



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
© Copyright by Darryl Duane Siemer (1969)

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
fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemistry

Approved:

Charles N. Campbell
Head, Major Department

Ray Woodruff
Chairman, Examining Committee

K. Goering
Graduate Dean

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. Woodruff 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.

TABLE OF CONTENTS

	Page
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	vii
I. INTRODUCTION.....	1
II. STATEMENT OF PROBLEM.....	3
III. EXPERIMENTAL.....	6
A. Electroplating Equipment.....	6
B. Emission Apparatus.....	8
C. Detection Apparatus.....	11
D. Sample Preparation.....	11
E. General Analytical Procedure.....	12
IV. RESULTS AND DISCUSSION.....	15
A. Typical Analytical Results.....	15
B. Effects of Experimental Parameters....	19
C. Possible Application to Other Metals..	25
V. CONCLUSIONS.....	28
VI. SUGGESTIONS FOR FUTURE WORK.....	28
VII. LITERATURE CITED.....	30

LIST OF TABLES

Table		Page
I.	Interferences of Some Other Heavy Metals.....	18
II.	Power Input to Oscillator versus Signal Level...	25
III.	Application of the Method to Other Metals.....	26

LIST OF FIGURES

Figure		Page
1.	Electroplating Apparata.....	7
2.	Emission and Detection Apparata.....	9
3.	Emission Tube.....	10
4.	Snapshot of a Typical Signal.....	14
5.	Analytical Curve for Silver.....	16
6.	Analytical Curve for Silver.....	17
7.	Plating Curve.....	20
8.	Helium Flow versus Signal.....	23
9.	Filament Temperature versus Signal.....	24

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.

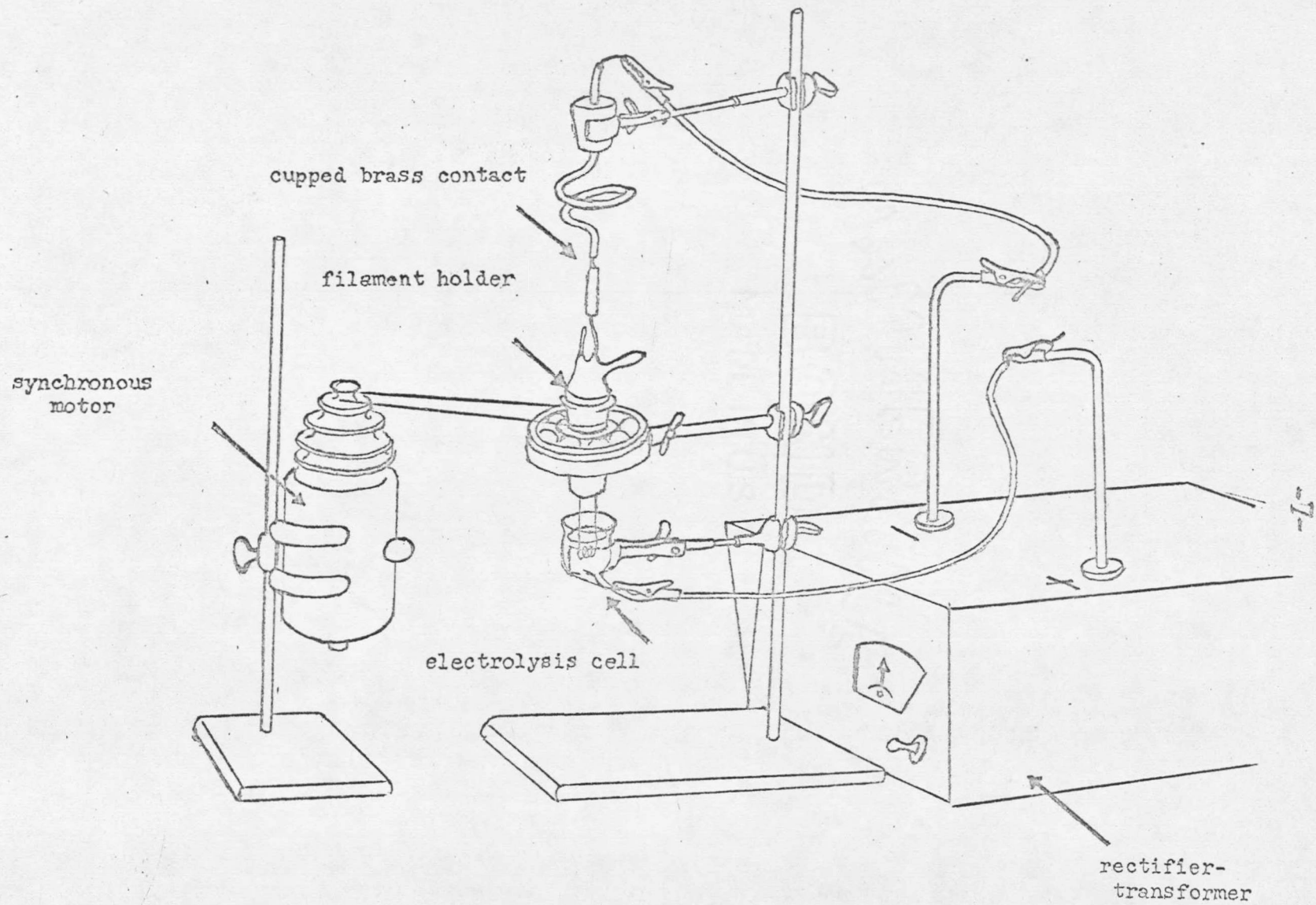


Figure 1: Electroplating Apparatus

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.

