordinary
110-volt power line.
       N is a neon warning lamp to show when the
circuit is closed.
       R stands for the receptacles for heating
elements (600 watts each).
       A_1 measures the primary current.
       A_2 measures the secondary or arc current.
       1 and 2-7 are various taps for the primary
coil.
       8 and 9 are the outlets for the high
potential.

Fig. 2. The heater circuit in position.

       The copper tube electrode at top.
       The aluminum cone electrode below the arc.
       The heater element is a platinum ribbon spot
welded to the nichrome sheets, which are mounted
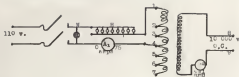on an asbestos rock board insulating holder.

PLATE I

Fig. 1
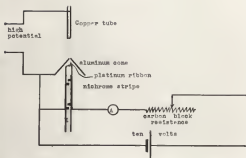Source for low-frequency, high-potential

Fig. 2
First heater element circuit

nature relatively free from irregularities. Failure in its performance can arise only in fluctuations in the line voltage. During week-days the line voltage remained fairly constant, and no measures were taken to stabilize it.

As the initial step in correcting variations in the arc, two 1/4-in. aluminum rods were placed in holders connected across the terminals of the transformer and the arc observed. The arc covered a small part of the space between the electrodes at any one instant but constantly moved its position until, at one time or another, it had appeared in a large portion of the space in the vicinity of the electrodes. As the electrodes were moved wider apart, the flame from the arc projected upward and climbed up the side of the top electrode. Starting with a distance of 2.5 mm. and increasing the space between the electrodes for each test, it was noticed that the size of the arc increased at the center as the distance between the electrodes was increased, and that the flame extended up past the end of the top electrode a greater distance as the space between the electrodes was increased. The space of widest electrode separation was 43 mm. At this separation the flame occasionally extended about 20 mm. up the side of the electrode. The flame of the arc also appeared intermittently below the top surface of the bottom electrode. Not only did the climbing flame spread the source over a larger area, but also it caused the amount of light sent to the spectrograph to vary as the flame revolved about a line joining the electrodes.

This placed the flame behind the electrode part of the time.

To correct this wandering feature of the arc, a 1/4-in. copper tube was hammered out at the end, leaving an opening about 1/8 in. in diameter. The top electrode was replaced by this copper tube and the house vacuum was attached to it. Air was drawn through the tube and the arc terminated at the end of the electrode, seeming to be drawn into the opening with the stream of air. A Sargent Wet Test Meter from the Precision Scientific Company of Chicago with a dial reading in thousandths of a cubic foot was connected between the house vacuum system and this copper tube electrode. After making a series of tests with various amounts of air flow, results showed that the arc was properly stabilized with an air flow of from one to one and one-half cubic feet per minute through the tube. Less than one cubic foot per minute was not able to hold the end of the arc steady, while more than one and one-half cubic feet per minute did not better the result that had already been obtained.

After a few minutes of operation the end of the tube became red hot. This arc is high in energy and much of the energy appears as heat in the electrodes. A longer piece of copper tubing was coiled to fit inside a jar which was filled with water. This water cooler allowed the arc to be used for long intervals.

A series of eight photographs of this arc was made, part of them without the vacuum connection and part with the vacuum pump pulling air into the tube. In Plate II, Figure 3,

a picture of the arc without air flow is shown. The flame of
the arc sputtered, sometimes seeming almost to jump free from
the upper electrode, and it kept moving around the end of the
electrode. In Plate II, Figure 4, the current of air produced
by the vacuum pump caused the arc to terminate at the bottom
of the copper electrode. This arc was more quiet in action
and was constant in position and in illumination. The intro-
duction of this constant air flow had stabilized the arc so
that it could be relied upon to produce a definite optical
density on spectroscopic negatives when the arc was used as
the excitation source.

