ANALYSIS OF CONTAMINANTS COMMONLY FOUND IN ELECTRODEPOSITION SOLUTIONS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

by

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ABSTRACT

ANALYSIS OF CONTAMINANTS COMMONLY FOUND IN ELECTRODEPOSITION SOLUTIONS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

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The efficient functioning of electrodeposition solutions is governed by the application of current which induces the deposition of metal. Any interference with this current can cause an electrodeposition solution to become inefficient. Inorganic impurities are the primary interferents causing solutions not to function. An increase in the concentration of inorganic impurities may be caused by contaminated raw materials, carry-over of previous electrodeposition solutions, improper rinsing, spray, and other processes of contamination,

The acid copper electrodeposition solution is the most common solution employed for the deposition of copper metal at a cathode, The primary impurities of the acid copper electrodeposition solution include zinc, nickel, manganese, aluminum, silicon, silver, iron, tin, lead, titanium, vanadium, and palladium.

Inductively coupled plasma emission spectrometry provides a rapid, sensitive technique for the analysis of inorganic impurities at levels which are encountered in an acid copper electrodeposition solution. The Multiquant^{TM} analysis program, when coupled with an

inductively coupled plasma emission spectrometer, provides a simplified technique of contaminant determination. However, interfering element and internal standardization corrections were not able to be incorporated into the Multiquant program. An alternate program was then constructed using the basic operations program supplied with the IL Plasma-200 emission spectrometer. This enabled interelement interference and internal standardization corrections.

In this study it was found that the analytical error generally increased as the copper concentration within the solution increased. The analyses performed by the Multiquant version proved unsuccessful. Using the basic operations program analysis was possible for the less easily oxidized elements. Determination of the more easily oxidizable elements again proved unsuccessful.

ACKNOWLEDGEMENTS

I wish to thank Dr. Daryl W. Mincey for his continued guidance and support throughout this entire study.

I would also like to express my appreciation to Dr. Francis W. Smith and Dr. R. C. Phillips for their helpful suggestions regarding the compilation of this work.

Finally, I dedicate this thesis to my parents, without whose constant confidence, support, and guidance this study would not have been possible.

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LIST OF SYMBOLS

SYMBOL	DEFINITION
AES	Atomic Emission Spectrometry
amp-hr	Ampere-hour
cm	Centimeter
e^-	Electron
E^o	Ground state energy level
E^*	Excited state energy level
g	Gram
(g)	Gaseous state
HG	Option of analysis with mercury lamp (0=lamp off; 1=lamp on)
ICP	Inductively Coupled Plasma
ICP-ES	Inductively Coupled Plasma Emission Spectrometry
K	Degrees Kelvin
kW	Kilowatt
L/min.	Liters per minute
MHz	Megahertz
mL/min. or ML/M	Milliliters per minute
mm	Millimeter
nm	Nanometer
oz/gal	Ounces per gallon
P#	Program number
PDLY	Pump delay time

SYMBOL	DEFINITION
pH	Negative log of hydrogen ion concentration
ppm	Parts per million
PWR	Power level
(s)	Solid state
sec	Second
sp-gr	Specific gravity
sq-ft	Square foot
TM	Trade mark
uL	Microliter
V	Volt
WP	Write protect option (0=write protect off; 1=write protect on)
*ANAL	Number of analyses (0=1 analysis)
*RDG	Number of readings (0=1 reading)
Δ	"Change in" or difference

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CHAPTER I

INTRODUCTION

Electroplating, a combination of both science and art, has made its presence felt in almost every area of our world. "Electroplating was born from science that demonstrated the remarkable ability of electric current to reduce metal salts to metal. It soon aided the production of beautiful objects and it became an art that was dependent on the masters who learned how to coax attractive coatings from homely solutions."[1]

The process of electroplating entails the deposition or "plating" of metals from solutions of the metal. As a voltage of magnitude specific to the metal being plated is applied to a system a metal anode is dissolved or oxidized. In the process of oxidation -the metal ionizes and thereby takes on a positive (+) charge. The positive ions are then attracted to the negatively (-) charged cathode, where they are then reduced back to the elemental metal (zero charge) state, and plated onto the cathode.

The actual process of electrodeposition is quite complex and as a result electrodeposition has emerged as a separate field of electrochemistry, with its "masters" still attempting to completely understand the process. A complete knowledge of the solutions involved, the electrodes, current, current density, deposition potentials, and other variables, as well as the conditions at which the above are most efficient, is necessary to successfully perform electrodeposition.

However, even when all conditions are optimized, plating can still be inefficient or impossible due to the presence of contaminants in the electrodeposition solution, commonly referred to as an electroplating bath. Contaminants present perhaps some of the greatest problems in the electrodeposition process and must be constantly monitored in order to maintain their concentrations at a minimum.

In the past contaminants were monitored and their concentrations measured by such methods as titrations, voltammetry, potentiometry, and polarography. While being dependable methods, they can also be very involved and time-consuming. Therefore, a simpler method of solution analysis for the presence of contaminants in electrodeposition solutions has long been sought. Atomic emission spectroscopy appears to be a very likely candidate for a much simplified analytical technique.

Atomic emission spectroscopy (AES) became a useful analytical tool in the analysis of electrodeposition solutions with the development of the flame emission spectrometer. Although it was a very useful technique, it did have its drawbacks, in that the flame emission spectrometer could only perform single element analyses, and then only after somewhat long standardization processes. Therefore, analysis for several contaminants could be time-consuming. Furthermore, analysis of some elements was often difficult; flames did not provide high enough temperatures to accomodate their atomization. With the introduction of the inductively coupled plasma (ICP) these drawbacks have been practically eliminated. The inductively coupled plasma excitation-atomization source allows for much higher temperatures, making possible the atomization, and thereby the analysis, of species which could not be handled by traditional emission techniques. With the development of the Multiquant™ program, a program allowing for the sequential analysis of thirty different analytical lines without long standardization processes, analysis has been even more greatly facilitated. Therefore, with these great advantages, it is only natural that ICP emission spectroscopy would be considered as a possible tool of the electroplater.

Statement of the Problem

Traditional methods of analysis of metal or metalloid solutions can be very time-consuming. The scope of this research entails the use of the inductively coupled plasma emission spectrometer and the Multiquant program to successfully analyze acid copper electrodeposition solutions for contaminants, which when present in the solution, would make the deposition of copper metal inefficient or impossible. ICP techniques have the advantages of increased temperatures and more sensitive detection limits. Such an analytical method could provide both quicker and possibly more dependable results than those methods presently available.

CHAPTER II

HISTORICAL REVIEW

Electrodeposition

Electrodeposition, commonly termed electroplating, is a branch of the field of chemistry known as electrochemistry, that is, the field of chemistry in which chemical reactions occur due to the application of an electric current, or in which electricity is produced by chemical reactions.[2] Electrodeposition is the process by which a substance is deposited at an electrode due to the flow of current through the solution.[1]

Electrochemical processes can be of two distinct types: (1) electrolytic, in which current is applied directly to the medium in order to induce the chemical reaction, or (2) galvanic, in which the reaction species themselves generate the electric current necessary, thereby forming a cell.[2] The electrolytic system is the basis of electrodeposition.

In the electrolytic system three components are essential for electrodeposition to occur: (1) electrodes (anode and cathode), (2) electrolyte, and (3) external voltage source. In order for electricity to flow between the electrodes in an electrochemical system the anode and cathode must first be connected externally to permit the flow of electrons, and the two electrolytic solutions (those of the anode and cathode) must be in contact with each other, again to allow the flow of electrons and ions.[3]

In an electrochemical system, whether electrolytic or galvanic, two chemical reactions, reduction and oxidation, occur. The relationship between these two reactions is illustrated in general by the following reaction equation:

$$\begin{matrix}\text{Oxidized} \\ \text{Species}\end{matrix} + ne^- \rightleftharpoons \begin{matrix}\text{Reduced} \\ \text{Species}\end{matrix} \qquad (1)$$

A typical electrochemical cell is illustrated in Figure 1.

The quantity of electricity used in the process of electrodeposition is of great concern to the electroplater "since the number of units of electricity that pass through the electrolyte during electrolysis determines the quantity of product formed at the cathode."' Instead of dealing directly with the applied voltage, the electroplater commonly deals with the amount of current which flows in a system. The two variables, potential(voltage) and current, are related through the following equation:

$$E = IR \qquad (2)$$

where E is potential expressed in volts, I is current expressed in amperes, and R is resistance expressed in ohms.

The ampere unit simply relates the strength of a current. It is usually combined with a time factor, e.g., ampere-hours, in order to relate the quantity of metal which will deposit at the cathode in a given period of time. For every 26.806 ampere-hours of electric current, one gram equivalent weight (gram atomic weight divided by number of valence electrons in an ionic species) will be deposited at the cathode.[1] For example, the amount of copper metal which will deposit at the cathode from Cu^{2+} ions in 26.806 ampere-hours will be the gram atomic weight of copper, 63.57 g, divided by the valence number on the cationic species, or 2. Therefore, 63.57 g/2 = 31.78 g of copper metal will be deposited at the cathode in 26.506 ampere-hours. Knowing

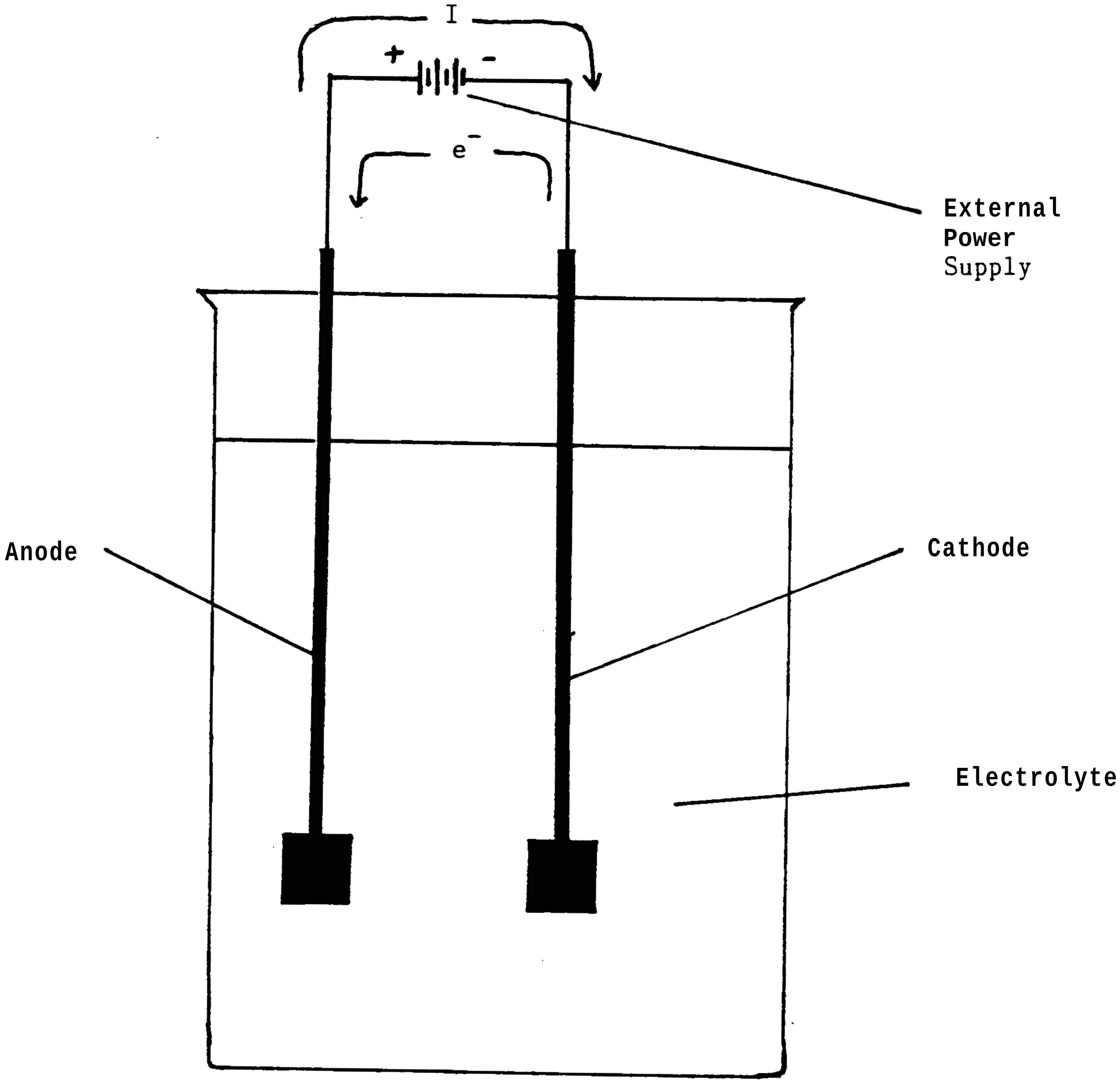


Figure 1. Representation of an electrolytic cell.

the ampere-hour factor, the plating rate of the solution can also be calculated.

$$\text{Plating Rate} = \frac{\text{amp-hr}}{\text{sq-ft}} \times \%\ \text{efficiency} \qquad (3)$$

As the electroplater is most commonly concerned with the thickness of a deposit, Equation 3 together with the cathode efficiency can be used to calculate the plating thickness. The cathode efficiency is that percentage of the current that deposits metal.[1]

$$\frac{\text{equivalent weight}}{\text{amp-hr}} = \frac{\text{equivalent weight}}{26.8} \qquad (4)$$

$$= \frac{\text{g}}{\text{amp-hr}} \quad \text{at 100\% efficiency} \qquad (5)$$

$$\frac{\text{g}}{\text{amp-hr}} \times \frac{\text{amp-hr*}}{\text{sq-ft}} = \frac{\text{g}}{\text{sq-ft}} \qquad (6)$$

(* Plating rate from Equation 3)

$$\frac{\text{g}}{\text{sq-ft} \times 144} \times \frac{1{,}000}{16.4 \times \text{sp-gr}} = \text{mils thickness} \qquad (7)$$

With a knowledge of these basic principles the electroplater is able to not so mysteriously produce metal at a cathode from a liquid solution of a metal.

