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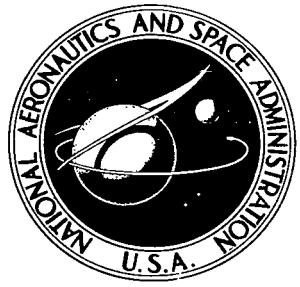

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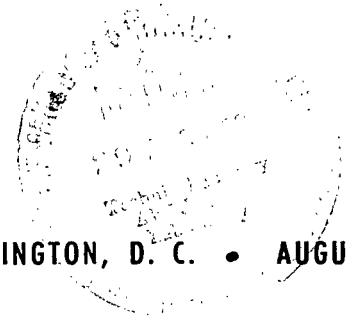
A SERVOCONTROLLER FOR PROGRAMMING SAMPLE VAPORIZATION IN DIRECT CURRENT ARC SPECTROCHEMICAL ANALYSIS

by William A. Gordon

Lewis Research Center
Cleveland, Ohio



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ABSTRACT

A new method was developed for controlling atomic emission and sample vaporization in dc arc spectrochemical analysis. Automatic adjustments in arc current were made to cause the rate of atomic emission to follow a prescribed program. With a stabilized arc in argon the vaporization of silver chloride was repeatable to about 1 percent. The control system consisted of a spectrometer with multiplier-phototube detector, a curve-following programmer, a controller, a dc current supply, and an argon arc chamber. The control system was used with a stabilized arc in argon and also with a wandering arc in air.

A SERVOCONTROLLER FOR PROGRAMMING SAMPLE VAPORIZATION IN DIRECT CURRENT ARC SPECTROCHEMICAL ANALYSIS

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SUMMARY

A new method was developed for controlling the light emitted from samples vaporized in a dc arc. This method is intended to minimize errors caused by nonrepetitive sample vaporization and thus to improve the precision of dc arc spectrochemical analysis. The control method was applied both to stabilized arcs in argon and to wandering arcs in air. The best results were obtained with the stabilized arc in argon. In this case the vaporization of 4.0 milligrams of silver chloride from the anode cavity was repeatable with a precision of about 1 percent, relative standard deviation. The precision of 30-second integrations of background emission from the controlled arc averaged about 2 percent for 15 wavelength positions in the 2100- to 4250-Å (or 10^{-10} m) range.

The control instrumentation consisted of a spectrometer with a multiplier-phototube detector, a curve-following programmer, a controller with proportional, derivative, and integral modes of control, a phase-sensitive dc current supply, and an argon arc chamber. These components were connected to form a closed-loop control system.

In operation, a selected spectral line was monitored by the multiplier-phototube and produced a voltage, the emission signal, which was proportional to the line intensity. Another voltage, the reference signal, was produced by a curve-following programmer. During sample vaporization, the emission signal was compared with the reference signal in the controller. Any difference between the emission and reference voltages produced a control signal that caused instantaneous and continuous adjustments in arc current so as to make the voltage difference zero. Thus, the spectral line emission precisely followed the prescribed program entered on the curve-following programmer.

The instrumentation is described in detail and procedures are outlined for obtaining control of emission from stable and wandering arc sources.

INTRODUCTION

In the spectrochemical analysis of materials using the dc arc the specimen is vaporized by the heat generated at a graphite anode containing the specimen. The excitation of atomic spectra from the vaporized sample occurs in the arc column. The anode temperature and rate of sample vaporization are primarily determined by the arc current, anode material, anode geometry, sample form, and the composition and pressure of the atmosphere. Variations in any of these factors between analyses can adversely affect the reproducibility of the sample vaporization and the analytical results.

In practice these factors are kept constant, insofar as possible, for each analytical procedure. Electronic control of arc current has been used (ref. 1) to ensure a constant current level regardless of changes in vapor composition in the arc column. Close tolerances of electrode geometry and densities are maintained by suppliers of spectrographic electrodes. The use of uniform samples with respect to weight, particle size, and density is also common practice. In spite of these precautions, erratic sample vaporization can cause spectral intensities to vary approximately from 10 to 50 percent, relative standard deviation (RSD)[1], for repetitive arcings. Because of these analytical errors, the direct arcing procedure is seldom used for quantitative analysis.

Some improvement of analytical precision can be achieved by using the internal standard technique to partly compensate for experimental variations. This compensation is achieved by taking the ratio of the analytical line intensities to the line intensity of an element (the internal standard) that is present in all samples at a constant concentration. With this internal standard procedure, precisions of 5 percent (RSD) can be obtained under favorable conditions. However, there are practical limitations in the internal standard technique caused by the difficulty of achieving good compensation for many elements with a single internal standard. A significant amount of the total effort in developing new spectrochemical procedures is spent in selecting appropriate materials and spectral lines to serve as internal standards. Further improvement in analytical precision, of

[1]The relative standard deviation (RSD) is given by the following equation:

$$\text{RSD} = \frac{\sqrt{\frac{\Sigma(\bar{x} - x)^2}{n - 1}}}{\bar{x}} \times 100$$

where n is the number of determinations, x is the value of the determination, and $\bar{x}$ is the arithmetic average.

the order of 1 to 2 percent, and elimination of the need for internal standards would greatly increase the usefulness of the arc for chemical analysis.

If this improvement is to be achieved, the problem of nonrepeatable vaporization of samples into the arc column must be solved. A new method for precisely controlling and programming sample vaporization is described in this report. This method makes use of a control system to control the spectral light emission from an arc electronically. With this method, errors caused by nonrepeatable sample vaporization were reduced to as low as 1 percent. The method also improves the prospects for performing quantitative analyses without internal standards.

The control system developed in this work was tested on a stabilized arc in argon and also on a wandering arc in air. The work with the arc in argon was a continuation of work reported in references 2 and 3. In reference 2, conditions were reported for detecting nanogram (10^{-9} g) amounts of metals with a dc arc in argon. In reference 3, a special tantalum (Ta)-tipped graphite cathode was developed which stabilized the argon arc. The use of the control system with the argon arc and with the arc in air demonstrated its usefulness with both spatially stable and spatially unstable arcs for improving the repeatability of sample vaporization.

APPARATUS

The instruments required for the control of arc light intensities were added to a conventional facility that included both a direct-reading spectrometer and a spectrograph. However, only the spectrometer was directly involved in this work. (Later references to the photographic instrument are made only to explain aspects of the optical system involving both the spectrometer and the spectrograph.) This facility also included a dc arc source, a conventional air arc-spark stand, and a gas-tight chamber for conducting arcs in argon atmospheres. However, the original dc arc source was modified by replacing the mercury vapor rectifier tubes with thyratron tubes, so that the current output could be controlled by a voltage at the thyratron grid. The control instruments that were added to this facility consisted of a controller and a curve-following programmer.

These instruments were connected to form a closed-loop control system for providing instantaneous and continuous control of light emission during the arcing cycle. Table I is a summary of the components used in the electronic control system. Detailed descriptions of these components are restricted to modifications of commercial designs and to their optical and electronic connections.

TABLE I. - SUMMARY OF INSTRUMENTATION

Instrument	Description
Controlled-atmoshpere arc chamber:	Shown in figure 1.
Anode	Prepurified graphite, cupped-undercut ASTM type S-14 (ref. 4).
Cathode	Ta-tipped graphite (ref. 3).
Atmosphere	Argon, nominally 99.995 percent pure; pressure, 345 torr.
External optics	Shown in figure 3.
Spectrometer	Focal length, 1.5 meter; grating, 1180 grooves per millimeter; optical mount, Paschen-Runge; entrance slit, 25 micrometers; exit slit, 75 micrometers.
Electronic readout:	
Multiplier phototube	Radio Corporation of America, Type 1P28; selected for sensitivity and precision, and operated at 700 to 800 volts.
Electrometer amplifier	Jarrell- Ash Co., Model 26-770-A; operated in 10^{-6}-ampere range at about 2 to 4 millivolts output; time constant, about 20 milliseconds.
Strip-chart recorder	Voltage, 0 to 10 millivolts (full scale); four pen; 11 inches (full scale).
Controller	Research Incorporated, Model TC-5192-RR (modified schematic shown in fig. 4).
Curve-following programmer	Research Incorporated, Model FGE-5110-HS-10; voltage, 0 to 10 millivolts (full scale).
dc current source	Spectro Equipment Inc., Model 40750-SP; modified to thyratron control (fig. 4); current range, 0 to 40 amperes; open-circuit voltage, 150 to 250 volts, dependent on firing angle of thyratons as discussed in text; arc voltage, 18 to 20 volts.

Operating Principles of Control System

Figure 1 is a block diagram of the components of the servoloop. Samples were vaporized from the anode cavity of the dc arc source, with simultaneous excitation of atomic spectra in the arc column. The emitted light was passed into the spectrometer where it was dispersed and detected by multiplier phototubes. The current signal from a selected multiplier phototube, usually alined on an atomic line emitted by a major element in the sample, was applied to the electrometer amplifier.

