



Electrodeposition on a filament with subsequent thermal atomization followed by excitation for spectroscopic analysis
by Darryl Duane Siemer

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemistry
Montana State University
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Abstract:

Electrodeposition was studied as a method for placing silver onto an iridium filament from which it was subsequently thermally displaced into a radio frequency wave induced helium plasma. The logarithm of the intensity of the light emitted from the silver was found to be directly proportional to the logarithm of the amount of silver over the range of 10^{-11} to 10^{-7} gram of metal. Under the conditions of the study the method proved to be an extremely interference-free as well as sensitive way of determining silver.

Instrumental and other analytical parameters were varied and the effect upon the silver determination was studied. The effect of the presence of several other heavy metals in the plating solution was also investigated.

A cursory study of the probable potential of the method toward the estimation of several other metals was made. Mercury, gold, and copper as well as silver will likely, upon optimization of conditions, prove to be readily analyzable by this method.

ELECTRODEPOSITION ON A FILAMENT WITH SUBSEQUENT
THERMAL ATOMIZATION FOLLOWED BY EXCITATION
FOR SPECTROSCOPIC ANALYSIS

by

DARRYL DUANE SIEMER

A thesis submitted to the Graduate Faculty in partial
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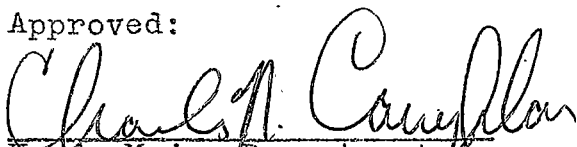
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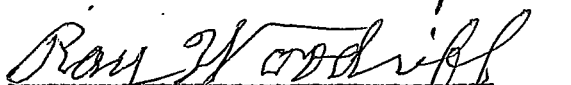
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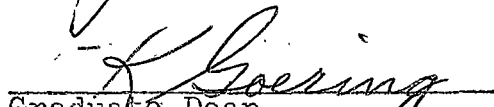
in

Chemistry

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MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1969

ACKNOWLEDGEMENT

I would like to thank Montana State University and the National Science Foundation for their financial assistance during the last two years.

I am grateful for the assistance and suggestions I received from Drs. R. A. Woodriff and J. R. Amend.

The moral support, as well as the time devoted to the typing of this thesis, that I received from my wife Judy is especially appreciated.

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ABSTRACT

Electrodeposition was studied as a method for placing silver onto an iridium filament from which it was subsequently thermally displaced into a radio frequency wave induced helium plasma. The logarithm of the intensity of the light emitted from the silver was found to be directly proportional to the logarithm of the amount of silver over the range of 10^{-11} to 10^{-7} gram of metal. Under the conditions of the study the method proved to be an extremely interference-free as well as sensitive way of determining silver.

Instrumental and other analytical parameters were varied, and the effect upon the silver determination was studied. The effect of the presence of several other heavy metals in the plating solution was also investigated.

A cursory study of the probable potential of the method toward the estimation of several other metals was made. Mercury, gold, and copper as well as silver will likely, upon optimization of conditions, prove to be readily analyzable by this method.

INTRODUCTION

Trace analysis of minute quantities of the heavy metals in water has been an intriguing subject to chemists for many years. The new surge in interest in the effect of these metals on man's environment has spurred much research in more sensitive methods of trace quantity analysis. Some methods commonly used are: colorimetry, electrochemical "stripping" coulombmetry, flame emission spectroscopy, arc or spark spectroscopy, atomic absorption spectroscopy, and neutron activation. Of these methods the most sensitive in terms of the absolute minimum mass of metal detectable is neutron activation analysis (11).

Several recent publications have discussed the use of high frequency induced plasmas in atmospheric pressure gases for spectral excitation of metals (3, 8, 10, 12, 13). Extremely good sensitivities on the order of 10^{-10} to 10^{-13} gram of metal were reported (3, 10, 12). Some methods of introducing the sample into the discharge were: placing a solid sample into a graphite cup and heating the cup inside of an induction coupled gas plasma, introducing it as an aerosol into the discharge, and evaporating the sample from a heated filament into the gas inlet of the discharge chamber (8, 10, 12, 15).

It was thought that if these metals could be electroplated onto a filament readily and subsequently evaporated into a discharge this method would be a very sensitive analytical

tool. The following study is directed at evaluating this technique for the analysis of silver.

STATEMENT OF PROBLEM

The use of atmospheric pressure inert or diatomic gas plasmas as a source for spectral excitation of metals has been studied by several workers (3, 8, 10, 12, 13). Cooke and co-workers used a low wattage microwave discharge for atomic and band emission excitation of F, Cl, S, N, as well as C in organic samples eluted from a gas chromatograph (7). Bache and Lisk used this method for the identification of halogen and phosphorous bearing insecticides (2). This method was estimated by Cooke to be capable of detecting 10^{-16} gram of carbon.

As a tool for the analysis of heavy metals in water the method as described by the above mentioned workers suffers from awkward and sensitivity limiting sample introduction procedures. Fassel and Hume describe a method of sample introduction similar to that used in some atomic absorption units (15). The solution sample is introduced as a liquid aerosol through the use of an ultrasonic dispersing element. Sample introduction rates are limited to tenths of a milliliter per minute¹ which greatly reduces the utility of the method.

If the production of photons in the discharge and of photoelectrons at the photocathode are random processes conforming to a Poisson distribution, then, if a number N of photoelectrons is produced, the standard deviation of N is \sqrt{N} . However, during the time t that N photoelectrons are being

¹More material than this extinguishes the discharge.

produced, there are also from random background "noise" a number nt of photoelectrons being created. Therefore, the total standard deviation of the signal is $\sqrt{N + nt}$. It is obvious that at low signal levels and for long sample introduction times, the total standard deviation can be much greater than \sqrt{N} . Because the detection limit of an analytical method is usually defined as that amount of sample which gives a signal equal to two or three times the standard deviation of the blank ($\sqrt{N_{\text{blank}} + nt}$), slow introduction of an element into an excitation source seriously limits the sensitivity of a method (4).

For this reason the slow evaporation of a sample from a graphite cup into the discharge described by Mavrodineau and Hughes also limits the potential of their procedure. Of course, evaporation of a relatively large volume of water to a volume suitable for placing into a graphite cup is also a step fraught with potential errors.

To circumvent the statistical problem caused by slow introduction of sample, several workers describe techniques in which the sample is introduced into the discharge by its sudden evaporation from a heated metal filament (3, 10, 12, 13). Sensitivities at the picogram level were reported. However, their technique required that sample introduction onto the filament be performed by pipeting a few microliters of solution onto the wire. For analysis of waters which contain ex-

tremely low levels of the metals in question, this step would necessitate extensive preconcentration measures.

