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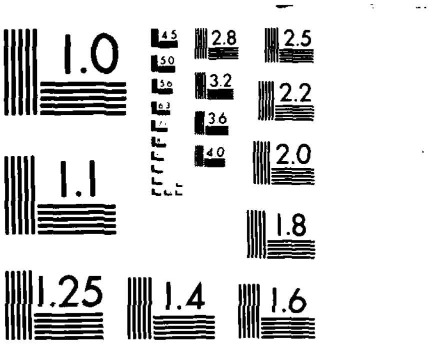

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ESTABLISHMENT OF PRODUCTION CLEANLINESS CRITERIA AND PROCESSES FOR PRINTED WIRING BOARDS AND ASSEMBLIES

Contract DAAK-40-78-C-0114

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December 1981

Final Report for Period 26 April 1979 through 23 Decmeber 1981, Phase II

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Printed Wiring (PW)	Specific conductance (κ)
Printed Wiring Board (PWB)	Concentration in parts-per-million(PPM)
Printed Wiring Assembly (PWA)	Concentration in parts-per-billion(PPB)
Specific Resistivity (ρ)	Concentration in μ/g / cm^2

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Phase I Final Technical Report (FTR) (24 April 1978 through 26 April 1979) of the program suggested that a systems approach be used to solve the problem of contamination on printed wiring (PW). The solution was to design, assemble, and integrate a system giving a detailed profile of practically all of the ionic contaminant species. Profiling a species means detecting it (qualitative) and measuring its' concentration (quantitative). The system was to consist of various pieces of analytical instrumentation suitable for profiling individual species and a minicomputer.

19. Key Words (continued)

Ionic Species
Contaminant Profiling
Contaminant Profiling (C/P) System
Systems Analysis
Direct surface analysis techniques (SEM/EDX,AES,ESCA).
Solvent Extraction/Analysis Techniques (ICP-ES,IC).
Inductively coupled plasma emission/graphite furnace atomic absorption spectrophotometry
Ion chromatography
Minicomputer
System Control
Cost/benefit analysis
Data base

20. Abstract (continued)

The Minicomputer's purpose was for final analysis of the results, overall systems control of the analytical instrumentation, and final report generation. The two most promising methods of profiling contaminants on PW were direct surface analysis techniques and solvent extraction/analysis techniques. An experiment was performed to decide the better of the two extraction/analysis techniques were better. Thus the contaminant profiling (C/P) system was assembled and built using solvent extraction/analysis instrumentation coupled to a minicomputer. The main components of the C/P system are the:

1 Inductively-coupled plasma emission spectrophotometer/graphite furnace atomic absorption spectrophotometer;
2 Ion chromatograph;
3 Minicomputer and computing integrator unit;
4 Extraction tank/pumping unit;
5 Water purification unit.

As a continuation of the present program, it is recommended this system be used to build a data base for printed wiring contamination.

Letter on file

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APPENDIX 1

1.0 GENERAL INTRODUCTION

A summary of the most important findings of the Phase I effort - The Contaminant Profiling System

1.1 The Problem

Contaminants on printed wiring boards and assemblies cause electrical malfunction and/or failure. The most harmful class of contaminants are ionic species. During the course of producing a PW assembly, many different ionic species appear on the PW surface. Hopefully, the many ionic species on the PW surface are removed by the cleaning processes to which the PW entity is exposed during fabrication and assembly.

The only methods which were even roughly quantitative are those measuring a parameter whose value is dependent upon the gross amount of ionic material. These methods are the extract resistivity test (ERT) and the insulation resistance test (IRT). An investigation of these methods formed the basis of Phase I of MIRADCOM program "Establishment of Production Cleanliness Criteria and Processes for Printed Wiring Boards and Assemblies" (DAAK40-78-C-0114). The principal purpose of Phase I was to investigate applying the above methods to establish cleanliness criteria and to critique their application. The contractual definition of Phase I made it clear that any other appropriate physical, chemical, or electrical test suitable as a production cleanliness criterion might legitimately be investigated. The outcome of Phase I indicated that a physico-chemical method suitable as a fully quantitative, in-line production cleanliness test did exist, but to make it fully implementable required an additional prototype development phase.

The Phase I Final Technical Report (FTR) (24 April 1978 through 26 April 1979) of the program covered the current state-of-the-art in testing for contaminants remaining on the surface of printed wiring[1] (PW) after processing. The extract resistivity test is based on measuring the specific resistivity, ρ , or its reciprocal, κ , the specific conductance , of an isopropyl alcohol/water extract solution of a PW entity. For an ionic contaminant levels $\geq 5 \mu$g NaCl or equivalent/cm^2 of PW surface area, the devices measuring this parameter are probably adequate provided special precautions are taken. But such devices are notoriously susceptible to absorption of carbon dioxide (CO_2) from the atmosphere followed by its ionization in solution. This results in deterioration of the instruments' accuracy. Insulation resistance testing (IRT) is another common method of testing PW for cleanliness. In this test method a voltage bias is applied across pads on a test PW with subsequent degradation of the PW insulation resistance.

The chief criticism of both the extract resistivity test and the insulation resistance test is this. Both indicate the presence of ions and affort only a rough order of magnitude of the ionic concentration,

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.1 SEM/EDX

2.2.1.4 Discussion of Results

SEM/EDX USEFUL IN DETECTING GROSS DEFECTS AND/OR CONTAMINANTS RESULTING DURING PW MANUFACTURE

The SEM/EDX data indicate SEM/EDX is a useful technique for detecting gross defects in PW and/or contaminants resulting during the PW manufacture, but it is not an optimal method for surface contaminant analysis.

The first four sets (sets #1-#4; 12 samples total) all have similar surface morphologies and composition as revealed by SEM and EDX. Striations caused by the abrasive nonwoven aluminum oxide brush (deburring and scrubbing operations) are evident at magnifications of 100x and greater. For these samples, Cu (copper) is the major component with a small amount of Si (silicon) on each spectrum. It is believed that the Si originates in the glass fiber in the base epoxy (recall that the electron beam can "see" quite deeply into the material). Traces of Fe (iron) appear in all spectra and are artifacts of the analysis system. The samples from sets #1 and #3 (the cleaned sets) also show signs of graininess at 3,000x and 10,000x, no doubt indicating copper oxide formation. It is speculated that the demineralized water used in cleaning these particular PWBs hastened oxide formation on the copper surface (see, for example, Figures 1 and 2). Samples from sets #5 and #6 (apply resist, electrolytic plating, strip resist) have spectra obtained at the solder/Cu interface. Intensities for Cu, Sn (tin), and Pb (lead) vary quite a bit from sample to sample.

The photomicrographs often indicate crystalline material on the solder pads; this is probably composed of oxides of Sn and Pb. A deposit on sample 5B appears to be Pb leached from the solder. It is interesting to note that no Sn appears in the EDX spectrum for this particular sample. It is concluded that for this particular sample the electrolytic solder plating resulted in an insufficient deposit of Sn. Al (aluminum) was observed in small concentrations on the three samples from set #6. The fact that Al shows up is also substantiated by the ESCA data, indicating it is a direct surface contaminant (see below). The Al may arise from contamination from the plating baths, or it comes from the nonwoven aluminum oxide brushes used to scrub and deburr. The cleaned samples from set #5 show much less Al.

Proceeding to the samples of sets #7 to #11 (etch off copper, solder reflow, and flux/solder), EDX indicates several new elements in addition to the elements found in the first six sets, namely Br (bromine), Cl (chlorine), S (sulfur), P (phosphorus), Ca (calcium) and Cr (chromium)

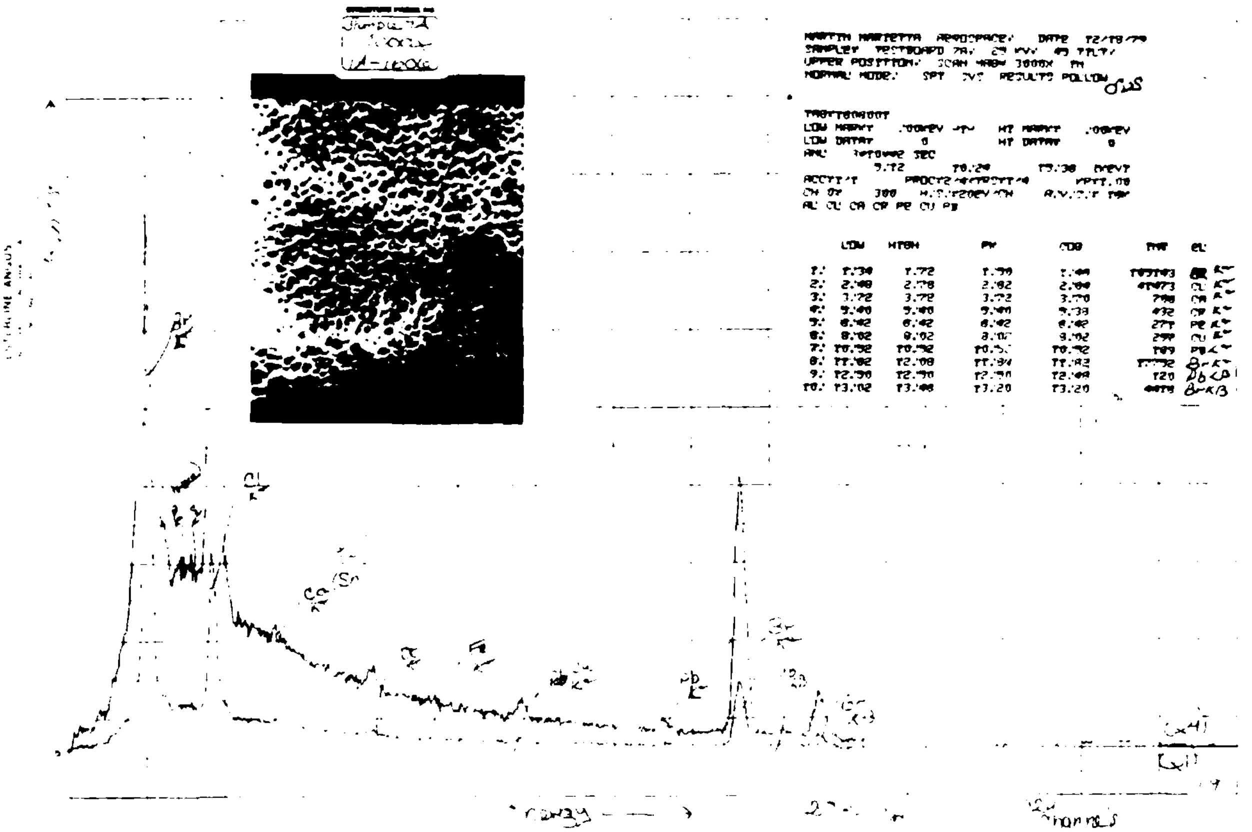

Figure 3. SEM photomicrograph + EDX readout for Sample 7A (from Set #7).

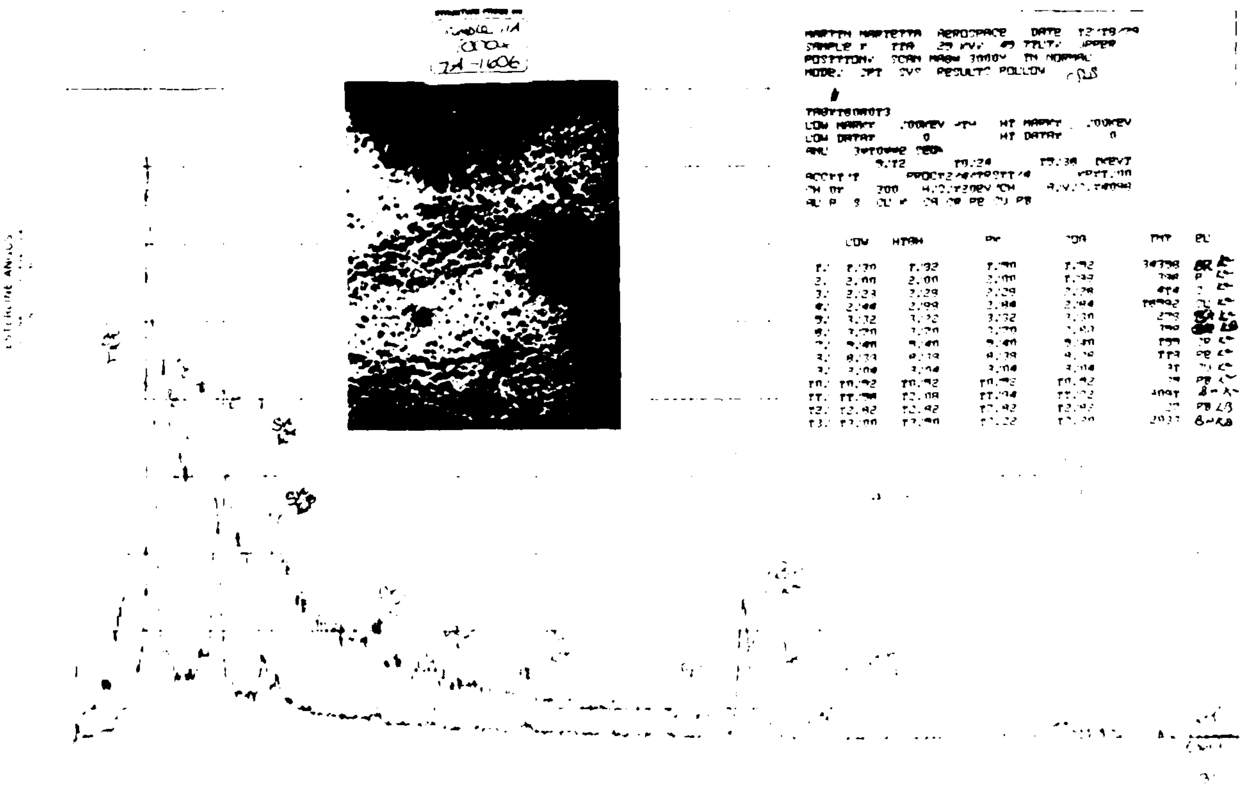

Figure 4. SEM photomicrograph + EDX readout for Sample 11A (from Set #11)

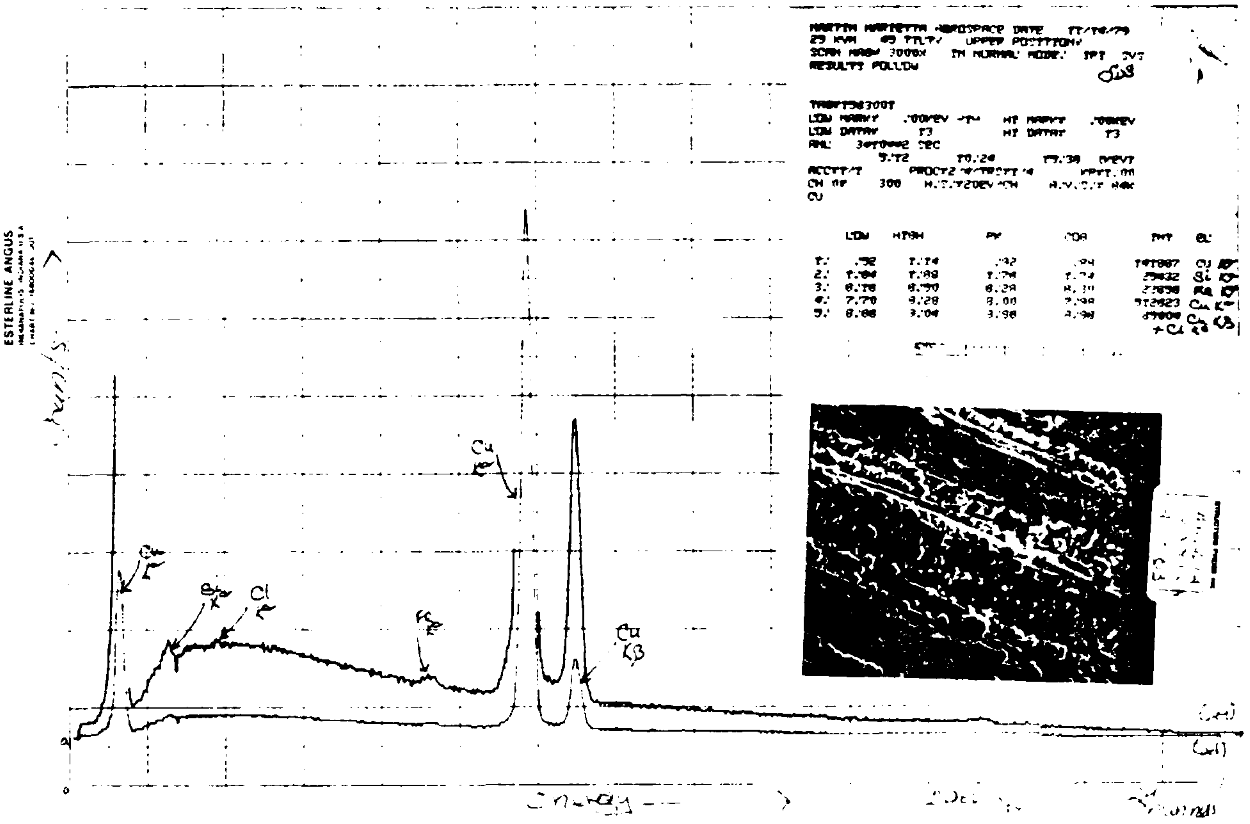

Figure 1 SEM photomicrograph + EDX readout for Sample 1A (from Set #1).

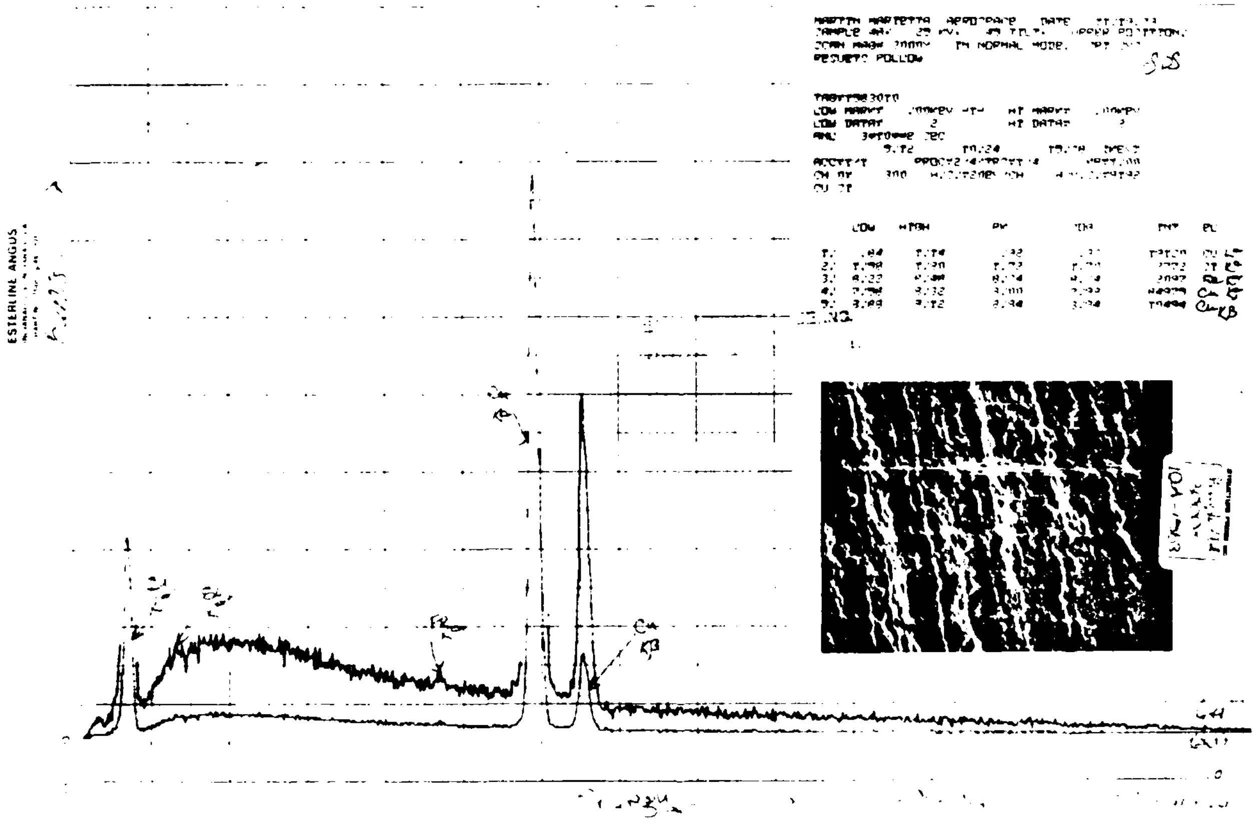

Figure 2 SEM photomicrograph + EDX readout for Sample 4A (from Set #4).

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.1 SEM/EDX

2.2.1.2 Procedure

HIGHLY FOCUSED ELECTRON BEAM FROM SEM ENABLES FORMATION OF PHOTOMICROGRAPHS

The SEM electron beam produces a secondary electron image of the surface revealing general surface morphology.

Photomicrographs were taken at 100x; 300x; 1,000x; 3,000x (and some at 10,000x) for the samples from all sets. The purpose of this was to record in photographic form the general surface morphology of the printed wiring at different stages during the manufacturing process. Three samples were used from each set. Since 12 sets were used, there are 36 (12x3) separate EDX readouts.

2.2 DIRCET SURFACE ANALYSIS TECHNIQUES

2.2.1 SEM/EDX

2.2.1.3 Data

DATA CONSISTS OF PHOTOMICROGRAPHS PLUS EDX READOUTS

The SEM/EDX data consists of select photomicrographs plus 36 EDX readouts.

Since it is not feasible here to present all 36 EDX readouts, four have been chosen as representative of the technique. These are Figures 1-4. Figure 1 gives the EDX readout for one of the samples from set #1 + SEM photomicrograph at 3,000x magnification; Figure 2 the EDX readout for a sample from set #4 + SEM photomicrograph; Figure 3 for a sample from set #7; and Figure 4 for a sample from set #11. The EDX spectra are displayed at two different intensities, i.e., x1 and x4.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.1 SEM/EDX

2.2.1.1 Discussion of Method

SCANNING ELECTRON MICROSCOPY (SEM) MAKES USE OF HIGHLY FOCUSED ELECTRON BEAM

The SEM produces a highly focused electron beam inciting the production of x-ray from the sample which leads to a semiquantitative indication of how much of the x-ray emitting element is present.

Scanning Electron Microscopy (SEM) makes use of a highly focused electron beam (less than 100 A diameter) which can be scanned in a raster on the sample surface. The intensity of the secondary electrons produced at each point is used to form a picture of the sample. Magnification factors from 10x to 100,000x can be obtained. The depth of the field is inherently quite large, allowing the micrographs to be in focus at all points across a rough surface. In addition, the SEM does not suffer from the light microscope problem of light reflecting off at odd angles and being lost from view.

Energy dispersive electron probe microanalysis (EDX) was used to analyze for the principal components as well as low-level (0.1%) contaminants in relatively thick layers (several micrometers, µm, i.e., about 10,000 to 50,000 A). It must be emphasized that this method of analysis cannot be considered a form of direct surface analysis since the electron bean "sees" quite deeply into the sample. The bombarding SEM electron beam will incite the production of x-ray from the sample. The resulting x-ray spectrum is normally displayed as an intensity versus x-ray emission energy plot. The vertical scale is x-ray intensity at each energy position, and the intensity level provides a semiquantitative indication of how much of the x-ray emitting element is present. Each element emits x-rays of characteristic energies so it is a simple matter to relate an x-ray peak to its corresponding element using a table of major x-ray emission energies. This analysis, like any making use of EDX, does not include elements lighter than Na (sodium; At No. 11) since these cannot be detected by this method.

Direct surface analysis techniques were used to examine the surfaces of test PW after each of the above stages. Three samples were chosen from each set for examination by the direct surface analysis techniques. Since there were two sets per stage, there was a total of 36 PW samples. The purpose of this investigation was to compare the surface characteristics between the samples with respect to physical morphology and elemental composition.

A total of three[5] different surface analysis technical were employed:

1 Scanning Electron Mi croscopy coupled with Energy Dispersive Spectroscopy (e^- in, x-ray photons out), SEM/EDX[6]

2 Auger Electron Spectroscopy (e^- in, e^- out), AES[7]

3 Electron Spectroscopy for Chemical Analysis, (x-ray photons in, e^- out), ESCA (sometimes referred to as X-ray Photoelectron Spectroscopy, XPS).[8]

Solvent extraction/analysis techniques were used to analyze solvent extracts of test PW after each of the above stages. Two samples were chosen from each set for examination by each solvent extraction/analysis technique. For this investigation the goal was to compare elemental and ionic composition among samples at the different manufacturing stages.

A total of two[9] different solvent extraction/analysis techniques were employed:

1 Inductively-Coupled Plasma Emission Spectrophotometry, ICP-ES[10]

2 Ion Chromatography, IC[11].

Each one of these techniques has its own particular strengths and weaknesses; it is appropriate at this point to discuss them and the results gleaned from each.

Scale of Effectiveness. The scale of effectiveness will be the extent of analytical fulfillment of each of the viable alternative. For this purpose an experiment was performed to aid in deciding between the alternatives. The design plan of this experiment called for testing PW at six distinct stages during the manufacturing process. These six stages were:

1 Drill, deburr, chemical and mechanical clean

2 Electroless plate

3 Apply resist, develop image, electrolytic plate with copper and solder, strip resist

4 Etch image (alkaline etchant)

5 Solder reflow and rout to size

6 Stuff components and flux/solder.

After each stage one set of PWBs was cleaned using conventional PW cleaning methods, viz., solvent degrease (1,1,1-trichloroethane used at all stages except the sixth-there 1,1,1-trichloroethane followed by 1,1,2-trichloro-2,2,1-trifluoroethane was employed) followed by a thorough rinse with demineralized water. One set of PWBs after each stage was left as is, i.e., not cleaned at all.

To summarize, PWBs in sets #1 and #2 were processed through stage 1; PWBs in sets #3 and #4 were processed through stage 2; sets #5 and #6 through stage 3; sets #7 and #8 through stage 4; sets #9 and #10 through stage 5; and sets #11 and #12 through stage 6.[2] The PWBs in odd numbered sets were cleaned by the conventional PW cleaning techniques[3] whereas the PWBs in the even numbered sets received no cleaning.[4] All PWBs used for this experiment were fabricated and assembled at Martin Marietta's Ocala PW facility in the actual production mode.

2.1 EXPERIMENT FOR PROFILING PW CONTAMINANTS USED TWO SEPARATE PROFILING METHODS

The PW in the experiment were tested for contaminants using direct surface analysis techniques and solvent extraction/analysis techniques.

Two distinct methods of profiling for residual contaminants on PW were employed:

1 Direct surface analysis techniques

2 Solvent extraction/analysis techniques.

information on the kind and concentration of all solvated ionic species at levels far below what can be achieved by ERT. To meet the objective as we have restated it then implies that a contaminant profiling system must be assembled and intergrated.

However, this is not to suggest that the laser scanning system has no merit. Clearly it does. A laser scan evaluation of the PW surface can reveal many common and serious PW defects such as edge ply separation, missing holes, solder bridging, cold solder joints, dewetting, etc. It is thus evident that PW evaluation by a laser beam scanning system can be used to great advantage for assuring proper process control over critical portions of the PW manufacturing process. It cannot, however, in its present state-of-the-art discern submicroscopic quantities of residues left on the surface during the PW processing. Thus, although laser beam PW evaluation cannot at the present level of the art meet the objective, it can be used in a complementary fashion to contaminant profiling. That is, it can be used for more rigorous process control for PW defects above a certain dimension ($> 10^{-4}$cm). With this assessment of laser scanning for PW evaluation, we pass to the third alternative.

By direct surface analysis techniques, we mean those techniques capable of focusing on and examining a minute portion of the PW surface. An analysis of the different elements present on the surface is the normal outcome, but one of the techniques (ESCA) can yield some valence information. A total of three different surface analysis techniques hold promise:

1 Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (e^- in, x-ray photons out), SEM/EDS

2 Auger Electron Spectroscopy (e^- in, e^- out), AES

3 Electron Spectroscopy for Chemical Analysis (x-ray photons in, e^- out), ESCA (sometimes referred to as X-ray Photoelectron Spectroscopy, XPS).

There is no technical reason to suggest that direct surface analysis techniques cannot be used to achieve the objective. Hence, they must be considered a viable alternative at this point.

Solvent extraction/analysis techniques represent the fourth alternative. By this we shall mean those techniques capable of analyzing a solvent extract of PW for the kind and concentration of various ionic species. There are two different solvent extraction/analysis techniques:

1 Inductively-Coupled Plasma Emission Spectrophotometry, ICP-ES

2 Ion Chromatography, IC.

Again, there is no technical reason to suggest that solvent extraction/analysis techniques cannot be used to achieve the objective. Therefore, they too must be considered as a viable alternative for developing a contaminant profiling system.

Let us briefly discuss the four alternatives presented above and examine to what extent they are likely to help us achieve the objective. The first alternative is the extract resistivity test (ERT). It is based on measuring the specific resistivity, ρ, or its reciprocal,κ,the specific conductance, of a solvent extract of PW. There are several commercial devices now available on the market which perform one variation or another of this test. Such devices are notoriously susceptible to the absorption of carbon dioxide (CO_2) from the atmosphere followed by its subsequent ionization in solution. This can result in a serious deterioration of the instruments' accuracy. And no variation of the ERT affords any indication whatsoever of the specific ionic species causing the degradation of the parameter being measured (either ρ or κ). The ERT is quantitative only for the general class of all ionic species, or at least those species most soluble in the solvent used in the test (typically a mixture of water/2-propanol). But for greater product reliability and improved field performance and also for better process control, it is highly desirable to be able to identify each particular species causing degradation and to be able to measure its corresponding concentration. This the ERT in any variation cannot do. Hence, in terms of meeting the above objective, the effectiveness of the ERT is low.

The second alternative is laser beam scanning of the PW surface. It would seem at first that this method might hold high promise for meeting the above objective. However, a moment's consideration causes a realization that here a distinction must be made. A reexamination of the objective as stated reveals an ambiguity. Of what level of contamination are we speaking? In the present state-of-the-art analytical instrumentation can detect and measure nanogram (ng) and in some cases even picogram (pg) quantities of material. A careful technical consideration of the approach to the problem by this method suggests that only a laser beam of x-ray frequency could detect contaminants at the atomic and molecular scale (10^{-8} - 10^{-7} cm). Ordinary visible light laser techniiques probably cannot distinguish anything beyond about 1 μm. Therefore, if the original objective is meant to deal with submicroscopic amounts of contaminants, then clearly a lasar beam scanning system will not accomplish the objective.

The objective can be made unambiguous by specifying that by detecting contaminants and measuring their concentrations we mean submicroscopic quantities of material. Visible or microscopic defects of the PW manufacturing process shall not be considered a form of contamination. Rather, by contaminants we shall mean identifiable chemical species. With this in mind, the effectiveness of the laser beam scanning system for meeting the objective as modified is very low.

In order to clarify the discussion, let us establish several definitions. Designate the act of detecting contaminant species and assaying their individual concentrations as contaminant profiling. We are especially concerned with the profiling of all ionic species. Profiling the contaminated surfaces of PW to ascertain their cleanliness will provide

2.0 A SYSTEMS APPROACH FOR DETERMINING PRODUCTION CLEANLINESS OF PRINTED WIRING

Systems analysis used to determine the preferred method for detecting contaminants on PW.

Systems analysis normally takes place in five overlapping stages[1]:

1 Formulation - the issues are clarified and the elements of the problem identified.

2 Search - information is gathered and alternatives generated.

3 Evaluation - the alternatives are evaluated against a selected criterion. The criterion is used to weigh performance versus cost.

4 Interpretation - the alternatives are ranked in order of preference based on the criterion. Either a deterministic or a probabilistic criterion can be used depending on the nature of the problem.

5 Verification - the results are verified against real-world situations.

Phase I of the program constituted the formulation stage since the issues involved in PW contamination testing were carefully examined and clarified.

The Objective. Develop a systems approach to deal with PW contaminants. This approach necessitates testing for contaminants. This entails both detecting the contaminants (qualitative analysis) and measuring their concentrations (quantitative analysis). The approach discussed here will deal chiefly with ionic contaminants.

The Alternatives. A careful examination reveals four alternatives to achieving the objective:

1 The extract resistivity test (ERT)

2 Laser beam scanning of the PW surface

3 Direct surface analysis techniques

4 Solvent extraction/analysis techniques.

Recalling that the objective is to both detect and measure the amount of specific contaminant species, one must now ask to what extent each alternative will meet this objective. The scale of effectiveness will be the extent of analytical fulfillment of each of the alternatives. Against this scale the corresponding costs must be superimposed.

NOTES

1. This term is generic and refers to detail printed wiring of any type: (1) rigid printed wiring boards (PWBs), (2) flexible printed wiring, (3) rigid-flex. It also refers to flux/soldered printed wiring assemblies (PWAs) and conformally coated printed wiring assemblies (PWAs).

2. 2.0 MΩ·cm is the lowest acceptable resistivity for a PW extract following MIL-P-28809 procedures. See MIL-P-28809 or above mentioned report.

3. It is anticipated that higher reliability will be required for PWAs routinely having <5 unit line widths/line spacings.

Indeed, a recent paper claims that five micrometer (5 μm) lines can be achieved on a variety of substrates using a semi-additive process. See Luke R. Volpe, "A Method for Manufacturing High Density Conductive Interconnect Circuits", Intern J. Hyb. Microelec., Vol. 4, No. 2, October (1981), 246-50.

The system was to consist of various pieces of analytical instrumentation suitable for profiling individual species and a minicomputer. The minicomputer's purpose was for final analysis of the results, overall systems control of the analytical instrumentation, and final report generation.

After the system was developed, it was implemented in the Contractor's PW facility located in Ocala, Florida. An Industry Demonstration took place on 10 December 1981 to interested members of the PW industry. The remainder of this report deals with the steps taken to develop and implement this system. The system is called a contaminant profiling (C/P) system.

1.3 The Benefits

Identification of individual contaminant species is the first step in understanding contaminant mechanism, pathways (the various process steps), and synergistic effects. A C/P system will prove necessary to meet the tighter packaging requirements of future PW. The PW industry is being driven by advances in the microelectronics industry, and advances in integrated circuits (ICs) leads to increased demands for packaging the ICs which leads to further demands for PW to interconnect and support packaged ICs. The trend in PW is towards reduced line widths/line spacings and greater component densities.[3] All of this means improved cleaning processes and ways of assuring that the PW is clean. It will be necessary to detect contaminant species in the submicrogram ($<10^{-6}$g) region. For these reasons the contaminant profiling system was developed.

The potential sources of PW contamination are many. These may be summarized as:

1 The substrate material prior to fabrication

2 The various operations involved in the fabrication process such as plating and etching

3 Packaging and/or transferring the PW (often referred to as printed wiring boards at this stage) to the assembly area

4 The various operations involved in the assembly process, of which soldering is undoubtedly the most important, both from the standpoint of producing a workable PW and from the aspect of introducing serious contaminants on the PW surface

5 The components used--especially the component leads

6 Inspection and reworking

7 Final inspection and packaging

8 Ambient shop conditions.

The most harmful class of contaminants are clearly ionic species since their presence in the PW surface will actively degrade the electrical properties of PW, especially in the presence of moisture. Contaminant species such as salts of copper and lead produce green and white residues on the PW surface. These and other salts, if not removed by suitable cleaning processes, can lead to electrical malfunction and/or circuit failure. Even though PWAs may be conformally coated, no conformal coating is competely impermeable to moisture. Moisture (water vapor, H_2O) is attracted to hygroscopic materials left on the PW surface, such as certain salts and organic materials. This attraction of moisture for hygroscopic materials can result in vesication (mealing), especially under certain conditions of temperature and humidity. Vesication refers to the formation of blisters under the conformal coating but on top of the PW surface. Vesication indicates the existance of hygroscopic materials left on the PW surface.

1.2 The Solution

The Final Recommendation section (11.0) of the Phase I FTR suggested a systems approach to solving the problem of PW contaminants. The solution was to design, assemble, and integrate a system giving a detailed profile of practically all of the ionic contaminant species. Profiling a species means detecting it (qualitative) and measuring its concentration (quantitative).

but neither gives any indication whatsoever of the specific ionic species causing the degradation. Both methods can be characterized as quasi-quantitative and non-specific. Neither method is ion-specific; hence, neither method can be used for detailed profiling of ionic species. Further, neither method can be used to detect non-ionic species, let along profile them. This criticism can also be directed towards another common cleanliness test: temperature/humidity cycling. It is not ion-specific nor is it even quantitative. At best it indicates the presence of hygroscopic species on the PW surface after the surface has a conformal coating. Table O summarizes this situation. This summarizes the most important results obtained in Phase I of the subject contract. Although the results as they stand by themselves seemed disappointing, they did suggest a more rigorous quantitative test method to check the cleanliness of PW substrates.

TABLE O. Deficiencies in Current Test Methodology

TEST	DEFICIENCY	RESULT
RESISTIVITY	PWAs WITH LESS THAN 1 μg/CM^2 NaC OR EQUIVALENT WILL NOT FAIL 28809	FOR PWAs WITH 5 MIL LINE WIDTHS/5 MIL LINE SPACINGS, THEY WILL PASS 28809 BUT MAY FIELD FAIL
RESISTIVITY	SOME IONIC CONTAMINANTS SUCH AS CHLORIDE, Cl^-, ARE MUCH WORSE THAN OTHERS	NO RESISTIVITY TEST DISTINGUISHES ONE ION FROM ANOTHER
TEMPERATURE/ HUMIDITY	SOME COMPOUNDS ARE WORSE IN PROMOTING BLISTERING BECAUSE OF THEIR ATTRACTION FOR WATER	TEMPERATURE/HUMIDITY TEST DOES NOT DIFFERENTIATE BETWEEN SPECIES
TEMPERATURE/ HUMIDITY	NOT QUANTITATIVE	DOES NOT REVEAL AMOUNTS OR KINDS OF SPECIES CAUSING BLISTERING

Extract resistivity/conductivity testing (MIL-P-28809) may not even be applicable once PW line widths/line spacings pass a certain point. Indeed, as a conductor spacings become smaller than 0.009 inch, say 0.002 inch, a threshold value of 1.0 μg of NaClor equivalent/cm^2 of PW surface is expected to be too high a value of allowable quantity of ionic material on the PW surface. A simple linear shrinkage factor alone would suggest a value of 0.22 μg/cm^2. Thus, as conductor spacings on PW shrink to 2 mils, a lower limit of at least 7.0 or preferably 8.0 MΩ·cm will be required rather than 2.0 MΩ·cm.[2] It is questionable whether the accuracy of devices designed to measure the extract resistivity are capable of performing at this higher suggested limit. It is further questionable whether their accuracy is such that they can effectively monitor all other probable ionic species, some highly insoluble, likely to be formed on PW.

in addition to Cu, Sn and Pb (see Figures 3 and 4). The Br and P are undoubtedly part of the epoxy substrate (FR-4 fire retardant epoxy used). The Cr may come from the glass coupling agent or from the passivating agent used on the copper and remaining on the surface after the copper has been etched away. If the former, it is within the epoxy substrate; if the latter, on it. See 2.2.3.4, Discussion of Results, ESCA, for evidence that some of the Cr is to be found on the epoxy surface, i.e., its source is the passivating agent. The Cl, S and Ca may be true surface contaminants or they may be contaminants within the epoxy laminate[12]. Further, the photomicrographs reveal several interesting items. Crystalline-type structures were observed by SEM on a number of solder areas on samples from sets #7, #11, and #12. Figure 5 is a SEM photomicrograph of heavy deposit of these structures observed on sample 11A. Dot, or elemental distribution, maps of Pb, Sn, Cu and Br were made in this area.[13]. No increase in intensity was observed, indicating the lack of these elements. Au (gold) also appeared on the spectrum because Au was used as a coating applied for the purpose of reducing charging effects on the samples. A dot map for Au also revealed no increase in intensity in the crystalline deposit regions. Since these elements were the major ones observed in that area as evidenced by the EDX spectra, it is concluded that the deposited material is organic in nature. It is probably flux.

SEM/EDX is useful in detecting gross defects and/or contaminants resulting during PW manufacture. SEM photomicrographs at 3,000x and 10,000x often reveal different surface morphologies, especially when surface oxides are present. EDX is useful for characterizing the major elements involved and can sometimes spot defective boards, as, for example, the gross lack of Sn in sample 5B. However, the fact that the electron beam for EDX penetrates so deeply into the material (1-5 μm) precludes it from being an optimal method for surface contaminant analysis where the species being examined should be within a few angstroms of the "true" surface.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.2 AES

2.2.2.1 Discussion of Method

AUGER ELECTRON SPECTROSOCOPY (AES) MAKES USE OF FOCUSED ELECTRON BEAM TO KNOCK OUT CORE LEVEL ELECTRONS IN SAMPLE

AES uses a focused electron beam to knock out core level electrons in the sample resulting in so-called Auger electrons; this technique is a true surface analysis technique.

The excitation source in Auger Electron Spectrosocpy (AES) is a focused beam of electrons with an energy on the order of 1-10 KeV and a current of 1-30 μA. The primary electrons from the beam bombard the sample, knocking out core level electrons. The vacancy in the core level is rapidly filled by an outer level electron (the transition generally takes place in picoseconds or less). Since an energy difference is involved for each such transition, there must be some way to release that exact quantum of energy. The emission of a characteristic x-ray is one possibility, but the ejection of an outer shell electron called an Auger electron is a competing quantized phenomenon. Those Auger electrons which are produced within 20 A of the surface can escape with their full energy and result in a characteristic Auger spectrum for each element. Therefore, AES is a true surface analysis technique since it reveals elemental composition down to roughly 20 A (approx. 20 monolayers compared to EDX depths of 10,000-50,000 A). Only H (hydrogen) and He (helium) are excluded since they have no outer shell electrons to eject.

If the thin film analysis capability of Auger is combined with the material removing capability of ion beam etching, then the composition variation with depth into the sample can be investigated and/or extraneous surface contamination can be removed.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.2 AES

2.2.2.2 Procedure

AUGER SPECTRA OBTAINED AT TWO INDEPENDENT POINTS ON SAMPLE SURFACE AND AUGER DEPTH PROFILES MADE ON ONE SAMPLE FROM EACH OF 12 SETS

Auger elemental scans were made at two independent points on each sample; surface Auger depth profiles were made on one sample from each of the 12 sets.

Auger and ESCA spectra were obtained at the surface level from each sample. Further, Auger spectra were obtained at two independent points for each sample. Since there are three samples per set and a total of 12 sets, there are 72 individual AES elemental scans. For sets #7-#12, the Auger spectrum was obtained at a metallic surface since AES cannot be used on organic materials such as epoxy because the primary electron beam has sufficient energy to rapidly destroy organic materials. Auger depth profiles were made on one sample from each of the 12 sets. ESCA high resolution spectra were obtained from selected sample areas to explore the chemical bonding information available. In addition, ESCA elemental survey scans were made at a point on the epoxy surface for each of the three samples in sets #7-12. Thus, there are 18 individual ESCA elemental scans.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.2 AES

2.2.2.3 Data

DATA CONSISTS OF AES ELEMENTAL SCANS AND DEPTH PROFILES

The AES data consists of 72 elemental scans and 12 depth profiles to reveal contaminants on test PW.

To give an example of the method of computing atomic percents, sample 1A (AES) is chosen.

Example of *intensity/concentration conversion calculations:* For sample 1A-AES, as received, atomic concentration C_X of element X may be estimated by:

$$C_X = \frac{I_X/S_X}{\sum_i I_i/S_i} \times 100$$

where I_X is the peak-to-peak height of the Auger electron signal, or the peak height of the ESCA photoelectron signal, for element X divided by the proper scale amplification, and S_X is the elemental sensitivity factor as found in appropriate references. Where peaks other than those referenced have been used, their sensitivity factors have been corrected using the ratio of the measured peak height to the reference peak height. Note that these calculations are of a semiquantitative nature only. The absolute accuracy is no better than ±30 percent. Relative accuracy for similar surfaces is ±5 percent.

Element	Ix (cm)	Sx	Ix/Sx	Cx (atomic %)	Rounded to
S	1.1	0.74	1.49	0.85	0.9
Cl	1.8	1.00	1.80	1.03	1.0
C	10.2	0.14	72.86	41.57	41.6
Ca	0.1	0.40	0.25	0.14	0.1
N	0.53	0.21	2.52	1.44	1.4
O	12.8	0.40	32.00	18.26	18.3
Cu	15.4	0.24	64.17	36.61	36.6
Na	0.05	0.25	0.20	0.11	0.1
	$\sum_i I_i/S_i$ =		175.29	100.01	100.0

The data are presented in Table 1. However, since the data in Table 1 are unwieldy, it was thought appropriate to compute the arithmetic mean for the data for each set and present these in tabular form (see Table 2).

Table 1

Estimated Atomic Compositions (%) From AES Data

Set	Sample	Pb	S	Cl	C	Ca	N	Sn	O	Cu	Na	Al	Si	Fe	F
#1	1A	-	0.9	1.0	41.6	0.1	1.4	-	18.3	36.6	0.1	-	-	-	-
	1A	-	0.6	0.7	58.6	0.3	1.5	-	12.3	25.8	0.2	-	-	-	-
	1B	-	0.7	1.9	36.8	0.2	1.5	-	20.9	38.0	-	-	-	-	-
	1B	-	0.8	1.2	38.1	0.2	1.4	-	24.2	34.0	0.1	-	-	-	-
	1C	-	0.9	1.4	40.8	0.2	1.5	-	18.3	36.8	0.1	-	-	-	-
	1C	-	1.4	3.9	32.0	0.2	1.6	-	20.2	40.7	-	-	-	-	-
#2	2A	-	0.8	2.9	37.1	0.6	0.9	-	16.5	40.7	0.5	-	-	-	-
	2A	-	1.1	2.6	39.4	0.2	0.9	-	15.9	39.5	0.4	-	-	-	-
	2B	-	1.2	3.5	34.7	0.2	0.7	-	16.0	43.7	-	-	-	-	-
	2B	-	0.9	2.6	39.6	0.2	0.8	-	15.7	40.2	-	-	-	-	-
	2C	-	1.8	4.7	34.3	0.1	0.6	-	15.7	42.8	-	-	-	-	-
	2C	-	0.9	2.6	39.1	0.2	0.9	-	15.9	40.3	0.1	-	-	-	-
#3	3A	-	1.5	4.0	32.1	0.2	1.5	-	20.2	40.5	-	-	-	-	-
	3A	-	1.5	4.3	33.1	0.2	1.1	-	20.0	39.6	0.2	-	-	-	-
	3B	-	1.7	5.5	28.4	0.3	1.3	-	20.5	42.3	-	-	-	-	-
	3B	-	1.3	4.9	31.0	0.2	1.6	-	20.1	40.9	-	-	-	-	-
	3C	-	0.6	2.6	44.0	0.3	1.2	-	16.2	35.1	-	-	-	-	-
	3C	-	0.4	1.8	39.0	0.2	1.4	-	19.0	38.2	-	-	-	-	-
#4	4A	-	1.6	6.2	30.2	0.1	1.0	-	18.8	42.1	-	-	-	-	-
	4A	-	1.8	6.0	29.4	0.2	1.0	-	19.1	42.2	0.3	-	-	-	-
	4B	-	1.8	4.0	32.6	0.2	1.4	-	18.7	41.3	-	-	-	-	-
	4B	-	2.0	6.7	25.1	0.2	1.0	-	20.5	44.2	0.3	-	-	-	-
	4C	-	1.5	6.1	30.0	0.2	1.1	-	19.0	42.1	-	-	-	-	-
	4C	-	1.2	6.6	30.1	0.1	1.2	-	18.7	42.1	-	-	-	-	-
#5	5A	32.8	1.0	8.3	16.8	-	2.4	2.9	27.0	8.8	-	-	-	-	-
	5A	29.2	1.0	10.5	32.8	-	0.6	0.3	18.2	7.4	-	-	-	-	-
	5B	9.4	1.2	3.0	42.5	-	-	17.1	22.5	1.2	-	3.1	-	-	-
	5B	11.9	0.8	3.7	56.1	-	-	5.1	15.9	6.0	0.5	-	-	-	-
	5C	16.0	1.6	9.9	41.3	0.2	-	2.8	19.2	8.4	0.6	-	-	-	-
	5C	37.1	0.7	9.3	18.6	-	-	3.0	26.4	4.5	0.4	-	-	-	-
#6*	6A	5.3	2.4	7.5	28.2	1.3	1.8	1.5	18.8	30.6	0.9	-	-	-	-
	6A	1.7	1.1	3.9	60.5	-	4.3	3.7	9.8	15.0	-	-	-	-	-
	6B	2.9	0.7	3.0	51.0	2.7	4.4	1.5	10.8	12.2	-	7.5	-	-	3.3
	6B	1.7	1.1	2.6	57.5	0.4	1.7	3.7	11.5	12.0	0.4	5.9	-	-	1.5
	6C	1.2	0.7	1.6	59.4	0.8	4.4	0.3	6.1	12.0	-	9.3	-	-	4.2
	6C	1.3	0.9	2.6	51.1	1.6	4.8	1.6	10.3	13.7	0.4	8.1	-	-	3.6

* The peak for N and the peak for Sn interfer with each other in the Auger spectra. The chances are these values and those corresponding to Sn should probably be changed as follows:

	N	Sn
6A	1.8	1.5
6A	1.7	6.3
6B	1.8	4.1
6B	1.7	3.7
6C	1.8	2.9
6C	1.8	4.6

Table 1 (Cont.)