USE OF THIRD ELECTRODE TO REMOVE AIR LINES

In an arc or spark, current must pass from one electrode
to the other. This current is carried by ions and electrons.
In the simple low-potential arc, the density of ions is rela-
tively high, and there are from one to ten more positive ions
than electrons (6, p. 610). In the spark the ions are more
evenly divided and there are not so many of them. If the elec-
trodes in the spark are far apart and not easily volatilized,
most of the ions at the center of the discharge must be fur-
nished by the air. It is the lines and bands from these air
ions which dominate much of the spectrum, especially the vis-
ible end, and mask the lines belonging to the sample. These
bands and lines may under certain conditions mask as much as
two-thirds of the spectrum and hence make useless about

Fig. 3. The arc without vacuum pump.

Photographed with Eastman view camera, f32,
time, 5 seconds.
Shows play of arc as it covers space
between electrodes.

Fig. 4. The arc with vacuum pump operating.

Photographed as above.
Shows top of arc definitely ending at the
end of copper tube where it is pulled by suction
created by vacuum pump.

PLATE II

Fig. 3

Fig. 4

two-thirds of the entire spectrogram. A good example of this masking is shown in the first spectrogram of Figure 5. It was hoped that these troublesome air lines might be obliterated through the action of ions from some easily volatilized substance which ordinarily gives a simple spectrum.

With this in mind a third electrode of an oven type was constructed. Its purpose was to supply vapors for the discharge and replace the air. Several oven electrodes were built. In the first one the bottom aluminum rod electrode described in Plate II, Figure 3, was replaced by a cone of sheet aluminum with a small opening in the small upper end of the cone. Under this cone was mounted a ribbon filament heater element. A schematic diagram of this assembly is shown in Plate I, Figure 2. A pair of nichrome sheet strips 3 in. long and 1 in. wide were cut and fitted to an insulating asbestos rock board 1/2 in. wide and 1/4 in. thick. A strip of platinum foil 0.001 in. thick and about 2 mm. wide was spot welded to the polished nichrome sheets. A small depression was pressed into its center to hold the sample. This heater was connected to the circuit of a ten-volt battery and its temperature regulated by a carbon block resistance. The heater element was set in position under the cone so that it did not touch the metal. A photograph shown in Plate IV, Figure 11, was taken after the heater element had been lowered into view.

Four different electrode arrangements were tried to see

Fig. 5.   The first exposure is the scale. This scale
         is marked in units of 100 angstroms each.

         1. Spectrogram of ordinary arc between copper
            and aluminum electrodes taken July 5, 1940.

         2. Spectrogram taken a few minutes later. In
            the meantime a sample of potassium salt was
            placed on the ribbon heater and evaporated
            into the arc. The lines of the normal arc
            are eliminated.

Fig. 5

EXPLANATION OF PLATE III

Fig. 6. Horizontal aluminum rod as bottom electrode.

        C - copper tube electrode.
        A - aluminum rod.
        H - heater ribbon.
        x,y,z - various positions of arc.

Fig. 7. V-shaped metal strip to test fumes.

        H - heater ribbon with fumes ascending.
        s - smallest space fumes ascended.

Fig. 8. Helical furnace of soapstone, with nichrome wire,
        and central cavity for sample.

Fig. 9. Oven mounted inside lower electrode.

        A - aluminum cone.
        B - brass ring.
        C - coil of nichrome wire.
        TW - water-cooling tube.
        P - porcelain base.
        I - insulating stand.

Fig. 10. Platinum cup to hold sample mounted on
        inverted platinum cup to fit oven.
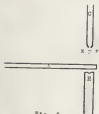
PLATE III

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

EXPLANATION OF PLATE IV

Fig. 11. Showing detail of copper tube, aluminum cone,
          and platinum ribbon heater.

Fig. 12. Assembly of apparatus.

          Copper tube coiled in can of water at top.
          Aluminum cone adjustable on frame.
          Adjustable heater element.
          Leg screws to lift and lower apparatus.