Electrodeposition directly onto the filament both as a separation and as a preconcentration measure had not been reported by other investigators. Because electrodeposition of metals at the nanogram level has been shown to be successful, at least on mercury surfaces, it was thought that it would be an ideal approach to placing sample onto the electrode (1, 9, 16). Silver was chosen to be the metal studied for this project both because it has ideal electrochemical behavior and because a difficult analytical problem to which the method might be immediately applicable was available--the analysis of the silver in precipitation due to cloud seeding with silver salts. The presently utilized method, neutron activation, requires access to a nuclear reactor with high neutron flux (14).

EXPERIMENTAL

The apparatus used for this study may be separated into three main categories: electroplating equipment, emission source, and detector.

Electroplating Equipment

Figure 1 illustrates the electroplating apparatus utilized for collecting most of the data described in this paper. An 1800 rpm synchronous motor with a step pulley spins the electrode filament holder which is, itself, held in a glass joint centered in a wheel bearing. Electrical contact is made by bending one of the heavy tungsten wires of the filament holder coincidental with the axis of revolution and letting a cupped brass contact ride over it. The electrolysis vessel of about 8 cubic centimeter capacity is made of pyrex and has a platinum wire sealed into it to serve as an anode. The electrolysis voltage source is a simple rectifier transformer unit common to sophomore chemistry laboratories.

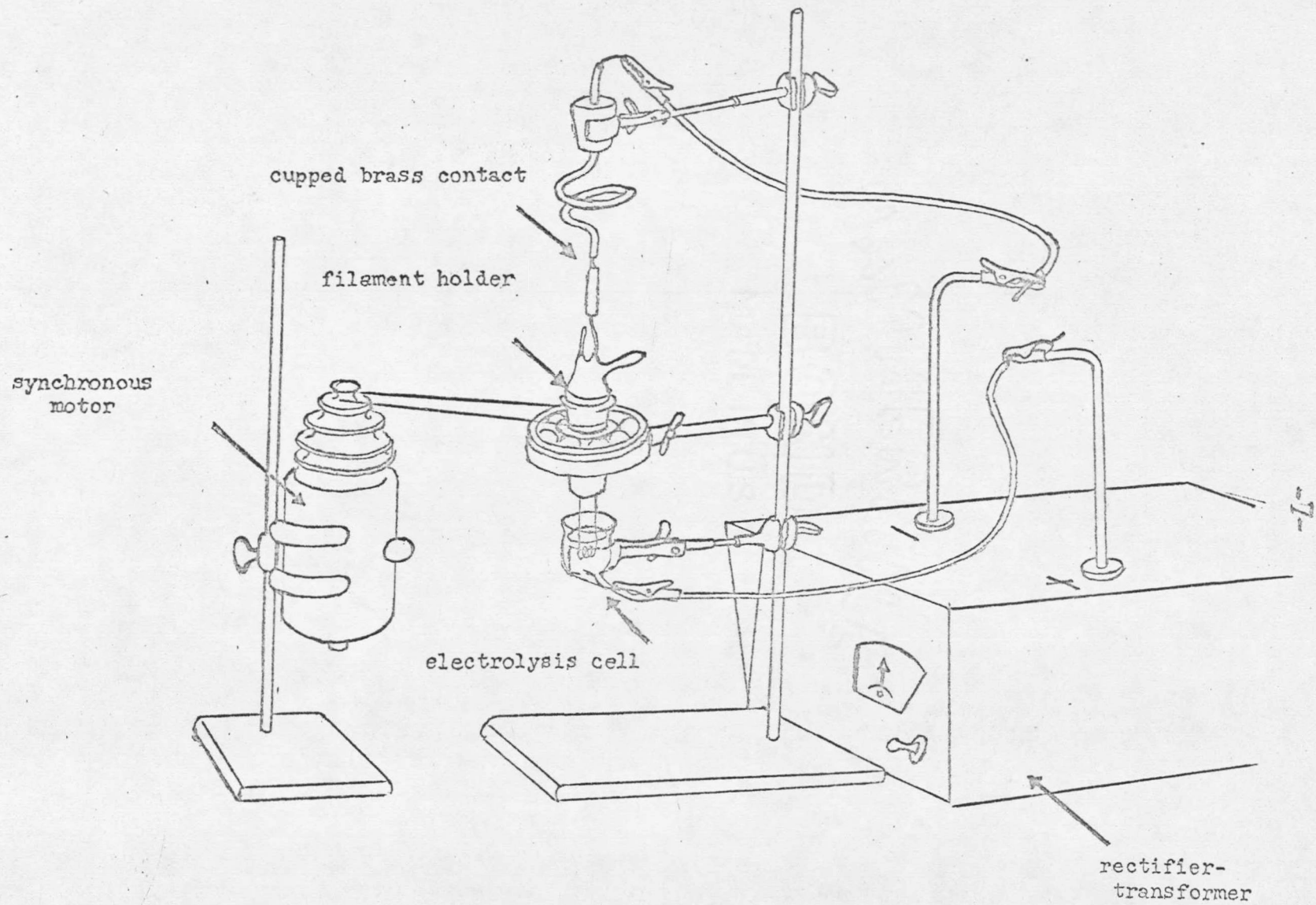


Figure 1: Electroplating Apparatus

Emission Apparatus

Figure 2 depicts all of the emission and detection apparatus and figure 3 illustrates the tube in which the discharge takes place. The tube is made of pyrex and consists of two parts. The first, the filament holder, is a male 19/22 pyrex joint through which is sealed two heavy tungsten wires. A helium inlet is also sealed onto the side. To the ends of the tungsten wires is clamped, by means of two soft steel clips, the 0.020 cm. diameter iridium wire filament. Iridium was chosen because of its chemical inertness and high melting point of 2454 degrees C. The other part of the tube is a female pyrex joint with a constricted discharge chamber at right angles to it. A quartz lens collimates the light emitted from the chamber.

The radiofrequency generator is a Fischer and Co., type SP diathermy machine. The oscillation frequency is 23.8 M Hz, and the power input to the oscillator circuit is adjustable in steps of 27, 51, and 91 watts. The output leads to the discharge tube are inductively coupled to the tank coil of the oscillator circuit. A pi-section filter was constructed to smooth the oscillator supply voltage in order to prevent 120 cycle modulation of the discharge. The iridium filament heater was a low voltage transformer (hot wire glass tubing cutter) in series with a large autotransformer.