Electrodeposition Solutions

The primary electrodeposition solution studied in this work was the acid copper solution. Copper deposition is one of the oldest electrodeposition techniques in use today. Copper is the most abundant of all noble metals, and is highly corrosion resistant, ductile, and highly conductive.[1] Therefore, copper plating is not limited to decorative uses, but is also utilized in the electronics industry.

In the acid copper plating solution a copper salt, usually cupric sulfate ($CuSO_4$) is dissolved in a water/sulfuric acid mixture. Copper is then anodically dissolved, or oxidized to Cu^{2+} with a maximum anode efficiency. Since copper is easily reduced, and since a maximum anode efficiency is initially achieved, it can therefore be expected that the cathodic reaction (electrodeposition) will proceed with approximately the same maximum efficiency.[1] Since copper is a "noble metal" it will preferentially deposit over more base metals which could be present in the solution as contaminants, such as zinc or iron.[1]

The various acid copper plating solution formulations are all very similar, usually differing only in the acid and copper compound used. Three of the most common acid copper plating solutions include the sulfuric acid solution, the fluoboric acid solution, and the pyrophosphate solution. The sulfuric acid solution is the most commonly used of the three formulations. The pyrophosphate bath consists of copper pyrophosphate, potassium pyrophosphate, and ammonia, and is usually operated in a pH range of eight to nine. Typical formulations for the sulfuric acid and fluoboric acid solutions are the following[1]:

Sulfuric Acid Solution

Constituent	g/L	oz/gal
$CuSO_4 \cdot 5H_2O$	200-250	27-33
H_2SO_4	45-75	6-10

Fluoboric Acid Solution

Constituent	g/L	oz/gal
$Cu(BF_4)_2$	330-360	44.0-48.0
HBF_4	20-25	2.7-3.3
H_3BO_3	20-25	2.7-3.3

Specific gravity = 1.27-1.29
pH = 0.6-0.9

Copper deposits are easily formed from these three electrodeposition solutions, however the grain tends to be rather rough. The grain can be softened by the use of addition agents.[1]

Contaminants

Although use of the acid copper electrodeposition solutions is a relatively simple and efficient method of plating copper, contamination of the bath solution can easily cause the plating process to be inefficient or even impossible. Some of the more common contaminants as well as their limits and effects are listed in Table 1.4

TABLE 1

COMMON CONTAMINANTS OF ACID COPPER ELECTRODEPOSITION SOLUTIONS

Element	Lower Limit	Effects
Aluminum	10 ppm	Used as guideline on cleanliness of bath. Uncertain of effects upon deposit.
Iron	60 ppm	Degrades physical properties of deposit. Degrades performance of solution
Lead	1-2 ppm	Precipitates, becoming incorporated into the deposit.
Manganese	0 ppm	Degrades physical properties of deposit.
Molybdenum	-----	Degrades physical properties of deposit.
Nickel	10 ppm	Degrades physical properties of deposit.
Palladium	5 ppm	Causes surface staining.
Silicon	10 ppm	Uncertain of effects upon deposit.

Element	Lower Limit	Effects
Silver	0 ppm	Attacks brighteners within solution.
Tin	10 ppm	Degrades physical properties of deposit.
Titanium	1 ppm	Catalyzes decomposition of solution constituents.
Vanadium	1 ppm	Catalyzes decomposition of solution constituents.
Zinc	10 ppm	Deactivates organics in solution. Degrades physical properties of deposit.

CHAPTER III

METHODOLOGY

Inductively Coupled Plasma Emission Spectrometry

Inductively coupled plasma emission spectrometry is a relatively new branch of emission spectroscopy, which began in the early 1960's. Emission spectroscopy itself is based upon the emission of electromagnetic radiation by atomic particles.[5] In an emission spectroscopic method, a sample is initially nebulized into a heat source where it is vaporized and atomized. The most common atomization sources are electric arc and spark devices, flames, and plasmas. Once the sample is atomized, its outermost electrons absorb energy, thereby raising the atom from its ground state to an excited state of higher energy. This is known as the excitation process. The excited state to which an atom can be raised is very specific to each element. Once raised to an excited state, the atoms release the excess energy which they absorbed. Just as the amount of energy absorbed by atoms of different elements is usually specific to each element, so too then is the amount of energy (radiation) which is emitted by atoms of different elements. The process of emission spectroscopy is illustrated pictorially in Figure 2.[6]

The radiation which is emitted in the emission process is of a particular wavelength(s), depending on the transitions undergone by the valence electrons. These wavelengths are usually unique to each

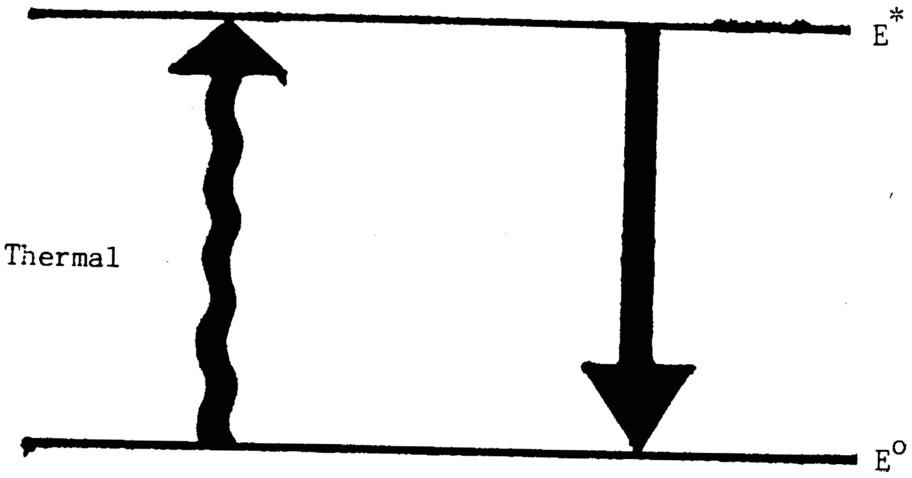


Figure 2. Pictorial representation of emission process.[6]

element. This difference in wavelength makes it possible to distinguish radiation of one element from that of another, thus rendering emission spectroscopy a qualitative technique. By using a spectrometer and measuring the quantity of emitted radiation at a given wavelength, it should be possible to quantitate the concentration of an element present in a sample. The amount of radiation emitted is proportional to the concentration of the solution. Standard curves of emission intensities versus concentration can then be used to determine the concentration of a solution of unknown concentration. Thus, emission spectroscopy can be considered a quantitative technique as well. Similar procedures can be performed on most metal or metalloid elements.

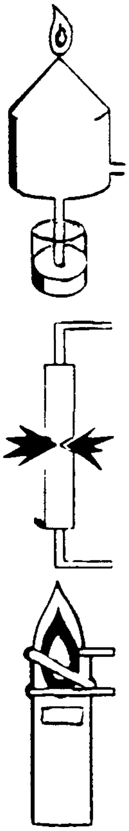
In the atomic emission process, the atomization and excitation of the sample are the major steps which first must be successfully accomplished. The major characteristic of interest in the atomization-excitation process is the temperature which can be obtained by the source. The temperatures which can be obtained by using various atomization-excitation sources are illustrated in Figure 3.[7] Temperature is an essential variable of the excitation process, in that the temperature, along with other minor variables, determines the degree to which excitation of the sample occurs. This temperature dependence is best illustrated by the Boltzmann Equation:[5]

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp\left(\frac{-E_j}{kT}\right) \qquad (8)$$

where N_j = number of atoms in excited states

N_Θ = number of atoms in ground state

k = Boltzmann constant (1.38 x 10^{-16} erg/deg)



FLAME

- SIMPLE SPECTRA
- 2000 TO 3000 K

ELECTRICAL DISCHARGES

- >8000 K
- DC AND AC ARCS
- HV SPARKS

INDUCTIVELY -COUPLED
AND DC PLASMAS

- ELECTRICAL HEATING OF GASES
- 6000 TO 10,000 K

Figure 3. **Comparison of Excitation Sources.**[7]

T = temperature in degrees kelvin

E_j = energy difference in ergs between the excited state and the ground state.

P_j and P_o = statistical factors that are determined by the number of states having equal energy at each quantum level.

As can be seen from this relationship, the higher the temperature of the atomization-excitation source, the larger will be the ratio of the number of atoms in the excited state to the number of atoms in the ground state. Higher temperatures provide greater efficiency in the atomization-excitation process, and thereby provide greater sensitivity in the qualitative and quantitative determinations of elements.

Since the excitation source is of such great importance, a source which could surpass the temperatures attainable with an ordinary flame was long sought. Although the flame was able to reach relatively high temperatures (ca. 3000 K), the flame itself was a chemical environment which often affected the sample, often adversely. By the end of the 1950's a new excitation source was being considered--the capacitatively, or inductively coupled plasma. In the early 1960's the first working plasma was constructed. Early in its development the advantages of the ICP were already recognized: "(1) high atomization temperatures, (2) capability of being sustained in noble gas environments (important from free-atom lifetime considerations), and (3) freedom from contamination from electrodes, since none were required."[8] By the 1970's spectrometers were being designed to accommodate these new atomization-excitation sources.

"By definition, plasmas are gases in which a significant fraction of their atoms or molecules is ionized."[9] In an inductively coupled plasma source argon flows through three concentric quartz tubes (Figures 4 through 6).[9] Around the top of this tube is placed a water-cooled induction coil, which is powered by a radio frequency generator. This high-frequency generator normally operates in the 4-50 MHz range, producing 2-5 kW of energy. When power is supplied to the generator, nothing initially happens to the flowing argon. Once the tube is "tickled" with a Tesla coil, or by some other mechanism, the argon becomes "seeded" with electrons. The argon gas then spontaneously ionizes, forming the plasma, which thereafter is capable of sustaining itself until the power is again switched off. The ions of the plasma interact with the high frequency currents in the induction coil causing the ions and electrons to flow in closed annular paths inside the quartz tube, resulting in the formation of so-called eddy currents. The resistance of the ions and electrons to flow in this way results in Joule or ohmic heating. The temperatures achieved by such a plasma can be so great (9000-10,000 K), that it becomes necessary to thermally isolate the plasma from the outer quartz tube. This thermal isolation is accomplished by tangentially flowing argon around the outside wall of the quartz tube. By so doing, the inside walls of the tube are cooled, forcing the plasma to be centered radially.[5,9]

The sample, usually a liquid solution, is then carried into the hot plasma by either a pneumatic, ultrasonic, or cross-flow nebulizer (Figure 7).[8,10] (A cross-flow nebulizer was used in this study.) The sample is then carried through the plasma. Often nebulizers are capable of handling different types of samples, including aerosols, thermally generated vapors, or fine powders.[5] Alterations in nebulizers may be

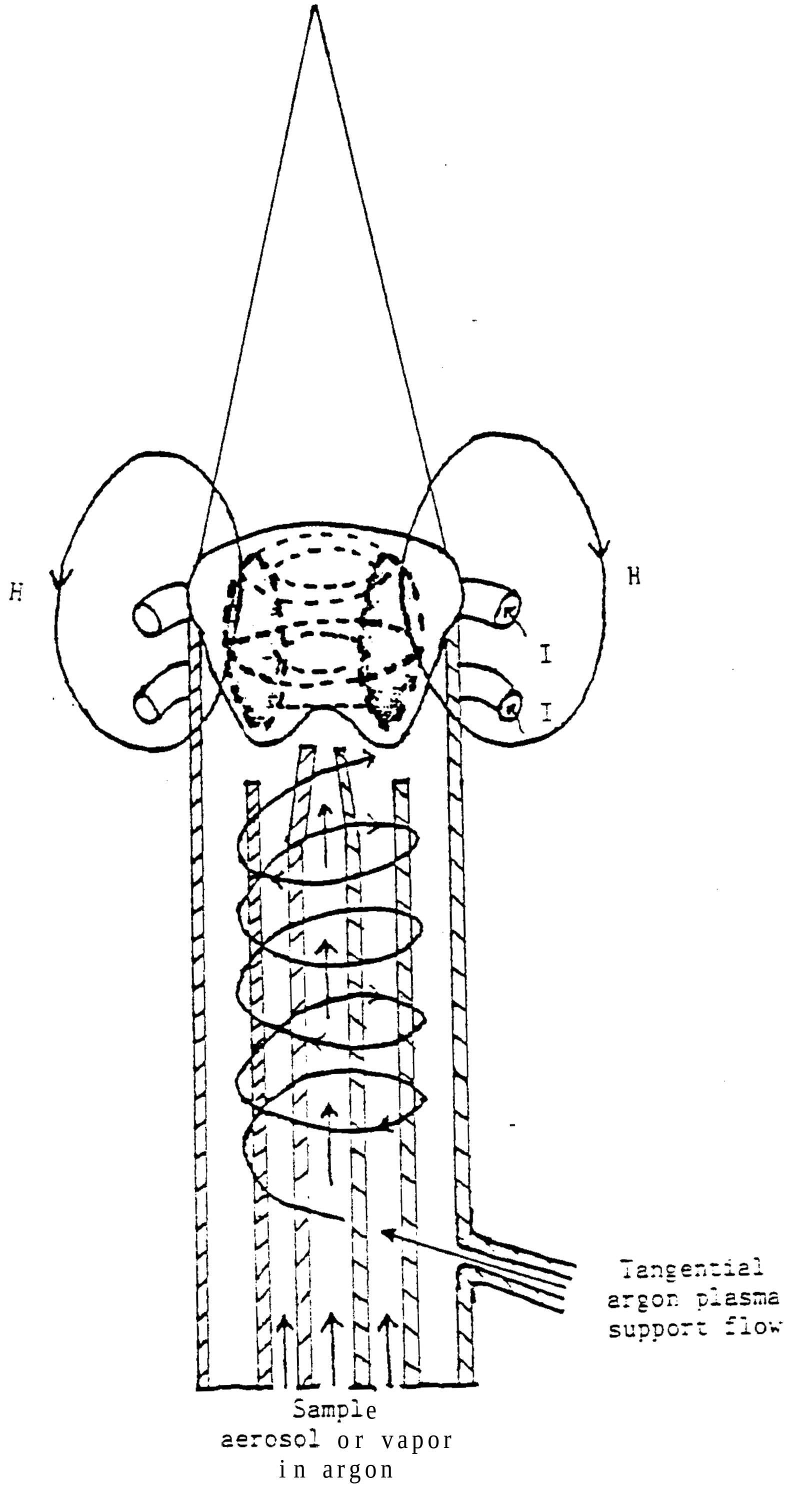


Figure 4, Representation of an inductively coupled plasma source.'

