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MM&T PROGRAM TO ESTABLISH PRODUCTION TECHNIQUES FOR THE AUTOMATIC DETECTION AND QUALIFICATION OF TRACE ELEMENTS PRESENT IN THE PRODUCTION OF MICROWAVE SEMICONDUCTORS

> SECOND QUARTERLY REPORT 23 November 1977 to 28 February 1978

AUG 2 .1978

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Placed by

Production Division, Procurement and Production Directorate USAECOM, Fort Monmouth, New Jersey 07703

Contract DAAB07-77-C-0561

Harris Corporation, PRD Electronics Division 6801 Jericho Turnpike, Syosset, New York 11791

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and MMAT PROGRAM TO ESTABLISH PRODUCTION TECHNIQUES FOR THE AUTOMATIC DETECTION AND QUALIFICATION OF TRACE ELEMENTS PRESENT IN THE PRODUCTION OF MICROWAVE SEMICONDUCTORS. SECOND QUARTERLY REPORT. no. dy 23 November 4077-to 28 Februar

Object of Study

Establish production technique for the automatic detection and concentration quantification of the trace elements (impurities) in the organic and inorganic compounds and solutions that are used in the fabrication of microwave semiconductors and the deter-

mination of acceptable impurity levels. Contract No. : DAAB07-77-C-0561 Report Prepared by: Roy W. Spacie Distribution Statement

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ABSTRACT

This is the second quarterly progress report of a US Army sponsored study which had as its objective the improvement of product yields in the manufacture of microwave semiconductor devices by establishing the correlation between the electrical performance of such devices and the levels of trace element contamination in the materials used in the manufacturing process. The quarter primarily was devoted to the acquisition, assembly and calibration of the analytic tools to be used and the training of operating personnel and the development of computer programs for the statistical analysis of the test data.

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GLOSSARY

Aliquot: contained an exact number of times in another, fractional. Analysis of Covariance: a statistical technique that combines the features of variance and regression. a set of equations and/or logic statements, generally Analytic Model: implemented on a computer, which quantitatively represents the interrelationships that characterize a given system. A unit of length (wavelength) equal to one ten-billionth Angstrom: of a meter, i.e., 10-10m. Boule: a pear-shaped mass formed synthetically in a special furnace with the atomic structure of a single crystal. Clustering: statistical procedures which classify data into recognizable sub-groups according to a defined criterion function. a statistical procedure to find a lower-dimensional Factor Analysis: representation that accounts for the correlation among variables. Epitaxial: having orientation controlled by the crystalline substrate - used of crystals and of the relationship between them and their substrate. Ionize: to cause a change in the number of electrons in the outer orbits of an atom such that it exhibits a net electrical charge. that within which something else originates or develops, Matrix: e.g., a format for developing computer instructions. Mesa: (~ transistor) structured as a mesa - an isolated hill having steeply sloping sides and a level top. one billionth of a gram. (Also used are femtogram Nanogram: [one quadrillionth], picogram [one trillionth] and microgram one millionth .)

GLOSSARY (Contd)

PIN:

Plasma:

Principal Component Analysis:

Regression Analysis:

Variance:

(~ diode) an acronym formed from ''positive-intrinsicnegative'' - a semiconductor device consisting of heavily doped p^+ and n^+ end regions separated by a lightly doped region which can be regarded as intrinsic.

a gas in which a significant fraction of its atoms or molecules are ionized.

a statistical procedure for finding a lower-dimensional representation that accounts for the variance among an ensemble of data.

a statistical method concerned with the prediction of one or more variables on the basis of information provided by other measurements or concomitant variables.

the weighted average of the squared deviation of the values in a population from the population mean, numerically equal to the square of population's standard deviation.

PURPOSE

The objective of the present Manufacturing Methods and Technology (MM&T) Project is the reduction of microwave semiconductor manufacturing costs through increased product yields. This will be achieved by establishing the correlation between contaminant levels in process materials and their effect upon product yields. These relationships will be used to optimize the manufacturing process toward maximum product yields and minimum unit costs. The project will result in the following developments:

1. An analytical model of the manufacturing process. The model will be implemented in a computer program which will serve as an optimizing control system for the process.

2. A system of batch or lot identification to maintain traceability of contaminants throughout the process, from receiving inspection to the final product.

3. A quantitative chemical analysis system to evaluate contaminants in the materials used in the manufacturing process.

4. A performance specification for an improved manufacturing process control and data management system incorporating these techniques.

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SECTION I INTRODUCTION

1.1 BACKGROUND

The objective of this program is to improve product yields and consequently lower production costs in the fabrication of microwave semiconductor devices. The yield improvement is predicated on improved control of trace element contamination occurring in process chemicals and reagents. The program will correlate the electrical characteristics of the semiconductor device to measured concentration levels of the elements known to adversely affect the product's performance. The causal relationships between them will then be quantified and employed in a mathematical model of the process. The model in turn will be used to minimize the manufacturing costs of the semiconductor product. A thorough discussion of the project's plans and objectives may be found in the project's First Quarterly Report entitled "MM&T Program to Establish Production Techniques for the Automatic Detection and Quantification of Trace Elements Present in the Production of Microwave Semiconductors," Report Number ECOM 0561-1.

In the manufacture of microwave semiconductor devices, such as high voltage PIN diodes which are used in military electronic systems, the production yields are very low, typically in the order of 5 to 10 percent. These poor yields are attributed in part to the inclusion of trace amounts of contaminants within the crystalline structures of the devices. Contaminating elements in the order of a few parts per billion are often sufficient to degrade, if not destroy, the performance of the device. Currently the military is spending \$28 million annually for devices of this type. Any improvement in production yields is reflected in lower unit costs. At present usage rates, it is expected that this could represent significant cost savings to the military.

1.2 THE MANUFACTURE OF MICROWAVE SEMICONDUCTOR DEVICES

Typically, the manufacture of microwave semiconductor devices is accomplished as a series of batch processing steps. For example, ultrapure silicon is procured as a raw material. A quantity of this material is melted and recrystallized into a boule. The boule is entered into stock. Sometime later a boule is drawn from stock and sliced into many wafers. The wafers are ground and polished and returned to stock. Small lots of the wafers are drawn from stock as required. The process continues in this manner through 50 to 60 production steps (refer to flow diagram in Appendix A). Similarly, the reagents used in the various process steps are prepared and dispensed in relatively small batches or lots. A single store of partially processed devices may serve as a source for several different product lines.

Because the manufacture of microwave semiconductors is a batch process, it is difficult to maintain traceability of the end product. If an end item should fail to perform properly because of some intrinsic impurity, it is often impossible to trace the impurity back to its source or point of ingress. However, to control impurity levels to a few parts per billion, it is essential that precise traceability be achieved. Therefore, a fundamental part of the present program must be to devise and implement a system of automatic record keeping and data processing so that yields can be correlated with measurable impurity levels at each step of the process.

Table 1-1 is a partial list of those chemical elements known to adversely affect the performance of microwave semiconductor devices. These impurities may enter interstitially into the crystalline structure of the device, enter on a substitutional basis replacing atoms in the normal crystalline matrix, or react chemically with some of the semiconductor materials. In some cases these elemental impurities may migrate to an interface, inducing effects disproportionate to their average concentrations. In most cases, the effects of these impurities upon the electrical performance of the semiconductor device can be predicted with a high degree of accuracy if one knows the concentration of each. Unfortunately, the concentrations of these elements within the semiconductor material can be measured at only a few points in the manufacturing process. Where tests can be made on the semiconductor material they are generally destructive and analytical data must be gathered on a sampling basis.

Aluminum	Copper	Molybdenum	
Antimony	Fluorine	Nickel	
Arsenic	Gallium	Oxygen	
Bromine	Germanium	Palladium	
Boron	Gold	Phosphorus	
Cadmium	Iodine	Potassium	
Calcium	Iron	Rubidium	
Carbon	Lead	Silver	
Cesium	Lithium	Sodium	
Chlorine	Magnesium	Tin	
Chromium	Manganese	Zine	
Cobalt	Mercury		

TABLE 1-1. CRITICAL CONTAMINANTS

The chemical impurities may enter the semiconductor material at any of many points in the manufacturing process. They may be induced from the solvents used for cleaning and etching the crystalline wafers, from the materials used in the formation of epitaxial layers, or from the reagents used in any of the 50 to 60 steps of the manufacturing process.

It must be assumed that all of these contaminants are present to a greater or lesser extent in all of the reagents used in the manufacturing process. However, the semiconductor material is not equally susceptible to contamination at each step of the process. For example, the silicon is susceptible to contamination by oxygen only at elevated temperatures. Therefore, it is not sufficient to only know the concentration of these contaminants in each reagent, but one must also know the transfer ratio associated with each element at each step of the process. That is to say, one must know the quantitative relationship between the level of a contaminant in the reagent and the amount of contamination it can be expected to induce into the semiconductor material. Little is known about these transfer ratios at this time. A major task of the present project is to explicitly define the manufacturing process in terms of the interrelationships between the reagents and the semiconductor material and to quantify the transfer ratios of pollutants. Once the ratios are established, it remains to set threshold levels consistent with acceptable yields.

Theoretically, one might analyze the chemical composition of the semiconductor material at each step of the manufacturing process, aborting a batch if it is found to be execessively contaminated. Unfortunately such an approach is neither practical nor economical. The semiconductor material is available for testing at only a relatively few points in the manufacturing process, and, where it is available, it is in a solid form which does not readily lend itself to chemical analysis. Further, chemical analyses of elements to a few parts per billion are generally extremely expensive and require highly skilled technicians operating with meticulous care. Thus, the costs associated with such an approach would soon outrun any economic gains which may accrue from improved yield. For these reasons, a fundamental part of this program must be to develop a testing program which is capable of providing the necessary control data within the economic constraints of improved yields.