Estimated Atomic Compositions (%) From AES Data

Set	Sample	Pb	S	Cl	C	Ca	N	Sn	O	Cu	Na	Al	Si	F	Zn	K
#7	7A	11.6	1.4	2.8	35.5	1.6	-	17.1	26.3	-	2.1	1.4	-	0.2	-	-
	7A	11.7	0.8	2.0	36.5	1.4	-	17.8	29.4	-	0.4	-	-	-	-	-
	7B	7.4	0.5	0.8	44.2	0.4	-	15.9	29.3	1.2	0.3	-	-	-	-	-
	7B	9.3	0.4	1.1	33.9	0.4	-	18.3	32.3	-	0.4	-	3.9	-	-	-
	7C	12.4	0.7	3.8	32.2	0.6	-	14.1	30.0	-	2.3	-	-	-	-	3.9
	7C	18.4	-	-	6.1	0.3	-	23.1	44.1	-	0.6	-	6.9	-	-	0.5
#8	8A	2.2	0.8	0.8	50.3	0.2	-	14.0	25.5	5.0	1.1	-	-	-	-	-
	8A	12.1	1.6	2.4	37.5	-	-	13.4	27.6	5.1	0.3	-	-	-	-	-
	8B	1.2	0.9	1.0	46.9	1.8	-	9.3	24.2	14.4	0.3	-	-	-	-	-
	8B	2.1	2.3	3.3	32.6	2.2	-	8.2	26.6	22.1	0.6	-	-	-	-	-
	8C	-	0.5	1.3	53.8	1.4	-	3.0	17.3	21.8	0.9	-	-	-	-	-
	8C	7.2	1.4	1.9	45.0	-	-	17.0	25.9	1.6	-	-	-	-	-	-
#9	9A	10.8	1.0	6.2	27.1	2.2	-	5.8	24.4	1.0	15.6	3.7	-	-	-	2.2
	9A	12.5	0.5	2.0	26.4	0.4	-	21.4	36.0	-	-	-	-	-	0.8	-
	9B	7.7	0.5	0.8	35.5	0.7	-	16.8	31.0	-	-	-	4.0	-	3.0	-
	9B	6.5	0.3	1.0	42.6	1.7	-	15.6	29.6	-	-	-	-	-	2.7	-
	9C	5.8	0.5	0.9	61.6	1.3	-	10.0	19.0	-	0.9	-	-	-	-	-
	9C	11.8	1.0	1.4	26.2	0.1	-	19.8	34.9	-	-	-	4.1	-	0.7	-
#10	10A	1.4	0.8	1.9	40.9	1.9	-	21.6	28.6	-	2.9	-	-	-	-	-
	10A	3.1	0.9	2.8	49.7	0.2	-	18.8	22.8	-	1.7	-	-	-	-	-
	10B	-	0.2	1.6	46.1	0.5	-	23.2	26.1	-	2.3	-	-	-	-	-
	10B	-	-	0.5	49.6	0.6	-	18.0	22.3	-	1.1	-	8.0	-	-	-
	10C	-	0.1	0.6	45.7	0.3	-	25.5	26.9	-	-	-	-	-	0.9	-
	10C	-	0.1	-	61.0	0.4	-	18.2	19.4	-	-	-	-	-	0.9	-
#11	11A	8.1	0.7	1.8	48.1	-	-	13.5	27.8	-	-	-	-	-	-	-
	11A	8.3	0.1	3.9	40.0	-	-	17.2	30.5	-	-	-	-	-	-	-
	11B	4.7	0.3	3.5	70.7	-	-	9.0	11.8	-	-	-	-	-	-	-
	11B	9.7	-	1.4	50.9	-	-	12.6	25.4	-	-	-	-	-	-	-
	11C	4.2	-	1.7	49.4	0.1	-	19.0	25.6	-	-	-	-	-	-	-
	11C	7.5	0.4	2.7	54.4	-	-	12.7	22.3	-	-	-	-	-	-	-
#12	12A	-	-	-	98.4	-	-	-	1.6	-	-	-	-	-	-	-
	12A	-	0.1	0.1	95.9	-	-	-	2.6	1.3	-	-	-	-	-	-
	12B	-	-	-	98.9	-	-	-	1.1	-	-	-	-	-	-	-
	12B	-	0.1	-	99.2	-	-	-	0.7	-	-	-	-	-	-	-
	12C	-	0.2	0.1	99.1	-	-	-	0.7	-	-	-	-	-	-	-
	12C	-	0.1	0.1	99.3	-	-	-	0.5	-	-	-	-	-	-	-

Table 2

Set	Pb	S	Cl	C	Ca	N	Sn	O	Cu	Na	Al	Si	F	Zn	K
1	—	0.9	1.7	41.3	0.2	1.5		19.0	35.3	0.1	—	—	—	—	—
2	—	1.1	3.1	37.4	0.2	0.8		15.9	41.2	0.2	—	—	—	—	—
3	—	1.2	3.8	34.6	0.2	1.3		19.3	39.4	0.0	—	—	—	—	—
4	—	1.6	5.9	29.6	0.2	1.1		19.1	42.3	0.1	—	—	—	—	—
5	22.7	1.0	7.4	34.7	0.0	0.5	10.4	21.5	6.0	0.2	0.5	—	—	—	—
6	2.4	1.1	3.5	51.3	0.1	1.8	3.8*	11.2	15.9	0.3	5.1	—	2.1	—	—
7	11.8	0.6	1.8	31.4	0.8	—	17.7	31.9	0.2	1.0	0.2	1.8	0.0	—	0.7
8	4.1	1.2	1.9	44.3	0.9	—	10.8	24.5	11.7	0.5	—	—	—	—	—
9	9.2	0.6	2.0	36.6	1.1	—	14.9	29.1	0.0	2.7	0.6	1.3	—	1.2	0.4
10	0.7	0.4	1.2	48.8	0.6	—	20.9	24.4	—	1.3	—	1.3	—	0.3	—
11	7.1	0.2	2.5	52.2	0.0	—	14.0	23.9	—	0.0	—	—	—	—	—
12	—	0.1	0.1	98.5	0.0	—	0.0	1.2	0.2	0.0	—	—	—	—	—

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*Using the suggested change in values given for N and Sn for set #6.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.2 AES

2.2.2.4 Discussion of Results

AES, A TRUE SURFACE ANALYSIS TECHNIQUE, IS USEFUL IN DETECTING ELEMENTS ON PW

AES is a true surface analysis technique since Auger electrons can only be detected for the first 20-30 A of a surface; it is a useful technique for detecting elements on the surface of PW.

The only thing truly startling about the above data is the large amount of C (carbon) and O (oxygen) detected by AES. Neglecting the samples from set #12, on which was left a gross amount of rosin flux, all the other samples still have relatively large amounts of carbon. For the cleaned samples it is possible to show statistically (analysis of variance) that the null hypothesis: $\mu_1 = \mu_3 = \mu_5 = \mu_7 = \mu_9 = \mu_{11}$ (for 1 carbon) can be accepted at a 1 percent level of significance. This means we can presume the population mean for cleaned samples to be the same, with a 1 percent chance that we will be in error by accepting this hypothesis. Thus, accepting the null hypothesis, μ (cleaned samples) = 38.5 (for C).[14]. It can further be shown by similar statistical techniques that $\mu_1 = \mu_3 = \mu_5$ (for oxygen) can be accepted at a 1 percent level of significance for the cleaned copper-clad samples and that $\mu_7 = \mu_9 = \mu_{11}$ (for oxygen) can be accepted at a 1 percent level of significance for the cleaned copper-etched samples. Thus, for sets #1, #3, #5 we can accept the null hypothesis and μ = 19.9 (for oxygen) for these sets. for sets #7, #9, #11 we can accept the hypothesis null and μ = 28.3 (for oxygen) for these latter sets.

This means for the first three cleaned sets, on the average C and O account for 58.4% of the atomic composition as determined by AES and for the latter three cleaned sets C and O account for 66.8% of the atomic composition on the average as determined by AES. This means that of all the elements detected on cleaned PW by AES, C and O account for just about two-thirds. The C on the samples is probably mostly chemisorbed CO, CO_2, and hydrocarbons from the atmosphere or adsorbed solvent (1,1,1-trichloroethane). These materials adhere tenaciously to the PW surface, even under high vacuum, because they chemisorb. No doubt some of the O also comes from chemisorbed gases, including H_2O, while some of it is probably associated with various metals, Cu, Pb, Sn, as metallic oxides.

Another contaminant found on every set (although in far lesser a percentage) is S (sulfur). Again, using the F test, it is likely (1 percent level of significance) there is no difference between the amount of S on sets #1-#9 inclusive so μ=0.1 (for sulfur) for these sets. The S probably comes from the atmosphere and is absorbed onto the PW surface.

Nitrogen gas (N_2) is also found on the PW surface, particularly in the first six sets. Since N_2 is physically absorbed, there was undoubtedly much more on the surface initially but it came off under high vacuum.

In addition to the above, Cl (chlorine), Ca (calcium) and Na sodium) are found on the PW at every stage (except stage 6, sets #11 and #12, for Ca and Na). Some of the Cl may come from the 1,1,1-trichloroethane which was used initially on all sets to degrease the PW before processing. It is known that C has a strong affinity for Cl. However, some of the Cl undoubtedly exists as chloride ions, Cl^-. Further, the Na and Ca are likely to exist as ions, viz., Ca^{2+} and Na^+. Other positive ions, Al^{3+} (aluminum), Zn^{2+} (zinc), and K^+ (potassium) are also noted at various stages. The Al seems chiefly associated with electrolytic plating or possibly from the nonwoven aluminum oxide scrubbing brush. The Zn probably arises from the Zn used to promote better adhesion between the copper and epoxy substrate during lamination and is thus exposed after the copper has been etched away. This seems borne out by the fact that Zn is observed chiefly at stages 4 and 5. Na and Ca may come from the undemineralized water used at almost every stage of PW fabrication. Note that their concentrations drop to 0 during stage 6, at least as determined by AES. Si (silicon) is also found on some sets. It, like Zn, seems to appear on the PW surface after the copper has been etched away. It is probably Si from the glass fibers that has become exposed after etching.

Turning to the in-depth profiling, several interesting results are seen (see Figures 6-11 for representative samples). The depth profiling was performed by simultaneously sputtering away a portion of the surface with Ar^+ while applying the Auger electron beam. Only 12 samples were used, one from each set. Samples from sets #1-#4 show variation in the oxide thickness on the Cu but no other interesting results (see Figures 6 and 7). Again, the cleaned samples (1,1,1-trichloroethane followed by demineralized water) show much more oxide formation. Further, the amount of oxide runs much deeper (>1,500 A) in the two cleaned samples than it does in the uncleaned. In the uncleaned samples the oxide layer falls off almost to 0 by 300 A. Again, it is speculated that the water used in the cleaning process greatly accelerated the formation of oxides on the PW surface. The sample from set #5 (Figure 8) shows a chloride layer near the surface and a thick oxide-chloride trailoff. The sample from set #6 (Figure 9) is about the same as that from set #5 with respect to the final Cu:Sn:Pb relative intensities but lacks the surface chloride and thick oxide-chloride trailoff. In addition, a layer of Sn (oxide?) is observed at the surface of this sample.

The samples from sets #7-#12 have radically varying profiles. Examination of these shows depleted Pb on the sample from set #7, a 300 A thick organic on the sample from set #8, good solder with little contamiination on the sample from set #9 (Figure 10), a surface layer of Pb tapering off to the expected composition in the sample from set #10, a surface Sn chloride-oxide over a high Pb region in the sample from set #11 (this is the cleaned sample after flux/solder - presumably "clean" and ready for conformal coating, see Figure 11), and a very thick (>2,000 A) organic layer on the sample from set #12 (this is uncleaned flux).

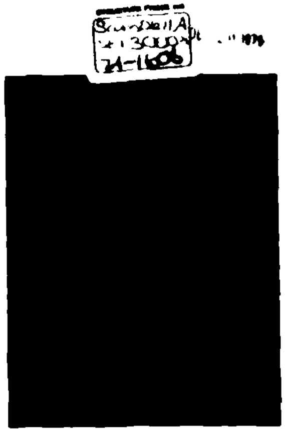

Figure 5. SEM photomicrograph of crystalline deposit on Sample 11 A (from Set # 11).

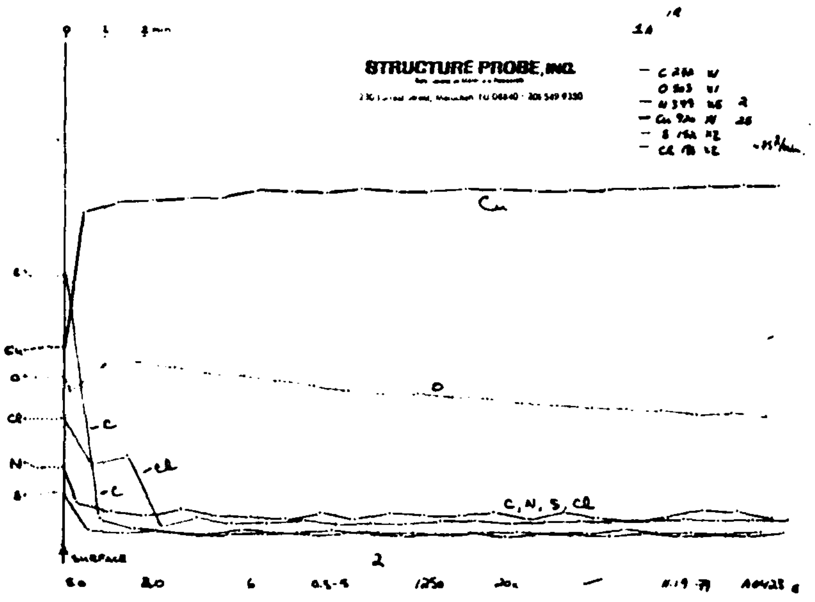

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Figure 6. Auger depth profile of Sample 1A (from Set # 1).

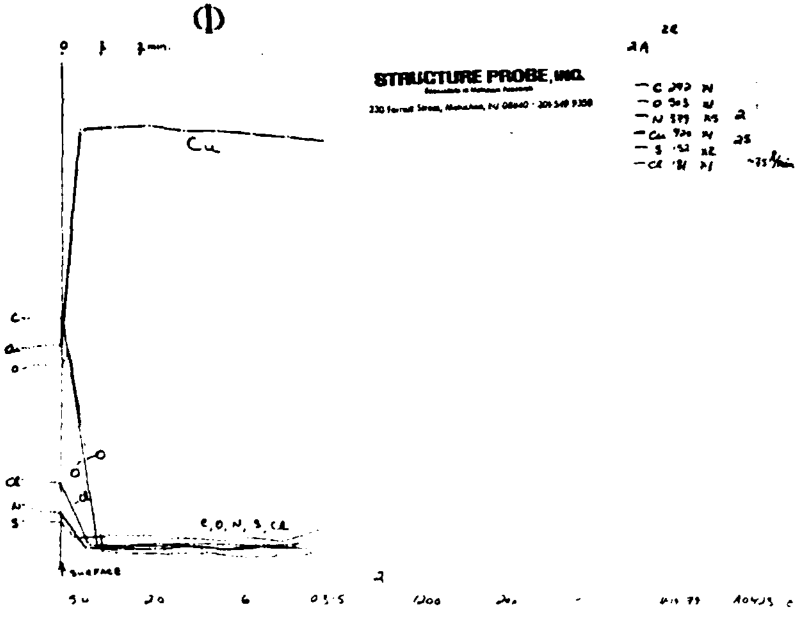

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Figure 7. Auger depth profile of Sample 2A (from Set # 2).

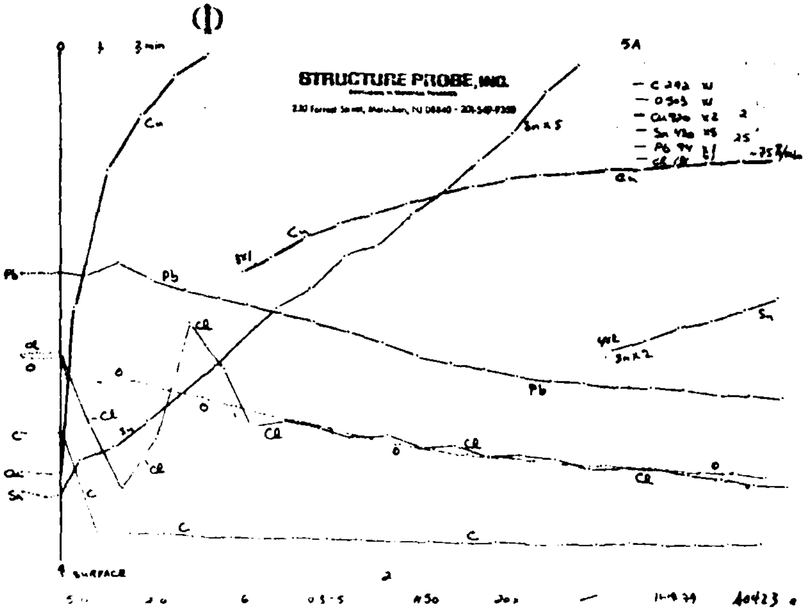

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Figure 8. Auger depth profile of Sample 5A (from Set # 5).

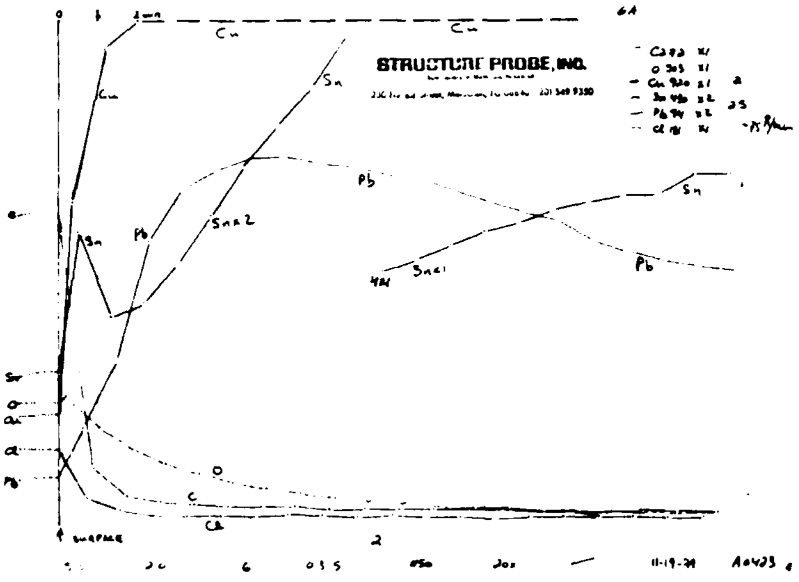

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Figure 9. Auger depth profile of Sample 6A (from Set # 6)

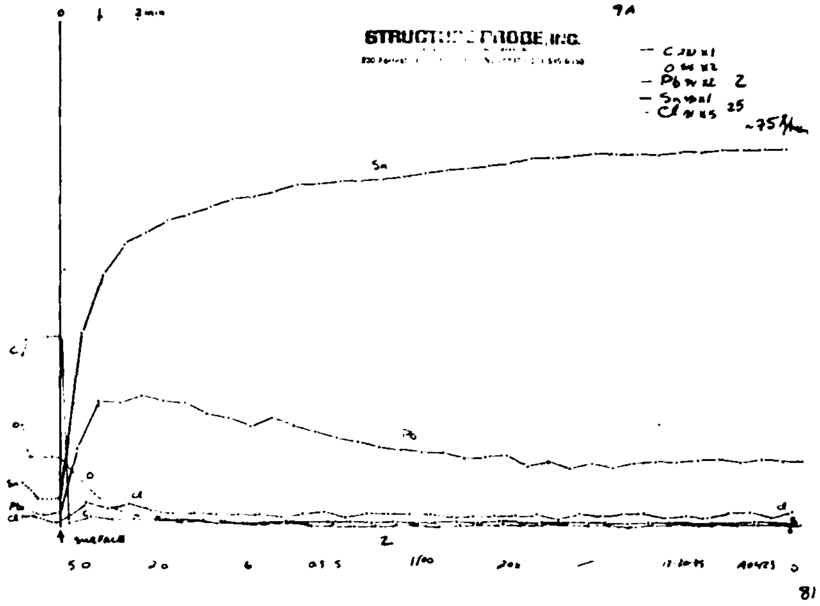

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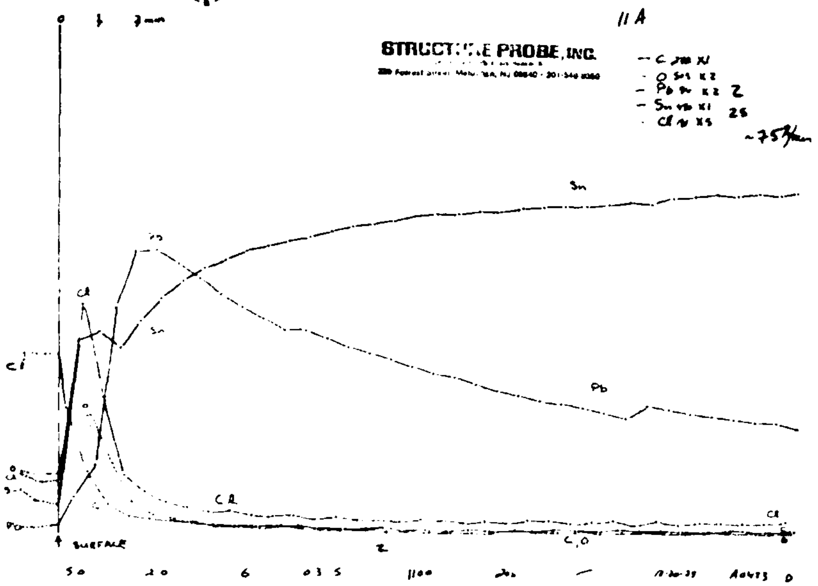
Figure 10 Auger depth profile of Sample 9A (from Set # 9)



83

Fig. [illegible] Auger [illegible] profile [illegible] le 11A [illegible] Set #1

Figure 12. SEM photomicrograph of epoxy surface at 7,000X.

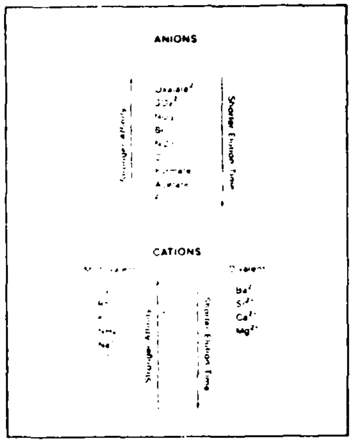


Figure 13 Normal Elution Sequence For Common Ions Using Ion Chromatography

Like the SEM/EDX, AES is useful in detecting elements on PW. However, unlike EDX, AES is as true surface analysis technique since Auger electrons can only be detected for the first 20-30 A of a given surface. Thus AES is useful in defining the surface elements on PW. The chief problem with this technique is choosing a representative spot on the surface. The Auger beam covers an area typically 200-300 μm^2. Since the surface of PW is very large compared to the area covered by the Auger beam, a PW having an area of 100 cm^2 will have a ratio of about 3 x 10^{-8} of beam area: PW area. That is, the Auger beam covers about 1/100,000,000 of the board surface. Examining three or four spots on several separate but identically manufactured PWBs will provide more confidence in this analytical technique, but this is more expensive.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.3 ESCA

2.2.3.1 Discussion of Method

ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA) MAKES USE OF A MONOENERGETIC X-RAY BEAM TO IRRADIATE SAMPLE SURFACE

The ESCA uses a monoenergetic x-ray beam to irradiate the PW surface knocking out electrons (photoelectrons) from core shells of atoms.

Electron Spectroscopy for Chemical Analysis (ESCA) or as it is sometimes called, X-ray Photoelectron Spectroscopy (XPS), makes use of a monoenergetic beam of x-rays to irradiate a sample surface. The excitation source in ESCA is an x-ray beam of predominantly $MgK\alpha$ x-rays. The x-rays (photons) possess sufficient energy to knock out electrons from core shells of atoms in the sample. Electrons from atoms within the top 20-30 A of the surface have enough energy to escape and are available for detection as photoelectrons. The energy equation governing these photoelectrons is:

K. E. ($1/2\ mv^2$) of the photoelectron = $h\nu - B.E. - \phi_w$.

where $h\nu$ is the energy carried by the photon, B.E. is the binding energy and ϕ_w is the work function of the surface. The ESCA spectra are plotted with binding energy on the horizontal axis and electron intensity on the vertical axis. ESCA has an advantage over AES, namely, it can be applied to polymeric surfaces whereas AES cannot, the electron beam being too highly destructive of organic material to gain useful information. With ESCA, elemental identification is possible by merely comparing the measured electron peak energy to the tabulated values. As with AES, all elements except H (hydrogen) and He (helium) can be detected. However, ESCA is a potentially more powerful method than AES, chiefly because the photoelectron binding energy can be measured so precisely that shifts in energy due to changes in chemical bonding can be studied resulting in much information about chemical compounds present in the analyzed layer. This method is known as High Resolution (HR) ESCA.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.3 ESCA

2.2.3.2 Procedure

ESCA SPECTRA OBTAINED AT ONE POINT ON PW EPOXY SURFACE AND EIGHT HIGH RESOLUTION ESCA MADE AT SELECTED POINTS

ESCA elemental scans were made at one independent point on each sample surface; high resolution ESCA were made at select sample sites on PW surfaces.

See 2.2.2.2 Procedure.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.3 ESCA

2.2.3.3 Data

DATA CONSISTS OF ESCA ELEMENTAL SCANS AND HIGH RESOLUTION PROFILES

The ESCA data consists of 18 elemental scans and 3 high resolution profiles to reveal bonding information of elements on PW surfaces.

The data for ESCA presenting the elemental analyses were taken at a particular point on the epoxy surface as opposed to AES, where the data were derived necessarily from a metallic portion of the PW. See Figure 12 for a SEM photomicrograph of an epoxy surface at 7,000x. The calculations of the ESCA data are basically the same as for AES. The data are presented in Table 3. Again, since the data in Table 3 are unwieldy, the arithmetic mean for the data for each set was computed and is presented in Table 4. Table 5 gives the results for the high resolution ESCA.

concentrations. The amount of copper detected by the ICP was actually somewhat less for the uncleaned samples than for those cleaned. This may be because the water rinse after each fabrication stage solubilizes more of the copper which subsequently appears in the extract. Also, the amount of copper falls precipitously in stage 3 whereas the amount of lead rises quite dramatically. At this stage (copper and solder deposited on PW surface electrolytically), apparently, much less of the copper forms ionic species whereas the lead does. No doubt lead ionization also suppresses copper ionization, probably through a common ion (anion) effect. After the etching operation the amount of copper falls considerably, which is to be expected; during and after this stage lead salts constitute the major form of contaminant in the PW extracts. The tin in the extracts naturally starts occurring at stage 3, only in relatively small amounts though (<0.1 ppm). Phosphorus and silicon show up in many of the PW extracts after the etching operation. They may arise as extraneous contamination or they may somehow come from the glass fiber portion of the epoxy laminate. The zinc that is observed during and after stage 4 undoubtedly arises from that used to promote better adhesion between the copper and epoxy substrate during lamination and is thus exposed after the copper has been etched away. Chromium, which was detected by ESCA (but not AES) was not detected by the ICP, possibly because its concentration was too far below the detection limit of the instrument.

The most severe metallic contaminants per the ICP on the PW surface are:

1 Copper in stages 1 and 2 especially

2 Lead in stages 3 through 6

3 Calcium, stage 3 especially

4 Phosphorus in stages 5 and 6 especially

5 Silicon in stages 5 and 6 especially.

There are several things to be said regarding the ICP emission spectrophotometer used in the experiment. Although this device makes very rapid analyses (it can easily analyze for more than 40 separate elements in a liquid sample and report their concentrations in ppm in less than one minute), it also suffers several drawbacks.

The chief drawback of the ICP is this. Even though values for the elements aluminum, Al; potassium, K; phosphorus, P; palladium, Pd; iron, Fe; and sodium, Na, were detected in the PW extracts, the values obtained ≈ detection limit concentration.[17] Hence, the precision of such measurements is poor. It is presumed the accuracy will also be poor. The detection limits on the ICP are:

Table 8

Element	Detection Limit in ppm
Al	0.030
Ca	0.010
Cr	0.006
Cu	0.004
Fe	0.006
K	0.300
Na	0.010
P	0.080
Pb	0.050
Pd	0.080
Si	0.025
Sn	0.050

The detection limit of an element is typically defined as the concentration in solution of that element which can be detected with 95 percent certainty. This is that quantity of the element that gives a reading equal to twice the standard deviation of a series of at least ten determinations at or near blank level. This means that at concentrations near the detection limit an element may be detected with reasonable statistical certainty. However, the precision of determinations at such low concentrations will normally not be satisfactory for normal quantitative purposes.

It is speculated that the aluminum arises form the mechanical cleaning operation since a non-woven abrasive aluminum oxide brush was used both for deburring the PW panels and for mechanical scrubbing. The amount of aluminum seems relatively independent of whether the board was cleaned or not. The calcium and sodium probably arise from the undemineralized water used to wash PWBs during processing. Note the steadily increasing rise in calcium concentrations, especially on the two PWBs from set #6. After the etching operation (stage #4), the amount of calcium drops considerably. Note some of the test boards have sodium, always in small concentrations, and some do not. Note also the copper

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.3.1 ICP-ES

2.3.1.4 Discussion of Results

WITHIN BOUNDS ICP USEFUL IN PROFILING CONTAMINANTS IN PW EXTRACTS

The results demonstrate that in general the ICP can profile contaminants in PW extracts, but for some elements its detection limits may be too high.

The results obtained using the ICP are indeed startling. Perusing especially Table 7, it can readily be seen that the number of micrograms of positive ions/cm^2 of PW surface ($\mu g/cm^2$) is quite high even during the initial two first stages (1 drill, deburr, chemical and mechanical clean; 2 electroless plate). It is quite apparent this is due to copper salts (generally only moderately soluble) which went into solution. During stage 3 (apply resist, develop image, electrolytic plate with copper and solder, strip resist), the number of $\mu g/cm^2$ rises due now to both lead and copper salts going into solution. Note that lead salts now account for much of the corresponding $\mu g/cm^2$ figure. Also note that tin salts play very little part.

Proceeding to stage 4 (etch image), the removal of the copper off the surface by the etchant is seen to cause the number of $\mu g/cm^2$ to drop drastically. Proceeding to the next two stages (solder reflow and routing; stuff components and flux/solder), there is a definite increase in the number of $\mu g/cm^2$ so that the total amount of contaminants at stage 6 for the cleaned PWAs (set #11) is practically the same as for the uncleaned PWBs of set #1. Again, note that lead salts account for a great percentage of the positive ion contamination in set #11 (this is the cleaned set after flux/solder - presumably "clean" and ready for conformal coating). It is obvious that the uncleaned rosin flux left on the PWAs in set #12 prevented a fair amount of the contaminants from entering the extract solution (demineralized water).

From perusing Tables 6 and 7, it is seen that the only elements present for certain in the PW solvent extracts are: calcium, Ca; copper, Cu; lead, Pb; silicon, Si; tin, Sn; and zinc, Zn. It is also highly likely that aluminum, Al; potassium, K; phosphorus, P; palladium, Pd; iron, Fe; and sodium, Na, are to be found. The only elements to occur in the extracts in quantities >0.1 ppm are: calcium, Ca, in Set #6; copper, Cu, in Sets #1-#5, Set #8 and Set #10 (sample 2); and lead, Pb, in Sets #5-#12.

Table 6

Results from ICAP in ppm (parts-per million)*

Element Analyzed For	Stage 1				Stage 2				Stage 3				Stage 4				Stage 5				Stage 6			
	Set #1 Cleaned		Set #2 Not Cleaned		Set #3 Cleaned		Set #4 Not Cleaned		Set #5 Cleaned		Set #6 Not Cleaned		Set #7 Cleaned		Set #8 Not Cleaned		Set #9 Cleaned		Set #10 Not Cleaned		Set #11 Cleaned		Set #12 Not Cleaned	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al	-	-	0.017	-	0.002	0.015	0.014	0.025	0.019	0.024	0.035	0.038	0.005		0.007	0.018	0.013	0.007	-	-	-	-	-	0.003
Ca	0.007	0.006	0.023	0.022	0.006	0.009	0.054	0.046	0.061	0.072	0.277	0.243	0.006		0.025	0.032	0.018	0.033	0.029	0.036	0.028	0.022	0.013	0.037
Cr	-	-	-	-	-	-	0.001	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Cu	2.318	1.740	1.678	1.438	2.186	2.294	1.929	1.524	0.942	0.147	0.027	0.012	0.066		0.521	0.530	0.098	0.028	0.016	0.133	0.028	0.013	0.019	0.017
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	0.006	0.005	-	-	0.004	0.003	-	-
K	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	0.275
Na	0.001	-	0.004	0.002	0.001	0.002	0.003	0.004	0.004	0.003	0.008	0.009	0.001		0.014	0.108	0.002	0.004	0.014	0.014	0.002	0.004	0.077	0.118
P	-	-	0.003	-	0.013	-	-	-	-	-	-	-	-		0.108	0.073	0.062	0.077	0.045	-	0.046	0.068	0.024	0.010
Pb	-	-	-	-	-	-	-	-	1.876	1.929	2.696	2.353	0.253		0.287	0.335	1.185	1.183	1.524	1.243	1.791	1.826	0.932	0.562
Pd	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	0.006	0.032	-	-	0.025	0.015	-	0.045
Si	-	0.015	0.064	-	-	-	-	-	-	-	-	-	0.020		0.014	0.009	0.027	0.054	0.004	0.012	0.049	0.029	-	0.029
Sn	-	-	-	-	-	-	-	-	-	-	0.039	0.085	-		-	-	-	0.025	-	-	0.018	0.004	-	0.028
Ba													-		-	-	-	-	-	-	-	-	-	-
Zn													0.035		0.031	0.027	-	-	0.016	0.005	0.048	0.050	0.016	-
Mg													-		-	-	-	-	-	-	-	-	-	-

*Two samples were used from each set. The second sample for Set #7 was destroyed in transit, hence, no results under that column. Values are in ppm after the average blank values have been subtracted out. A - = not detectible. The ICAP has a given sensitivity for each individual element. The figures reported above take this into account and only significant values are included.

Table 7

Results from ICAP in µg/cm² (micrograms-per-square-centimeter)**

Element Analyzed For	Stage 1				Stage 2				Stage 3				Stage 4				Stage 5				Stage 6			
	Set #1 Cleaned		Set #2 Not Cleaned		Set #3 Cleaned		Set #4 Not Cleaned		Set #5 Cleaned		Set #6 Not Cleaned		Set #7 Cleaned		Set #8 Not Cleaned		Set #9 Cleaned		Set #10 Not Cleaned		Set #11 Cleaned		Set #12 Not Cleaned	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al	-	-	8	-	1	7	7	12	9	12	17	19	2		3	9	6	3	-	-	-	-	-	1
Ca	3	3	11	11	3	4	27	23	30	36	138	121	3		12	16	9	16	14	18	14	11	6	18
Cr	-	-	-	-	-	-	1	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Cu	1159	870	839	719	1093	1147	965	762	471	73	13	6	33		260	265	49	14	8	66	14	6	9	8
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	3	2	-	-	2	1	-	-
K	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	137
Na	1	-	2	1	1	1	1	2	2	1	4	4	1		7	9	1	2	7	7	1	2	38	59
P	-	-	1	-	6	-	-	-	-	-	-	-	-		54	36	31	38	22	-	23	34	12	5
Pb	-	-	-	-	-	-	-	-	938	964	1348	1176	126		143	167	592	591	762	621	895	913	466	281
Pd	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	3	16	-	-	12	7	-	22
Si	-	7	32	-	-	-	-	-	-	-	-	-	10		7	4	13	27	2	6	24	14	-	14
Sn	-	-	-	-	-	-	-	-	-	-	19	42	-		-	-	-	12	-	-	9	2	-	14
Ba													-		-	-	-	-	-	-	-	-	-	-
Zn													17		15	13	-	-	8	2	24	25	8	-
Mg													-		-	-	-	-	-	-	-	-	-	-
$\sum$ µg	1163	880	893	731	1104	1159	1001	799	1450	1086	1539	1368	192		501	519	707	721	823	720	1018	1051	539	559
$\sum$ µg/cm²	9.46	7.15	7.26	5.94	8.98	9.42	8.14	6.50	11.79	8.83	12.51	11.12	1.56		4.07	4.22	5.75	5.86	6.69	5.85	8.28	8.25	4.38	4.54

** The area of the test printed wiring used = 123 cm².

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.2.1 ICP-ES

2.3.1.3 Data

DATA FROM ICP REPORTED IN PARTS-PER-MILLION FOR DIFFERENT CONTAMINANT SPECIES

The data from the ICP consists of concentrations of the different contaminant elements reported in ppm; these values were converted to ug/cm^2 of PW surface.

Table 6 contains the data for PW extracts run on the ICP. The results are given in parts-per-million (ppm).[15] Since 500 ml of each sample was used in the experiment, it is easy to convert the values given in ppm (Table 6) into so many micrograms (μg)/cm^2 of PW area for each element. Summing these values for any given sample yields the total number of μg/cm^2 for any given sample. See Table 7. The significance for reporting the results in μg/cm^2 stems from a recently published paper stating that 1.0 μg/cm^2 of sodium chloride or its equivalent represents the threshold concentration of ionic material beyond which functional degradation of PW takes place.[16]

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.2.1 ICP-ES

2.3.1.2 Procedure

PW EXTRACTS FROM TWO SAMPLES PER SET ANALYZED BY ICAP-ES

The ICP was used to profile twelve different elements in PW extracts during the first three stages and fifteen elements the last three stages.

Two samples per set were used in the experiment. The extracts were prepared by allowing the test PW to remain in pure demineralized water for six days in 500 ml polypropylene mason jars. After six days the PW were then carefully removed from the jars and the extracts therein were analyzed on the ICAP.

This device was used to profile PW extracts in pure demineralized water prepared from PW test boards. The extracts for the first three stages were analyzed for the following twelve elements: aluminum, Al; calcium, Ca; chromium, Cr; copper, Cu; iron, Fe; lead, Pb; palladium, Pd; phosphorus, P; potassium K; silicon, Si; sodium, Na; and tin, Sn. Many, if not all, of these particular elements were expected to occur on PW surfaces after each successive stage during the manufacturing process. The elements barium, Ba; zinc, Zn; and magnesium, Mg, were also run for the last three stages.

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.3.1 ICP-ES

2.3.1.1 Discussion of Method

INDUCTIVELY-COUPLED PLASMA (ICP-ES) ANALYZES LIGHT EMITTED BY CONTAMINANT ELEMENTS

The ICP is a system utilizing a plasma generated torch and nebulizer system to analyze emitted light for contaminant elements.

Because of the drawbacks suggested above regarding direct surface analysis techniques for profiling contaminants on the surface of PW, another method strongly recommends itself. This method can be called *solvent extraction/contaminant profiling* because it first necessitates making a solvent extraction of the PW followed by analyzing the solvent extract for various contaminants. Not only should the presence of a particular contaminant be detected (qualitative analysis) but the amount of the particular contaminant in question should be quantified (quantitative analysis).

Inductively-Coupled Plasma Emission Spectrophotometry (ICP-ES) makes use of an inductively-coupled argon plasma flame and nebulizer system to atomize a liquid sample and thermally excite the atoms in the sample. Thus excited, the different atomic species emit light at determined frequencies. A precisely aligned optical system collimates and directs the emitted light through an entrance slit onto a concave grating surface. The grating diffracts the different wavelengths of light to a series of exit slits precisely positioned along the spectrometer's focal curve. Photomultiplier tubes behind these exit slits convert the emitted light into electrical energy proportional to the intensity of the spectral lines. A computer converts the signals into desired concentration units (generally parts-per-million).

The chief problem of any of the above methods as applied to the analysis of PW is this. Surface analysis techniques by their very nature can be applied only to an exceedingly small area of the total PW surface area. Data from several (>3) areas would undoubtedly have to be gathered and, even then, there might exist some question as to whether these data were truly representative of the surface as a whole. Further, the necessary equipment is quite expensive (approximately $300K-500K) and requires a highly skilled operator to perform the analyses. In addition, the results from the direct surface analysis techniques are expressed in atomic percent concentrations which cannot be converted into µg of contaminant/cm^2 of PW surface.

Surface analysis techniques do have limitations associated with their application to ascertaining production cleanliness of PW. Their use may provide relevant information in solving some of the problems associated with PW contamination.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.4 GENERAL DISCUSSION

SURFACE ANALYSIS TECHNIQUES CAN BE USED TO PROFILE CONTAMINANTS ON PW BUT ARE VERY EXPENSIVE

Surface analysis techniques can be applied only to exceedingly small areas of total PW surface area.

The surface analysis techniques outlined above, viz., SEM/EDX, AES, ESCA (survey and high resolution) can be used to profile contaminants left on PW. Something positive can be said of each method.

With SEM/EDX photomicrographs of the surface can be made along with a general analysis of the chief elements down to about 10,000-50,000 A. On occasion the SEM may reveal an anomalous surface morphology and EDX may reveal gross abnormalities in composition. To cite two examples, the SEM was used to detect crystalline-like deposits on the solder surface, on PWAs of set #11. The concurrent use of elemental distribution maps indicates the material is most probably organic in nature. It is speculated that is is flux which did not come off by the conventional cleaning techniques. Further, the use of EDX revealed a case where the amount of tin in a tin/lead trace was grossly deficient.

It is often not clear, however, whether a given morphology is anomalous or not. This is the chief problem with SEM. In the case of EDX, it is not a true surface analysis technique since it "sees" far into the material.

With AES only elemental analysis is possible. However, AES is a true surface method since the analysis extends only 20-30 A into the material. AES also suffers from the limitation that it cannot be used on polymeric surfaces because it is too destructive of these surfaces.

ESCA is more versatile than AES. ESCA can be applied to both metallic and nonmetallic surfaces. It is a true surface method since the analysis likewise extends only 20-30 A into the material. Further ESCA data (photoelectron spectra) lend themselves more readily to yielding different chemical states of the elements, thus suggesting molecular groupings. Of the three methods outlined above, it is the most powerful in terms of the amount of useful surface information it affords.

Both AES and ESCA can be used in conjunction with sputtering of the surface. AES may be performed simultaneously with the sputtering whereas the sputtering must precede ESCA analysis. However, there is one caution. Sputtering often changes the valence states of the atoms at or near the area being sputtered. Thus, identification of the remaining chemical states may not accurately reflect the initial composition.

On the spot from a board from set #6 (6A Solder/Cu) HR-ESCA again revealed adsorbed material some of which is undoubtedly hydrocarbon in nature, a Sn (tin) oxide, metallic and/or ionic copper, Cu° or Cu^+, and lead chloride-organic (organo-metallic).

On the spot from the board from set #8 made on the epoxy (8A Epoxy) HR-ESCA revealed again adsorbed material some of which is organic in nature, some evidence of a metal oxide of some kind, and again a lead chloride-organic (organo-metallic). On the spot made at the solder/epoxy interface (8A Solder/Epoxy) HR-ESCA revealed, in addition, traces of metallic and ionic copper, Cu° and Cu^{2+}, Sn oxide, and evidence of a tin chloride-organic (organo-metallic).

From the board from set #10 made on the epoxy (10A Epoxy) HR-ESCA revealed adsorbed material, a metal oxide of some kind and elemental tin, Sn°. From the spot made at the solder/epoxy interface (10A Solder/Epoxy) HR-ESCA showed in addition Sn oxide and a tin chloride-organic (organo-metallic).

Finally, from the board from set #11 made on the epoxy (11A Epoxy) HR-ESCA exhibited adsorbed organic material, Sn oxide, Pb oxide, lead chloride-organic and evidence of a organic chloride (probably 1,1,1-trichloroethane). On the spot made at the solder/epoxy interface (11A Solder/Epoxy) basically the same was found as at 11A Epoxy.

The boards from set #11 represent those that were flux/soldered and cleaned using conventional PW cleaning techniques. Presumably they were "clean" and were now ready for conformal coating. However, evidence from HR-ESCA indicates that such PWAs still have a wide variety of compounds and materials on the PW surface, albeit in relatively small amounts. The presence of these compounds may not be sufficient to degrade the electrical, mechanical, or chemical properties of the PW in the present state-of-the-art. However, their presence and formation should be noted.

2.2 DIRECT SURFACE ANALYSIS TECHNIQUES

2.2.3 ESCA

2.2.3.4 Discussion of Results

ESCA, A TRUE SURFACE ANALYSIS TECHNIQUE, IS USEFUL IN DETECTING ELEMENTS ON PW AND REVEALING BONDING INFORMATION

ESCA is as true surface analysis technique since ESCA photoelectrons are only detectable from the first 20-30 A of a surface; it is a useful technique for detecting elements on the surface of PW and revealing bonding information.

Keeping in mind that the elemental analyses for the ESCA were made only on the epoxy surface (thus only sets #7-#12 were involved), it is evident some elements show up here that did not with AES. Here the amount of C (carbon) and O (oxygen) is even higher (approx. 82%) since the analysis takes place directly on the epoxy surface. The analyses were made at a fair distance from the Sn/Pb pads and conductor traces. Note that a fair amount of Sn and Pb occurs even on the bare epoxy. Cr (chromium) occurs on all samples except samples from set #12 where the flux was purposely left on the PW. The Cr undoubtedly appears on sets #7-#11 because at this point the copper has been etched away, revealing Cr. Chromium oxide was used by the laminator as a passivating agent in treating copper. In similar fashion Zn (zinc) arises after the copper has been etched away. The Zn is used to treat the copper surface to which the epoxy will be bonded to improve adhesion. Br (bromine) also appears after the copper has been etched away. The Br is incorporated into the epoxy structure and acts as a fire retardant. Cl (chlorine) as appears, either as ionic or possibly from adsorbed chlorocarbon compounds, such as 1,1,1-trichloroethane. Note that on some of the sets Cu (copper), Ba (barium - why this appears is not yet certain), P (phosphorus - possibly from exposed glass), Si (silicon - same source as P) and S (sulfur - probably adsorbed) also appear.

High Resolution (HR) ESCA was performed on eight samples. A representative sample from the first four sets was chosen (4A). This board still had its Cu surface. Another was chosen from set #6 (6A) which had copper and solder traces. The HR-ESCA was performed at a solder/Cu interface. Two different spots on a board from set #8 were chosen (8A Epoxy and 8A Solder/Epoxy), two different spots from a board from set #10 (10A Epoxy and 10A Solder/Epoxy), and two different spots from a broad from set #11 (11A Epoxy and 11A Solder/Epoxy).

On the spot from the board form set #4 (4A) HR-ESCA revealed adsorbed material some of which is undoubtedly hydrocarbon, metal oxide (undoubtedly a form of copper oxide) and evidence of Cu^+. Perhaps the copper oxide is Cu_2O.

Table 5

Summary of High Resolution ESCA Results

Sample	Corrected Element Binding Energy (eV)		Possible Identification
4A	Cls	284.6	Adsorbed/hydrocarbon
	Ols	531.5	Metal oxide or organic
	$Cl2p_{3/2}$	199.3	Metal or organic chloride
	$Cu2p_{3/2}$	932.7	Cu^0 or Cu^+
	Cu Auger	337.0	Cu^+
6A Solder/Cu	Cls	284.6	Adsorbed/hydrocarbon
	Ols	531.6	Metal oxide or organic
	$Sn3d_{5/2}$	486.7	Sn oxide
	$Pb4f_{7/2}$	138.7	Pb-Cl organic
	$Cu2p_{3/2}$	932.3	Cu^0 or Cu^+
8A Epoxy	Cls	284.6	Adsorbed/hydrocarbon
	Ols	525.6	?
		528.5	?
		530.7	Adsorbed or metal oxide
	$Pb4f_{7/2}$	139.7	Pb-Cl organic
8A Solder/Epoxy	Cls	284.6	Adsorbed/hydrocarbon
		286.4	Methyl organic
	$Cu2p_{3/2}$	930.6	Cu^0?
		933.2	Cu^{2+}
	$Pb4f_{7/2}$	140.9	Pb-Cl organic
	$Sn3d_{5/2}$	487.7	Sn oxide/Sn-Cl organic
10A Epoxy	Cls	284.6	Adsorbed/hydrocarbon
	Ols	528.1	?
		530.4	Adsorbed or metal oxide
	$Sn3d_{5/2}$	484.7	Sn^0
10A Solder/Epoxy	Cls	284.6	Adsorbed/hydrocarbon
	Ols	532.0	Adsorbed or organic
		533.7	Adsorbed or organic
	$Sn3d_{5/2}$	486.5	Sn oxide
		487.0	Sn oxide/Sn-Cl organic
11A Epoxy	Cls	284.6	Adsorbed/hydrocarbon
	Ols	528.2	?
		530.5	Adsorbed or metal oxide
	$Sn3d_{5/2}$	486.2	Sn oxide
	$Pb4f_{7/2}$	138.5	Pb oxide/Pb-Cl organic
	Cl2p	198.2	Metal or organic chloride
11A Solder/Epoxy	Cls	284.6	Adsorbed/hydrocarbon
	Ols	530.9	Adsorbed or metal oxide
		531.7	Metal oxide or organic
	$Sn3d_{5/2}$	486.7	Sn oxide
	$Pb4f_{7/2}$	138.4	Pb oxide/Pb-Cl organic
		138.8	Pb-Cl organic

Table 4

Sample	Cu	Ba	Cr	O	Sn	C	Zn	Cl	Br	S	Pb	P	Si
7	—	—	3.7	29.8	4.4	58.0	0.2	1.4	1.2	—	0.7	0.5	—
8	2.5	—	5.2	34.6	4.1	46.1	0.2	1.7	0.5	1.1	0.3	0.7	—
9	—	0.6	2.9	30.5	12.2	49.3	0.0	1.7	0.8	—	2.0	—	—
10	—	—	2.0	24.4	4.2	67.9	0.1	0.4	1.0	—	0.2	—	—
11	—	—	1.5	19.3	15.3	60.6	—	1.3	0.3	—	1.6	—	—
12	—	—	—	1.7	—	97.7	0.1	—	—	—	—	—	0.5

Table 3

Estimated Atomic Compositions (%) From ESCA Data

Set	Sample	Cu	Ba	Cr	O	Sn	C	Zn	Cl	Br	S	Pb	P	Si
#7	7A	-	-	3.0	27.9	3.6	61.8	0.2	1.2	1.3	-	1.0	-	-
	7B	-	-	3.5	27.8	4.8	59.7	0.2	1.0	1.3	-	0.2	1.5	-
	7C	-	-	4.7	33.8	4.7	52.6	0.2	2.1	0.9	-	1.0	-	-
#8	8A	2.6	-	3.8	35.2	3.7	50.2	0.2	1.6	0.5	1.1	0.3	0.8	-
	8B	1.4	-	6.4	39.8	4.4	43.3	0.3	1.4	0.4	0.9	0.3	1.4	-
	8C	3.6	-	5.3	37.9	4.1	44.9	0.2	2.0	0.5	1.2	0.3	-	-
#9	9A	-	0.6	4.0	34.0	4.6	52.8	0.1	1.8	0.7	-	1.4	-	-
	9B	-	0.7	2.8	27.2	13.9	51.0	-	1.5	0.9	-	2.0	-	-
	9C	-	0.6	1.9	30.2	18.0	44.1	-	1.8	0.8	-	2.6	-	-
#10	10A	-	-	2.5	24.6	6.8	63.7	0.1	1.1	0.9	-	0.3	-	-
	10B	-	-	1.9	24.5	3.5	68.8	0.1	-	1.1	-	0.1	-	-
	10C	-	-	1.7	23.9	2.2	71.0	0.1	-	1.0	-	0.1	-	-
#11	11A	-	-	1.6	21.2	12.3	61.0	-	1.4	0.4	-	2.1	-	-
	11B	-	-	1.4	16.6	22.6	57.8	-	0.9	-	-	0.7	-	-
	11C	-	-	1.6	20.2	10.9	63.0	-	1.6	0.6	-	2.1	-	-
#12	12A	-	-	-	2.5	-	96.4	0.1	-	-	-	-	-	1.0
	12B	-	-	-	1.4	-	98.0	-	-	-	-	-	-	0.6
	12C	-	-	-	1.3	-	98.6	0.1	-	-	-	-	-	-

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.3.2 IC

2.3.2.1 Discussion of Method

ION CHROMATOGRAPHY (IC) ANALYZE IONS IN SOLUTION

The IC uses a system involving ion exchange separation followed by eluent suppression and conductivity detection to analyze for ions in solution.