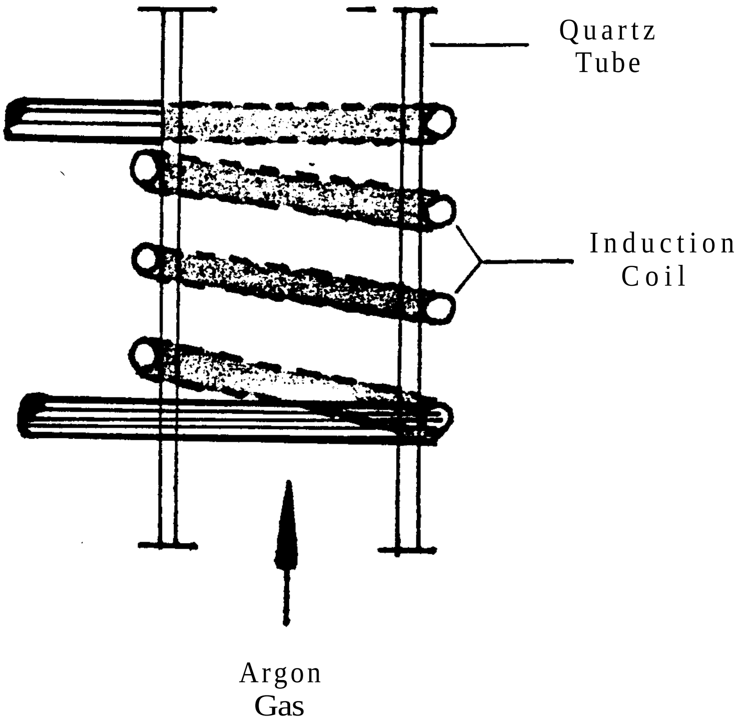


Figure 5. Cross-sectional view of an inductively coupled plasma.[7]

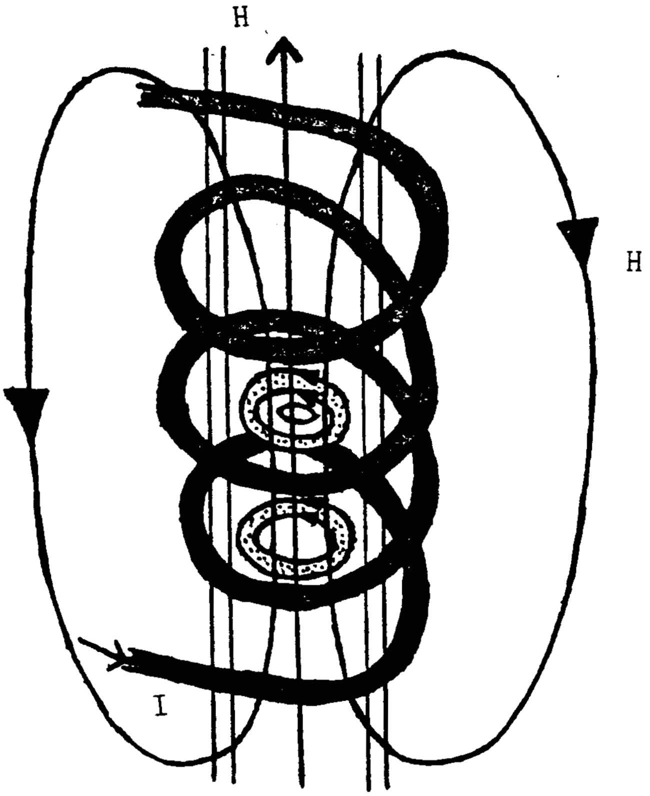


Figure 6. Magnetic fields and eddy currents generated by an induction coil.[9]

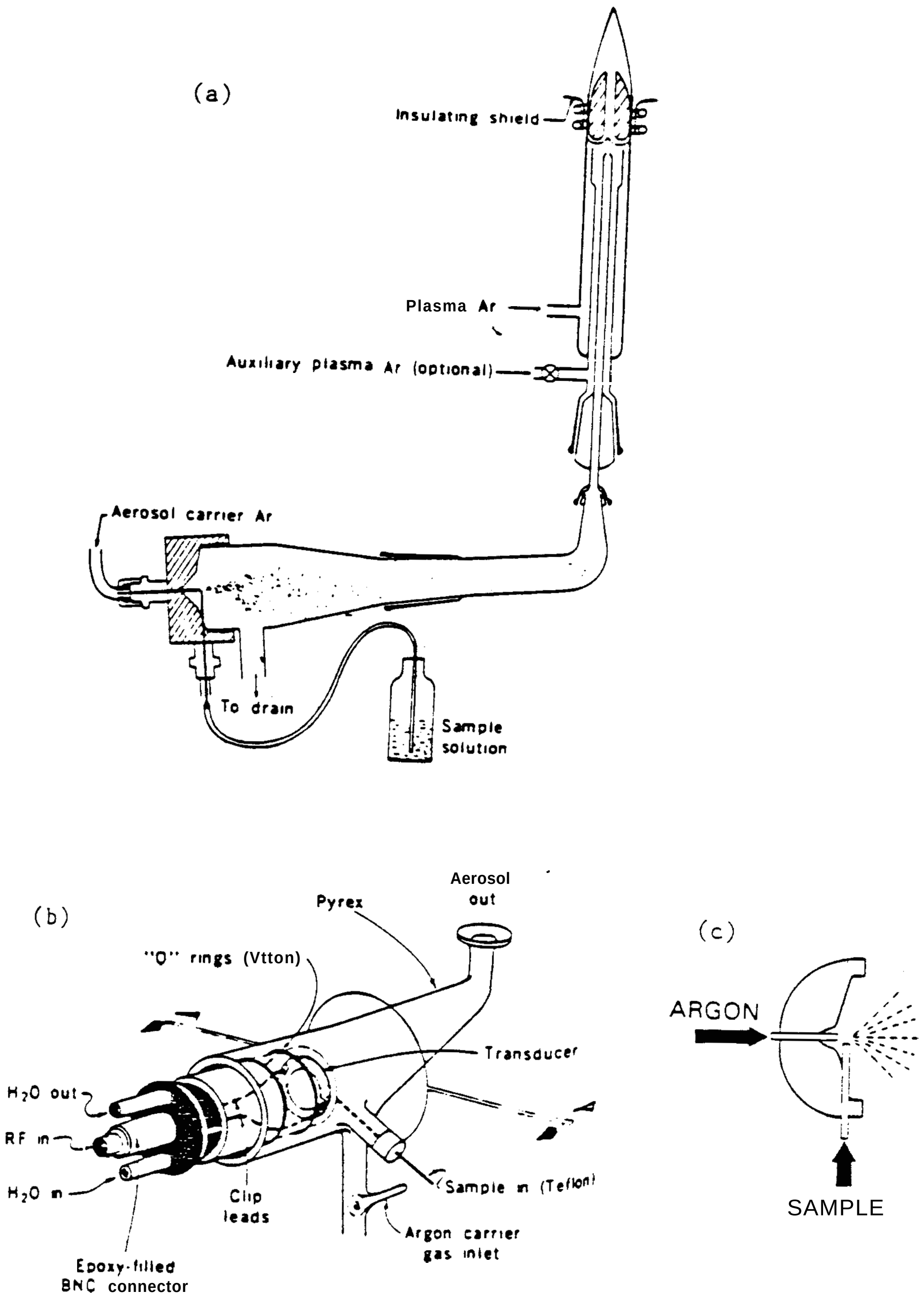
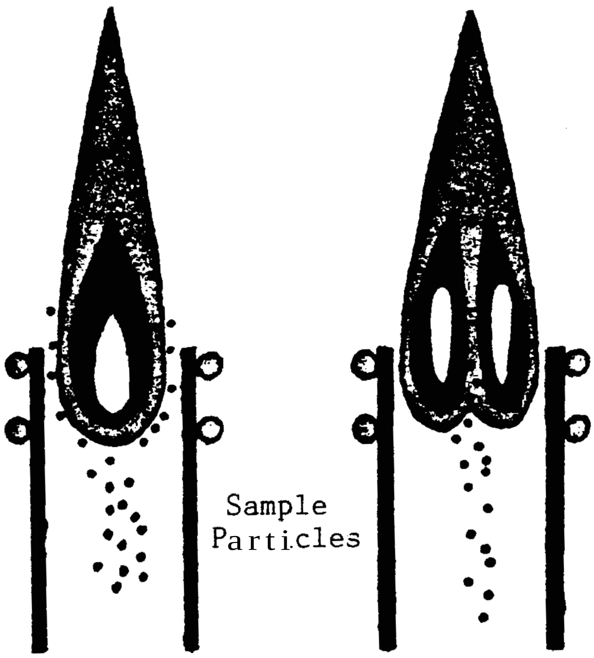


Figure 7. Typical nebulizers used in Inductively Coupled Plasma Emission Spectrometry: (a) pneumatic nebulizer, (b) ultrasonic nebulizer, and (c) cross-flow nebulizer. 9,10

necessary in order to accomodate these different types of samples. Although the sample is carried through the plasma, it is currently under debate as to whether the sample actually reaches the hottest part of the plasma. In the tube the plasma conforms to a doughnut shape. The doughnut represents the hottest part of the plasma. The sample is believed to pass through the hole of the doughnut, avoiding the highest temperatures of the plasma. However, the temperatures encountered in the plasma still exceed those of conventional atomization sources.

The plasma itself takes on a very flame-like appearance, as can be seen in Figure 8.[5] Normally, the plasma consists of a very bright white, nontransparent core. On top of this core extends a flamelike tail. The core itself extends only a few millimeters above the tube. This core is composed of a continuum upon which the spectrum of argon is superimposed. The argon spectrum originates basically due to the recombination of argon ions and electrons. Approximately 10-30 mm above the core the plasma becomes transparent due to the fading of the spectrum continuum. Spectral analyses are usually performed in this region, normally between 15-20 mm, since background interferences due to argon are minimal in this region.[5] As is evident from Figure 9, in the region of analysis the temperatures obtained in the plasma are approximately five to six times hotter than those obtained in commonly used gas flames.[5] This increased temperature provides for a more efficient atomization-excitation process, adding greater sensitivity to the technique.

Since such high temperatures can be achieved in the plasma, it has become an ideal excitation source. Due to the high temperatures and the constant flow of hot argon, common spectral interferences such as



Low
Frequency

High
Frequency

Figure 8. Sample particle paths for two different "flame-like" plasma shapes.[5]

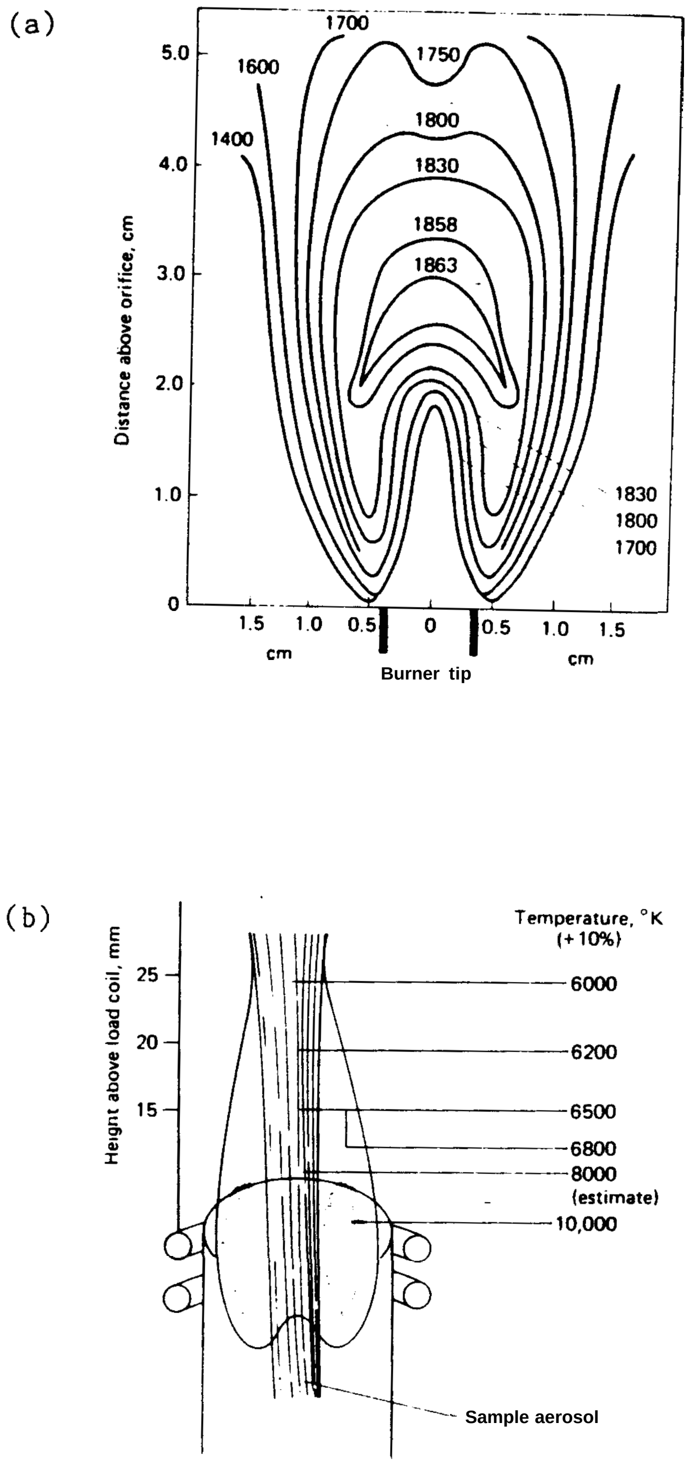


Figure 9. Comparison of temperature profiles for (a) a natural gas-air flame, and (b) an inductively coupled plasma.

self-absorption, reversal effects, molecular interferences, and interelement interferences are virtually eliminated. As a direct consequence thereof, calibration curves of concentration versus emission intensity performed using an ICP tend to be linear, whereas those obtained using flame sources tend to have an upward curvature at very high concentrations due to such spectral interferences as listed above.