1.3 THE SPECIFIC PROBLEM

There are uncertainties in processing semiconductor devices in reasonable yields consistently. Controls for times and temperature are known to be quite good. The most significant unknown is the variability of the chemical reagents and deionized water used in wafer fabrication. In addition, although ambient conditions are usually considered to be quite well-controlled with laminar flow, ultrafiltration and frequent particle counts, the chemical nature of airborne contamination is probably the next most significant unknown. The well-known cyclical history of the manufacture of certain microwave semiconductor devices bears these facts out. Frequently, certain devices go out of production; the company is said to have "lost the recipe" temporarily. Then, as mysteriously as the problem arose, its nature being such, the problem disappears; yields return to original levels and production once again returns. The cost to the Government in these situations is significant. Did the problem disappear because a particular lot of reagent material was used up, or replaced? The problem could have been caused by variability within the manufacturer's specification of some critical contaminant in a reagent, as no quantitative tool is available to monitor on-line each batch for impurity levels and types.

The present project will form the basis for an automatic test and control system, which will include all the appropriate sensors to detect impurity levels in the chemical reagents and particulate matter which might be present in a microwave semiconductor process. This control system will have the capability of analyzing all the chemical inputs to the process: solid, liquid and gaseous. The functions of this detection and control system will be several: to provide warning of excessive contamination as early in the process as possible; to allow contaminated material to be discarded, rather than accrue further manufacturing costs; to be able to identify specifically the critical contaminants to microwave technology, and the threshold levels necessary to precisely control the process; to provide lot traceability throughout the process so that final yields of end products can be correlated with known contamination levels and appropriate yield improvements can be made.

The benefit to the Government and to the microwave industry arising from this project is significant. The keystone of an overall process control and monitoring system is the analytical tool necessary to provide the answers as to what contaminants affect device yields, what are their allowable levels and what steps are to be taken to minimize their effects upon semiconductor yields.

The present project could readily be extended at some future date to include other sensors. Temperature, flow rates, real-time gas stream analysis, pressure, residual atmosphere under high vacuum are all areas which can be readily controlled and monitored by a computerized system. Historical information on the performance of a piece of equipment, comparison with present performance, and trend information are all readily available.

1.4 METHOD OF SOLUTION

The approach to the solution of this problem will be a joint effort between Harris Corporation/PRD Electronics Division, Syosset, New York, acting as prime contractor, and Microwave Associates, Inc., Burlington, Massachusetts, serving as

principal subcontractor. Microwave Associates will provide and operate a standard production facility and process for the manufacture and test of PIN diode chips having specific electrical performance characteristics. An atomic emission spectrometer will be employed as the principal means of chemical analysis. Microwave Associates will monitor the impurity levels of each process chemical as it is used in the production process.

A set of experiments will be designed in which the normal operation of the process is deliberately perturbed to allow evaluation of the effects of impurities upon product yields.

Microwave Associates will gather all pertinent analyses, test data and observations and will transmit them to PRD Electronics on a daily basis. PRD Electronics will analyze these data to evaluate the impact of contamination levels upon the electrical characteristics of the device and upon the product yields.

Material and lot traceability will be meticulously maintained throughout the program to facilitate the accurate correlation of contaminant levels with yields. As correlation is established between contaminant level and yield, a mathematical model of the process will be developed which will provide an independent yield analysis for a particular production run.

Finally, a technical report and demonstration will be developed and presented which will indicate critical process steps, reagents and contaminant levels, the appropriate correlations, the frequency of measurements, and the number and types of sensors needed to control the process to minimize product costs.

1.5 FIRST QUARTER ACTIVITIES

During the first quarter of the program, a computer-controlled spectrometer capable of measuring elements in concentration as low as 20 parts per billion was procured. The instrument will serve as the principal measuring device with which the quality of the chemicals will be monitored. A high voltage PIN diode (e.g., JANTX-1N5710) was selected as the device on which the study would be based and a computer model of its manufacturing process was designed. A technique was developed

for maintaining material and lot traceability throughout the program. All ancillary materials were ordered, facilities were allocated and personnel assigned.

SECTION II

INSTRUMENTATION

2.1 SPECTROMETER INSTALLATION

A plasma emission spectrometer from the Jarrell-Ash Division of Fisher Scientific Company was delivered to Microwave Associates, Burlington, Massachusetts on 29 November 1977. Installation and calibration of the instrument were started on 5 December 1977 and completed on 16 December 1977. The installation and calibration were performed by Jarrell-Ash technicians under the terms of the purchase contract and required approximately 100 man-hours of effort. Dr. George P. Allendorf of Microwave Associates was in attendance throughout the period and received valuable instruction in the operation and maintenance of the instrument. The instrument met or exceeded the performance specifications. The installation was made in the area designated to become an analytical laboratory but delays in the construction of the laboratory were encountered and as of the end of February the laboratory had not been completed. It is not anticipated that the delay will adversely affect the progress of the project.

Upon completion of the installation, practice analyses were performed on a variety of substances including nitric and hydrochloric acids and various water samples. The analyses which were performed were reproducible and the instrument appeared to be stable over an 8-hour period. The main thrust during the remaining weeks of December and early February was to gain familiarity with the instrument. Microwave Associates' personnel developed facility with the operation of the instrument's computer, the loading of programs and the development of matrices.

2.2 SPECTROCHEMICAL MATRICES

In its broadest sense a matrix is something within which something else originates or develops. In geology, for example, it refers to the natural material in which a fossil, metal or crystal is embedded. In chemistry it may be a substance in which a solute or colloid is dispersed. Within the context of the Jarrell-Ash

spectrometer it refers to a format in which a set of computer instructions is developed. Specifically, it refers to the instruction set which the computer is to use in performing the analysis of a prescribed list of chemical elements occurring in a chemical solution.

A spectrometer matrix essentially instructs the computer as to the type of data it is to develop and the format in which it is to be printed. It specifies the spectral line intensities to be measured and the computations it is to make in converting the measured line intensities to concentration levels. The latter requires the input of scaling factors and slope and offset data for each element of interest.

The preparation and calibration of a new matrix is an exacting process requiring careful attention and precise accuracy. It requires a well-planned and meticulously formulated set of standard solution. The adjustment of the slope and offset constants is an interactive process. Using the computer's operating system the matrix is standardized and the primary standards rerun. The measured concentrations are then compared with the stated concentration and corrections applied to obtain improved accuracy. The corrections are edited and the process repeated until the desired accuracy is obtained. The matrix, after some inspection, is then typed manually into the computer. Once in the computer, and corrected in format, a permanent record is made in supplementary memory (disc) and a copy is also made on paper tape.

Typically, with 28 channels to be calibrated the process requires a week or more. By the end of February 1978 the following matrices had been written:

MATRIX NAME	MEDIUM
GAAQ	Aqueous (water)
TRIC	Trichloroethylene
ACET	Acetone
MECL	Methylene Chloride
XYLN	Xylene
ISOP	Isopropyl Alcohol
METH	Methyl Alchol

An example of one of these matrices is presented as Figure 2-1, GAAQ Matrix Printout, located on page 2-7 with apron to permit viewing while reading the entries in the printout which are interpreted as follows:

Line 1 Command to print a matrix data base (PR).

- 2-3 Submatrix name, limited to four characters. The first two characters are unique to the particular matrix and the second two identify the submatrix.
- 4 Number of logic channels, i.e., the number of chemical elements (LCN:28) and the number of submatrices (SM'S:1).
- 5 Mode, i.e., the type of data to be developed, concentrations (CN). Alternative options include intensities, intensity ratios, and concentration ratios.
- 6 FORMAT This line is used to specify the format in which the analytical data are to be printed. The format is limited to five lines. The number of entries per line is to be specified. In this case the computer is instructed (e.g., 19991) to print one channel on the first line, nine channels each on lines 2, 3 and 4, and one channel on the fifth line. The first channel always is the internal standard. The last channel is number 28 XX, the unused channel.
- 7-10 Up to four internal standards may be used. Only one was selected and it occupied "physical channel" number 26 (PCN:26). A format priority 1 (PRTY:1) was assigned (see Note 1), as was a preburn of 1 second (PREBRN:1) on an exposure of 10 seconds (EXPOSR:10) (See Notes 2 and 3).
- 11-15 Five standard solutions were specified (HAR1----HAR5)

17-43 <u>COLUMN</u>	SUBJECT	
a	Logical Channel Number - order of printout	
ь	Heading - element symbol	
c	Physical Channel Number - the physical location in the	
	spectrometer of the photomultiplier tube for that element	
d	Internal Standard Channel Number	
	Location of Bakegroud Line - not applicable here	
f	High Standard - which bottle of solution contains this	
	element	
g	Low Standard - the "blank" solution (here #1)	
h	Significant Figure Format - number of significant figures	
	to be printed	
,	Priority Level - 1 through 7 - can modify printout by	
	specifying priority; instrument will print out priority 2	
will state and no Gara	Name of Analytical Curve	
at longer to had with	Name of Analytical Curve	
k	Background Constant (here 0) to be applied for correction	
1	Intensity Ratio of High Standard (10 ppm = 10) Absolute Intensity	
	Intensity Ratio is: Internal Standard	
m	Intensity Ratio of Low Standard (blank)	
n	Gain - Correction applied to each element after standardiza-	
	tion - compensates for instrumental drift; given as G_L in	
	equation (1) below	
P	Offset - Correction applied to each element after	
	standardization - coefficient A_L in equation (1)	

$$\frac{\frac{1}{1}}{\frac{1}{S}}_{O} = \begin{bmatrix} \frac{1}{\frac{1}{S}} \\ \frac{1}{\frac{1}{S}} \\ \frac{1}{\frac{1}{S}} \end{bmatrix}_{m}^{O} = \frac{1}{S} \begin{bmatrix} \frac{1}{\frac{1}{S}} \\ \frac{1}{S} \end{bmatrix}_{m}^{O}$$
$$= G_{L} \begin{pmatrix} \frac{1}{\frac{1}{S}} \\ \frac{1}{S} \end{bmatrix}_{m}^{O} + A_{L}$$

where

 $\left(\frac{1}{1s}\right)$

 $\left(\frac{l_{L}}{l_{S}}\right)$

designates the intensity ratio measured at the time of standardizetion for the high secondary standardi and

AL

(1)

represents the intensity ratio for this standard during calibration.

46 Name of the calibration curve used (AQUE)

47 "High" intensity ratio (1000.00) followed by a corresponding"High" concentration (1000.00) (See Note 4.)