Although an ICP or equivalent spectrophotometer is useful for analyzing the positive ionic species in PW extracts, another method must be employed to profile the negative ionic species in such extracts. It is suggested that an ion chromatograph be used for making such an analysis.

An IC analyses ions in solution. It accomplishes this by an ion exchange separation followed by eluent suppression and conductivity detection. For an ion analysis, the eluent (usually 0.003M $NaHCO_3$/0.0024M Na_2CO_3) and separator column (containing an anion resin in the HCO_3^-/CO_3^{2-} form) cause the sample ions to split into distinct bands. The retention time of each anion is governed by the affinity of that ion, the eluent used, the length of column, and the eluent flow rate. Figure 13 shows the relationship between affinity and relative retention time for both anions and cations.

The effluent from the separator column is then fed to the suppressor column. Two reactions occur in the suppressor. First, the resin (a strong acid resin in hydrogen form) removes Na^+ and protonates the HCO_3^-/CO_3^{2-} to H_2CO_3, viz.,

$$NaHCO_3 + R\text{-}H \longrightarrow R^- + Na^+ + H_2CO_3$$

$$Na_2CO_3 + 2R\text{-}H \longrightarrow 2R^- + 2Na^+ + H_2CO_3.^{18}$$

Second, all the sample anions exit from the suppressor as an acid since the sample cations are exchanged for H^+ in the suppressor.

$$Na^+X^- + R\text{-}H \longrightarrow R^- + Na^+ + H^+X^-.$$

The analysis of cations utilizes the same physical design. However, the separator column contains a cation resin and the suppressor column contains an anion resin in hydroxide form. In this case, the acidic element is neutralized by the suppressor resin and the cations are detected as hydroxides.

Using the 0.3 μMHO full scale sensitivity of the ion chromatograph and a 250 μl sample loop, the minimum detection limits (MDL)[19] for several ions of interest are as follows:

Ion	MDL
Na^+, NH_4^+, K+	5-20 pb
Mg^{2+}, Ca^{2+}	
F^-, Cl^-	5-10 ppb
PO_4^{3-}, NO_3^-, SO_4^{2-}	20-30 ppb.

For normal samples, these MDLs are more than sufficient. However, for certain applications it is necessary to analyze at 1 ppb or less; the use of concentrator columns is necessary to achieve this.

A concentrator column is a short (3 x 50 mm) column that replaces the sample loop. When a large amount of sample water is passed across an anion concentrator column, the anions are stripped out and held on the concentrator column. Then when the loaded column is switched into the eluent stream, the ions are eluted from the concentrator column and separated as usualy by the separator column. If the initial loading onto the concentrator were 25 ml, the concentration factor would be 100 when compared to the 250 μl sample loop. Hence, the MDLs can be lowered by a factor of 100, and analysis at less than 1 ppb can be done routinely.

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.3.2 IC

2.3.2.2 Procedure

PW EXTRACTS FROM TWO SAMPLES PER SET ANALYZED BY IC

The IC was used to profile nine different ionic species in PW extracts.

Two samples per set were used in the experiment. The extracts were prepared by allowing the test PW to remain in 75% demineralized water/25% Reagent Grade isopropyl alcohol for six days in 500 ml polypropylene mason jars. After six days the PW were then carefully removed from the jars and the extracts therein were analyzed on the IC. The extracts were analyzed for the following cations: sodium, Na^+; ammonium, NH_4^+; potassium, K^+; calcium, Ca^{2+}; and magnesium, Mg^{2+}. The same samples were also analyzed for the following anions: chloride, Cl^-; phosphate, PO_4^{3-}; nitrate, NO_3^-; and sulfate, SO_4^{2-}.

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.3.2 IC

2.3.2.3 Data

DATA FROM IC REPORTED IN PARTS-PER-MILLION FOR DIFFERENT CONTAMINANT SPECIES

The data from the IC consists of concentrations of different contaminating ionic species reported in ppm; these values were converted to $\mu g/cm^2$ of PW surface.

Table 9 contains the data for PW extracts run on the IC. The results are given in parts-per-million (ppm). Again, the values given wre converted into so many micrograms (μg)/cm^2 of PW area for each element. Summing these values for any given sample yields the total number of $\mu g/cm^2$ for any given sample. See Table 10.

Table 9

Results from IC in ppm (parts-per-million)*

	Stage 1				Stage 2				Stage 3				Stage 4				Stage 5				Stage 6			
Ion	Set #1 Cleaned		Set #2 Not Cleaned		Set #3 Cleaned		Set #4 Not Cleaned		Set #5 Cleaned		Set #6 Not Cleaned		Set #7 Cleaned		Set #8 Not Cleaned		Set #9 Cleaned		Set #10 Not Cleaned		Set #11 Cleaned		Set #12 Not Cleaned	
Analyzed For	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Na^+		0.130	0.120	0.110				0.120	0.090		0.170	0.130		0.070	0.090	0.110	0.160		0.120	0.120	0.150	0.120		
NH_4^+		0.030	0.030	0.030				0.080	0.030		0.050	0.030		0.060	0.070	0.080	0.060		0.060	0.060	0.080	0.050		
K^+		0.020	0.010	0.010				0.020	0.130		0.010	0.010		0.010	0.010	0.020	0.030		0.010	0.030	0.020	0.020		
Ca^{2+}		0.004	0.014	0.012	0.009		0.031	0.033	0.017		0.052	0.080		0.036	0.035	0.021	0.034	0.017	0.044	0.033	0.044	0.024		
Mg^{2+}		-	-	-	-			-	-		-	-		-	-	-	-		-	-	-	-		
Cl^-		0.015	0.019	0.012	0.011			0.018	0.012			0.025		0.060	0.060		0.070		0.045			0.200		
PO_4^{3-}		-	-	-	-			-	-			-		-	-		0.200		-			-		
SO_4^{2-}		0.005	-	0.010	0.006			0.135	0.012			0.018		0.075	0.075		0.008		0.008			0.030		
NO_3^-		-	-	0.003	0.003			0.005	0.005			0.006		0.004	0.003		-		0.005			0.008		

---

*Two samples were used from each set. However, many of the samples were partially or totally destroyed in transit. All blank spaces under a particular column indicate the sample was destroyed. Values are in ppm after the average blank values have been subtracted out. A- = not detectible.

Table 10

Results from IC in $\mu g/cm^2$ (micrograms-per-square-centimeter)**

	Stage 1				Stage 2				Stage 3				Stage 4				Stage 5				Stage 6			
Ion	Set #1 Cleaned		Set #2 Not Cleaned		Set #3 Cleaned		Set #4 Not Cleaned		Set #5 Cleaned		Set #6 Not Cleaned		Set #7 Cleaned		Set #8 Not Cleaned		Set #9 Cleaned		Set #10 Not Cleaned		Set #11 Cleaned		Set #12 Not Cleaned	
Analyzed For	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Na^+		65	60	55				60	45		85	65		35	45	55	80		60	60	75	60		
NH_4^+		15	15	15				40	15		25	15		30	35	40	30		30	30	40	25		
K^+		10	5	5				10	65		5	5		5	5	10	15		5	15	10	10		
Ca^{2+}		2	7	6	4		15	16	8		26	40		18	17	10	17	8	22	16	22	12		
Mg^{2+}		-	-	-				-	-		-	-		-	-	-	-		-	-	-	-		
Cl^-		7	9	6	5			9	6			12		30	30		35		22			100		
PO_4^{3-}		-	-	-	-			-	-			-		-	-		100		-			-		
SO_4^{2-}		2	-	5	3			67	6			9		37	37		4		4			15		
NO_3^-		-	-	1	1			2	2			3		2	1		-		2			4		
$\sum \mu g$		101	96	93				204	147			149		157	170		281		145			226		
$\sum \mu g/cm^2$		0.82	0.78	0.76				1.66	1.20			1.21		1.28	1.38		2.28		1.18			1.84		

**The area of the test printed wiring used = 123 cm^2.

2.3 SOLVENT EXTRACTION/ANALYSIS TECHNIQUES

2.3.2 IC

2.3.2.4 Discussion of Results

THE IC USEFUL FOR PROFILING IONIC CONTAMINANTS IN PW EXTRACTS

The results show that the IC can profile ionic contaminants in PW extracts but more work needs to be done to better define the process.

In terms of μg/cm^2 of ionic material as determined by the IC, the results are much lower. Note, however, that no heavy metal ion concentrations such as copper, lead, tin, or zinc could be made using the IC. The results for sodium and potassium differ considerably from those obtained on the ICAP. This is probably because of the rather high detection limits for those two elements on the ICAP. Except for those in stage 3, the calcium values are in reasonably good agreement. The chloride values show a marked steadily rising increase from stage 1 through stage 6. Except for a few exceptions, phosphate and sulfate do not constitute serious contaminants. Nitrate as a contaminant is practically nonexistent. It might be pointed out there were several unidentified peaks in the chromatograms. It is suspected one of the peaks belongs to fluoride (F^-) but further investigation is needed to confirm this. Also, no attempt was made to check for organic anions, some of which might have been present.

2.4 SURFACE ANALYSIS TECHNIQUES SOMETIMES USEFUL BUT SOLVENT EXTRACTION/CONTAMINANT PROFILING ANALYSIS OF PW EXTRACTS MORE PROMISING

A general discussion of the merits of surface analysis techniques versus solvent extraction/analysis techniques.

At this point we shall summarize the key points regarding direct surface analysis techniques versus solvent extraction/analysis techniques.

Surface analysis techniques can be applied only to exceedingly small areas of the total PW surface area. These techniques, viz., SEM/EDS, AES, and ESCA (survey and high resolution) can be used to profile contaminants left on PW. Something positive can be said of each method.

With SEM/EDS photomicrographs of the surface can be made along with a general analysis of the chief elements down into the surface to about 10,000-50,000 A ($\approx 10^{-4}$cm). On occasion the SEM may reveal an anomalous surface morphology and EDS may reveal gross abnormalities in composition. To cite two examples, the SEM was used to detect crystalline-like deposits on the solder surfaces on some of the PWAs of set #11. It is highly probable that the material was organic in nature.

It is speculated that it was flux which did not come off by the conventional cleaning techniques. The use of EDS revealed a case where the amount of tin in a tin/lead trace was grossly deficient.

It was often not clear, however, whether a given morphology was anomalous or not. This is the chief problem with employing SEM. In the case of EDS, it is not really a true surface analysis technique since it "sees" far into the material.

With AES only elemental analysis is possible. However, AES is a true surface analysis method since the analysis extends only 20-30 A into the material. AES also suffers from the limitation that it cannot be used on polymeric surfaces because its electron beam is too destructive of these surfaces.

ESCA is more versatile than AES. ESCA can be applied to both metallic and nonmetallic surfaces. It too is a true surface method since the analysis likewise extends only 20-30 A into the material. Further, ESCA data (photoelectron spectra) lend themselves more readily to yielding different chemical states of the elements, thus suggesting molecular groupings and arrangements. Of the three direct surface analysis techniques, it is the most powerful in terms of the amount of useful surface information it affords.

Both AES and ESCA can be used in conjunction with sputtering of the surface. AES may be performed simultaneously with the sputtering whereas the sputtering must of necessity precede ESCA analysis. However, there is one caution. Sputtering often changes the valence states of the surface atoms at or near the area being sputtered. Thus, identification of the surface chemical states may not accurately reflect the initial composition.

The chief problem of all of the direct surface analysis methods as applied to profiling contaminants on the surface of PW is this. Surface analysis techniques by their very nature can be applied only to an exceedingly small area of the total PW surface area. Data from several (>3) areas would undoubtedly have to be gathered and, even then, there might exist some question as to whether these data were truly representative of the surface as a whole. The problem is compounded by the lack at the present time of adequate ways of standardizing the instruments. In addition, the results from the direct surface analysis techniques are expressed in atomic percent concentrations which cannot be converted into µg of contaminant/cm^2 of PW surface.

The conclusion is that direct surface analysis techniques do have definite limitations associated with their application for determining production cleanliness of PW. However, their use can provide relevant and useful information, and they will sometimes prove beneficial in solving problems of PW contamination. In point of fact, it is estimated that approximately 5% of all PW contamination problems will require direct surface analysis techniques for successfully resolving the problem.

The data generated from the experiment on production PW also indicate that the solvent extraction/analysis techniques will also function adequately as contaminant profiling devices for determining production cleanliness of PW. In particular, they do not suffer from the chief drawback of the direct surface analysis techniques, for the solvent extraction is made over the entire surface. The only problem with their application is to establish the proper extraction time to ensure that the contaminants have been rinsed into the extract and no longer remain on the PW surface. The results, normally reported in ppm (parts-per-million), can easily be converted into micrograms of contaminant/cm^2 of PW surface (μg/cm^2) provided the volume of extract is measured. It is estimated that approximately 95% of all PW contamination problems will be amenable by solvent extraction/analysis techniques.

2.5 THE COSTS

A cost analysis of the different methods of detecting surface contaminants on PW can be performed.

The conclusion drawn from the PW experiment data is that both direct surface analysis techniques and solvent/extraction/analysis techniques can be used successfully to profile contaminants on the surface of PW. It is estimated that the solvent extraction/analysis techniques are somewhat superior because they have less problems attendant to their use. However, it is appropriate now to turn to the costs.

We first construct an effectiveness versus cost scale, which is presented in Figure 14. Bear in mind that

Alternative 1 = extract resistivity testing (ERT)

Alternative 2 = laser beam scanning

Alternative 3 = direct surface analysis techniques (SEM, AES, ESCA)

Alternative 4 = solvent extraction/analysis techniques (ICP-ES, IC).

Since alternative 2 is not viable, it does not appear in Figure 14.

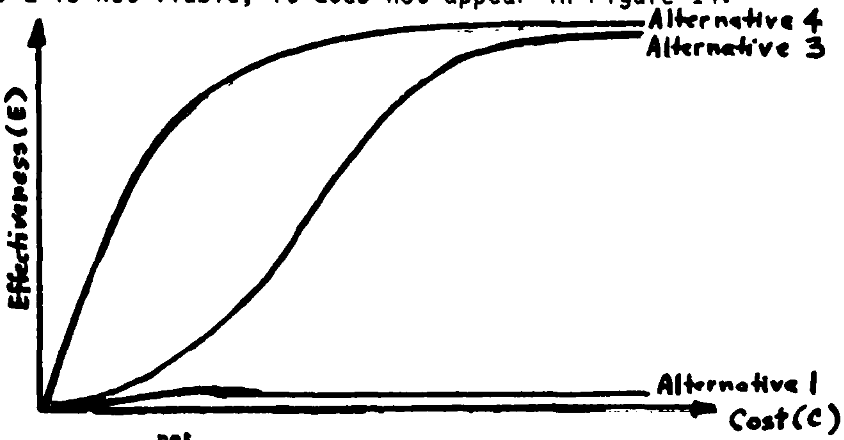


Figure 14. Effectiveness vs. cost for the three alternatives.

Using the terminology of capital budgeting, we are here dealing with mutually exclusive alternatives. That is, each alternative under consideration represents an alternative method for meeting the same objective. Once one alternative is chosen to do the job, the others will be dropped from consideration. Applying discounted cash flow techniques to the above two alternatives holding the highest promise, viz., direct surface analysis techniques and solvent extraction/analysis techniques, we obtain the following table below. The net present worth (NPW) technique is employed to compare the two alternatives.[20]

Table 11

Net Present Worth for Two Mutually Exclusive Projects

	Direct Surface Analysis Techniques	Solvent Extraction/ Analysis Techniques
First Cost:	$328K	$174K
Life:	10 yr	10 yr
Salvage value	25K	10K
Annual operating disbursements	29K	22K
Minimum return in investment = 14%		
First Cost:	$328K	$174K
First replacement		
= (328-25) (P/F, 14%, 10):	82K	
= (174-10) (P/F, 14%, 10):		45K
Operating disbursements		
= 29 (P/A, 14%, 10):	152K	
= 22 (P/A, 14%, 10):		115K
Less salvage value @ 10		
= 25 (P/F, 14%, 10):	-7K	
= 10 (P/F, 14% 10):		-3K
Net present worth cost	$555K	$331K

The cost analysis of the two competing projects leads us to choose alternative 4, solvent extraction/analysis techniques (ICP-ES and IC).

2.6 THE BENEFITS

The benefits for selecting the solvent extraction/analysis techniques are widespread for PW manufacturing.

The most desirable method to pursue detecting contaminants on the surface of PW is seen from the above discussion to be solvent extraction/analysis techniques. It is suggested that such a system be put together where the analytical instrumentation is directly combined with a minicomputer. This system will be called a contaminant profiling (C/P) system. It will provide a higher degree of confidence in PW cleaning and manufacturing processes.

On-line monitoring of the types and levels of various contaminants, especially the ionic contaminants, by means of a contaminant profiling system under the direct control of a minicomputer will result in the rapid detection of processes, manufacturing and/or cleaning, out of control. It will also lead to improved field performance and higher PW reliability. Such a system can be designed to function with a GO/NO GO test procedure affording early detection of a failure situation. Thus, the manufacturing process in question can be halted before a great number of faulty PW are produced.

Such a system will give a high degree of statistical confidence to the manufacturing and cleaning processes used. The sensitivity of the contaminant profiling system based on solvent extraction/analysis instrumentation will be such that detection of submicrogram ($<10^{-6}$g) quantities of various contaminant species in an extract solution will be feasible. This resolving power far exceeds that obtainable by present methods. Such an integrated system is not only applicable now, but will be even more pertinent in the future when conductor line widths/spacings are expected to be $\leq$0.002 in.

The use of a minicomputer to integrate the system will result in automatic calibration, system process control, fault diagnosis, and analysis and computation of the resulting data. Thus, the contaminant profiling (CP) system will fit easily within an on-line PW manufacturing production line where it will provide efficient monitoring of the production and cleanliness processes. The establishment of this system will substantially reduce failures of PWAs due to contaminants remaining on their surfaces.

2.7 THE CRITERION

The cost/benefits analysis for the two competing projects was made.

In the case of ascertaining the production cleanliness of PW, it is clear that Alternative 4 (solvent/extraction/analysis techniques) dominates the others at all levels of investment and effectiveness. Based on this outcome of benefits and effectiveness versus costs, Alternative 4 is the preferred method for realizing the objective.

2.8 THE SOLUTION

Build a contaminant profiling (C/P) system to detect and quantify contaminants on the surface of PW.

Design, assemble, and integrate a system having the capability of yielding a detailed profile of all ionic contaminant species. Very little fabrication of parts is expected since all parts, or components, needed for the system already exist as separate entities with the exception of the extraction tank/pumping component. The contaminant profiling (C/P) system will consist of:

1. Inductively-coupled plasma spectrophotometer/graphite furnace
2. Ion chromatograph
3. Minicomputer and computing integrator unit
4. Extraction tank/pumping unit
5. Water purification unit.

The inductively-coupled plasma (ICP)/graphite furnace unit will be used to detect and quantify the levels of metallic and quasi-metallic elements, such as copper, tin, lead, chromium, phosphorus, silicon, etc., which are routinely expected to be found in extracts made from production PW. The ion chromatograph will be employed to detect and quantify anionic species such as chloride, fluoride, sulfate, and small organic acid anions appearing in many fluxes, both rosin-based and water-based. The extraction tank/pumping unit will be used to contain the PW during the extraction phase of the test cycle. The water purification unit will ensure the highest purity water for preparing the PW extracts. The computing integrator unit will be employed in conjunction with the ion chromatograph. It will automatically compute and integrate the areas under the curve which is the case for chromatographic data. Finally, the minicomputer will be used for C/P system control, data handling and analysis, and total system integration. Data and programs can be displayed on the CRT. Data handling and analysis will include statistical treatment of all data generated to ensure the secure foundation of a data base for PW production cleanliness criteria. A schematic of the C/P system is presented in Figure 15.

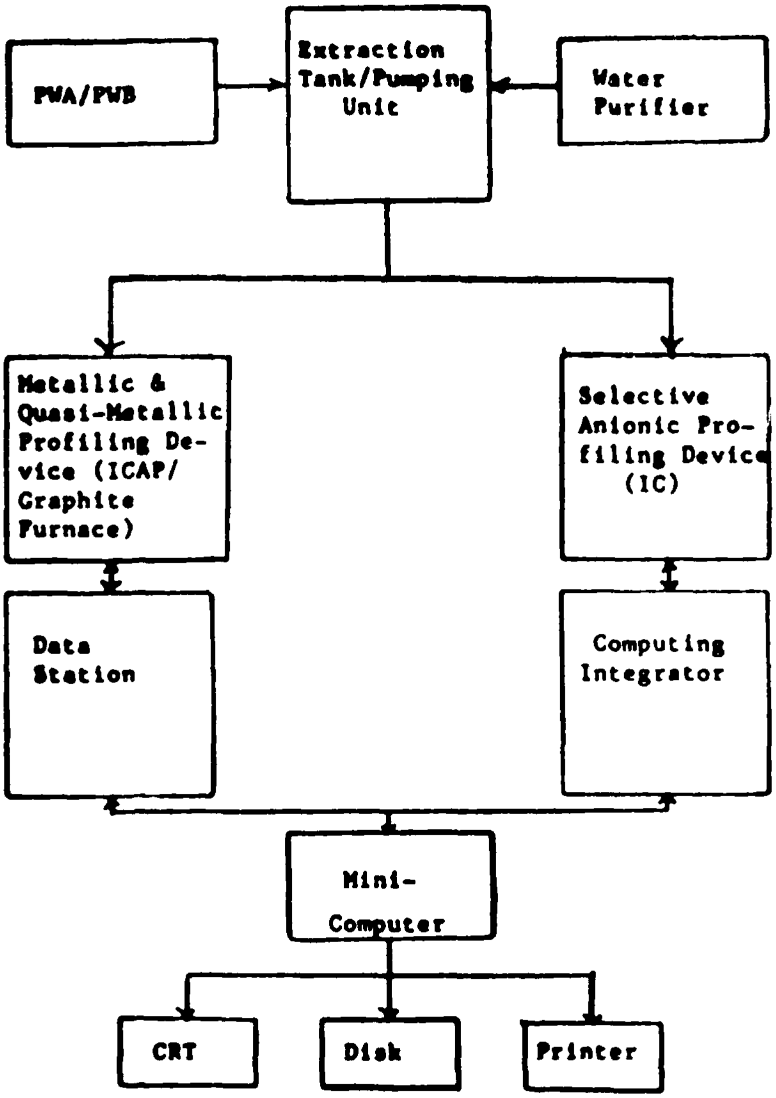


FIGURE 15. Schematic Diagram of The Mini Computer-Controlled Contaminant Profiling System

This concludes the systems analysis approach to determining the production cleanliness of PW. One can see during the discussion how the five phases of the systems approach were interweaved in the process of selecting the most appropriate alternative to build a C/P system. These five phases were:

<u>1</u> Formulation

<u>2</u> Search

<u>3</u> Evaluation

<u>4</u> Interpretation

<u>5</u> Verification.

NOTES

1. See E.S. Quade and W.I. Boucher, Systems Analysis and Policy Planning (New York: Elsevier, 1968), pp. 12-13.

2. Each individual set consisted of 18 test PWBs whose size was 2.375" x 4.0".

3. All of the test PWBs (except those in Set #11) in the cleaned sets (odd numbered) were cleaned following this procedure:

   1 2 minutes over boil sump

   2 2 minutes spray rinse - each side of the board sprayed 1 minute

   3 Each test individually rinsed 1 minute on each side with demineralized water.

   In steps 1 and 2, the degreaser contained stabilized 1,1,1-trichloroethane.

   The test PWAs in set #11, however, were batch cleaned following this procedure:

   1 2 minutes complete immersion in stabilized 1,1,1-trichloroethane

   2 2 minutes over boil sump (raised every 30 seconds to cool then lowered over boil sump again)

   3 2 minutes immersion in rinse sump

   4 2 minutes spray rinsed with solvent - each side of the assembly sprayed 1 minute

   5 Each test PWA individually rinsed 1 minute on each side with demineralized water.

   In steps 2-4, the degreaser contained stabilized 1,1,2-trichloro-2,2,1-trifluoroethane.

4. All panels used in the experiments were initially cleaned before any fabricated steps following this procedure:

   1 2 minutes over boil sump

   2 2 minutes spray rinse - each side of the panel sprayed 1 minute.

   The degreaser contained stabilized 1,1,1-trichloroethane. However, only the test PWBs in the odd numbered sits were cleaned after reaching the end of the appropriate manufacturing stage (six stages). See note 3 for the cleaning procedure used.

5. Transmission Electron Microscopy (TEM) was also employed; however, except for revealing not especially noteworthy differences in morphological characteristics among samples, the TEM is not a useful technique for profiling contaminants on PW. Hence, no discussion of the TEM or the results obtained therewith are included in this report.

6. Model JSM-U3 scanning electron microscope (marketed by JEOL, USA, Inc. of Peabody, MA). EDX spectra were obtained from areas of interest using a Si(Li) detector (manufactured by Princeton Gamma Tech, Inc. of Princeton, NJ) coupled to a Proxan III energy analysis system (marketed by Elscint, Inc. of Hackensack, NJ).

7. Model 549 ESCA/AES/SAM surface analysis (manufactured by Perkin-Elmer, Physcial Electronics Division of Eden Prairie, MN).

8. Same as Note. 7.

9. An Ionograph (Alpha Metals) was also used to test the PW for the Extract Resistivity Test (ERT). The ERT is based on measuring the specific resistivity, ρ, or its reciprocal κ (the specific conductance), of an isopropyl alcohol/water extract solution of PW. Two ERT devices widely used throughout the PW industry are the Omega-Meter and the Ionograph. The Ionograph is calibrated to read directly in micrograms of sodium chloride (ug NaC) or equivalent. Dividing the reading by the PW surface area in cm^2 yields the amount of μg NaCl or equivalent/cm^2. These are the results found using the Ionograph. All data are given in μg/cm^2 (the figures give here are based on taking the arithmetic means of the readings).

Results from IONOGRAPH in μg/cm^2

	Cleaned	Not Cleaned
	Set #1	Set #2
Stage 1	0.02	0.07
	Set #3	Set #4
Stage 2	0.01	1.13
	Set #5	Set #6
Stage 3	0.06	1.06
	Set #7	Set #8
Stage 4	0.07	0.29
	Set #9	Set #10
Stage 5	1.19	1.30
	Set #11	Set #12
Stage 6	2.72	25.1

However, the ERT merely indicates the presence of ions and affords only a rough order of magnitude of the ionic concentration. It does not give any indication whatsoever of the specific ionic species causing the PW degradation. Since ERT is nonspecific regarding the

```
   530 WRCUR(256*LINE+47):
           INPUT"",P(N)
   540 IF P(N)<1 OR P(N)>6 OR P(N)<>INT(P(N)) THEN WRCUR(5642):
           PRINT"ILLEGAL PROGRAM NUMBER":
           WRCUR(256*LINE+47):
           PRINT"      ":
           GOTO530
   550 WRCUR(5642):
           PRINT
   560 NEXT N
570 WRCUR(5642):
       INPUT "PRESS HOLD - PRINT ON 5000. PRESS RETURN TO CONTINUE
         ",O$:
       WRCUR(5642):
       PRINT
580 WRCUR(5642):
       PRINT"READING ELEMENT FILES"
590 FOR N=1TOI
   600 F$="MFD1:"+ELE$(N)+".GR"
   610 ON ERROR GOTO 830
   620 OPEN "I",#2,F$
   630 LINPUT #2,P$(N)
   640 PRINT #6:
           PRINT #6,"PROGRAM #";P(N),"ELEMENT FILE NAME:
            ";ELE$(N):
           PRINT#6,P$(N)
   650 CLOSE #2
   660 NEXT N
670 PRINT#4,"A":
       INPUT#5,CHK$
680 FOR N=1TO I
   690 LET A$="P"+RIGHT$(STR$(P(N)),1)
   700 PRINT#4,A$
   710 INPUT#5,CHK$
   720 PRINT#4,P$(N)
   730 INPUT#5,CHK$
   740 NEXT N
750 PRINT#6
760 PRINT#6,"THE FOLLOWING PROGRAMS HAVE BEEN LOADED INTO THE 5000: ";
       PRINT#6
770 PRINT#6,TAB(25);"ELEMENT","PROGRAM":
       PRINT#6
780 FOR N=1TOI
   790 PRINT#6,TAB(25);ELE$(N);TAB(50);P(N)
   800 NEXT N
810 PRINT#6
820 CLOSE:
       GOTO20
830 P$(N)="0000100000100000100005110001100000100005105000500100000700038000
       1100010001040000000027"
840 PRINT#6:
       PRINT#6,ELE$(N);"  NOT IN LIBRARY.  PROGRAM LOCATION ";P(N);
       "WILL CONTAIN 5000 DEFAULT VALUES."
850 ELE$(N)="DEFAULT"
860 RESUME 650
870 RESUME 370
```

FIGURE 20C.

```
240 WRCUR(256*7+10):
        PRINT "PRESS HOLD - PRINT ON 5000."
250 WRCUR(256*8+10):
        PRINT "PRESS RETURN ON DATA STATION TO STORE IN LIBRARY."
260 INPUT "",W$
270 PRINT#4,"A":
        INPUT#5,CHK$
280 PRINT#4,"D1"
290 LINPUT #5,P$
300 ON ERROR GOTO 870:
        F$="MFD1:"+ELE$+".GR":
        OPEN"I",#2,F$:
        CLOSE #2
310 WRCUR(5642):
        PRINT ELE$;:
        INPUT"  ALREADY EXISTS IN LIBRARY. OVERWRITE (Y/N) ",O$
320 IF O$="Y" GOTO 370
330 IF O$<>"N" GOTO 310
340 WRCUR(5642):
        INPUT "NEW ELEMENT FILE NAME (PRESS RETURN TO EXIT).......",ELE$
350 IF ELE$="" GOTO 90
360 WRCUR(1034):
        PRINT ELE$:
        WRCUR(5642):
        PRINT
370 OPEN "O",#2,F$
380 PRINT#2,P$
390 CLOSE #2
400 PRINT #6:
        PRINT #6,ELE$
410 PRINT #6:
        PRINT #6,P$
420 CLOSE:
        GOTO 20
430 PRINT C$:
         WRCUR(529):
        PRINT#3,INIT$
440 WRCUR(256*7+17):
        INPUT "NUMBER OF ELEMENTS (6 MAX.)...",I
450 IF I<1 OR I>6 OR I<>INT(I)THEN WRCUR(1809):
               PRINT:
               GOTO440
460 PRINTC$:
        WRCUR(529):
        PRINT#3,INIT$
470 WRCUR(256*5+23):
        PRINT "ELEMENT           PROGRAM # (1-6)"
480 WRCUR(256*6+23):
        PRINT "-------           -------------- "
490 FOR N=1TOI
   500 LINE=6+N
   510 WRCUR(256*LINE+24):
          INPUT"",ELE$(N):
          IF LEN(ELE$(N))>5 OR LEN(ELE$(N))=0 THEN WRCUR(5642):
               PRINT"ILLEGAL ELEMENT FILE NAME":
               WRCUR(256*LINE+24):
               PRINT"      ":
               GOTO510
   520 WRCUR(5642):
               PRINT
```

FIGURE 20B.

```
 DATE   80/11/14            <<<<<<<<<<MFD1:GFLOD.BA>>>>>>>>>> TIME 10:04

1  REM    ***   ICP/5000 LOADING ROUTINE    ***
2  REM    THIS PROGRAM IS A COMMUNICATIONS ROUTINE THAT PERMITS:
3  REM            1)CREATION AND STORAGE OF ELEMENT PARAMETER FILES
4  REM            2)LOADING THOSE FILES ONTO THE MODEL 5000 6 AT A TIME
5  REM
6  REM    FILES ARE CREATED BY ENTERING PARAMETERS INTO THE MODEL 5000
7  REM    AND STORING IN PROGRAM LOCATION 1.  THE DATA STATION READS
8  REM    THE FILE ONTO THE LIBRARY DISK IN DRIVE #1.
9  REM
10 REM    IN THE LOADING OPTION, UP TO 6 ELEMENT FILES MAY BE READ FROM
11 REM    THE LIBRARY DISK AND LOADED INTO PROGRAM LOCATIONS 1-6.
12 REM
13 REM
14 REM
20 CLEAR 900
30 DEFINT I
40 OPEN "O",#4,"COMW:"
50 OPEN "I",#5,"COMR:"
60 OPEN "O",#6,"AUXW:"
70 OPEN "O",#3,"SCRN:"
80 C$=CHR$(27)+CHR$(75)
90 PRINT C$
100  WRCUR(529):
        INIT$=CHR$(136)+"ICP 5000 PARAMETER COMMUNICATION ROUTINE"+CHR$( ..
        ):
        PRINT#3,INIT$
110  WRCUR(256*7+20):
        PRINT "ENTER:
           L = LOAD 5000"
120  WRCUR(256*8+29):
        PRINT "F = FILE CREATE"
130  WRCUR(256*9+29):
        INPUT "E = EXIT          ",O$
140  IF O$="F" GOTO 180
150  IF O$="L" GOTO 430
160  IF O$="E" THEN PRINT C$:
              CLOSE:
              SYSTEM
170  GOTO 110
180  PRINTC$:
        WRCUR(529):
        PRINT#3,INIT$:
        WRCUR(256*7+17):
        INPUT "ELEMENT FILE NAME (5 CHARS. MAX.)...",ELE$
190  IF LEN(ELE$)>5 THEN WRCUR(5642):
              PRINT"ILLEGAL FILE NAME":
              FOR I=1TO2000:
                     I=I:
                     NEXT I:
              GOTO180
200  IF ELE$=""THEN 180
210  WRCUR(256*7):
        PRINT
220  WRCUR(256*4+10):
        PRINT ELE$
230  WRCUR(256*6+10):
        PRINT "LOAD PARAMETERS INTO 5000. STORE IN PROGRAM LOCATION #1.
```

FIGURE 20A. Program for Loading Various Atomic Absorption Operating Parameters in BASIC

```
  DATE   80/11/14            <<<<<<<<<<MFD1:CR.BA   >>>>>>>>>> TIME 10:07

10 C$=CHR$( 27 )+CHR$( 75 )
20 PRINT C$
30 WRCUR( 256*1 )
40 PRINT"   Communication Routine"
50 PRINT
60 PRINT"   Data Station - Model 5000"
70 PRINT
80 PRINT"   Enter character string to be sent to Model 5000"
90 PRINT"   after prompt."
100 PRINT
110 PRINT"   Model 5000's reply will be printed."
120 OPEN "O",#4,"COMW:"
130 OPEN "I",#5,"COMR:"
140 CLEAR 200
150 WRCUR( 256*12 ):
          PRINT:
          WRCUR( 256*12 )
160 INPUT "STRING....",A$
170 PRINT #4,A$:
          INPUT #5, CHK$
180 WRCUR( 256*14 ):
          PRINT:
          PRINT:
          WRCUR( 256*14 )
190 PRINT CHK$
200 OPEN "O",#1,"AUXW:":
          PRINT#1:PRINT#1,A$:
          PRINT#1,CHK$:
          PRINT #1:CLOSE#1
210 GOTO140
```

FIGURE 19. Program for Establishing Two-Way Communication between 5000 and Data System in BASIC

```
760 FOR I=1TON
      770 CALL HSYMB(@E,@H(I),@V(I),@SYM$)
      780 NEXT I
790 V1=(125*M+B):
          V2=(625*M+B)
800 H1=(25-B)/M:
          H2=(200-B)/M
810 IF V1>=0 GOTO 850
820 IF V2<=200 GOTO 840
830 CALL LINE(@E,@H1,25,@H2,200,1):
          GOTO 880
840 CALL LINE(@E,@H1,25,625,@V2,1):
          GOTO 880
850 IF V2<=200 GOTO 870
860 CALL LINE(@E,125,@V1,@H2,200,1):
          GOTO880
870 CALL LINE(@E,125,@V1,625,@V2,1)
880 WRCUR 256*20+25:
          PRINT USING "CORRELATION COEFFICIENT = #.####";RHO
890 GOTO590
900 WRCUR 256*20+14:
          PRINT CHR$(136);"MAXIMUM ENTRY = NINE POINTS";CHR$(128):
          GOTO590
910 CALL GRINIT(@E):
          CLOSE:
          PRINT C$:
          WRCUR 256*1
920 SYSTEM
```

FIGURE 18C.

```
                        NEXT I
310 Y=Y(1)
320 FOR I=2 TO N:
                    IF Y<Y(I) THEN Y=Y(I):
                        NEXT I
330 FOR I=1 TO N:
                X(I)=X(I)/X*500+125:
                Y(I)=Y(I)/Y*175+25:
                H(I)=X(I)+44:
                V(I)=Y(I)+24:
                NEXT I
340 FOR I=1 TO 5:
                S(I)=0.0:
                NEXT I
350 FOR I=1TON
      360 S(1)=S(1)+X(I)
      370 S(2)=S(2)+Y(I)
      380 S(3)=S(3)+X(I)*Y(I)
      390 S(4)=S(4)+X(I)*X(I)
      400 S(5)=S(5)+Y(I)*Y(I):
                NEXT I
410 THETA=N*S(3)-S(1)*S(2)
420 PHI=N*S(4)-S(1)*S(1)
430 CHI=N*S(5)-S(2)*S(2)
440 Q1=CHI/N
450 Q2=THETA↑2/(N*PHI)
460 Q3=N-2
470 M=THETA/PHI
480 B=(S(2)-M*S(1))/N
490 M2=(Q1-Q2)/Q3
500 SB=SQR(ABS(M2*N/PHI))
510 SA=SQR(ABS(V2*S(4)/PHI))
520 RHO=THETA/SQR(PHI*CHI)
530 REM INTERCEPT =B +/- SA
540 REM SLOPE     =M +/- SB
550 REM CORREL. COEFF.=RHO
560 GOTO650
570 WRCUR 256*20+14:
          PRINTCHR$(136);"DATA INSUFFICIENT FOR LINEAR REGRESSION";CHR$(128)
580 RESUME 590
590 CLOSE
600 OPEN "O',#1,"CNSL:":
          PRINT#1,"STRIKE";CHR$(136);'RETURN";CHR$(128);"TO CONTINUE...'
610 WRCUR 256*24+36:
          INPUT"",X$
620 PRINT C$
630 PRINT #1,"LR
640 GOTO50
650 PRINT C$
660 WRCUR 256*23+10:
          PRINT CHR$(136);'GRAPHICS MODE";CHR$(128)
670 CALL LINE(@E,125,25,125,200)
680 CALL LINE(@E,121,200,125,200,1)
690 CALL LINE(@E,125,25,625,25)
700 CALL LINE(@E,625,22,625,25,1)
710 H$="CONCENTRATION"
720 CALL HSYMB(@E,380,25,@H$)
730 V$="ABSORBANCE"
740 CALL VSYMB(@E,125,100,@V$)
750 SYM$="*"
```

FIGURE 18B.

```
 DATE  80/11/14          <<<<<<<<<<MFD1:LR.BA   >>>>>>>>>> TIME 10:06

1    REM         *** GRAPHITE FURNACE STANDARDS SELECTION ROUTINE ***
2    REM
3    REM   THIS PROGRAM IS DESIGNED TO AID THE ANALYST IN THE SELECTION OF
4    REM   STANDARDS FOR THE HGA-500 GRAPHITE FURNACE.
5    REM
6    REM   ABSORBANCE VALUES FOR UP TO 9 STANDARDS MAY BE ENTERED.
            THE
7    REM   PROGRAM WILL PERFORM A LINEAR REGRESSION ANALYSIS
           OF THE ENTERED
8    REM   VALUES AND PLOT THE RESULTS ON THE SCREEN, USING THE GRAPHICS
9    REM   CAPABILITIES OF THE MODEL 3500 DATA STATION.  THE CORRELATION
10   REM   COEFFICIENT IS ALSO DISPLAYED.
11   REM
12   REM   PRINTER OUTPUT IS NOT AVAILABLE AT THIS TIME.
13   REM
14   REM
20 DEFINT H,V
30 LIBRARY "GRUTL.LB"
40 ON ERROR GOTO 570
50 C$=CHR$(27)+CHR$(75)
60 HOLD
70 F=0
80 CALL GRINIT(@E)
90 PRINT C$:
           WRCUR 256*2+20
100 PRINT "GRAPHITE FURNACE METHODS DEVELOPMENT"
110 WRCUR 256*4+21
120 PRINT "LINEAR REGRESSION GRAPHICS ROUTINE"
130 WRCUR 256*23+10:
          PRINT CHR$(136);"DATA ENTRY MODE";CHR$(128)
140 CLOSE:
          OPEN"O",#1,"CNSL:":
          PRINT#1,"ENTER";CHR$(136);"0";CHR$(128);"TO EXIT

150 WRCUR 256*8:
          INPUT"ENTER NUMBER OF STDS...(2-9)...",N
160 PRINT#1,"LR                                    ":
          CLOSE
170 IF N=0 THEN 910
180 IF N<2 THEN ERROR 10
190 IF N>9 GOTO 900
200 WRCUR 256*8
210 PRINT ,"STANDARD #","CONC. (PPB)","ABSORBANCE"
220 PRINT ,"----------","-----------","----------"
230 PRINT ,"  BLANK"
240 FOR I=1 TO N:
                PRINT,"    ";I:
                NEXT I
250 N=N+1
260 FOR I=1 TO N:
                WRCUR 256*(I+9)+31:INPUT"",X(I)
    270 WRCUR 256*(I+9)+45:
                INPUT "",Y(I)
    280 NEXT I
290 X=X(1)
300 FOR I=2 TO N:
                       IF X<X(I) THEN X=X(I):
```

FIGURE 18A. Linear Regression Analysis Program for Data from graphite Furnace in BASIC

4 RF Power Supply

5 Data System

6 HGA-500 Graphite Furnace

7 AS-40 Autosampler (for furnace)

8 PR-80 Printer.

The emission spectrophotometer, i.e., plasma torch, will be used to detect high to fairly high levels of the metallic and quasi-metallic elements ($\approx$0.5 ppm and greater), whereas the furnace will be employed only for levels lower than those detectable using the torch.

The other units making up the ICP 5000 are auxiliary units. The RF Power Supply is required to supply the energy needed to decompose Argon (Ar) gas into a plasma. The autosamplers are used to hold sample cups and to present the appropriate sample to be analyzed to the torch or to the furnace, as the case may be. Light emitted by the torch must pass into the 5000 Spectrophotometer via the Optical Interface for optical, hence elemental, analysis. Light absorbed in the Graphite Furnace must also be analyzed in the 5000 Spectrophotometer; however, the furnace is an integral part of the 5000 as constructed and requires no special Optical Interface. The Data System is a microcomputer having two I/O devices attached directly on it - a CRT and a keyboard. Accompanying this is a Printer which is software selectable to produce up to 132 characters per line of hardcopy.

Figures 18A, B, C display a program in the BASIC language for performing a linear regression analysis of data obtained from the Graphite Furnace. Using this program, it is possible to plot on the CRT standard concentrations versus absorbances and to visually display the linearity of the resulting graph. In this way discrepancies and deviations from linearity can easily be checked.

The operation of the 5000 is completely controlled by its built-in microprocessor, or it may be controlled by the external Data System through a two-way RS-232C interface. Figure 19 shows a BASIC program used to establish two-way communication between the 5000 and the Data System. In this way, the 5000 becomes controllable through the Data System.

Figures 20 A, B, C represent a BASIC program for loading various atomic absorption operating parameters, e.g., absorbance wavelength, slit width, lamp current, etc., for Graphite Furnace use into the 5000 from the Data System. Figures 21 A, B represent the hardcopy output of the various parameters for the different elements to be run in the furnace. Note that the long number strings are the particular way the 5000 stores its parameters.

4 Allowance of cause/effect correlation by determining the species source and species related latent failures

5 Allowance of the use of water-soluble fluxes since contaminant levels can be determined with confidence.

It is a truism that printed wiring assemblies (PWAs) are rapidly becoming more complex. Driven by tighter packaging requirements and the necessity for greater component densities, product lines for advanced missile systems will soon be almost exclusively PWAs having smaller line widths/line spacings and having ceramic chip carriers (C^3s) as components. See Figure 17 for an illustration of this trend in PW manufacturing. It is anticipated that the C/P system will greatly aid in testing for cleanliness for such complex PWAs.

3.1 THE INDUCTIVELY COUPLED PLASMA EMISSION/ATOMIC ABSORPTION SPECTROPHOTOMETER

One of the most important analytical instruments in the contaminant profiling system is the inductively coupled plasma emission/atomic absorption spectrophotometer.