An additional advantage resulting from the increased temperatures provided by an ICP source is the sensitivity which can be achieved in analyses. Using conventional flame methods, analyses were commonly only possible for major to trace constituents (parts per million level). When using an ICP source one is able to perform analyses often as low as the ultratrace level (parts per billion level). This added sensitivity has definitely guaranteed the ICP atomization source a principal role in the field of analytical chemistry in the future.

Multiquant Program

Simultaneous multielement analysis is not uncommon in the field of inductively coupled plasma emission spectrometry. Traditional multielement analysis is performed by using a direct reading, multichannel polychromator (Figure 10).[8] While definitely having its advantages, such an instrument requires a separate detector for each element of interest. In order to add or change elements, detectors had to be added or changed. With the advent of the scanning monochromator, analyses could be performed at various wavelengths with relative ease, simply by programming the instrument to analyze at a given wavelength by means of a computer. This made multiwavelength, and thereby

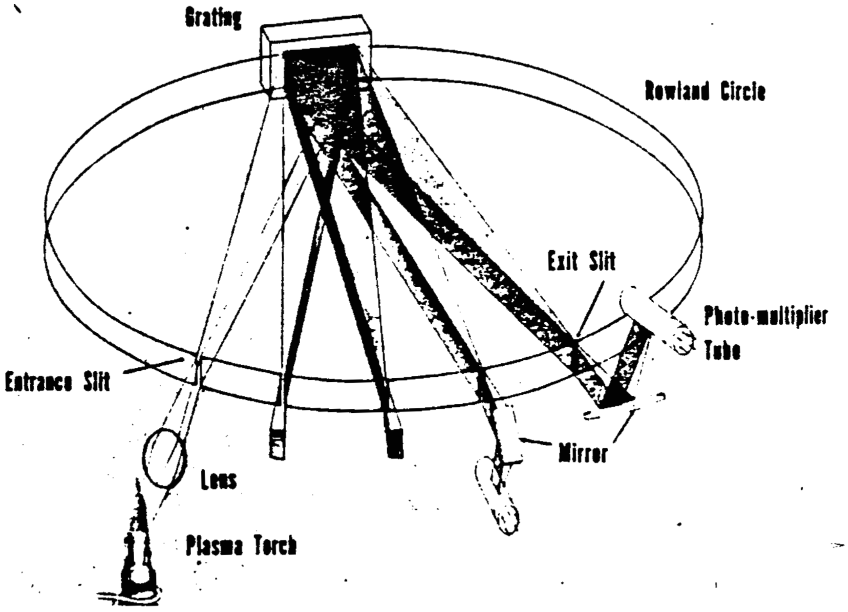


Figure 10. Schematic of a typical polychromator for multielement analysis.[8]

multielement, analysis a relatively simple task; however simultaneous multielement analysis with a scanning monochromator was still not possible. In the early 1980's an analytical program called Multiquant TM was developed for the Instrumentation Laboratory Plasma-200TM ICP emission spectrometer. The program enables the rapid sequential analysis of several elements at various wavelengths, eliminating the time and trouble consumed by multielement analysis performed in the traditional manner. The program provides qualitative and semiquantitative analysis. Also, an automated wavelength scan and graphic analysis at each wavelength are possible.[11]

The original Multiquant program consists of twenty-nine different elements measured at thirty different wavelengths; barium is included in the program twice (Table 2).[11] Calibration of the instrument is accomplished by using a blank and a three-element standard. The three-element standard is composed of the three so-called header elements, whose analytical lines are scattered across the spectrum accessible to the ICP emission spectrometer. The header elements and their corresponding wavelengths are: Zn (213.86 nm), Cu (324.75 nm), Ba (233.53 nm and 455.40 nm). The three-element standard consists of 10 ppm Zn, 10 ppm Cu, and 5 ppm Ba.[11]

As part of the start-up procedure of the Multiquant program the three-element standard is first run, followed by the blank. Intensities for the remaining elements in the program are then related to these three standard elements and their emission intensities. Each element in the program is then referenced to the header element of nearest wavelength. Each line is then calibrated to this header element by a predetermined ratio, which is entered into the program.[11] Before the

TABLE 2

ELEMENTS IN MULTIQUANT PROGRAM

Element	Wavelength (nm)
Ag	328.07
Al	396.15
As	193.70
B	249.77
Ba	455.40
Ba	233.53
Be	313.04
Bi	223.06
Ca	317.93
Cd	214.44
Co	230.79
Cr	205.55
Cu	324.75
Fe	259.94
Li	670.78
Mg	285.21
Mn	257.61
Mo	202.02
Na	589.59
Ni	231.60
Pb	220.35
Pd	340.46
Pt	265.95
Sb	206.83
Se	196.03
Si	251.61
Sr	407.77
Tl	351.92
V	290.88
Zn	213.86

program can be successfully run, standard solutions of all elements listed in the program must be run to determine the correct ratio of nearest header element intensity to analyte intensity. When the correct ratio has been determined the standardization process is complete.

The program itself can hold up to thirty analytical lines. The four header element lines must be included in every Multiquant program, however the program itself can be edited to contain other elements or other emission lines. The usual variables present in any inductively coupled plasma emission spectrometric method including torch observation height, and background correction must also be optimized in the Multiquant program. The usual advantages of Inductively Coupled Plasma Emission Spectrometry (ICP-ES), including minimizing of chemical and vaporization interferences and analysis in the trace to ultratrace levels, are retained in the Multiquant program.

CHAPTER IV

MATERIALS AND INSTRUMENTATION

Materials

Table 3 provides a list of all reagents used in this study. All were used without further purification. The water used in the preparation of all standard solutions was deionized water which was consecutively passed through three additional deionizing columns. Actual samples of contaminated acid copper electrodeposition solutions were used as confirmation of the success of this study. The acids used (nitric acid and hydrochloric acid) were double distilled, high purity acids, stored in teflon bottles.

Instrumentation

All analyses in this study were performed on an Instrumentation Laboratory Plasma-200 Inductively Coupled Plasma Emission Spectrometer.

Instrument Specifications[12]

1. RF Generator. The IL Plasma-200 is equipped with a two kilowatt RF Generator. The frequency of the system is crystal controlled at 27.12 MHz.

2. Torch. The torch used in this study is constructed from three concentric quartz tubes (Figure 11). The outer tube has a diameter of 20 mm, while the inner tube, which is responsible

TABLE 3

REAGENTS

Element	Concentration (ppm)	Grade	Manufacturer
Ag	1000	Certified AA Standard	Fisher Scientific
Al	1000	Certified AA Standard	Fisher Scientific
Ba	1000	Certified AA Standard	Fisher Scientific
Cu	1000	Certified AA Standard	Fisher Scientific
Fe	1000	Certified AA Standard	Fisher Scientific
Mn	1000	Certified AA Standard	Fisher Scientific
Ni	1000	Certified AA Standard	Fisher Scientific
Pb	1000	Certified AA Standard	Fisher Scientific
Pd	500	--------------------	---------------
Si	1000	Certified AA Standard	Fisher Scientific
Sn	1000	Certified AA Standard	Fisher Scientific
Ti	1000	Certified AA Standard	Fisher Scientific
V	1000	Certified AA Standard	Fisher Scientific
Zn	1000	Certified AA Standard	Fisher Scientific
Zr	1000	--------------------	---------------
Triton X-100	----	....	Fisher Scientific
HCl	----	Triple Distilled	---------------
HNO_3	----	Triple Distilled	---------------

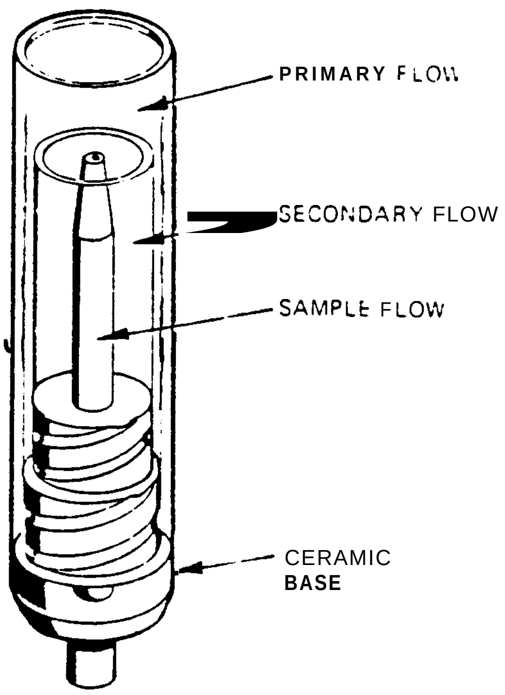


Figure 11. Schematic of the standard IL Plasma–200 torch.

for sample introduction into the plasma, has a diameter of 1.5 mm. Argon flows tangentially between the outer and middle tubes at 14-18 L/min. The tangential argon flow between the middle and inner tubes is approximately 0.5 L/min.

3. Sample Introduction. A computer controlled peristaltic pump is responsible for sample introduction into the plasma. Sample flow to the torch varies between 0.1 and 2.2 mL/min., the selected flow rate being programmed into the microcomputer. A cross-flow nebulizer with sapphire gas and sample orifices was used.

4. Optics for Air Monochromator. The optical system of the IL Plasma-200 consists of a double monochromator (Figure 12). "The primary monochromator is a 1/3 meter Ebert-Fastie design used in conjunction with a 1/6 meter Ebert-Fastie premonochromator. This . . . provides resolution of 0.02 nm by the Raleigh Criteria (second order) and stray light exclusion of $1:10^6$."[12] Two separate wavelength drive mechanisms are incorporated into the monochromator. A rapid scan grating drive functions as a coarse adjustment with a minimum step size of 0.005 nm. A refractor drive functions as a fine adjustment with a minimum step size of 0.001 nm. The optical system of the instrument operates in second order from 190 nm to 365 nm. Operation in first order occurs from 365 nm to 900 nm. Initial calibration of the instrument is performed using a mercury source and scanning a mercury triplet located at 365.02 nm.

5. Peak Search Window. The peak search window can be varied

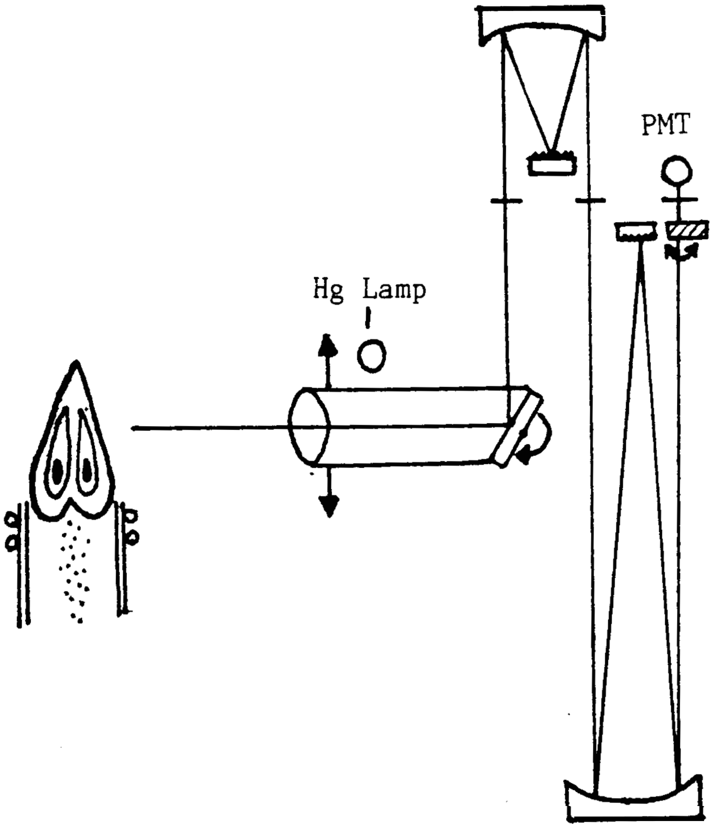


Figure 12. Schematic of the double monochromator optical system found in the IL Plasma-200.[12]

between narrow (0.033 nm), medium (0.067 nm), and wide (0.10 nm). Window size is programmed through the microcomputer.

6. Microcomputer. The instrument is controlled by a built-in microcomputer based on an Intel 80/16 single board computer using an 8080A microprocessor. Readout appears on a graphics printer and a 23 cm x 17 cm video screen with full graphics capability.

7. Software. The primary software used in this study consisted of the Multiquant program and the basic operations program provided with the IL Plasma-200.