Legend

- A. Diathermy Machine
- B. Pi-section Filter With DC Voltmeter
- C. Autotransformer
- D. Discharge Tube
- E. DU Monochromator
- F. Tektronix Oscilloscope
- G. Power Supply of Photomultiplier
- H. Photomultiplier Housing

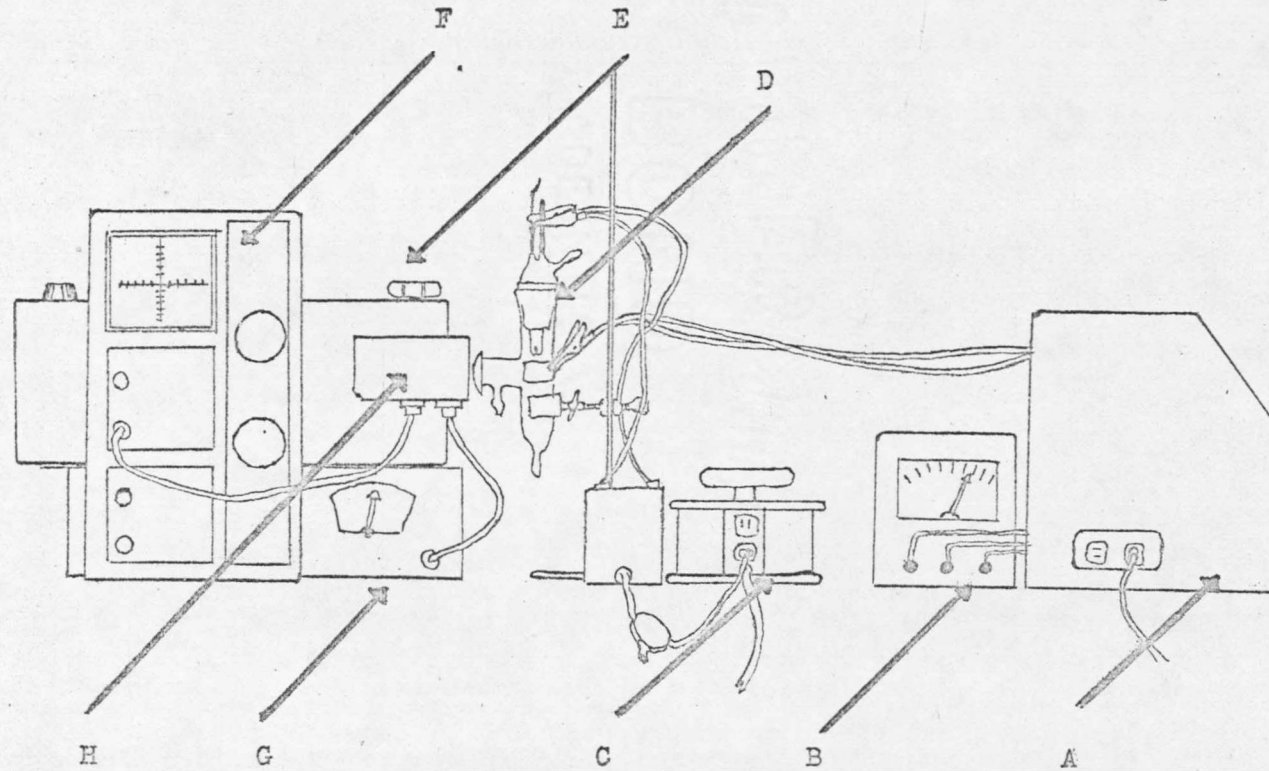


Figure 2: Emission and Detection Apparata

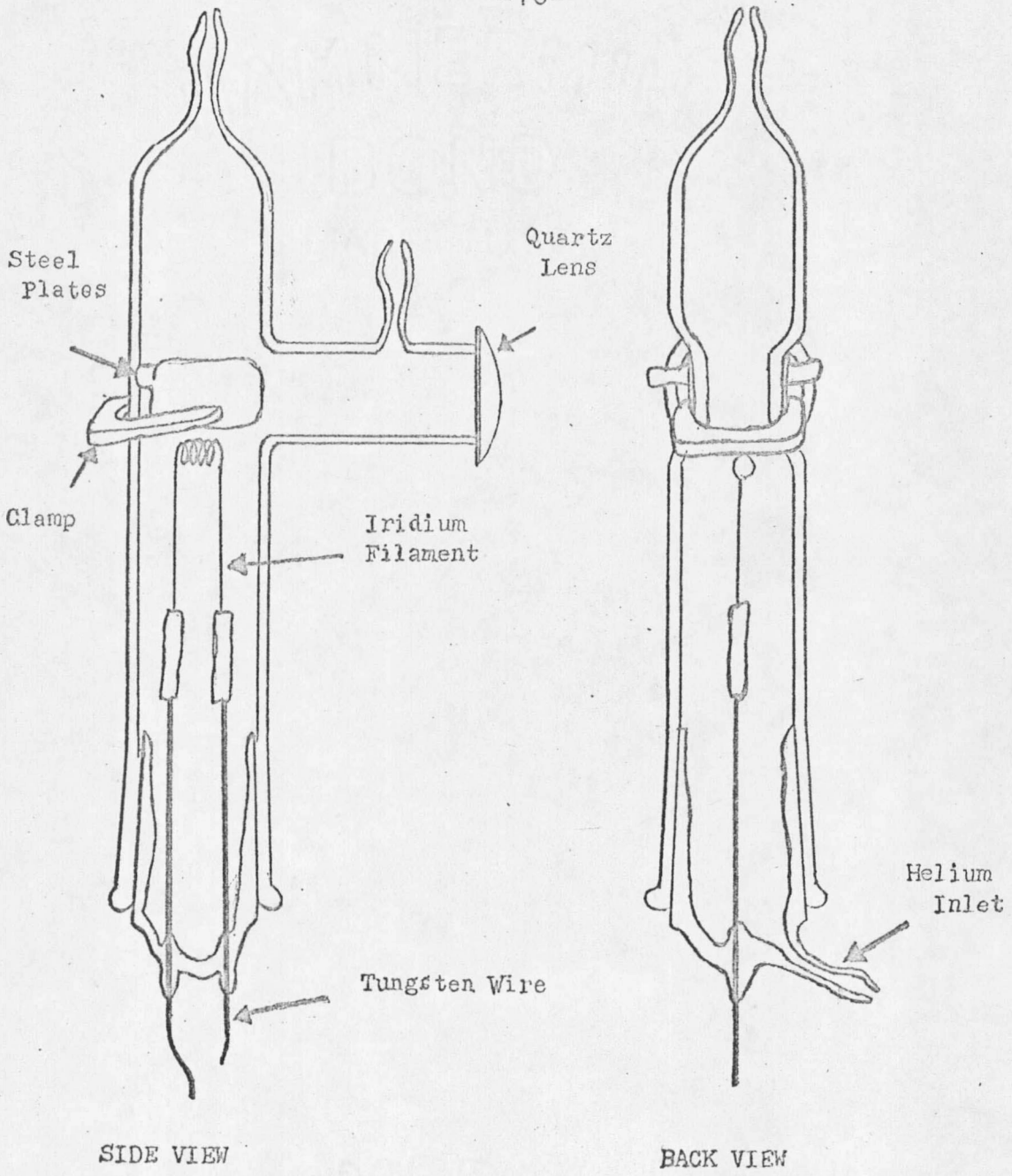


Figure 3: Emission Tube

Detection Apparatus

The detection apparatus consisted of a Beckman DU monochromator with a Sylvania IP28 photomultiplier and a Tektronix, type 564 storage oscilloscope. An Atomic Instrument Co. power supply variable from 0 to minus 1500 volts powered the phototube. A 2 microfarad capacitor was placed across the two megohm load resistor of the phototube to filter off high frequency noise from the diathermy machine. Because a relatively high and steady background signal of about twenty to one hundred millivolts² prevented the use of the more sensitive settings of the oscilloscope, a "dark voltage" nulling device was interposed into the signal leads. This device consisted of a penlite battery in parallel with a potentiometer.