48 "Low" intensity ratio (0) followed by "Low" concentration ratio (0)

49-53 Space reserved in computer core memory for future calibration curves, should they be required

55 Submatrix name (AQ for aqueous) and the assigned priority (2)

56-64 Scaling factor for each element in the submatrix (see Note 5). The list of 28 Logic Channel numbers was truncated at 9 to save space in printing

NOTES

1. PRIORITY: The AtomComp spectrometer provides several forms in which concentration data can be reported. In the matrix a priority is assigned to each element. Then, at time of analysis, the operator can determine the element concentrations to be printed by specifying a priority level. Elements assigned a priority rating of 1 will always be printed. Elements assigned a priority of 7, the lowest rating, will be printed only when a priority of 7 is specified. An element will be printed only when the priority level specified by the operator is equal to or greater than its assigned rating.

- 2. PREBURN: In some of the antecedents of the Inductively Coupled Argon Plasma AtomComp spectrometer, such as the Direct Current Arc spectrometer, it was necessary to allow time for the sample excitation to stabilize before a meaningful measurement could be made. Provision was made in the computer program to delay any measurement for a specified time to achieve satisfactory operating conditions. The inductively coupled plasma does not require time to stabilize but the software provided with the instrument, being an adaptation of that developed for the earlier instruments, retains this requirement. It is necessary, therefore, to specify a PREBURN time, even though it may be specfied as zero.
- 3. EXPOSURE: Exposure time is the interval during which the photomultiplier/integrator circuitry is permitted to respond to the refracted light emanating from the plasma. The period chosen should be long enough to span the expected temporal variations in the intensity of the plasma, but short enough to assure that the high concentration expected will not saturate the integrating or counting circuits.
- 4. LINE SEGMENTS: The AtomComp spectrometer uses a series of straight line segments to represent its "working" or "conversion" curves. The software will accommodate from 1 to 10 line segments per curve. Each line segment is specified by its end points, starting with the highest value and proceeding to the lowest. In the example, GAAQ Matrix Printout, only one line segment was specified for the intensity ration curve as well as for the concentration curve, each extending from 0 to 1000.00.
- 5. SCALING FACTORS: Scaling factors for each element in the submatrix are accommodated by the AtomComp software. They are particularly useful when testing aliquot diluents or concentrates.

2.3 STANDARDIZATION

After the instrument is turned on and stabilized for several minutes, a standardization procedure is carried out. Standarization involves returning the

	PR				
	MX NAME: GAAQ				
	# OF ICN'S:28 #	OF SM	1.5. 1		
5	MODE : CN	-			
	FORMAT: 1 9 9	9 1			
	IS# 1 PCN:26 PR	TY: 1	PREBRN: 1 EX	POSR: 10	
	15# 3				
10	1S# 4				
	STD# 1 HAR1				
	STD# 3 HAR3				
	STD# 4 HAR4				
15	STD# 5 HAR5				
	a b c d e f	g	n i j	* /	m n p
	1 1 40 1 0 3	1	4 1 AQUE	0 10.00	0 1.144037
	2 CU 12 1 0 2	1	4 1 AQUE	0 10.00	0 1.419066
	3 MG 9 1 0 2	1	4 1 AQUE	0 10.00	0 1.694008
20	4 LD 5 1 0 2 5 8 6 1 0 4	1	4 1 AQUE	0 10.00	0 4.363080
	6 GE 49 1 0 4	1	4 3 AQUE	0 10.00	0 1.000 0
	7 P 20 1 0 4	1	4 1 AQUE	0 10.00	0 6.339 -1.11
25	9 EE 43 1 0 4	1	4 1 AQUE	0 10.00	0.8953158 0.4.546329
	10 NA 41 1 0 3	i	4 1 AQUE	0 10.00	0 4.808165
	11 AG 42 1 0 2	1	4 1 AQUE	0 10.00	0 .2910102
	12 CA 11 1 0 2 13 HG 44 1 0 5	1	4 1 AQUE	0 10.00	0 4.351410 0 5.594808
30	14 AL 10 1 0 3	i	4 1 AQUE	0 10.00	0 .6735819
	15 SN 1 1 0 3	1	4 1 AQUE	0 10.00	0 1.279415
	16 AS 2 1 0 4		4 1 AQUE	0 10.00	0 2.278448 0 3.263113
	18 CO 46 1 0 2	i	4 1 AQUE	0 10.00	0 1.439149
35	19 K 39 1 0 5	1	4 1 AQUE	0 10.00	0 4.951 -7.07
	20 AU 45 1 0 5	1	4 1 AQUE	0 10.00	0 1.566166 0 1.585 - 036
	22 PD 15 1 0 5	i	4 3 AQUE	0 10.00	0 1.000 0
	23 GA 18 1 0 5	1	4 3 AQUE	0 10.00	0 1.000 0
40	24 PB 47 1 0 2	1	4 1 AQUE	0 10.00	0 3.643782
	25 58 4 1 0 3 26 MN 7 1 0 2	1	4 1 AQUE	0 10.00	0 .9358021
	27 NI 23 1 0 3	1	4 1 AQUE	0 10.00	0 1.341130
	28 XX 50 1 0 0	0	4 1 AQUE	0 0	0 1.000 0
40	CURVE NAME : AQUE				
	1000.00 1000.00				
	0 0				
50	CURVE NAME INTOE				
the second second	CURVE NAME				
	CURVE NAME				
	CURVE NAME				
55	SM NAME: AQ PRTY:	2			
	1 1.000				
	3 1.000				
	4 1.000				
60	5 1.000				
	6 1.000				
	8 1.000				
	9 1.000				
\$2-R-76-23	Figure	2-1.	GAAQ Matrix	Printout	

A COLUMN TO A COLUMN

2-7

1

day's intensity ratio points for two different concentrations of each element back to those points obtained during initial calibration, thus reestablishing the original concentration curve. This is a computer function, and results in correction factors referred to as gains and offsets. These new gains and offsets will then remain in effect until the instrument is re-standarized.

An example of the standardization procedure is given below for the matrix GAAQ. The following standard solutions are formulated weekly:

STD	COMPOSITION
HAR-1	Blank
HAR-2	10 ppm of Ag, Ca, Cd, Co, Cu, Mg, Mn, Pb, Zn
HAR-3	10 ppm of Al, Fe, Li, Mo, Na, Ni, Sb, Sn
HAR-4	10 ppm of As, B, Cr, Ge, P
HAR-5	10 ppm of Au, Ga, Hg, Pd, 100 ppm of potassium(K)

Solutions are prepared from stock solutions of Fisher certified standards, 1,000 ppm; aliquot portions are pipetted into chemically cleaned volumetric flasks and the volumes adjusted with D. I. water. Accuracy of solution makeup is known to be better than 1%. Solutions are stored in plastic containers which have been chemically cleaned ("Triton - X - 100, a low metallic content detergent, followed by aqua regia treatment, followed by deionized water rinses"). Shelf time of 1 to 10 ppm standards is generally low: 1 to 2 days for 1 ppm; 1 week for 10 ppm. Precipitation, leaching and absorption are some of the mechanistic reasons for standard concentrations changing.

The actual standardization process is then performed, and the output data for each standard is shown below. Note that the units are absolute intensities and net concentrations. Also note the antimony (Sb) channel had malfunctioned and three channels, Ga, Pd and Ge, were not standardized on this run (due to unavailability of these standards). The printout of gains and offsets based on a standardization run is shown in Figure 2-2. For comparison, gains and offsets from the previous days are shown in Figure 2-3. Generally, the numbers should be within 20% of one another from day to day; large variations of fluctuations signal problems. Procedures are then available to reestablish proper operating conditions. The standardization

*EGIGIGI	GIAIN/H	AR1							(SEE NOTE 1)
G			H	AR-1 - BL	ANK				
BURN # 1 I	GAAQ	11	:42 1	8FE 878					
IS 4012									(SEE NOTE 2)
LI	cu	MG	CD	В	GE	Р	CR	FE	
170	295	29	358	110	4277	982	1177	469	
217	2341	618	904	6118	1511	1194	221	692	
ĸ	AU	ZN	PD	GA	PB	SB	MN	NI	
8922	722	145	9158	3325	1349	2030	146	614	
^^9									(SEE NOTE 3)
G									
BURN # 2	GAAQ	11	:43 1	BFEB78					
1 15									
4013									
166	288	MG 29	357	B 109	6E 4173	950	1146	FE 458	
NA	AG	CA	HG	AL	SN	AS	MO	co	
213	2300	606	875	6075	1473	1174	219	677	
8729	710	2N 138	8906	GA 3250	1298	SB 2022	MN 142	NI 590	NOTES
XX			0,00	52.70	12.70	LULL		2.00	1. PERTINENT COMPUTER COMMANDS
8 G									STAND BY TO RECEIVE INSTRUCTIONS E EDASE DATA IN BURN BUFFERS
BURN # 3	GAAQ	11	:44 1	BFEB78					G GO, BURN A SAMPLE
15									A AVERAGE DATA IN BURN BUFFERS
4013			~ ~		~~		~~		N AVERAGE STANDARDIZATION
167	285	28	346	107	4022	925	1134	456	SAMPLE
NA	AG	CA	HG	AL	SN	AS	MO	co	/ DESIGNATES THAT WHICH FOLLOWS TO BE COMMENTARY.
212	2272	596	874	6000	1469	1118	215	672	NOT TO BE INTERPRETED AS A COMMAND.
8674	698	137	8795	3207	1305	2214	MN 138	NI 605	2. IS: THE INTENSITY OF THE
XX				520.			1.50	005	PRINTED. IT HAS A PRIORITY OF 1.
12									3. THE ATOMCOMP SPECTROMETER PROVIDES A SPECIAL EXIT SLIT
0									FOR USE WITH AN EXTERNAL REFRACTOMETER. THE CHANNEL
BURN # 4	GAAQ	11	:44 10	BFEB78					NORMALLY IS UNCALIBRATED. ITS POSITION IS DICTATED BY MOUNTING
1 15									BY ANY CONSTRAINT TO INTERCEPT
4014									PRESENT APPLICATION THE CHANNEL
LI	CU	MG	CD	B	GE	P	CR	FE	WAS NOT USED. THE MEASURED
NA NA	294 AG	CA	HG	162	4159 SN	967	MD	468	MEANING INASMUCH AS THE CHANNEL
220	2342	621	905	6160	1457	1164	221	690	COULD HAVE BEEN SUPRESSED HAD
K	AU	ZN	PD	GA	PB	SB	MN	NI	RATHER THAN "1".
8836 XX	126	140	9139	3319	1312	1987	146	628	
8									
A									
AVERAGE	GAAQ	11 :	:45 18	BFEB78					
IS									
4013	C 11		~~				~~		
169	290	29	353	109	4158	956	1159	463	
NA	AG	CA	HG	AL	SN	AS	MO	co	
215	2314	610	889	6088	1477	1162	219	683	
8790	714	140	8999	GA 3275	1316	2063	MN 143	609	
XX		1.0	•	5215	1910	2005	145	007	
N 9									
	-								