CHAPTER V

PROCEDURE AND RESULTS

Preparation of Standard Solutions

Standard solutions of all elements listed in the program were prepared according to Table 4. All solutions were prepared with 0.05 uL/100 mL Triton-X and deionized water (water preparation described in Chapter IV). Three additional solutions, a three element standard (the calibration solution for Multiquant), a standard consisting of all elements provided in the program (basic operations program calibration solution), and a blank, were also prepared as listed in Table 5. All solutions were prepared in advance except single element solutions of silver, paladium, silicon, tin, and titanium, which tend to be unstable and were prepared immediately before use. All solutions were stored in polystyrene bottles. All glassware used in this study was first cleaned for at least twenty-four hours in a nitric acid solution. Immediately before use, all glassware was rinsed with deionized water.

Creation of Acid Copper Analysis Program

Multiquant Version

The initial program created in this study was an edited version of the original Multiquant program. Wavelengths of the various contaminating elements listed in Table 1 were included in the program. as well as those of the four header element lines which must be included in

TABLE 4

PREPARATION OF STANDARD SOLUTIONS

Element	Volume of 1000 ppm Standard (mL/1000mL)	Final Concentration (ppm)
Ag	10.00	10.00
Al	10.00	10.00
Ba	10.00	10.00
Cu	10.00	10.00
Fe	10.00	10.00
Mn	10.00	10.00
Ni	10.00	10.00
Pb	10.00	10.00
Pd	20.00 (500 ppm)	10.00
Si	10.00	10.00
Sn	10.00	10.00
Ti	10.00	10.00
V	10.00	10.00
Zn	10.00	10.00
Zr	10.00	10.00
Triton X-100	0.50	-----
*HCl	20.00	-----
HNO_3	10.00	-----

*HCl added only for solutions of Ag, Si, Sn, Ti.

TABLE 5

PREPARATION OF MULTIQUANT THREE ELEMENT STANDARD

Constituent	Volume (mL/1000mL)	Final Concentration (ppm)
Ba	5.00 (1000 ppm)	5.00
Cu	10.00 (1000 ppm)	10.00
Zn	10.00 (1000 ppm)	10.00
Triton X-100	0.50	-----
HNO_3	10.00	-----

PREPARATION OF BLANK

Constituent	Volume (mL/1000mL)	Final Concentration (ppm)
Triton X-100	0.50	-----
HNO_3	10.00	-----

PREPARATION OF CALIBRATION SOLUTION FOR BASIC OPERATIONS PROGRAM

Constituent	Volume (mL/1000mL)	Final Concentration (ppm)
Al	10.00(1000 ppm)	10.00
Cu	10.00(1000 ppm)	10.00
Fe	10.00 (1000 ppm)	10.00
Mn	10.00 (1000 ppm)	10.00
Mo	10.00 (1000 ppm)	10.00
Ni	10.00(1000 ppm)	10.00
Pb	10.00 (1000 ppm)	10.00
Pd	2.00 (500 ppm)	1.00
Sn	10.00(1000 ppm)	10.00
Ti	10.00(1000 ppm)	10.00
V	10.00(1000 ppm)	10.00
Zn	10.00 (1000 ppm)	10.00
Zr	2.00(1000 ppm)	10.00
Triton X-100	0.50	———

Constituent	Volume (mL/1000mL)	Final Concentration (ppm)
HCl	20.00	-----
HNO_3	10.00	-----

all Multiquant analysis programs. The wavelengths used in this study were selected according to Boumans Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometery and the Instrumentation Laboratory Methods Manual. All lines were selected on the basis of maximum sensitivity combined with minimal interelement interference. Zirconium was also entered into the program for use as an internal standard. The initial choice of wavelengths used in this study is listed in Table 6.

Calibration of Program Variables

The calibration of the variables involved in the Multiquant program was completed in a five step process: (1) calibration of each line to its nearest header element wavelength, (2) trimming of analyte lines, (3) correction for background interference, (4) adjustment of torch observation height, and (5) emission ratio adjustment. The following variables were held constant for all analyte lines: (1) analysis on channel A since a single channel instrument was used, (2) an integration time of 1.0 sec (except for palladium which had an integration time of 2.0 sec), (3) concentration unit of parts per million (ppm), (4) medium window size, (5) concentrations expressed to two digits beyond the decimal point. In addition, the following variables are program specific and chosen for this program: (1) moderate power level setting of three (of possible six), supporting an approximate delivery power of 1.2 kW of power and an approximate coolant flowrate of 13 L/min., (2) aspiration rate of 1.0 mL/min., (3) pump delay rate (pump washout cycle) of 30 sec, and (4) mercury lamp on during analysis.

TABLE 6

INITIAL MULTIQUANT VERSION OF ACID COPPER ANALYSIS PROGRAM[a]

```
 P#   WP  PWR NAMED
  1    0    3 ACID COPPER

ML/M PDLY HG   *ANAL *RDG
 1.0    30  1      0     0

 # EL       NM ORD CH MM BC   SEC
 1 ZN  213.86    2  A 10  L   1.0
 2 BA  233.53    2  A 10  L   1.0
 3 CU  324.75    2  A 10  L   1.0
 4 BA  455.40    1  A 12  L   1.0
 5 NI  231.60    2  A 10  B   1.0
 6 NI  232.00    2  A 10  B   1.0
 7 MN  257.61    2  A 10  L   1.0
 8 AL  396.15    1  A 14  L   1.0
 9 SI  251.61    2  A 10  B   1.0
10 AG  328.07    2  A 12  B   1.0
11 FE  238.20    2  A 10  L   1.0
12 FE  239.56    2  A 10  B   1.0
13 FE  234.35    2  A 10  R   1.0
14 ZN  206.20    2  A  8  N   1.0
15 ZN  481.05    1  A  8  R   1.0
16 SN  242.95    2  A 12  R   1.0
17 SN  284.00    2  A 14  B   1.0
18 PB  220.35    2  A 10  B   1.0
19 PB  217.00    2  A 12  L   1.0
20 PB  283.31    2  A 14  B   1.0
21 TI  307.86    2  A 10  L   1.0
22 TI  337.28    2  A 12  N   1.0
23 V   310.23    2  A 10  L   1.0
24 V   311.84    2  A 10  L   1.0
25 PD  284.89    2  A 22  B   2.0
26 ZR  343.82    2  A 10  L   1.0
27 ZR  327.31    2  A 10  N   1.0
```

[a] P# = **program number**
PWR = **power level**

PDLY = **pump delay in seconds**
*ANAL = **number of analyses**

WP = **write protect option**
ML/M = **aspiration rate in milliliters per minute**
HG = **mercury lamp option**
*RDG = **number of readings**

Trimming of Analyte Lines

For each element a specific wavelength value was entered into the program. When a standard sample of an element was aspirated the emission peak maximum may not have occurred within the peak search window precisely at the wavelength desired. A trim routine was performed, specifying the precise wavelength within the window at which the emission intensity was a maximum. This then specified the wavelength where analysis should be performed. The effect of performing a trim routine on a nickel solution is illustrated in Figure 13.

Background Correction

"Background correction has three primary uses: (1) to compensate for background shift between standards and samples caused by continuum emission, wing broadening, stray light, or viscosity differences; (2) to compensate for thermal drift in the background when determinations near the detection limit are to be made; and (3) to compensate for partially resolved matrix line spectral overlap."[10]

To choose the point where background correction should be performed, both a standard element solution and the blank were analyzed and their emission curves displayed simultaneously. The position chosen for background correction was that position free of all matrix interferences, that is, where the baseline of the standard and the blank coincided. The procedure is illustrated in Figure 14.

Observation Height Selection

The optimal observation height chosen for analysis of each wavelength was selected as the height giving the best signal-to-noise

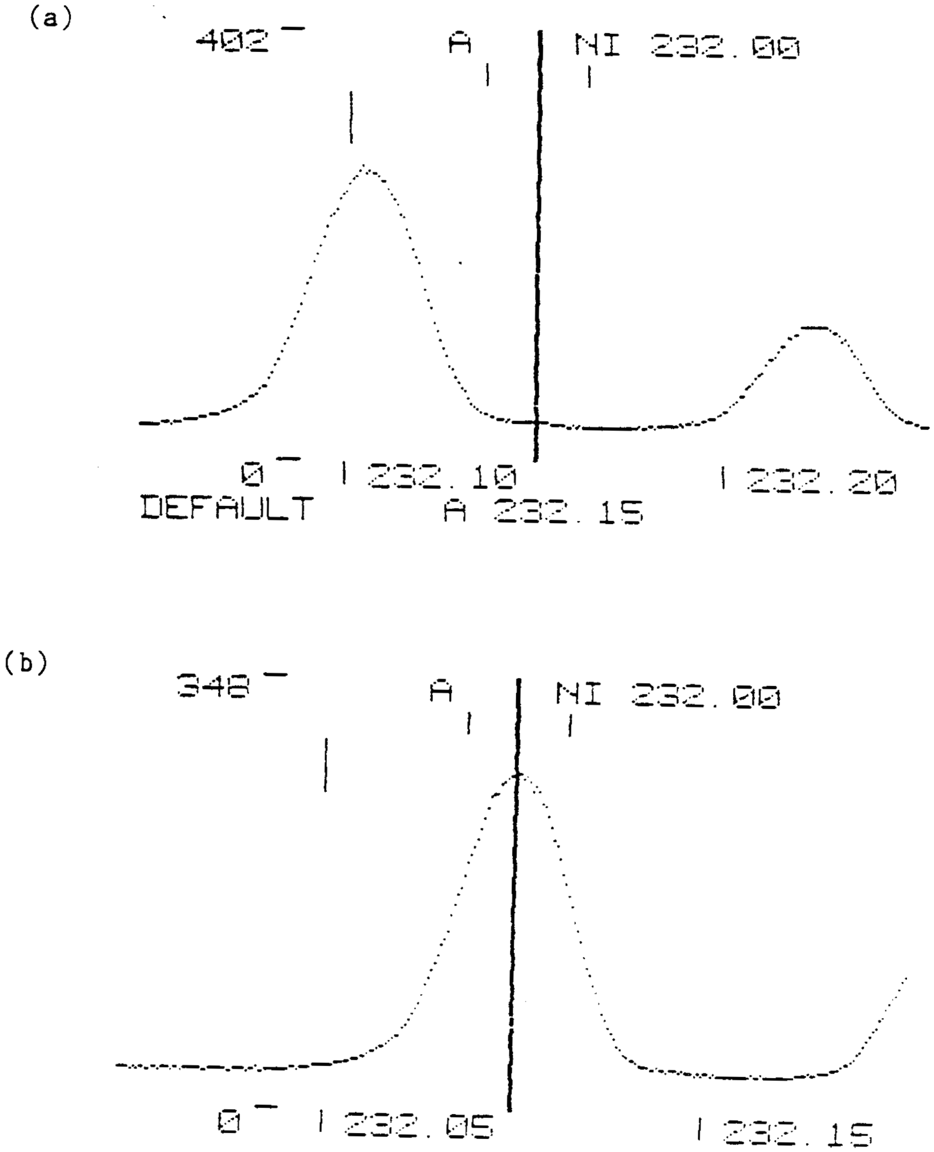


Figure 13. Representation of the effect of performing a trim routine on the nickel 232.00 nm line: (a) untrimmed line; (b) trimmed line.

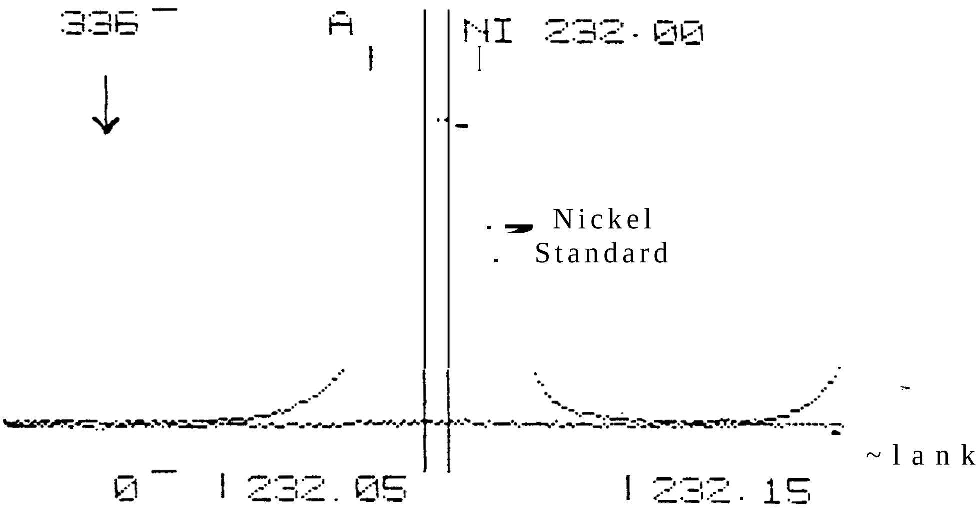


Figure 14. Illustration of background correction technique for the nickel 232.00 nm line by simultaneous overlay of a 10 ppm nickel standard and a blank. The point selected for background correction is marked by the arrow.

ratio. The optimal observation height was chosen by performing a torch profile of a standard element solution coupled with a torch profile of the blank. The torch profiles of both standard and blank were displayed simultaneously. The optimal observation height was chosen as the height in the torch where the distance between the signal from the standard and the signal from the blank was maximized. The procedure is illustrated in Figure 15 for a nickel solution.