The amplified emission signal E_1 was applied to the controller. Also applied to the controller was E_2, the reference voltage generated by the curve-following programmer. During sample vaporization, any difference between E_1 and E_2 was detected by the controller. From this difference signal a resultant control signal $\mathscr{E}$ was produced

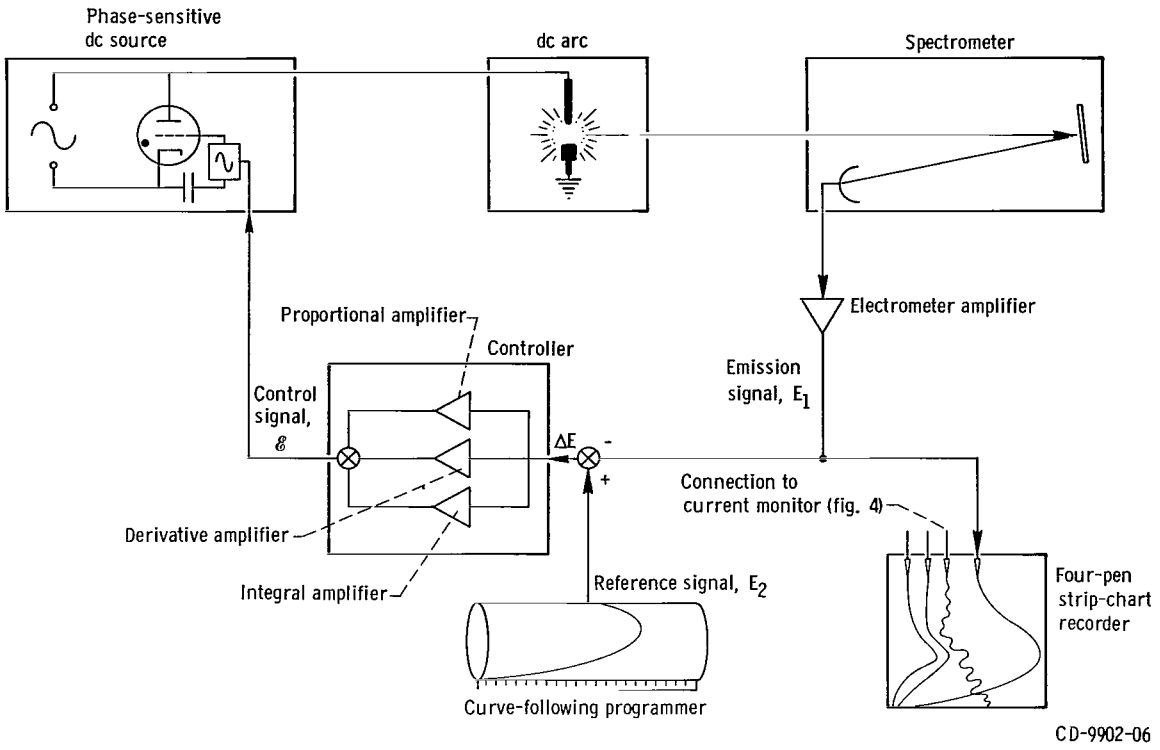


Figure 1. - Block diagram of dc arc control loop.

by the controller. This resultant control signal was produced by three modes of control: proportional, derivative, and integral as represented in figure 1 by the three amplifiers in the controller. The control signal $\mathscr{E}$ regulated the output of the current source by controlling the conduction phase angle of the thyratron tubes. The instantaneous and continuous action of the changing current resulted in an increase or decrease in sample vaporization and emission signal as required to match voltages E_1 and E_2.

The emission signal E_1 was also recorded by a strip-chart recorder, which was not part of the control loop. The strip chart recorded the intensity of the spectral line that was selected for control and also recorded the current and any two additional spectral line signals. Both the strip-chart recorder and the curve-following programmer were 0- to 10-millivolt (full-scale) instruments. Therefore, the percentage displacement of the strip-chart recorder was always the same as that of the curve-following programmer when the program conditions were met, that is, $E_1 = E_2$. Thus, with ideal control, the trace of light emission on the strip-chart recorder was the same in time and amplitude as the program entered on the curve-following programmer. Similarly, repetitive traces of spectral light intensities from subsequent arcings were the same.

Controlled-Atmosphere Chamber

The controlled-atmosphere chamber used in this investigation (fig. 2) is basically the same as that described in references 2 and 3. Only the essential features of the chamber and some recent modifications are described herein.

The chamber was a gas-tight enclosure which was evacuated to about 10^{-3} torr and backfilled with argon to about 345 torr prior to each sample arcing. The arc was conducted in a static argon atmosphere between the cathode and an anode positioned under it. A sample positioning knob attached to a gear drive was used to position the anodes under the cathode. In this way, 11 samples contained in the anodes were arced in sequence without opening the chamber. A bellows seal above the cathode was used to adjust the interelectrode spacing.

The cathode used in the arc chamber was a Ta-tipped graphite rod. The preparation and use of this cathode is described in reference 3. This special cathode stabilized the arc and eliminated the electrical noise originating from arc wander.

The anode was a high-purity cupped graphite rod with the same shape as the electrode designated S-14 by the American Society for Testing Materials (ref. 4). The sample was contained in the lower electrode which was always the anode in this investigation. However, for other applications, switch S1 (fig. 4, p. 10) was used for switching the polarity of the lower electrode and at the same time maintaining ground potential through the clamp to the optical bar.

The vacuum seal between the quartz cylinder and the Viton gasket was achieved by hand grinding the ends of the quartz cylinder to a 5-micrometer polish on a flat plate. Final polishing was then done on a metallographic polishing wheel using 0.05-micrometer-diameter alumina. The quartz cylinder was rotationally alined so that each time the chamber was reassembled the arc light was always transmitted to the spectrometer through the same area on the cylinder.

The chamber in figure 2 included a modification that minimized cumulative fogging of the quartz cylinder caused by the sequential vaporization of 11 samples. The chamber was modified by inserting a specially constructed quartz tube between the arc discharge and the transmitting area of the quartz cylinder, in figure 2. The binocular design of the antifog tube allowed optical transmission along separate optical axes to the spectrograph and to the spectrometer. The larger ends of the tubes were open but were shaped to fit against the circumference of the quartz cylinder. This contact between the antifog tube and the quartz cylinder was adequate to prevent penetration of vapor onto the window area. The opposite end of the tube was cut out slightly larger than the respective optical apertures of the spectrograph and the spectrometer. The relatively small open areas of the antifog tube effectively limited fogging of the optical window to less than 2 percent for vaporization of 44 milligrams of silver chloride (AgCl) (11 vaporizations of 4 mg of AgCl each).