52-R-76-24

1000

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 1 of 5)

```
EGIGIGIGIAIN/HAR2
E
G
                            HAR-2
BURN # 1 GAAQ
                    11:46
                            18FE878
1
   15
  4013
                MG
32174
                                                       CR
1253
   LI
          CU
                          CD
                                         GE
                                                                FE
                                  B
                                                 P
   169
        27739
                        28252
                                 118
                                        4208
                                               1177
                                                                532
                                                                CO
          AG
                  CA
                                         SN
                                                 AS
                                                        MO
                          HG
                                 AL
   NA
   245 164790
               14041
                         1273
                                6456
                                        1535
                                                1206
                                                         232
                                                              40104
                                GA
3234
                                         PB
                                                SB
2449
                          PD
                                                        MN
         AU ZN
1127 37489
                                                                N1
756
   K
  8668
                         9116
                                       15830
                                                      56630
   XX
     8
G
BURN # 2 GAAQ
                 11:47 18FEB78
   15
  4014
   LI
          CU
                  MG
                          CD
                                         GE
                                                        CR
                                                                FE
                                 B
                                                 P
   170
                                                1129
        27369
                31960
                        28307
                                 119
                                        4268
                                                       1280
                                                                542
   NA
          AG
                  CA
                          HG
                                 AL
                                         SN
                                                 AS
                                                        MO
                                                                co
   250 162958
                13963
                         1285
                                6495
                                        1501
                                               1253
                                                        234
                                                              39810
          AU
                  ZN
                          PD
                                 GA
                                         PB
                                                 SB
                                                        MN
                                                                NI
   K
  8825
         1141 37270
                         9253
                                3322
                                      15708
                                                2396
                                                      56152
                                                                757
   XX
     9
G
BURN # 3 GAAQ
                 11:47 18FE878
1
   IS
  4014
   LI
          CU
                  MG
                          CD
                                 B
                                         GE
                                                P
                                                        CR
                                                                FE
        27486
                        27796
                                 114
                                                1140
                                                       1230
   166
                31478
                                        4193
                                                                522
   NA
          AG
                  CA
                          HG
                                 AL
                                         SN
                                                 AS
                                                        MO
                                                                CO
   237 162597
                13710
                         1250
                                6366
                                        1483
                                                1201
                                                        229
                                                              39361
   K
          AU
                  ZN
                          PD
                                 GA
                                         PB
                                                 SB
                                                        MN
                                                                NI
                         8879
  8607
         1111
               36670
                                3219
                                       15609
                                                2303
                                                      55432
                                                                729
   XX
     9
G
BURN # 4 GAAQ
                 11:48 18FE878
   15
  4013
                       CD
28575
                                        GE
4242
                                                       CR
1252
   LI
          CU
                  MG
                                 B
117
                                                 P
                                                                FE
                                               1163
   169
                                                                534
        28014
                32240
                                                        MO
   NA
          AG
                CA
14078
                         HG
                                 AL
                                         SN
                                               AS
1220
                                                                0.0
   238 165159
                                                        230
                                6504
                                        1521
                                                              40256
                         1266
               ZN
37574
                                 GA
                                         PB
   K
          AU
                         PO
                                                 SB
                                                        MN
                                                                NI
  8659
         1137
                                3247
                         8978
                                       15835
                                               2357
                                                      56738
                                                                740
   XX 8
A
                 11:48 18FEB78
AVERAGE
          GAAQ
1
   15
  4013
          CU
                  MG
   LI
                          CD
                                 B
                                         GE
                                                 P
                                                        CR
                                                                FE
                                               1152
   168
        27652
               31963
                        28232
                                        4228
                                                       1254
                                                                532
                                 117
                                       SN
1510
                                               AS
1220
                  CA
                                                        MO
                                                                co
          AG
                         HG
   NA
                                 AL
               13948
                         1268
                                6455
                                                        231
   242 163876
                                                              39883
                  ZN
                          PD
                                 GA
                                         PB
                                                SB
                                                        MN
                                                                NI
   K
          AU
  8690
         1129 37250
                         9056
                                3255
                                      15745
                                               2376
                                                      56238
                                                                745
   XX
     8
N
ENTER STD ID HAR2
```

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 2 of 5)

```
EGIGIGIGIGIAIACN/HAR3
E
G
                             HAR-3
BURN # 1 GAAQ
                    11:51
                             18FE878
   15
  4011
                                                        CR
1246
                  MG
                          CD
                                                 P
                                                                 FE
   LI
           CU
                                  8
                                          GE
                          407
                                  138
                                                1046
                                                             11139
           505
                   62
                                         4600
 22035
                                AL
61324
                  CA
                                                         MO
                                                                 co
                          HG
                                          SN
                                                 AS
   NA
           AG
                                       23015
                                                1671
                                                       13575
  5934
          2546
                   692
                         1115
                                                                 861
  K
8947
                                  GA
                                                         MN
                                                                 NI
           AU
                   ZN
                          PD
                                         PB
                                                 SB
                         9333
                                                              37177
           762
                   358
                                 3392
                                         1465
                                               11183
                                                         342
   XX 9
G
BURN # 2
           GAAQ
                    11:52 18FEB78
   15
  4011
                                  8
138
                  MG
                          CD
                                         GE
                                                 P
                                                         CR
   LI
           CU
                                                                 FE
                                                1050
 24361
           458
                          396
                                         4508
                                                        1204
                                                               11153
                   60
                  CA
   NA
           AG
                          HG
                                          SN
                                                 AS
                                                                 co
                                  AL.
                                                         MO
                  674
2N
                                62805
                                       23181
  6573
          2466
                         1082
                                                1626
                                                       13748
                                                                 828
           AU
                          PD
                                  GA
                                         PB
                                                 SB
                                                         MN
                                                                 NI
   ĸ
  8727
           746
                   345
                                               13321
                         8997
                                 3288
                                         1458
                                                              37371
                                                         334
   XX 9
G
BURN # 3
          GAAQ
                   11:53 18FEB79
   15
  4013
   LI
           CU
                  MG
                          CD
                                  8
                                         GE
                                                 P
                                                         CR
                                                                 FE
                                  137
                                                1047
 22902
           433
                   58
                          405
                                         4594
                                                        1208
                                                              11092
   NA
           AG
                  CA
                          HG
                                  AL
                                          SN
                                                 AS
                                                         MO
                                                                 CO
  6137
          2482
                  674
                         1084
                                61763
                                       23132
                                                1638
                                                       13657
                                                                 829
                          PD
                                 GA
                                         PB
                                                 SB
                                                         MN
                                                                 NI
           AU
                  ZN
   ĸ
  8811
           749
                   338
                         9084
                                 3312
                                         1452
                                               14731
                                                         330
                                                              37119
  ××
G
BURN # 4
          GAAQ
                    11:53 18FE878
1
   15
  4013
                                                              FE
11159
                  MG 58
                                 B
149
                                                        CR
1269
           CU
                                                 P
   LI
                          CD
                                         GE
                                                1092
                                         4840
 22582
           438
                         1042
                  CA
                                         SN
                                                                CO
   NA
           AG
                          HG
                                  AL
                                                 AS
                                                         MO
          2547
                                                2274
                                61751
                                       25521
                                                       13919
  6097
                  701
                         1130
                                                                 901
  K
9065
           AU
                  ZN
                          PD
                                 GA
                                         PB
                                                 SB
                                                         MN
                                                                 MI
           772
                                3420
                  800
                         9452
                                         1617
                                                    *
                                                         337
                                                              37420
   XX
   10
4
AVERAGE
           GAAQ
                    11:54
                           18FE878
   15
   4012
                                                 P
   11
          cu
                  MG
                          CD
                                  8
                                         GE
                                                         CR
                                                                FE
                                       4635
SN
23712
                                                        1232
 22970
                                 140
                                                1059
           458
                   60
                          562
                                                              11133
   NA
          AG
                  CA
                          HG
                                                 AS
                                                         MO
                                                                 co
                                 AL
  6185
          2510
                  685
                                                1802
                                                       13725
                                                                 855
                         1103
                                61911
                                        PB 58
1498 624053
                                                                 NI
                                 GA
          AU
757
                  ZN
                          PD
                                                         MN
   ĸ
  8887
                                                              37271
                  460
                         9216
                                 3353
                                                         336
   XX
4
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Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 3 of 5)

EGIGIGIGI	IAIACN/	HAR4						
G			H	AR-4				
BURN # 1	GAAQ	11:	57 1	8FEB78				
15 4010								
LI 103	CU	MG	CD	8	GE 4557	P 0304	CR 60247	162
NA	AG	CA	HG	AL	SN	AS	MO	co
4319	2514	670	981	6413	1619	24195	281	79
K	AU	ZN	PD	GA	P8	SB	MN 179	NI 77
XX	151	429	9410	3409	1401	3104	110	
9								
G								
BURN # 2	GAAQ	11:	58 1	8FE878				
15								
4012								
LI	202	MG	CD	B 10274	GE 4407	P	CR 41422	166
NA	AG	CA	HG	AL	SN	AS	MO	CO
4429	2570	680	998	6515	1633	24754	277	81
ĸ	AU	ZN	PD	GA	PB	SB	MN	NI
12726	778	439	9678	3527	1449	3229	182	11
^^ <u>9</u>								
G								
BURN # 3	GAAQ	11:	58 1	8FEB78				
I								
4011								
LI	CU	MG	CD	В	GE	ρ	CR	FE
180	337	36	381	10360	4438	9668	61575	163
NA	AG	CA	HG	AL	SN 1414	AS	MO 243	00
480G	AU	ZN	PD	GA	PB	SB	MN	NI
12688	758	436	9330	3417	1402	2989	176	67
xx								
6 9								
•								
BURN # 4	GAAQ	11:	59 1	8FE 878				
15								
4012	cu	MG	CD	B	GE	P	CR	FF
184	340	37	385	10421	4714	9665	62210	165
NA	AG	CA	HG	AL	SN	AS	MO	co
4374	2536	677	987	6447	1633	25087	262	80
12685	781	444	9995	3517	1469	2823	180	70
XX								
A 9								
	~~~~							
AVERAGE	GAAQ	1111	24 1	Brebia				
15								
4011								
LI	CU	MG	CD	10295	GE	P	CR	FE
NA	AG	CA	HG	AL	SN	AS	MO	03
4432	2522	672	984	6458	1625	24689	271	80
×	AU	ZN	PD	GA	PB	SB	MN	NI
12634	768	437	9618	3483	1430	3186	179	70
^^ <u>9</u>								
N								