Other necessary apparatus include a Taylor gas flow meter, an optical pyrometer for measuring filament temperatures, and an interval timer. The flowmeter is calibrated for compressed air, and had to be recalibrated for helium.

Sample Preparation

The stock silver solutions were made up of the carefully dried reagent grade nitrate salt dissolved in 0.1 M doubly distilled nitric acid. Working solutions were made up daily by dilution with distilled water. These solutions were stored

²This background voltage depended upon the voltage per stage applied to the photomultiplier.

during use in polyethylene bottles to forestall possible adsorption onto glass vessels (9).

The working solutions of the other metals were prepared as needed by dilution of one molar stock solutions with distilled water, or, if needed to prevent hydrolysis, nitric acid.

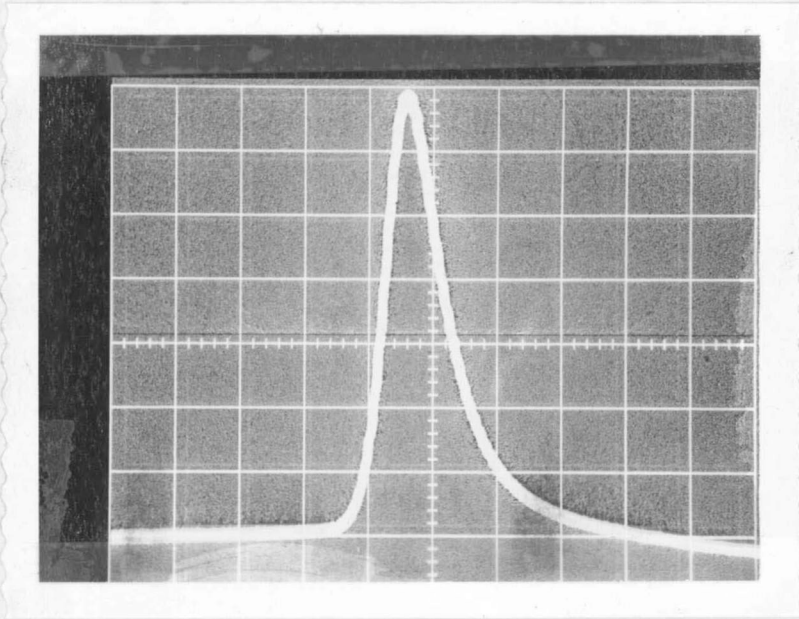
General Analytical Procedure

The first part of the procedure followed is the electroplating step. The working solution was pipeted into the electrolysis cell and distilled water was added to a level indicated by a crayon mark on the cell. The belt was placed onto the correct pulley in order to give the desired mixing speed and the filament holder was placed into the wheel bearing spindle. Then the lead from the positive side of the electroplating voltage supply was attached to the anode and the cupped cathode contact was fitted over the end of the coaxial tungsten lead. The stirring motor was started and then the voltage was turned on at the same time that the interval timer was actuated. At the end of the plating period, the electrolysis vessel was lowered away from the spinning filament while a stream of distilled water was played over the surface of the filament to rinse off any adhering solution.

The second part of the procedure is the excitation and measurement step. The filament was placed into the discharge tube and the heater leads and helium tube attached. The he-

lium valve was turned on to give the desired flow rate and the filament heater was adjusted to a low level to dry the filament. After the filament was dried, the heater was turned off and the autotransformer adjusted to give the filament temperature desired for the final step. Then the diathermy machine was turned on and the discharge initiated. A check was made of the oscilloscope trace level and the "storage" mode activated. Finally, the heater circuit was closed and the sample evaporated into the discharge. The peak emission intensity in millivolts was recorded and is the "signal" referred to in the remainder of this paper. Figure 4 is a Polaroid snapshot of a typical signal stored on the screen of the oscilloscope.

An integrating circuit consisting of a capacitor paralleling a solid state operational amplifier was tried and evinced promise of extending the sensitivity of the method over another order of magnitude. However, insufficient time prevented development to the point that results could appear in this thesis.



Conditions:

silver	10^{-8} g
filament temperature	1600 degrees C
helium flow	75 cc/sec
photomultiplier voltage	990 Volts
entrance slit	0.030 mm
plating time	6 minutes
abscissa scale	200 m sec/major division
ordinate scale	20 mV/ major division

Figure 4: Snapshot of a Typical Signal

RESULTS AND DISCUSSION

My discussion of this new method of analysis will concern itself primarily with typical results and their precision, with the effect of varying experimental parameters upon those results, and possible application of the method to different samples.