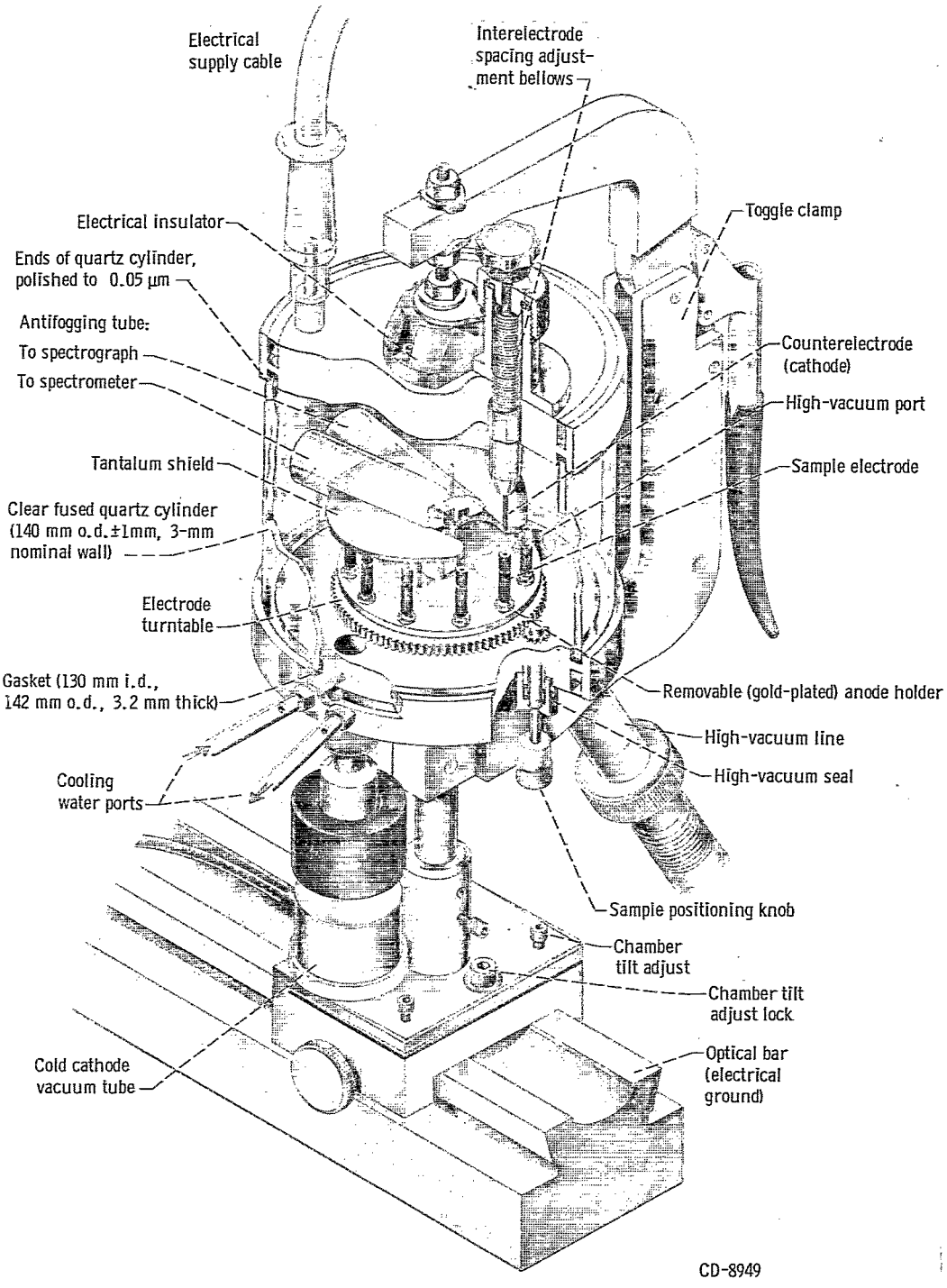


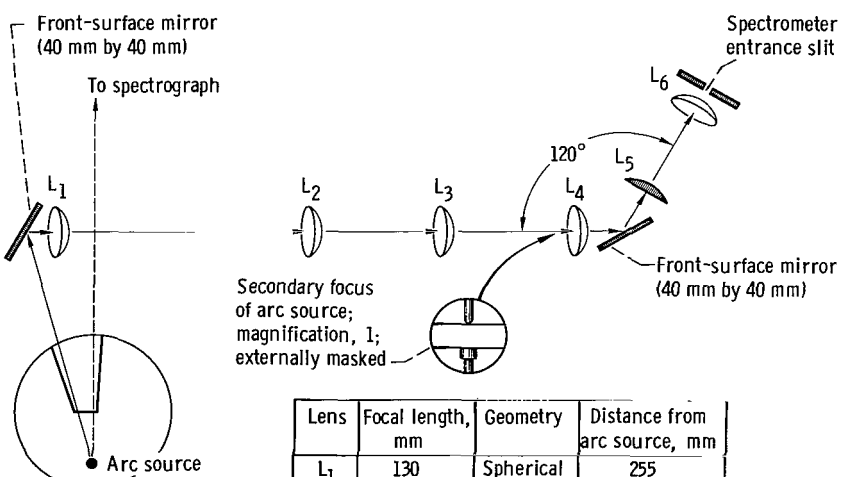
Figure 2. - Controlled-atmosphere arc chamber. (Top of chamber is at high voltage during instant arc is spark ignited. Precautions must, therefore, be taken to prevent contacting chamber top at this time.)

Another modification made to the arc chamber was the method of elevating the sample electrode with respect to the other chamber. This elevation was necessary to allow vertical alinement of the sample electrode with the optical axis of the spectrometer without interference of the optical aperture by the other structures in the chamber. The necessary elevation of the anode was obtained by tilting the chamber slightly forward, as shown in figure 2.

Source-to-Spectrometer Optics

The optical paths between the arc chamber and the spectrograph and spectrometer are shown in figure 3. These optics were designed to allow simultaneous viewing of the arc light with both the spectrometer and the spectrograph.

The electrodes were critically positioned on the spectrometer axis by projecting images of the electrodes on L4 (fig. 3). Index marks on a mask at L4 were used for both vertical spacing (interelectrode spacing) of the electrodes and for horizontal alinement of the anodes as they were rotated into arcing position. The external mask at L4 also served to prevent the bright electrode radiation from entering the spectometer. A similar external mask (not shown) was located in the optics to the spectrograph.



Lens	Focal length, mm	Geometry	Distance from arc source, mm
L_1	130	Spherical	255
L_2	87	Spherical	510
L_3	67	Spherical	645
L_4	80	Spherical	780
L_5	50	Cylindrical	875
L_6	165	Spherical	970

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Figure 3. - Schematic diagram of source-to-spectrometer optics. Lens diameter, 30 millimeters.

Controller

The controller, described in table I, produced an error signal from the voltage difference between two input signals. With this controller, three modes of control, proportional, derivative, and integral, were used to generate a resultant control signal. The actions of the three modes of control produced the resultant control signal $\mathscr{E}$ of figure 1. The gain controls of the proportional, derivative, and integral stages of amplification were adjusted to yield sensitive and stable control of light intensities from the arc column. These conditions were determined empirically by changing the R (resistance) and C (capacitance) values in all three circuits for a series of sample arcings. The R and C values selected in this way were incorporated into the circuits of the controller. A more detailed description of the controller, including a circuit diagram, the gain control circuits, component values, and gains, is given in appendix A.

The voltages and currents applied to the controller were 0 to 10 millivolts and 0 to 10 microamperes. The output control signal from the controller to the phaser (fig. 4) was 0 to 1 volt (dc), and 0 to 1 milliampere.

Direct-Current Arc Source

The schematic circuit of the full-wave-rectified, thyratron-controlled dc source and its connections to the electrodes in the arc chamber is shown in figure 4. The current capacity of the thyratrons was about 40 amperes. Open-circuit voltage between the arcing electrodes was variable, being dependent on the conducting phase angle of the thyratron tubes. This voltage ranged from 150 volts for 10 amperes (conduction late in the half cycle) to about 220 volts for 40 amperes (conduction over the complete half cycle).

The dc source contained a phaser (fig. 4) for controlling the current through the thyratrons. Connections to positions A or B in figure 4 allowed the thyratron current to be controlled by voltages applied at these points. The voltage at A was supplied by a Zener-regulated dc source (not shown) and was used to set a small bias voltage on the phaser to establish a minimum current level during operation. The use of this control prevented the arc current from going to very low currents which could cause the arc to extinguish during operation. The voltage at position B was the control signal $\mathscr{E}$ produced by the controller. The 0- to 1-volt range of $\mathscr{E}$ was sufficient to change the arc current from the minimum allowed by the bias voltage at A to the maximum current capacity of the thyratrons.

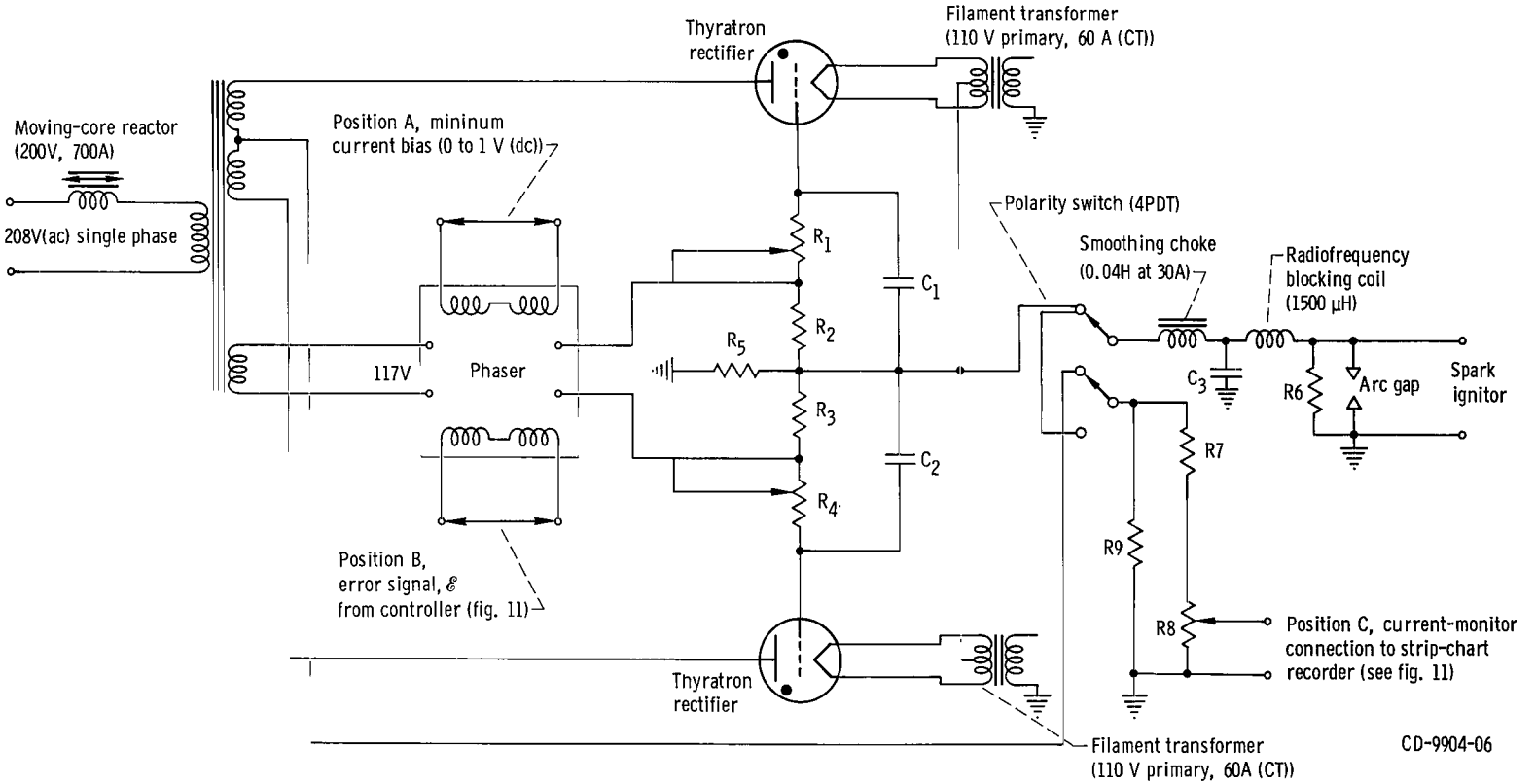


Figure 4. - Schematic diagram of phase-sensitive dc source. C_1 and C_2, 0.005 microfarad, 600 volts dc; C_3, 0.05 microfarad, 600 volts; R_1 and R_4, 1 megohm (variable); R_2 and R_3, 82 kilohms, 1 percent; R_5, 500 ohms, 40 watts; R_6, 1 megohm, 5 watts; R_7, 10 megohms, 0.5 watt; R_8, 20 kilohms, variable; R_9, 0.5 ohm, 500 watts. Phaser, Vectrol series VV60/901, type C, Vectrol Engineering Inc..