PLATE IV

Fig. 11

Fig. 12

if this arrangement of getting ions from the heater into the
arc could be improved. In the first one a brass screen re-
placed the aluminum cone. While the screen permitted the
passage of a larger flow of the vapor, it had to be discarded
because it was melted full of holes as soon as the arc was
formed. In the second, a 3/16-in. aluminum rod was mounted
horizontally just above the heater element, as shown in Plate
III, Fig. 6. The arc followed the vapor which rose on either
side of the horizontal aluminum rod only part of the time.
Most of the time the vapor carried the arc to one side of the
opening at the end of the tube and the flame climbed up the
side of the copper tube from one to two inches, broke, and
again started up. This made the arc very erratic. A third
modification consisted of a strip of sheet aluminum about 4 in.
long and 1 in. wide which was bent at right angles along a line
running lengthwise through its axis, making a V-shaped trough.
This bent strip was mounted in an inverted position as shown
in Plate III, Figure 7. A bevel was ground off the narrow part
of the V, leaving a wedge-shaped opening that gradually wid-
ened to about 1/4 in. at the open end. With this strip mounted
as the bottom electrode, it was moved along above the heater
to find the most desirable width to carry a steady stream of
vaporized particles from the heater below. The test showed
that the vapor moved up unimpeded through the opening from
the wide end of the wedge back to the place marked s, as
indicated in the figure, where the opening was about 1/16 in.

The stream of vapor refused to pass through the narrow end of the opening. The next arrangement tried was a cone electrode larger than the first one used. Since the volume of this cone was larger, more pressure from the hot vapor was expected at its tip and a hole 1/32 in. in diameter was drilled through the tip. This cone was placed over the heater element. After the heater had been in operation for a short time, a white deposit was found on its inside walls, and it was noted that very few vapor particles were getting through the opening at the top. Some fumes even began to appear at the outer edge and to approach the discharge from outside the cone. When the arc was operating, the vapor was not supplied fast enough to carry the discharge constantly. A larger hole, about 1/8 in. in diameter, was drilled in the top of the cone, and then enough ions came through to carry the discharge. This arrangement was photographed as shown in Plate IV, Figure 11.

Several different ovens were also built and tested. In the original oven the depression in the platinum ribbon strip was so small that it required reloading for each test. To correct this, a new oven was constructed by winding a helix of number 24 nichrome wire around a brass screw bolt, the screws making an evenly spaced coil. Into this wire form was placed a block of soapstone having a small hole drilled part way through it. The helical heating coil with the soapstone oven is shown in Plate III, Figure 8. The ends of this wire were spot welded to the nichrome strips which had previously

supported the platinum ribbon element. Samples placed in this furnace were easily volatilized.

With the information gained from the performance of these four electrodes and ovens, a new design for an electrode-oven assembly was drawn and the apparatus constructed. A brass cylinder 1 cm. thick with a diameter of 5 cm. had the central 2-1/2 cm. removed. In one of the walls of this brass ring a hole was bored for a 1/4-in. copper tube to carry water through the brass. This water line kept it from getting too hot during operation. Photographs of this oven and its parts are shown in Plates V and VI, Figures 13 to 16. A machined cone of aluminum 1 mm. thick was accurately fitted into the brass ring, and a hole was bored by a number 50 twist drill through the peak of the cone. A porcelain heater element employed commercially as a cigar lighter was used for the oven. It consisted of a porcelain base into which a small coil of nichrome wire of diameter 0.035 in. had been sealed. One end connected through the center of the porcelain to the tip, and the other end was connected to a metal strip around the outside of the porcelain. This is shown in section in Plate III, Figure 9.

This heater element was inserted into a hole bored through an asbestos rock board, and the brass ring described above was placed around it and fastened with screw bolts. A thin mica plate covered the top of the coil of nichrome wire heater, insulating the wire coil from metals placed on it. A platinum dish fashioned from 0.004-in. platinum foil was made

Fig. 13. Parts of oven electrode.