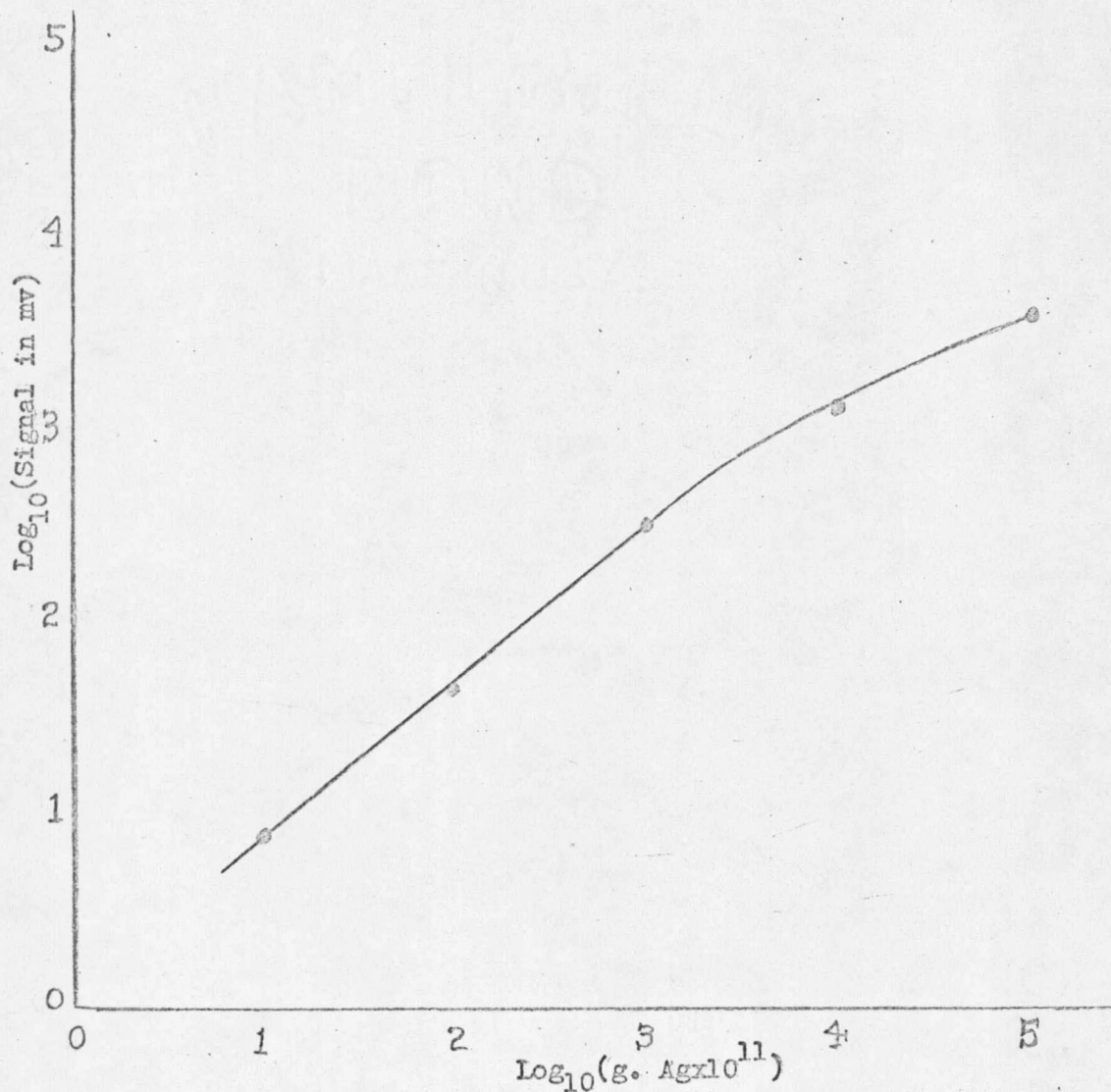
Typical Analytical Results

Figure 5 is a typical analytical curve for silver over four orders of magnitude. At very high levels of silver the curve tails off; this is likely due to a longer time being required to drive the larger amounts of silver from the electrode. An integrating readout system would decide the matter. Figure 6 depicts another analytical curve for silver over a range from 5×10^{-11} gram to 5×10^{-10} gram of silver. A sensitivity limit (here defined as that quantity of silver giving a deflection of three times the standard deviation of the blank) of 3.5×10^{-11} g. was calculated. A series of five determinations of ten nanograms of silver under similar conditions gave a coefficient of variation of 4.5%. The coefficient of variation is calculated as follows:

$$V = (S/\bar{X}) \times 100\%$$

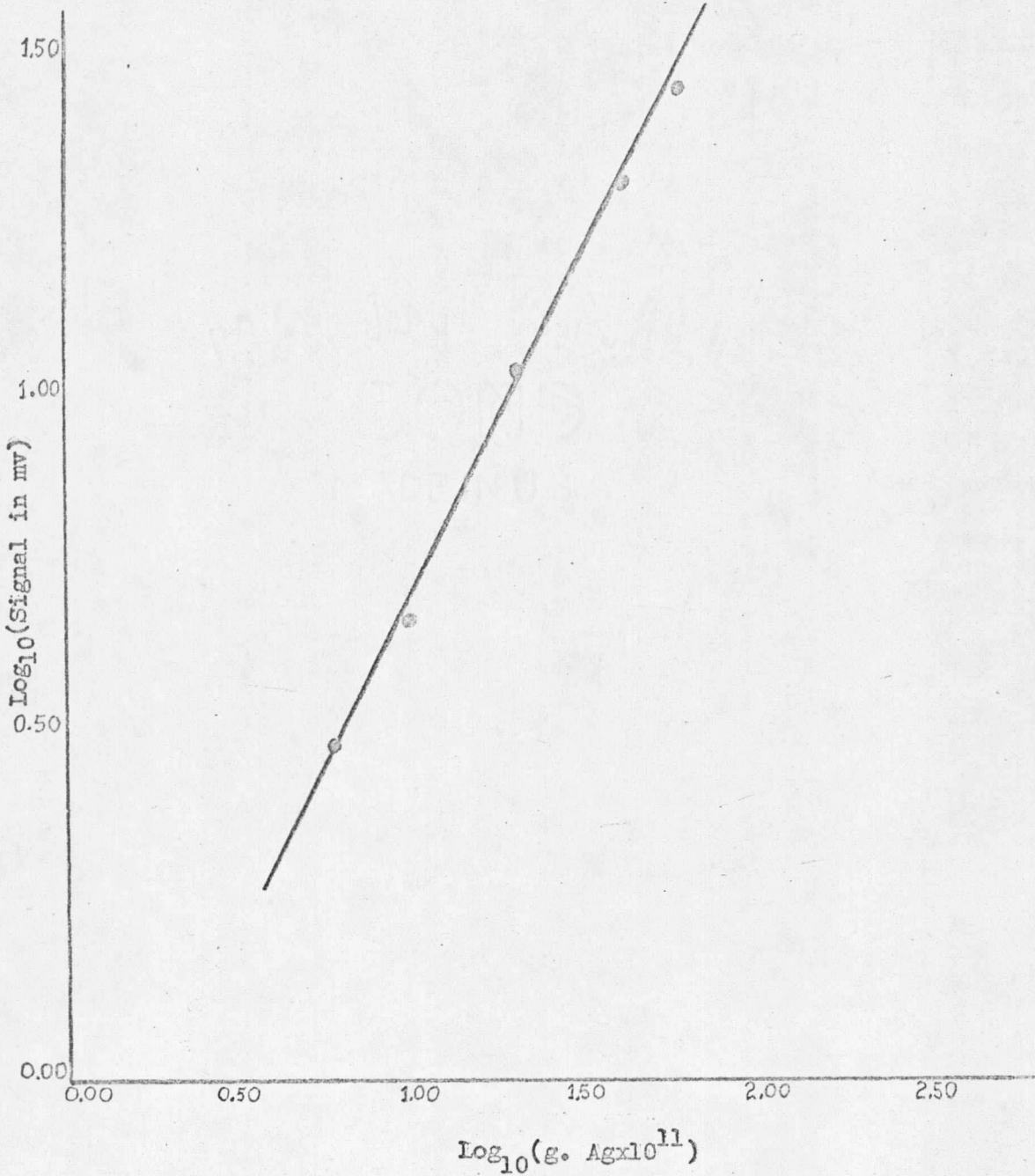
where \bar{X} = mean signal in millivolts and S = signal standard deviation in millivolts

Table 1 shows the results of an experiment aimed at determining the effect of having other heavy metals present in



Conditions:	Filament temperature	1500°C.
	helium flow	75cc/sec
	power	51 watts
	photomultiplier voltage	1070 Volts
	plating time	10 minutes
	monochromator slit	0.0175 mm.