PROCEDURE

Procedures were established for controlling light intensities from the dc arc by use of the apparatus of figure 1. These procedures involved selecting the spectral light to be controlled, establishing a program representing the desired time dependency of light emission, and determining the best gain settings in the controller.

When the apparatus is applied to control light emission in existing dc arc methods, no single control procedure can serve for all cases. Factors which were important in the control procedures, such as the time dependency of light emission, can be different for each arc method. For this reason, some generalized procedures were established for both time-dependent and non-time-dependent light emission and also for spatially stabilized and unstabilized light emission. Thus, these procedures can serve for approximating the control conditions for other dc arc methods.

Control of Time-Dependent and Spatially Stable Light Emission

In this type of control, stable light emission was produced by a stabilized dc arc operated in an argon atmosphere. The specifications for the electrodes and for the argon atmosphere are listed in table I (p. 4). In this investigation, an arc current of about 60 amperes was used to prepare the Ta spheres on the graphite cathode as compared with 30 amperes used in reference 3. The Ta spheres prepared at 60 amperes were about 2.3 millimeters in diameter. The Ta-tipped cathode was offset with respect to the cathode-anode centerline, as shown in figure 5. The reason for using the offset in cathode alinement is discussed in the section DISCUSSION OF RESULTS.

With the use of this stabilized argon arc, the control system was applied to the control of vaporization of silver chloride (AgCl) following the procedure for microanalysis described in reference 2.

Selection of spectral light. - The spectral line selected for control was silver (Ag), 3502 Å (or 10^{-10} m). This line was selected because it was relatively free of interferences from other atomic lines and also free of self-absorption with the conditions reported in this investigation. A multiplier phototube located at this spectral position in the spectrometer provided the emission signal E_1, which was proportional to the Ag line intensity. Another multiplier phototube located at 7004 Å detected the same line emission, but in second order, and was used to obtain time-integrated values for the Ag line intensity.

During vaporization of AgCl in the arc the Ag line intensity initially increased to a maximum and then dropped to zero as the AgCl was completely vaporized. Thus, the vaporization rate of the AgCl and its spectral light intensity were time dependent. The

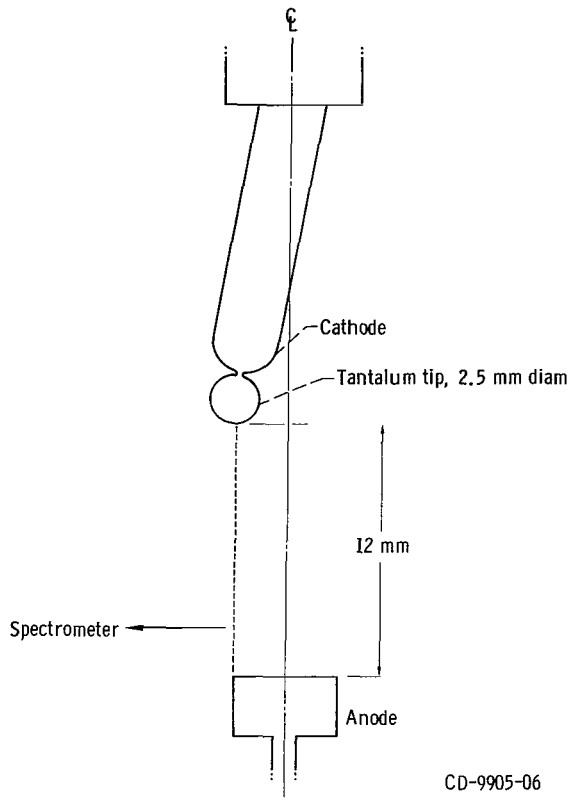


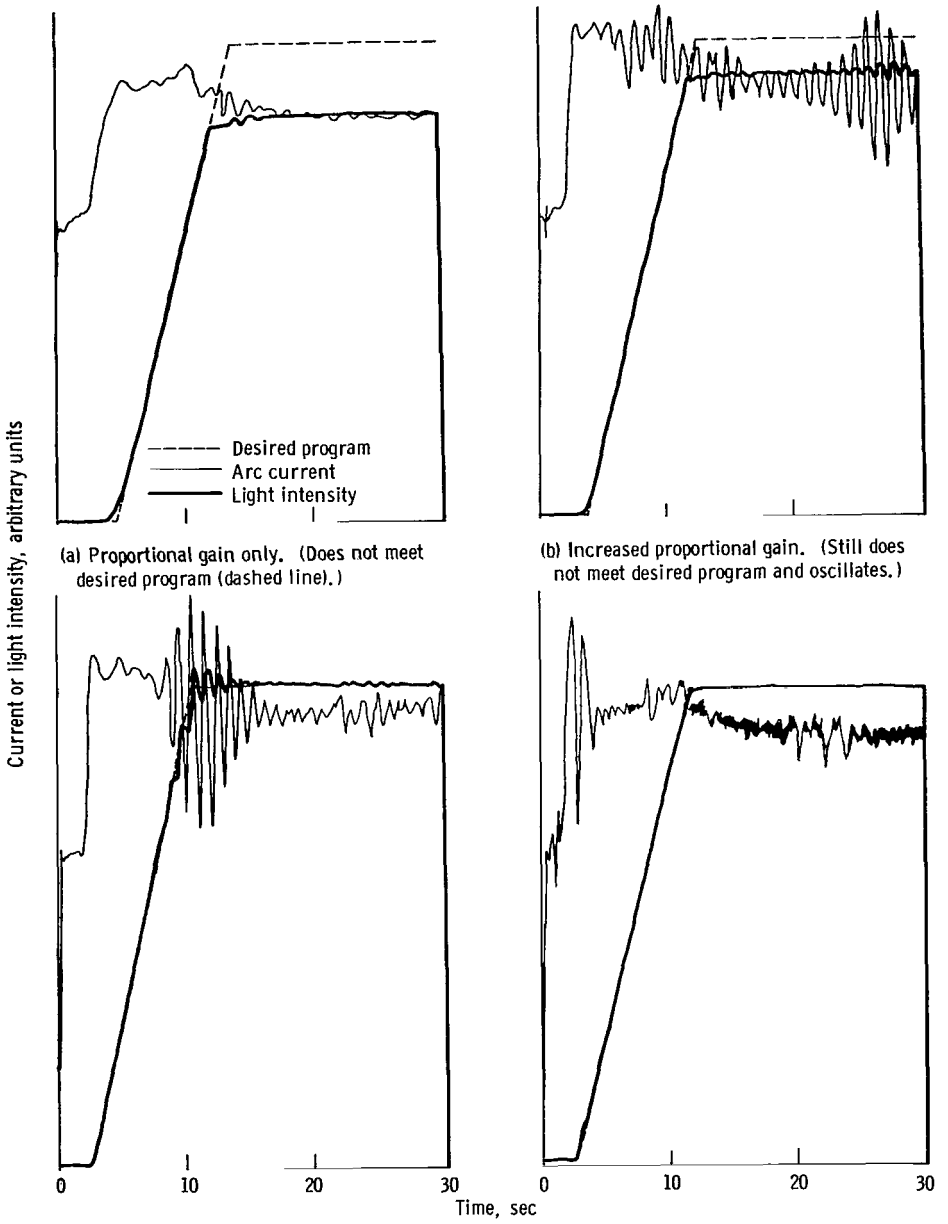
Figure 5. - Electrode orientation in argon arc chamber for achieving optimum control with servocontroller. (Offset from centerline may be either toward spectrometer or away from spectrometer.)

time required for total vaporization of four milligrams of AgCl was about 20 seconds at an arc current of 30 amperes.

Establishing the control program. - The vaporization of AgCl was controlled by programming the intensity of the silver line emission. The stepwise procedure for establishing this program and for achieving stable control of Ag emission was as follows:

(1) Samples of AgCl (about 4 mg) were vaporized from the anode with a constant-current 30-ampere arc in argon. A strip-chart-recorder trace was made of the Ag line intensity plotted against time. Several of these strip-chart traces were used to estimate an average vaporization profile for AgCl for the conditions used. Precise averaging of the vaporization profiles was advantageous only when good control was difficult to achieve. However, when control precision was not a problem, a rather crude approximation of the average profile, such as is shown in figure 6, was adequate.

(2) This averaged vaporization profile was traced on the metallized chart of the curve-following programmer. The speed of rotation of the chart drum was so geared that the drum rotated about one revolution for each sample vaporization. The rotation of the drum generated the reference signal E_2 of figure 1.



(a) Proportional gain only. (Does not meet desired program (dashed line).)

(b) Increased proportional gain. (Still does not meet desired program and oscillates.)