Calibration to Nearest Header Element and Ratio Adjustment

This procedure is unique to the Multiquant program. Emission ratios are used to calibrate all wavelengths in the program except the four header element lines. Each dependent element line in the program is referenced to that header element line to which it is closest. For example the nickel line at 232.00 nm was referenced to the barium header element line at 233.53 nm. The concentration of a solution would be determined by multiplying the measured emission intensity- by some emission ratio specific to each line. Emission ratios were determined by first setting an arbitrary ratio for an element, such as 1.000. A standard sample was then analyzed and its uncorrected concentration determined. The corrected emission ratio was determined according to the following equation:

$$\text{Adjusted Ratio} = \frac{\text{Concentration Found}}{\text{True Concentration}} \times \text{Original Ratio} \qquad (9)$$

Evaluation of Program

Once the program variables were optimized the analyte lines were evaluated according to minimal background emission, minimal interelement interference, and maximum sensitivity. The analyte lines were evaluated

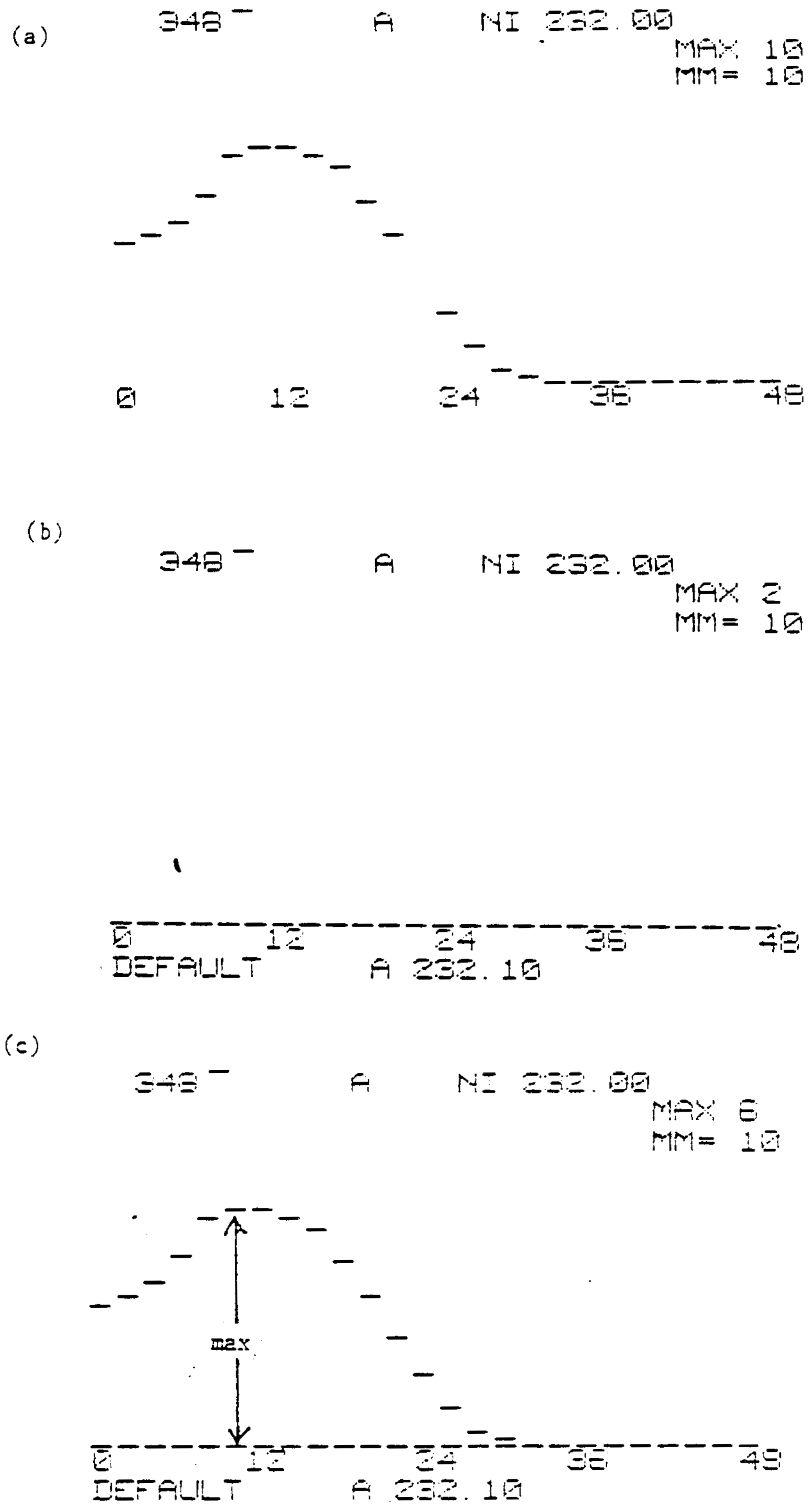


Figure 15. Representation of selection of optimal torch observation height for the nickel 232.00 nm line by performing torch profiles on (a) 10 ppm nickel standard, (b) blank, (c) simultaneous overlay of nickel standard and blank. 10 mm was chosen as the optimum torch observation height.

by analyzing 10 ppm standards of all elements individually and obtaining concentration readings for all lines in the program. A sample approximating that of a commercial copper electrodeposition solution matrix (150 g $CuSO_4 \cdot 5H_2O$/L) was prepared and analyzed. Finally a 10:1 dilution of this approximated copper matrix was analyzed. Emission intensities for all standard solutions as well as the two additional copper solutions at all analyte lines are listed in Table 7.

Once the emission intensities in Table 7 were obtained the program was further edited to accommodate any problems with analyte emission lines. It was expected that the emission intensities for elemental lines of elements not present in a given 10 ppm standard solution would have read a concentration of zero. This was not the case for several elements. Due to high background emission during analysis of most of the 10 ppm standards the following lines were deleted from the program: nickel (231.60 nm), zinc (481.05 nm), vanadium (310.23 nm), and zirconium (327.31 nm). High matrix interference was encountered with palladium (284.89 nm) for all standard 10 ppm solutions analyzed. Therefore a new palladium wavelength at 229.65 nm was entered into the program to replace the palladium line at 484.89 nm. All 10 ppm standard solutions were then analyzed at the new palladium line. Elemental interferences of a lesser degree were also encountered with zinc (213.86 nm), silver (328.20 nm), iron (238.20 nm, 239.56 nm, and 234.35 nm), tin (242.95 nm), lead (217.00 nm), and palladium (229.65 nm) in high copper matrices, and palladium (229.65 nm) in a nickel matrix. The interference of copper with zinc at 213.86 nm was a major problem since this zinc line was a header element line upon which other lines in the program were referenced. The optimum zirconium line at 343.82 nm

TABLE 7

EMISSION INTENSITIES OF STANDARD SOLUTIONS

Wavelength (nm)	Blank	Zn 10 ppm	Ba 10 ppm	Ni 10 ppm	Mn 10 ppm	Al 10 ppm
Zn 213.86	0.00	----	0.00	0.05	0.00	0.00
Ba 233.53	0.00	0.00	----	0.00	0.00	0.00
Cu 324.75	0.33	0.00	0.00	0.00	0.00	0.00
Ba 455.40	0.00	0.00	----	0.00	0.00	0.00
Ni 231.60	0.39	0.38	0.44	----	0.44	0.43
Ni 232.00	0.00	0.00	0.00	----	0.00	0.00
Mn 257.61	0.00	0.00	0.00	0.00	----	0.00
Al 396.15	0.07	0.07	0.10	0.07	0.05	----
Si 251.61	0.05	0.04	0.06	0.08	0.01	0.06
Ag 328.07	0.36	0.12	0.01	0.01	0.02	0.00
Fe 238.20	0.00	0.01	0.00	0.04	0.02	0.02
Fe 239.56	0.00	0.01	0.00	0.00	0.02	0.01
Fe 234.35	0.02	0.03	0.04	0.16	0.03	0.04
Zn 206.20	0.12	----	0.15	0.16	0.15	0.15
Zn 481.05	0.29	----	0.00	0.67	0.00	0.00
Sn 242.95	0.00	0.04	0.00	0.00	0.00	0.00
Sn 284.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb 220.35	0.02	0.01	0.06	0.01	0.00	0.00
Pb 217.00	0.13	0.22	0.15	0.00	0.14	0.00
Pb 283.31	0.00	0.00	0.00	0.00	0.00	0.00
Ti 307.86	0.20	0.22	0.00	0.00	0.00	0.00
Ti 337.28	0.18	0.18	0.20	0.22	0.20	0.20
V 310.23	0.30	0.33	0.33	0.00	0.32	0.32
V 311.84	0.00	0.00	0.00	0.00	0.00	0.00
Pd 284.89	10.03	10.05	10.05	9.80	9.94	9.93
Pd 229.65	0.01	0.09	0.00	16.58	0.00	0.10
Zr 343.82	0.00	0.00	0.00	0.00	0.00	0.00
Zr 327.31	0.49	0.49	0.54	0.59	0.56	0.53

Wavelength (nm)	Si 10 ppm	Ag 10 ppm	Fe 10 ppm	Sn 10 ppm	Pb 10 ppm	Ti 10 ppm
Zn 213.86	0.00	0.00	0.00	0.00	0.01	0.02
Ba 233.53	0.00	0.00	0.00	0.00	0.00	0.00
Cu 324.75	0.00	0.00	0.00	0.00	0.00	0.00
Ba 455.40	0.00	0.00	0.00	0.00	0.00	0.00
Ni 231.60	0.44	0.40	0.44	0.41	0.46	0.45
Ni 232.00	0.00	0.02	0.00	0.01	0.00	0.01
Mn 257.61	0.00	0.00	0.03	0.00	0.00	0.00
Al 396.15	0.09	0.10	0.00	0.07	0.08	0.14
Si 251.61	----	0.08	0.06	0.07	0.08	0.07
Ag 328.07	0.02	----	0.00	0.03	0.00	0.01
Fe 238.20	0.02	0.01	----	0.03	0.03	0.01
Fe 239.56	0.01	0.01	----	0.02	0.04	0.01
Fe 234.35	0.04	0.04	----	0.01	0.03	0.04
Zn 206.20	0.13	0.12	0.16	0.13	0.16	0.16
Zn 481.05	0.32	0.00	0.00	0.00	0.18	0.02
Sn 242.95	0.00	0.00	0.00	----	0.00	0.00
Sn 284.00	0.00	0.00	0.00	----	0.00	0.00
Pb 220.35	0.01	0.01	0.00	0.02	----	0.00
Pb 217.00	0.23	0.13	0.05	0.26	----	0.23
Pb 283.31	0.00	0.00	0.00	0.00	----	0.00
Ti 307.86	0.00	0.00	0.00	0.00	0.00	----
Ti 337.28	0.20	0.17	0.21	0.18	0.21	----
V 310.23	0.34	0.32	0.32	0.31	0.33	0.32
V 311.84	0.00	0.00	0.00	0.00	0.00	0.00
Pd 284.89	10.05	10.36	9.39	9.85	10.06	9.86
Pd 229.65	0.01	0.04	0.05	0.00	0.01	0.05
Zr 343.82	0.00	0.00	0.00	0.00	0.00	0.00
Zr 327.31	0.54	0.50	0.55	0.51	0.56	0.56

Wavelength (nm)	V 10 ppm	Pd 10 ppm	Zr 10 ppm	Cu 10 ppm	Cu 100 ppm	**Cu** Matrix
Zn 213.86	0.04	0.00	0.04	0.03	0.23	60.90
Ba 233.53	0.04	0.00	0.00	0.00	0.00	0.00
Cu 324.75	0.00	0.00	0.00	----	----	----
Ba 455.40	0.00	0.00	0.00	0.00	0.00	0.00
Ni 231.60	0.53	0.40	0.49	0.40	0.41	0.87
Ni 232.00	0.02	0.00	0.00	0.01	0.00	0.00
Mn 257.61	0.00	0.00	0.00	0.00	0.00	0.01
Al 396.15	0.03	0.10	0.10	0.04	0.05	0.16
Si 251.61	0.11	0.07	0.01	0.05	0.05	0.06
Ag 328.07	0.11	0.02	0.07	0.36	0.36	1.83
Fe 238.20	0.01	0.03	0.01	0.03	0.01	1.88
Fe 239.56	0.02	0.03	0.02	0.03	0.00	1.74
Fe 234.35	0.04	0.03	0.03	0.04	0.04	1.82
Zn 206.20	0.18	0.13	0.19	0.14	0.13	0.56
Zn 481.05	0.00	0.00	0.00	0.35	0.12	0.00
Sn 242.95	0.00	0.00	0.00	0.00	0.00	1.70
Sn 284.00	0.00	0.00	0.00	0.00	0.00	0.02
Pb 220.35	0.00	0.00	0.00	0.00	0.00	0.00
Pb 217.00	0.30	0.21	0.26	0.04	0.00	8.55
Pb 283.31	0.00	0.00	0.00	0.00	0.00	0.00
Ti 307.86	0.00	0.00	0.00	0.20	0.19	0.24
Ti 337.28	0.24	0.28	0.23	0.18	0.17	0.24
V 310.23	----	0.33	0.33	0.28	0.28	0.35
V 311.84	----	0.00	0.00	0.00	0.00	0.21
Pd 284.89	11.37	----	10.08	9.80	10.06	10.04
Pd 229.65	0.00	----	0.00	0.01	0.00	5.46
Zr 343.82	0.00	0.00	----	0.00	0.00	0.00
Zr 327.31	0.63	0.50	----	0.50	0.60	30.69

was selected as the line to be used as the internal standard. The lines of the final program are listed in Table 8.

Sample Analysis

Actual copper electrodeposition solution samples containing the various contaminants were analyzed using the completed program. All samples were diluted by a 10:1 ratio and spiked with the various contaminants. Samples 1A and 1B were composed of a 10:1 dilution of the same copper electrodepositon solution sample but differed in the contaminating elements which were spiked into the sample. The same is true of samples 2A and 2B, however the spikes were of a higher concentration (10 ppm) in samples 2A and 2B than in samples 1A and 1B (1 ppm). Sample 3 contained a 1 ppm spike of all contaminating elements in a 10:1 diluted copper sample, while sample 4 contained a 10 ppm spike of all contaminating elements in yet another 10:1 diluted copper sample. 10:1 dilutions of all four unspiked copper solution samples used were also prepared as blanks to determine if the spikes could be successfully recovered.