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\$2-R-76-27

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 4 of 5)

#### EGIGIGIGIAIN/HAR5 ε G HAR-5 BURN # 1 GAAQ 12:01 18FE878 15 4011 MG 30 CR 1104 FE 423 LI 158 B 124 GE 3887 cu CD P 872 310 324 CA CD HG AS 1159 NA 20 AL 5755 SN MO 612 217 2003 563 7694 1401 203 PD κ AU ZN GA PB SB MN NI 58365 27853 7903 2946 2199 130 554 130 1165 XX 12 G BURN # 2 GAAQ 12:02 18FE878 15 4011 FE LI cu MG CD GE P CR B 416 121 1098 161 320 31 318 3868 846 CA HG MO co NA AG AL SN AS 5816 218 2630 569 7821 PD 1400 PB 1144 205 626 GA AU ZN SB MN NI ĸ 58878 2968 1157 565 28433 130 7992 2118 130 XX 12 G BURN # 3 GAAQ 12:02 18FEB78 15 4006 LI cu MG CD GE CR FE B P 160 323 30 324 121 3901 921 1118 425 NA AG CA HG AL SN AS MO CO 220 2560 580 7800 5755 1417 1173 208 634 PD PB AU ZN GA SB MN NI ĸ 56490 28371 132 8159 3039 2207 1217 133 580 XX 12 G BURN # 4 GAAQ 12:03 18FE878 1 15 cu CD GE CR FE LI MG 8 P 894 32 160 326 331 118 4026 1110 432 CA NA AG HG AL SN AS MO CD 220 2476 580 8060 5922 1457 1169 205 633 AU ZN PD GA PB 58 MN NI ĸ 61651 29123 132 8134 3026 1216 2026 134 550 XX 12 A AVERAGE GAAQ 12:04 18FE878 15 4009 8 121 LI CU MG CD GE P CR FE 321 3920 883 160 31 321 1107 424 CA NA AG MG SN AS MO CO AL 2617 219 573 7844 5812 1419 205 1161 659 PD AU ZN GA PR SB MN NI ĸ 58846 28445 8047 2995 1189 2137 562 131 132 XX 12 N

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Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 5 of 5)

52-R-76-28

*W W GAINS GAAQ 10:09 23FE878 15 0 P CR FE CD GE LI CU MG B .9296 1.371 1.280 2.254 3.760 -203 6.168 .7537 3.758 CO MO NA AG CA HG AL SN AS .2557 3.214 5.169 .6044 .9132 2.156 2.646 .8525 4.000 PB PD GA SB MN NI AU ZN K 22.47 1.268 -34-99 -580-2 4.889 3996E .6867 1.093 1.468 XX 1.000 OFFSETS GAAQ 10:10 23FEB78 15 0 LI CU MG CD B GE P CR FE 200-9 -1.257 -.1546 -.3056 -.0310 -.0695 -.0078 -.1226 -.0793 NA CA HG AL SN AS MO CO AG -.1450 -.0987 -.3383 -.7789 -.6752 -.2981 -.4614 -.0942 -.1339 K AU ZN PD GA PB SB MN NI -34.54 -.1729 -.0274 108-2 321-2 -. 6336 -106-2 -.0175 -.1119 XX 0 *+W tW * W GAINS 14:21 22FEB78 CAAQ IS 0 MG CD GE P CR FE LI CU B 6.904 .8561 1.247 1.330 1.342 4.752 -38-45 .9486 4.662 CA HG SN AS H.J. CO NA AG AL 2.950 .7798 3.351 5.648 .6485 2.588 3.564 .2550 1.098 ZN PD GA PB SB MN NI K AU 24.59 1.276 -19-04 -57-72 3.591 .0000 .7554 1.478 1.337 XX 1.000 OFFSETS GAAQ 14:22 22FEB78 15 0 LI CU MG CD B GE P CR FE -.0238 -.0701 -.0085 -.2734 -.1028 28-91 -1.241 -.2125 -. 4145 NA AG CA HG AL SN AS MO CO -.1395 -.1070 -.3783 -. 9467 -.8240 -. 4627 -. 6924 -.1375 -.1365 PD PB MN K AU ZN GA SB NI -41.31 -. 2006 -. 0575 32-15 34-85 -. 7977 -. D000 -. 0202 -. 1473 XX 0 NOTE 2. THE ANTIMONY (Sb) CHANNEL MALFUNCTIONED AND THE THREE CHANNELS, GALLIUM (Ga), PALLADIUM (Pd) AND GERMANIUM (Ge), WERE NOT STANDARDIZED ON THIS RUN, BECAUSE AT THE TIME CHEMICAL STANDARDS WERE NOT AVAILABLE FOR THOSE ELEMENTS. THE MEANINGLESS RECORDS WERE MANUALLY X-ED OUT. NOTE 1. COMPUTER INSTRUCTIONS . STAND BY TO RECEIVE INSTRUCTIONS. W WRITE CURRENT GAINS AND OFFSETS. IW WRITE CURRENT MATRIX ON SUPPLEMENTARY MEMORY.

\$2-R-76-29

Figure 2-3. Gains and Offsets, 23 and 22 February 1978 Runs

can then be checked by rerunning any of the standards, or a solution made up to be of some intermediate concentration of elements (e.g., 5 ppm). In our experience to date, accuracy of this procedure has been impressive.

#### 2.4 LIMITS OF DETECTABILITY

Included in the software provided is a statistical program which allows a sequence of up to 10 burns to be performed and which then calculates the average, the standard deviation, and the relative standard deviation. By definition, the limits of detectability are twice the standard deviation of the blank. An example of a statistical run on a blank solution is included (Figure 2-4). Note that the standard deviations in most cases push the limit of detectability to the low parts per billion range. Also included are the average, standard deviation and relative standard deviation for a statistical run of one of the standards (Figure 2-5); note that the relative standard deviation for the elements of interest are all better than 1%. The units recorded in this statistical presentation are concentrations in parts per million (ppm).

#### 2.5 ANALYSIS OF ORGANIC MATERIALS

A variety of problems was encountered in the analysis of organic media. First, while chemical standards in aqueous solutions were readily available from several chemical supply houses, standards in organic solutions were not. After much searching, standards were obtained from a division of Continental Oil Company. These standards were formulated as typically 500 to 900 ppm of the metallic elements in a hydrocarbon oil. These standards were used as aliquots and diluted in the appropriate organic base, without the need for solubilizers. Second, when running organics, molecular carbon was deposited on the inner surfaces of the plasma torch. The carbon absorbed the infrared radiation causing the glass of the torch to overheat. The torch was designed to provide a protective shield of argon gas around the plasma. This served to cool the glass and to flush the molecular carbon away. It was found that by careful adjustment of the gas flow, the rate of carbon accumulation could be greatly reduced but not totally eliminated. As a result, when organic materials were analyzed, the torch required frequent cleaning and adjusting. The gas flow was controled by means of an uncalibrated pressure control valve. An indicated pressure of

WC (SEE NOTE 1) BURN NO.O GAAQ 11:03 23FEB78 IS 3988 MG CD B GE P CR FE 0028 .0164 .0093 0 0 .0300 .0647 LI CU .0147 .0028 .0164 .0093 .0115 SN AS MO CO NA AG CA HG AL .0647 .0557 .0313 .0694 .0203 .0647 .1556 .0810 .0315 AU ZN PD GA PB SB MN NI K .0030 6.472 .0384 .0073 0 0 .2172 .1394 .0245 XX .0023 BURN NO.1 GAAQ 11:04 23FE878 3987 (SEE NOTE 2) .0094.0130.0025.0114.00340.0259.0270.0563.0316.0173.0551.1247.0678.0438.0751.0398.02825.980.0311.006000.2015.1663.0028.0259 .0023 11:05 23FEB78 BURN NO.2 GAAQ 3987 .0034 .0137 .0028 .0142 .0112 0 0.0303 .0620 .0201 .0656 .1506 .0584 .0359 .0060 0 0 .0486 .0756 .0345 .0273 .0326 0 .2591 .1663 .0032 .0210 6.414 .0359 .0060 .0023 BURN ND.3 GAAQ 11:06 23FEB78 3988 
 093
 0
 .0163
 .0274
 .0623

 510
 .0472
 .0533
 .0311
 .0303

 0
 .02246
 .1394
 .0028
 .0196
 .0130 .0025 .0136 .0093 .0187 .0615 .1387 .0510 .0336 .0060 0 .0082 .0335 6.382 .0336 .0060 0 .0023 11:07 23FEB78 BURN NO.4 GAAQ 3987 .0144 .0023 .0181 .0093 .0201 .0648 .1506 .0782 .0352 .0063 0 0 0 0 .0316 .0582 .0408 .0762 .0292 .0307 0 .0075 .0296 0 0 .2248 .1663 .0032 .0246 5.918 .0025 BURN NO.5 GAAQ 11:07 23FEB78 3987 .0075 .0137 0 .0025 .0142 .0093 0 .0312 .0563 .0195 .0616 .1455 .0641 .0285 .0788 .0252 .0370 .0060 0 0 .2444 .1663 .0038 .0282 .0346 .0196 6.674 .0370 .0060 .0023 11:08 23FE878 BURN NO.6 GAAQ 3987 0 .0304 .0544 .0068 .0134 .0025 .0142 .0093 0 .0296 .0198 .0632 .1390 .0656 .0310 .0583 .0232 .0290 .0341 .0057 0 .2505 .1663 .0030 .0232 6.414 0 .0023 NOTE 1. WC IS A COMPUTER INSTRUCTION WHICH WHEN USED WITH THE ATOMCOMP STATISTICAL PACKAGE COMMANDS THE SYSTEM TO MAKE 10 BURNS AND TO PRINT THE AVERAGE CONCENTRATIONS.