(c) Introduction of integral gain with proportional gain to meet desired program. (System still oscillates.)

(d) Introduction of derivative gain with proportional and integral gains to damp oscillations, resulting in precise control.

Figure 6. - Strip-chart traces illustrating typical stepwise stabilization of closed-loop controller. Arc atmosphere, argon; pressure, 345 torr; sample, 4.0 milligrams of AgCl in anode cavity; spectral line controlled, Ag, 3502 A.

(3) The current range was set from the maximum current capacity of the thyratrons (approx. 40 A) to some arbitrary minimum current. The minimum current was established at about 18 amperes by a bias of about 0.18 volt at position A, figure 3.

Determination of gain parameters. - The conditions for stable control of spectral light were determined by adjusting the gain controls of the controller while arcing a series of samples. The general procedure that was followed for establishing the program is outlined in the following steps (1), (2), and (3). These steps are illustrated in figure 6. The traces are representative of current and intensity of the 3502 Å line, as they appear on the strip-chart recorder. The dashed lines in figure 6 represent the programmed intensity level determined in step (2) of the preceding section.

(1) Several samples were first arced with only proportional control. In this series of arcings, the proportional gain was gradually increased between arcings from a condition illustrated by figure 6(a) to the point of oscillation illustrated by figure 6(b). The proportional gain was then set at some intermediate point between that used in figures 6(a) and (b). Typically, after this procedure the light intensity did not meet the desired program level represented by the dashed lines.

(2) The sample arcings were continued with both proportional and integral gain. The integral gain control was increased until the average light intensity was approximately the same as the desired program level. As shown in figure 6(c), increasing the integral gain did aid in achieving the programmed level but also caused the system to oscillate.

(3) The oscillations caused by the use of integral gain were minimized by gradually increasing derivative gain. The stabilizing effect of the correct amount of derivative gain is shown in figure 6(d).

Each of the three steps required arcing 10 to 20 samples to determine the optimum gain levels for stable control. After conditions had been established for stable operation of a sample-anode combination, the same gain settings were used for arcing all subsequent samples of the same type.

Control of Non-Time-Dependent and Spatially Stable Light Emission

Control of light emitted from the stable argon arc, with no sample in the anode, was achieved with a non-time-dependent program. The light used for this control was the spectral continuum at 3500 Å.

Control with a non-time-dependent program was advantageous when the main constituents in a sample were vaporized at an approximately constant rate. In such cases the initial increase in light intensity was ignored, with the integration time starting when the light intensity reached a constant programmed level. The following procedure for

control of the spectral continuum, therefore, also typifies a method for using the controller with samples vaporized at a constant rate.

The procedure for controlling non-time-dependent light intensities from the argon arc was, in general, the same as that given for time-dependent light intensities. However, because the light intensity was relatively constant with time, the control voltage E_2 was also constant rather than time-dependent. Thus, the curve-following programmer was not used for this control. With non-time-dependent light the conditions for stability were more easily determined than with a time-dependent emission because the gain adjustments were made with the arc operating continuously, and it was therefore unnecessary to use as many repeat arcings as with time-varying light.

The gain values of the controller were determined for stable and sensitive control of the spectral continuum at 3500 Å.

Control of Spatially Unstable Light Emission (Wandering Arc in Air)

The dc arc in air between graphite electrodes is typical of spatially unstable arcs. Stable control of this arc was not achieved because of random light fluctuations caused by arc wander. But the light output of the unstable arc was controlled by operating the arc in a nonperiodic oscillating mode. The oscillations of light intensities were caused by deliberately increasing the proportional gain to near maximum. At high proportional gain both the current and the spectral light intensities oscillated rapidly. The maxima and minima of the light intensity fluctuations occurred at approximately the programmed level. The procedure for controlling the vaporization of analytical specimens in the oscillating mode is as follows:

(1) Samples, in the form of either metal turnings or powders, were packed into a cupped anode and arced in air. The signal from the multiplier phototube, alined on the major element, was used to generate E_1, as with stable light emission.

(2) Conditions were next established for achieving smooth vaporization of samples from the anode cavity by using a dc arc in air. Conditions such as sample weight, anode type, current, and exposure time were selected by using the same general procedures as in conventional dc arc analysis.

(3) A strip-chart-recorder trace was made of sample vaporization with time by using an uncontrolled arc at the desired current.

(4) The control voltage E_2 was then set at a constant value (non-time-dependent) equal to the average magnitude of E_1 determined from the deflection of the strip-chart pen in step (1) in this section. A convenient method of setting the value of E_2 was to displace the probe of the curve-following programmer an equal distance to the displacement of the strip-chart pen when measuring E_1.

(5) Samples were arced with the proportional gain near maximum, and with sufficient integral gain to achieve control at the programmed level; that is, the displacement of the strip-chart-recorder pen and the curve-following programmer were the same.

RESULTS

Control of Time-Dependent and Spatially Stable Light Emission

The closed-loop controller proved effective for control of time-dependent Ag light intensity emitted from samples of AgCl vaporized in the dc arc. Compared with samples vaporized at constant current, both the instantaneous and the time-integrated intensities were more repeatable when the control system was used. Figure 7 illustrates the effectiveness of instantaneous control of Ag line emission at 3502 Å as compared with a conventional arcing procedure at constant current.

Figure 7(a) shows a typical superposition of five repetitive vaporizations of 4.0 milligrams of AgCl from the anode cup at a constant current of 30 amperes. The poor repeatability of the instantaneous light emission can be seen in the traces. The relative standard deviation of the intensities integrated over the total vaporization times was 7.5 percent. Similar experiments gave relative standard deviations ranging from about 6 to 11 percent.

Five vaporizations were superimposed in figure 7(b) by using the new method of controlling light intensities with variable current feedback. The initial shape of this program approximated the vaporization rate at constant current as shown in figure 7(a). However, after the initial increase in light intensity to about 70 percent of the peak of the lowest trace of figure 7(a), the programmed level was made constant to the end of the integration time. The arc was terminated before completion of vaporization, and thus the amount of AgCl placed into the anode was not critical. This program gave an adequate approximation of the average vaporization profiles at constant current.

With the silver light emission controlled, the instantaneous intensity closely followed the prescribed program. The relative standard deviation of the time-integrated emission was 0.9 percent. This value was typical of the precision obtained for repetitive arcings on the same day.

Fluctuations in the current levels in figure 7(b) were indicative of the amount of current correction required to keep the Ag emission intensity at the programmed level.

Precise control of Ag emission in the arc column also improved the source precision with respect to continuous background emission. A summary of precision data for Ag emission and continuous background emission at various spectral positions is shown in

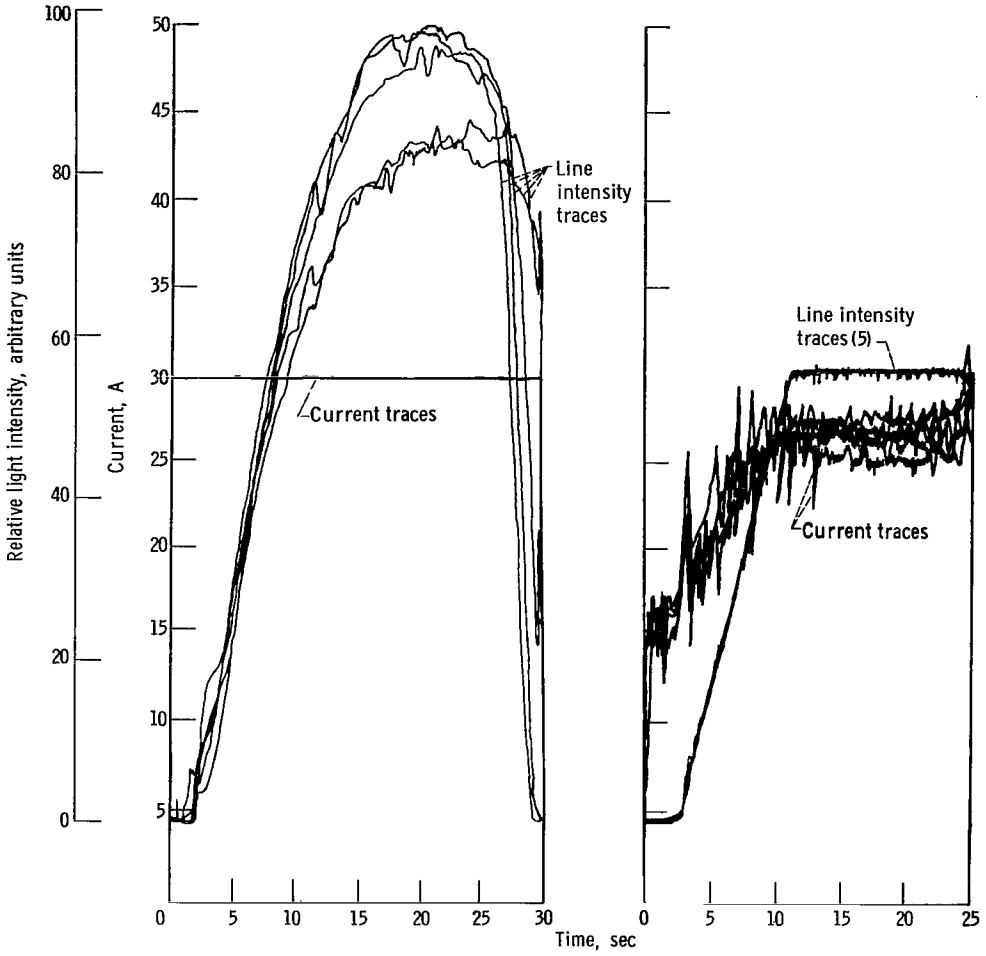


Figure 7. - Comparison of repeatability of silver light emission with time. Arc atmosphere, argon; pressure, 345 torr; cathode, Ta-tipped graphite; sample, 4.0 milligrams of AgCl in anode cavity; spectral line controlled, Ag, 3502 Å.

figure 8. Comparative precision data at the listed wavelengths are shown for (1) the wandering arc in argon between graphite electrodes, (2) an arc in argon spatially stabilized with a Ta-tipped graphite cathode, and (3) an intensity controlled arc. Shown in figure 8(d) is the instrument precision of the integrating readout system when a constant light source is used. The differences between the repeatability obtained in figures 8(a), (b), and (c) and that obtained in 8(d) are indicative of repeatability of the arc sources alone.