       Aluminum cone.
       Heater element.
       Brass ring with water pipe.

Fig. 14. Oven electrode, partly assembled.

       Aluminum cone.
       Brass ring with water cooler.
       Electrode holder with oven electrode in place.
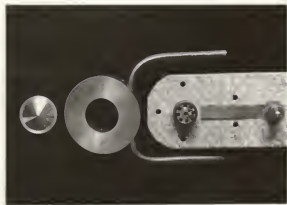   High-potential terminal.

PLATE V

Fig. 13

Fig. 14

EXPLANATION OF PLATE VI

Fig. 15. Oven electrode assembled.

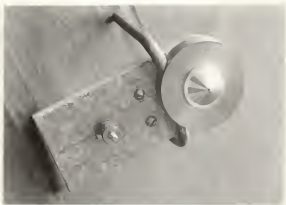Fig. 16. Parts of oven electrode assembly.

PLATE VI

Fig. 15

Fig. 16

to fit over the end of the heater coil, and a smaller cylin-
drical cup of platinum foil was spot welded to the center of
the first one as shown in Plate III, Figure 10. The rim of
the larger cup slipped over the top of the oven coil, holding
the sample in the smaller dish directly in the center of the
space above the oven, as shown in Plate III, Figure 9. The
asbestos rock board base upon which this oven electrode had
been mounted was placed in a horizontal position on the adjust-
able lower electrode holder shown in Plate IV, Figure 12. This
electrode-oven itself, picture in Plate VI, Figure 15, had
three electrical connections: the high-potential lead con-
necting to the brass ring and the two leads which connect the
oven heater. This new heater element was designed for use
with 110-volt a.c. circuit, and a variable wire coil resist-
ance of 180 ohms was used to regulate the temperature of the
oven. An a.c. ammeter was also placed in this line, as well
as a toggle switch.

In order to get the oven hot enough to vaporize the
sample, a current was used which burned out the coil. A new
helix of the same diameter was then made using nichrome wire
of 0.080-in. diameter. The wire was then heated to redness
on the iron core used in forming it. This heating of the
helix also caused it to set in its new shape so that it could
be handled easily.

PROCEDURE

It was decided that an alkali salt would be most desirable as the substance to be vaporized into the arc. In general, these salts have low vaporization temperatures and the spectra are relatively simple. Crystals of common salt (NaCl) were placed on the platinum ribbon filament described previously and the ribbon heated hot enough to cause fumes to appear above the crystals. It required nine amperes of current to make the vaporization visible. When the arc was viewed through a Gaertner prism spectrometer, the yellow sodium D line was plainly visible. Tests were made with a number of other samples, but most of them were unsuccessful. A piece of metallic zinc placed on the platinum ribbon ignited and burned almost instantaneously. A piece of lead melted on the ribbon and caused it to fuse and burn out. After installing a new platinum ribbon, cadmium metal was tried but gave the same result as lead. Then a calcium salt was placed on a new ribbon, but it volatilized so little that the result was unsatisfactory. A barium salt was tried next, but it did not volatilize readily and was also discarded. A salt of potassium (KNO_3) fused readily, and at a higher temperature produced a steady stream of ions. Viewed through the spectrometer, this spectrum was simpler than any previously tested.

The apparatus was placed in position in front of a Bausch and Lomb medium quartz spectrograph with a range of from 2000

to 7000 angstrom units. This instrument photographs the spectrum on a ten-inch plate. The plates used were Wratten and Wainwright panchromatic and Eastman 50. In some pictures a screen of metal was placed between the slit of the spectrograph and the arc, allowing only a portion of the arc to record on the spectrogram. All the negatives were developed in Eastman Kodak elon-hydroquinone developer, number D-11, and fixed in a chrome alum fixing bath, Eastman F-16.