NOTE 2. THE SPECTROMETER IS TIME CONSTRAINED BY ITS ASSOCIATED PRINTER, I.E., IT TAKES MUCH LONGER TO PRINT THE RESULTS OF AN ANALYSIS THAN IT DOES TO COMPLETE THE ANALYSIS. TO SAVE TIME, HEADINGS AND LABELS ARE CUSTOMARILY OMITTED WHENEVER THE MEANING OF THE DATA IS NOT OBSCURED BY DOING SO.

sz-m-76-30 Figure 2-4. Statistical Package, Blank Solution (Sheet 1 of 2)

BURN NO.7 GAAQ 11:09 23FEB78 3987 .0151 0 0 .0354 .0648 .0028 .0198 .0121 .0068 .0619 .0783 .0259 .0737 .1766 .0630 .0356 .0224 .0303 0 0 .2346 .1663 .0035 .0221 .0407 .0060 7.643 .0023 BURN NO.8 GAAQ 11:10 23FEB78 3987 .0105 .0369 .0028 .0164 .0121 0 .0714 .0075 .0154 .0530 .0227 .0761 .1882 .0744 .0643 .0232 .0365 .0336 .0410 .0063 0 0 .2260 .1663 .0035 .0265 7.203 .0025 BURN NO.9 GAAQ 11:10 23FEB78 3987 
 .0147
 .0025
 .0153
 .0121
 0
 .0354

 .0224
 .0721
 .1675
 .0795
 .0931
 .0491
 .0225

 .0407
 .0063
 0
 0
 .2689
 .1663
 .0035
 .0066 .0582 .0314 .0356 7.079 .0246 .0023 AVERAGE IS 3987 MG P CR FE LI CU CD B GE .0053 .0316 .0080 .0141 .0027 .0154 .0183 0 .0609 AS HG SN MO CO NA AG CA AL .0328 .0200 .0658 .1537 .0683 .0517 .0673 .0318 .0303 PB GA SB MN NI K AU ZN PD .0368 .0062 0 0 .2352 .1609 .0032 .0232 6.618 XX .0028 STANDARD DEVIATION IS υ FE LI CU MG CD В GE P CR .0002 .0015 .0009 .0024 0 .0093 .0033 .0052 .0015 SN NA AG CA HG AL AS MO CO .0098 .0192 .0026 .0022 .0017 .0064 .0109 .0103 .0191 K AU ZN PD GA PB SB MN NI .0113 0 0 .0003 .5441 .0034 .0004 .0205 .0025 XX .0001 * RELATIVE STANDARD DEVIATION IS U LI CU MG CD В GE P CR FE 0 175.5 10.51 6.360 15.85 14.40 8.531 18.44 6.178 SN AS MO CO NA AG CA HG AL 8.548 9.689 12.41 14.41 37.06 16.23 33.20 8.558 6.740 GA K AU ZN PD PB SB MN NI 8.221 9.259 6.897 0 0 8.733 7.037 8.656 10.72 XX 4.590

52-R-76 31

Figure 2-4. Statistical Package, Blank Solution (Sheet 2 of 2)

AVERAGE 15 3876 CD CR CU AU B CA CO AG AL AS .0296 10.09 10.08 9.752 9.972 .6017 .0281 .1181 .0008 10.01 MG MN MO NA ĸ FE GA GE HG LI .3653 .1214 0155 .2251 -1.753 -.0004 10.02 9.723 .0026 -1.407 NI P PB PD SB SN ZN 10.04 .0108 .0349 -.0329 10.02 .0264 -.1591 STANDARD DEVIATION 15 U CO CR CU CA CD AG AL AS AU В .0019 .0010 .0744 .0427 .0262 .0045 .0441 .0574 .0011 .0603 MG NA FE GA GE GH K LI MN MO .0486 .0012 .0067 .0092 .1363 .0497 .0079 .0059 .1269 .0007 NI P PB PD SB SN ZN .0024 .0303 .0685 .0163 .0078 .0104 .0322 **\$ RELATIVE STANDARD DEVIATION** 15 U CR CU AG CA CD CO AL AS AU B .5751 .4522 3.606 .4235 15.89 1.648 124.0 .7430 . 5986 4.360 FE GA GE HG ĸ LI MG MN MO NA . 4963 .4996 45.31 -.4781 6.527 -37.90 56.38 2.515 -7.776 -176.7 P PB PD SB SN ZN NI 9.185 -19.07 .6816 150.1 22.46 -31.50 .3211

*

82-8-76-32

Figure 2-5. Statistical Data, Standard No. 2

2 Kg/sq. cm. (28.5 psi) was found to be satisfactory. Excessive flow rates were found to make the plasma unstable or to extinguish it. Insufficient flow allowed carbon to rapidly accumulate.

A third problem was concerned with attaining a constant aspiration rate for the sample. The organic solvents of interest generally are highly volatile. When these materials were introduced into the aspirator, the aspiration rate was found to be unstable and quenched the plasma torch. In the Jarrell-Ash spectrometer, the sample was normally drawn through a capillary tube by a negative pressure created by the Venturi effect of the aspirator. The aspiration rate was controlled by regulating the pressure of the argon gas fed to the Venturi jet. For samples which had high vapor pressures the rapid reduction of pressure in the immediate vicinity of the Venturi tended to vaporize rather than atomize the material, thus resulting in erratic pressure variations. The operator was constantly striking a balance between the loss of aspiration and blowing out the flame with a burst of material. One solution was to introduce the sample material under positive rather than negative pressure. This could be accomplished by using a positive displacement pump to inject the material at a precisely controlled rate. To minimize any pulsation in the flow which might be induced by the pumping action, a peristaltic type pump was selected.

A fourth problem in analyzing organics was concerned with the intense green color observed at the base of the plasma torch. Upon investigation it was found to be the product of molecular carbon species. To minimize possible interference from those bands, it was found that the plasma torch had to be precisely positioned to assure that the region of maximum atomic emission was scanned. The intense green color suggested that its principal energy bands were between 5250Å and 5750Å and fortunately the spectrometer, as configured for this application, did not monitor any line between 4632Å (Ni) and 5890Å (Na). Furthermore, second order dispersion of the green would fall (above 10, 500Å) in the far infrared, beyond the range of the spectrometer's optical system and beyond 7664Å (K), the highest line which was monitored. However, carbon, which is a major constituent of all organics, exhibits a strong line at 1930Å just 6Å from the 1936Å line of arsenic, a trace element of interest. For any element whose emission is 2500Å or less, corrections must be

made for emissions from such molecular products as C=N, C=C and O=H. This would include nearly half of the 27 trace elements of interest. To help resolve these interferences, the elements which are to be analyzed and the appropriate wavelengths under investigation were identified to scientists at the Analytical Chemistry Laboratory at Watertown Arsenal. They will identify the possible interferences. Where interferences exist, quantitative techniques are available for automatically correcting the data in the computer to improve the accuracy of the analysis.

#### 2.6 SPECTRUM SHIFTER

The project will determine quantitatively what levels of impurities in process chemicals affect device performance. From what is known at this time, it would appear that meaningful data must be obtained on concentrations in the partsper-billion range. These levels approach the limit of detection for the spectrometer. At such concentration levels the background emission intensity at a given exit slit may be more than 50 to 75% of the total intensity falling upon the photomultiplier tube. In making accurate measurements in the parts-per-billion range, it is necessary to compensate for the background emission falling on each exit slit, as well as for any slow instrumentation drift. This is accomplished by frequently standardizing the instrument against standard solutions having compositions closely approximating those of the sample under test. This technique is very exacting and time-consuming. It works well in compensating for slow instrumentation drifts and for changes in background levels which are proportional to the line intensity or to the intensity of the internal standard. It presupposes however that the chemical and physical characteristics of the sample are comparable to those of the standard. If, for any of a variety of reasons, e.g., a sample of different viscosity, the background intensity varies independently of the signal, a significant error may be introduced. A more effective method would be to measure the background at each exit slit each time the line intensity (i.e., line plus background) is measured.

Jarrell-Ash presently manufactures a device which automatically corrects for background illumination at each exit slit each time a measurement is made. It dynamically rotates the spectral array through a very small angle so that the photomultiplier tube senses first the intensity of the spectral line plus the background and

then the spectral array shifts and the photomultiplier senses only the background intensity immediately adjacent to the line. The device consists of a small (approximately 3 mm thick) glass plate inserted in the polychromic light beam immediately behind the entrance slit. The plate is rotated about a vertical axis, normal to the optical plane. The plate, driven by an electrical stepping motor, alternately assumes one of two angular positions, shifting the spectrum a few angstroms from right to left and back again. This permits alternately making a set of measurements at the peak of each line response followed immediately by a similar set offset from the peak by a fixed amount. The computer compares the value of intensity at the peak of each line to the measured value of background interference immediately adjacent to each line rather than to some assumed (standardized) level. The device dramatically improves the accuracy of the spectrometer at low concentration levels.

A spectrum shifter of this type was purchased from Jarrell-Ash and was scheduled for delivery and installation on 4 April 1978.

#### 2.7 ANCILLARY EQUIPMENT

Standards for all elements of interest (except palladium) were received, and standard solutions are being prepared weekly.