The constancy of the background at the various spectral positions shown was improved to about 2 percent, relative standard deviation, by controlling the Ag emission. The readout repeatability for the constant light source averaged about 0.5 percent, relative standard deviation.

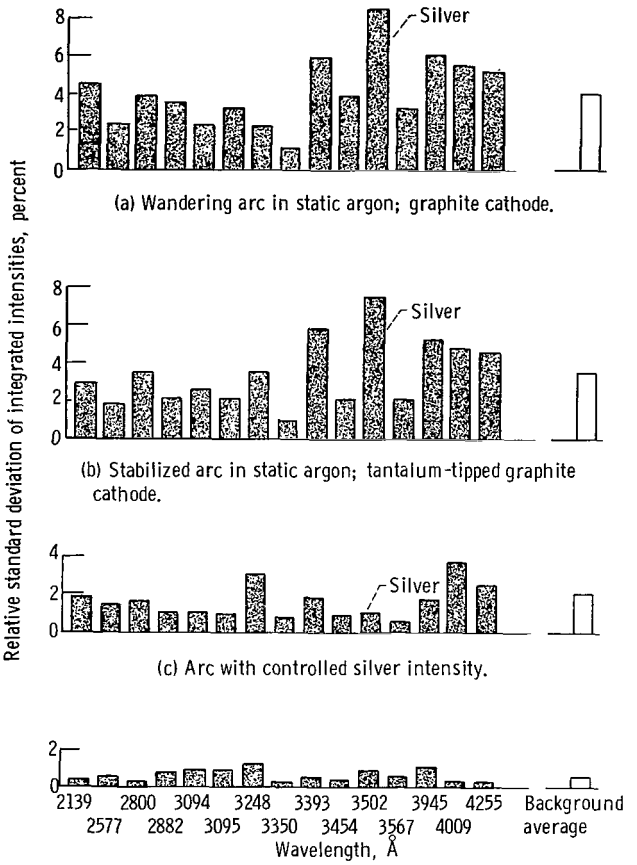


Figure 8. - Repeatability of spectral background and silver emission. Integration time, 30 seconds; sample, 4 milligrams of AgCl in anode cavity.

Control of Non-Time-Dependent and Spatially Stable Light Emission (Argon Continuum at 3502 Å)

In the control of continuous background emission from the stabilized argon arc without a sample in the anode, the system response was sensitive and rapid. To illustrate this control, traces of light intensity at constant arc current were compared with traces made with the light controller in operation. Figure 9(a) shows a gradual upward drift of arc light intensity with time. The arc was operated in the enclosed chamber at a constant level, and the drift was caused by heating effects in the chamber. The placement of an optical filter (90 percent transmission) in the optical path at the positions indicated caused a 10 percent attenuation in the light intensity, as shown in the trace.

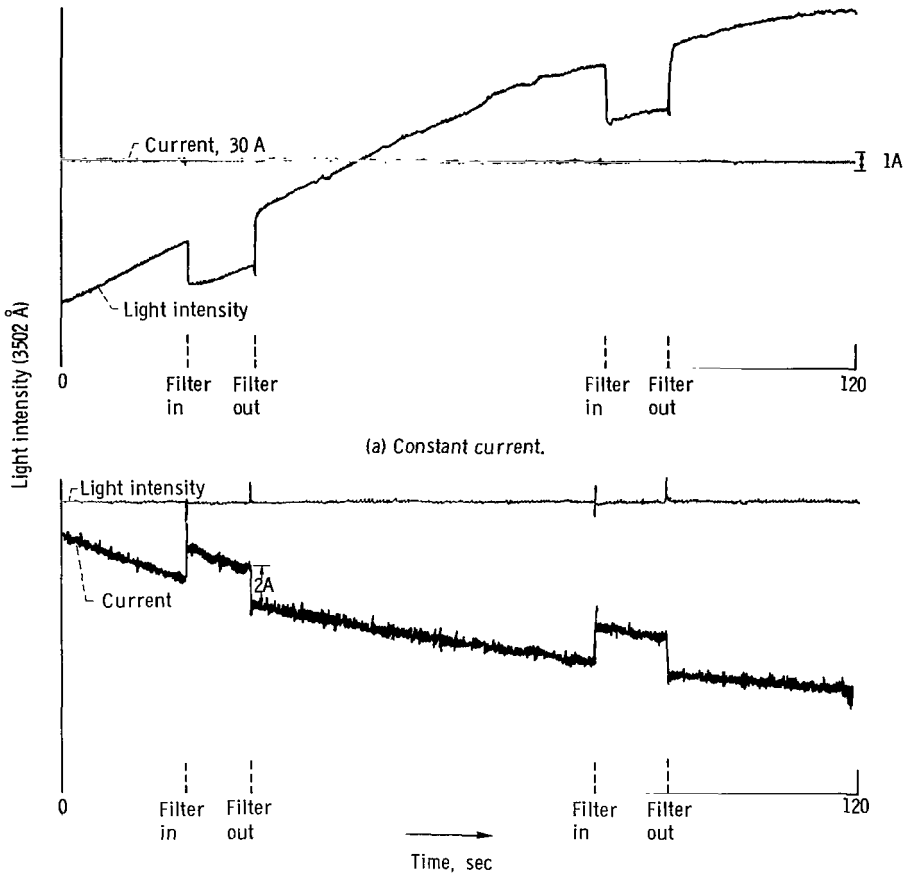


Figure 9. - Effect of light attenuation on arc current and light intensity for constant-current arc and intensity controlled arc. (With constant-current arc, insertion of filter (90 percent transmission) attenuated light intensity, whereas insertion of filter with intensity controlled arc caused compensating increase in arc current. Only disturbance when filter was inserted in case (b) was light spikes at positions when filter was inserted and removed from optical path.)

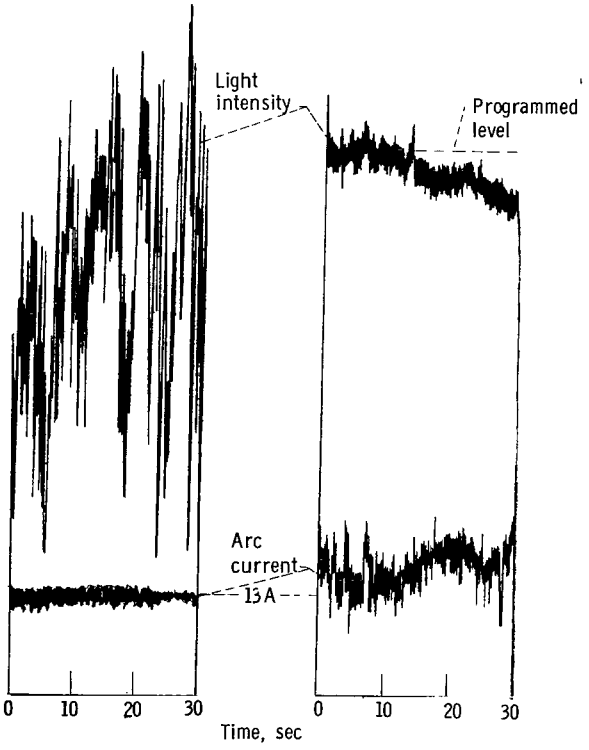
Figure 9(b) represents the same experiment as 9(a) except that the arc light intensity, rather than the arc current, was controlled. As shown, the light intensity remained constant as the current changed slowly to compensate for the increased light emission from the arc. When the filter was inserted with these conditions, the current increased rapidly to compensate for the light attenuation caused by the filter. The only disturbances noted in the traces of light intensity were the spikes at the positions where the filter was inserted and again when it was removed.

Control of Spatially Unstable Light Emission (Wandering Arc in Air)

The experimental results for control of unstable light emission are illustrated in figure 10. Strip-chart traces were made with the use of an arc in air at constant current (fig. 10(a)) and also with controlled light intensity (fig. 10(b)). In these tests the sample, about 50 milligrams of a titanium (Ti) alloy (National Bureau of Standards No. 173), was vaporized at a current of about 13 amperes. The light intensity controlled was titanium (Ti) line emission at 3349 Å.

A comparison of figure 10(a) with figure 10(b) shows that the instantaneous fluctuations of the titanium line intensity were reduced when controlled light intensities were used as in figure 10(b). Furthermore, the average light intensity in figure 10(b) was near the desired program level represented by the dashed line.