RESULTS

Over 70 spectrograms were taken under varying conditions to determine the best set of conditions for suppressing the air lines and bands. In analyzing the spectrograms, the lines used to indicate the presence of aluminum originating in the lower electrode were the persistent lines,

Al - 3944 angstrom units
Al - 3961 angstrom units

Those used to indicate the copper of the copper electrode were the persistent lines,

Cu - 3247 angstrom units
Cu - 3274 angstrom units

The presence of potassium was shown by the presence of the two persistent lines,

K - 4044 angstrom units
K - 4047 angstrom units

Other lines encountered were the two persistent lines of sodium,

Na - 5889 angstrom units
Na - 5896 angstrom units

The first spectrograms to be analyzed in detail are shown in Figure 5. They were taken under the following conditions:

Slit opening . . . . . . 200 microns.
Slit length . . . . . . 7 mm.
Discharge length . . . . 21 mm.
Slit to discharge . . . . 31 cm.
Time of exposure . . . . 3 minutes.
Type of plate . . . . . Eastman 50.

The scale occupies the first position on the plate. The first spectrogram is that of the arc only, and in it appear the persistent lines of the copper and the aluminum electrodes with air lines and bands. For the second spectrogram the ribbon platinum heater was used. It required a current of 12.5 amperes to furnish the stream of vapor for the arc. This stream of ions caused the arc to contract laterally and to assume a faint purplish red color. As can be seen from the figure, the spectrogram shows a marked reduction in air lines and air bands. In their place appear the one strong potassium line and also a sodium D line, doubtless from some trace of sodium salt in the sample used.

The next series of spectrograms were taken to show the influence of the oven temperature on the elimination of the air lines and bands. This plate was made by photographing the arc between the aluminum cone and the copper tube, using the original platinum ribbon filament heater as described previously. This spectrogram is reproduced so that position No. 1 is at the left, as shown in Figure 17. The data

rslating to the exposure of the plate are as follows:

          Slit opening . . . . . . 100 microns.
          Slit length . . . . . .   5 mm.
          Discharge length . . .   15 mm.
          Slit to discharge . . . 21 cm.
          Time of exposure . . . . 3 minutes.
          Type of plate . . . . . Wratten and Wainwright
                                     panchromatic.

Table 1 details the conditions under which this series of
spectrograms was taken.

Table 1. Heater currents and temperatures for
spectrograms in Figure 17.

Position	Sample	Current on ribbon heater in amperes	Temperature indicated by optical pyrometer
1	Scale	- - -	- -
2	Arc only	- - -	- -
3	Arc and KNO_3 crystal	10.00	827° Kelvin
4	Arc and KNO_3 crystal	10.30	843
5	Arc and KNO_3 crystal	10.67	877
6	Arc and KNO_3 crystal	11.00	920
7	Arc and KNO_3 crystal	11.31	958
8	Arc and KNO_3 crystal	11.61	989
9	Arc and KNO_3 crystal	11.91	1009
10	Arc and KNO_3 crystal	12.20	1022
11	Scale	- - -	- -

The fact that the air bands faded out in exposure No. 3
(Table 1) is hard to explain. For some reason enough potassium
ions were present to mask out most of the air lines and bands.
In exposure No. 8 and the remaining ones the potassium ions
carried most of the discharge, and the former air lines and
bands were replaced by the 4044-4047 potassium doublet and
the 5889-5996 sodium line. The sodium line was undoubtedly

Fig. 17. Spectrogram, various temperatures of oven.

     1. Scale.
     2. Arc only.
     3. Arc with heater, 10.00 amperes current.
     4. Arc with heater, 10.30 amperes current.
     5. Arc with heater, 10.67 amperes current.
     6. Arc with heater, 11.00 amperes current.
     7. Arc with heater, 11.30 amperes current.
     8. Arc with heater, 11.61 amperes current.
     9. Arc with heater, 11.81 amperes current.
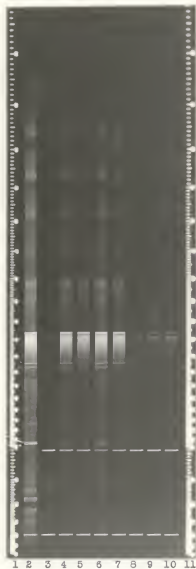   10. Arc with heater, 12.20 amperes current.
   11. Scale.