In order to better place the following discussion in perspective, it is appropriate to describe in greater detail the PW contaminant profiling (C/P) system. Recall that this system consists of five major components:

1 Inductively-coupled plasma spectrophotometer/graphite furnance, ICP/GF

2 Ion chromatograph, IC

3 Minicomputer and computing integrator unit

4 Extraction tank/pumping unit

5 Water purification unit.

However, some of the above C/P system components can be considered a system in their own right, i.e., they can be further decomposed or broken down into subunits or subcomponents. The best case in point is the ICP/GF (Perkin-Elmer ICP 5000). The ICP 5000 can be considered a system in its own right composed of the following units:

1 Model 5000 Spectrophotometer

2 ICP Source (torch)

3 Optical Interface between 1 and 2

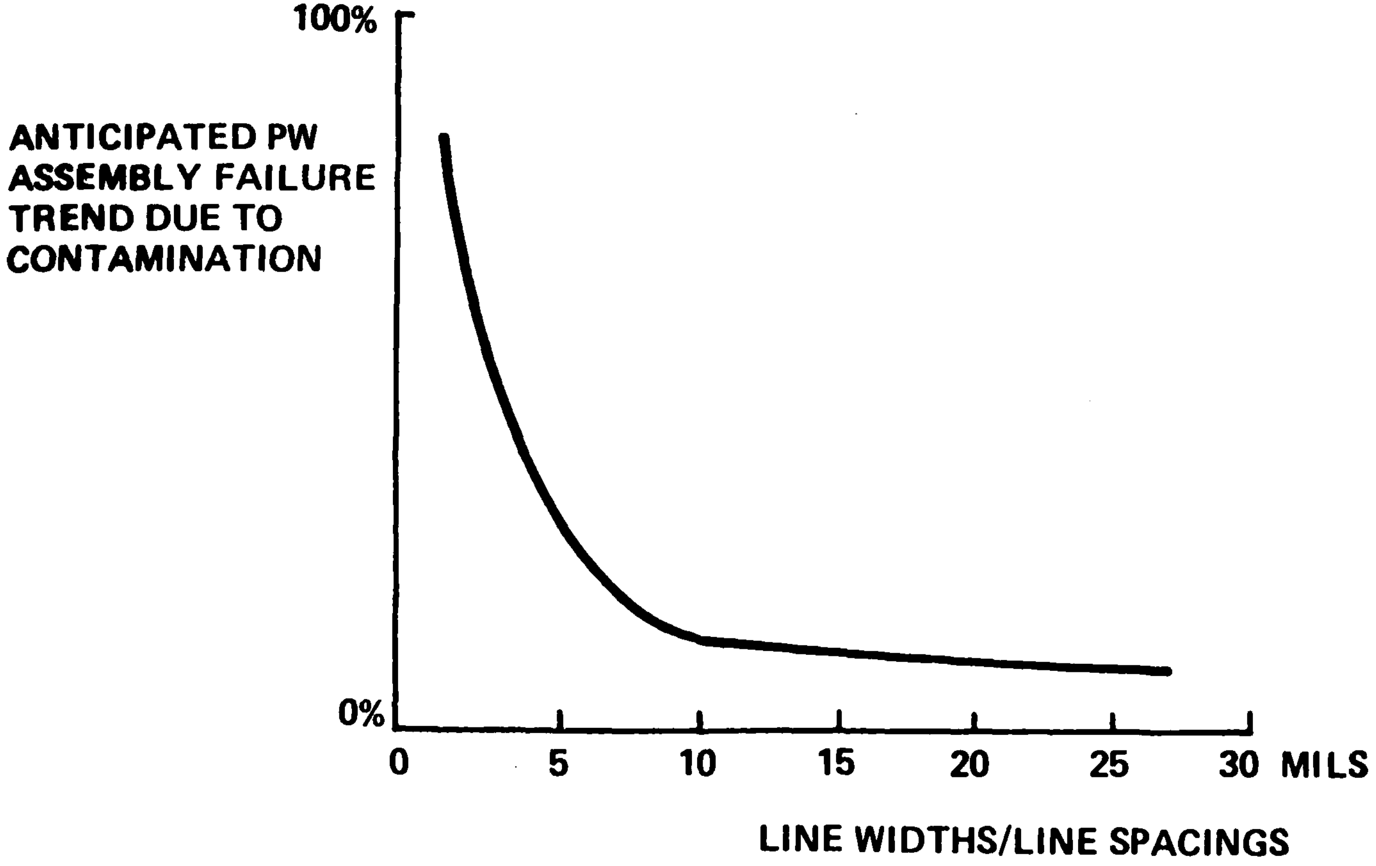


FIGURE 17. Implications of Advanced Packaging Trends

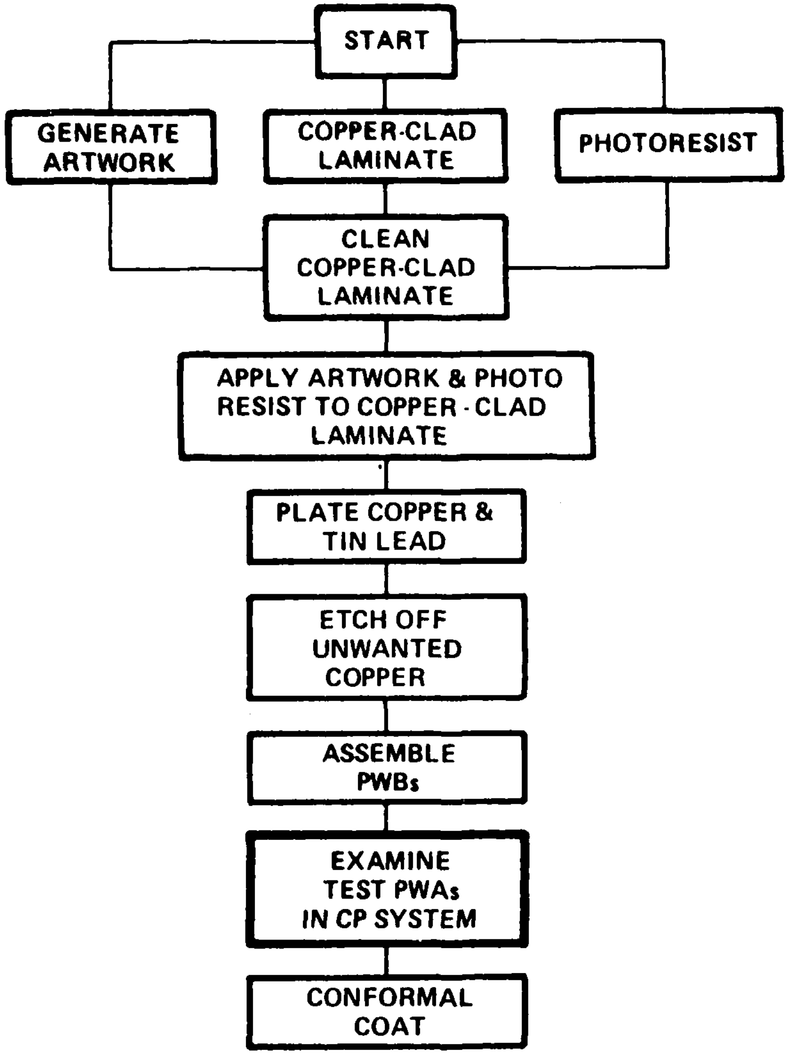


FIGURE 16. Position of Contaminant Profiling System in Double-Sided Printed Wiring Manufacturing Line

3.0 DEVELOPMENT OF THE CONTAMINANT PROFILING SYSTEM

Based on the results of systems analysis, a contaminant profiling (C/P) system for establishing printed wiring cleanliness criteria was designed and integrated.

To produce highly reliable PW requires a more rigorous method for detecting and quantifying contaminants on PW. This method will provide a much higher degree of confidence in PW cleaning and manufacturing processes. The method is called Contaminant Profiling.

Designate the act of detecting contaminant species and assaying their individual concentrations as Contaminant Profiling (C/P). One will be especially concerned with the detailed profiling of all ionic species, allowing a rapid determination to indicate if a particular process is in control or not. If it is not in control, C/P will indicate this and allow remedial steps to be taken without too great a loss in time. Hence, it will be cost-saving and economical in the long run. Further, C/P of special solvent extract solutions of PW entities to ascertain their cleanliness will provide information of the kind and concentration of all solvated ionic species at levels far below what can be achieved by extract resistivity or insulation resistance testing. Contaminant Profiling, then, will reveal whether the cleaning processes used on PW entities are truly performing as they ought. This technique will be an absolute must to ensure adequate cleanliness levels for PW assemblies having 0.002 inch conductor spacings or less.

The task objectives were:

1 Develop and build a contamination detection and measuring system for printed wiring (PW).

2 Increase PW reliability by in-line testing and monitoring of PW production cleanliness.

3 Implement the contamination detection and measuring system in a PW manufacturing environment.

Figure 16 shows an abbreviated typical manufacturing process for double-sided PW boards and the inclusion of the C/P system into the manufacturing line.

The advantages of the C/P systems are:

1 Identification of different contaminant species

2 Quantification of the contamination level of each species

3 In-line detection - modular and minicomputer controlled

15. By definition, 1 ppm = 1 milligram/liter = 1 microgram/milliliter, i.e., 1 ppm = 1 μg/ml. Also note that 1 ppm = 1000 ppb (parts-per billion).

16. According to a recent investigator, Dr. W. Bernard Wargotz, 1.0 μg/cm^2 represents the threshold concentration beyond which rapid and progressive deterioration of the PW electrical functions begins. See Wargotz, "Quantification of Contaminant Effects upon Electrical Behavior of Printed Wiring", IPC Technical Paper, Sept. (1977), 13. In his experiment, Wargotz used PW having conductor spacings of 0.009 inch. He used sodium chloride as the ionic material to produce the degradation. Sodium chloride, NaCl, however, is a readily soluble salt. Whether the 1.0 μg/cm^2 figure represents a threshold concentration for only slightly soluble ionic salts (such as many of those of copper, lead, and tin) remains to be determined. It may even be that 1.0 μg of NaCl or equivalent/cm^2 of PW surface is too high an acceptable limit for PW. It is easy to show that this amount of sodium chloride amounts to 7 to 10 monolayers of salt assuming completely even distribution over the surface area. As conductor spacings become narrower, we may want to limit the acceptable amount to less than this.

17. For some of the elements in PW extracts, an atomic absorption spectrophotometer (AAS) with an accompanying graphite furnace (GF) would be better because of improved detection limits.

18. When the CO_3^{2-}/HCO_3^- eluent is used, a negative "water dip" is observed on the chromatogram before the Cl^- peak.

19. Defined as twice the noise level.

20. See John R. Canada, Intermediate Economic Analysis for Management and Engineering (Englewood Cliffs, N.J.: Prentice Hall, Inc., 1971, Chap. 4, pp. 48-59.

ionic species, it cannot be classified as a detailed contaminant profiling test. See Table 7 for a comparison of these figures with those found using the ICP.

10. Model 965 Plasma Atom Comp emission spectrophotometer (marketed by Jarrell-Ash of Waltham, MA).

11. Models 12 and 14 AutoIon ion chromatographs (marketed by DIONEX Corporation of Sunnyvale, CA).

12. A dicussion with the laminate vendor revealed that the following elements may be observed from the materials used to make the glass fiber cloth within the epoxy: B (boron as B_2O_3, 5-10%, rarely observed), Ca (calcium as CaO, 16-25%), Al (aluminum as Al_2O_3, 2-16%), Si (silicon as SiO_2, 52-56%) Na and K (sodium and potassium as Na_2O and K_2O, 0-2%), Ti (titanium as TiO_2, 0-0.8%), Fe (iron as Fe_2O_3, 0.05-0.4%), P (phosphorus, 0-1%). Br (bromine) shows up in epoxy functioning as a fire retardant.

13. Elemental distribution maps can be obtained to show the distribution on the sample of an element of interest. The brightness of the recording CRT is modulated such that a series of dots apears on the photograph with their density related to the concentration of the element, i.e., more dots indicate more of the element. The elemental distribution shown on the photograph (dot map) can then be qualitatively related to the sample topography shown in a SEM secondary electron photograph taken of the same area. It shold be emphasized that only differences in dot density are significant since some dots will be produced by the white radiation background. For the crystalline-like material in question, elemental distribution maps were made for Pb, Sn, Cu and Br in this area since these were the major elements in that area. The distribution maps revealed that the crystalline material was not composed of any of these elements.

14. To show this statistically, the so-called F function must be calculated where:

$$F = \frac{\text{estimate of } \sigma^2 \text{ based on variation among } \overline{X}\text{s}}{\text{estimate of } \sigma^2 \text{ based on variation within samples}}$$

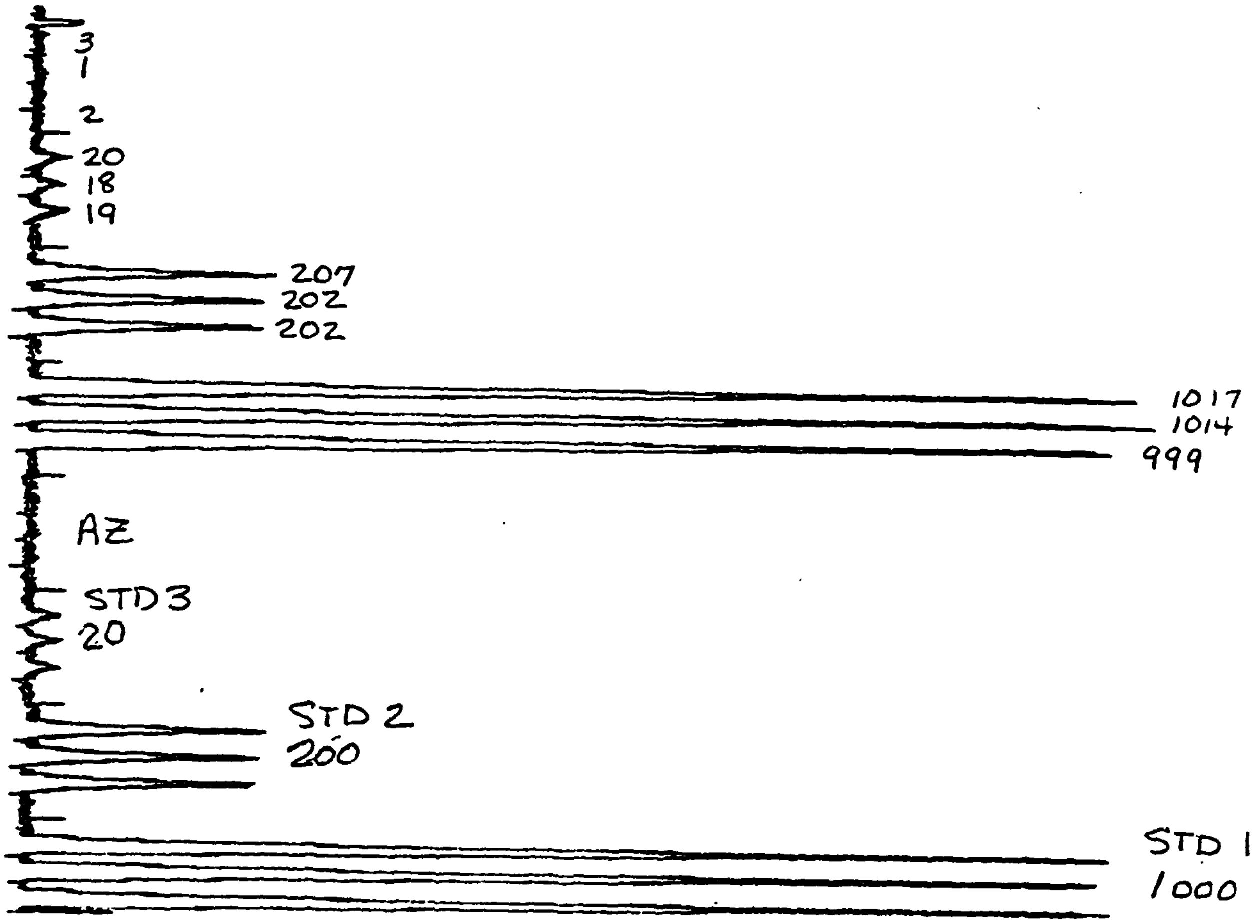
For the percent of C on the cleaned samples (sets #1, #3, #5, #7, #9, #11), it can be shown that estimate of σ^2 based on variation among $\overline{X}$s = 335.03 and estimate of σ^2 based on variation within samples = 135.68. There are six sets of size 6; therefore, the number of degrees of freedom of the numerator is 5 (6-1) and the number of degrees of freedom of the denominator is 30 (6x5). Now $F = 335.03/135.68 = 2.47 < 3.70$ where $F_{.01} = 3.70$.

```
PROGRAM # 1                   ELEMENT FILE NAME: AL001
000010000001000000100005100001100000100500120000000010000708030932222??0111009109130
000==

PROGRAM # 2                   ELEMENT FILE NAME: K001
000010000001000000100005100001100000100500120000000020000708076652122??0112009109130
000<4

PROGRAM # 3                   ELEMENT FILE NAME: P001
000010000001000000100005100001100000100500120000000030000208021362022??0113009309130
00095

PROGRAM # 4                   ELEMENT FILE NAME: PB001
000010000001000000100005100001100000100500120000000040000708021702222??0114009109130
00009

PROGRAM # 5                   ELEMENT FILE NAME: SN001
000010000001000000100005100001100000100500120000000050000708022462222??0115009109130
00030

PROGRAM # 6                   ELEMENT FILE NAME: ZN001
000010000001000000100005100001100000100500120000000060000708021372222??0116009109130
0003<

THE FOLLOWING PROGRAMS HAVE BEEN LOADED INTO THE 5000:

                         ELEMENT              PROGRAM

                         AL001                   1
                         K001                    2
                         P001                    3
                         PB001                   4
                         SN001                   5
                         ZN001                   6


PROGRAM # 1                   ELEMENT FILE NAME: CA001
000010000001000000100005100001100000100500120000000011000708042272222730121009[illegible]
000[illegible]

PROGRAM # 2                   ELEMENT FILE NAME: CR001
000010000001000000100005100001100000100500120000000022500708035792222550122009[illegible]
00065

PROGRAM # 3                   ELEMENT FILE NAME: CU001
000010000001000000100005100001100000100500120000000031500708032472222?0123009[illegible]
00087

PROGRAM # 4                   ELEMENT FILE NAME: FE001
000010000001000000100005100001100000100500120000000043000208024832222780125009[illegible]
00089

PROGRAM # 5                   ELEMENT FILE NAME: NA001
0000100000010000001000051000011000001005001200000000508004080589023222[illegible]
00[illegible]3

PROGRAM # 6                   ELEMENT FILE NAME: MG001
[illegible]0001000000100005101000130000100500120000000060000708028522022??01260093[illegible]
```

FIGURE 21A. Hardcopy Output of Parameters to Run Furnace

```
THE FOLLOWING PROGRAMS HAVE BEEN LOADED INTO THE 5000:

                              ELEMENT             PROGRAM

                              CA001                  1
                              CR001                  2
                              CU001                  3
                              FE001                  4
                              NA001                  5
                              MG001                  6


PROGRAM # 1                   ELEMENT FILE NAME: NI001
0000100000100000100005100001100000100500120000000125002080232022227001310091.=030
00077

PROGRAM # 2                   ELEMENT FILE NAME: AU001
00001000001000001000051000011000001005001200000002100070802428222281013200%: -030
000:0

PROGRAM # 3                   ELEMENT FILE NAME: SI001
0000100000100000100005100001100000100500120000000340002080251622227801330077. -030
000=8

PROGRAM # 4                   ELEMENT FILE NAME: PD001
000010000010000010000510000110000010050012000000043000208024762222300134007. =030
0007?

EMPTY  NOT IN LIBRARY.  PROGRAM LOCATION  5 WILL CONTAIN 5000 DEFAULT VALUES.

EMPTY  NOT IN LIBRARY.  PROGRAM LOCATION  6 WILL CONTAIN 5000 DEFAULT VALUES

THE FOLLOWING PROGRAMS HAVE BEEN LOADED INTO THE 5000:

                              ELEMENT             PROGRAM

                              NI001                  1
                              AU001                  2
                              SI001                  3
                              PD001                  4
                              DEFAULT                5
                              DEFAULT                6
```

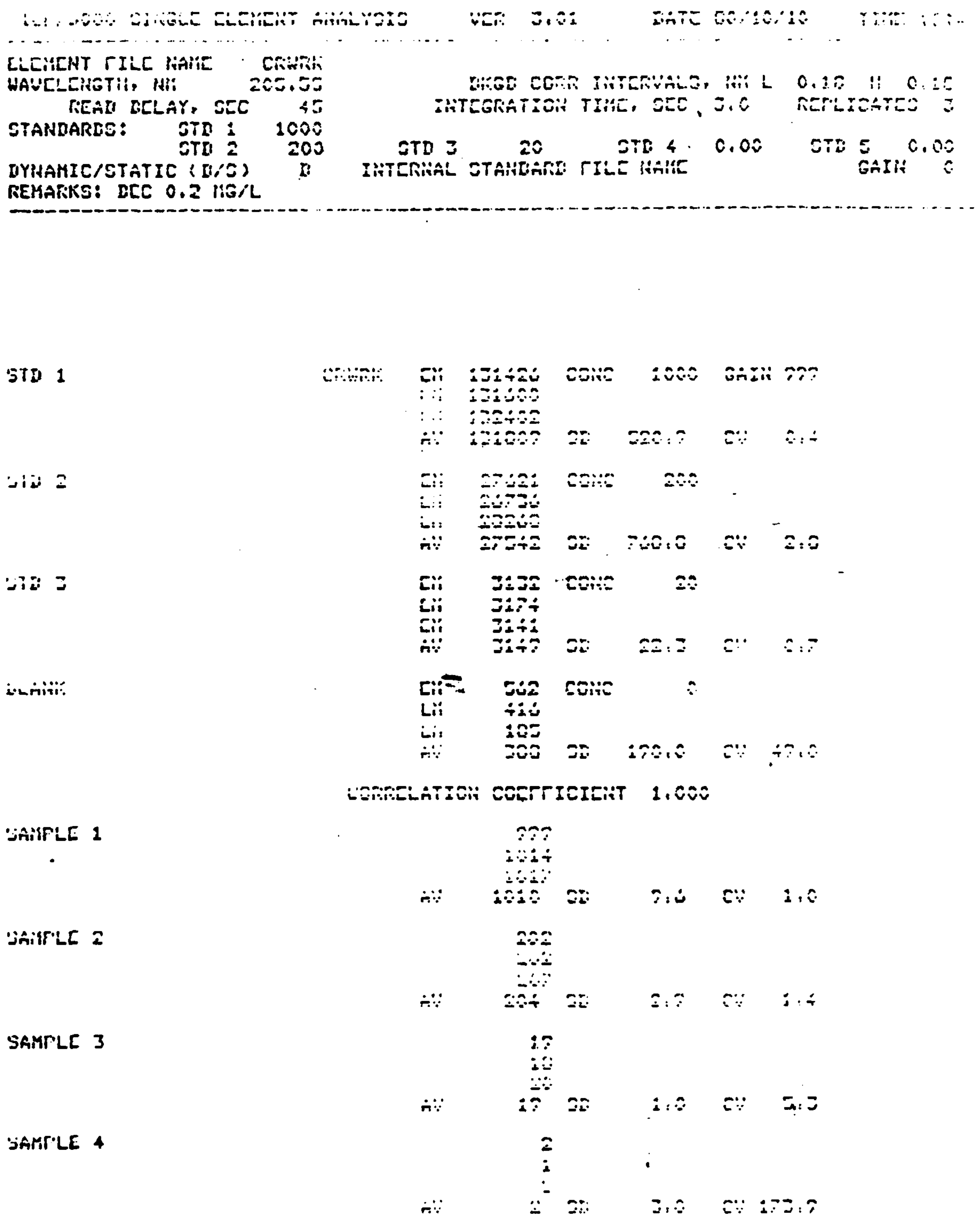
FIGURE 21B.



Cr Analysis

STD1 1000PPB-AZ, Read Same Order
" 2 200PPB
" 3 20PPB

FIGURE 22A. Torch Analysis of Chromium



```
ICP/6000 SINGLE ELEMENT ANALYSIS     VER  3.01      DATE 80/10/10     TIME [illegible]

ELEMENT FILE NAME     CRWRK
WAVELENGTH, NM       205.55          BKGD CORR INTERVALS, NM L  0.10  H  0.10
   READ DELAY, SEC     45          INTEGRATION TIME, SEC  3.0    REPLICATES  3
STANDARDS:     STD 1  1000
               STD 2   200     STD 3      20      STD 4   0.00    STD 5   0.00
DYNAMIC/STATIC (D/S)    D    INTERNAL STANDARD FILE NAME               GAIN   0
REMARKS: DEC 0.2 MG/L
--------------------------------------------------------------------------------




STD 1                        CRWRK   EM  131426  CONC    1000  GAIN 999
                                     EM  131600
                                     EM  132402
                                     AV  131809  SD     520.6   CV    0.4

STD 2                                EM   27621  CONC     200
                                     EM   26736
                                     EM   28268
                                     AV   27542  SD     760.0   CV    2.8

STD 3                                EM    3132  CONC      20
                                     EM    3174
                                     EM    3141
                                     AV    3149  SD      22.3   CV    0.7

BLANK                                EM     562  CONC       0
                                     EM     416
                                     EM     185
                                     AV     388  SD     190.0   CV   49.0

                              CORRELATION COEFFICIENT  1.000

SAMPLE 1                                    999
                                           1014
                                           1017
                                     AV    1010  SD       9.6   CV    1.0

SAMPLE 2                                    202
                                            202
                                            207
                                     AV     204  SD       2.9   CV    1.4

SAMPLE 3                                     17
                                             18
                                             16
                                     AV      17  SD       1.0   CV    5.9

SAMPLE 4                                      2
                                              1
                                              -
                                     AV       2  SD       3.0   CV 173.9
```

FIGURE 22B. Data System Printout of Figure 22A

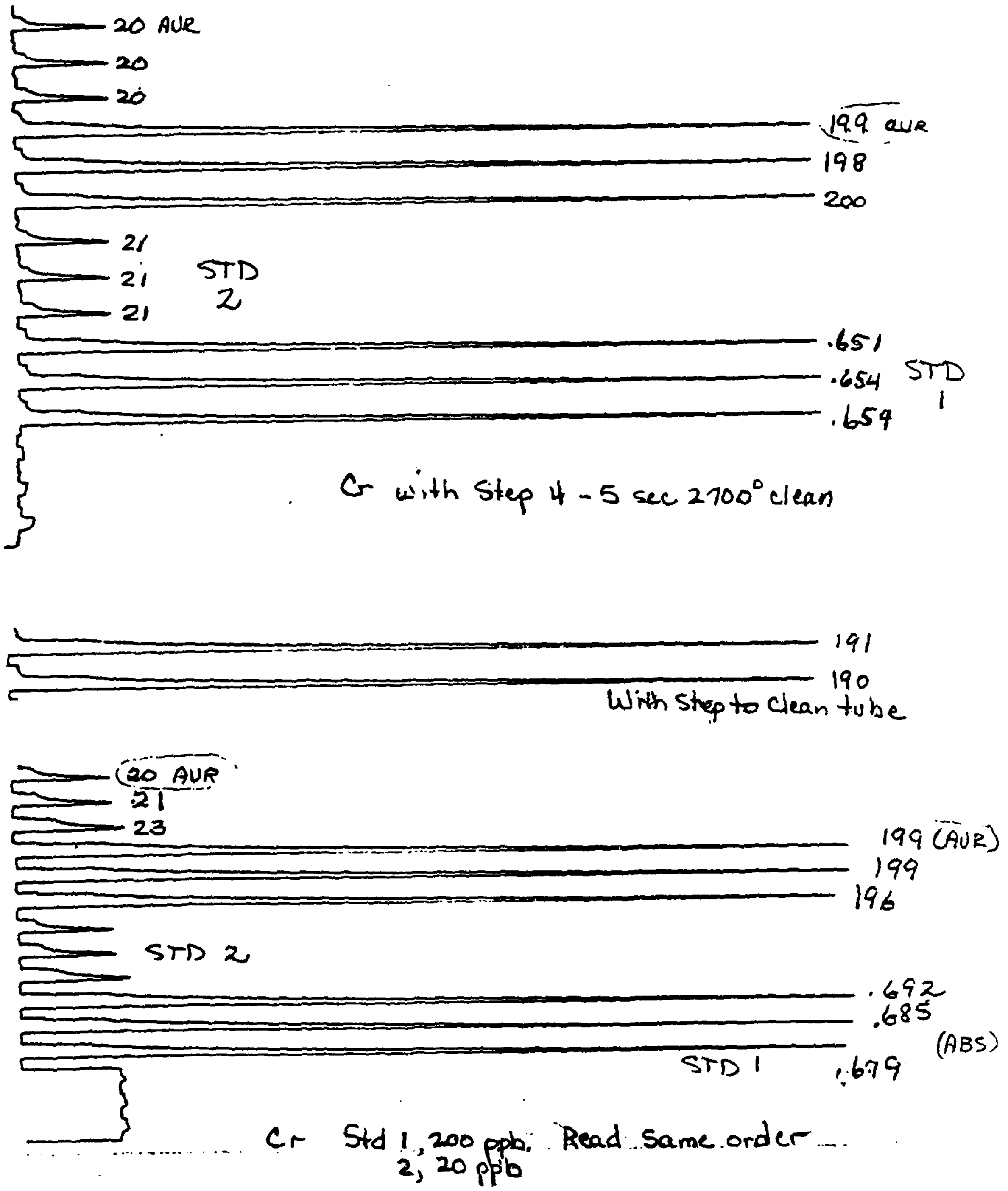
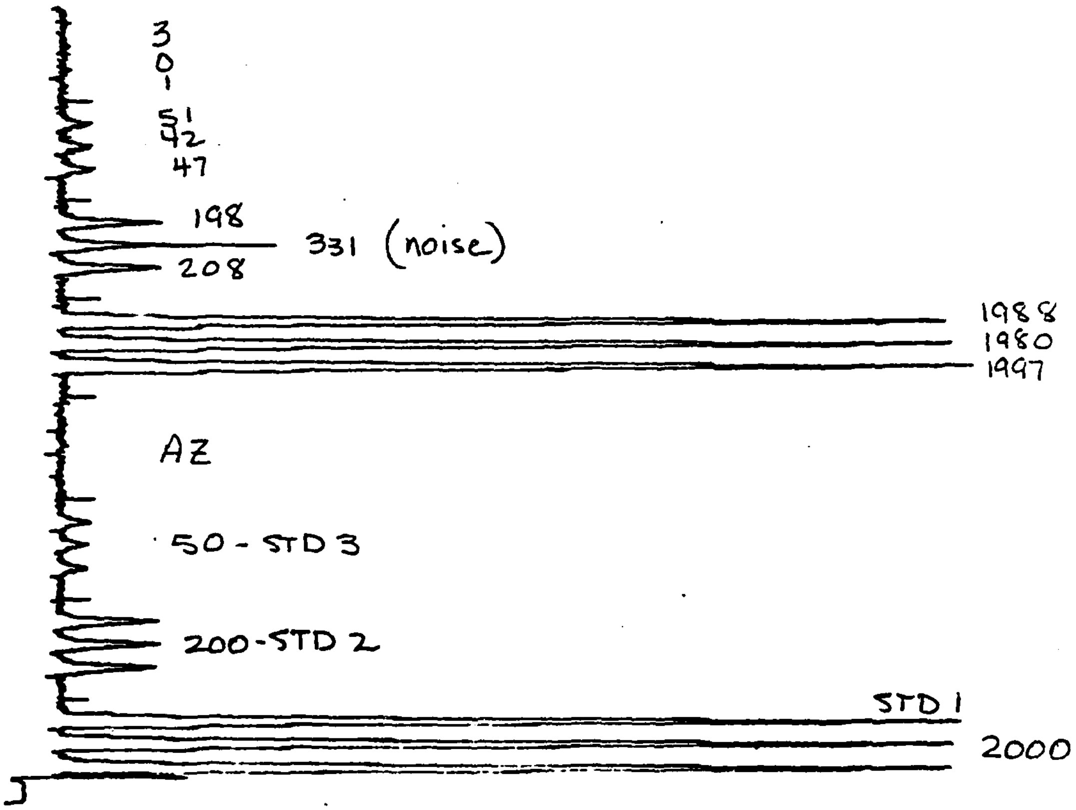


FIGURE 22C. Furnace Analysis of Chromium

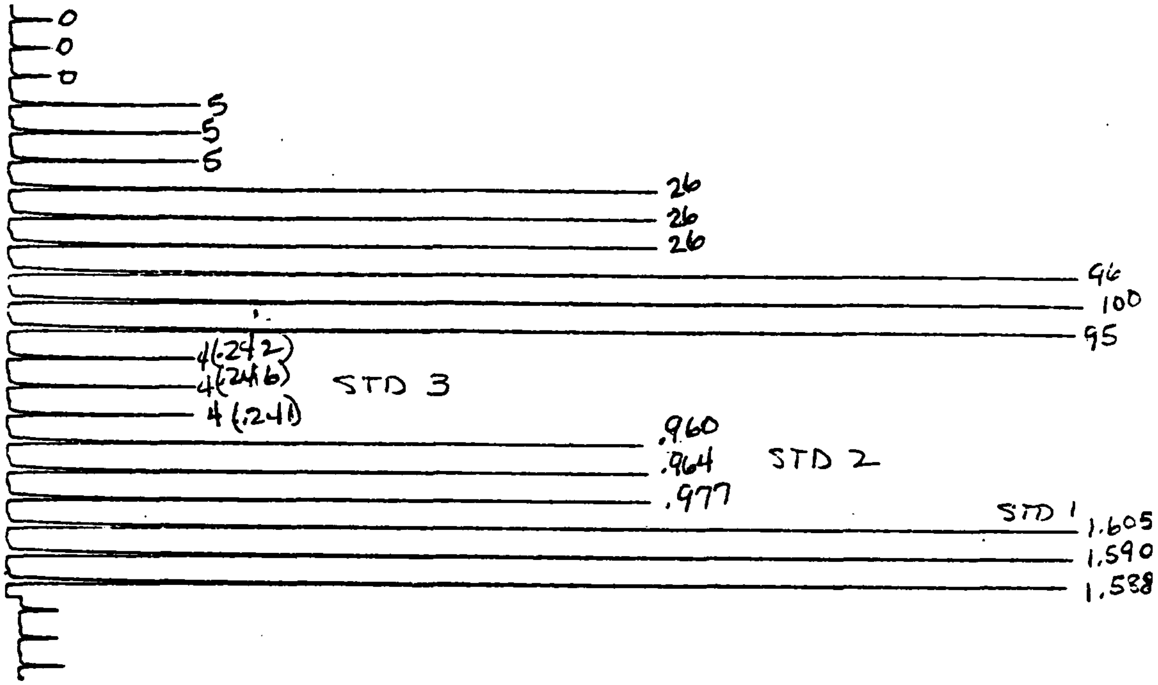


Cu Analysis Std 1 - 2000 ppb
2- 200 ppb
3 - 50 ppb

FIGURE 23A. Torch Analysis of Copper

```
STD 1                     CUWRK   CN  122140  CONC   2000  GAIN 921
                                  CN  123054
                                  CN  121776
                                  AV  122325  SD   660.1   CV    0.5

STD 2                             CN   12540  CONC    200
                                  CN   13272
                                  CN   13113
                                  AV   12978  SD   385.6   CV    2.7

STD 3                             CN    3446  CONC     50
                                  CN    3421
                                  CN    3432
                                  AV    3433  SD    12.5   CV    0.4

BLANK                             CN     151  CONC      0
                                  CN     525
                                  CN     545
                                  AV     407  SD   222.1   CV   54.6

                       CORRELATION COEFFICIENT  1.000

SAMPLE 1                                1707
                                        1706
                                        1700
                                  AV    1700  SD     6.6   CV    0.4

SAMPLE 2                                 238
                                         331
                                         170
                                  AV     246  SD    73.7   CV   30.1

SAMPLE 3                                  47
                                  [illegible]
                                  [illegible]
                                  AV      47  SD     4.3   CV    9.2

SAMPLE 4                                   1
                                  [illegible]

                                  AV       1  SD     1.6   CV 277.7

 ICP/5000 SINGLE ELEMENT ANALYSIS     VER  3.01      DATE 06/10/83    TIME 10:5
--------------------------------------------------------------------------------
ELEMENT FILE NAME     CUWRK
WAVELENGTH, NM       224.70          BKGD CORR INTERVALS, NM L  0.15  H  0.15
     READ DELAY, SEC     45        INTEGRATION TIME, SEC  3.0     REPLICATES  3
STANDARDS:     STD 1   2000
               STD 2    200      STD 3      50      STD 4   0.00     STD 5   0.00
DYNAMIC/STATIC (D/S)     D    INTERNAL STANDARD FILE NAME                GAIN    0
REMARKS: DCC 0.2 MG/L
--------------------------------------------------------------------------------
```

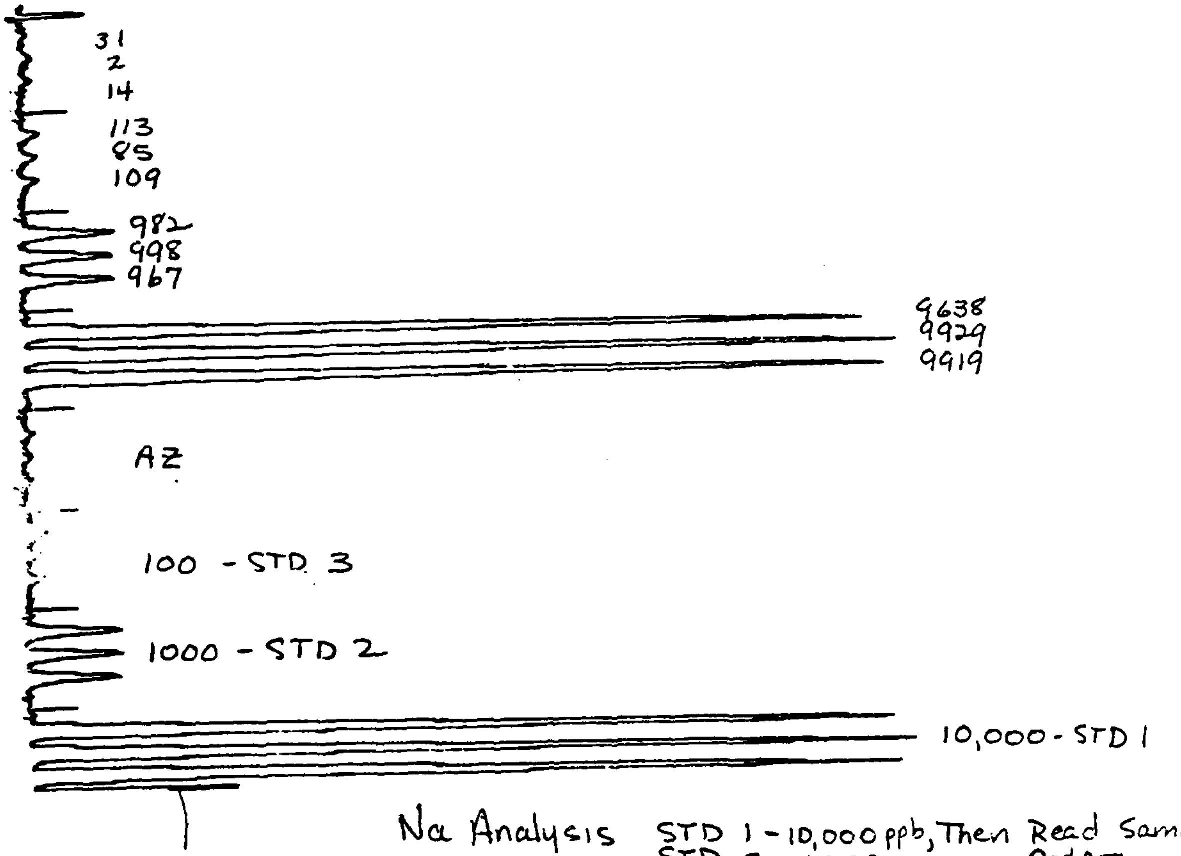
FIGURE 23B. Data System Printout of Figure 23A



Cu Analysis

Std 1 100 ppb Then read same order.
2 25
3 5

FIGURE 23C. Furnace Analysis of Copper



Na Analysis STD 1 - 10,000 ppb, Then Read Same Order
STD 2 - 1000
STD 3 - 100

FIGURE 24A. Torch Analysis of Sodium

UNCLASSIFIED

```
 [illegible] SINGLE ELEMENT ANALYSIS     VER  3.01       DATE [illegible]     TIME [illegible]

ELEMENT FILE NAME     NAWRK
WAVELENGTH, NM        589.59            BKGD CORR INTERVALS, NM L  0.25  H  0.15
     READ DELAY, SEC     45          INTEGRATION TIME, SEC  3.0    REPLICATES  3
STANDARDS:      STD 1  10000
                STD 2   1000      STD 3     100       STD 4   0.00    STD 5   0.00
DYNAMIC/STATIC (D/S)     D    INTERNAL STANDARD FILE NAME                GAIN   0
REMARKS: DEC 2 MG/L
--------------------------------------------------------------------------------



STD 1                          NAWRK   EM  116007  CONC  10000  GAIN 677
                                       EM  118303
                                       EM  116661
                                       AV  117204  SD  1125.7   CV   1.0

STD 2                                  EM   12633  CONC   1000
                                       EM   12527
                                       EM   12645
                                       AV   12602  SD    65.2   CV   0.5

STD 3                                  EM    2072  CONC    100
                                       EM    2082
                                       EM    2068
                                       AV    2074  SD     7.2   CV   0.3

BLANK                                  EM    1271  CONC      0
                                       EM     923
                                       EM    1282
                                       AV    1159  SD   204.0   CV  17.7

                                CORRELATION COEFFICIENT  1.000

SAMPLE 1                                     7717
                                             7729
                                             7636
                                       AV    7627  SD   105.2   CV   1.7

SAMPLE 2                                      767
                                              779
                                              762
                                       AV     769  SD    11.7   CV   1.2

SAMPLE 3                                      107
                                               85
                                              113
                                       AV     102  SD    15.1   CV  14.7

SAMPLE 4                                       14
                                               -2
                                               31
                                       AV      14  SD    16.3   CV 114.0
```

FIGURE 24B. Data System Printout of Figure 24A

The next set of figures (22 A-C, 23 A-C, 24 A-B) pertain also to the inductively-coupled spectrophotometer (plasma torch)/graphite furnace. Recall that this component of the C/P system is being used to detect and quantify levels of metallic and quasi-metallic elements. Based on the experiment performed on actual production PW, these will be the elements sought for using the ICAP torch/furnace:

aluminum, Al

calcium, Ca

carbon, C

chromium, Cr

copper, Cu

gold, Au (only if applicable)

iron, Fe

lead, Ph

magnesium, Mg

nickel, Ni (only if applicable)

palladium, Pd

phosphorus, P

potassium, K

silicon, Si

sodium, Na

tin, Sn

zinc, Zn

The emission spectrophotometer, i.e., the plasma torch, will be used to detect high to fairly high levels of the above elements ($\approx$0.5 ppm and greater) whereas the furnace will be employed only for levels lower than those detectable on the torch. Figures 22 A-C deal with the analysis of chromium, Cr, on both the torch and the furnace. Figure 22 A presents the torch analysis of chromium. Three standards were run to determine the low level limit of the torch. These standards were 1000 ppb, 200 ppb, and 20 ppb. Note the excellent reproducibility and the extremely stable and reproducible peaks in the lower range. From these data, the torch lower limit for Cr is estimated at <20 ppb. Figure 22 B is a Data System printout of A. Figure 22 C deals with the furnace analysis of Cr. Two standards were run to determine the acceptable point to cross over from torch analysis to furnace analysis. In the first run (bottom portion of figure), heavily tailing peaks in conjunction with peak height buildup on high level samples and falloff on low level samples indicate incomplete atomization. The addition of a 5 sec. 2700° cleaning step after atomization resulted in consistent peaks (top portion of graph). A cross-over from torch to furnance is suggested at 50 ppb, which should allow a single standard to be used on the furnace.

Figures 23 A-C deal with the analysis of copper, Cu, on both the torch and the furnace. Again, three standards were run to determine the low level limit of the torch. In this case these standards were 2000 ppb, 200 ppb, and 50 ppb. A preliminary run with a standard of 20 ppb indicates lack of reproducibility at that level. The noise peak in one of the 200 ppb standards (upper portion of figure) was caused by nebulizer drainage. Again, Figure 23 B is a Data System printout of 23 A. Three standards were run to determine the acceptable point to cross over from torch to furnace. The extreme sensitivity of the furnace to Cu suggests use of the lowest possible cross-over point and multiple standards since the linear range for furnace analysis 10 ppb. A cross-over from torch to furnace is indicated at 100 ppb with a minimum of three standards used during furnace analysis.

Figures 24 A-B deal with the analysis of sodium, Na, on the torch only. Three standards were used: 10,000 ppb (10 ppm), 1000 ppb, and 100 ppb. There is good freedom from noise down to 100 ppb. Figure 24 B is a Data System printout of 24 A.

The utilization of the ICP 5000 (plasma torch) requires the development of specific analytical techniques to assure the accuracy and reproducibility of the results. Plasma torch parameter optimization is one of the most important of these. Using manganese (Mn) as a calibration element, the Background Equivalent Concentration (BEC), measure of the signal to noise ratio (S/N ratio), was measured for a multi-dimensional variable matrix consisting of viewing height, power, nebulization pressure, and plasma argon flow. The combination of these variables giving the lowest BEC and hence, the best S/N ratio, is to be used in all further development.

For any given torch/load coil configuration, there is one set of operating parameters that gives the best S/N ratio for the system. S/N in a plasma system is measured as the BEC which is defined as the concentration of analyte species that gives an emission signal equal to the background emission at the wavelength of interest. It may be calculated from the emission signal at any concentration by the formula:

$$\frac{(\text{Background})(\text{Concentration})}{(\text{Analyte - Background})}$$

Where:

Background = background emission at λ

Concentration = [analyte species]

Analyte = emission for [analyte species] at λ

λ = wavelength of interest

1 ppm manganese is chosen as the analyte for convenience. Four parameters influence the BEC:

1 viewing height in the plasma

2 plasma power

3 nebulizer pressure

4 argon flow.

Preliminary development work suggests varying the parameters in the order given above.

Figures 25A 1-3 show the results of varying the viewing height while holding power at 1250 W, neb. pressure at 30 psi and argon flow at 15 liters/min. A viewing height of 13 mm gave the best (lowest) BEC and was chosen as the optimum viewing height on this basis. Figures 25 B 1-2 show the result of varying the power of the torch while holding the viewing height at 13 mm. 1000 W was chosen as optimum torch power. Figures 25 C 1-2 show the results of varying neb. pressure. View ht = 13 mm, power = 1000 W. 28 psi gave the lowest BEC. Figures 25D 1-2 show the result of varying argon flow. 17 liters/min was chosen as optimum. Figures 25 D 1 and 3 show a test run with the final parameters of:

View height = 13 mm

Power = 1000 W

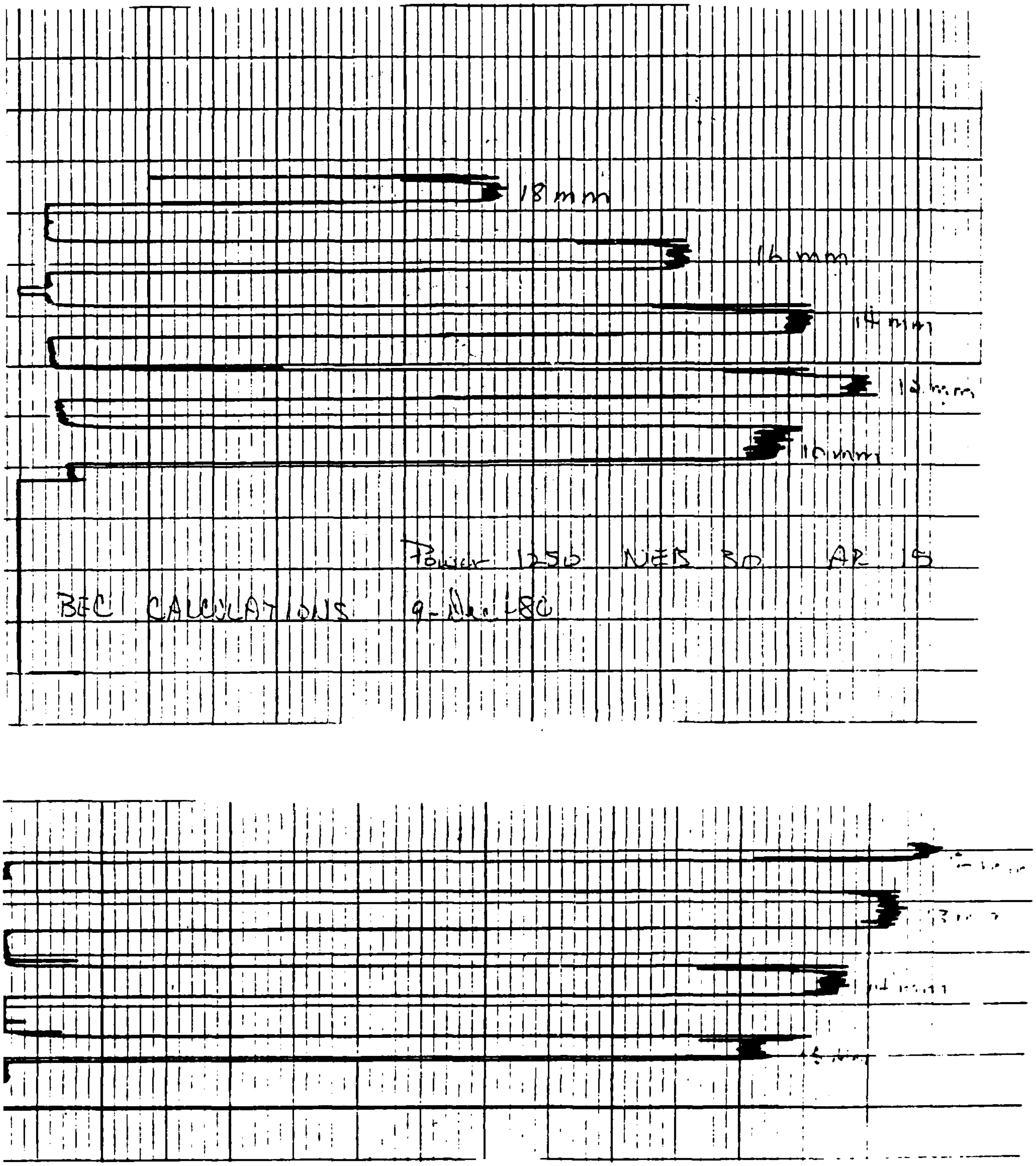
Neb pressure = 28 psi

Argon flow = 17 1/min.

Good torch stability and excellent BEC (.022 ppm avr) were obtained. The manufacturer's guaranteed BEC for Mn is .05 ppm. Optimization has resulted in a 2X increase in the sensitivity of the torch.

Standards were procurred from SPEX Industries that contain all 16 elements of interest (Al, Ca, Cr, Cu, Fe, Na, Pb, Mg, Zn, Ni, Pd, Sn, K, P, Si, Au) in a single matrix. This will permit the multi-element analysis to be run on the ICP-5000 using one standardization without the necessity of correcting for the comtamination resulting from compiling a mixed element matrix from single-element standards.