These traces were typical of the control achieved for a variety of samples vaporized with the arc in air. Samples arced in this way included argillaceous limestone, low-



(a) Vaporization at constant current.

(b) Vaporization by controlled light intensity.

Figure 10. - Strip-chart traces showing control of light intensity from dc arc in air. Sample, 50 milligrams of Ti alloy, National Bureau of Standards No. 173, vaporized from anode cavity; spectral light controlled, Ti, 3349 Å.

carbon steels, iron ores, titanium alloys, cobalt-base alloys, bismuth metal, and tin metal.

Although both the arc light intensity and the current appeared to oscillate rapidly in this form of control, no fundamental frequency was found with an oscilloscope. The repetition rate in this oscillating mode of control appeared to vary randomly between about 2 and 10 hertz.

DISCUSSION OF RESULTS

Arc Stability and Controllability

The experimental tests of the controller with the stable argon arc and with the wandering arc in air demonstrated the application of the controller to arc sources with widely differing stabilities. From the results of these experiments, some generalizations may be made for arcs of intermediate stabilities.

Control of the background continuum emission from the stable arc in static argon atmospheres exemplified the best control that was achieved. However, no analytically useful free-running arcs have such high stability. Control of this arc, therefore, demonstrated the control system capability when arc instabilities were not limiting. The high control accuracy and the rapid and sensitive system response for this arc were shown in figure 9.

The relatively smooth vaporization of AgCl in a stable argon arc was also controlled with good precision. In this case an arcing procedure similar to that reported in reference 2 was used for determining trace metals weighing as little as 1 nanogram. Control of silver vaporization in this arc, therefore, typified the best that was achieved with an analytically useful arc. The precision of the time-integrated Ag line and background intensities, when Ag line emission was controlled, averaged 2 percent with a range from about 0.6 to 3.7 percent for the 15 detection channels tested. These precision figures do not represent precision of analyses because no metal elements were present in the anode. However, they do indicate the best precision obtainable from this procedure without internal standards.

The control of Ti light emission from the wandering arc was a useful type of control that can be used with very unstable arcs. This arc had a poorer stability than will usually be encountered with arcs in air because no attempt was made to produce a smooth vaporization of Ti. In many arc methods the vaporization of samples into the arc column induces a degree of stability. Therefore, the source stability of these arc methods will be intermediate between the wandering arc in air and the stabilized arc in argon. In general, those arc procedures yielding the smoother sample vaporization will also yield the better possibilities for control of spectral intensities.

Validity of Controlling Sample Vaporization by Controlling Spectral Line Intensities

In applying current feedback to control sample vaporization, spectral line intensities were used as a direct measure of vapor concentration in the arc column. Thus, the precision of the counts from the spectrometer readout were used to indicate directly the precision of controlling sample vaporization. The reason for using a direct relation between light intensities and the amount of sample vaporized from the anode is discussed in this section.

The relation between spectral line intensities and vapor concentration in the arc column is given by

$$I = kC^n \tag{1}$$

where

I intensity from emitting element

k constant

C concentration of element in arc column

n empirical factor (ideally n = 1)

This equation is the basis for quantitative spectrochemical analysis. From equation (1), the spectral intensity I is directly proportional to vapor concentration C only when n = 1. However, n can have any value from about 0 to 1 depending on the conditions of the experiment. When n is maximal, the light intensities are most sensitive to changes in vapor concentration. For values of n less than 1 the control of spectral intensities can still be used to control sample vaporization, but with less control sensitivity.

Whatever the value of n is, the control of sample vaporization by using current-feedback is best done if n is independent of arc current. The dependency of n on arc current was determined experimentally for the vaporization of AgCl in the argon arc. These experiments showed that n was independent of arc current and that, therefore, the control of silver spectral light emission provided direct control of AgCl vaporization. A description of these experiments and the results thereof are summarized in appendix B.

Determination of Conditions for Control Stability at Optimum Gain

One of the limitations of the control method described herein was the necessity for empirically establishing conditions for sensitive and stable control for various arc con-

ditions. Because of the number of variables involved, it was not practicable to establish an exact procedure for stabilizing the controller for all arcing conditions. In the application of stable light control to various combinations of anode, sample, and current, the general procedure outlined previously was useful for approximating the best gain parameters for stable control. However, final adjustments of proportional, derivative, and integral gains were made by trial and error while the samples were arced.

An important consideration when new sample-anode combinations were arced was the gain of the arc column itself. This gain can be expressed as the incremental change of the current required to produce an incremental change in atomic emission of the line for control, that is, di/dI. Because this gain parameter was determined by both vaporization and excitation phenomena, it was subject to change for every sample-anode combination.

In addition, the arc gain may change throughout the vaporization cycle. For example, the initial heating of the sample to produce atomic emission is a low-gain condition. In this early portion of the cycle a higher current was required to produce measurable light intensities. Later, when the thermal inertia of the anode was overcome, the arc column gain was relatively higher. Likewise, the arc gain was less when the sample passed the maximum intensity in the normal vaporization cycle. This variable-gain condition encountered in sample vaporization was difficult to evaluate quantitatively and was a primary reason for the use of an empirical approach.

Variations in optical gain (transmittance) can also affect system stability and sensitivity. In the system described, there were 23 optical surfaces (two surfaces per lens) between the arc and the photocathode. Dust deposits on these surfaces decreased the transmittance of the optics and resulted in lower system gain. Conversely, cleaning the lenses can result in higher system gain, which can cause a previously stable arc to oscillate. However, these optical effects can be reduced to tolerable limits by wiping the lens surfaces regularly.

The fogging of the quartz window was also detrimental to the operation of the controller. When the transmittance of the interior surface of the quartz window was reduced by vapor deposits, the control system automatically corrected for decreased light intensity by raising the average arcing current for each succeeding arcing. This correction was undesirable because it was not directly related to Ag concentration in the arc column. The purpose of the antifog tube, therefore, was to minimize changes in the transmission of the optical window of the arc chamber that can occur during a series of sample arcings. By using the antifog tube, no systematic drift in average current was observed for a series of 11 sample arcings. The quartz surface was wiped with tissue when loading each group of 11 samples into the arc chamber.

One of the important conditions for achieving maximum control sensitivity of Ag in the argon arc was the cathode offset alinement shown in figure 7. Proportional gains

from four to five times higher were used with the offset cathode as compared with the conventional axial alinement of the electrodes. However, with the pure argon arc containing no sample in the anode, the best control conditions did not appear to be dependent on the cathode orientation. The cause of this effect is unknown. Possibly the gas flow from the cathode (cathodic gas streaming) and the sample vapors from the anode interacted to cause local disturbances in the arc column. The gas flow in the arc column appeared to be more laminar with the offset alinement than with axial alinement of the cathode.

Applications of Controller to Existing Direct-Current Arc Methods

Investigations of the effect of vaporization control on analytical precision of dc arc analysis are in the preliminary stage. If the emission of the major element in the sample is directly controlled, the minor elements can be indirectly controlled. Factors that are believed to be important in the indirect control of minor elements are (1) a more reproducible vapor composition resulting in a more reproducible excitation in the arc column, and (2) a more reproducible temperature at the anode. These factors can lead to improved analytical precision, even for elements that are selectively vaporized during arcing. Thus, in principle, the need for internal standards can be decreased and possibly eliminated by sufficiently precise control of a major element in the sample.

The control apparatus and procedures can be adapted to conventional dc sources and to existing analytical methods. Improved analytical precision will thereby result for those methods in which sample vaporization is a major cause of error. However, in most analytical methods the total analytical error is usually known, but neither the causes of error nor their distribution are known. Unless the vaporization error is known, it is impossible to predict accurately the effect of controlling light emission on analytical precision. An empirical test of the controller for specific analytical methods must therefore be performed. When the controller is tested on specific analytical procedures, any improvement in precision can be assumed to result from a decrease in the vaporization error. Similiarly, when improvements in analytical precision are not observed with precise control of sample vaporization, it can be assumed that other causes of error predominate. In this case, attention can be given to other causes or errors, such as sampling, blank, chemical reaction, etc., to improve analytical precision.

CONCLUDING REMARKS

With the electronic control technique described in this report, spectral emission from samples vaporized in a dc arc was made more repeatable compared with uncon-

trolled arcs. The controller automatically adjusted the arcing current to cause the emission of a selected spectral line to follow a prescribed program. When spectral line intensities were a direct measure of element concentration in the arc column, the controller allowed direct control of sample vaporization from the anode. In the most favorable case the errors caused by nonrepeatable sample vaporization were reduced to about 1 percent (RSD). This was about the precision limit of the spectrometric system used in this investigation. The controller was best used with a stabilized arc in argon but was also useful with unstable arcs in air. Although closed-loop control systems are used widely, the application of this method to control spectral light intensities and sample vaporization in emission spectroscopy has not been previously reported.