Fig. 17

caused by a slight amount of some sodium salt as an impurity
in the sample. According to these results, the proper vapor-
ization temperature for the oven when heating potassium ni-
trate is between 925° and 957° Kelvin. There seems to be
nothing gained by raising the oven to any higher temperature.

Another series of spectrograms was taken to compare the
discharge in various sections of the arc. For this purpose
three lag screws were fitted into the base of the apparatus
as shown in Plate IV, Figure 12, so that they could be used
to lift and lower the arc in front of the spectrograph slit.
Photographs were then made in which light from certain sections,
taken horizontally across the arc, was chosen. A metal screen
was placed between the arc and the spectrograph slit which
limited the record to that section of the arc. This test was
made with the platinum ribbon heater previously described.
The spectrograms obtained are shown in Figure 18. Data re-
garding these exposures are as follows:

<pre>
Slit opening . . . . 150 microns.
Slit length . . . . 4 mm.
Discharge length . . . .   16 mm.
Slit to discharge . . . . 18 mm.
Air flow through tube . . 1.5 cu. ft./min.
Oven current . . . . . .   11 amperes
Time of exposure . . . .   2 minutes
Type of plate . . . . . . Wratten and Wainwright
                             panchromatic.
</pre>

Each pair of spectrograms was taken of a different section of
the arc. The first one of each pair was taken with the normal
arc discharge, and the second one of the pair was taken while
the oven heater was in operation. A comparison of the two

Fig. 18. Spectrogram, sections of arc.

1. Aluminum end, arc only.
2. Aluminum end, arc with K^+ ions.

3. Next higher section, arc only.
4. Same as 3, arc with K^+ ions.

5. Higher section, arc only.
6. Same as 5, arc with K^+ ions.

7. Copper end, arc only.
8. Copper end, arc with K^+ ions.
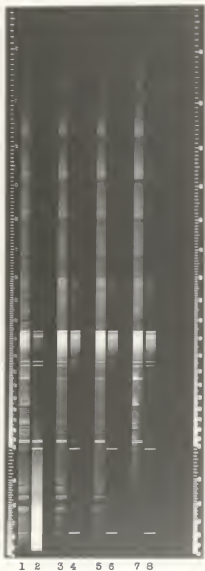
1 2 3 4 5 6 7 8

Fig. 18

spectrograms in each pair shows the effect of the potassium ions on the discharge in that section of the arc.

A sketch of the arc showing the section covered by each exposure is shown in Figure 19. Exposures numbered 1, 3, 5, and 7 were taken first; then 8, 6, 4, and 2, in that order. The approximate size of the normal arc is shown by the light shading and the size of the arc produced by the potassium ion stream is approximately that indicated by the heavy shading in the center of the arc. Distances given at the margin refer to the height of the bottom board of the apparatus from the table top while that section of the arc was photographed.

The spectrogram series reproduced in Figure 20 was taken using the final oven electrode assembly as previously described. It represents the most successful attempt to remove the bands and air lines. The primary circuit in the transformer operating the arc, shown on diagram in Plate I, Figure 1, was connected through only three heater coils, giving an ammeter A_1 reading of 15 amperes. In a previous test the enclosed oven had been charged with pure potassium nitrite (KNO_2). The discharge was partially screened by a metal shield having a 7-mm. opening. This shield was placed directly in front of the discharge and screened the electrodes. The data relating to this plate are as follows:

                    Slit opening . . . . . . 150 microns.
                    Slit length . . . .   4 mm.
                    Discharge length . . . . 12 mm.

Fig. 19. Sections of arc.