During the development of the ICP 5000 torch, it did not prove feasible to analyze 15 distinct elemental species by one software file. Accumulating evidence and a consultation with the vendor's leading appliations chemist indicated it would be more profitable in terms of error reduction to switch to three separate analyte files, each accommodating five (5) elemental species. After the decision had been made to switch to three separate files, an error analysis was conducted to determine realistic torch lower limits. To keep total analysis time at a minimum and to promote torch stability, the three 5 element files were grouped in order of increasing analyte wavelength. To generate the error analysis, concentration levels of 5,000; 1,000; 200, and 50 parts-per-billion (ppb), or expressed in parts-per-million (ppm), 5.000; 1.000; 0.200; and 0.050, for each analyte element were run in quadruplicate-- two (2) times as a single file of 15 elements and two (2) times as three files of 5 elements. The results were hard-copy printed by the comtaminant profiling (C/P) system's printer and shown in Figures 26A, 26B, and 26C. In the figures, the phrase "single run"

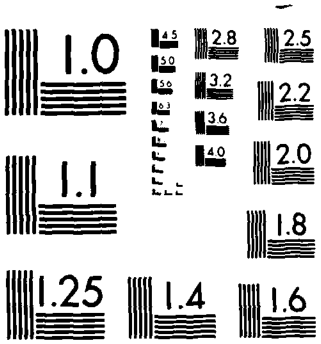


RESULTS OF FIRST RUN - VIEW HEIGHT

FIGURE 25A. 1. Varying the View Height to Optimize BEC

AD-A151 952 ESTABLISHMENT OF PRODUCTION CLEANLINESS CRITERIA AND PROCESSES FOR PRINTE..(U) MARTIN MARIETTA AEROSPACE ORLANDO FL J K BONNER DEC 81 OR-16668 2/3

UNCLASSIFIED DAAK-40-78-C-0114 F/G 9/5 NL

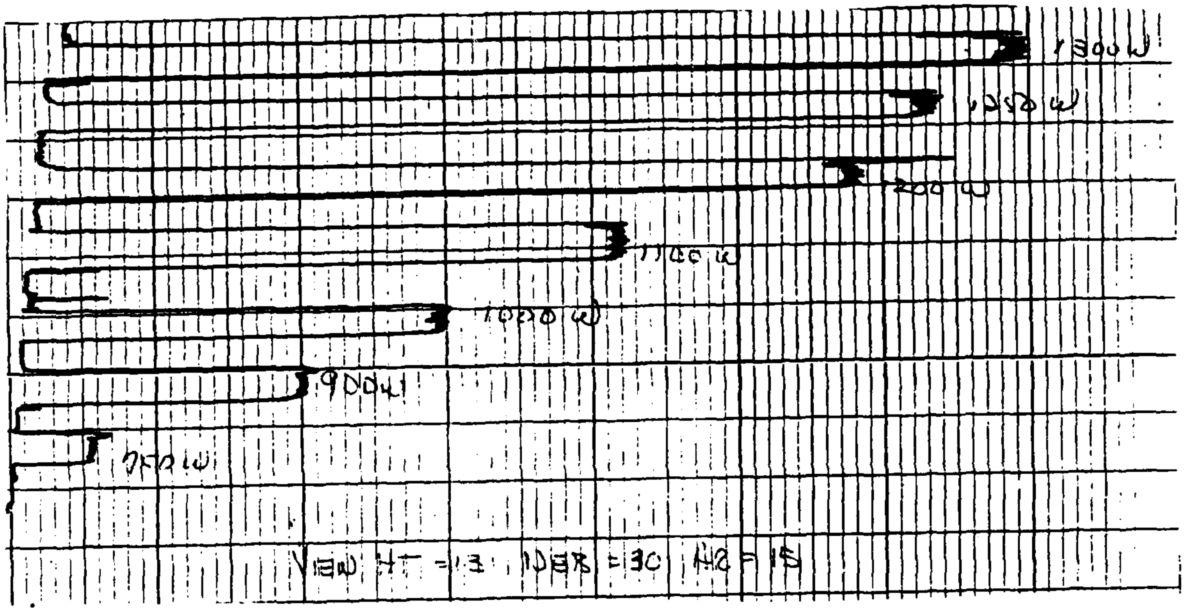

1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

```
****************** BEC CALCULATIONS ******************

 VIEW HT = 10MM (POWER = 1250  NEB = 30  AR = 15)

BACKGROUND READING =   84.
ANALYTE READING    = 1194.
BEC                = 0.07568


 VIEW HT = 12

BACKGROUND READING =   65.
ANALYTE READING    = 1329.
BEC                = 0.05142


 VIEW HT = 14

BACKGROUND READING =   52.
ANALYTE READING    = 1237.
BEC                = 0.04388


 VIEW HT = 16

BACKGROUND READING =   48.
ANALYTE READING    = 1045.
BEC                = 0.04814


 VIEW HT = 18

BACKGROUND READING =   43.
ANALYTE READING    =  744.
BEC                = 0.06134
```

FIGURE 25A. 2.

```
******************** BEC CALCULATIONS ********************

 VIEW HT = 12MM

BACKGROUND READING =   56.
ANALYTE READING    = 1511.
BEC                = 0.03849


 VIEW HT = 13MM

BACKGROUND READING =   51.
ANALYTE READING    = 1453.
BEC                = 0.03638


 VIEW HT = 14MM

BACKGROUND READING =   49.
ANALYTE READING    = 1367.
BEC                = 0.03718


 VIEW HT = 15MM

BACKGROUND READING =   52.
ANALYTE READING    = 1237.
BEC                = 0.04388
```

FIGURE 25A. 3.

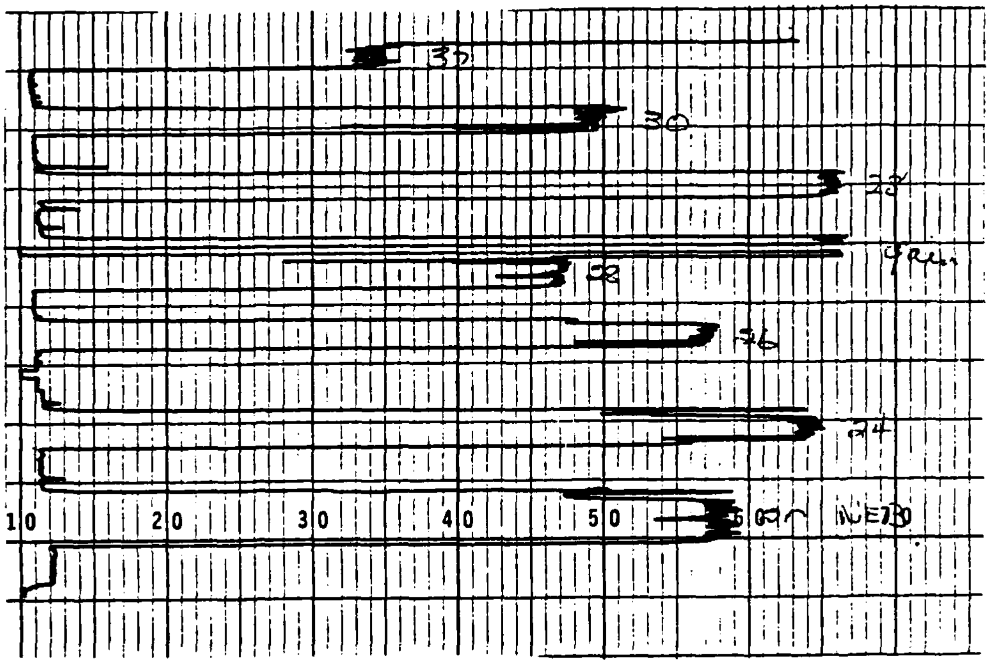


RESULTS OF SECOND RUN - POWER

FIGURE 25B. 1. Varying the Power to Optimize BEC

```
****************** BEC CALCULATIONS *******************

 POWER = 750 (VIEW HT = 13MM  NEB = 30  AR = 15)

BACKGROUND READING =    6.
ANALYTE READING    =  112.
BEC                = 0.05660


 POWER = 900

BACKGROUND READING =   11.
ANALYTE READING    =  408.
BEC                = 0.02771


 POWER = 1000

BACKGROUND READING =   16.
ANALYTE READING    =  597.
BEC                = 0.02754


 POWER = 1100

BACKGROUND READING =   25.
ANALYTE READING    =  850.
BEC                = 0.03030


 POWER = 1200

BACKGROUND READING =   39.
ANALYTE READING    = 1174.
BEC                = 0.03436


 POWER = 1250

BACKGROUND READING =   46.
ANALYTE READING    = 1278.
BEC                = 0.03734


 POWER = 1300

BACKGROUND READING =   54.
ANALYTE READING    = 1398.
BEC                = 0.04018
```

FIGURE 25B. 2.

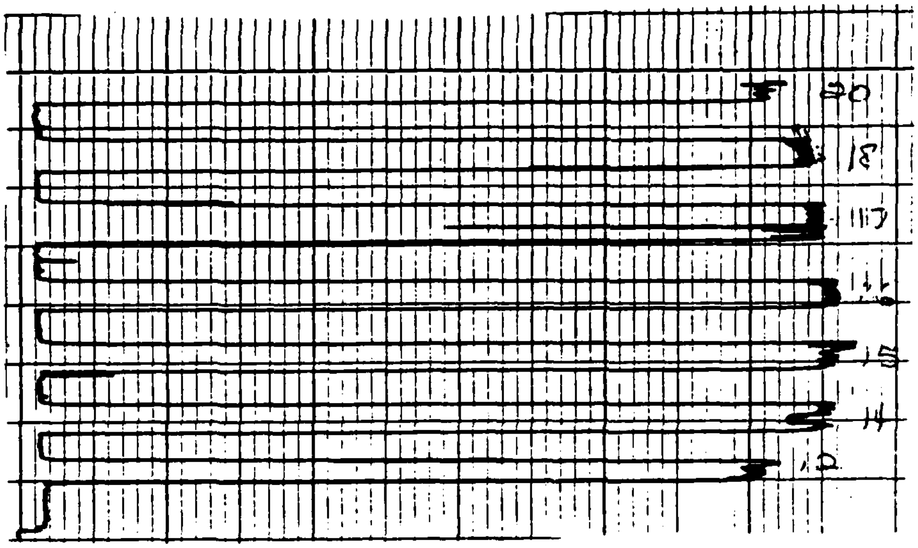


RESULTS OF THIRD RUN – NEBULIZER PRESSURE

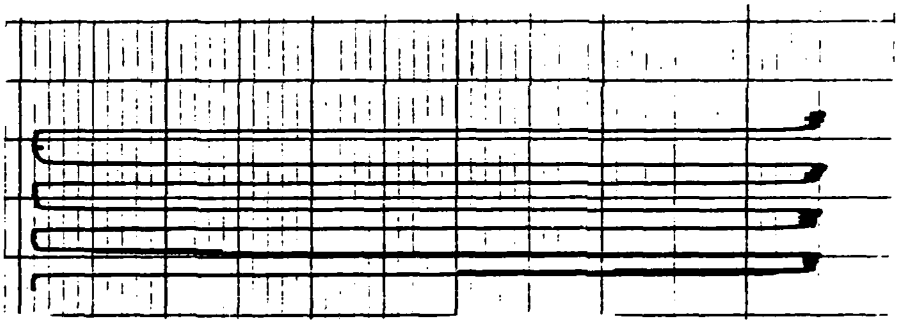
FIGURE 25C. 1. Varying the Nebulizer Pressure to Optimize BEC

```
******************** BEC CALCULATIONS ********************


 NEB = 20 (POWER = 1000  VIEW HT = 13  AR = 15)

BACKGROUND READING =   47.
ANALYTE READING    =  975.
BEC                = 0.05065


 NEB = 24

BACKGROUND READING =   29.
ANALYTE READING    = 1096.
BEC                = 0.02718


 NEB = 26

BACKGROUND READING =   25.
ANALYTE READING    =  957.
BEC                = 0.02682


 NEB = 28

BACKGROUND READING =   19.
ANALYTE READING    =  756.
BEC                = 0.02578


 NEB = 28 AUTO-GAIN

BACKGROUND READING =   28.
ANALYTE READING    = 1131.
BEC                = 0.02539


 NEB = 30

BACKGROUND READING =   22.
ANALYTE READING    =  796.
BEC                = 0.02842


 NEB = 32

BACKGROUND READING =   18.
ANALYTE READING    =  496.
BEC                = 0.03766
```

FIGURE 25C. 2.



RESULTS OF FOURTH RUN - ARGON FLOW



RESULTS OF FINAL RUN - TEST
VIEW HT = 13mm POWER = 1000W
NEBULIZER PRESSURE = 30 PSI
ARGON FLOW = 17 LITERS | MIN

FIGURE 25D. 1. Varying the Argon Flow to Optimize BEC

```
****************** BEC CALCULATIONS *******************

 AR = 12 (POWER = 1000  VIEW HT = 13  NEB = 28)

BACKGROUND READING =   37.
ANALYTE READING    = 1024.
BEC                = 0.03749


 AR = 14

BACKGROUND READING =   31.
ANALYTE READING    = 1105.
BEC                = 0.02886


 AR = 15

BACKGROUND READING =   29.
ANALYTE READING    = 1125.
BEC                = 0.02646


 AR = 16

BACKGROUND READING =   28.
ANALYTE READING    = 1132.
BEC                = 0.02536


 AR = 17

BACKGROUND READING =   26.
ANALYTE READING    = 1112.
BEC                = 0.02394


 AR = 18

BACKGROUND READING =   28.
ANALYTE READING    = 1093.
BEC                = 0.02629


 AR = 20

BACKGROUND READING =   26.
ANALYTE READING    = 1038.
BEC                = 0.02569
```

FIGURE 25D. 2.

```
******************** BEC CALCULATIONS ********************

 001    VIEW HT = 13  POWER = 1000  NEB = 28  AR = 17


BACKGROUND READING =   24.
ANALYTE READING    = 1109.
BEC                = 0.02212



 002

BACKGROUND READING =   23.
ANALYTE READING    = 1109.
BEC                = 0.02118



 003

BACKGROUND READING =   25.
ANALYTE READING    = 1111.
BEC                = 0.02302



 004

BACKGROUND READING =   25.
ANALYTE READING    = 1115.
BEC                = 0.02294
```

FIGURE 25D. 3. Test Run with Final Torch Parameters

```
                         ERROR ANALYSIS

*****      SN      **********      SN      **********      SN      *****

                   5000         1000         200          50

SINGLE RUN 1     4.86 %        2.6 %        5.5 %       -104 %
SINGLE RUN 2     5.38 %        3.9 %        16 %        -8 %
METHOD RUN 1     9.1 %         21.6 %       68.5 %       62 %
METHOD RUN 2     5 %           11.6 %       0 %          4 %

*****      CR      **********      CR      **********      CR      *****

                   5000         1000         200          50

SINGLE RUN 1     2.9 %         .4 %        -5 %         -28 %
SINGLE RUN 2     4.28 %        4.5 %        4 %         -12 %
METHOD RUN 1     9.24 %        11.3 %       10 %         6 %
METHOD RUN 2     3.1 %         8.9 %        6 %          18 %

*****      SI      **********      SI      **********      SI      *****

                   5000         1000         200          50      ~3000

SINGLE RUN 1     5.34 %       -13.7 %      -81 %        -678 %
~~SINGLE RUN 2    -100 %        -100 %       -100 %       -100 %~~
METHOD RUN 1     5.78 %        64.3 %       269 %        880 %
METHOD RUN 2    -4.66 %        70.1 %       222 %        880 %

*****      ZN      **********      ZN      **********      ZN      *****

                   5000         1000         200          50

SINGLE RUN 1     .7 %          .1 %        -4 %         -24 %
SINGLE RUN 2     .72 %         .5 %        -5.5 %       -24 %
METHOD RUN 1     3.52 %        5.9 %        3 %         -4 %
METHOD RUN 2     1.46 %        4 %          2 %         -8 %

*****      PB      **********      PB      **********      PB      *****

                   5000         1000         200          50

SINGLE RUN 1    -.16 %         8.5 %        14 %         208 %
SINGLE RUN 2    -100 %        -100 %       -100 %       -100 %
METHOD RUN 1     5.38 %       -7.9 %       -94 %        -270 %
METHOD RUN 2     4.16 %       -3.3 %       -32.5 %      -222 %

*****      CU      **********      CU      **********      CU      *****

                   5000         1000         200          50      ~100

SINGLE RUN 1     .92 %        -1.5 %       -13.5 %       0 %
SINGLE RUN 2    -1.08 %        .7 %         0 %          8 %
METHOD RUN 1     .94 %         1.5 %        7.5 %        14 %
```

FIGURE 26A. Torch Development Using Three Separate Analyte Files

```
METHOD RUN 2   1.16 %    1.9 %     13.5 %    42 %

*****     NI      **********    NI      **********     NI      *****

               5000      1000      200       50

SINGLE RUN 1   1.3 %     2.6 %      4.5 %   -22 %
SINGLE RUN 2   1.08 %    3.4 %      6 %      10 %
METHOD RUN 1   3.14 %    8.4 %      4 %      24 %
METHOD RUN 2   .58 %     3.6 %      13 %     6 %

*****     AU      **********    AU      **********     AU      *****

               5000      1000      200       50               ~-100

SINGLE RUN 1   1.82 %    4.9 %     -4.5 %   -46 %
SINGLE RUN 2  -100 %    -100 %    -100 %   -100 %
METHOD RUN 1   2.58 %    3.4 %      8 %      26 %
METHOD RUN 2  -.28 %    -.1 %     -6.5 %    -36 %

*****     FE      **********    FE      **********     FE      *****

               5000      1000      200       50

SINGLE RUN 1   6.4 %     6.5 %      11 %     18 %
SINGLE RUN 2  -.2 %      1.1 %      4.5 %    22 %
METHOD RUN 1   4.58 %    7 %        11.5 %   32 %
METHOD RUN 2   .1 %      2.9 %     -1 %     -4 %

*****     MG2       **********    MG2       **********     MG2      *****

               5000      1000      200       50

SINGLE RUN 1   2.02 %    2.6 %     -3 %      6 %
SINGLE RUN 2  -.14 %     2.4 %     -3.5 %   -10 %
METHOD RUN 1   6.78 %    9.1 %      7 %      14 %
METHOD RUN 2   3.38 %    5.3 %      4 %      10 %

*****     PD      **********    PD      **********     PD      *****

               5000      1000      200       50

SINGLE RUN 1  -3.28 %   -1.5 %      10 %    -56 %
SINGLE RUN 2  -.46 %    -1.9 %     -9 %     -176 %
METHOD RUN 1   6.96 %    6.9 %      10.5 %  -72 %
METHOD RUN 2   4.68 %    4.5 %     -6 %     -48 %

*****     CA2       **********    CA2       **********     CA2      *****

               5000      1000      200       50

SINGLE RUN 1  -2.66 %   -1.5 %     -3 %      8 %
SINGLE RUN 2  -2.2 %     1.6 %     -2.5 %    8 %
METHOD RUN 1   9.34 %    13.7 %     14.5 %   44 %
```

FIGURE 26B.

```
METHOD RUN 2   3.82 %     6.9 %      7 %        22 %

*****     AL2      **********     AL2     **********     AL2     *****

                 5000       1000      200        50

SINGLE RUN 1    .78 %      3.4 %    -10 %      -32 %
SINGLE RUN 2  -1.66 %     -.7 %     -28.5 %   -126 %
METHOD RUN 1   13.42 %    11.7 %    -2 %       -64 %
METHOD RUN 2   3.46 %     2.1 %     -21 %      -114 %

*****     NA     **********     NA     **********     NA     *****

                 5000       1000      200        50

SINGLE RUN 1   -.24 %      1.1 %    -4 %       -108 %
SINGLE RUN 2   -.4 %      -1.8 %    -11 %      -164 %
METHOD RUN 1   -3.34 %    -9.3 %    -5.5 %     -62 %
METHOD RUN 2    2.12 %    -1.4 %    -40 %      -156 %

*****     K     **********     K     **********     K     *****

                 5000       1000      200        50

SINGLE RUN 1   -.72 %     -12.9 %   -92 %      -282 %
SINGLE RUN 2   -100 %     -100 %    -100 %     -100 %
METHOD RUN 1   -1.44 %    -42.9 %   -172 %     -674 %
METHOD RUN 2    3.94 %    -27.4 %   -280.5 %   -1166 %
```

FIGURE 26C.

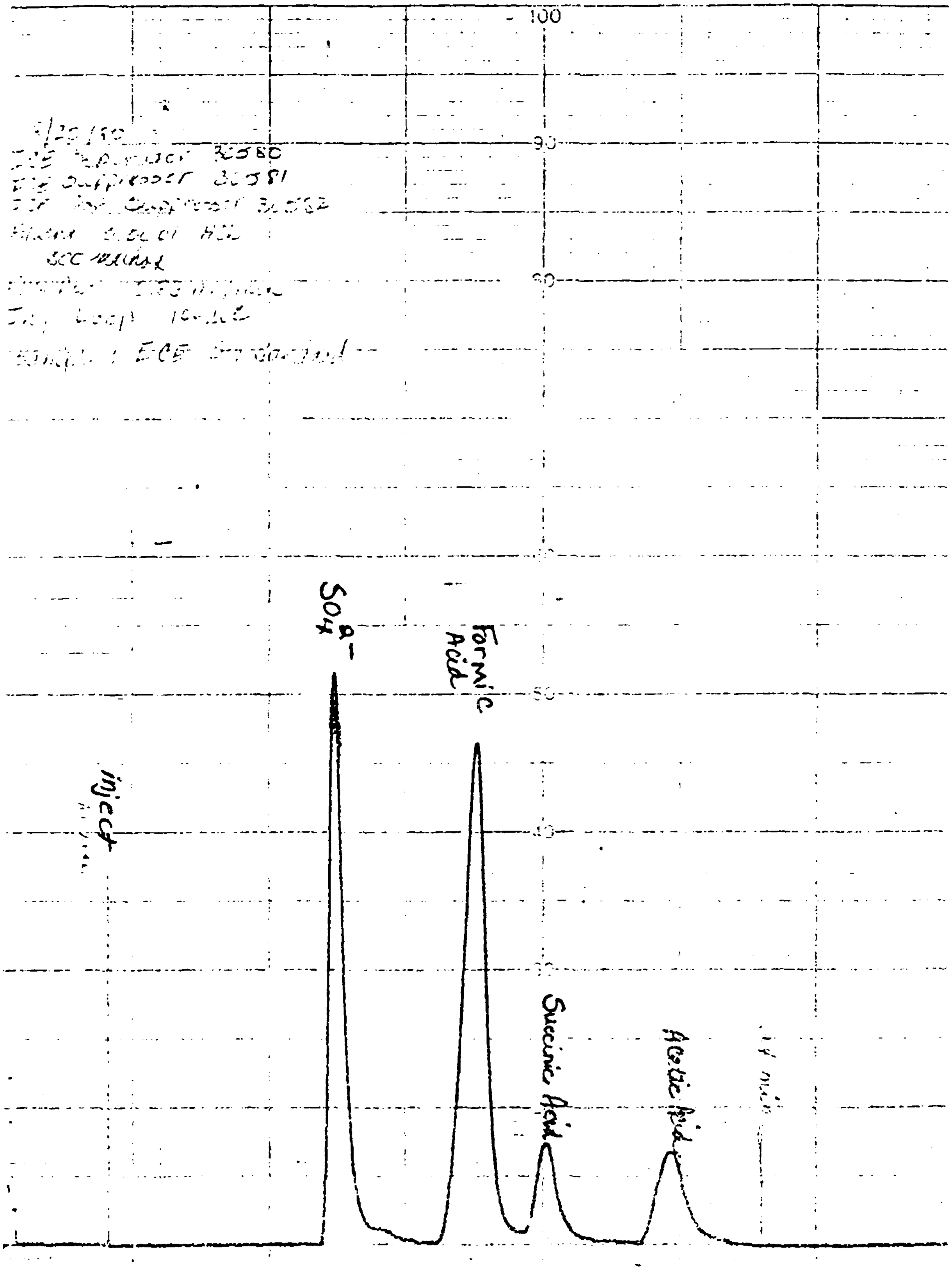


FIGURE 31. Analysis of a Standard Small Organic Anion Sample on the Ion Chromatograph

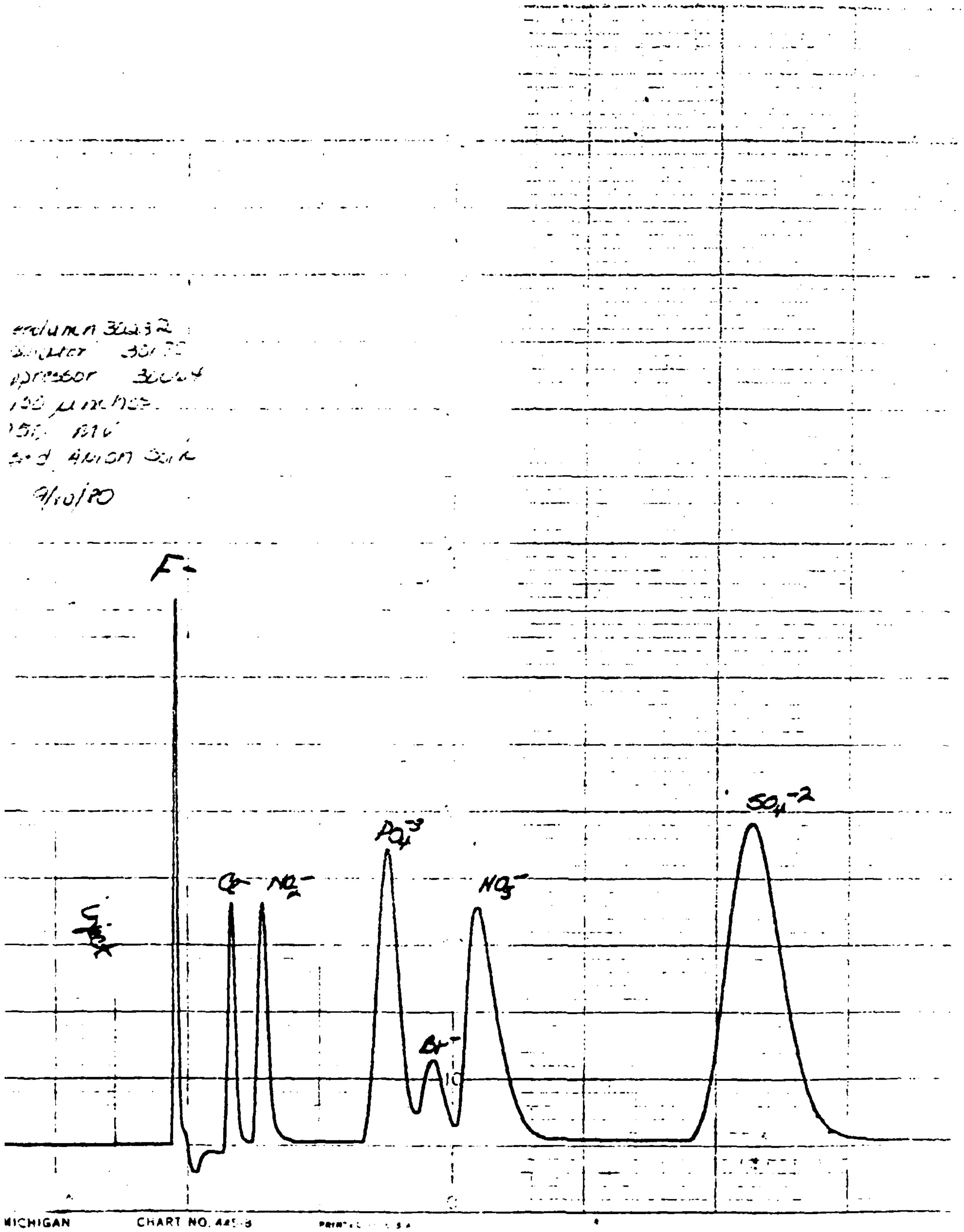


FIGURE 30. Analysis of a Standard Anion Sample on the Ion Chromatograph

3.2 THE ION CHROMATOGRAPH

The second most important analytical instrument in the contaminant profiling system is the ion chromatograph.

The ion chromatograph (IC) is the system component being used to detect and quantify individual negative ionic species (anions).

The next four figures deal with development work on the IC. Figure 30 illustrates the analysis of a standard anion sample using appropriate anion columns. Note that the peaks indicating each kind of anion are well defined and exhibit good resolution. The following anions with their respective concentrations were separated by the IC: fluoride (F^-), 3 ppm; chloride (Cl^-), 4 ppm; nitrite (NO_2^-), 10 ppm; phosphate (PO_4^{3-}), 50 ppm; bromide (Br^-), 10 ppm; nitrate (NO_3^-), 30 ppm; and sulfate (SO_4^{2-}), 50 ppm. Figure 31 presents the analysis of a standard small organic anion sample using different columns (ICE columns; ICE = Ion Chromatograph Exclusion Mode). Again, excellent resolution is obtained for each peak. The following small organic anions with their respective concentrations were separated by the IC: sulfate (SO_4^{2-}), 10 ppm (the only nonorganic); formate ($HCOO^-$), 20 ppm; succinate [$CH_2COO^-)_2$], 20 ppm; and acetate (CH_3COO^-), 20 ppm.

Naturally, it will be necessary to run such standards each day analyses are performed in order to calibrate the IC to run unknown samples. Once the standards are run, then unknown samples can be. The unknown samples will be extracts made from production PW. The computer-integrator (C/I) attached to the IC is used to make the identification and compute the concentrations of ionic species found in the unknown sample. Basically, the C/I compares retention times of ionic species in the unknown sample with the retention times of ionic species in the standard. If the retention time[4] of an ionic species in the unknown sample is the same as the retention time of chloride ion in the standard, say, then the unknown sample has chloride ion in it. In this way qualitative identification is made. To determine the quantitative amount, the C/I integrates the areas under the curves for the ionic species in the standard and compares these to the integrated areas under the curves for ionic species in the unknown sample. Figures 32 and 33 show two successive analyses of the same flux, in this case a water-based flux. An analysis was made only of the common anions, not small organic acid anions. In the case of this particular flux, only fluoride (F^-) and chloride (Cl^-) ion were detected by the IC. The results are:

6	Phosphorus, P^3	Analytical group 2, turret #2
7	Silicon, Si	
8	Calcium, Ca	
9	Sodium, Na	
10	Potassium, K	
11	Copper, Cu	
12	Zinc, Zn	Analytical group 3, turret #3
13	Lead, Pb	
14	Tin, Sn	

As noted, each analytical group has corresponding to it a turret number.

The atomic absorption operating parameters are shown in Figures 27 A, 27 B, and 27 C. Taking the first element, chromium, Cr, its absorbance wavelength is 357.9 nm; lamp 1 is the Cr lamp operating on a current of 25mamps; 3 standards are used - 100 ppb, 25 ppb, 10 ppb; the operation mode is AA-BC (background correction)/concentration; the integration time is 6 sec; low (L) slit widths used for furnace work; 3 replicates are used to determine the mean and the coefficient of variation (CV) is determined.

At this point, it becomes necessary to determine the maximum analyte level permissible for each of the above species as determined by the achievement of a 0.6 Absorbance (ABS) signal. Due to relatively high analytical limits for certain elements (notably Si, K, Pb, and Sn) it is likely that less sensitive lines for these elements will allow avoidance of gaps in their analytical range.

Figures 28 and 29 A and 29 B illustrate the preliminary HGA-500 (graphite furnace) settings for all analyte species.

This concludes the section on the inductively-coupled plasma emission spectrophotometer/graphite furnace. It is now appropriate to turn to the development of the ion chromatograph.

ELEMENT	TYPE TUBE	INJ. VOL.	STEP	TEMP	RAMP	HOLD	GAS	REC.	READ
Ni (AA-BG)	pyro coated	20	1	110	10	10			
			2	250	10	5			
			3	1000	10	5			
			4	2300	0	5	50	-10	X
			5	20	1	5		X	
Au (AA-BG)	pyro coated	20- 100 (greater volume for sensitivity)	1	110	10	10	(if >20ul injection volume used,		
			2	250	10	5	add 10 sec to steps 1-3.)		
			3	600	10	10			
			4	1600	0	5	0	-10	X
			5	2600	1	5		X	
Fe (AA-BG)	pyro coated	20	1	110	10	10			
			2	250	10	5			
			3	1200	10	10			
			4	2000	0	5	50	-10	X
			5	20	1	5		X	
Mg (AA-BG)	pyro coated	20	1	110	10	10			
			2	250	10	5			
			3	1000	10	10			
			4	2400	1	5	50	-10	X
			5	20	1	5		X	
Pd				Should be determined on the ICP/5000					
Ca (AA-BG)	standard	20	1	110	10	10			
			2	250	10	5			
			3	1200	10	5			
			4	2600	1	5	50	-10	X
			5	20	1	5		X	
Al (AA-BG)	pyro coated	20	1	110	10	10			
			2	250	10	5			
			3	1500	10	5			
			4	2400	0	5	50	-10	X
			5	20	1	5		X	
Na (AA-BG)	standard	20 severe environmental contamination	1	110	10	10			
			2	250	10	5			
			3	900	10	5			
			4	2600	1	5	50	-10	X
			5	20	1	5		X	
K (AA-BG)	standard	20	1	110	10	10			
			2	250	10	5			
			3	950	10	5			
			4	2600	1	5	50	-10	X
			5	20	1	5		X	

FIGURE 29B.

ELEMENT	TYPE TUBE	ul INJECTION VOL.	STEP	TEMP	RAMP	HOLD	GAS	REC.	READ
Sn (AA-BG)	standard	20	1	110	10	10			
			2	250	10	5			
			3	500	5	5			
			4	2500	1	5	50	-10	X
			5	20	1	5		X	
Cr (AA-BG)	pyro coated	20	1	110	10	10			
			2	250	10	5			
			3	1200	10	5			
			4	2300	0	5	0	-10	X
			5	20	1	5		X	
Si (AA-BG)	standard	20	1	110	10	10			
			2	250	10	5			
			3	1400	10	5			
			4	2700	0	5	50	-10	X
			5	20	1	5		X	
Zn (AA-BG)	standard	20 severe environmental contamination	1	110	10	10			
			2	250	10	5			
			3	400	5	5			
			4	2200	1	5	50	-10	X
			5	20	1	5		X	
Pb (AA-BG) EDL	standard	20	1	110	10	10			
			2	250	10	5			
			3	500	5	5			
			4	2300	1	5	2-300	-10	X
			5	20	1	5		X	
P (AA-BG) EDL	standard -ADD EQUAL VOL. °F .1% La as La$(NO_3)_2$	20	1	110	10	10			
			2	250	10	5			
			3	1400	10	5			
			4	2700	0	5	50	-10	X
			5	20	1	5		X	
Cu (AA-BG)	standard	20	1	110	10	10			
			2	250	10	5			
			3	900	10	5			
			4	2600	1	5	50	-10	X
			5	20	1	5		X	

FIGURE 29A. Preliminary Graphite Furnace Settings for Analyte Species (continued)

ELEMENT	PYRO COATED TUBE	ATOMIZE TEMP	RAMP	SET PHOTODIODE AND ATOMIZE TEMP	
Cr	(Specify Ringsdorf tubes)	2300	0	2400	ANALYTICAL GROUP 1 5000 set with 6 sec integration time, peak height or peak area
Ni	↓	2300	0	2400	
Au	↓	1600	0	2400	
Fe	↓	2000	0	2400	
Al	↓	2400	0	2400	
Mg		2400	1	----	
P	Standard tube	2700	1	2700	ANALYTICAL GROUP 2 5000 set with 6 sec t, peak height or peak area
Si	↓	2700	0	2700	
Ca	↓	2600	1	----	
Na	↓	2600	1	----	
K	↓	2600	0	----	
Cu	↓	2600	1	----	
Zn	Standard tube	2200	1	----	ANALYTICAL GROUP 3 5000 set with 6 sec t, peak height or peak area
Pb	↓	2300	1	----	
Sn	↓	2500	1	----	

MULTI-ELEMENT ANALYSIS

FIGURE 28. Preliminary Graphite Furnace Settings for Analyte Species

ANALYTICAL GROUP 3; TURRET #3

```
                                  PARAMETERS
                                  ==========

12:07       81/06/10

                      ZN IN PROGRAM MEMORY #1
WAVELENGTH  213.9 LAMP  1            CURRENT  0         INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25          STD 3  10          SLIT 0.70 L


                      PB IN PROGRAM MEMORY #2
WAVELENGTH  217   LAMP  2            CURRENT  0         INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  1000       STD 2  200         STD 3  50          SLIT 0.70 L


                      SN IN PROGRAM MEMORY #3
WAVELENGTH  224.6 LAMP  3            CURRENT  0         INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  1000       STD 2  200         STD 3  50          SLIT 0.70 L
```

FIGURE 27C. Analytical Group 3,
Turret #3

ANALYTICAL GROUP 2; TURRET #2

```
                                  PARAMETERS
                                  ==========


12:07        81/06/10

                      P IN PROGRAM MEMORY #1
WAVELENGTH  213.6 LAMP  1            CURRENT  0         INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  1000       STD 2  250         STD 3  100         SLIT 0.20 L


                      SI IN PROGRAM MEMORY #2
WAVELENGTH  251.6 LAMP  2            CURRENT  40        INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  2000       STD 2  500         STD 3  250         SLIT 0.20 L


                      CA IN PROGRAM MEMORY #3
WAVELENGTH  422.7 LAMP  3            CURRENT  10        INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25          STD 3  10          SLIT 0.70 L


                      NA IN PROGRAM MEMORY #4
WAVELENGTH  589   LAMP  4            CURRENT  8         INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25          STD 3  10          SLIT 0.40 L


                      K IN PROGRAM MEMORY #5
WAVELENGTH  766.5 LAMP  5            CURRENT  0         INT TIME  6
STATS CV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  1000       STD 2  200         STD 3  50          SLIT 0.70 L


                      CU IN PROGRAM MEMORY #6
WAVELENGTH  324.7 LAMP  6            CURRENT  15        INT TIME  6
STATS AV          AVERAGE  3         MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25          STD 3  10          SLIT 0.70 L
```

FIGURE 27B. Analytical Group 2,
Turret #2

ANALYTICAL GROUP 1; TURRET #1

```
                          PARAMETERS
                          ==========

12:07      81/06/10

                   CR IN PROGRAM MEMORY #1
WAVELENGTH  357.9 LAMP  1          CURRENT  25        INT TIME  6
STATS CV          AVERAGE  3       MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25        STD 3  10          SLIT 0.70 L


                   NI IN PROGRAM MEMORY #2
WAVELENGTH  232   LAMP  2          CURRENT  25        INT TIME  6
STATS CV          AVERAGE  3       MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25        STD 3  10          SLIT 0.20 L


                   AU IN PROGRAM MEMORY #3
WAVELENGTH  242.8 LAMP  3          CURRENT  10        INT TIME  6
STATS CV          AVERAGE  3       MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25        STD 3  10          SLIT 0.70 L


                   FE IN PROGRAM MEMORY #4
WAVELENGTH  248.3 LAMP  4          CURRENT  30        INT TIME  6
STATS CV          AVERAGE  3       MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25        STD 3  10          SLIT 0.20 L


                   AL IN PROGRAM MEMORY #5
WAVELENGTH  309.3 LAMP  5          CURRENT  0         INT TIME  6
STATS CV          AVERAGE  3       MODE AA-BG,CONC    SIGNAL PEAK HT
STD 1  100        STD 2  25        STD 3  10          SLIT 0.70 L
```

FIGURE 27A. Analytical Group 1,
Turret #1

Condition 1 - Analyte concentration gap between torch and furnace.

FLL $\leq$ Concentration (1) of analyte species$_1$ $\leq$ FUL $<$

Concentration (2) of analyte species$_1$ $<$TLL $\leq$

Concentration (3) of analyte species$_1$.

That is, since concentration (2) falls somewhere between the furnace upper limit (FUL) for that species and the torch lower limit (TLL), concentration (2) would be undetectable by either furnace or torch. Steps are being taken to avoid this situation. What we want to achieve is this:

Condition 2 - No analyte concentration gap between torch and furnace.

FLL $\leq$ Concentration (1) of analyte species$_1$ $\leq$ FUL

$\approx$ TLL $\leq$ Concentration (2) of analyte species$_1$

The use of the symbol $\approx$ indicates there is no concentration range lying between the FUL and the TLL, hence, no gap.

As a departure point for the development, the principal spectral lines for each analyte species have been chosen per the HGA-500 (graphite furnace) Methods Development Manual. Also it must be remembered that the graphite furnace method utilizes atomic absorption as opposed to the torch which is atomic emission. This was the principal reason for choosing the ICP-5000, it combined the analytical capabilities of both atomic emission and atomic absorption. The real contaminant profiling (C/P) system lower limits are the furnace lower limits (FLLs). The FLLs are expected to be about 1 part-per-billion (1 ppb) for most of the analyte elements.

The fact that we are using atomic absorption techniques for the furnace dictates that a light source (analyte lamp) having as its cathode the analyte element in question must be used for each separate analyte element to be detected by use of the graphite furnace. These lamps must be loaded into a lamp turret (maximum no. of lamps per turret = 6). It is assumed that we will be operating in the non-linear portion of the absorbance curve for most elements. Therefore, a multilevel calibration with non-linear curve fitting has been chosen. This requires that several analyte standards be run for each element. The analyte species that will be detected by the graphite furnace are:

1 Chromium, Cr
2 Nickel, Ni
3 Gold, Au
4 Iron, Fe
5 Aluminum, Al

} Analytical group 1, turret #1

Regarding the type of line, symbols I and A, ion lines (I) are the better of the two. Ion lines are less sensitive to torch conditions; therefore, elements determined using one of their ion lines are less likely to exhibit significant analysis error. To achieve ion line analyses, low gas flows, low nebulizer pressures, and high torch viewing heights are necessary. The latter three conditions result in longer residence times of the sample's elemental species in the torch flame, and longer residence times are more likely to give rise to the formation of analyte ions. In short, it is easier to optimize the torch running conditions using ion lines. However, for some elements, such as gold, palladium, sodium, etc., atom lines must be used since either there are no ion lines available for such elements within the ICP 5000's wavelength range capacity (175 to 900 nm) or the ion lines, if they exist, are of too low sensitivity for the 5000. In either case, one of the analyte's atom lines must be used.

Regarding the TLLs, it must be kept in mind that these do not represent the C/P system's lower limits for such analyte species. Rather, the TLLs serve merely to mark the necessary switch from torch analysis mode to graphite furnace analysis mode. That is, if a given analyte element's concentration in a PW extract is less than its TLL, the MINC will prompt the analyst that further analysis will be required on the ICP 5000 graphite furnace, which has the capability of detecting concentrations of elements less than the TLLs. For example, suppose during a torch analysis the concentration of copper, Cu, is below 75 ppb (0.075 ppm). This information would be communicated to the MINC which would then call the graphite furnace routing (FURNCE) for analysis of copper. Thus, the graphite furnace lower limits (FLLs) rather than the torch lower limits (TLLs) represent the C/P system's real lower limits. The FLLs are about 1 ppb for most of the analyte elements.

As suggested before, a suitable data base of PW contaminants ought to be established. This data base would relate specific contaminant species and their amounts in PW extracts to PW manufacturing processes and to PW failures, both in the test mode and the field service mode. Building such a data base will allow C/P to be used as an improved statistical control tool and enable the PW industry to proceed in confidence (statistically speaking) to manufacture PWAs with increased component densities and decreased line widths/line spacings. Such PWAs will be mandatory for high reliability military/aerospace advanced missile systems.

The analytical limits for the ICP torch have been established. These are the torch lower limits (TLLs). Methods had to be developed for the graphite furnace that will permit a continuous range of instrumental analytical capability of all analyte levels. That is, the furnace upper limits (FULs) should be as coterminous as possible with the TLLs for each analyte species; otherwise, a concentration gap would exist in which the analyte element(s) in question would be undetectable by either torch or furnace. This can perhaps more readily be illustrated like this:

Table 12

	Element[2]	Torch Lower Limit (TLL), in ppb	Wavelength (w) in nm	Type of Line[1]
File 1	(1) Tin, Sn	1000	189.99	I
	(2) Chromium, Cr	50	205.55	I
	(3) Silicon, Si	3000	212.41	A
	(4) Zinc, Zn	50	213.86	A
	(5) Lead, Pb	1000	220.35	I
File 2	(6) Copper, Cu	75	224.70	I
	(7) Nickel, Ni	50	231.60	I
	(8) Gold, Au	100	242.80	A
	(9) Iron, Fe	50	259.94	I
	(10) Magnesium, Mg	50	279.55	I
File 3	(11) Palladium, Pd	200	340.46	A
	(12) Calcium, Ca	50	393.37	I
	(13) Aluminum, Al	200	396.15	A
	(14) Sodium, Na	200	589.59	A
	(15) Potassium, K	1000	766.50	A

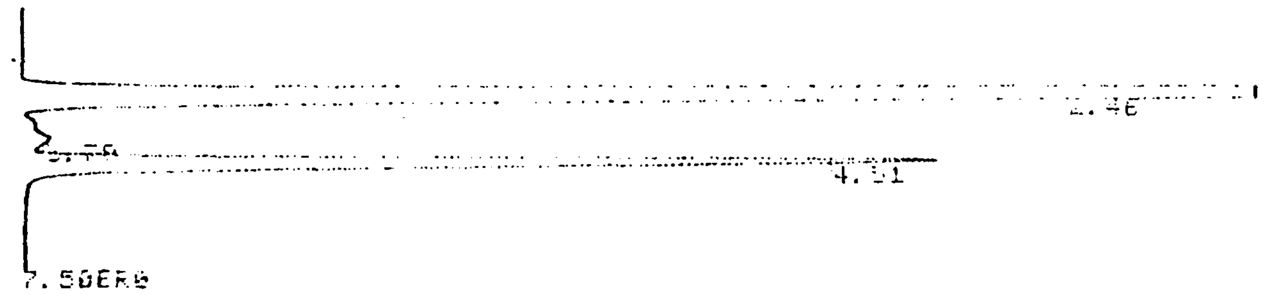
refers to a single file run of 15 elements and the phrase "method run" to one of the three files of 5 elements. Actually, the results in the error analysis are averages, i.e., arithmetic means. Three separate readings in each case were averaged. Consider the case of tin, Sn, the first element presented in Figure 26A. At 5000 ppb for single run 1, the error of 4.86% is in reality the arithmetic mean of three (3) separate readings. Hence, in point of fact for each numerical error datum there were three (3) readings per element per concentration per file. The results of each analysis were automatically compared by the C/P system's MINC minicomputer to the known concentration. The MINC then computed the error percents (3) for each analysis, computed the arithmetic mean for each analysis, and printed the results in hard-copy form utilizing the C/P system's on-line printer. The torch lower limits (TLLs) are presented in Table 12 below in order of ascending analyte wavelength.