All chemical glassware was received for accurate standard solution preparation as were all sampling vials, syringes and labels.

#### 2.8 TRAINING

During the installation of the spectrometer at Microwave Associates, service engineers from Jarrell-Ash provided training in many aspects of the instrument, including sample preparation, matrix construction, operation, troubleshooting, and preventive maintenance. As an extension of that training, three people attended a 1-week intensive course of study at the facilities of Jarrell-Ash Division, Waltham, Massachusetts. The formal training course emphasized spectrochemical theory and refinements in analytical technique. As a consequence of the formal training, and of the experience accrued from almost constant operation of the instrument from the time of its installation, the analytic skills required for the project were developed.

# SECTION III DATA PROCESSING

#### 3.1 DATA TRANSMISSION

The project plan called for Microwave Associates to analyze each of the process chemicals and to measure the product's electrical characteristics. These data were to be transmitted to PRD Electronics, where they would be analyzed in the UNIVAC 1108 computer facility.

An unexpected technical problem arose with regard to transmitting the spectrometer's analytical data from Burlington, Massachusetts, to Syosset, New York. It was originally planned to store the data on the unused magnetic disc (Floppy-Disk) in the spectrometer and periodically transmitting it, via the PDP-8A computer in the spectrometer and a modem, over telephone lines to Syosset. This was to be accomplished by making a minor modification to the Jarrell-Ash software to permit writing and reading a file on the unused disc. In attempting to implement the plan, it was discovered that the Jarrell-Ash software was written in assembly language. was poorly documented without annotation, and was considered by Jarrell-Ash to be proprietary. Were Jarrell-Ash to write the software modification, it would need to be done by the original authors at Jarrell-Ash who were currently dedicated to a company program which precluded their being available for a minimum of 6 months. Were PRD to write the new software it would require several months to decipher the undocumented coding. A tentative solution was adopted which consisted of leasing a small cassette recorder. The data was to be written on the magnetic tape as it was printed on the LA-36 Decwriter and subsequently transmitted via modem over a telephone line to Syosset.

The particular cassette recorder chosen was a Techtran 815 Datacassette manufactured by Techtran Industries, Inc., Rochester, New York. The device was leased from Computrend, Inc., Burlington, Massachusetts, which also provided a maintenance and service contract to support its operation.

The operating features and general specification of the device were as

follows:

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Capacity per cassette:

145,000 characters

#### Media:

Phillips-type cassette

#### Coding:

ASCII, 8-level

#### Transmission:

Half/Full Duplex

#### Speeds:

110/300 baud switch selectable

#### Interfaces:

Terminal-RS 232C/CCITT/20 ma Modem/CPU-RS-232C/CCITT

**Operating modes:** 

Read, Write, Fast Forward

#### Remote control:

Read, Write, Rewind, Fast Forward, Edit

#### Source control:

Automatic

#### Data edit:

Character delete

#### CR delay:

Fixed; 360 ms

#### Size:

5 x 7 1/4 x 11 Inches

#### Weight:

6 lbs.

Power:

115 VAC 60 Hz (100/230 V, 50 Hz optional)

To correct transmission errors, the PDP-8 computer in the spectrometer was programmed to read out all significant analytical data, i.e., average concentrations, wafer identification and station names, in triplicate. These data, together with appropriate heading and operator commentary, were recorded on the tape cassette. Upon reception at PRD Electronics, the significant data were corrected for transmission errors prior to their being entered into the data base file. Insofar as could be determined by trial runs, the data transmission system worked satisfactorily.

#### 3.2 DATA BASE FILE

As they are received at PRD Electronics, the analytical data are checked for errors. The transmission errors are corrected and the corrected data filed on a FASTRAND disc. Subsequently, these data are recorded in a permanent backup file on magnetic tape. The data from the FASTRAND are stripped of all superfluous legends and mnemonic symbols and entered into a data base file. Periodically the unprocessed data are transcribed on magnetic tape as a permanent record and purged from the FASTRAND disc.

Two types of data base files were designed. The first was configured under the control of a UNIVAC DMS 1100 (FORTRAN) data management system. The second was a simple sequential file in which data were recovered by screening the file (in its entirety or partially) against a limited set of prescribed single dimensional criteria. The former had the advantage of almost unlimited flexibility at the cost of relatively high program administrative overhead. The latter had the advantage of simplicity and low overhead at the cost of longer search times and the possibility of its failing to satisfy some unforeseen sorting requirement.

Until such time as a sizeable quantity of test data are assembled, and one technique has clearly demonstrated its advantage over the other, both filing systems will be used.

#### 3.3 STATISTICAL ANALYSES

Considerable effort was devoted to designing an experiment strategy to minimize the number of tests while maximizing the amount of pertinent information. The model of the manufacturing process incorporated 50 process steps and 27 chemical elements to be considered as possible contaminants at each process step. To evaluate only first-order effects, excluding all interactions, would require the solution of 1.350 simultaneous equations. To solve these equations deterministically, assuming no measurement errors and no factors overlooked, would require that a minimum of 1.350 wafers be processed. This was considered to be an unrealistic task to be accomplished in the time which was available. Alternatively, a stochastic approach was planned. Statistical tests of the data were planned to determine the relative significance of each variable. That is, a screening process was selected to determine which contaminants at which stations exhibited the largest effects on the dependent variable, yield. The results would show only main or first-order effects - only the sensitivity of yield to significant changes in the independent variables, contaminant levels. Initially, interactions between elements and second-order effects would not by analyzed. The screening would also serve to show the degree to which the product yield was dependent upon factors outside the experiment, that is, factors other than chemical contamination.

The screening process was designed to rank the independent variables in the order of most probable significance. This does not mean that any variable is to be excluded from the analysis, but simply that the probability of discovering highly significant variables early in the process will be enhanced. Initially, the ranking will be based upon the physical chemistry of the process. The most sensitive stations will be assumed to be those involving high processing temperatures since the adsorbtion rates of most elements are higher at elevated temperatures. On this basis it was assumed that the most critical process steps would be those involving and immediately preceding the formation of thermal oxide layers and P-N junctions. Process steps Nitride Etch P20 and Thermal Oxidation P25, for example, were ranked high on the priority list for early attention.

The system input is in the form of wafers which already have undergone a number of processing steps. From a statistical point of view, each wafer will have built-in variations as evidenced by such parameters as: resistivity of the substrate, thickness of epitaxial layer, resistivity, epitaxial run number, and orientation within the boule source. These variables are measured and recorded. The design of the experiment must account for these variations. This will be accomplished by block randomization and analysis of covariance.

As used in this context, block randomization is an experimental procedure that reduces experimental errors due to variability of the specimen. It will be accomplished by systematically mixing wafers with different initial properties to produce a homogeneous mix, rather than allowing a batch of wafers with relatively uniform but strongly biased initial properties to be processed. This mixing or randomization of batches of wafers will serve to reduce the experimental error due to specimen variability. Block randomization also will be used to control variability due to external factors such as personnel variability and processing variability, e.g., time, temperature, etc.

Analysis of covariance is an analytic procedure for controlling the effects of specimen variability by adjusting the observed response variables of the system for effects of the observed specimen variations. The procedure is a combination of analysis of variance and regression analysis.

In addition to specimen variability of the input, measurement of yield will be biased also by variability of processing characteristics. The electrical measurements, which will determine the final product acceptance, will be controlled carefully since variation in the measurements of these parameters could seriously affect yield figures and confound the response due to contaminant levels.

#### SECTION IV

#### PROGRAM SCHEDULE

#### 4.1 PROGRAM STATUS

As of the end of February 1978, the project was approximately 10 weeks behind the schedule anticipated in the original planning and delineated in the project's PERT chart (refer to page 2-5/2-6 in the First Quarterly Report). That is to say, the project as of 28 February had achieved a majority of the planned objectives through 15 December 1977.

One cause for the delay was in training operators in the use of the spectrometer, which was originally thought to be the pacing item on the critical path. While the spectrometer was delivered on 16 December 1977, a month ahead of the schedule, the operators' training course scheduled by the manufacturer for 14-18 November for PRD and Microwave Associates personnel was postponed until 9-13 January, at which time Dr. George P. Allendorf of Microwave Associates was unable to attend.

It was expected that the time allocated for the course would be sufficient to train operators in the use of the instrument to a proficiency level where consistently accurate analysis could be performed. The course provided by the manufacturer was adequate for teaching the operator to turn on the spectrometer and operate it, but was inadequate in areas involving the preparation of standards, the generation of matrices (i.e., control computer operating programs), the analysis of organic materials, the aspiration of volatile liquids and making analyses at concentration levels approaching the resolution of the instrument.

Another cause of the delay was the excessive snowfall in the Northeast during January and February, which resulted in several days of plant closings at both Microwave Associates and PRD. These had a disruptive effect upon the project far beyond just the direct loss of man-hours. Microwave Associates was delayed in

finishing the construction of the laboratory area because of problems arising out of the need to coordinate such an activity with other moves within the plant, all of which were delayed by the weather. Because of the small staffs involved in the project, both at Microwave Associates and at PRD, any absences among the personnel had an extensive and profound effect upon progress of the work.

The inaccessibility of the software supplied with the spectrometer and the difficulty of coordinating modifications through the manufacturer to facilitate the automatic transmission of analytical data between the spectrometer in Burlington, Massachusetts, and the UNIVAC 1108 computer in Syosset, New York, indirectly delayed the project. While the lack of an adequate data transmission system did not curtail the operation of the spectrometer, the implementation of an alternate means of data transmission did occupy much of the time of the project's key personnel and thus delayed the project work.

As of the end of February 1978, the following tasks were completed:

1. The spectrometer was installed, demonstrated and accepted.

2. The manufacturing facilities were designated and scheduled, with the exception that the laboratory in which the spectrometric analyses were to be made was not completed.

3. The expendable materials were on hand with the exception of a few organic standards.

4. The ancillary instrumentation was at hand with the exception of a **spectrum shifter needed** to enhance the resolution of the spectrometer.