Figure 5: Analytical Curve for Silver



Conditions: 1600°C., 75 cc/second, 51 watts, 1070 V,
10 minutes plating, 0.0175 mm

Figure 6: Analytical Curve for Silver

Table I.: Interference of Some Other Heavy Metals

Conditions: He flow 75 cc/sec, Temperature 1600°C., 1×10^{-8} g. Ag, 1070 V., 0.015 mm slit, 5 minute plating period

Metal	g. Metal	Signal
--	0	341
--	0	350
--	0	345
Sn	10^{-6}	327
Hg	10^{-6}	465
Hg (no silver)	10^{-6}	125
Pb	10^{-6}	320
Sb	10^{-6}	334
Bi	10^{-6}	340
Ni	10^{-6}	305
--	0	325
Ni	10^{-6}	320
Cu	10^{-6}	325

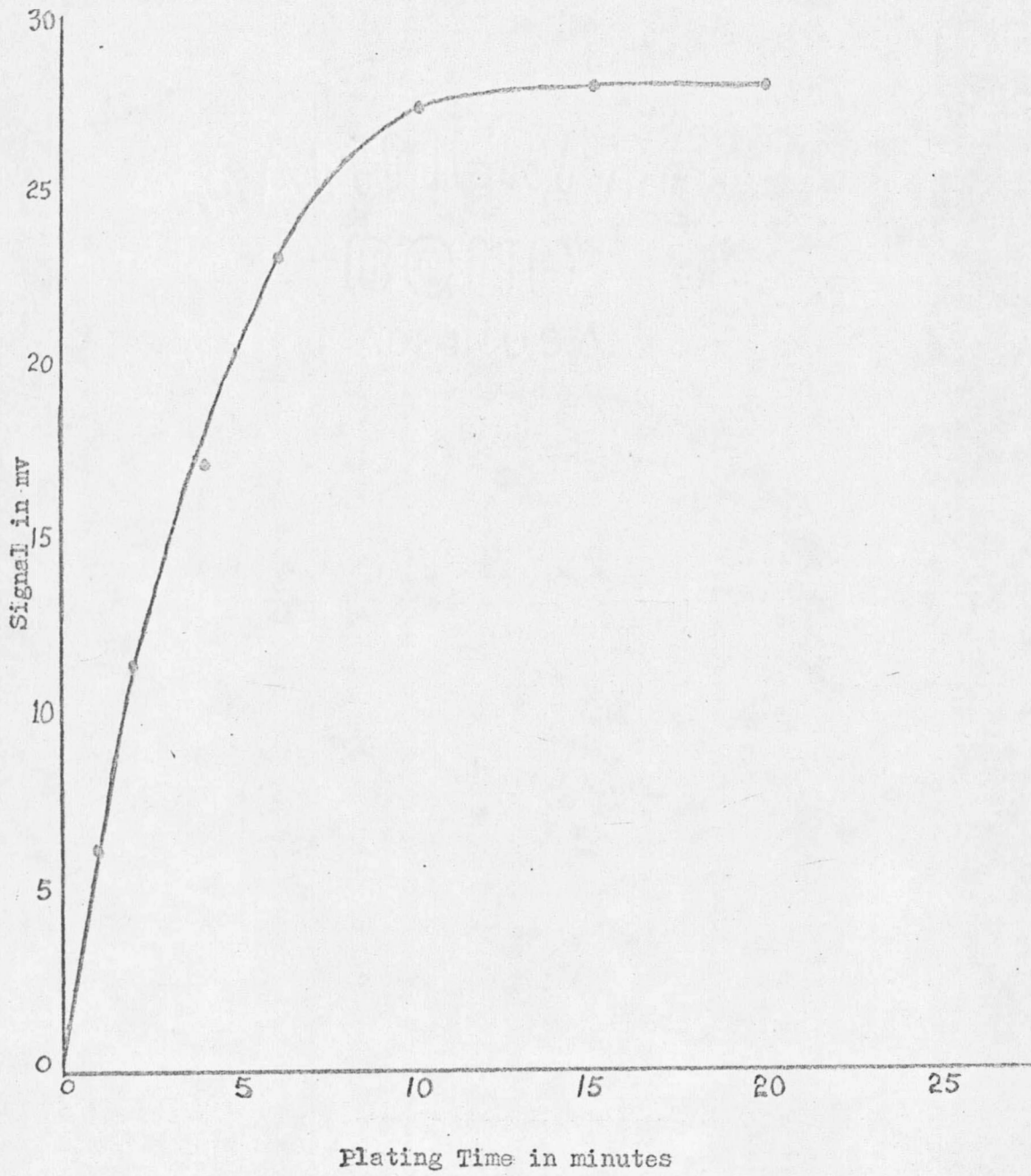
Standard deviation of silver determination alone 14.8 mv
 Mean value of silver-alone signal 333 mv
 95% confidence interval 303--363 mv

the plating solution. One microgram of tin, lead bismuth, antimony nickel, copper, or mercury had no statistically significant effect upon the determination of ten nanograms of silver. The mercury solution used was rather badly contaminated with silver. At lower filament temperatures copper interfered with the silver determination markedly (17). However, the volatility reduction of the silver by coplated copper at higher temperatures did not seem to affect the peak silver emission.

Effects of Experimental Parameters

This section of the discussion may be broken into two main categories: plating parameters and excitation parameters. The method of study used in all cases was to hold all but one parameter constant and study the effect of varying that parameter. In some cases where there may exist parameter interactions, this is not statistically the most desirable approach; however, it suffices to give first order optimization values at least.

Plating parameters studied were the effect of stirring rate, applied voltage, and differing solutions upon the speed of the plating process. Figure 7 gives a curve obtained by plating out one nanogram of silver from a neutral aqueous solution for differing times. It does not fit exactly the theoretically predicted first order decrease of concentration with



Conditions: 10^{-9} g. silver, 0.015 mm slit, 990 Volts, 51 watts,
1500 C., 2150rpm mixing speed

Figure 7: Plating Curve

time curve for a constant potential electrolytic separation (6). It follows that the times necessary to complete 90% deposition of a sample varied with the level of silver present. Six minutes were required (at 2150 rpm) to plate 90% of the silver from a solution containing 10 nanograms, 7.5 minutes for a one nanogram solution, and about 11 minutes for a 100 picogram solution.