SC A0622 010

Spectra-Physics

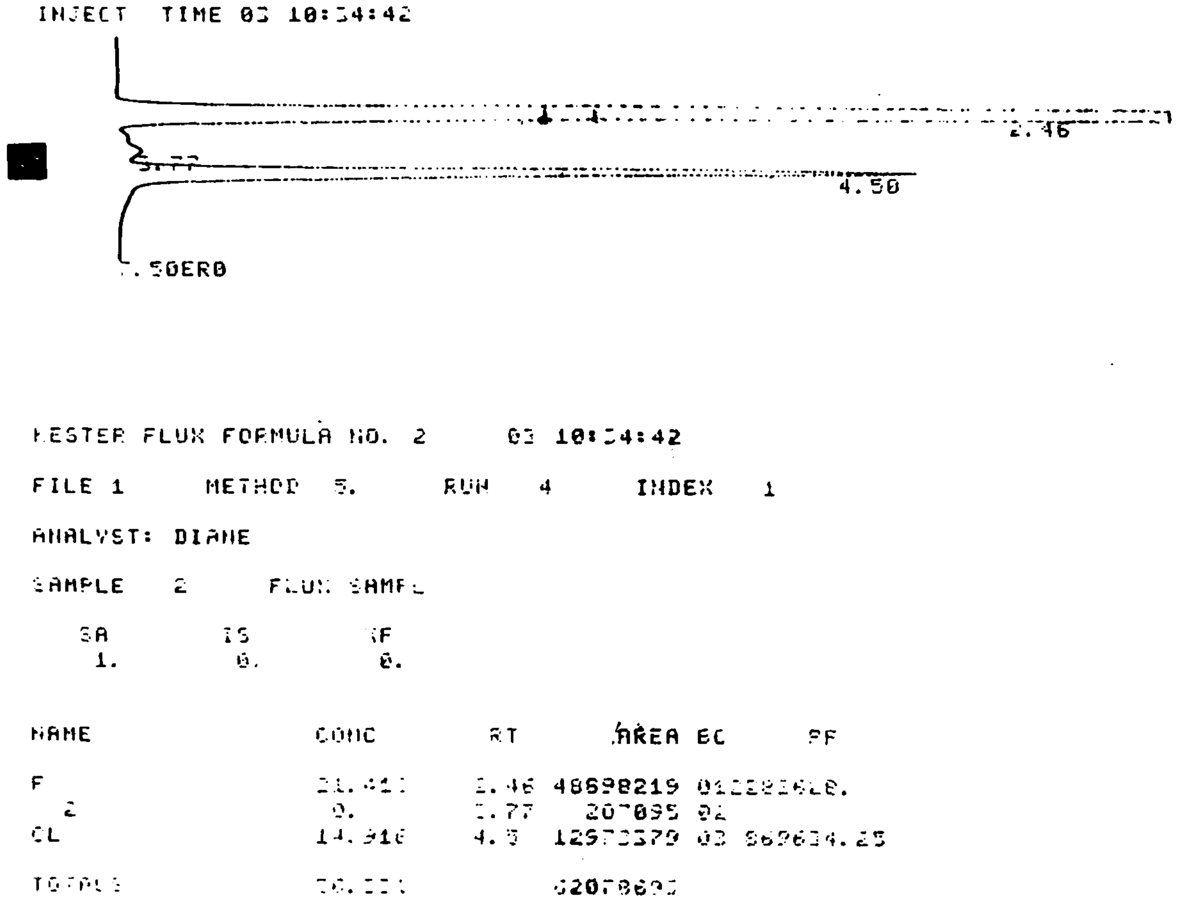
091

```
INJECT  TIME 03 10:25:58
```



```
KESTER FLUX FORMULA NO. 1300   03 10:25:58

FILE 1      METHOD  5.      RUN   3      INDEX   1

ANALYST: DIANE

SAMPLE   1      FLUX SAMPL

   IA         IS         MF
    1.         0.         0.

NAME                CONC       RT       AREA BC      RF

                    21.172     2.46 48805444 01 2231626.
  2                  0.        3.79   247531 02
OL                  14.621     4.51 12715247 01 969634.25

TOTALS              35.793          61768222
```

FIGURE 32. Analysis of a Water-Based Flux, #1



```
INJECT  TIME 03 10:34:42
```

```
KESTER FLUX FORMULA NO. 2      03 10:34:42

FILE 1      METHOD  5.      RUN   4      INDEX   1

ANALYST: DIANE

SAMPLE   2     FLUX SAMPL

    SA         IS          RF
     1.         0.          0.

NAME                 CONC        RT       AREA BC      RF

F                    21.411     2.46 48698219 01228162.
  2                   0.        3.77   207095 02
CL                   14.916     4.5  12973379 03 869634.25

TOTALS               36.327          62078693
```

FIGURE 33. Analysis of a Water-Based Flux, #2

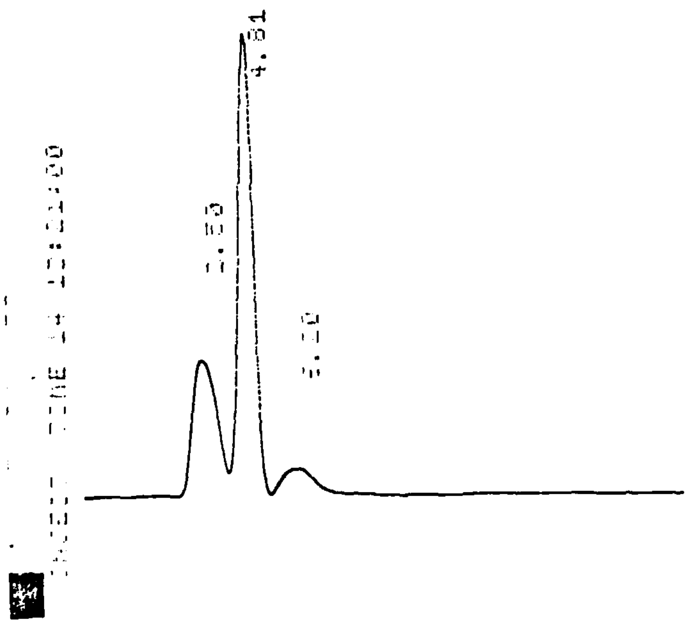


FIGURE 34., Chromatogram of a Typical RMA Flux

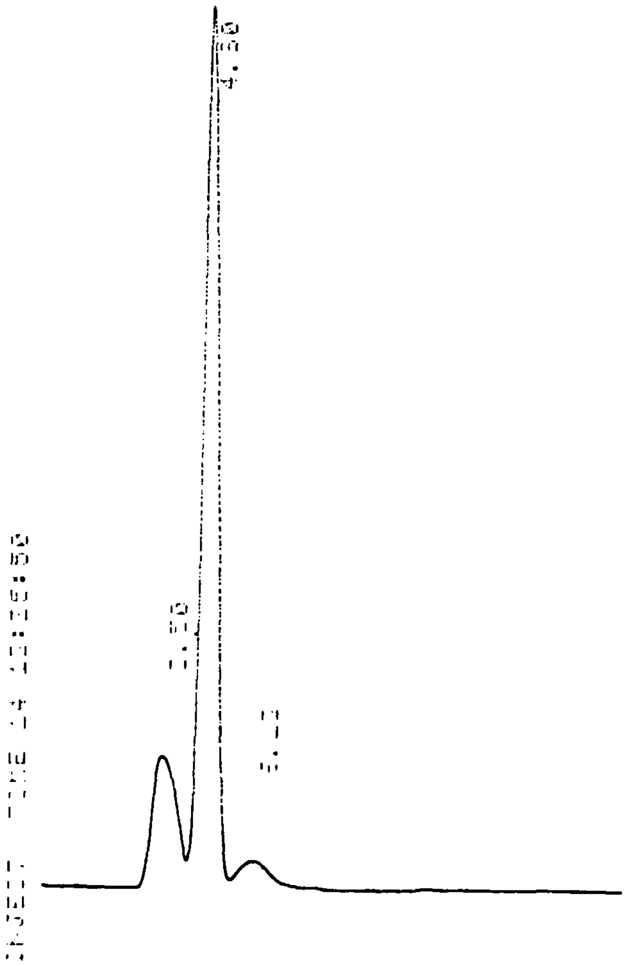


FIGURE 35. Chromatogram of a Typical RMA Flux Spiked with 10 ppm Cl^-

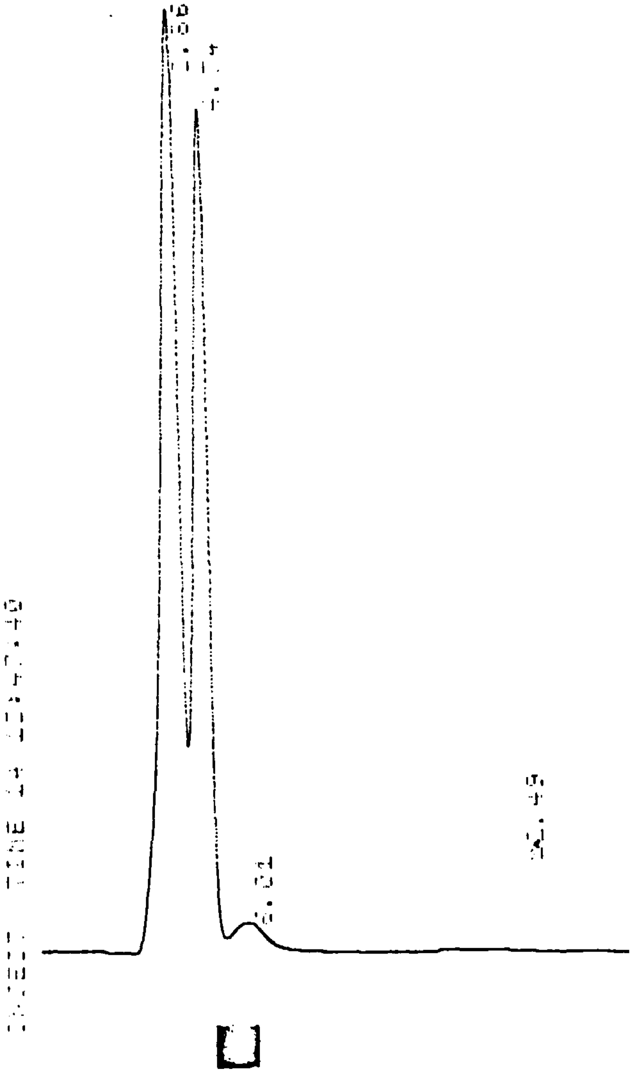


FIGURE 36. Chromatogram of a Typical RMA Flux Spiked with 20 ppm F^-

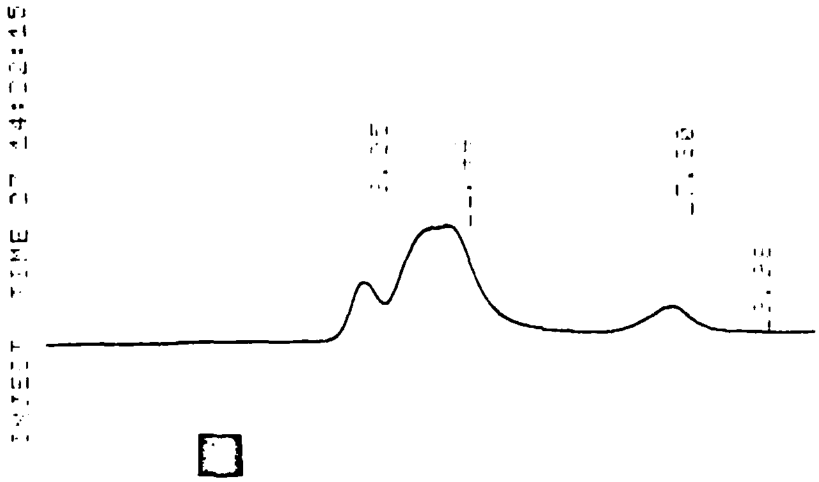


FIGURE 37. Chromatogram of a Typical RMA Flux Using ICE Column to Detect Small Organic Acids

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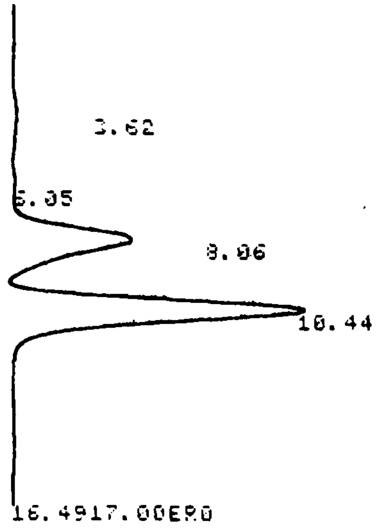
INJECT  TIME 12 13:18:46
```



```
ANIONS                              12 13:18:46

FILE 1      METHOD  5.      RUN    2       INDEX  2      CALIB

ANALYST: D.HILLYER

NAME                    CONC*         RT        AREA BC        RF

  1                        0.        3.62     125072 01
  2                        0.        6.05      67889 02
F                        250.        8.06    3473262 02   13893.048
CL                       500.       10.44    6984416 03   13968.832
  5                        0.       16.49      56038 21

TOTALS                   750.               10706677

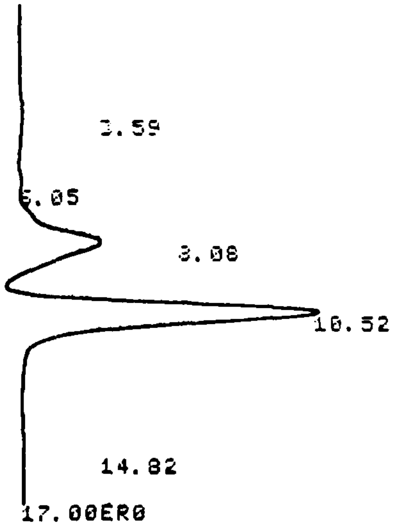
NEW FILE:

NAME             RF             RT

F            14263.598        8.05
CL           14527.652       10.42
```

FIGURE 38. Analysis of a Standard of Cl^- and F^- on the Ion Chromatograph

```
INJECT  TIME 12 13:46:14
```



```
ANIONS                            12 13:46:14

FILE 1      METHOD  5.      RUN    3      INDEX    1

ANALYST: D.HILLYER

SAMPLE   1      KESTER RMA

   SA        IS        RF
    1.        0.        0.


NAME                 CONC *      RT       AREA BC       RF

  1                   0.       3.59    122334 01
  2                   0.       6.05    110121 02
F                   215.728    8.08   3077059 02  14263.598
CL                  508.458   10.52   7386704 03  14527.652
' 5                   0.      14.82     64002 21

TOTALS              724.186          10760220
```

FIGURE 39. Analysis of a Flux Sample on the Ion Chromatograph, #1

```
INJECT  TIME 12 14:29:15
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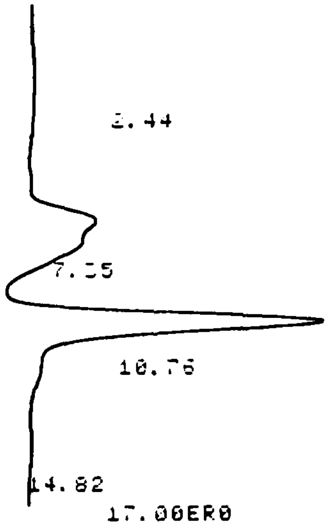
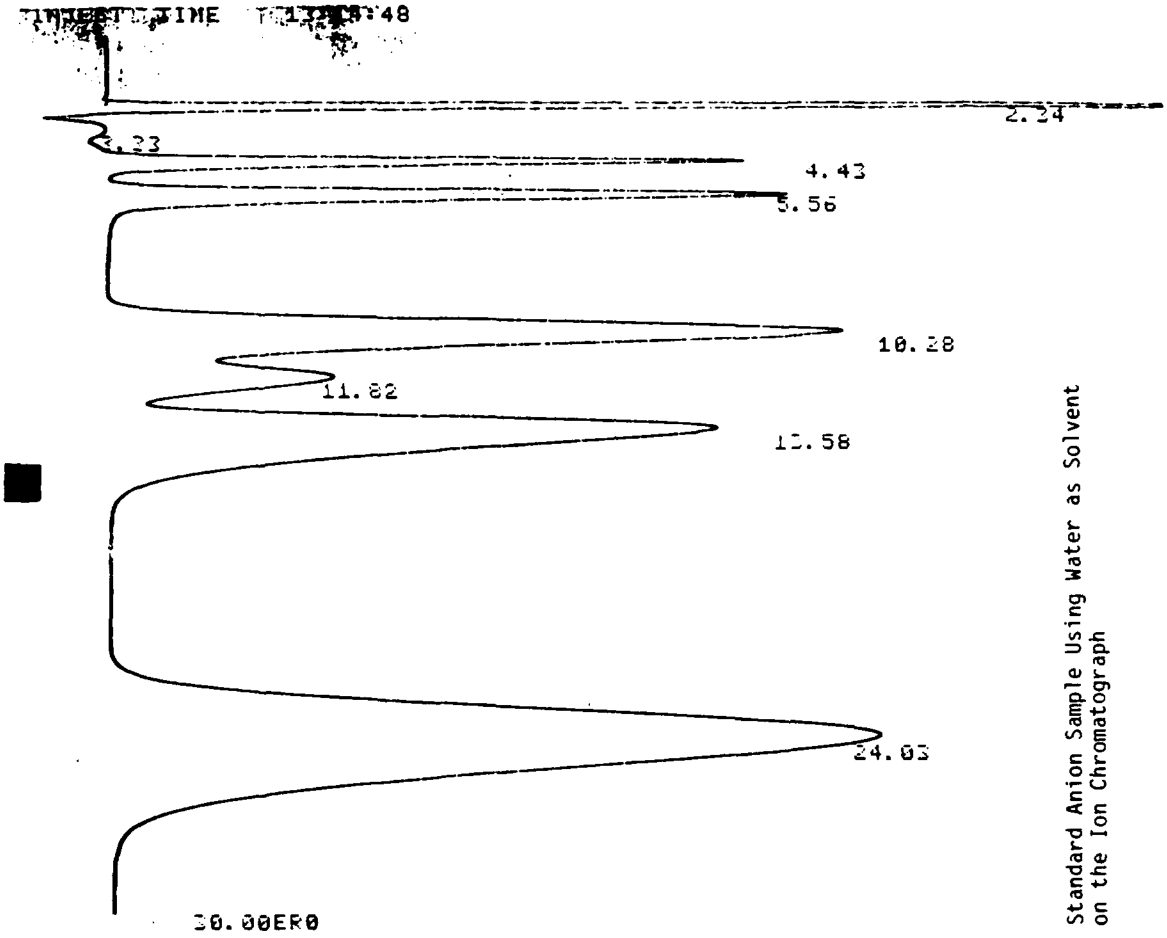


```
ANIONS                           12 14:29:15

FILE 1     METHOD  5.      RUN   4      INDEX   1

[illegible]NALYST: D.HILLYER

SAMPLE   2      KESTER RMA

   SA         IS         XF
    1.         0.         0.

NAME                 CONC*     RT      AREA BC     RF

  1                   0.      2.44   1300483 02
F                   333.441   7.35   4756062 02  14263.598
CL                  534.99   10.76   7772152 02  14527.652
  4                   0.     14.82    204370 23

TOTALS              868.431          14033067
```

FIGURE 40. Analysis of a Flux Sample on the Ion Chromatograph, #2



```
COMMON ANIONS                          13:14:48

FILE 1      METHOD  5.      RUN    8      INDEX   1

ANALYST: VK

SAMPLE   1       SAMPLE

    SA         IS          XF
     1.         0.          0.


NAME                   CONC         RT        AREA BC       RF

FL                     1.919      2.24   6451751 012210309.
  2                    0.         3.33    885841 02
CL                     4.207      4.43   6396565 021520287.75
NO2                   10.025      5.56   8255665 03 823508.9
PO4                   47.975     10.28  19276823 02 401813.54
BR                     9.778     11.82   5700875 02 583036.4
NO3                   29.095     13.58  22170529 03 762000.433
SO4                   48.194     24.03  50521410 011048300.06
```

FIGURE 41. Standard Anion Sample Using Water as Solvent on the Ion Chromatograph

```
ANIONS                              13 13:25:13

FILE 1      METHOD  5.      RUN   4     INDEX   1

ANALYST: D.H.

SAMPLE   2      SAMPLE 2

   SA        IS        KF
    1.        0.        0.

NAME                CONC        RT        AREA BC      RF

F                   3.441     7.96   1856120 02 539354.667
CL                  5.444    10.25   3043975 03 559133.75
NO2                13.744    14.68 19001469 011382530.8
SO4                80.497    40.73 30188821 21 375032.22

TOTALS            103.126          54090405
```

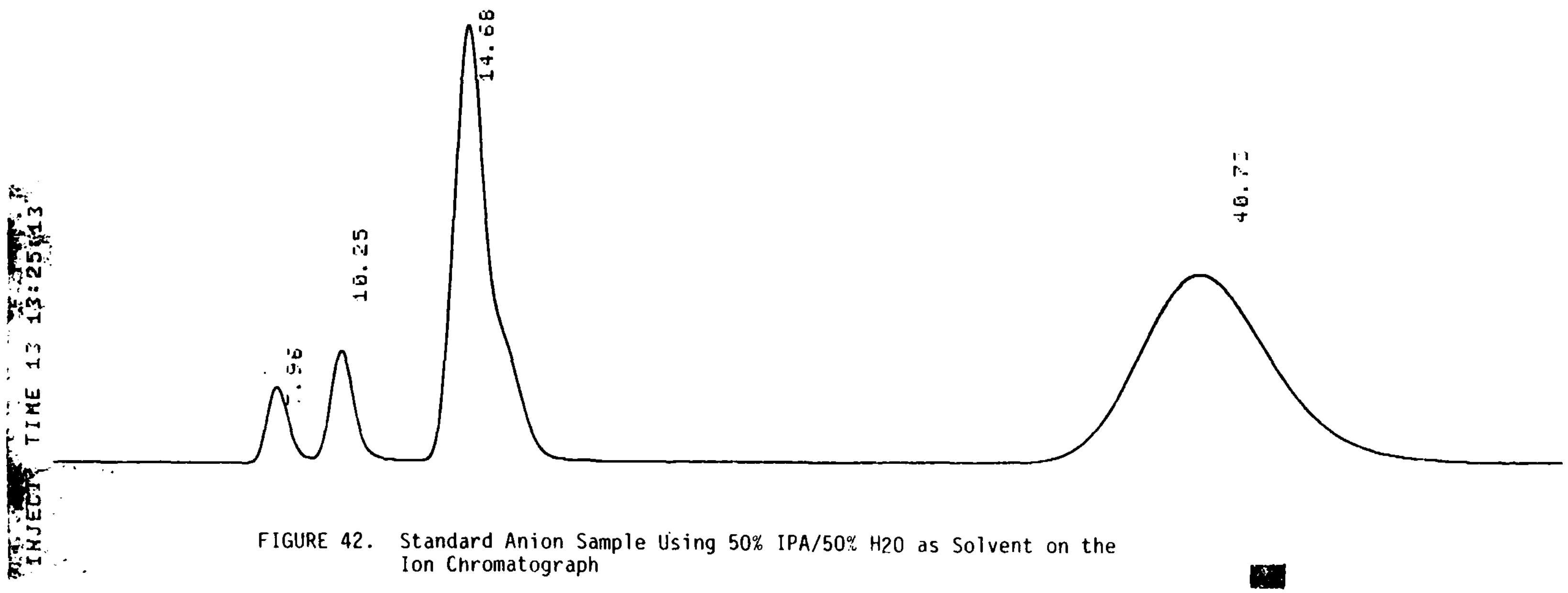


FIGURE 42. Standard Anion Sample Using 50% IPA/50% H2O as Solvent on the Ion Chromatograph

	Analysis 1	Analysis 2
Concentration of F^-	21.372 ppt	21.413 ppt
Concentration of Cl^-	14.621 ppt	14.918 ppt

where ppt = parts-per-thousand. Note the excellent reproducibility. Also note the high quantities of F^- and Cl^-. The strongly reinforces the point that such fluxes are extremely corrosive.

The next four figures, Figures 34-37, illustrate some of the work performed on the IC in the ongoing attempt to characterize RMA fluxes. As remarked previously, a great deal of developmental work must be done to satisfactorily characterize rosin-base fluxes. Figure 34 shows a chromatogram of a typical RMA flux run on the IC using 50% H_2O/50% IPA. The flux was run through the standard anion columns. Recall that such columns are to be used to detect such species as: fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), bromide (Br^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}). Note that the flux is chiefly characterized by two peaks, one at 3.50 minutes and a second at 4.81 minutes.

Figure 35 is the same flux sample as in Figure 34, except that the sample was spiked with 10 ppm Cl^-. As can easily be discerned by the figure, the second peak is considerably larger indicating that the component of the flux represented by the second peak is Cl^-. Figure 36 is the same flux sample as in Figure 34, except that the sample was spiked with 20 ppm F^-. Now the first peak seen in Figure 34 is considerably larger, indicating that F^- is a component of the flux represented by the first peak.

Figure 37 shows the same flux run through the ICE columns to detect small organic acids, etc. Note that three peaks appear although they are relatively poorly defined. Their identity as yet is not known.

On the IC one of the major developmental procedures was to attempt to condition the chromatographic columns to isopropyl alcohol (IPA). The columns used with the Dionex IC are normally run with water only as the solvent. 50% IPA/50% H_2O was tried as a solvent to run flux samples. The columns had to be conditioned to IPA gradually or the column resins would have swelled. Then the pressure would have become too great to run the samples.

By using a concentrator column, it is possible to carry analyses of samples on the IC into the parts-per-billion (ppb) range. Figure 38 represents the analysis of a standard with a known concentration of fluoride (F^-) ion and chloride (Cl^-) ion. The standard contained 250 ppb F^- and 500 ppb Cl^-; it was prepared using 50% IPA/50% H_2O as the solvent. The standard was used to calibrate the SP 4100 Computing Integrator. A sample of an RMA flux was then run. The flux sample was prepared by diluting 1 ml (milliliter) of flux to 1000 ml in 50% IPA/50% H^2O. Figures 39 and 40 represent two successive analyses of the same flux sample. Note the data following each chromatogram under the column headed "CONC". It is seen that the F^- concentration in the two runs is 333 ppb and 215 ppb. The large variation in the F^- concentration for the same sample confirms the fact that the concentration column cannot be used to quantify the amount of F^-. The F^- ion, unlike other anions, is not retained on the anion separator columns; therefore, during the concentration column loading process much of the F^- is flushed out as waste. This suggests it will not prove feasible to quantify F^- concentrations <1-4 ppm. However, it will still be feasible to detect F in the ppb range qualitatively. The chloride, Cl^-, concentrations for the two runs are 508 ppb and 534 ppb, which agree within 4.7%.

As pointed out, the chromatographic columns of the ion chromatograph (IC) had to be conditioned to isopropyl alcohol (IPA). The columns used with the IC are normally run with water only as solvent. A solvent mixture composed of 50% IPA/50% H_2O was intended to be used for samples having rosin flux.

Figure 41 represents a chromatogram obtained when a standard anion sample is run on the IC using water as the solvent for both the sample run and the eluent. The sample contained seven components - fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), bromide (Br^-), nitrate (NO_3), and sulfate (SO_4^{2-}). The amount of each component in the sample was: F^-, 3 ppm; Cl^-, 4 ppm; NO_2^-, 10 ppm; PO_4^{3-}, 50 ppm; Br^-, 10 ppm; NO_3, 30 ppm; SO_4^{2-}, 50 ppm. It can be seen from the chromatogram that each component has a corresponding peak which is well defined and that the concentrations reported agree closely with the actual concentrations. The chromatogram exhibits good baseline resolution. The time necessary to complete the run was 30 minutes.

Figure 42 represents a similar standard anion sample. The major difference between this and the sample used for Figure 41 is that PO_4^{3-} was left out and the solvent used was 50% IPA/50% H_2O. It can be seen that the first two peaks representing F^- and Cl^- are much smaller and less well defined than is seen in Figure 41. Judging from the size of the third peak and the fact that it shows a shoulder peak on the right, it is thought this peak represents NO_2^-, Br^- and NO_3^-, all eluting at approximately the same time. The last peak, that of SO_4^{2-}, is much broader and less well defined than that seen in Figure 41. The reason why peaks are less well defined in 50% IPA/50% H_2O is because IPA represses ionization of the sample components. The run time necessary for this sample was 55 minutes. This increased run time is because the flow rate must be reduced since IPA increases the back pressure. Column breakage may occur if the flow rate is not adjusted properly.

From the information supplied by the two chromatograms, it is evident that there are many disadvantages using 50% IPA/50% H_2O as the solvent for the IC. Chief among these are:

1 smaller, less well defined peaks on the chromatogram

2 poor separation of components into distinct peaks (NO_2^-, Br^-, NO_3^-)

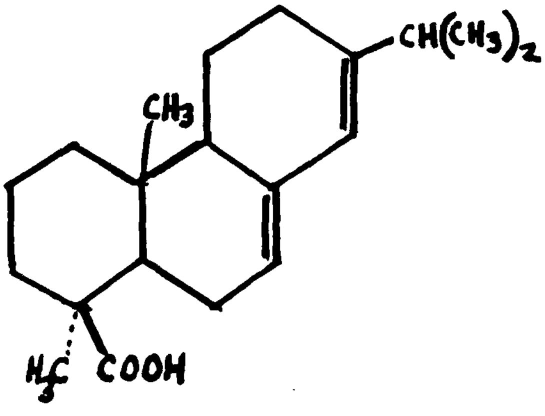
3 longer run time.

Using 50% IPA/50% H_2O as solvent, it will probably not be possible to carry analyses of samples on the IC into the parts-per-billion (ppb) range. This is truly unfortunate. To get away from using IPA in the solvent, i.e., using pure water as solvent, is one of the principal reasons using a water soluble flux is highly recommended. One is definitely not going to obtain as good results using 50% IPA/50% H_2O as one would using pure water.

The use of 50% isopropyl alcohol (IPA)/50% water as a solvent system for cleaning PW samples having rosin flux on them was mentioned. There are, however, attendant problems of a serious nature using IPA as was pointed out.

Further, a solvent system of 50% IPA/50% H_2O proved unsuitable as the solvent matrix for the metallic and quasimetallic species that must be aspirated through the nebulizer of the ICP 5000 torch in order that the species' spectral properties can manifest themselves. Serious torch instabilities ocurred causing the torch to extinguish suddenly. Because of these attendant difficulties, an alternative method was to solubilize any remaining rosin flux on the PWA at hand.

Two approaches seemed viable. Rosin, of course, is a complex mixture of organic acids, the principal constituent of which is abietic acid, having the following structural formula:



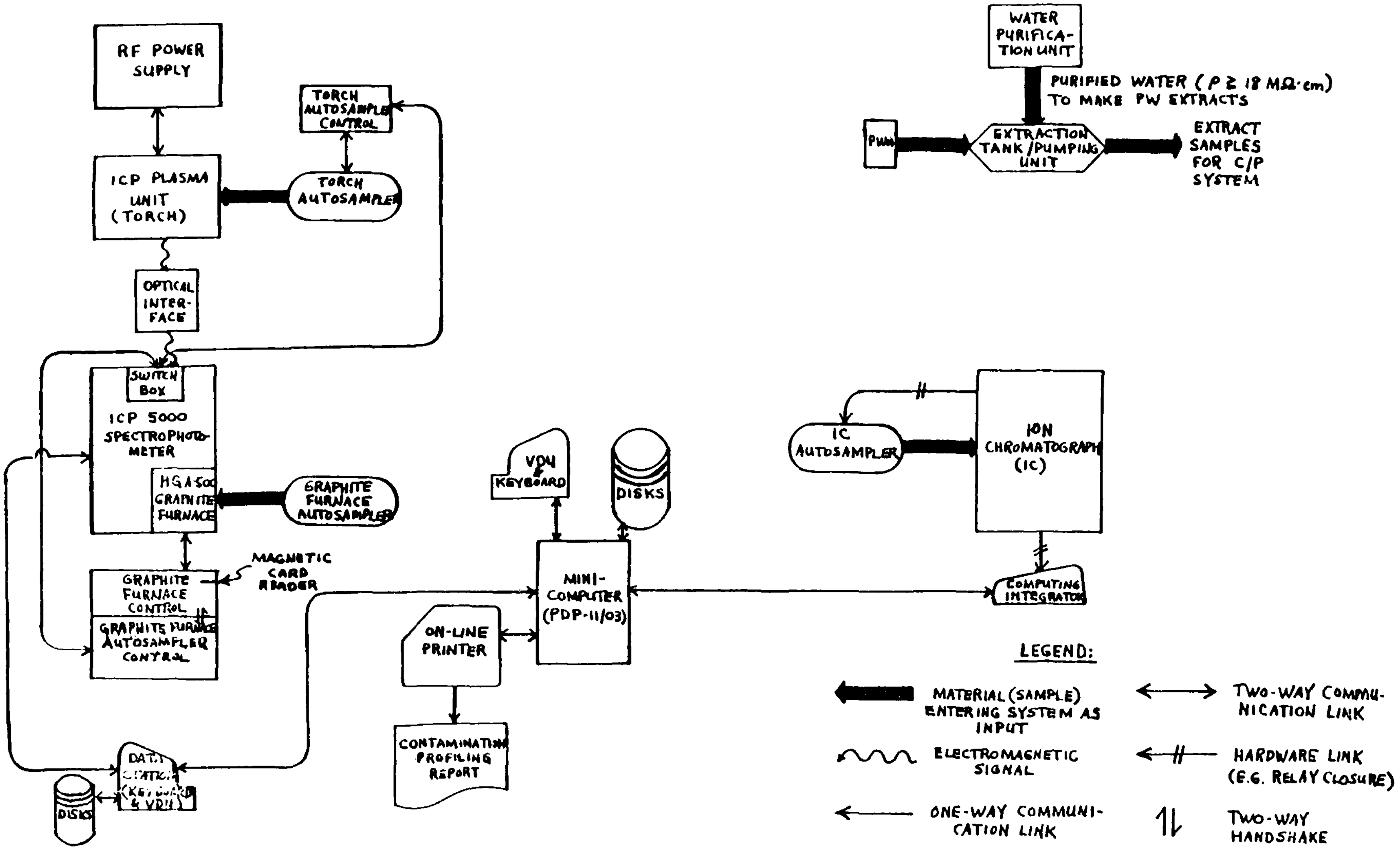


FIGURE 46. Present C/P System Hardware Configuration with Key Data Links

Turning back to the system hardware, Figure 46 illustrates the present hardware configuration of the C/P system. It also depicts the extent of total system integration, a phrase signifying the extent to which system control is effected through the system's minicomputer (MINC-11)., At present the C/P system is not fully integrated system (nor will it be by contract's end) due to certain hardware features beyond the control of the project personnel. It must be kept firmly in mind, however, that this in no way detracts from the C/P system's chief function, viz., to operate as an effective system for profiling different contaminant species found on PW surfaces. Further, total integration is not required for implementation or etticient system operation. The fact that it is not fully integrated (not 100%) merely means the anslyst/operator will have to pay more attention to some of the operating details in order to avoid errors. For example, to use the ICP-5000 Grahpite Furnace, the operator will have to manually insert a magnetic card into the Graphite Furnace Control unit and he (or she) will have to manually enter certain items for the sampling procedure via the keyboard on the AS-40 Autosampler Control unit. However, the MINC-11 will prompt the operator to perform these items by prompting him on the MINC VDU (CRT).

In view of the above, one might legitimately ask why were the above particular pieces of hardware chosen as systems components for the C/P system. There are two reasons:

1 The hardware performs the job intended, i.e., the analytical equipment allows detection of individual contaminant species.

2 The hardware chosen is the only hardware on the market that will allow for individual contaminant species detection in an extract solution.

The fact that the C/P system cannot be fully integrated at this point merely illustrates the unfortunate situation among analytical instrumentation vendors. They are not at present properly designing their equipment for integration with a host computer. They must recognize, and soon, that the trend today is for computer system integration and control and the construction of a data base for the computer system. In all fairness to the vendor of the ICP-5000, his system does go far in achieving this goa. Full integration, however, implies that the MINC-11 would exercise all or practically all ($\geq$97%) control functions and execute all error functions. At contract's end, 75% will be under minicomputer control. It is appropriate to discuss those hardware features that at present negate total system integration.

The ICP-5000 is itself deficient as a self-contained system in its own right, and its deficiencies prevent it from functioning optimally as a key unit in a fully computerized system using a host computer, notwithstanding the vendor's claims to the contrary. Its deficiencies center on several particular points. They are:

FURNCE instructs the ICP-5000 via its Data Station of the 5000 operating parameters for execution on the ICP-5000/furnace. The specific furnace parameters for any given element, e.g., furnace ashing and atomization times, must be fed into the HGA-500 furnace control via magnetic cards. FURNCE instructs the 5000 of all necessary spectrophotometric parameters for a given element on the furnace, e.g., the wavelength at which the element absorbs (the furnace operates in the atomic absorption mode), its elemental slit width, etc. FURNCE must also access HEAR, for it too must "listen" for any data feedback from the ICP-5000/furnace. After the FURNCE routine is through, all necessary data have been generated from a particular run. Since the IC is much slower than the ICP-5000/torch and furnace combined, ION is represented in the time sequence as extending from the time when INSTRU is initially called up by ICPEX to the time that FURNCE is completed. Since INSTRU is wiped out by DECIDE and DECIDE by FURNCE, both DECIDE and FURNCE each repectively in its turn must also call forth ION.

After all data have been collected, REPORT performs further manipulations on them (statistical treatment) and generates a final hard-copy print-out report.

It is strongly recommended that as contamination profiling proceeds on PWAs, a data based be constructed for future comparisons and further statistical treatment of the data. In this fashion, meaningful cutoff limits for each contaminant species can be established given the relevant PW design and process parameters, e.g., line widths/line spacings, circuitry density, plating and etching processes required, flux used, etc. In this way PW contaminant profiling can be founded on a firm scientific basis through the use of computer control, the proper analytical instrumentation, and an ever-broadening data base.

Regarding system hardware integration, work has been accomplished getting the IC/SP4100 computing integrator on line with the MINC-11 minicomputer. Recently the SP4100 was successfully interfaced with the MINC. To effect this, one of the MINC RS232 ports had to be manually converted to a 20 mA current loop. It was also found that the SP4100 must be run in the manual mode rather than the automatic since the IC, as is true of most other chromatographs, is subject to long range drift, i.e., a steady upward draft of the baseline. The SP4100 in automatic mode interprets this drift as a distinct chromatographic peak, which in reality it is not, and integrates it.

Regarding software development, the systems subroutines required to make use of the three MINC laboratory modules-- 1) digital-in mode, 2) digital-out mode, and 3) real-time clock--have been generated and stored in the total system library via floppy disk. These laboratory module subroutines enable the MINC to communicate with the IC. In particular, the routine ION in the MINC's main memory will call the lab module subroutines off disk as required, to talk to the IC.

the CRT screen, e.g., how wide or how narrow the characters are to be, the physical spacing of alphanumeric data on the screen, etc. HEAR is the routine to indicate to the MINC whether its hardware devices (the system hardware-- the ICP-5000/torch-furnace, IC) are sending data to the MINC. FPRINT refers to File Print and signifies the routine required to print out on the line printer all constant parameters of the system while in operation, e.g., wavelength settings, furnace operating parameters, tank extraction time, etc.

Going now to Segment 1 (intermediate addresses in memory), there is first SETUP. This is the first routine called into main memory by ICPEX. SETUP creates the CRT screen format and information (as opposed to the screen's physical qualities--CURSOR) to instruct its human operator what necessary steps must be initiated to start contamination profiling on an actual hardware printed wiring assembly (PWA). After SETUP has been executed, ICPEX calls up EXTRCT, which defines the necessary steps required to make a physical extraction in the extraction tank/pumping unit. Once the extraction phase has been completed, i.e., a physical extract has been made from the sample PWA, ICPEX calls up INSTRU. Of course, each time ICPEX calls up a routine into Segment 1, it wipes out the previously held routine. That is, INSTRU wipes out EXTRCT as EXTRCT wiped out SETUP and as DEFINE will wipe out INSTRU. No harm is done though as all the Segment 1 routines are kept in secondary storage on disk. INSTRU activates the ICP-5000/torch via the ICP Data Station. INSTRU defines the necessary operations needed to process sample extracts through the ICP-5000/torch. It sets all parameters and gives instructions to the torch through the Data Station. In the meanwhile, INSTRU also calls forth ION, the routine to initiate and define the various operations of the IC. Both INSTRU and ION must be linked to HEAR, i.e., they must both be "listening" whether their respective hardware units are producing data and attempting to send them to the MINC. As data are being generated by the torch, INSTRU must manipulate them appropriately and store them. The same is true of ION regarding data emanating from the IC. As data are generated by the IC, ION must manipulate them and store them.

As the sample is being physically treated by the ICP-5000, it is anticipated that the torch (emission spectrophotometer) will not suffice to perform the entire analysis for the sixteen analyte elements. No doubt some of the analyte concentrations will be too low to be detected by the torch. After the torch has passed its data to the MINC, DECIDE must be called up by ICPEX. DECIDE examines all data derived from INSTRU. Limits of concentration will have been previously set. If the concentration of a particular analyte species is at or below the acceptable torch detection limits, DECIDE will file the element's name and designate that the sample extract is to be run on the furnace for that particular element. After DECIDE has examined all data and "decided" which elements are to be analyzed for on the ICP-5000/furnace, ICPEX calls up FURNCE. FURNCE is the routine for the graphite furnace.

In addition to the effort required to patch together the RT-11--the specific RT-11 system for the C/P MINC had to be literally built up, or patched, from selecting different prepackaged portions provided by DEC--in addition to this, a great deal of effort has been expended on the writing of the C/P software operating system (as opposed to the MINC's indigenous operating system, the RT-11). The C/P operating system is being written in the FORTRAN programming language and will allow the MINC to operate and monitor the C/P hardware modules (ICP-5000/torch, ICP-5000/furnace, IC, computing integrator). It will, in addition, allow the MINC to interpret and manipulate all data it receives from its hardware modules. It will also support and execute the generation of a final hard-copy print-out displaying the following: the particular sample PWA's (1) part number (P/N), (2) serial number (S/N), and (3) lot number (LOT), (4) the date, (5) the time, and (6) the analyst. The analysis data themselves will appear on a separate print-out page. The analysis data will consist of: (1) element designated by its chemical symbol, (2) its concentration (mean value) as determined from three separate aliquots, (3) the standard deviation, s, and (4) the coefficient of variation, CV. Figure 44 lists the FORTRAN routines required for the C/P operating system. Approximately 60% of these routines have been completed.

Figure 45 illustrates in diagrammatical form the C/P software operating system stored in the MINC's main memory locations. The principal routines stored in Root, i.e., OTS, CURSOR, ICPEX, HEAR, and FPRINT, are kept in permanent main memory locations at low addresses in the memory. In addition, the routine ION is stored in permanent memory but at high addresses, hence, that portion in which it is stored is designated Segment 2. The other chief routines, SETUP, EXTRCT, INSTRU, DECIDE, FURNCE, and REPORT are called into main memory off disk storage by the system's executive routine, ICPEX, which calls each in turn as required. That is, each of the routines listed in Segment 1 of main memory does not permanently reside there but is called into memory sequentially with respect to time as required from disk storage.

Let us briefly describe the chief routines constituting the C/P software operating system. OTS (Object Time System) is the FORTRAN operant system, enabling all the other routines to be written in the FORTRAN programming language. Note its box in Figure 45 is marked with a ③. All other routines in the diagram (Figure 4) necessarily must be linked to this routine in order to be executed. This is indicated in the diagram in two different ways. Either a two-way arrow, ⟷, is employed or the symbol ③⟷ is used. It is not feasible in such a diagram to make use only of two-way arrows since the diagram would become unnecessarily cluttered, hence, the use of the symbol ③⟷ to indicate linking of a particular routine with OTS. The same significance is attached to the symbols ①⟷ , ②⟷ , and ④⟷ . ICPEX is the executive routine controlling when the various Segment 1 routines will be called off disk storage and placed into main memory for execution. CURSOR is the routine governing the physical attributes of

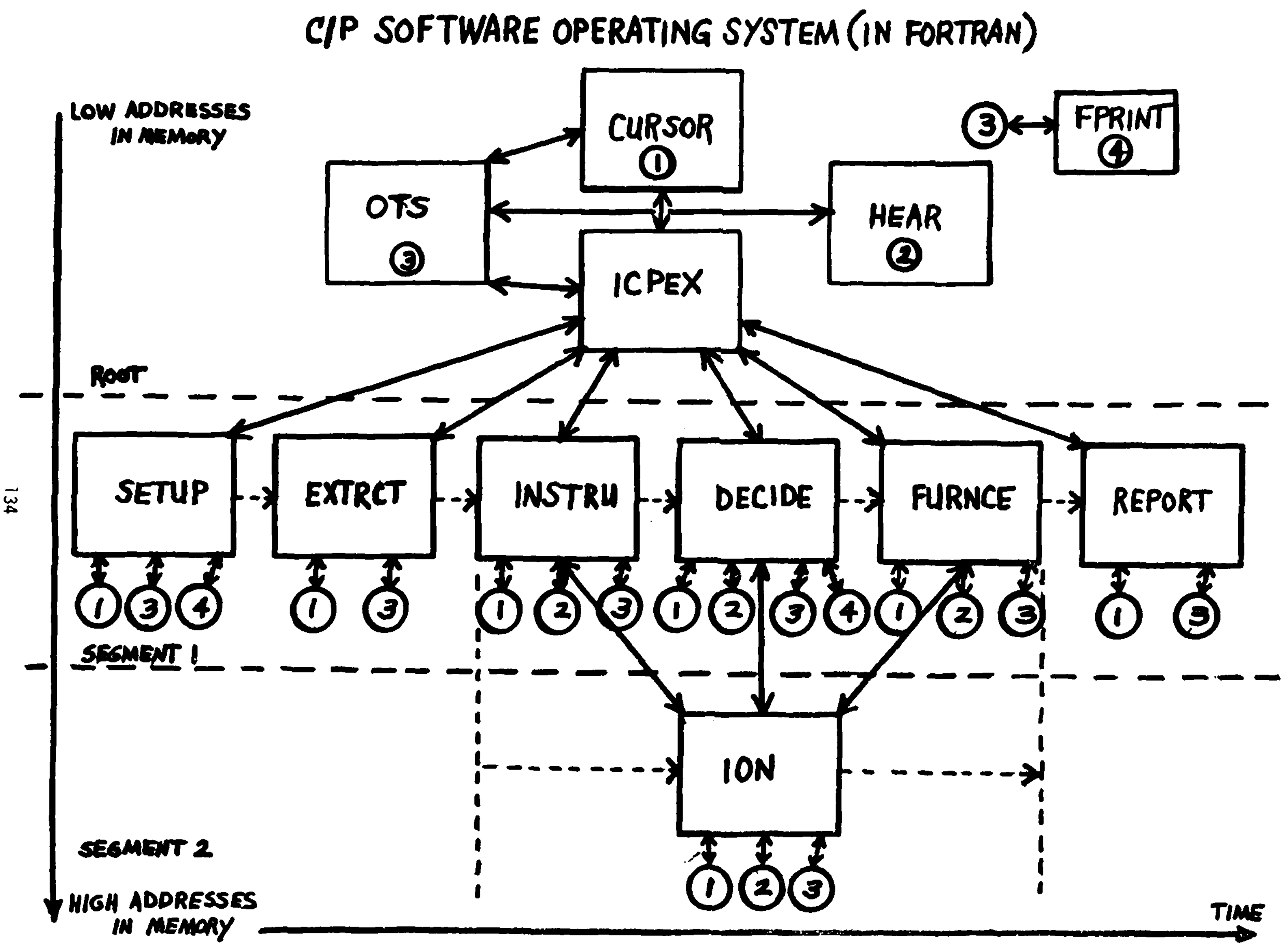


FIGURE 45. C/P Software Operating System in the MINIC's Main Memory Locations

```
 12-Feb-81
ALL    .COM     1  12-Feb-81       FPRINT.FOR     4  11-Feb-81
ATTRIB.FOR      2  11-Feb-81       FPRINT.OBJ     7  11-Feb-81
ATTRIB.OBJ      5  11-Feb-81       FURNCE.FOR     2  11-Feb-81
BELL   .FOR     2  11-Feb-81       FURNCE.OBJ     4  11-Feb-81
BELL   .OBJ     4  11-Feb-81       HEAR   .FOR    5  11-Feb-81
BINCOM.SAV     10P 08-Jan-81       HEAR   .OBJ    5  11-Feb-81
CK1    .LST     2  12-Feb-81       ICPEX  .BAK    6  12-Feb-81
CK2    .LST     2  12-Feb-81       ICPEX  .COM    1  12-Feb-81
CK3    .LST     3  12-Feb-81       ICPEX  .FOR    6  12-Feb-81
CLEAR  .FOR     1  11-Feb-81       ICPEX  .OBJ    5  12-Feb-81
CLEAR  .OBJ     5  11-Feb-81       ICPEX  .SAV   55  12-Feb-81
CLOCK  .SAV    17  03-Jan-81       INIT   .COM    1  05-Feb-81
CLRSTR.FOR      1  10-Feb-81       INIT   .SAV   18  29-Jan-81
CLRSTR.OBJ      4  11-Feb-81       INSTRU.FOR    21  11-Feb-81
COMPIL.COM      1  09-Feb-81       INSTRU.OBJ    17  11-Feb-81
CONVRT.FOR      1  11-Feb-81       ION    .FOR    3  11-Feb-81
CONVRT.OBJ      4  11-Feb-81       ION    .OBJ    5  11-Feb-81
CREATE.COM      1  12-Feb-81       LNKNO  .COM    1  11-Feb-81
CREF   .SAV    6P  08-Jan-81       LNKYES.COM     1  11-Feb-81
CURSOR.HLP      4  04-Jan-81       MOVCUR.FOR     3  11-Feb-81
DAILY  .COM     1  12-Feb-81       MOVCUR.OBJ     6  11-Feb-81
DATTIM.COM      1                  NOW    .COM    1  11-Feb-81
DECIDE.FOR      2  11-Feb-81       OLDICP.SAV    47  10-Feb-81
DECIDE.OBJ      4  11-Feb-81       PAT    .SAV   8P  08-Jan-81
DISK   .BAK     2  12-Feb-81       PATCH  .SAV  10P  08-Jan-81
DISK   .FOR     2  12-Feb-81       REPORT.FOR    11  11-Feb-81
DISK   .OBJ     5  12-Feb-81       REPORT.OBJ    13  11-Feb-81
DISK   .SAV    15  12-Feb-81       REPORT.SAV    22  11-Feb-81
DOUBLE.FOR      6  11-Feb-81       SAVE   .LST    1  11-Feb-81
DOUBLE.OBJ      6  11-Feb-81       SCROLL.FOR     4  11-Feb-81
DUMP   .SAV    8P  08-Jan-81       SCROLL.OBJ     6  11-Feb-81
EACHR  .COM     1  12-Feb-81       SEQ    .DAT    1  12-Feb-81
ERASED.FOR      2  11-Feb-81       SETUP  .FOR   21  11-Feb-81
ERASED.OBJ      5  11-Feb-81       SETUP  .OBJ   20  11-Feb-81
ERASEL.FOR      2  11-Feb-81       SIPP   .SAV  20P  08-Jan-81
ERASEL.OBJ      5  11-Feb-81       SLP    .SAV   9P  08-Jan-81
EXTRCT.FOR     12  11-Feb-81       SRCCOM.SAV   13P  08-Jan-81
EXTRCT.OBJ     10  11-Feb-81       STARTS.BAK     1  12-Feb-81
FILE   .BAK     2  12-Feb-81       STARTS.COM     1  12-Feb-81
FILE   .FOR     2  12-Feb-81       TALK   .FOR    3  05-Feb-81
FILE   .OBJ     5  12-Feb-81       TCHAO  .LST    5  12-Feb-81
FILE   .SAV    15  12-Feb-81
 83 Files, 582 Blocks
 392 Free blocks
```

FIGURE 44. FORTRAN Routines for the C/P Operating System

```
   12-Feb-81
  SWAP  .SYS    25P 07-Oct-80  → LP    .SYS      2P 08-Jan-81
  NL    .SYS     2P 08-Jan-81  → DY    .SYS      4P 08-Jan-81
  RT11SJ.MAP    21P 08-Jan-81    RT11FB.MAP     28P 08-Jan-81
→ RT11SJ.SYS    71P 08-Jan-81    RT11FB.SYS     85P 08-Jan-81
  SYCND .MAC     5P 08-Jan-81    SYSTBL.MAC     21P 08-Jan-81
  SYSBLD.COM     1P 08-Jan-81    MONBLD.COM      3P 08-Jan-81
  DEVBLD.COM     2P 08-Jan-81  → SRCCOM.SAV     13P 08-Jan-81
  BINCOM.SAV    10P 08-Jan-81    SLP   .SAV      9P 08-Jan-81
→ DUMP  .SAV     8P 08-Jan-81    SIPP  .SAV     20P 08-Jan-81
  PATCH .SAV    10P 08-Jan-81    PAT   .SAV      8P 08-Jan-81
  ERROUT.SAV    17P 08-Jan-81    QUEMAN.SAV     13P 08-Jan-81
  HELP  .SAV   107P 08-Jan-81  → PIP   .SAV     23P 08-Jan-81
→ DUP   .SAV    41P 08-Jan-81  → FORMAT.SAV     19P 08-Jan-81
  RESORC.SAV    15P 08-Jan-81  → DIR   .SAV     17P 08-Jan-81
→ KED   .SAV    60P 08-Jan-81    MACRO .SAV     51P 08-Jan-81
  CREF  .SAV     6P 08-Jan-81    LINK  .SAV     41P 08-Jan-81
→ LIBR  .SAV    22P 08-Jan-81    SYSMAC.SML     42P 08-Jan-81
  SYSLIB.OBJ    47P 08-Jan-81    ODT   .OBJ      9P 08-Jan-81
  STARTS.COM     1P 08-Jan-81    BACKUP.COM      1  08-Jan-81
  P     .COM     1               DUPLIC.COM      1  08-Jan-81
  Q     .COM     1  13-Jan-81    A     .COM      1  13-Jan-81
   42 Files, 884 Blocks
 _ 90 Free blocks
```

FIGURE 43. Disk Dump of the Various RT-11 Routines

The conclusion of this is it would be much easier to characterize water-soluble fluxes than rosin-based organic fluxes because

1 there would be no deleterious solvent problem as regards the chromatographic columns because pure water would be the extractant

2 this kind of flux is man-made, not natural, hence the characteristic composition will be fixed according to specific manufacturing procedures

3 they probably are not as complicated chemically as regards the number of distinct chemical species as rosin-based fluxes.