5. The experiments were designed.

6. The data communication link was installed but exhibited some malfunctioning.

7. The data management system was designed and programmed but not debugged.

8. The data reduction plan was developed but not programmed. (It was decided to make maximum use of existing statistical software program packages provided by UNIVAC and by the Biomedical Department of the University of California and programmed to run on the UNIVAC 1108.)

9. The analytical model was designed but not programmed.

10. An adequate staff of trained personnel was available at Microwave Associates to conduct the chemical analyses.

Before the "Analysis of Baseline" could be initiated, the following remained to be accomplished:

1. The preparation of a set of chemical solutions to be used as calibration standards.

2. Completion of the set of spectrometer control "matrices."

3. Techniques developed for the handling and analysis of organic chemicals.

4. Techniques developed for aspirating highly volatile liquids.

5. Techniques developed for sampling and analyzing gases, particularly where high flow rates were involved as in the gaseous reactors.

Before any automatic data processing could be initiated the following remained to be accomplished:

1. Preparation of computer programs for checking transmission errors in transmitted data in the absence of parity bits.

2. Preparation of computer programs for identifying, extracting and filing pertinent data.

3. Preparation of job control language programs for inputting statistical data into available statistical program packages.

The program delays accrued through February 1978 were significant enough to warrant a major revision of the PERT plan.

### 4.2 PROGRAM PLAN

In view of the delays encountered through the end of the second quarter, it was planned to develop and submit for approval a new PERT chart which would reorient the project's activities while holding to the project's major objectives and the submittal data for the final report. This would be accomplished by reducing the time allotted to Production Process Monitoring from nominally 15 weeks to 6 weeks and deferring the Development of System Specification so that it would be delivered after the project's final report.

Until such time as a significant ensemble of analytical test data is assembled, the pacing item will be the manufacturing and testing of the PIN diodes. Figure 4-1, Wafer Processing Schedule, is a plan for acquiring those data. The plan calls for six series of wafers to be run. The first series of wafers, the Unperturbed Runs, will consist of not less than 20 wafers. It will be divided into 10 batches of two wafers each. A new batch will be introduced into the manufacturing process each day for 10 work days. These wafers will be processed as in a normal manufacturing operation except that more highly skilled technicians may be used to help resolve procedural problems which may arise from the imposition of the new and more exacting testing routines. Because only standard processing materials will be used in their manufacture and no reagent will be purposely contaminated or doped, the group will experience only incidental contamination.

The second series of runs, the Pre-High Temperature Station Sensitivity Runs, is designed to explore the effects of contamination in those operations which immediately precede operations performed at elevated temperatures. The plan is to start with a relatively large batch of wafers (say 40). The large batch will be processed as a unit in a normal manner up to the step under investigation. At that point the large batch will be divided into smaller batches, e.g., 20 sub-batches of two wafers each. Each sub-batch will be exposed to a different level of contamination during the processing operation. Upon completion of the operation the sub-batches will be reassembled into a single large batch and proceed through the remaining steps of the manufacturing process. The stratagem will permit one to correlate





directly the changes in yield to specific groups of contaminating elements at a specific process step or position. Refer to flow diagram in Appendix A. The second series will consist of four runs and will address Rinse P04, Rinse P11, Photoresist Stripping P19 and Rinse P24. It is planned to investigate the following nine groups of elements:

(1)	(2)	(3)
Lithium (Li)	Copper (Cu)	Magnesium (Mg
Sodium (Na)	Iron (Fe)	Cadmium (Cd)
Potassium (K)	Gold (Au)	Calcium (Ca)
(4)	(5)	(6)
Silver (A_)	Boron (B)	Phosphorus (P)
Zinc (Zm)	Aluminum (Al)	Arsenic (As)
Mercury (Hg)	Gallium (Ga)	Antimony (Sb)
(7)	(8)	(9)
a state an and the fatter in		Makel AR

Germanium (Ge) Lead (Pb) Tin (Sn) Chromium (Cr) Molybdenum (Mo) Cobalt (Co) Nickel (Ni) Manganese (Mn) Palladium (Pd)

A tenth sub-batch will be used as a control and will receive only incidental exposures. Two levels of concentrations of each of the nine groups of elements will be used, e.g., 10 ppm and 100 ppm.

The fourth series, the High Temperature Station Sensitivity Runs, will closely parallel those of the second series, the Pre-High Temperature Station Sensitivity Runs. They will address the high temperature operations directly. The series will include operating positions: Boron Deposit P05, Boron Diffusion P06, Boron Redistribution P07, Deposit Silicon Nitride P12, Etch Nitride (Plasma) P20 and Thermal Oxidation P25. Also included in this series, although run at room temperatures, is the final Clean P50.

The fourth series presents some as yet unsolved implementation problems. Techniques for sampling and quantitatively measuring the contamination levels in high flux gases remain to be developed as do techniques for uniformly introducing controlled levels of contamination and subsequently purging the reactors.

The third and fifth series, the Selectively Perturbed Runs (Series A and B), are designed to address specific process steps which the statistical analyses will identify as critical to the building of the mathematical model.

The sixth and final series, the Normal Production Runs, like those of the first series will involve only incidental contamination. They will differ from the first series only in that they may use normal manufacturing personnel and procedures. The series will provide those statistics against which the mathematical model will be adjusted and verified.

It is planned to initiate the gathering of analytical data on or about 10 April 1978, at which time the first two-wafer batch of the Unperturbed Runs will be processed.

Consistent with the schedule for gathering the statistical data, the schedule for reducing the data and building the analytical model is presented as Figure 4-2, Data Reduction and Model Building Schedule. The reduction of the data and fitting of a model to the data must necessarily be a reiterative process of estimating and evaluating the factors which affect the yield. The steps of the process are outlined in Figure 4-3, Data Processing Flow Diagram.







Figure 4-3. Data Processing Flow Diagram

4-11/4-12

# SECTION V FUTURE PROGRAM ACTIVITIES

# 5.1 PROBLEMS TO BE ADDRESSED IN THE THIRD QUARTER

A major problem which will be addressed early in the third quarter involves the analysis of organic materials, particularly those having high vapor pressures such as acetone. The molecular carbon species and complex ions present in the plasma of the spectrometer during the analysis of organic materials give rise to relatively high and variable background illumination. This, in turn, adversely affects the limits of detectability. The high vapor pressure, which most of the organic solvents of interest exhibit, create problems with the control of the aspiration rate of the sample into the plasma torch of the spectrometer.

To ameliorate the first of these problems, a dynamic spectrum shifter (Jarrell-Ash Model No. 90-555) will be procured and installed in the spectrometer. The device will allow an intensity measurement to be made at the peak of each spectral line, and then, by shifting the spectral blaze slightly, permit a measurement of the background intensity immediately adjacent to each line. The computer within the spectrometer will then compensate each intensity measurement for the background level at each spectral line.

To solve the second problem, a positive displacement pump will be added to the sample injection system of the spectrometer. This will be used to inject the sample into the nebulizer under positive pressure.

A third problem to be addressed during the early weeks of the third quarter will be to resolve procedural incompatibilities which remain in the interface between the spectrometer's computer, the cassette recorder, the Decwriter and the data line to the UNIVAC 1108 computer. These problems, while they are minor and presently do not impede the work of the project, are a source of annoyance and if unresolved will become significant when the volume of data to be transmitted increases and reaches its peak during the third quarter. Fortunately, all of these incompatibilities appear to be amenable to changes in software and operating procedures.

#### 5.2 PROGRAM FOR THE THIRD QUARTER

The month of March 1978 will be devoted primarily to resolving the problems cited above and to establishing the accuracy of the spectral analysis. In the data reduction area, the time will be devoted toward readying the data management system and toward completing the search for effective statistical procedures which can be implemented on the UNIVAC 1108 computer.

The major thrust of the program during April and May will be directed toward the amassing of a statistical data base which will permit the correlation of measured electrical performance with analytical levels of trace-element contamination in the process reagents. During April and May, approximately 40 percent of the test data will be gathered. Some 820 wafers will be introduced into the manufacturing process of which approximately 380 will be completely processed. The wafers will be processed according to the schedule depicted in Figure 4-1, Wafer Processing Schedule.

The last week of April and the first week of May will be devoted to preliminary exploratory analyses of the test data as it is received from the processing of the wafers into PIN diodes. These steps are outlined in Figure 4-3, Data Processing Flow Diagram.

The remainder of May will be devoted to clustering and dimensionality reduction.

# SECTION VI

# PUBLICATIONS AND REPORTS

(There were no publications, conferences or talks made during the period covered by this report on or associated with the work performed under Contract No. DAAB07-77-C-0561.)

# SECTION VII

# PERSONNEL IDENTIFICATION

# 7.1 PERSONNEL ASSIGNMENTS

Persons working on the program and the hours worked through the report period were as follows:

NAME	AFFILIATION	HOURS 1ST QTR	HOURS 2ND QTR	TOTAL HOURS
Roy W. Spacie	PRD Electronics	408	560	968
Dr. George Allendorf	Microwave Associates	164	436	600
Albion Weeks	Microwave Associates	120	508	628
Dr. Demir S. Zoroglu	Microwave Associates		112	112
Peter Barnett	PRD Electronics		80	80
H.R. Bedrosian	Microwave Associates		30	30
Dr. David Levine	PRD Electronics		15	15

# APPENDIX A

PIN DIODE MANUFACTURING PROCESS











PIN Diode Manufacturing Process (Sheet 1 of 3)

A-3/A-4

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PIN Diode Manufacturing Process (Sheet 2 of 3)

A-5/A-6

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52-R-76-3





LEGEND



ELECTRICAL, PHYSICAL OR CHEMICAL MEASUREMENT

COMPUTED OR DERIVED INDIRECT MEASUREMENT TRANSFER RATIO OR COUPLING COEFFICIENT

# PXX - PROCESS STEP IDENTIFICATION

- TXX ELECTRICAL TEST IDENTIFICATION
- MEASURED OR DERIVED CONTAMINANT CONCENTRATION LEVEL A
- VALUE OF TRANSFER RATIO K

alben Bil

ELEMENTAL SPECIES PROCESS STEP × .K.

PIN Diode Manufacturing Process (Sheet 3 of 3)

A-7/A-8 2