One drawback of the Multiquant program which was encountered was that interfering element and internal standard corrections could not be directly performed by the instrument during analysis. All corrections were performed by the operator after analysis. The results of the analyses of the various samples are listed in Tables 9 through 14. The average error involved in the analyses of the spiked samples at the various wavelengths is included in Table 15.

Upon reviewing the results in Tables 9 through 14 two trends become apparent. First, those elements referenced on the copper 324.75

TABLE 8

FINAL MULTIQUANT VERSION OF ACID COPPER ANALYSIS PROGRAM

```
 P#   WP  PWR  NAMED
  1    0    3  ACID COPPER

ML/M  PDLY  HG   *ANAL  *RDG
 1.0    30   1      0     3

  # EL        NM  ORD  CH  MM  BC   SEC
  1 ZN  213.86     2   A  10   L   1.0
  2 BA  233.53     2   A  10   L   1.0
  3 CU  324.75     2   A  10   L   1.0
  4 BA  455.40     1   A  12   L   1.0
  5 NI  232.00     2   A  10   B   1.0
  6 MN  257.61     2   A  10   L   1.0
  7 AL  396.15     1   A  14   L   1.0
  8 SI  251.61     2   A  10   B   1.0
  9 AG  328.07     2   A  12   B   1.0
 10 FE  238.20     2   A  10   L   1.0
 11 FE  239.56     2   A  10   B   1.0
 12 FE234.35       2   A  10   R   1.0
 13 ZN  206.20     2   A   8   N   1.0
 14 SN  242.95     2   A  12   R   1.0
 15 SN  284.00     2   A  14   B   1.0
 16 PB  220.35     2   A  10   B   1.0
 17 PB  217.00     2   A  12   L   1.0
 18 PB  283.31     2   A  14   B   1.0
 19TI   307.86     2   A  10   L   1.0
 20 TI  337.28     2   A  12   N   1.0
 21 V   311.84     2   A  10   L   1.0
 22 PD  229.65     2   A  10   B   1.0
 23 ZR  343.82     2   A  10   L   1.0
```

TABLE 9

RESULTS OF ANALYSIS--SAMPLE 1A

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Zn	213.86	5.41	7.03	1.62	1.00
Cu	324.53	----	31,010.00	----	----
Ni	232.00	0.72	1.73	1.01	1.00
Mn	257.61	0.13	1.20	1.07	1.00
Al	396.15	16.65	16.99	0.34	1.00
Si	251.61	3.61	4.50	0.89	1.00
Zn	206.20	1.05	2.12	1.07	1.00

TABLE 10

RESULTS OF ANALYSIS--SAMPLE 1B

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Ag	328.07	0.57	1.23	0.66	1.00
Cu	324.75	----	31,010.00	----	----
Fe	238.20	10.52	9.33	-1.19	1.00
Fe	239.56	10.22	11.31	1.09	1.00
Fe	234.35	10.42	9.06	-1.36	1.00
Sn	242.95	0.00	0.00	0.00	1.00
Sn	284.00	0.63	1.32	0.69	1.00
Pb	220.35	0.00	0.02	0.02	1.00
Pb	217.00	0.00	0.00	0.00	1.00
Pb	283.31	0.00	0.62	0.62	1.00

Element	**Wavelength** (nm)	**Blank Concentration** (ppm)	**Sample Concentration** (ppm)	Δ ppm	**Actual ppm Added**
Ti	307.86	2.39	3.03	0.64	1.00
Ti	337.28	2.54	3.14	0.60	1.00
V	311.84	0.00	0.86	0.86	1.00
Pd	229.65	1.50	2.09	0.59	1.00

TABLE 11

RESULTS OF ANALYSIS--SAMPLE 2A

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Zn	213.86	4.08	14.16	10.08	10.00
Cu	324.75	----	23,290.00	-----	-----
Ni	232.00	5.31	15.04	9.73	10.00
Al	396.15	0.23	10.99	10.76	10.00
Zn	206.20	0.25	11.18	10.93	10.00
Sn	242.95	2.17	11.78	9.61	10.00
Sn	284.00	2.06	11.94	9.88	10.00
Pb	220.35	0.00	10.14	10.14	10.00
Pb	217.00	0.00	0.00	0.00	10.00
Pb	283.31	0.00	10.08	10.08	10.00
Ti	307.86	0.27	9.62	9.35	10.00
Ti	337.28	0.23	9.84	9.61	10.00
Pd	229.65	9.00	35.25	26.25	10.00

TABLE 12

RESULTS OF ANALYSIS--SAMPLE 2B

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	A ppm	Actual ppm Added
Cu	324.75	----	23,290.00	----	-----
Mn	257.61	0.07	9.75	9.68	10.00
Si	251.61	0.73	10.02	9.29	10.00
Ag	328.07	0.57	5.44	4.87	10.00
Fe	238.20	1.07	1.07	0.00	10.00
Fe	239.56	0.90	10.39	9.49	10.00
Fe	234.35	1.13	10.59	9.46	10.00
V	311.84	0.00	10.13	10.13	10.00

TABLE 13

RESULTS OF ANALYSIS--SAMPLE 3

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Zn	213.86	52.43	53.44	0.97	1.00
Cu	324.75	-----	22,150.00	----	----
Ni	232.00	3.84	4.62	0.78	1.00
Mn	257.61	0.17	1.19	1.02	1.00
Al	396.15	0.25	1.44	1.19	1.00
Si	251.61	1.66	2.71	1.05	1.00
Ag	328.07	0.88	1.63	0.75	1.00
Fe	238.20	15.36	16.16	0.80	1.00
Fe	239.56	14.88	15.77	0.89	1.00
Fe	234.35	14.83	14.96	0.13	1.00
Zn	206.20	50.53	51.45	0.92	1.00
Sn	242.95	11.03	11.50	0.47	1.00
Sn	284.00	13.19	14.27	1.08	1.00

Element	**Wavelength** (nm)	**Blank Concentration** (ppm)	**Sample Concentration** (ppm)	**Δ** ppm	**Actual ppm Added**
Pb	220.35	0.00	0.39	0.39	1.00
Pb	217.00	0.00	0.00	0.00	1.00
Pb	283.31	0.00	0.00	0.00	1.00
Ti	307.86	0.57	1.63	1.06	1.00
Ti	337.28	0.74	1.94	1.20	1.00
V	311.84	0.00	0.76	0.76	1.00
Pd	229.65	6.52	8.81	2.29	1.00

TABLE 14

RESULTS OF ANALYSIS--SAMPLE 4

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Zn	213.86	4.15	16.06	11.91	10.00
Cu	324.75	-----	19,420.00	----	----
Ni	232.00	0.02	10.96	10.94	10.00
Mn	257.61	0.03	10.50	10.47	10.00
Al	396.15	0.76	12.25	11.49	10.00
Si	251.61	0.40	10.81	10.41	10.00
Ag	328.07	0.60	6.74	6.14	10.00
Fe	238.20	5.35	17.20	11.85	10.00
Fe	239.56	5.21	16.46	11.25	10.00
Fe	234.35	5.14	17.02	11.88	10.00
Zn	206.20	0.62	12.23	11.61	10.00
Sn	242.95	0.00	8.77	8.77	10.00
Sn	284.00	0.31	9.44	9.13	10.00

Element	**Wavelength** (nm)	**Blank Concentration** (ppm)	**Sample Concentration** (ppm)	**Δ** ppm	**Actual ppm Added**
Pb	220.35	0.00	10.51	10.51	10.00
Pb	217.00	0.00	0.00	0.00	10.00
Pb	283.31	0.00	9.12	9.12	10.00
Ti	307.86	0.49	9.43	8.94	10.00
Ti	337.28	0.66	10.20	9.54	10.00
V	311.84	0.00	9.77	9.77	10.00
Pd	229.65	0.00	28.46	28.46	10.00

TABLE 15

COMPARISON OF ANALYTICAL ERROR--SAMPLES 1-4

Element	Wavelength (nm)	Sample 1	Sample 2	Sample 3	Sample 4	Average Error
Zn	213.86	62.00	0.80	3.00	19.10	21.23
Ni	232.00	1.00	2.70	22.40	9.40	8.78
Mn	257.61	7.00	3.20	3.00	4.70	4.22
Al	396.15	66.00	7.60	19.00	14.90	26.88
Si	251.61	11.00	7.10	5.00	4.10	6.80
Ag	328.07	34.00	51.30	25.00	38.60	37.22
Fe	238.20	219.00	100.00	20.00	18.50	89.38
Fe	239.56	9.00	5.10	11.00	12.50	9.40
Fe	234.35	236.00	5.40	87.00	18.80	86.80
Zn	206.20	7.00	9.30	8.00	16.10	10.10
Sn	242.95	100.00	3.90	53.00	12.30	42.30
Sn	284.00	31.00	1.20	8.00	8.70	12.22

Element	**Wavelength** (nm)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Average Error**
Pb	220.35	98.00	1.40	61.00	5.10	41.38
Pb	217.00	100.00	100.00	100.00	100.00	100.00
Pb	283.31	38.00	0.80	100.00	8.80	36.90
Ti	307.86	36.00	6.50	6.00	10.60	14.78
Ti	337.28	40.00	3.90	20.00	4.60	17.12
V	311.84	14.00	1.30	23.00	2.30	10.15
Pd	229.65	41.00	162.50	129.00	184.60	129.28

nm header element line tended to exhibit the least amount of error in the various analyses, as 67% of all lines referenced on the copper header element line fell within the 25% error range, which is recommended as the acceptable error range when using the Multiquant program. Lines referenced on header element lines increasingly farther away from the copper line exhibited an error which increased with the distance of the header element line from that of the copper header element line. 50% of all lines referenced on the barium line at 233.53 nm were within the recommended error range, while 33% of all those referenced on the zinc line at 213.86 nm and 0% of those referenced on the barium line at 455.50 nm fell within the recommended 25% error range. Secondly, the analysis error tended to increase as the copper concentration in the samples increased. It was thus apparent that analyte concentration determinations using the Multiquant program would be dependent upon the concentration of copper in the samples. It was therefore decided to abandon use of the Multiquant program and to attempt to devise a program using the basic operations program provided with the IL Plasma-200.

<u>Creation of Acid Copper Analysis Program Using Basic Operations Program</u>

The basic operations program provided with the IL Plasma-200 differs from the Multiquant program mainly in that the analyte lines used in the program are not referenced upon other lines(header element lines) in the program. The same calibration variables as in the Multiquant program for the analyte lines also had to be determined using the basic program. Sequential element analysis was still possible using the alternate program, however a somewhat more complex calibration process was required. In the basic operations program a calibration curve of emission intensity versus concentration must be obtained for each element in the initial calibration procedure. The concentration of an unknown sample is then extrapolated from this calibration curve. Interfering element and internal standardization correction techniques were performed by the instrument and are included in the final results.

An attempt was again made to construct a program which could be used in concentrated copper matrices. The lines used in the Multiquant program were re-evaluated; some lines were incorporated into the new program, while others were rejected due to difficulty of analysis within the given matrix or due to interelement interferences. Some changes were also made to the elements to be included in the program. Silicon was excluded from this new program. An alumina torch, which is necessary for the analysis of silicon, was not available. As a result silicon tended to be leached from the torch causing silicon concentration values to be erroneous, and making silicon determination impossible. Silver was also excluded from the new program. Silver solutions tend to be unstable and to form complexes easily. It is believed that one, if not both, of these tendencies caused the silver concentration determinations to contain such large error. Accurate determination of silver concentrations would be impossible. Molybdenum was included in this program. Although molybdenum contamination is minimal in acid copper electrodeposition solutions low levels of molybdenum can interfere with the analysis of nickel and aluminum. With these changes in mind a new program was constructed. The initial program is listed in Table 16. All program specific variables remained the same as in the Multiquant program except the power setting. It was

TABLE 16

INITIAL BASIC OPERATIONS VERSION OF ACID COPPER ANALYSIS PROGRAM

```
 P#   WP PWR NAMED
  1    0   4 ACID COPPER

ML/M PDLY HG  *ANAL *RDG
 1.0   30  1      0    3

  # EL       NM ORD CH MM BC  SEC
  1 CU  222.78    2  A 14  B  1.0
  2 NI  232.00    2  A 10  L  1.0
  3 ZN  213.86    2  A 10  L  1.0
  4 ZN  206.20    2  A  8  R  1.0
  5 AL  396.15    1  A 14  B  1.0
  6 FE  238.20    2  A 10  L  1.0
  7 FE  239.56    2  A 10  R  1.0
  8 MN  257.61    2  A 10  L  1.0
  9 SN  189.99    2  A 10  L  1.0
 10 PB  220.35    2  A 10  L  1.0
 11 TI  334.94    2  A 12  L  1.0
 12 V   292.40    2  A 10  R  1.0
 13 V   290.88    2  A 14  L  1.0
 14 V   311.84    2  A 14  B  1.0
 15 MO  203.84    2  A 10  R  1.0
 16 PD  344.14    2  A 10  L  1.0
 17 ZR  343.82    2  A 14  B  1.0
```

power setting of four for the program. At this power level the amount of power delivered is the same as that in power level three (as was used in the Multiquant program) but the argon coolant flowrate is increased by 5 L/min. to 18 L/min.. This change in argon coolant flowrate minimizes the background emission interferences caused by nitrogen oxide molecular band emission.