Now Requirement 5 of Mil-Std-454E states that an R or RMA flux shall be used except that an RA flux may be used if cleanliness testing per Mil-P-28809 is applied. It is hoped that the military requirements can be extended to cover water-soluble fluxes since an adequate method can be used to ascertain production cleanliness of PW after flux/soldering, viz., contaminant profiling via the C/P system.

3.3 THE MINICOMPUTER CONTROL SYSTEM

Probably the most important piece of equipment in the contaminant profiling system in the minicomputer for final analysis and system control.

With the printed wiring contaminant profiling (PW C/P) system we necessarily concentrated heavily on software development. This is especially critical since the C/P hardware is to be run and monitored by the system's minicomputer (the DEC MINC-11). In addition, all data handling, manipulation, and printout are to be performed by the MINC. The MINC operating system, the RT-11 (RT = Real Time) comprises a monitor/executive program for MINC system control and supervision; several device handlers (programs), one for each of the supported hardware devices; a variety of utility support routines for system software routines/data manipulation; and finally, the interfaces necessary to support programming language processors. Figure 43 depicts a disk dump of the various RT-11 routines. Some of its chief routines are:

RT11SJ.SYS	single job monitor
DUMP .SAV	dump memory
DUP .SAV	file management
KED .SAV	editor
LIBR .SAV	library
LP .SYS	line printer handler
DY .SYS	disk handler
SRCCOM.SAV	compares two files
PIP .SAV	file exchange
FORMAT.SAV	formats disks
DIR .SAV	prints directory.

The results indicate that ammonia < surfactant $\approx$ 50 percent surfactant + 50 percent monoethanolamine $\approx$ rosin saponification product 1 $\approx$ rosin saponification product 2; $\approx$ signifies "about equal to" where < signifies "worse than". Note that items 2-5 give almost identical results. However, since the surfactant is a pure substance whereas the others (surfactant/monoethanolamine and rosin saponification products 1 and 2) are mixtures, it seemed preferable to use only surfactant alone since it does an equally good job.

The problem with using the surfactant is that a thorough qualification test must be performed before it can routinely be used in military PW. Further, although the surfactant itself is nonionic, its method of production involves ionic catalysts which proved impossible to remove. Naturally this interferred with the analysis. For this reason, the only solvent that will be used at present will be pure demineralized water. It is assumed that most harmful ionic species will come off the PW surface in the water. If there are any entrapped under polymerized rosin, these probably would not prove troublesome. It is highly unlikely they would leach out of the polymerized rosin.

It is not out of place to say a few words about fluxes at this point. At present MMC is employing RMA fluxes for the soldering process. Rosin fluxes are, of course, complex mixtures composed of many weakly acidic species, such as abietic acid, neoabietic acid, pimaric acid, etc. Rosin is a natural product. It is the non-steam volatile portion of pine gum, and its specific composition will vary depending on the source of the raw rosin. In short, the RMA flux marketed by a particular manufacturer is likely to vary depending on where he obtained his raw gum rosin.

Further, it is well known that both exposure to oxygen and to heat will change the chemical structure of some of the components of rosin. The abietic-type acids (abietic, neoabietic, levopimaric, palustric), for example, are more prone to take up oxygen because of their conjugated double bonds than the pimaric-type acids (pimaric, isopimaric). Further, heating of abietic acid will cause a disproportionation to a pyroabietic acid mixture containing dehydroabietic and tetrahydroabietic acids, both of which are chemically inert and therefore resistant to oxidation. These known facts of rosin fluxes are likely to make them difficult to characterize chemically on the ion chromatograph.

In addition, any particular manufacturer's RMA flux will contain a small amount of proprietary activators (e.g., halides, non-rosin organic acids, amines, amides, etc.). These too must be characterized.

Finally, the solvent that must be used to dissolve the rosin flux must be carefully considered. It was expected that a 50% H_2O (water)/50% IPA (isopropyl alcohol) extractant would prove feasible to both dissolve the rosin flux and to lead to no problems with the chromatographic columns. However, it is recognized that the ion-exchange resins used in the chromatographic columns are often sensitive to other solvents, and this can sometimes lead to their subsequent deterioration if water alone is not used. For reasons pointed out above, 50% H_2O/50% IPA did not prove satisfactory.

As displayed in the test matrix, all methods of rosin removal were effective when the extraction time was two (2) hours. For a one (1) hour extraction time, however, it is seen that LFF > NFF > NH_3 where > signifies "better than". The flux supplied by vendor 2 can be removed easier by all three methods than flux supplied by vendor 1. Actually, it would be more correct to say that the flux batch produced by vendor 2 was removed easier than the flux batch of vendor 1. This way of specifying the situation is necessary since rosin fluxes are derived from natural sources and their compositions can and do vary somewhat due to fluctuations in supply conditions. By this is meant that a particular given rosin flux of a particular given vendor will probably have a slightly varying composition from batch to batch due to supply factors (it may contain a fixed proportion of activator, however). It seems evident, therefore, that the use of a natural source product such as rosin in the manufacturing of PWBs will always necessitate a qualification test to be repeated at certain intervals, i.e., if high reliability PWBs are the desideratum. Hence, a suitable method of chromatography (liquid or preferably FID gas) should be employed to qualify the use of LFF surfactant to remove rosin. The chromatographic technique will be used to fingerprint both rosin and surfactant and to demonstrate removal of surfactant. Although the surfactant is nonionic, it is wise to ascertain that the nonionic surfactant species has been completely removed from the PW surface.

Regarding the extraction procedure to be used for the printed wiring (PW), five different materials were used to clean rosin from PWB substrate. A volume of 50 μl of rosin (2 different RMA rosin fluxes were used in the experiment) was applied to a 1 in x 1.5 in coupon. The flux was then heated to solder temperature by passing the coupons through a solder belt reflow machine. An attempt was then made to clean the coupons in the PW extraction tank using each of the five different materials. These materials included:

1 Ammonia, NH_4OH

2 Surfactant (low foaming)

3 50 percent surfactant + 50 percent monoethanolamine (common ingredient of rosin saponification formulations)

4 Rosin saponification product 1 (produced by vendor 1)

5 Rosin saponification product 2 (produced by vendor 2).

The PWB substrate material was then tested for rosin using the Liebermann-Storch (L/S) test.

Table 13
TEST MATRIX

Method of Extraction \ Time	T_1 1 hour	T_2 2 hours
	F_{11} +	F_{11} -
NH_3	F_{12} +	F_{12} -
	F_{21} +	F_{21} -
	F_{22} -	F_{22} -
	F_{11} +	F_{11} -
NFF	F_{12} +	F_{12} -
	F_{21} -	F_{21} -
	F_{22} -	F_{22} -
	F_{11} +	F_{11} -
LFF	F_{12} -	F_{12} -
	F_{21} -	F_{21} -
	F_{22} -	F_{22} -

The fluxes were allowed to dry in air for 48 hours.

Blanks were also run in duplicate in all cases and consistently tested negative for rosin by the L/S test as expected.

Surfactants 1 and 2 are both produced by the same vendor because no other vendor's surfactants appeared promising based on preliminary evaluations. Two different extraction times were used--1 hour and 2 hours. The Liebermann-Storch test was employed to check for traces of rosin ≥ 75 parts-per-billion (ppb). Each flux was run in duplicate. The results are summarized in the test matrix displayed below.

<u>LEGEND</u>

<u>1</u> ++ = positive L/S test for rosin

+ = faintly positive L/S test for rosin

\- = negative L/S test for rosin

<u>2</u> RMA flux 1, trial #1 = F_{11}

RMA flux 1, trial #2 = F_{12}

<u>3</u> RMA flux 2, trial #1 = F_{21}

RMA flux 2, trial #2 = F_{22}

There are other organic acids containing in rosin in addition to abietic, and most are isomeric to abietic. Natural rosin also contains a small amount of inert materials, probably polymeric in nature. Based on its chemical constituents, the two approaches to solubilizing rosin are these:

1 Seek a suitable surfactant having the ability to solvate the rosin using essentially the same mechanism by which organic "dirts" are removed by soaps and detergents. That is, the surfactant should possess a hydrophobic and a hydrophilic end, the hydrophobic responsible for the dissolution of the rosin. Preferably, the surfactant would have near neutral pH. Thus, the use of a nonionic surfactant was suggested.

2 Use an alkaline material ($pH>7$) to saponify the rosin, causing it to go into water solution as rosin salts.

After trying approximately twelve different commercial nonionic surfactants, one particular kind was found to remove rosin quite well. Its chemical type is: ethoxylated tridecylalcohol. The solution concentration needed is 2-5%. Further investigation is required to choose the optimal concentration; however, preliminary work indicates that a 5% solution will be necessary. Regarding alkaline material, a 1% solution of ammonia (NH_3) will also successfully remove rosin. Although the pH 10, no apparent harm is caused the PWA, apparently because the ammonia volatilizes. However, further investigation is required before one can say this positively. *The IC can be used to check* the efficient removal of the ammonia since it has the capability to perform an analysis for ammonia.

Both approaches proved to be successful.

The materials used were these:

1 Ammonia, NH_3 or NH_4OH (in aqueous solution)

2 Surfactant 1, normal foaming formulation (NFF)

3 Surfactant 2, low foaming formulation (LFF)

4 RMA flux 1, F_1 (produced by vendor 1)

5 RMA flux 2, F_2 (produced by vendor 2).

1 The ICP-5000 Data Station (6800 microcomputer) is powerful and can communicate effectively with the 5000 Spectrophotometer. It passes control and program information to the 5000 and receives back data for manipulation and storage which it passes to the MINC. The Data Station's disk storage holds the furnace files, the torch files, and the operating files to run the torch and furnace. The Data Station, however, exercises no control over the Graphite Furnace Control unit. This must manually be operated by a magnetic card. Nor does the Data Station exert control over the Graphite Furnace Autosampler Control unit (operated manually by a keyboard) or the Torch Autosampler Control unit (has only ON/OFF switch). Since the Data Station with its 6800 chip microprocessor and RAM memory is the key element in linking the ICP-5000 system with a host computer (the MINC-11 in this case), the Data Station's failure to communicate with the Graphite Furnace Control unit and both Autosampler Control units means that the host computer cannot either. Hence, as far as the MINC is concerned, the Graphite Furnace Control unit and both Autosampler Control units are offline.

2 This second point concerns the IC. The way the IC was built, it contains a solid state programmer - not a microprocessor, makes it impossible to communicate with. The IC does not really talk to its Autosampler or to its Computing Integrator; rather, it merely hardwire activates realy closures to indicate it is ready to have samples fed to it by the Autosampler or when it is ready to dump data to the Computing Integrator after a run. This means, in effect, the real data control for the Computing INtegrator is via the IC, not the MINC, even though the MINC can talk directly to the Computing Integrator. So, as far as the MINC is concerned, the IC is offline also. This fact has necessitated a very careful software timing sequence during the torch/furnace data acquisition and manipulation by the MINC to ensure that the SP 4100 does not have a data set from a particular IC run wiped out by the IC (when it is ready to send more data to the SP 4100) before the SP4100 can transmit the data to the MINC.

It is appropriate to consider here the C/P system from the point of view of system control. Review again the system schematic as depicted in Figure 15 . The system control itself forms a hierarchy, and the major components of this hierarchy are depicted in Tables 14, 15, and 16.

This completes the discussion of total system hardware integration at this point. Hopefully, while building a contaminant profiling (C/P) data base, the problem of more complete integration of system hardware can be addressed and some of the equipment can be modified in a hardware fashion to permit this.

Table 14

CONTAMINANT PROFILING SYSTEM CONTROL HIERARCHY

SYSTEM CONTROL -- HIgh Level Command

- * MINC Mincomputer

INSTRUMENT CONTROL -- Middle Level Command

- * Perkin Elmer M3600 Data Station
- * Specta Physics SP-4100 Computing Integrator

MACHINE CONTROL -- Low Level Command

- * 6800 Microprocessor
- * 8008 Microprocessor
- * 4004 Microprocessor

Table 15

SYSTEM CONTROL TECHNICAL REQUIREMENTS

SYSTEM CONTROL

* Interface with human operator and Instrument Level Control.
* Decide which analyses are to be performed on each instrument (define task).
* Accept data and prepare reports.

INSTRUMENT CONTROL

* Interface with System Level Control and Machine Level Control.
* Have knowledge of analytical parameters for each elements for instrument.
* Compute analytical results from raw input data.

MACHINE CONTROL

* Interface with Instrument Level Control and machine devices (stepping motors, etc.).
* Have capability to operate stepping motors, valves, defraction gratings, temperature controllers, and the like.
* Read raw data and convert to digital form.

Table 16

INPUT / OUTPUT AT EACH SYSTEM LEVEL

SYSTEM CONTROL INPUTS

* From human: Commands (RUN), Identifying data (Board S/N, P/N, Operator's Name).
* From Inst. Level: Processed Data.

SYSTEM CONTROL OUTPUTS

* To human: Final reports.
* To Inst. Level: Control Commands (RUN CU)

INSTRUMENT CONTROL INPUTS

* From System Level: Control Commands
* From Mach. Level: Handshaking (Ready line), Raw Data Values (321453).

INSTRUMENT CONTROL OUTPUTS

* To System Level: Processed Data (2.01 PPB)
* To Mach. Level: Machine Control Commands (Step to 189.9 nm).

MACHINE CONTROL INPUTS

* From Inst. Level: Machine Control Commands
* From Components: Handshaking (Ready lines), Analog Data (0.476 v).

MACHINE CONTROL OUTPUTS

* To Inst. Level: Handshaking, Raw Data Values
* To Components: Component Level Commands (Logical 1 to Port OECH on line 3 for 5 ms.).

3.4 SETTING CONTAMINANT LIMITS WITH THE CONTAMINANT PROFILING SYSTEM

It is necessary to set initial contaminant levels using the contaminant profiling (C/P) system.

Attention was turned to addressing the problem of setting realistic limits, within the scope of our present knowledge, for the amount of contamination on a printed wiring assembly (PWA). As was pointed out, the comtaminant profiling (C/P) system instrumentation will detect and intepret the amounts of contaminant species in an extract in terms of parts-per-billion (ppb). This latter term, a concentration unit, can easily be converted into the number of micrograms per square centimeter ($\mu g/cm^2$) of each contaminant species, given that the total area of the PWA and the extract volume are entered into the C/P system's databank as system parameters.

It is agreed that what is required is to link the presence and amount of each species on the PW surface to PW degradation. A rigorous testing and evaluation shceduld in which the contribution to degradation and the concomitant threshold limits of each contaminant species should be performed for different PW configurations, packaging densities, and component types. The data generated from this extensive testing and evaluation phase can then be used to build a data base for C/P.

However, due to the time limitation imposed on the present program, the best approach to establishing meaningful first limits of contaminant species is to relate their toal amounts back to the existing military specification, MIL-P-28809. It was remarked in the Final Report for Phase I on the contract that the amount of NaCl (sodium Chloride) necessary to cause a resistivity change from 6.0 $M\Omega cm$ to 2.0 $M\Omega cm$ is $0.94\ \mu g/cm^2 \approx 1.0\ \mu g/cm^2$. This was assuming a PW whose surface area is A $inch^2$ (both sides included). Since 6.45 cm^2 = 1 $inch^2$, the PW surface = 6.45 A cm^2. This also presumes the entire quantity of NaCl is eluted into the test extract having a volume of 10 A ml since, according to MIL-P-28809, 1 $inch^2$ of PW surface = 10 ml of extract after washing. This amount is meaningful for PW having conductor line widths/line spacings $\geq$ 10 mils (0.010 inch) and average component densities (assuming no leadless components). This value, i.e., 1.0 $\mu g/cm^2$ as representing the threshold value for NaCl for the above conductor line widths/line spacings is also supported by the insulation resistance (IR) work of Dr. W. Bernard Wargotz (Dr. W. Bernard Wargotz, "Quantification of Contaminant Effects upon Electrical Behavior of Printed Wiring," IPC Technical Paper, Sept. (1977)).

However, it is obvious that NaCl will not be the only contaminant. Hence one must find the governing parameter for relating concentrations of different contaminant species back to MIL-P-28809. This parameter is the solution neutrality. The governing equation is

$$\kappa = 0.001\Lambda_o c + \kappa_{sol} \qquad (1)$$

where c is the concentration of ionizable material in equivalents/liter (normality); Λ_o, the equivalents conductance at infinite dilution, and and κ_{sol} the specific conductance of solution and pure solvent respectively. Further, the specific resistivity, ρ, is related to the specific conductance by the following equation:

$$\rho = 1/\kappa \qquad (2)$$

In the Final Report for Phase I, it was remarked that a concentration of $C = 10.41 \times 10^{-6}$N would result in a resistivity drop from 6 MΩ·cm to 2 MΩ·cm for an isopropyl alcohol (75%) /water (25%) solution as employed for MIL=P=28809. This concentration, then, will be used as the threshold concentration for contaminant species on a PWA. That is, when the total extract concentration equals to or surpasses this concentration, the PWA will have failed the C/P test.

To find the total extract normality, the number of μg/cm^2 of each contaminant species must be divided by the respective equivalent weight of each species, the result summed over all species and divided by 2 (since there are both positive and negative species). That is

$$\text{c (total normality)} = 645 \times 10^{-6} \left[\left(\sum_{i}^{\substack{\text{all}\\ \text{positive}\\ \text{species}}} C_i/\chi_i + \sum_{i}^{\substack{\text{all}\\ \text{positive}\\ \text{species}}} C_i/\chi_i\right)/2\right] \qquad (3)$$

where C_i is the respective concentration of species i in the μg/cm^2 and χ_i is its respective equivalent weight. The factor 645 arises because it is assumed the area, A, of the PWA was originally given in inch^2.

Based on calculations such as these, the following two reports (Figures 47 and 48)* illustrate the C/P report format showing

1 the PW part number (P/N), serial number (S/N), and lot number (LOT)
2 the date and time of analysis
3 the analyst
4 the instrumentation used for the cationic (positive) species - either inductively coupled Argon plasma emission spectroscopy (ICP-5000) or graphite furnance atomic absorption spectroscopy (5000-AA)
5 the instrumentation used for the anionic (negative) species - ion chromatography (IC)
6 the species analyzed for - using appropriate chemical symbolism
7 the species concentration in parts-per-billion (ppb) (This is a mean value based on three readings)

CONTAMINATION PROFILING
REPORT

P/N : AY0-12769-00000

S/N : 000034

LOT : N201

DATE: 07-JUL-81 TIME: 12:32:21

ANALYST ____________________________

V. A. DE GIORGIO

FIGURE 47. Contamination Profiling Report (Example) of a PWA Passing Test

Cations

- By Inductively Coupled Argon Plasma Emission Spectroscopy

ELEMENT	CONC./ WEIGHT	STD. DEV.	COEFF. OF VAR.	CONC./ BOARD AREA

Cations

- By Graphite Furnace Atomic Absorption Spectroscopy

ELEMENT	CONC./ WEIGHT	STD. DEV.	COEFF. OF VAR.	CONC./ BOARD AREA
P	10. PPB	+/- 0.9	9.04 %	0.016 ug/sq.cm
SI	9. PPB	+/- 2.1	23.54 %	0.014 ug/sq.cm
K	0. PPB	+/-******	***** %	0.000 ug/sq.cm
PB	70. PPB	+/- 4.1	5.91 %	0.109 ug/sq.cm
SN	35. PPB	+/- 0.8	2.34 %	0.054 ug/sq.cm
CR	11. PPB	+/- 0.1	0.68 %	0.017 ug/sq.cm
ZN	21. PPB	+/- 0.2	0.72 %	0.033 ug/sq.cm
CU	43. PPB	+/- 0.5	1.22 %	0.067 ug/sq.cm
NI	0. PPB	+/-******	***** %	0.000 ug/sq.cm
AU	0. PPB	+/-******	***** %	0.000 ug/sq.cm
FE	19. PPB	+/- 0.4	2.23 %	0.029 ug/sq.cm
MG	0. PPB	+/-******	***** %	0.000 ug/sq.cm
PD	7. PPB	+/- 0.9	12.57 %	0.011 ug/sq.cm
CA	46. PPB	+/- 0.1	0.30 %	0.071 ug/sq.cm
AL	10. PPB	+/- 0.1	1.15 %	0.016 ug/sq.cm
NA	46. PPB	+/- 4.5	9.84 %	0.071 ug/sq.cm

FIGURE 47. (continued)

```
                         Anions

                 - By Ion Chromatography

SPECIES   CONC./ WEIGHT   STD. DEV.   COEFF. OF VAR.   CONC./ BOARD AREA
-------   -------------   ---------   --------------   -----------------

  F            15. PPB    +/-   1.0          6.42 %      0.023 ug/sq.cm

  CL          188. PPB    +/-   9.8          5.23 %      0.291 ug/sq.cm

  NO2           0. PPB    +/-   0.1        100.00 %      0.000 ug/sq.cm

  NO3           0. PPB    +/-   0.5        100.00 %      0.000 ug/sq.cm

  BR           36. PPB    +/-   3.7         10.27 %      0.056 ug/sq.cm

  PO4          98. PPB    +/-   7.2          7.32 %      0.152 ug/sq.cm

  SO4          25. PPB    +/-   1.2          4.99 %      0.039 ug/sq.cm


                  TOTAL  CONTAMINANTS
                  -------------------

            Total Cationic Species =    0.507 ug/sq.cm

            Total Anionic  Species =    0.561 ug/sq.cm
                                       --------

                             TOTAL =    1.068 ug/sq.cm


 - Based on the above analysis, this PWB:
   PASSES  the Contaminant Profiling Test.
   ------
```

FIGURE 47. (continued)

CONTAMINATION PROFILING REPORT

P/N : AY0-12769-00000

S/N : 000067

LOT : N202

DATE: 07-JUL-81 TIME: 09:15:03

ANALYST ______________________

V. A. DE GIORGIO

FIGURE 48. Contamination Profiling Report (Example) of a PWA Failing Test

Cations

- By Inductively Coupled Argon Plasma Emission Spectroscopy

ELEMENT	CONC./ WEIGHT	STD. DEV.	COEFF. OF VAR.	CONC./ BOARD AREA
CU	231 PPB	+/- 5.1	2.2 %	0.358 ug/sq.cm
CA	430 PPB	+/- 4.7	1.1 %	0.667 ug/sq.cm
AL	200 PPB	+/- 4.8	2.4 %	0.310 ug/sq.cm
NA	543 PPB	+/- 57.6	10.6 %	0.842 ug/sq.cm

Cations

- By Graphite Furnace Atomic Absorption Spectroscopy

ELEMENT	CONC./ WEIGHT	STD. DEV.	COEFF. OF VAR.	CONC./ BOARD AREA
P	0. PPB	+/-******	***** %	0.000 ug/sq.cm
SI	24. PPB	+/- 0.8	3.40 %	0.037 ug/sq.cm
K	0. PPB	+/-******	***** %	0.000 ug/sq.cm
PB	45. PPB	+/- 2.1	4.77 %	0.070 ug/sq.cm
SN	70. PPB	+/- 1.0	1.42 %	0.109 ug/sq.cm
CR	5. PPB	+/- 0.1	1.04 %	0.008 ug/sq.cm
ZN	17. PPB	+/- 0.2	1.00 %	0.026 ug/sq.cm
NI	0. PPB	+/-******	***** %	0.000 ug/sq.cm
AU	0. PPB	+/-******	***** %	0.000 ug/sq.cm
FE	10. PPB	+/- 0.3	2.55 %	0.016 ug/sq.cm
MG	0. PPB	+/-******	***** %	0.000 ug/sq.cm
PD	3. PPB	+/- 0.2	5.93 %	0.005 ug/sq.cm

FIGURE 48. (continued)

```
                              Anions

                     - By Ion Chromatography

SPECIES   CONC./ WEIGHT   STD. DEV.   COEFF. OF VAR.   CONC./ BOARD AREA
-------   -------------   ---------   --------------   -----------------

  F            20. PPB    +/-   0.7        3.50 %         0.031 ug/sq.cm

  CL         2586. PPB    +/-  69.2        2.67 %         4.009 ug/sq.cm

  NO2           0. PPB    +/-   0.1      100.00 %         0.000 ug/sq.cm

  NO3           0. PPB    +/-   0.5      100.00 %         0.000 ug/sq.cm

  BR            0. PPB    +/-   0.0      100.00 %         0.000 ug/sq.cm

  PO4           0. PPB    +/-   0.1      100.00 %         0.000 ug/sq.cm

  SO4          70. PPB    +/-   2.6        3.76 %         0.109 ug/sq.cm


                      TOTAL CONTAMINANTS
                      ------------------

              Total Cationic Species =    2.447 ug/sq.cm

              Total Anionic  Species =    4.149 ug/sq.cm
                                        --------

                               TOTAL =    6.595 ug/sq.cm


 - Based on the above analysis, this PWB:
   FAILS     the Contaminant Profiling Test.
   -----
```

FIGURE 48. (continued)

8 the standard deviation (s) and coefficient of variation (s/$\overline{X}$) of the species concentration (ppb)
9 the species concentration in $\mu g/cm^2$
10 the total cationic species concentration in $\mu g/cm^2$
11 the total anionic species concentration in $\mu g/cm^2$
12 the grand total concentration of all species in $\mu g/cm^2$
13 statement as to whether given PWA passes or fails the C/P test (based on above total neutrality of extract).

3.5 THE CONTAMINANT PROFILING SYSTEM: AN OVERVIEW.HEREIN IS PRESENTED A FINAL OVERVIEW OF THE CONTAMINANT PROFILING (C/P) SYSTEM

To gain a better perspective, the total system hardware will be reviewed. Several of the contaminant profiling (C/P) system components can be regarded as systems in their own right since they can be further decomposed or broken down into a number of distinct subcomponents. Since the C/P system minicomputer is the host computer for the entire C/P system, the other components are called subsystems. These are:

1 One (1) inductively-coupled plasma (ICP) spectrophotometer (Perkin-Elmer ICP-5000). The ICP-5000 is a true C/P subsystem since it can be decomposed into distinct subunits.

a. Model 5000 Spectrophotometer
b. ICP Source (torch)
c. Optical Interface between a. and b.
d. RF Power Supply
e. Data Station (6800 microcomputer)

    1. Video display unit (VDU)
    2. Keyboard
    3. Disks (floppy)

f. HGA-500 Graphite Furnace
g. Graphite Furnace Control unit
h. AS-40 Autosampler(for furnace) + Control unit
i. AS-50 Autosampler(for torch) + Control unit
j. PR-80 Printer (line printer)

This instrument detects metallic and quasi-metallic species (cations).

---

*Figures 47 and 48 merely demonstrate the Report Generator software. They do not present actual PW data based on samples run in the C/P system. However, PWA samples should have similar profiles.

2 One (1) ion chromatograph (IC) (Dionex AutoIon^{TM} System 12 Analyzer). This can be considered a quasi-subsystem since it can be decomposed into subunits. It is ot, however, under the immediate control of its own microprocessor as the ICP-5000 is.

a. IC Autosmapler
b. Computing Integrator (Spectra Physics Moded SP 4100)

The ion chromatograph detects negative ionic species (anions). The computing integrator handles the data manipulation and peak integration for the ion chromatograph.

3 Minicomputer (Digital Electronic Corp. MINC-11, a PDP-11/03) with hardware modules for running laboratory equipment.

a. VDU
b. Keyboard
c. Disks (floppy).

¶ The minicomputer is for final data analysis, report generation, and overall system control.

4 Extraction Tank/Pumping unit (built in-house)

5 Water Purification Unit (Millipore)

The extraction .tank/pumping subsystem and water purification unit and for sample preparation and extraction.

Herein is given a summary of the major thrust in hardware/software development for the C/P system.

In the last few years, reductions in cost of microprogrammed processor arrays (microprocessors) have led to their increased use by system engineers in the design of laboratory analytical equipment. Along with the usual benefits of designing with micorprocessors, (primarily reduced cost of complex digital systems arrived at through the economies of scale), at least one additional function has been added to many state-of-the-art analytical instruments: the ability to communicate to the outside world through a standardized communications port. This, in turn, has simplified the connection of these instruments into automated analytical sytems; so much so, in fact, that the early 1980's are showing the promise of the development of the completely automated laboratory. The Contamination Profiling System, an automated analytical design for detecting contamination on printed wiring boards and assemblies, is a demonstration of this concept implementing as an on-line tool for use on the floor of a PWB/PWA manufacturing facility.

The design of such an automated facility involves concurrent exploration of several disciplines throughout the development of the project:

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:05:09                 PAGE 001

        SUBROUTINE CONVRT(IPARA,OPARA1,OPARA2)
        BYTE OPARA1,OPARA2
        IDIG=IPARA/10
        OPARA1=IDIG+48
        OPARA2=(IPARA-IDIG*10)+48
        RETURN
        END
```

```
FORTRAN IV        V02.5-2     Thu 03-Dec-81 02:04:31                    PAGE 001

0001            SUBROUTINE SCROLL(ISCTOP,ISCBOT)
0002            BYTE CONTRL(9)
0003            BYTE CLEAR(5)
0004            DATA CLEAR/"33,"133,"73,"162,"200/
0005            DATA CONTRL/"33,"133,0,0,"73,0,0,"162,"200/
0006            IF(ISCTOP.EQ.0)GO TO 100
0008            CALL CONVRT(ISCTOP,ISCTP1,ISCTP2)
0009            CALL CONVRT(ISCBOT,ISCBT1,ISCBT2)
0010            CONTRL(3)=ISCTP1
0011            CONTRL(4)=ISCTP2
0012            CONTRL(6)=ISCBT1
0013            CONTRL(7)=ISCBT2
0014            CALL PRINT(CONTRL)
0015            RETURN
0016      100   CALL PRINT(CLEAR)
0017            RETURN
0018            END
```

```
FORTRAN IV      V02.5-2     Thu 03-Dec-81 02:03:57                PAGE 001

0001            SUBROUTINE HEAR(IUNIT,IFLAG,HEARS)
0002            BYTE HEARS(83)
0003            CALL CLRSTP(HEARS)
0004            INDEX=1
0005      1     IFLAG=MTIN(IUNIT,HEARS(INDEX))
0006            IF(IFLAG.GT.0)RETURN
0008            DO 2,IPAUSE=1,500
0009      2     CONTINUE
0010            IF(HEARS(INDEX).EQ.10)RETURN
0012            IF(INDEX.GT.82)RETURN
0014            INDEX=INDEX+1
0015            GO TO 1
0016            END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:03:33                PAGE 001

        SUBROUTINE CLEAR
        BYTE CONTRL(8)
        DATA CONTRL/"33,"133,"110,"33,"133,"62,"112,"200/
        CALL PRINT(CONTRL)
        RETURN
        END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:03:09                PAGE 001

0001          SUBROUTINE CLRSTR(CLRS)
0002          BYTE CLRS(83)
0003          DO 1,KOUNT=1,83
0004          CLRS(KOUNT)=0
0005    1     CONTINUE
0006          RETURN
0007          END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:02:21              PAGE 001

0001            PROGRAM ICPEX
0002            BYTE REPLY
0003   1        ICPOS=0
0004            CALL SETUP(ICONT)
0005            IF(ICONT.EQ.1)GO TO 2
0007            CALL EXTRCT
0008            CALL INSTRU(ICPOS)
0009            CALL DECIDE(ICPOS)
0010            CALL FURNCE(ICPOS)
0011            CALL REPORT
0012   2        CALL MOVCUR(24.1)
0013            TYPE 1000
0014            ACCEPT 1001,REPLY
0015            IF(REPLY.EQ.'Y')GO TO 1
0017            CALL SCROLL(0,0)
0018            CALL CLEAR
0019            CALL EXIT
0020   1000     FORMAT(/ $Run another analysis (Y/N) ? ')
0021   1001     FORMAT(A1)
0022            END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:02:21

.LP:PROGRM=DK:PROGRM.FOR/O/A

OPTIONS IN EFFECT:

                     SOURCE
                     MAP
                   NOCODE
                   NOLEAPYEAR
                   NOREADONLY
                     LRECL=0136
                     STAT
                     ISNS
                   NOCOL80
                     USRSWAP
                   NODIAGNOSE
                   NOINTEGER*4
                     NLCHN=06
                   NODEBUG
                     VECTOR
                   NOWARN
                     CODE:FIS
                     LOG
```

4.0 CONTAMINANT PROFILING SYSTEM SOFTWARE

The Contaminant Profiling System software was designed to minimize the need for operator intervention.

The Contaminant Profiling System Software was designed to minimize the need for operator intervention during the course of PWB/PWA analysis. In order accomplish this goal, it was structured as a top-level manager for the C/P system. its tasks include:

1 Providing control commands to the various instrumentation including in the system.

2 Accepting data from these same instruments and storing that data for future utilization.

3 Analyzing the data from the ICP-5000 analysis and from it, deciding which elements require analysis by the HGA-500 Graphite Furnace.

4 Organizing the data from the instrumentation into a final report for each board analyzed.

5 Determining whether the analyte board has passed or failed the C/P System test.

The System Software was written in Fortran-IV to be executed on a Digital Equipment Corporation MINC 11/03 Minicomputer under the RT-11 (Version 4.0) Operating System. Extensive use of operating system calls was required both to enhance execution speed and to support the unique hardware configuration features of the MINC. Documentation for these calls is available from DEC as part of their RT-11 Support Manuals, and will not be included here.

A complete listing of the C/P System Software is contained on the following pages. In order to provide software maintainability, a modular approach was used. All Martin Marietta Corporation written routine are contained in the listing. However, in addition to these routines vendor-supplied software for the SP4100 Computing Integrator and the M3600 Data Station was modified for usage under the C/P System framework. Because this Software is proprietary to the vendors involved, it is not contained in this report.

NOTES

[1] I = ion line; A = atom line. For the significance, see below.

[2] Phosphorus, P, was deleted from the list of analyte elements to be run on the ICP 5000 torch because its best and most sensitive line is too far into the ultraviolet (UV). The entire ICP optical path must be purged with a UV-transparent gas, such as argon, to allow the determination of P at 177.50.

[3] Recall Note 2, viz., phosphorus, P, was deleted from the list of analyte elements to be run on the ICP torch because its best and most sensitive line is too far into the ultraviolet (UV). However, it can be run on the graphite furnace. Hence, it reappears in the above list.

[4] Retention time - time it takes for a particular species to pass through the IC's system and be detected by its detector.

form that can be understood by the host computer at execution time, programs written in this form take between 20 and 200 times as long to run as those in other (compiled) languages. Both of the instruments used in the C/P System were provided by the manufacturers with system software running in interpretive BASIC. The C/P System takes advantage of this fact, in that the controller software, written in FORTRAN IV, has more than enough time to receive, process, and store information from the several instruments concomitantly. Therefore, a general purpose laboratory minicomputer with FORTRAN IV capability and several communication ports was chosen as the system controller. While this increased hardware costs over that of using a smaller microcomputer system, it greatly reduced the development time/cost of the system software. Since the possibility of speading software costs over many units did not exist, this was deemed to be cost-effective in the development of this particular system.

The lack of portability of BASIC is due to syntactical differences amoung the various dealects of the language, and remains a probelm in the development of systems of this type. It results in increased development costs while the system programmer familiarized himself with these differences. There is a trend toward the use of faster, more powerful languages, such as FORTRAN IV and PASCAL in the design of laboratory instrumentation. Since these languages tend to be more standardized, this will, to some extent, alleviate the problem.

In Figure 49 is depicted the contaminent profiling (C/P) system in the MMC Ocala PW Facility. The C/P system is located in Building 1 in the Contamination Control Room adjacent to the Quality Chemistry Laboratory. It is under the jurisdiction of Quality in Ocala, and a person from Quality is being trained on the instrumentation.

In Figures 50 - 52 are photographs of the actual system hardware. In Figure 50 there is on the left the autosampler for the ion chromatograph (IC), the IC itself is the rectangular unit in the center, and the SP4100 computing integrator is seen on the right in Figure 50. In Figure 51 are seen the MINC-11 and the Perkin-Elmer spectrophotometric system. The MINC is seen in the center foreground. Directly to the left of it is the on-line printer for producing hard-copy. Behind the printer is the MINC visual display unit (CRT)/keyboard terminal. Behind that is the Perkin-Elmer ICP 5000 Data Sation (having its own keyboard/visual display unit), and behind that is the HGA-500 graphite furnace control unit. Finally, behind that is the ICP 5000/graphite furnace/torch unit itself. In the far left background, barely visible in Figure 51 is the torch RF power supply. Figure 52 shows the extraction tank/pump unit for making extractions for analysis from sample PWAs.

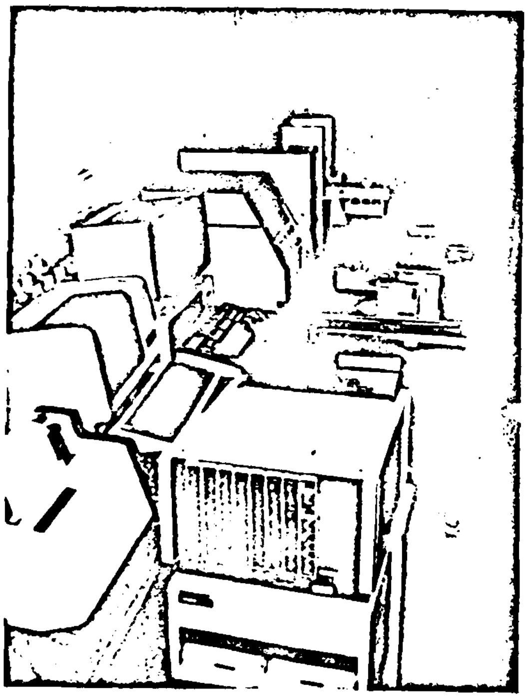


FIGURE 51. The Mini Computer, ICP with DAta System, Printer, Torch, and RF Power Supply

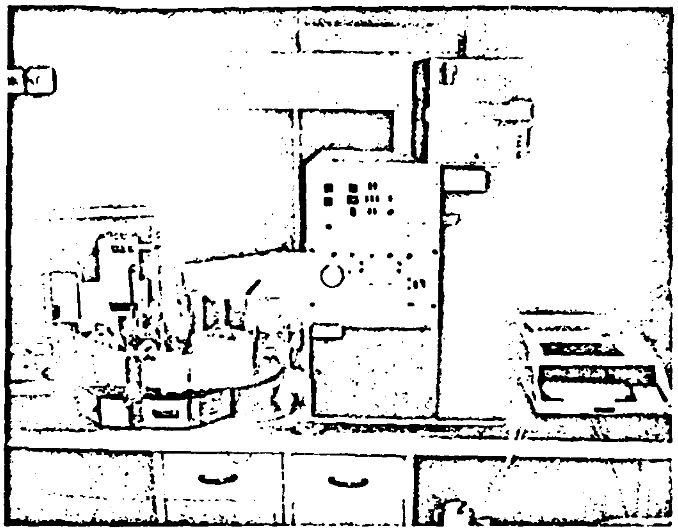


FIGURE 50. The Ion Chromatograph IC Autosample, and Computing Integrator

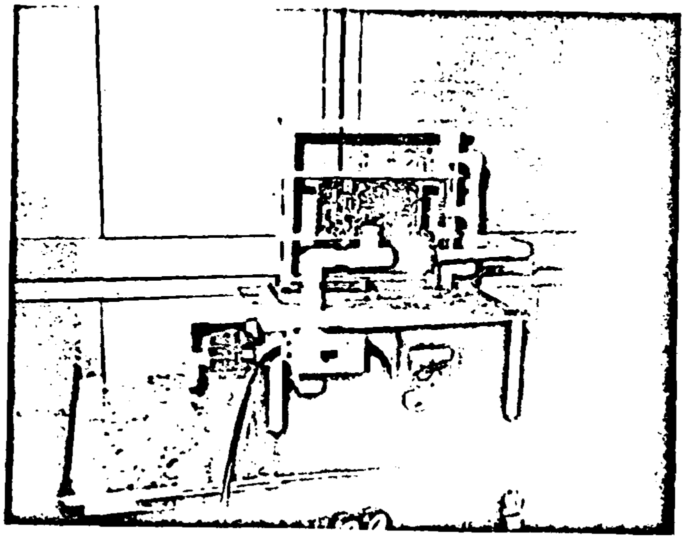
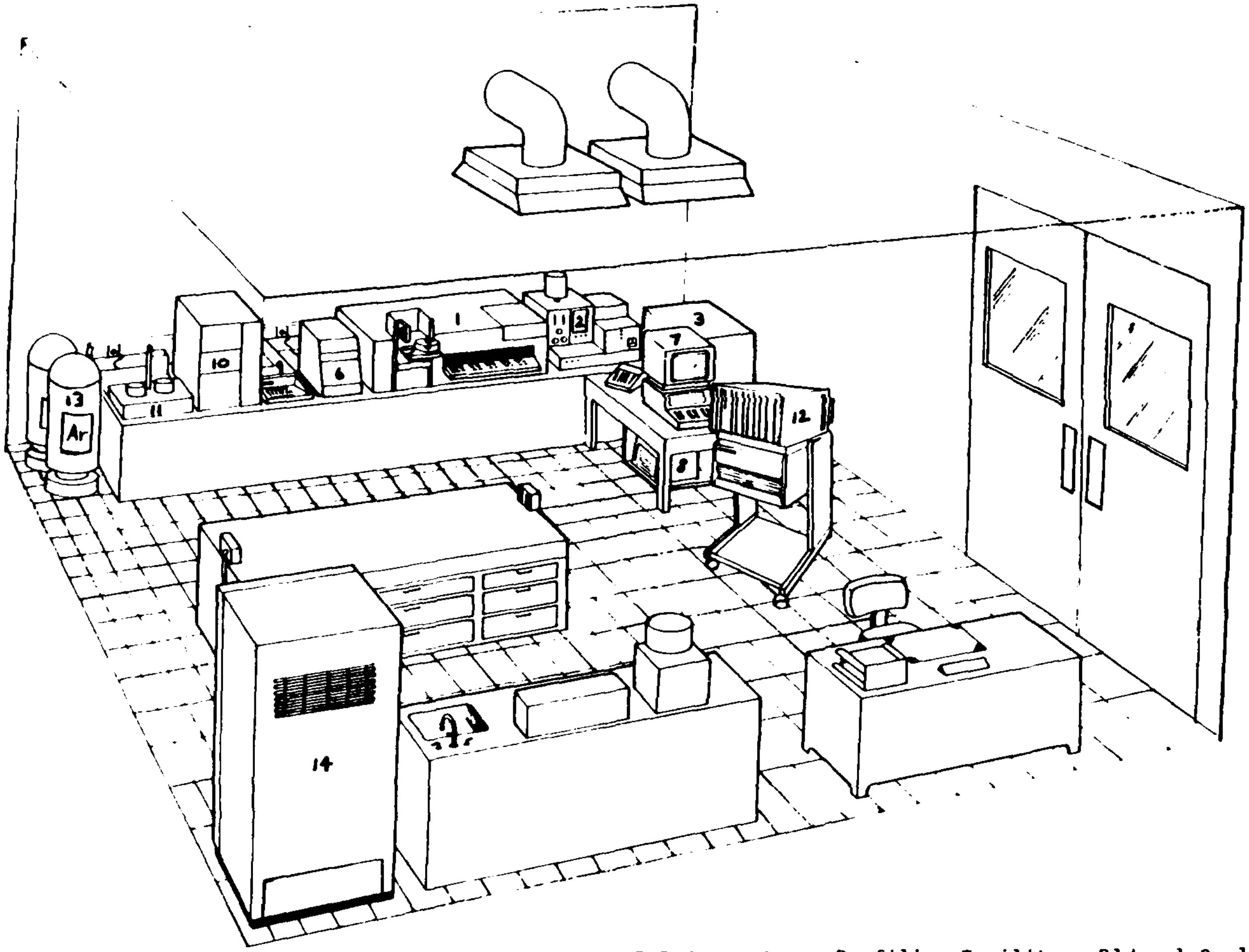


FIGURE 52. The Extraction Tank/Pumping Unit



ITEMS

1. ICP 5000
2. TORCH
3. RF POWER SUPPLY
4. FURNACE
5. FURNACE AUTOSAMPLER
6. FURNACE/AUTOSAMPLER CONTROL
7. DATA STATION
8. PRINTER
9. COMPUTING INTEGRATOR
10. ION CHROMATOGRAPH (IC)
11. IC AUTOSAMPLER
12. MINICOMPUTER
13. GAS CYLINDERS
14. REFRIGERATOR

FIGURE 49. PWB Contaminant Profiling Facility - Bldg. 1 Ocala

(1) Chemistry

The instrumentation to be used must be capable of fulfilling the requirements of the end system. While the analytical methodology involved will obviously play a large role in the choice of instrumentation, an automated system will require several additional factors to be considered within the total design. For example, since the C/P System was to have both cations (metals and semimetals) and anions (non-metallic species) determined in parallel, maximizing the system's throughout required that the total analytical time for each technique be balanced. Therefore, the ion chromatograph became the determinant instrument, since at two hours per run, it would require the bulk of the operating time. Within this timeframe, it was decided to use sequential inductively-coupled plasma emission spectrophotometry to determine the metals, backed up by graphite furnace atomic absorption, since the total run times would be approximately equal for most samples.

(2) Data Processing - Hardware

As has already been mentioned, state-of-the-art laboratory instrumentation is showing an increased implementation of miroprocessor-based, bus-oriented designs. However, it should be pointed out that the standardization of communication busses and system protocol has not yet arrived. In addition, the need for the availability of detailed technical information concerning these structures has not been fully recognized by many vendors. Therefore, the design of the C/P System required the purchase of equipment that while "computer compatible", was not totally designed to be used in a fully automated system. For these reasons, interfacing problems surfaced requiring hardware knowledge to solve. Particularly troublesome was the fact that certain pieces of equipment had no provision for external communication at all, which necessitated compromises in the data links within the system.

(3) Data Processing - Software

The most commonly available computer language for instrument control at this time is interpretive BASIC. While computer professionals usually feel that the disadvantages of this language limit its usefulness in all but the most casual of data processing situtation, interpretive BASIC holds several major advantages for the instrument manufacturer. It is, at this time, unusual to find personnel trained in both Analytical Chemistry and Computer Programming. Since the BASIC language was designed to rather easily learned, its use allows the instrument manufacturer to train personnel familiar with instrument operation in the programming of the computers needed to control them. The fact that the source program (program statements written in a form understandable to humans) resides within the computer at execution time also vastly simplifies program debugging and modification. The two major disadvantages of interpretive BASIC are its slow execution speed and its lack of protability. Since each BASIC statement must be translated to a

```
FORTRAN IV      V02.5-2    Thu 03-Dec-8. 02:05:33                PAGE 001

          SUBROUTINE ERASED(IEDOPT)
          BYTE CONTRL(5)
          DATA CONTRL/"33,"133,0,"112,"200/
          CONTRL(3)=IEDOPT+48
          CALL PRINT(CONTRL)
          RETURN
          END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:06:01                 PAGE 001

        SUBROUTINE ERASEL(IELOPT)
        BYTE CONTRL(5)
        DATA CONTRL/"33,"133,0,"113,"200/
        CONTRL(3)=IELOPT+48
        CALL PRINT(CONTRL)
        RETURN
        END
```

```
      SUBROUTINE MOVCUR(MOVLIN,MOVCOL)
      BYTE CONTRL(9)
      DATA CONTRL/"33,"133,0,0,"73,0,0,"110,"200/
      CALL CONVRT(MOVLIN,MVLIN1,MVLIN2)
      CALL CONVRT(MOVCOL,MVCOL1,MVCOL2)
      CONTRL(3)=MVLIN1
      CONTRL(4)=MVLIN2
      CONTRL(6)=MVCOL1
      CONTRL(7)=MVCOL2
      CALL PRINT(CONTRL)
      RETURN
      END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:07:03                  PAGE 001

0001            SUBROUTINE DOUBLE(IDOPT,IDLIN)
0002            BYTE CONTRL(4)
0003            DATA CONTRL/"33,"43,0,"200/
0004            IDBOPT=IDOPT
0005            IDBLIN=IDLIN
0006            IF(IDBOPT.EQ.0)IDBOPT=53
0008            IF(IDBOPT.EQ.1)IDBOPT=54
0010            IF(IDBOPT.EQ.2)IDBOPT=51
0012      5     CALL MOVCUR(IDBLIN,1)
0013            CALL ERASEL(2)
0014      4     CONTRL(3)=IDBOPT
0015            CALL PRINT(CONTRL)
0016            IF(IDBOPT.EQ.52)CALL MOVCUR(IDBLIN-1,1)
0018            IF(IDBOPT.NE.51)GOTO 2
0020            IDBOPT=52
0021            IDBLIN=IDBLIN+1
0022            GOTO 5
0023      2     RETURN
0024            END
```

```
0001        SUBROUTINE ATTRIB(IATOPT)
0002        BYTE CONTRL(5)
0003        DATA CONTRL/"33,"133,0,"155,"200/
0004        CONTRL(3)=IATOPT+48
0005        CALL PRINT(CONTRL)
0006        RETURN
0007        END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:08:08              PAGE 001