Times necessary to plate ninety percent of the silver from a one nanogram solutions were 7.5 minutes at 2150 rpm, 19 minutes at 1170 rpm, and a long but undetermined time at 390 rpm. Higher mixing speeds were not attempted because of the danger of overheating the stirring motor. These times were much shorter³ than those observed by Alvarez, whose electrolytic separation of silver from zinc onto a stationary graphite electrode required about six hours for the same degree of completion (1).

Varying the voltage difference applied between the filament and the anode over a range of 4 to 25 volts did not affect the degree of plating completion during a fixed electrolysis period.

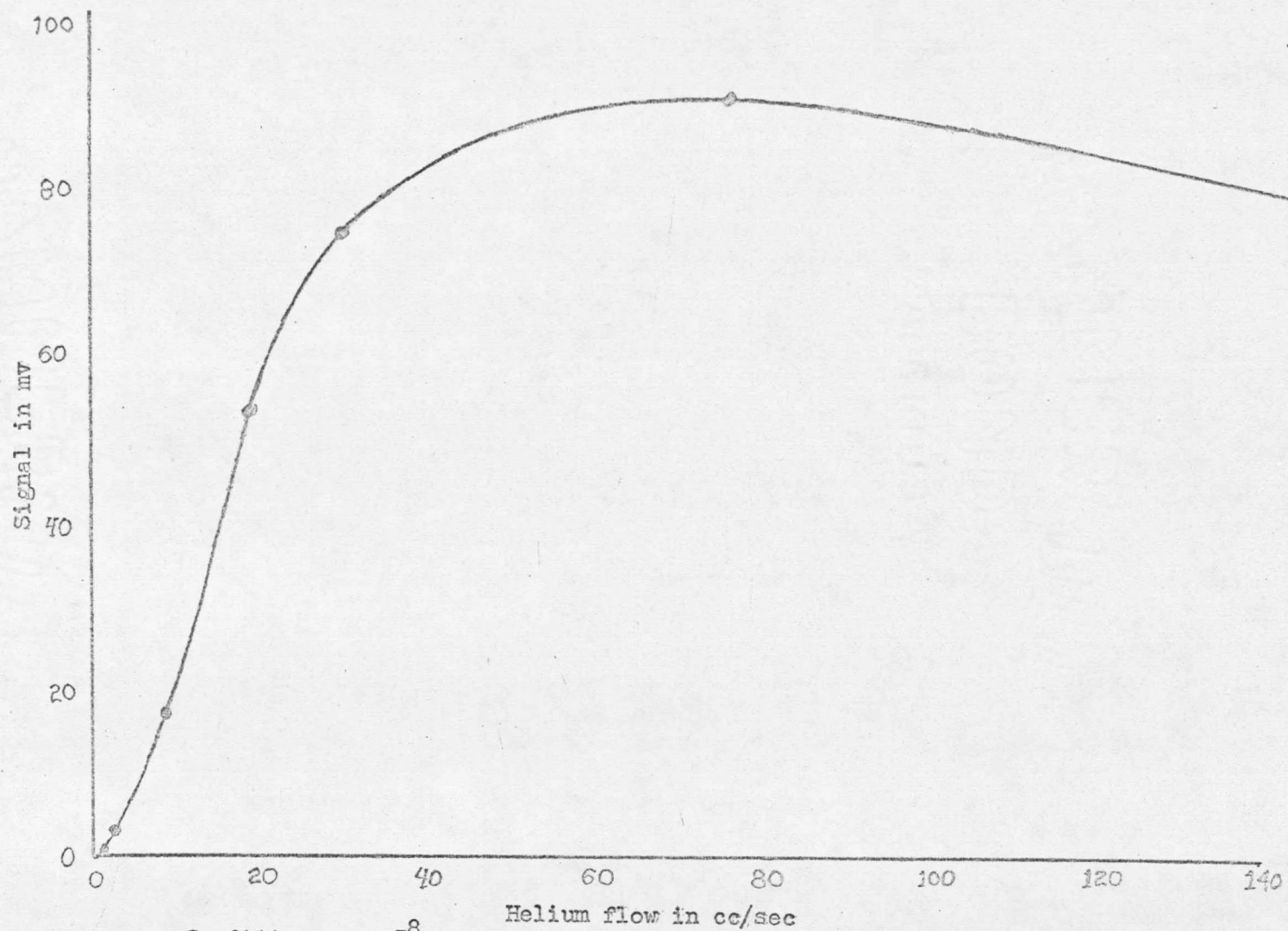
A cursory study of plating silver from 0.1 M nitric acid or 1/100 ammonium hydroxide solutions indicated that plating times were not significantly different in these media.

³Slightly fluting the walls of the electrolysis vessel to break up the vortex around the filament may lead to shorter plating periods.

Excitation parameters studied were the effect on signal level of varying the gas flow, filament temperature, and discharge power.