The control apparatus can be used for feedback control of spectral intensities with other sources in addition to dc arcs. In this control the light intensity can be emission from source continuum, molecular band emission, or atomic line emission. It is suggested that automatic feedback control of emission from hollow-cathode discharge lamps and also from microwave-induced discharges could improve the analytical uses of these sources. In the case of the microwave-induced plasmas there is some basis for controlling excitation conditions in the plasma by controlling atomic line intensity ratios. These sources appear to have a relatively linear relation between source power and plasma temperature (as measured by atomic line intensities) (refs. 5 and 6). This characteristic provides the means for controlling plasma temperature by controlling line intensity ratios with source power used as the feedback parameter. Advantages in chemical analysis could result from such control because shifts in excitation temperature that can occur with changes in plasma composition would be reduced.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 6, 1968,
129-03-14-04-22.

APPENDIX A

SCHEMATIC DIAGRAM AND SELECTED GAIN PARAMETERS FOR CONTROLLER

The schematic diagram of the controller circuit is shown in figure 11. This diagram is a revision of the commercial controller listed in table I (p. 4). The circuit excludes nonessential circuitry of the commercial amplifier and includes component modifications made for this investigation.

Shown in the upper left corner of the diagram is the circuit for comparing the emission signal E_1 with the reference signal E_2. The magnitude of E_2 was determined by the 0- to 100-ohm potentiometer that was mechanically driven by the curve-following programmer, as illustrated. In the lower right corner of the diagram is the resultant control signal $\mathscr{E}$ from the controller.

The resistance R and the capacitance C in the various gain circuits of the controller are located by the symbols R_a, R_b, C_b, R_c, and C_c, where a, b, and c designate the proportional, derivative, and integral circuits, respectively. The values given for these resistances and capacitances were selected for the control of AgCl vaporized in the argon arc with the conditions described in this report. When other samples and arcing conditions were used, the optimum values of R and C in these circuits were determined empirically by arcing a series of samples.

With the R and C values in figure 11, the voltage gains for the three amplifier types were measured. Table II summarizes the R and C values and approximate gains used to control Ag emission from the argon arc. These gain values can be useful in duplicating the results reported herein. However, this will be the case only when the electronic loop components such as multiplier phototube have comparable sensitivities to those used in this investigation.

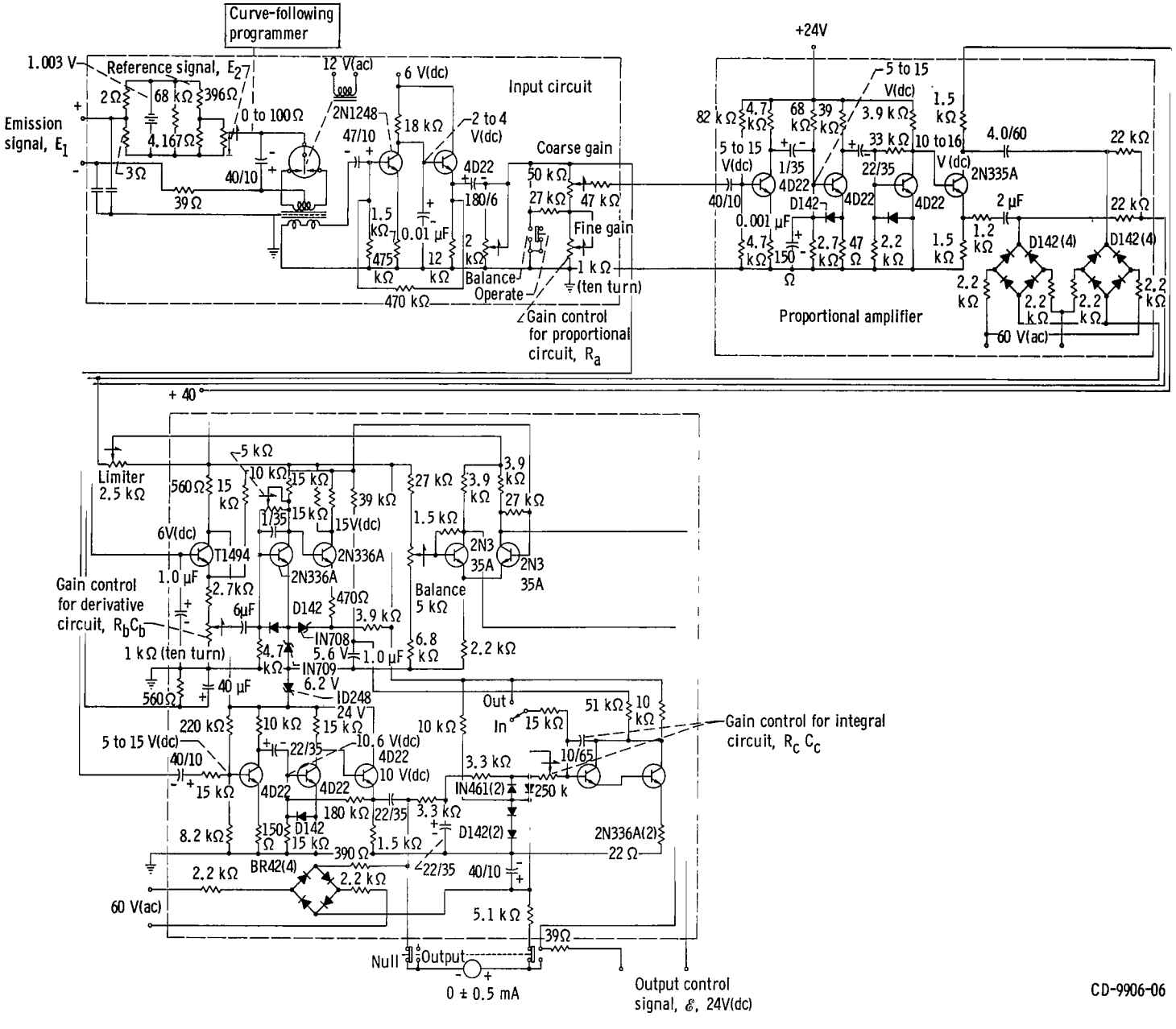


Figure 11. - Schematic circuit of controller amplifier. (Circuit was adapted from that of controller listed in table I.)

TABLE II. - CONTROLLER CONDITIONS FOR CONTROLLING SILVER EMISSION FROM VAPORIZATION OF SILVER CHLORIDE IN ARGON ARC

[Approx. loop gain, 26 V/V.]

Amplifier type	Resistance, Ω	Capacitance, μF	Approximate gain
Proportional	[a]1000	---	1300 V/V
Derivative	[b]400	[d]6	50 V/(V/s)
Integral	[c]60×10^3	[e]10	1000 V/(V)(s)

[a] R_a, fig. 11.
[b] R_b, fig. 11.
[c] R_c, fig. 11.
[d] C_b, fig. 11.
[e] C_c, fig. 11.

APPENDIX B

EXPERIMENTAL DETERMINATION OF n IN EQUATION (1) AND ITS CURRENT DEPENDENCY

Experiments were conducted to determine the value of n and its current dependency for atomic emission of Ag from the vaporization of AgCl in the argon arc. The results of these experiments established that the intensity of Ag, 3502 Å, was directly proportional to the vapor concentration of Ag in the arc column. Furthermore, the relation between spectral line intensity and Ag concentration was independent of arc current. Thus, the control of Ag emission provided a valid control of AgCl vaporization in the argon arc.

Figure 12 shows the experimental data for these conclusions. The figure shows a plot of log I against log C of equation (1) for 4 milligrams of AgCl vaporized at various arc currents. In this plot the line intensity I was assumed to be proportional to the count rate (counts/sec) of the spectrometer readout. The concentration C was assumed to be proportional to the vaporization rate from the anode (mg/sec). From the plot it was concluded that n was 1 and was independent of arc current over the current range tested. Currents ranging from 20 to 36 amperes were used in this experiment, and this current range was somewhat greater than the current range that was required for precise control of AgCl vaporization.

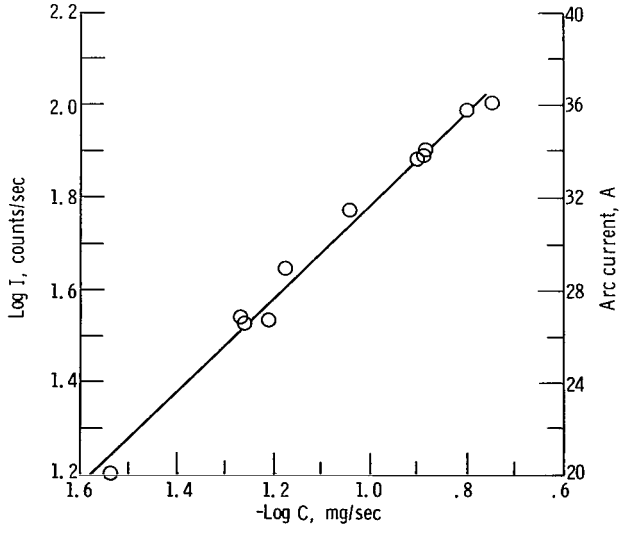


Figure 12. - Determination of n in equation (1) and its current dependency. (n is 1 and is independent of arc current.) Argon arc; pressure, 345 torr; integrating time, 22 seconds at 35 amperes to 137 seconds at 19 amperes.

Although the results of these experiments apply only to specific conditions in the argon arc, they can be explained in a general way. The independence of n and arc current is believed to result from the volume changes of the arc column accompanying changes in arc current. In the range of current and pressure used in this investigation, the volume of the arc column was approximately proportional to arc current. Because of these changes in volume, the average particle density in the arc column and also the apparent excitation efficiency for Ag atoms tended to be independent of arc current.

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