Spectrograms were taken at different
levels through the arc. The numbers at
the right refer to the height of the base
of apparatus from the table top. Odd-
numbered sections were views of the normal
arc. Even-numbered sections were views of
the potassium ion-charged arc.

section
7-8   4 mm

section
5-6   9 mm

section
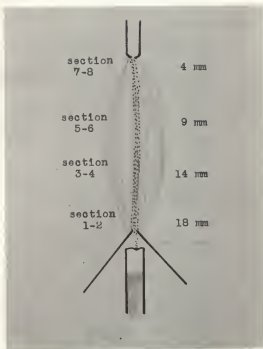3-4   14 mm

section
1-2   18 mm

Fig. 19

Fig. 20. Showing removal of air bands and lines
with oven heater.

1. Arc only.
2. Arc with heater, 0.6 amperes.
3. Arc with heater, 1.2 amperes.
4. Arc with heater, 1.4 amperes.
5. Arc only.

Fig. 20

1 2 3 4 5

Slit to discharge . . . 21 cm.
Time of exposure . . . 3 minutes.
Type of plate . . . . . Eastman 50.

The first spectrogram shows the arc when the heater element was not used. Most of the bands have their head toward the red end of the spectrum. The strongest band, a water band heading at 3064 angstroms, is very prominent. Probably the band at 2811 is also a water band. These water bands differ from most bands by having their head at the low angstrom reading and shading off at higher readings. The spectrum also shows the two persistent copper lines belonging to the upper electrode. These are the 3247 line and the 3274 line. The two persistent aluminum lines belonging to the lower electrode, lines 3944 and 3961, are also seen. The 4044-4047 doublet of potassium comes from the salt which had previously been used in the heater. Most of the other parts of the spectrum show the air lines and bands, nearly a continuous distribution.

The second spectrogram was taken while the oven current registered 0.6 ampere, and there was very little visual sign of the vaporized ions in the arc. The resulting spectrum also differs very little from the first one.

In the third spectrogram the only change in operation was to increase the temperature of the oven by increasing the heating current from 0.6 to 1.2 amperes. The potassium ions fed into the arc so slowly that the normal arc was only interrupted part of the time. When interrupted, the color changed to the reddish blue of the potassium ions. When it changed color, the

are assumed the shape of a narrow pencil instead of its former fuzzy brush-like appearance. The spectrogram shows an appreciable lessening in intensity of the air lines and electrode lines, but for some inexplicable reason the potassium line is also faint.

In the fourth spectrogram of the series the only change was an increase in the oven temperature which was accomplished by increasing the current in the heater to 1.4 amperes. This temperature was nearly, but not quite, high enough to maintain a continuous potassium ion arc. The spectrogram shows the strong potassium doublet, but the intensity of all other lines of the spectrum is less and most of the bands have disappeared.

During the taking of the final or control spectrogram, No. 5, the oven was not operating and only an occasional flicker of the reddish blue potassium arc was noticed. This spectrogram is practically the same as the first two. This series of spectrograms have shown how the potassium vapor eliminated the lines and bands of the air and water.

With the discharge 34 cm. from the slit in the spectrograph, a lens was placed 21 cm. from the discharge, focussing the arc on the slit. The arc was focussed so that the bright spot on the aluminum cone showed at one end of the slit. Then two spectrograms were taken, as shown in Figure 21. The remaining data for the exposure of this plate are as follows:

Slit opening . . . . . . 150 microns.
Slit length . . . . . . 9 mm.
Time of exposure . . . . 5 minutes.
Type of plate . . . . . Eastman 50.

Fig. 21. Arc focussed with lens.

      1. Arc only.
      2. Arc with heater.

Fig. 21

1   2

The first spectrogram was taken of the normal arc, and the bands are very prominent in most of the spectrum. The second spectrogram was taken with the heater on, but the potassium ions were not quite numerous enough to carry the discharge all the time. There was a sputter every time the character of the discharge shifted to the normal brush-like type. The bands are much fainter in this record, and the persistent lines have also been reduced in intensity.