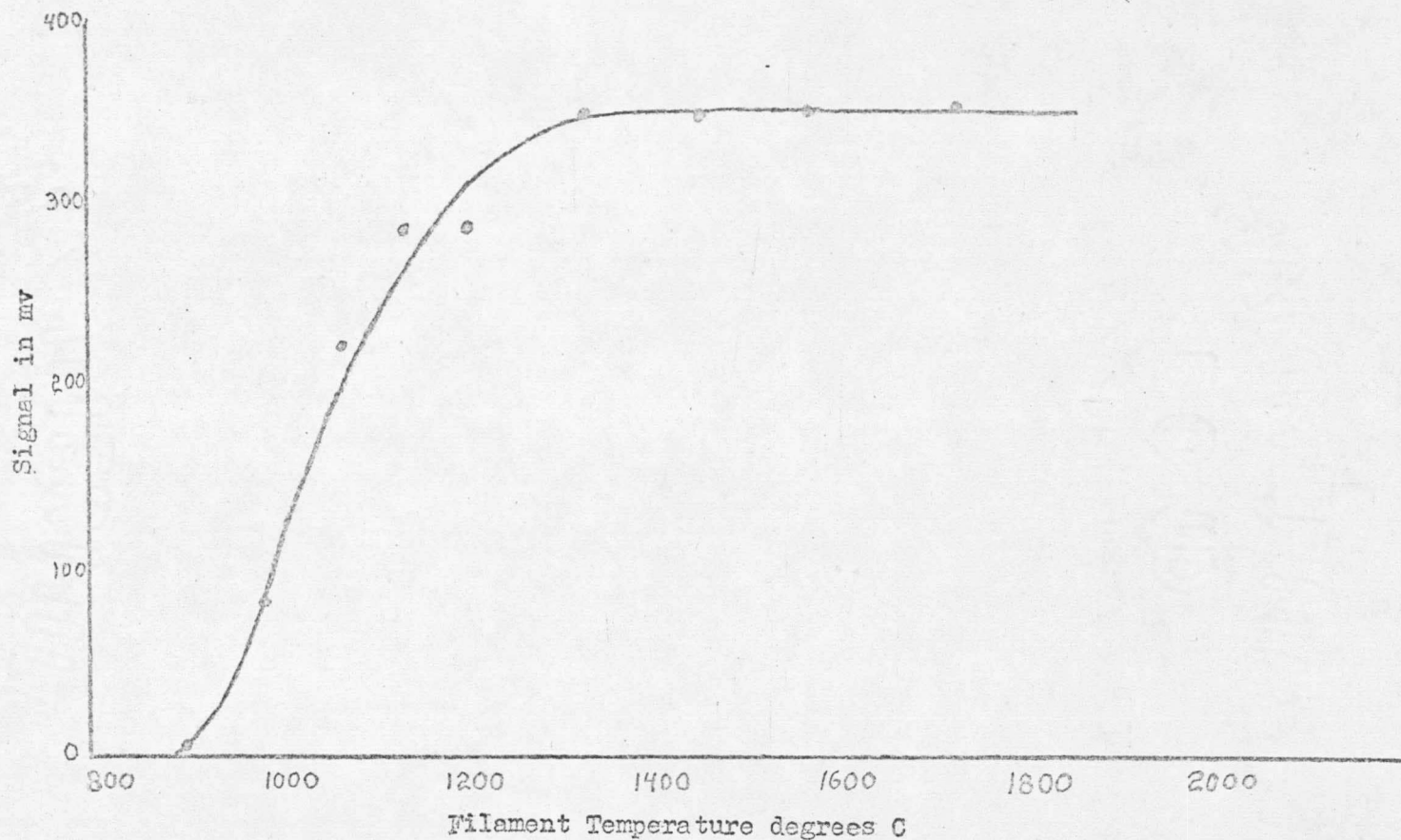
Figure 8 shows the relationship of flow rate in cc/sec to signal for one nanogram of silver. Apparently at low flow rates the sample is not carried into the discharge well and most of it deposits onto the sides of the tube. At very high rates of flow the intensity falls off, probably because the silver is carried through too quickly and/or because the discharge becomes less energetic at high flow rates. Neighboring helium spectral lines become less intense at increased rates of flow.

The results of the investigation of the effect of filament temperatures upon signal are depicted in figure 9. There is no signal at filament temperatures below 900 C.. From 900° C. to 1350° C. the signal increases rapidly. At this point it remains constant to at least 1720° C.. At 1350° C. the vapor pressure of pure silver is on the order of one millimeter of mercury. One would expect behavior similar to this for the integral of signal over time but not for the peak of the emission signal unless the time required for the silver to come off of the electrode is very short compared with the time that it is within the discharge chamber. Assuming a cross section of the discharge chamber to be 2 cm² and its length to be 3



Conditions: 10^{-8} g. Ag, 1500 C., 0.015 mm slit, 4 min. plating time

Figure 8: Helium Flow versus Signal



Conditions: 10^{-8} g. Ag, 0.015 slit, 1070 V., 75 cc/sec, 51 watts

Figure 9: Filament Temperature versus Signal

cm. and a helium flow of 75 cm.³/second, the time that the silver takes in coming off must be less than 0.08 second.⁴

The relationship of power input to the oscillator circuit to the signal is shown in table 2.

Table 2: Power Input to Oscillator Circuit Versus Signal

Conditions: 10^{-8} g Ag, 1600° filament temperature, 5 min. plating time, 1070 V. phototube voltage, 0.015 mm slit.

Power (watts)	Signal (millivolts)
27	230
51	350
91	690

Possible Application of This Method to Other Metals

A cursory study was made of the possible applications of this method to the determination of other heavy metals. The procedure followed was to set the monochromator on the wavelength of an intense emission line of the metal, start the helium flow, initiate the discharge, and see if there was appreciable background. Following this, one microgram of the metal in distilled water (acidified if necessary) was plated out for five minutes and the same excitation and measurement procedure used for silver followed. The results are in table 3.

⁴A direct determination of this time was not possible due to a large instrumental time constant of approximately 0.075 second.

Table 3: Application of the Method to Other Metals

Conditions: 0.030 mm slit, 75 cc/sec He flow, 51 watts, 1070 V. phototube voltage

Metal	Line (A)	Signal
Sn	2863.3	None
Hg	2536.5	Very strong
Pb	4057.8	Weak
Pb	2170.0	None
Au	2428.0	Very strong
Sb	2175.8	None
Bi	2230.6	Very weak
Cu	3247.5	Very strong
Ni	2320.0	None

It appears from the results obtained that mercury, gold, and copper, as well as silver, plate out of solution and are excited under the conditions used for this investigation. With further development this method of analysis may be found suitable for their determination. Anodic stripping analysis on mercury plated electrodes has been successful for the determination of cadmium, antimony, bismuth, and other metals at concentrations as low as 10^{-7} M (16). Because mercury seems to plate readily onto the iridium filament, it may be possible to plate metals other than gold, silver, mercury, and copper onto pre-plated mercury films and determine them also by this procedure.

CONCLUSION

This investigation has attempted to determine the feasibility of electrodeposition followed by radio frequency induced plasma excitation of metals as an analytical tool. The results indicate that it is a very sensitive and reproducible method of determining silver. The presence of microgram quantities of tin, nickel, mercury, copper, bismuth, lead, or antimony was demonstrated not to interfere with the determination of ten nanograms of silver under the correct experimental conditions. Also indicated was evidence of potential utility of the method for heavy metals other than silver.

SUGGESTIONS FOR FURTHER WORK

There is much more to be done before the full potential of this analytical procedure is realized even for the estimation of silver. An excitation tube with a long discharge through which the silver must pass and in which it may be more completely excited needs fuller investigation. Cooling of the phototube to reduce background noise should be helpful. Some means of cooling the discharge tube to permit higher discharge powers will increase sensitivity.

The potential of a signal integration type readout needs to be probed. This investigator is convinced that this step alone will increase sensitivities by an order of magnitude. An integrated signal should also reveal a more theoretically valuable picture of the relationship of experimental parameters

to emission than is made possible by measurement of the peak emission alone.

Of course the largest field for further work lies in the investigation of the applicability of the method for other metals. As was pointed out before, coplating of mercury will possible allow estimation of a wide range of metals. This, of course, needs to be checked out completely.

Another line of research would be electrodeposition followed by thermal atomization of metals into an inert gas atmosphere for atomic absorption measurements. One should get quite efficient atomization of metals as they boil off the filament.

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