After calibration of the program was completed, 1000 ppm solutions of all elements except palladium and zirconium were analyzed to determine which, if any, interelement interferences would occur. These results are listed in Table 17, where those values followed by an * indicate that interfering element correction was programmed in for interference with that element. For each interelement interference entered (two possible for each line) a scale factor had to be calculated. The interfering element scale factor, which determines the degree of interference from an element, is calculated by the following equation:

$$\text{Scale Factor} = \frac{\text{Apparent Analyte Concentration}}{\text{Actual Interferent Concentration}} \qquad (10)$$

Based on the results in Table 17 the zinc line at 213.86 nm was deleted from the program since all interelement interferences were unable to be corrected within the program. The zinc line at 206.20 nm showed no copper interference, making it a much more sensitive wavelength in a copper matrix. In addition, the vanadium (311.84 nm) and the iron (238.20 nm) lines were chosen as the most sensitive for the two given elements and were used in interfering element corrections. Changes were made in the program to facilitate interelement interference correction, in which the interferent must be listed in the program above

TABLE 17

EMISSION INTENSITIES OF STANDARD SOLUTIONS

Wavelength (nm)	Blank	Cu 1000 ppm	Ni 1000 ppm	Mn 1000 ppm	Fe 1000 ppm	Pb 1000 ppm
Ni 232.00	0.00	0.00	----	0.59	0.48	0.00
Zn 213.86	0.01	2.58	3.49	0.04	0.07	0.00
Zn 206.20	0.00	0.00	0.00	0.04	0.07	0.06
Al 396.15	0.00	0.01	0.17	0.00	0.00	0.03
Fe 238.20	0.00	0.00	0.01	0.00	----	0.00
Fe 239.56	0.00	0.00	0.00	0.95	----	0.00
Mn 257.61	0.00	0.00	0.00	----	3.10*	0.00
Sn 189.99	0.00	0.00	0.00	0.00	0.00	0.00
Pb 220.35	0.00	0.04	0.34	0.00	0.14	----
Ti 334.94	0.00	0.05	0.00	0.00	0.00	0.00
V 292.40	0.00	0.00	0.01	0.00	0.34	0.00
V 290.88	0.00	0.00	0.00	0.00	0.00	0.00
V 311.84	0.00	0.00	0.00	0.00	0.00	0.00
Mo 203.84	0.00	0.00	0.00	0.00	0.00	0.00
Pd 344.14	0.00	0.00	0.26	113.99*	0.29	0.00
Zr 343.82	0.00	0.00	0.00	0.00	0.06	0.00
Cu 222.78	0.07	1044.96	0.00	0.00	0.12	0.00

Wavelength (nm)	Al 1000 ppm	Zn 1000 ppm	Sn 1000 ppm	V 1000 ppm	Mo 1000 ppm	Ti 1000 ppm
Ni 232.00	0.00	0.00	0.11	0.60*	4.41*	0.00
Zn 213.86	0.11	----	1.13	6.52	0.00	0.91
Zn 206.20	0.11	----	1.48*	0.27	0.57	1.17*
Al 396.15	----	0.04	0.00	0.03	19.89*	0.00
Fe 238.20	0.04	0.05	1.03*	0.55*	0.00	0.45
Fe 239.56	0.04	0.05	1.03*	0.47	0.00	0.44
Mn 257.61	0.00	0.00	0.03	0.04	0.01*	0.02
Sn 189.99	0.02	0.00	0.00	0.45	0.49*	6.81*
Pb 220.35	1.38*	0.00	0.02	0.00	1.59*	1.26
Ti 334.94	0.00	0.00	0.00	0.00	0.00	0.00
V 292.40	0.00	0.00	0.00	----	0.95*	0.60*
V 290.88	0.00	0.00	0.00	----	0.00	0.00
V 311.84	0.00	0.00	0.01	----	0.00	0.00
Mo 203.84	0.00	0.00	0.00	0.78*	0.00	0.06
Pd 344.14	0.00	0.00	0.00	0.06	0.00	0.00
Zr 343.82	0.00	0.00	0.00	0.00	0.00	0.00
Cu 222.78	0.33	0.13	0.09	0.20	1.77*	0.00

the analyte line with which it interferes. The final program is listed in Table 18.

Six sample solutions similar to those analyzed using the Multiquant program were prepared and analyzed using this program. It was found that the error within the various wavelengths as well as the overall error had in general decreased (Tables 19-25). As a result 64% of the lines analyzed fell within the 25% error range, an improvement over the 53% found from using the Multiquant program. Significant'error resulted in the analysis of the easily oxidizable elements such as tin, titanium, and palladium. A large error was also encountered in the analysis of iron (238.20 nm and 239.56 nm) at low level concentrations, specifically in the 1 ppm spiked solutions. Alternate wavelengths were examined for these lines, but resulted in the same lack of analytical sensitivity. It was again observed that the average analysis error increased as the copper content in the samples increased. It was therefore decided that the latter program could successfully analyze for the less easily oxidized contaminants in an acid copper electrodeposition solution, however the elimination of matrix effects could only be reduced and not totally overcome.

TABLE 18

FINAL BASIC OPERATIONS VERSION OF ACID COPPER ANALYSIS PROGRAM

```
 P#  VP  PWR NAMED
  1   0    4 ACID COPPER

ML/M PDLY  HG   *ANAL  *RDG
 1.0    30  1       0     3

  # EL        NM ORD CH MM  BC  SEC
  1 V   311.84   2  A 14  B   1.0
  2 MO  203.84   2  A 10  R   1.0
  3 CU  222.78   2  A 14  B   1.0
  4 NI  232.00   2  A 10  L   1.0
  5 TI  334.94   2  A 12  L   1.0
  6 SN  189.99   2  A 10  L   1.0
  7 ZN  206.20   2  A  8  R   1.0
  8 AL  396.15   1  A 14  B   1.0
  9 FE  238.20   2  A 10  L   1.0
 10 FE  239.56   2  A 10  R   1.0
 11 MN  257.61   2  A 10  L   1.0
 12 PB  220.35   2  A 10  L   1.0
 13 V   292.40   2  A 10  R   1.0
 14 V   290.88   2  A 14  L   1.0
 15 PD  344.14   2  A 10  L   1.0
 16 ZR  343.82   2  A 14  B   1.0
```

TABLE 19

RESULTS OF ANALYSIS--SAMPLE 5A

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Cu	222.78	----	31,010.00	----	-----
Ni	232.00	0.71	2.01	1.30	1.00
Zn	206.20	0.83	1.82	0.99	1.00
Al	396.15	14.05	15.38	1.33	1.00
Mn	257.61	0.09	1.10	1.01	1.00

TABLE 20

RESULTS OF ANALYSIS--SAMPLE 5B

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
V	311.84	0.07	1.10	1.03	1.00
Mo	203.84	0.20	1.05	0.85	1.00
Cu	222.78	----	31,010.00	----	-----
Ti	334.94	2.24	3.45	1.21	1.00
Sn	189.99	0.32	1.51	1.19	1.00
Fe	238.20	9.87	12.27	2.40	1.00
Fe	239.56	9.94	12.27	2.33	1.00
Pb	220.35	0.05	1.11	1.06	1.00
V	292.40	0.05	1.13	1.08	1.00
V	290.88	0.06	1.07	1.01	1.00
Pd	344.14	0.00	0.05	0.05	1.00

TABLE 21

RESULTS OF ANALYSIS--SAMPLE 6A

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
Mo	203.84	0.11	7.31	7.20	10.00
Cu	222.78	----	23,290.00	----	-----
Ni	232.00	3.01	11.24	8.23	10.00
Ti	334.94	0.04	9.83	9.79	10.00
Sn	189.99	2.43	9.822	7.39	10.00
Zn	206.20	0.01	8.759	8.74	10.00
Al	396.15	0.11	9.433	9.32	10.00
Pb	220.35	0.18	8.51	8.33	10.00
Pd	344.14	0.00	0.00	0.00	10.00

TABLE 22

RESULTS OF ANALYSIS--SAMPLE 6B

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
V	311.84	0.00	11.02	11.02	10.00
Cu	222.78	----	23,290.00	----	-----
Fe	238.20	0.98	11.93	10.95	10.00
Fe	239.56	0.96	11.94	10.98	10.00
Mn	257.61	0.00	11.01	11.01	10.00
V	292.40	0.00	11.34	11.34	10.00
V	290.88	0.00	10.88	10.88	10.00

TABLE 23

RESULTS OF ANALYSIS--SAMPLE 7

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	A ppm	Actual ppm Added
V	311.84	0.02	1.01	0.99	1.00
Mo	203.84	0.19	1.31	1.12	1.00
Cu	222.78	----	22,150.00	----	-----
Ni	232.00	3.78	5.74	1.96	1.00
Ti	334.94	0.54	1.82	1.28	1.00
Sn	189.99	14.08	15.88	1.40	1.00
Zn	206.20	400.83	401.79	0.96	1.00
Al	396.15	0.03	1.43	1.40	1.00
Fe	238.20	14.07	15.77	1.70	1.00
Fe	239.56	14.43	16.36	1.93	1.00
Mn	257.61	0.03	1.13	1.10	1.00
Pb	220.35	0.01	1.07	1.06	1.00

Element	**Wavelength** (nm)	**Blank Concentration** (ppm)	**Sample Concentration** (ppm)	Δ ppm	**Actual ppm Added**
V	292.40	0.00	0.99	0.99	1.00
V	290.88	0.00	0.96	0.96	1.00
Pd	344.14	0.00	0.00	0.00	1.00

TABLE 24

RESULTS OF ANALYSIS--SAMPLE 8

Element	Wavelength (nm)	Blank Concentration (ppm)	Sample Concentration (ppm)	Δ ppm	Actual ppm Added
V	311.84	0.00	8.45	8.45	10.00
Mo	203.84	0.09	6.76	6.67	10.00
Cu	222.78	----	19,420.00	----	-----
Ni	232.00	0.10	10.41	10.31	10.00
Ti	334.94	0.38	8.55	8.17	10.00
Sn	189.99	0.66	12.52	11.86	10.00
Zn	206.20	0.09	8.79	8.70	10.00
Al	396.15	0.68	10.63	9.95	10.00
Fe	238.20	6.02	14.44	8.42	10.00
Fe	239.56	6.02	14.80	8.78	10.00
Mn	257.61	0.00	8.76	8.76	10.00
Pb	220.35	0.03	0.03	10.02	10.00

Element	**Wavelength** (nm)	**Blank Concentration** (ppm)	**Sample Concentration** (ppm)	Δ ppm	**Actual ppm Added**
V	292.40	0.00	8.69	8.69	10.00
V	290.88	0.00	8.51	8.51	10.00
Pd	344.14	0.00	0.00	0.00	10.00

TABLE 25

COMPARISON OF ANALYTICAL ERROR--SAMPLES 5-8

Element	Wavelength (nm)	Sample 1	Sample 2	Sample 3	Sample 4	Average Error
V	311.84	3.00	10.20	0.99	15.50	7.42
Mo	203.84	15.00	28.00	12.00	33.30	22.08
Ni	232.00	30.00	17.70	4.00	3.10	13.70
Ti	334.94	21.00	2.10	28.00	18.30	17.35
Sn	189.99	19.00	26.10	40.00	18.60	25.92
Zn	206.20	1.00	12.60	4.00	13.00	7.65
Al	396.15	33.00	6.80	40.00	0.50	20.08
Fe	238.20	240.00	9.50	170.00	15.80	108.82
Fe	239.56	233.00	9.80	193.00	12.20	112.00
Mn	257.61	1.00	10.10	10.00	12.40	8.38
Pb	220.35	6.00	16.70	4.00	0.10	6.70
V	292.40	8.00	13.40	1.00	13.10	8.88
V	290.88	1.00	8.80	4.00	14.90	7.18
Pd	344.14	5.00	100.00	100.00	100.00	76.45

CHAPTER VI

DISCUSSION AND CONCLUSIONS

Discussion of Results

In this study Inductively Coupled Plasma Emission Spectrometry was examined as a possible means for the analysis of acid copper electrodeposition solutions. It was hoped that a successful analysis program could be devised for the analysis of such copper solutions without any pretreatment being necessary before an analysis.

An analysis program was constructed using the Multiquant program. This program was unsuccessful. The high copper content of the solutions involved directly influenced the results, making accurate analysis impossible. The program was edited so that it contained lines of maximum sensitivity and minimal interference. Although interferences are minimal when using such high energy sources as an inductively coupled plasma, some interelement interferences were found to exist. The Multiquant program was not able to compensate for these interferences and made accurate analysis of such elements as manganese, nickel, and lead impossible. In addition, silver and silicon could not be determined as a result of reactions within the analysis system. Based on the results obtained from the program, lines were selected for the construction of an alternate program using the basic operations program provided with the IL Plasma-200 emission spectrometer. This program allowed lines of greater sensitivity to be used, since interfering element correction is possible. This program was more successful than the previous attempt. Determination of the more easily oxidized elements--tin, palladium, and titanium--still proved unsuccessful. Adequate sensitivity for these lines could not be provided by either program. The final program did prove to be successful in the analysis of the less easily oxidized elements.

Conclusions

It is believed that the final program offers a successful mode of analysis of the less easily oxidized contaminants in an acid copper electrodeposition solution. Since plasma sources offer the most successful excitation sources available, deficiencies in the successful analysis of the copper solutions studied may be attributed to the matrix effects caused by this high copper content.

Although the method developed was fairly straightforward, the interfering effects could have been minimized provided the copper could have been separated from the contaminants or the interfering effects of the copper matrix could have been eliminated. Elimination of the matrix effects was attempted with the use of internal standard and interfering element correction routines. However, the copper matrix was still found to influence analysis. An alternate method of initially removing the copper from the solutions before analysis could prove more successful. At present, an effective method of selectively removing copper from such a sample is not available. Methods of removing copper, such as the use of lanthanum nitrate as a precipitating agent of the contaminants, do exist. With the use of lanthanum nitrate several elements can be precipitated, leaving copper in solution. The precipitates are then separated from the supernatant liquid and redissolved. This technique, while successful for copper removal, is not totally selective for copper; contaminants would also be separated. These pretreatment techniques are both troublesome and time-consuming and would not offer any new advantages to industrial analysis. The development of a procedure to selectively remove copper from a solution is beyond the scope of this study, and will be left for future consideration.

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