DISCUSSION

In this investigation it has been proved that the arc can be stabilized as a source of steady excitation for spectrographic work. A vacuum pump operating at the rate of about one and one-half cubic feet of gas per minute on a tube that is also the top electrode of the arc will produce an arc of constant length and of constant intensity.

The second fact discovered by this investigation was that a stream of ionized vapor passed through the arc will suppress the air lines and bands. The plates submitted give that proof. But at the same time that the air lines and bands were masked out of the spectrogram, the lines pertaining to the specimen under study, in this case the lines of the electrodes used in the tests, were themselves diminished to such an extent that they would not make a very satisfactory plate under these conditions. The action of the potassium ions used in this investigation has changed the character of the arc.

Loeb (6, p. 610), in his discussion of the cathode fall
in the arc, reported that the high temperature of the arc
causes some thermionic emission from the cathode. This emis-
sion must be great enough to maintain the positive space
charge through the arc. But in the short cathode drop there
are many electrons needed to make one positive ion, so that
the arc must have a high current density. The stream of ions
from the hot potassium salt used in this investigation produced
a considerable density of positive ions. Loeb (6) gave an
equation for calculating the positive ion current density.
The equation reads,

$$j_+ = \sqrt{\frac{1}{9\pi}} \cdot \frac{2e}{M} \cdot \frac{V^{3/2}}{d^2}$$

in which e = charge on an electron,
          M = mass of the ions,
          V = potential across the cathode fall of the arc,
     and d = length of the fall.

This potential across the cathode is never more than twice
the ionization potential for the ions used and sometimes it is
just larger than the actual ionization potential.

In his table of ionization potentials of various elements,
Loeb (6, p. 655) gave, among others, the following:

Elements	Ionization potential
He	24.48
Ne	21.47
A	15.70
Hg	15.37
Mg	15.65
O₂	12.50
Cu	7.69

Elements	Ionization potential
Mg	7.61
Al	5.96
Li	5.37
Na	5.12
K	4.32

By comparing the ionization potentials of the nitrogen and
oxygen of the air with potassium, the table shows potassium to
be a little more than one-fourth that of the air. When the
arc was carried entirely by the potassium ions, the potential
difference was so low that the ions of air and even the me-
tallic ions of copper and of aluminum were not excited. With
a changing arc, partly the potassium ion arc and partly the
normal arc, the other ions were excited in those intervals
when the potassium ions did not hold the arc to the low
potential difference.

If it were possible to find an ion carrier that did not
have so low an ionization potential as potassium but a lower
ionization potential than the nitrogen and oxygen of the air,
it might be possible to mask the air lines and bands appre-
ciably and still have a high enough potential difference
across the arc to excite the lines of the specimen. This sub-
stance would still need to have a simple spectrum itself to be
of great value. If a substance of proper ionization potential
with a simple spectrum could be found, it might be possible
to improve the arc by masking out most of the air lines and
bands and still leave the persistent lines of the specimen
being tested. Since helium has a high ionization potential,

it might be a desirable substance to feed through the lower electrode to carry the discharge across the space between the electrodes. Helium is expensive to use in such experimental work and it was not tried. Magnesium is a metal with a rather high ionization potential, but it has a more complex series of its own spectral lines. Another difficulty with magnesium would be to find a salt that could be easily vaporized to feed the magnesium ions through the arc. There are a great number of other substances that might be tested as to their value for such a use, particularly the rare gases, all of which have relatively high ionization potentials.

SUMMARY

In this spectroscopic study of a low-frequency high-potential a.c. arc with auxiliary heater, evidence has been submitted to establish the following facts:

The arc discharge was stabilized in position and in intensity by using a tube for the top electrode and pulling through it a constant stream of air.

The character of the arc was changed by feeding a stream of positive ions from an oven into the arc through an opening in the bottom electrode. This stream of ions was able to suppress the normal lines in the arc by supplanting them with its own spectral lines.

ACKNOWLEDGMENT

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