0001            SUBROUTINE FPRINT(IFILNO,IFLAG)
0002            BYTE INSTR(80),FILE(11)
0003            DATA FILE/"123,"131,"72,"103,"113,0,"56,"114,"123,"124,0/
0004            NFILE=IFILNO
0005            IF(IFLAG.EQ.0)NFILE=1
0007            DO 5,ICOUNT=1,NFILE
0008            FILE(6)=ICOUNT+48
0009            IF(IFLAG.EQ.0)FILE(6)=IFILNO+48
0011            OPEN(UNIT=1,NAME=FILE,TYPE='OLD')
0012            IF(IFLAG.EQ.0)GO TO 1
0014            OPEN(UNIT=6,NAME='LP:',CARRIAGECONTROL='FORTRAN')
0015      1     DO 2 INDEX=1,80
0016            INSTR(INDEX)=0
0017      2     CONTINUE
0018            READ(1,1000,END=4)NCHRS,(INSTR(KOUNT),KOUNT=1,NCHRS)
0019            DO 6,INDEX=1,80
0020            IF(INSTR(INDEX).EQ.10)GO TO 3
0022      6     CONTINUE
0023      3     WRITE(6,1001)(INSTR(KOUNT),KOUNT=1,INDEX)
0024            GO TO 1
0025      4     CLOSE(UNIT=1)
0026            IF(IFLAG.EQ.0)GO TO 5
0028            CLOSE(UNIT=6)
0029      5     CONTINUE
0030            RETURN
0031      1000  FORMAT(Q,80A1)
0032      1001  FORMAT('+',80(A1,:))
0033            END
```

```
FORTRAN IV      V02.5-2    Thu 03-Dec-81 02:08:54                PAGE 001

            SUBROUTINE BELL
            BYTE CHR(2)
            DATA CHR/7,"200/
            DO 2,KOUNT=1,10
            CALL PRINT(CHR)
            DO 2,KOUNT1=1,10000
      2     CONTINUE
            RETURN
            END
```

```
              SUBROUTINE SETUP(ISTOP)
              BYTE ERR,DATE(9),CHR,REPLY,INSTR(34),TIMSTR(8)
              BYTE SEQ(13)
              INTEGER*4 SETSCR(18)
              DATA SETSCR/'OPR ',0,'DATE','TIME','P/N ',0,'LOT ','S/N ',
             1'SEQ ',0,0,0,'ICP ','HGA ','IC  ','TANK','MODE','   '/
              DATA SEQ/"104,"131,"61,"72,"103,"120,0,0,"56,"104,"101,"124,0/
        7     CALL CLEAR
              CALL SCROLL(15,24)
              CALL DOUBLE(1,1)
              CALL MOVCUR(1,6)
              CALL PRINT('CONTAMINANT PROFILING SYSTEM')
              CALL DOUBLE(1,14)
              CHR='-'
              TYPE 1006,(CHR,INDEX=1,40)
        1006  FORMAT('+',40A1)
              CALL ATTRIB(7)
              INDEX=1
              DO 4,ILIN=3,9,2
              DO 4,ICOL=1,61,20
              CALL MOVCUR(ILIN,ICOL)
              TYPE 1001,SETSCR(INDEX)
        1001  FORMAT('+',A4)
              INDEX=INDEX+1
        4     CONTINUE
              CALL MOVCUR(11,1)
              TYPE 1001,SETSCR(17)
              CALL MOVCUR(13,1)
              TYPE 1001,SETSCR(18)
              CALL ATTRIB(0)
              CALL MOVCUR(11,6)
              CALL PRINT('SET-UP')
              DO 5,ICOL=6,66,20
              CALL MOVCUR(9,ICOL)
              CALL PRINT('INACTIVE')
        5     CONTINUE
              OPEN(UNIT=1,NAME='SY:DATTIM.COM',TYPE='OLD')
              READ(1,1017)(DATE(INDEX),INDEX=1,9)
        1017  FORMAT(5X,9A1)
              CLOSE(UNIT=1)
              CALL MOVCUR(3,46)
              TYPE 1018,(DATE(INDEX),INDEX=1,9)
        1018  FORMAT('+',9A1)
              CALL TIME(TIMSTR)
              CALL MOVCUR(3,66)
              TYPE 1022,(TIMSTR(INDEX),INDEX=1,8)
        1022  FORMAT('+',8A1)
              CALL MOVCUR(24,1)
              IFILE=3
              TYPE 1002
        1002  FORMAT('$Is this the first run of the week (Y/N) ?  ')
              ACCEPT 1005,REPLY
        1005  FORMAT(A1)
              IF(REPLY.NE.'Y')IFILE=2
```

```
0055          IF(REPLY.EQ.'Y')GO TO 10
0057          TYPE 1029
0058   1029   FORMAT('$Is this the first run of the day  (Y/N) ?   ')
0059          ACCEPT 1005,REPLY
0060          IF(REPLY.NE.'Y')IFILE=1
0062   10     CALL MOVCUR(13,6)
0063          CALL ATTRIB(5)
0064          CALL PRINT('Printing Start-up Checklists')
0065          CALL ATTRIB(0)
0066          CALL MOVCUR(24,1)
0067          CALL FPRINT(IFILE,1)
0068          CALL MOVCUR(13,6)
0069          CALL ERASEL(0)
0070          CALL MOVCUR(24,1)
0071          ISTOP=1
0072          IF(IFILE.EQ.1) GO TO 20
0074          TYPE 1050
0075   1050   FORMAT('$Continue with the analysis         (Y/N) ?   ')
0076          ACCEPT 1051,REPLY
0077          IF(REPLY.EQ.'Y')GO TO 20
0079   1051   FORMAT(A1)
0080          ISTOP=1
0081          RETURN
0082   20     OPEN(UNIT=1,NAME='SY:SEQ.DAT',TYPE='OLD')
0083          READ(1,1023)ISEQ1,ISEQ2
0084          CLOSE(UNIT=1)
0085          OPEN(UNIT=1,NAME='SY:SEQ.DAT',TYPE='NEW')
0086          ISEQ2=ISEQ2+1
0087          IF(ISEQ2.LE.'71)GO TO 8
0089          ISEQ2='60
0090          ISEQ1=ISEQ1+1
0091   8      WRITE(1,1023)ISEQ1,ISEQ2
0092   1023   FORMAT(2I5
0093          CLOSE(UNIT=1)
0094          SEQ(7)=ISEQ1
0095          SEQ(8)=ISEQ2
0096          OPEN(UNIT=2,NAME=SEQ,TYPE='NEW',CARRIAGECONTROL='LIST')
0097          CALL MOVCUR(7,6)
0098          TYPE 1028,SEQ(7),SEQ(8)
0099   1028   FORMAT('+',A1,1X,A1)
0100          WRITE(2,1024)(DATE(INDEX),INDEX=1,9)
0101   1024   FORMAT(1X,9A1)
0102          WRITE(2,1025)(TIMSTR(INDEX),INDEX=1,8)
0103   1025   FORMAT(1X,8A1)
0104          CALL MOVCUR(24,1)
0105          TYPE 1040
0106   1040   FORMAT('$Enter Operator Name            ')
0107          CALL GETSTR(5,INSTR,33,ERR)
0108          CALL MOVCUR(3,6)
0109          CALL PRINT(INSTR)
0110          WRITE(2,1026)(INSTR(INDEX),INDEX=1,33)
0111   1026   FORMAT(1X,33A1)
0112          CALL MOVCUR(24,1)
0113          TYPE 1041
```

```
1041   FORMAT(//'$Enter Part Number                     ')
       CALL GETSTR(5,INSTR,33,ERR)
       CALL MOVCUR(5,6)
       CALL PRINT(INSTR)
       WRITE(2,1026)(INSTR(INDEX),INDEX=1,33)
       CALL MOVCUR(24,1)
       TYPE 1042
1042   FORMAT(//'$Enter Lot Number                      ')
       CALL GETSTR(5,INSTR,14,ERR)
       CALL MOVCUR(5,46)
       CALL PRINT(INSTR)
       WRITE(2,1027)(INSTR(INDEX),INDEX=1,14)
1027   FORMAT(1X,14A1)
       CALL MOVCUR(24,1)
       TYPE 1043
1043   FORMAT(//'$Enter Serial Number                   ')
       CALL GETSTR(5,INSTR,14,ERR)
       CALL MOVCUR(5,66)
       CALL PRINT(INSTR)
       WRITE(2,1027)(INSTR(INDEX),INDEX=1,14)
       CALL MOVCUR(24,1)
       TYPE 1044
1044   FORMAT(//'$Enter board length (cm)        ')
       ACCEPT*,FLEN
       TYPE 1045
1045   FORMAT('$Enter board width  (cm)         ')
       ACCEPT*,FWID
       AREACM=FLEN*FWID*2
       WRITE(2,1046)AREACM
1046   FORMAT(F10.2)
       TYPE 1047
1047   FORMAT('$Enter tank volume  (ml)         ')
       ACCEPT*,TVOL
       WRITE(2,1048)TVOL
1048   FORMAT(F10.2)
       CLOSE(UNIT=2)
       RETURN
       END
```

```
      SUBROUTINE EXTRCT
      BYTE REPLY,ERR,ENDFLG,CHR
      CALL MOVCUR(11,6)
      CALL ATTRIB(0)
      CALL PRINT('EXTRACTION')
      CALL MOVCUR(24,1)
      TYPE 1005
1005  FORMAT('$Enter extraction time (min.) ')
      ACCEPT *,RUNTIM
      CALL MOVCUR(13,6)
      CALL PRINT('Time remaining :       min       sec')
      CALL MOVCUR(13,25)
      IRUN=INT(RUNTIM)
      TYPE 1010,IRUN
1010  FORMAT('+',I2)
      CALL MOVCUR(24,1)
      CALL PRINT(' ')
      CALL PRINT('Fill extraction tank with DI water.')
      CALL PRINT('Place analyte board in tank.')
      CALL PRINT('Turn on extraction tank pump.')
      TYPE 1001
1001  FORMAT('$Press <RETURN> when ready to begin timing. ')
      ACCEPT 1002,REPLY
1002  FORMAT(A1)
      STTIM=SECNDS(0.)
      CALL MOVCUR(9,66)
      CALL PRINT('ACTIVE  ')
      CALL MOVCUR(13,6)
      CALL ATTRIB(5)
      CALL PRINT('Time remaining :')
1     ETIM=SECNDS(STTIM)
      SECTIM=RUNTIM*60-ETIM
      ISECT=INT(SECTIM)
      IMIN=ISECT/60
      ISEC=ISECT-IMIN*60
      CALL ATTRIB(0)
      CALL MOVCUR(13,25)
      TYPE 1008,IMIN
      CALL MOVCUR(13,34)
      TYPE 1008,ISEC
      IF(ETIM.LT.RUNTIM*60)GO TO 1
1008  FORMAT('+',I2)
      CALL MOVCUR(9,66)
      CALL PRINT('FINISHED')
      CALL MOVCUR(13,6)
      CALL PRINT('Time Remaining :')
      CALL MOVCUR(24,1)
      TYPE 1011
1011  FORMAT(' Extraction complete.  Turn off pump to
     1 Extraction Tank.'/)
      CALL BELL
      CALL MOVCUR(13,6)
      CALL ERASEL(0)
      CALL MOVCUR(24,1)
```

```
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55          RETURN
56          END
```

```
        SUBROUTINE INSTRU(LOAD1)
        BYTE REPLY,CHR,STRING(10),INSTR(83),OUTSTR(83),SEQ(14)
        INTEGER*2 JOB,SBLOK1(4),SBLOK2(4),HOLD1,HOLD2
        DATA SEQ/"104,"131,"61,"72,0,0,0,0,0,"56,"104,"101,"124,0/
        CALL MOVCUR(11,6)
        CALL ATTRIB(0)
        CALL PRINT('ANALYSIS  ')
1       CALL MOVCUR(24,1)
        CALL PRINT('')
        CALL PRINT('Verify CHECKLIST items complete.')
        CALL PRINT('Place extract samples in auto-samplers.')
        CALL PRINT('Start Data Station by typing ICP <RETURN>.')
        IER1=MTATCH(1,,JOB1)
        IF(IER1)GO TO 9999
        IER2=MTATCH(2,,JOB2)
        IF(IER2)GO TO 9999
        IF(MTGET(1,SBLOK1(1)).NE.0)GO TO 9999
        IF(MTGET(2,SBLOK2(1)).NE.0)GO TO 9999
        SBLOK1(1)=SBLOK1(1).OR."10000
        SBLOK2(1)=SBLOK2(1).OR."10000
        SBLOK1(1)=SBLOK1(1).OR."100
        SBLOK2(1)=SBLOK2(1).OR."100
        IF(MTSET(1,SBLOK1(1)).NE.0)GO TO 9999
        IF(MTSET(2,SBLOK2(1)).NE.0)GO TO 9999
        OPEN(UNIT=1,NAME='SY:SEQ.DAT',TYPE='OLD')
        READ(1,1004)ISEQ1,ISEQ2
1004    FORMAT(2I5)
        CLOSE(UNIT=1)
        HOLD1=0
        HOLD2=0
        LOAD1=0
        LOAD2=0
4       CALL ION(ISEQ1,ISEQ2,LOAD1)
        IF(LOAD2.EQ.1)GO TO 3
        IF(LOAD2.EQ.2)GO TO 5
2       CALL HEAR(2,HOLD2,INSTR)
        IF(HOLD2.EQ.1)GO TO 4
        SEQ(5)="124
        SEQ(6)="103
        SEQ(7)="110
        SEQ(8)=ISEQ1
        SEQ(9)=ISEQ2
        OPEN(UNIT=2,NAME=SEQ,TYPE='NEW',CARRIAGECONTROL='LIST')
        DO 99, IPUN = 1,3
        CALL MOVCUR(9,6)
        CALL ATTRIB(0)
        TYPE 1002,IPUN
1002    FORMAT('+GROUP',1X,I1,1X)
        CALL MOVCUR(24,1)
        CALL CLRSTR(OUTSTR)
        CALL SCOPY('MF (FL',OUTSTR)
        OUTSTR(3)=IPUN+48
        CALL MTPRNT(2,OUTSTR)
        TYPE 1003,IPUN
```

```
 1003  FORMAT('  ICP/5000 ready for Analytical Group #',I1/
      1' Please follow prompts on Data Station to begin analysis.'//)
       LOAD2=1
 3     CALL HEAR(2,HOLD2,INSTR)
       IF(HOLD2.EQ.1) GO TO 4
       IF(INSTR(1).EQ.'C')GO TO 999
 4     CALL CLRSTR(OUTSTR)
       CALL SCOPY('  RA',OUTSTR)
       CALL MTPRNT(2,OUTSTR)
       LOAD2=2
 5     CALL HEAR(2,HOLD2,INSTR)
       IF(HOLD2.EQ.1)GO TO 4
       IF(INSTR(1).EQ.' '.AND.INSTR(35).NE.'A')GO TO 5
       IF(INSTR(1).EQ.'C')GO TO 999
       IF(INSTR(35).EQ.'A')GO TO 7
       CALL CLRSTR(OUTSTR)
       CALL SUBSTR(INSTR,STRING,1,5)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       CALL CONCAT(OUTSTR,'   ',OUTSTR)
       CALL SUBSTR(INSTR,STRING,27,2)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       CALL CONCAT(OUTSTR,'  C ',OUTSTR)
       CALL SUBSTR(INSTR,STRING,53,5)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       CALL CONCAT(OUTSTR,' C ',OUTSTR)
       CALL SUBSTR(INSTR,STRING,65,3)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       CALL CONCAT(OUTSTR,'  ',OUTSTR)
       GO TO 5
 7     CALL SUBSTR(INSTR,STRING,39,7)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       CALL CONCAT(OUTSTR,' SD',OUTSTR)
       CALL SUBSTR(INSTR,STRING,51,7)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       CALL CONCAT(OUTSTR,' CV',OUTSTR)
       CALL SUBSTR(INSTR,STRING,63,5)
       CALL CONCAT(OUTSTR,STRING,OUTSTR)
       WRITE(2,1005)(OUTSTR(KOUNT),KOUNT=1,67)
 1005  FORMAT(1X,67A1)
       GO TO 5
 9     CALL HEAR(2,HOLD2,INSTR)
       IF(HOLD2.EQ.1)GO TO 9
 99    CONTINUE
       CLOSE(UNIT=2)
       CALL MOVCUR(9,6)
       CALL PRINT('FINISHED')
       RETURN
 999   IF(INSTR(2).NE.'C')GO TO 900
       CALL MOVCUR(13,6)
       CALL ATTRIB(5)
       CALL PRINT('Communications Error!')
       CALL MOVCUR(24,1)
       CALL ATTRIB(0)
       CALL BELL
```

AD-A151 952   ESTABLISHMENT OF PRODUCTION CLEANLINESS CRITERIA AND   3/3
PROCESSES FOR PRINTE..(U) MARTIN MARIETTA AEROSPACE
ORLANDO FL J K BONNER DEC 81 OR-16668
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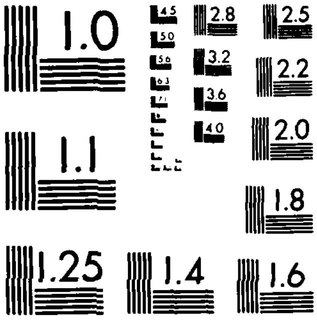

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

```
       TYPE 10001
10001  FORMAT(' $Correct Communication Problem.  Press <RETURN> to
     1 resume analysis. ')
       GO TO 9990
900    IF(INSTR(2).EQ.'E'.AND.INSTR(3).EQ.'N')GO TO 9
       IF(INSTR(2).NE.'D'.AND.INSTR(2).NE.'F'.AND.INSTR(2).NE.'M')
     1GO TO 901
       CALL MOVCUR(13,6)
       CALL ATTRIB(5)
       CALL PRINT('Error in Reading Disk!')
       CALL MOVCUR(24,1)
       CALL ATTRIB(0)
       CALL BELL
       TYPE 10004
10004  FORMAT('/' An error has occured in attempting to read from the
     1 disk in drive 1 of the'/' Data Station.  Make sure that the
     2 correct disk is inserted and that the door ' $to the drive
     3 is closed.  Press <RETURN> to resume analysis. ')
9990   ACCEPT 10003,REPLY
10003  FORMAT(A1)
       CALL MOVCUR(13,6)
       CALL ERASEL(0)
       CALL MOVCUR(24,1)
       IF(LOAD2.NE.2)GO TO 9991
       LOAD2=1
       CLOSE(UNIT=2)
       GO TO 3
9991   LOAD2=0
       GO TO 2
901    IF(INSTR(2).NE.'S')GO TO 9999
       CALL MOVCUR(13,6)
       CALL ATTRIB(5)
       CALL PRINT('Error in Reading Standards')
       CALL MOVCUR(24,1)
       CALL ATTRIB(0)
       CALL BELL
       TYPE 10006
10006  FORMAT('/  The Data Station has detected an error in the Stand
     1ardization Process.'/' Check Standard Preparation.  Refill
     2 AS-50 sample cups with fresh standards.'/' $Press <RETURN> to
     3 resume analysis.')
       ACCEPT 10003,REPLY
       CALL MOVCUR(13,6)
       CALL ERASEL(0)
       CALL MOVCUR(24,1)
       CLOSE(UNIT=2)
       LOAD2=1
       GOTO 3
9999   CALL MOVCUR(13,6)
       CALL ATTRIB(5)
       CALL PRINT('System Error')
       IER1=MTDTCH(1)
       IER2=MTDTCH(2)
       IF(LOAD2.EQ.2)CLOSE(UNIT=2)
```

```
0176            CALL MOVCUR(24,1)
0177            CALL ATTRIB(0)
0178            CALL BELL
0179            TYPE 10010
0180      10010 FORMAT(/' A fatal system error has occured.  Restart IC and
           1 ICP.'//'$Press <RETURN> to resume analysis.')
0181            ACCEPT 10003,REPLY
0182            CALL MOVCUR(13,6)
0183            CALL ERASEL(0)
0184            GO TO 1
0185            END
```

```
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0001            SUBROUTINE DECIDE(LOAD1)
0002            BYTE INSTR(83),OUTSTR(83),SEQ(14),TYPE,DATA(8),TURRET(18)
               1,LAMP(18),ELAMP,ETURRT,TDATA(10)
0003            INTEGER*2 HOLD3,NAME(18),ICROSS(18),FURNCE(18),ORDER(18),ENAME
               1,ECROSS,EORDER,EFURN,LOAD1
0004            DATA SEQ/"104,"131,"61,"72,"124,"103,"110,0,0,"56,"104,
               1"101,"124,0/
0005            DATA TDATA/"133,"131,"72,"124,0,"56,"114,"123,"124,0/
0006            CALL MOVCUR(11,6)
0007            CALL PRINT('DECISION  ')
0008            CALL MOVCUR(13,6)
0009            CALL ATTRIB(5)
0010            CALL PRINT('Determining Elements')
0011            CALL ATTRIB(0)
0012            CALL MOVCUR(24,1)
0013            DO 7,KOUNT=1,18
0014            LAMP(KOUNT)=0
0015            TURRET(KOUNT)=0
0016            NAME(KOUNT)=0
0017            ICROSS(KOUNT)=0
0018            ORDER(KOUNT)=0
0019            FURNCE(KOUNT)=-1
0020      7     CONTINUE
0021            OPEN(UNIT=1,NAME='SY:SEQ.DAT',TYPE='OLD')
0022            READ(1,1000)ISEQ1,ISEQ2
0023      1000  FORMAT(2I5)
0024            CLOSE(UNIT=1)
0025            SEQ(8)=ISEQ1
0026            SEQ(9)=ISEQ2
0027            CALL ION(ISEQ1,ISEQ2,LOAD1)
0028            OPEN(UNIT=1,NAME=SEQ,TYPE='OLD',CARRIAGECONTROL='LIST')
0029            OPEN(UNIT=2,NAME='SY:CROSS.LST',TYPE='OLD',CARRIAGE
               1CONTROL='LIST')
0030            READ(2,1002,END=2)(NAME(KOUNT),ICROSS(KOUNT),KOUNT=1,30)
0031      1002  FORMAT(A2,2X,I8)
0032      2     CLOSE(UNIT=2)
0033            IELE=KOUNT-1
0034      3     READ(1,1003,END=10)TYPE,INAME,(DATA(K),K=2,8)
0035      1003  FORMAT(2X,A1,4X,A2,13X,7A1)
0036            IF(TYPE.NE.'A')GO TO 3
0038            DATA(1)=DATA(8)
0039            DATA(8)=0
0040            DECODE(7,1004,DATA)IDATA
0041      1004  FORMAT(I7)
0042            CALL ION(ISEQ1,ISEQ2,LOAD1)
0043            DO 4,KOUNT=1,IELE
0044            IF(INAME.EQ.NAME(KOUNT))GO TO 5
0046      4     CONTINUE
0047            GO TO 3
0048      5     FURNCE(KOUNT)=0
0049            IF(IDATA.LT.ICROSS(KOUNT))FURNCE(KOUNT)=1
0051            GO TO 3
0052      10    CLOSE(UNIT=1)
0053            CALL MOVCUR(13,6)
```

```
0054          CALL ERASEL(0)
0055          CALL ATTRIB(5)
0056          CALL PRINT('Calling Data Station')
0057          CALL MOVCUR(24,1)
0058          CALL ATTRIB(0)
0059          CALL SCOPY('QUIT',OUTSTR)
0060          CALL MTPRNT(2,OUTSTR)
0061          LOAD2=0
0062    20    CALL ION(ISEQ1,ISEQ2,LOAD1)
0063          IF(LOAD2.EQ.1)GO TO 21
0065          IF(LOAD2.EQ.2)GO TO 22
0067    1     CALL HEAR(2,HOLD3,INSTR)
0068          IF(HOLD3.EQ.1)GO TO 20
0070          CALL SCOPY('GFLOD',OUTSTR)
0071          CALL MTPRNT(2,OUTSTR)
0072          LOAD2=1
0073    21    CALL HEAR(2,HOLD3,INSTR)
0074          IF(HOLD3.EQ.1)GO TO 20
0076          IF(INSTR(1).NE.'C'.AND.INSTR(2).NE.'E')GO TO 999
0078          CALL MOVCUR(13,6)
0079          CALL ERASEL(0)
0080          CALL ATTRIB(5)
0081          CALL PRINT('Calling Turret Information')
0082          CALL MOVCUR(24,1)
0083          CALL ATTRIB(0)
0084          DO 12,KOUNT=1,IELE
0085          IF(FURNCE(KOUNT).EQ.0)GO TO 12
0087          CALL CLRSTR(OUTSTR)
0088          CALL SCOPY(NAME(KOUNT),OUTSTR,2)
0089          CALL MTPRNT(2,OUTSTR)
0090          LOAD2=2
0091    22    CALL HEAR(2,HOLD3,INSTR)
0092          IF(HOLD3.EQ.1)GO TO 20
0094          IF(INSTR(1).EQ.'C')GO TO 999
0096          TURRET(KOUNT)=INSTR(1)
0097          LAMP(KOUNT)=INSTR(2)
0098          DECODE(2,1009,INSTR)ORDER(KOUNT)
0099    1009  FORMAT(I2)
0100    12    CONTINUE
0101          CALL MOVCUR(13,6)
0102          CALL ERASEL(0)
0103          CALL ATTRIB(5)
0104          CALL PRINT('Sorting Elements')
0105          CALL MOVCUR(24,1)
0106          CALL ATTRIB(0)
0107          INDEX=IELE-1
0108          DO 14,JINDEX=1,INDEX
0109          KINDEX=JINDEX+1
0110          DO 14,LINDEX=IELE,KINDEX,-1
0111          IF(ORDER(LINDEX).GT.ORDER(JINDEX))GO TO 14
0113          ELAMP=LAMP(LINDEX)
0114          ETURRT=TURRET(LINDEX)
0115          ENAME=NAME(LINDEX)
0116          ECROSS=ICROSS(LINDEX)
```

```
      EORDER=ORDER(LINDEX)
      EFURN=FURNCE(LINDEX)
      LAMP(LINDEX)=LAMP(JINDEX)
      TURRET(LINDEX)=TURRET(JINDEX)
      NAME(LINDEX)=NAME(JINDEX)
      ICROSS(LINDEX)=ICROSS(JINDEX)
      ORDER(LINDEX)=ORDER(JINDEX)
      FURNCE(LINDEX)=FURNCE(JINDEX)
      LAMP(JINDEX)=ELAMP
      TURRET(JINDEX)=ETURRT
      NAME(JINDEX)=ENAME
      ICROSS(JINDEX)=ECROSS
      ORDER(JINDEX)=EORDER
      FURNCE(JINDEX)=EFURN
      CALL ION(ISEQ1,ISEQ2,LOAD1)
14    CONTINUE
      DO 15,ITUR=1,3
      CALL ION(ISEQ1,ISEQ2,LOAD1)
      TDATA(5)=ITUR+48
      OPEN(UNIT=1,NAME=TDATA,TYPE='NEW',CARRIAGECONTROL='LIST')
      IFLAG=0
17    DO 16,KOUNT=1,IELE
      IF(TURRET(KOUNT).NE.TDATA(5).OR.FURNCE(KOUNT).EQ.0)GO TO 16
      IFLAG=1
      WRITE(1,1011)NAME(KOUNT),TURRET(KOUNT),LAMP(KOUNT),
     1FURNCE(KOUNT)
1011  FORMAT(A2,2X,A1,2X,A1,2X,I3)
16    CONTINUE
      IF(IFLAG.EQ.0)WRITE(1,1012)
1012  FORMAT('NODATA')
      CLOSE(UNIT=1)
15    CONTINUE
      CALL MOVCUR(13,6)
      CALL ERASEL(0)
      CALL MOVCUR(24,1)
      RETURN
999   TYPE 10000
10000 FORMAT(' ERROR IN CODING ROUTINES')
      CALL EXIT
      END
```

```
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0001            SUBROUTINE FURNCE(LOAD1)
0002            BYTE INSTR(83),OUTSTR(33),REPLY,SEQ(14),TURRET(6),LAMP(6),
               1TDATA(10),LSTSAM,ISTDS
0003            INTEGER*2 HOLD4,NAME(6)
0004            DATA SEQ/"104,"131,"61,"72,"106,"122,"116,0,0,"56,"104,
               1"101,"124,0/
0005            DATA TDATA/"123,"131,"72,"124,0,"56,"114,"123,"124,0/
0006            CALL MOVCUR(11,6)
0007            CALL PRINT('ANALYSIS  ')
0008            CALL MOVCUR(13,6)
0009            CALL ATTRIB(5)
0010            CALL PRINT('Opening Output File')
0011            CALL ATTRIB(0)
0012            CALL MOVCUR(24,1)
0013            OPEN(UNIT=1,NAME='SY:SEQ.DAT',TYPE='OLD')
0014            READ(1,1001)ISEQ1,ISEQ2
0015      1001  FORMAT(2I5)
0016            CLOSE(UNIT=1)
0017            CALL ION(ISEQ1,ISEQ2,LOAD1)
0018            SEQ(8)=ISEQ1
0019            SEQ(9)=ISEQ2
0020            OPEN(UNIT=2,NAME=SEQ,TYPE='NEW',CARRIAGECONTROL='LIST')
0021            CALL MOVCUR(9,26)
0022            CALL PRINT('ACTIVE  ')
0023            CALL MOVCUR(24,1)
0024            CALL ION(ISEQ1,ISEQ2,LOAD1)
0025            DO 1,ITUR=1,3
0026            CALL MOVCUR(13,6)
0027            CALL ERASEL(0)
0028            CALL ATTRIB(5)
0029            CALL PRINT('Reading Elements')
0030            CALL ATTRIB(0)
0031            CALL MOVCUR(24,1)
0032            TDATA(5)=ITUR+48
0033            OPEN(UNIT=1,NAME=TDATA,TYPE='OLD',CARRIAGECONTROL='LIST')
0034            KOUNT=1
0035      2     READ(1,1005,END=3)NAME(KOUNT),TURRET(KOUNT),LAMP(KOUNT)
0036      1005  FORMAT(A2,2X,A1,2X,A1)
0037            KOUNT=KOUNT+1
0038            IF(NAME(KOUNT-1).NE.'NO')GO TO 2
0040            CLOSE(UNIT=1)
0041            GO TO 1
0042      3     IELE=KOUNT-1
0043            CLOSE(UNIT=1)
0044            CALL ION(ISEQ1,ISEQ2,LOAD1)
0045            OPEN(UNIT=6,NAME='LP:',CARRIAGECONTROL='FORTRAN')
0046            CALL MOVCUR(9,26)
0047            CALL ATTRIB(0)
0048            TYPE 1015,ITUR
0049      1015  FORMAT('+TURRET ',I1)
0050            CALL MOVCUR(13,6)
0051            CALL ATTRIB(5)
0052            TYPE 1003,ITUR
0053      1003  FORMAT('+Printing Checklist - Turret #',I2)
```

```
0054          CALL MOVCUR(24,1)
0055          CALL ATTRIB(0)
0056          CALL FPRINT(4,0)
0057          WRITE(6,1004)ITUR
0058    1004  FORMAT(/' Lamp Turret / Analytical Sequence #',I2//' Be sure
             1Lamps are loaded in the following order :'//1X,'Lamp',20X,
             2'Turret Position'/11X,'----',20X,'---------------')
0059          CALL ION(ISEQ1,ISEQ2,LOAD1)
0060          DO 4,INDEX=1,IELE
0061          WRITE(6,1006)NAME(INDEX),LAMP(INDEX)
0062    1006  FORMAT(12X,A2,28X,A1)
0063    4     CONTINUE
0064          WRITE(6,1007)ITUR
0065    1007  FORMAT(/' Load Program Card # ',I1,' into HGA-500.'//' Load the
             1 following sequences into the AS-40 auto-sampler : //1X,'SEQ',
             2T11,'PROG',T22,'#',T32,'LAST',T41,'METHOD',T51,'SAMPLE',T61
             3,'INST',T71,'HGA'/2X,'#',T11,'DELAY',T21,'STDS',T31,'SAMPLE',
             4T43,'#',T52,'VOL',T61,'PROG',T71,'PROG'/1X,'---',T11,'-----',
             5T21,'----',T31,'------',T41,'------',T51,'------',T61,'----',
             6T71,'----')
0066          CALL ION(ISEQ1,ISEQ2,LOAD1)
0067          ISTDS='3'
0068          LSTSAM='1'
0069          METHOD=1
0070          IVOL=20
0071          IDELAY=2
0072          DO 5,INDEX=1,IELE
0073          WRITE(6,1008)INDEX,IDELAY,ISTDS,LSTSAM,METHOD,IVOL,INDEX,LAMP
             1(INDEX)
0074    1008  FORMAT(1X,I2,T13,I1,T22,A1,T33,A1,T43,I1,T52,I3,T62,I1,T72,A1)
0075    5     CONTINUE
0076          CALL ION(ISEQ1,ISEQ2,LOAD1)
0077          CALL MOVCUR(13,6)
0078          CALL ERASEL(0)
0079          CALL MOVCUR(24,1)
0080          CLOSE(UNIT=6)
0081          CALL BELL
0082          CALL PRINT(' ')
0083          TYPE 1012,ITUR
0084    1012  FORMAT('+Set up Model 5000 - HGA/500 for analytical sequence
             1 ',I1,'.'/'$Press <RETURN> to continue analysis ... ')
0085          ACCEPT 1013,REPLY
0086    1013  FORMAT(A1)
0087          CALL CLRSTR(OUTSTR)
0088          CALL SCOPY('* ,OUTSTR)
0089          CALL MTPRNT(2,OUTSTR)
0090          LOAD2=0
0091    20    CALL ION(ISEQ1,ISEQ2,LOAD1)
0092          IF(LOAD2.EQ.1)GO TO 21
0094          IF(LOAD2.EQ.2)GO TO 22
0096          IF(LOAD2.EQ.3)GO TO 23
0098          IF(LOAD2.EQ.4)GO TO 24
0100          IF(LOAD2.EQ.5)GO TO 25
0102          IF(LOAD2.EQ.6)GO TO 26
```

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0104  6      CALL HEAR(2,HOLD4,INSTR)
0105         IF(HOLD4.EQ.1) GO TO 20
0107         IF(INSTR(1).NE.'D'.AND.INSTR(3).NE.'U')GO TO 999
0109         CALL CLRSTR(OUTSTR)
0110         OUTSTR(1)=IELE+48
0111         CALL MTPRNT(2,OUTSTR)
0112         LOAD2=1
0113  21     CALL HEAR(2,HOLD4,INSTR)
0114         IF(HOLD4.EQ.1)GO TO 20
0116         IF(INSTR(1).NE.'D'.AND.INSTR(3).NE.'I')GO TO 999
0118         DO 8,INDEX=1,IELE
0119         CALL CLRSTR(OUTSTR)
0120         CALL SCOPY(NAME(INDEX),OUTSTR,2)
0121         CALL MTPRNT(2,OUTSTR)
0122         LOAD2=2
0123  22     CALL HEAR(2,HOLD4,INSTR)
0124         IF(HOLD4.EQ.1)GO TO 20
0126         IF(INSTR(2).NE.'O'.OR.INSTR(2).EQ.'B')GO TO 999
0128  8      CONTINUE
0129         LOAD2=3
0130  23     CALL HEAR(2,HOLD4,INSTR)
0131         IF(HOLD4.EQ.1)GO TO 20
0133         IF(INSTR(2).NE.'L')GO TO 999
0135         CALL CLRSTR(OUTSTR)
0136         CALL SCOPY(LSTSAM,OUTSTR,1)
0137         CALL MTPRNT(2,OUTSTR)
0138         LOAD2=4
0139  24     CALL HEAR(2,HOLD4,INSTR)
0140         IF(HOLD4.EQ.1)GO TO 20
0142         IF(INSTR(2).NE.'S')GO TO 999
0144         CALL CLRSTR(OUTSTR)
0145         CALL SCOPY(ISTDS,OUTSTR,1)
0146         CALL MTPRNT(2,OUTSTR)
0147         LOAD2=5
0148  25     CALL HEAR(2,HOLD4,INSTR)
0149         IF(HOLD4.EQ.1)GO TO 25
0151         IF(INSTR(2).NE.'S')GO TO 999
0153         LOAD2=6
0154  26     CALL HEAR(2,HOLD4,INSTR)
0155         IF(HOLD4.EQ.1)GO TO 20
0157         IF(INSTR(1).EQ.'D')GO TO 1
0159         WRITE(2,1014)(INSTR(INDEX),INDEX=1,44)
0160  1014   FORMAT(44A1)
0161         GO TO 26
0162  1      CONTINUE
0163         CALL MOVCUP(9,26)
0164         CALL PRINT('FINISHED  ')
0165         CALL MOVCUP(13,1)
0166         CALL ERASEL(0)
0167         CLOSE(UNIT=2)
0168         IER=MTDTCH(2)
0169  27     CALL ION(ISEQ1,ISEQ2,LOAD1)
0170         IF(LOAD1.NE.3)GO TO 27
0172         RETURN
```

```
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0173  999   CALL MOVCUR(24,1)
0174        TYPE 10000,(INSTR(INDEX),INDEX=1,30),(OUTSTR(INDEX),INDEX=1,30)
0175  10000 FORMAT('  ERROR!'/1X,30A1/1X,30A1)
0176        CALL EXIT
0177        END
```

```
      SUBROUTINE REPORT
      BYTE ENHANC,LF,FF,NORMAL,IDSEQ(13),IDSTR(112),CHR,SEQ(14)
     1,NAME(18,2),NAME1,NAME2,TYPE,STAT,DATA(8)
      INTEGER*2 ELEMNT
      INTEGER*4 ICSPEC
      DATA SEQ/"104,"131,"61,"72,0,0,0,0,0,"56,"104,"101,"124,0/
      DATA IDSEQ/"104,"131,"61,"72,"103,"120,0,0,"56,"104,"101,
     1"124,0/
      CALL MOVCUR(11,6)
      CALL ATTRIB(0)
      TYPE 1010
1010  FORMAT('+REPORT      ')
      CALL MOVCUR(24,1)
      OPEN(UNIT=1,NAME='SY:SEQ.DAT',TYPE='OLD')
      READ(1,1000)ISEQ1,ISEQ2
1000  FORMAT(2I5)
      CLOSE(UNIT=1)
      IDSEQ(7)=ISEQ1
      IDSEQ(8)=ISEQ2
      OPEN(UNIT=1,NAME=IDSEQ,TYPE='OLD',CARRIAGECONTROL='LIST')
      OPEN(UNIT=6,NAME='LP:',CARRIAGECONTROL='FORTRAN')
      ENHANC=14
      NORMAL=15
      FF="14
      LF="12
      CALL MOVCUR(13,6)
      CALL ATTRIB(5)
      TYPE 1011
1011  FORMAT('+Printing Final Report')
      CALL ATTRIB(0)
      CALL MOVCUR(24,1)
      WRITE(6,1001)(LF,KOUNT=1,9)
1001  FORMAT(1X,9A1)
      WRITE(6,1002)ENHANC,ENHANC
1002  FORMAT(1X,A1,8X,'CONTAMINATION PROFILING'/1X,A1,16X,'REPORT')
      READ(1,1003)(IDSTR(KOUNT),KOUNT=1,9),(IDSTR(KOUNT),KOUNT=10,
     117),(IDSTR(KOUNT),KOUNT=18,50),(IDSTR(KOUNT),KOUNT=51,83),
     2(IDSTR(KOUNT),KOUNT=84,97),(IDSTR(KOUNT),KOUNT=98,111),AREACM,
     3TVOL
1003  FORMAT(1X,9A1/1X,8A1/1X,33A1/1X,33A1/1X,14A1/1X,14A1/F10.2
     1/F10.2)
      CLOSE(UNIT=1)
      CONST=.001*TVOL/AREACM
      WRITE(6,1004)ENHANC,NORMAL,(IDSTR(KOUNT),KOUNT=51,83),ENHANC,
     1NORMAL,(IDSTR(KOUNT),KOUNT=98,111),ENHANC,NORMAL,(IDSTR(KOUNT),
     2,KOUNT=84,97),ENHANC,NORMAL,(IDSTR(KOUNT),KOUNT=1,9),ENHANC,
     3NORMAL,(IDSTR(KOUNT),KOUNT=10,17),ENHANC,NORMAL,(IDSTR(KOUNT),
     4KOUNT=18,50)
1004  FORMAT(////////7X,A1,' P/N : ',34A1///7X,A1,' S/N : ',15A1///
     17X,A1,' LOT : ',15A1//////7X,A1,' DATE: ',10A1,15X,A1,' TIME: ',
     29A1//////7X,A1,'ANALYST ____________________',A1//26X,33A1
      SEQ(5)="124
      SEQ(6)="103
      SEQ(7)="110
```

```
        SEQ(8)=ISEQ1
        SEQ(9)=ISEQ2
        OPEN(UNIT=2,NAME=SEQ,TYPE='OLD',CARRIAGECONTROL='LIST')
        SEQ(5)="106
        SEQ(6)="122
        SEQ(7)="116
        OPEN(UNIT=1,NAME=SEQ,TYPE='OLD',CARRIAGECONTROL='LIST')
        DO 3, IELE=1,18
        NAME(IELE,1)=0
        NAME(IELE,2)=0
  3     CONTINUE
        IELE=1
  5     READ(1,1008,END=4)NAME1,NAME2
  1008  FORMAT(42X,2A1)
        IF(NAME1.EQ.NAME(IELE,1).AND.NAME2.EQ.NAME(IELE,2))GO TO 5
        NAME(IELE,1)=NAME1
        NAME(IELE,2)=NAME2
        IELE=IELE+1
        GO TO 5
  4     CHR='-'
        WRITE(6,1005)ENHANC,(CHR,KOUNT=1,80)
  1005  FORMAT('1',A1,16X,'Cations'//' ',9X,'- By Inductively
       1 Coupled Argon Plasma Emission Spectroscopy'///4X,'ELEMENT',
       23X,'CONC./ WEIGHT',3X,'STD. DEV.',3X,'COEFF. OF VAR.',3X,
       3'CONC./ BOARD AREA'/4X,7A1,3X,13A1,3X,9A1,3X,14A1,3X,17A1)
        TOTAL1=0
        TOTAL2=0
  1     READ(2,1006,END=2)(IDSTR(KOUNT),KOUNT=1,47)
  1006  FORMAT(1X,47A1)
        IF(IDSTR(2).NE.'A')GO TO 1
        DO 6,IELEKT=1,IELE
        IF(NAME(IELEKT,1).EQ.IDSTR(7).AND.NAME(IELEKT,2).EQ.IDSTR(8))
       1GOTO 1
  6     CONTINUE
        CALL SUBSTR(IDSTR,DATA,21,8)
        DATA(1)=DATA(8)
        DATA(8)="56
        DECODE(8,1022,DATA)RCONC
  1022  FORMAT(F8.0)
        BDCONC=RCONC*CONST
        TOTAL1=TOTAL1+BDCONC
        WRITE(6,1007)(IDSTR(KOUNT),KOUNT=7,8),(IDSTR(KOUNT),KOUNT=22,28
       1),(IDSTR(KOUNT),KOUNT=32,37),(IDSTR(KOUNT),KOUNT=42,46),BDCONC
  1007  FORMAT('0',5X,2A1,7X,7A1,1X,'PPB',3X,'+/-',6A1,7X,5A1,1X,'%',
       16X,F8.3,1X,'ug/sq.cm')
        GO TO 1
  2     CLOSE(UNIT=2)
        REWIND 1
        WRITE(6,1012)ENHANC,(CHR,KOUNT=1,80)
  1012  FORMAT(//'0',A1,16X,'Cations'//13X,'- By Graphite Furnace
       1 Atomic Absorption Spectroscopy'///4X,'ELEMENT',3X,'CONC./ WEI
       2GHT',3X,'STD. DEV.',3X,'COEFF. OF VAR.',3X,'CONC./ BOARD AREA'
       3/4X,7A1,3X,13A1,3X,9A1,3X,14A1,3X,17A1)
  8     READ(1,1013,END=9)TYPE,STAT,CV,CONC,ELEMNT
```

```
1015  FORMAT(1X,A1,15X,A1,6X,F5.2,6X,F6.0,1X,A2)
      IF(TYPE.EQ.'A')GO TO 8
      IF(STAT.EQ.'E')CV=100.0
      SD=.01*CV*CONC
      IF(STAT.EQ.'E')SD=10000.0
      BDCONC=CONC*CONST
      TOTAL1=TOTAL1+BDCONC
      WRITE(6,1014)ELEMNT,CONC,SD,CV,BDCONC
1014  FORMAT('0',5X,A2,7X,F7.0,1X,'PPB',3X,'+/-',F6.1,7X,F5.2,
     11X,'%',6X,F8.3,1X,'ug/sq.cm')
      GO TO 8
9     CLOSE(UNIT=1)
      WRITE(6,1019)ENHANC,(CHP,KOUNT=1,60)
1019  FORMAT('1',A1,17X,'Anions',//28X,' - By Ion Chromatography'
     1///4X,'SPECIES',5X,'CONC./ WEIGHT',3X,'STD. DEV.',3X,'COEFF.
     2 OF VAR.',3X,'CONC./ BOARD AREA'/4X,7A1,3X,13A1,3X,9A1,3X,
     314A1,3X,17A1)
      SEQ(5)="111
      SEQ(6)="103
      SEQ(7)="110
      OPEN(UNIT=1,NAME=SEQ,TYPE='OLD',CARRIAGECONTROL='LIST')
10    READ(1,1020,END=11)ICSPEC,TYPE,CONC,SD,CV
1020  FORMAT(A4,11X,A1,2X,F10.1,4X,F10.3,4X,F10.3)
      IF(TYPE.NE.'A')GO TO 10
      BDCONC=CONC*CONST
      TOTAL2=TOTAL2+BDCONC
      WRITE(6,1021)ICSPEC,CONC,SD,CV,BDCONC
1021  FORMAT('0',5X,A4,2X,F10.0,1X,'PPB',3X,'+/-',F6.1,5X,F7.2,1X,
     1'%',6X,F8.3,1X,'ug/sq.cm')
      GO TO 10
11    WRITE(6,1050)ENHANC,ENHANC,TOTAL1,TOTAL2,TOTAL1+TOTAL2
1050  FORMAT(////' ',A1,11X,'TOTAL CONTAMINANTS'/' ',A1,11X,'------
     1-------------'/'0',18X,'Total Cationic Species =',F9.3,1X,
     2'ug/sq.cm'/'0',18X,'Total Anionic  Species =',F9.3,1X,'ug/
     3sq.cm'/44X,'--------'/'0',35X,'TOTAL =',F9.3,1X,'ug/sq.cm')
      CALL MOVCUR(13,6)
      CALL ERASEL(0)
      CALL MOVCUR(24,1)
      CALL MOVCUR(11,6)
      TYPE 1100
1100  FORMAT('+DONE        ')
      CALL MOVCUR(24,1)
      CLOSE(UNIT=6)
      RETURN
      END
```

REPORTS AND ARTICLES

Adams, Roger J. and Keane, David D. "Mechanical or Chemical Cleaning, Part 1." Industrial Finishing, Nov. (1971), 28-31.

Adams, Roger J. and Keane, David D. "Mechanical or Chemical Cleaning, Part 2." Industrial Finishing, Dec. (1971), 24-28.

Adams, Roger J. and Keane, David D. "Spectroscopy Reveals What Microscopy Leaves Untold." Circuits Manufacturing, Sept. (1971), 54-56.

Bonner, John K. "Establishment of Production Cleanliness Criteria and Processes for Printed Wiring Boards and Assemblies." Phase I Report (MICOM), April 1979.

Brous, J. and Cole, H. "Measurement of Residual Ionic Contamination on Printed Circuit Boards." Proceedings Of The Technical Program, NEPCON, Feb. (1974), 167-74.

Chung, B. C. and Eagle, J. G. "Detection Of Organic Components In Non-Rosin Fluxes."

Kenyon, Williams. "Fundamentals of Ionic Contamination Measurement Using Solvent Extract Methods." IPC Technical Paper, Sept. (1977).

McDonald, John C. "Ion Chromatography." American Laboratory, Jan. (1979), 45-55.

Tautscher, Carl J. "New Generation of Board and Assembly Cleanliness Tests." Insulation/Circuits, Dec. (1979), 15-19.

Taylor, P. R., Altavilla, P. L., and Simmons, G. J. "Solvent Extract Resistivity Testing -- Is It Meaningful?" IPC Technical Paper, Sept. (1974).

Volpe, Luke R. "A Method For Manufacturing High Density Conductive Interconnect Circuits." International Journal For Hybrid Microelectronics, Volume 4, No. 2, Oct. (1981), 246-50.

Wargotz, William B. "Ion Chromatography Quantification For Contaminant Ions In Water Extracts Of Printed Wiring." IPC Technical Paper, Sept. (1978).

Wargotz, William B. "Quantification Of Contaminant Effects Upon Electrical Behavior Of Printed Wiring." IPC Technical Paper, Sept. (1977).

BIBLIOGRAPHY

BOOKS

Adamson, Arthur W. Physical Chemistry of Surfaces, 3rd ed. New York: John Wiley and Sons, 1976.

Canada, John R. Intermediate Economic Analysis for Management and Engineering. Englewood Cliffs, N.J.: Prentice Hall, 1971.

Coetzee, J.F., and Ritchie, Calvin D. Eds. Solute-Solvent Interactions. New York and London: Marcel Dekker, 1969.

Constant, F. Woodbridge. Theoretical Physics. Vols. 1 & 2. Reading, MA: Addison-Wesley, 1958.

Coombs, Clyde E., Jr. ed. Printed Circuits Handbook, 2nd. ed. New York: McGraw-Hill, 1979.

Covington, A.K., and Dickinson, T. Eds. Physical Chemistry of Organic Solvent Systems. London and New York:

Czanderna, A.W., ed. Methods of Surface Analysis. Amsterdam: Elsevier, 1975.

Davis, Lawrence E. et al. Handbook of Auger Electron Spectroscopy, 2nd ed. Eden Pairie, Min.: Physical Electronics Ind., 1976.

McCrone, Walter C. and Delley, John G. The Particle Atlas, 2nd. ed. Vol. I, Principles and Techniques. Ann Arbor, Mich.: Ann Arbor Science, 1973.

McIntyre, N.S., ed. Quantitative Surface Analysis of Materials. Philadelphia: ASTM, 1978.

Quade, E.S., and Boucher, W.I. Eds. Systems Analysis and Policy Planning. New York: Elsevier, 1968.

Tautscher, Carl J. The Contamination of Printed Wiring Boards and Assemblies. Bothell, Wash.: Omega, 1976.

Wagner, C.D. et al. Handbook of X-Ray Photoelectron Spectroscopy. Eden Prairie, Minn: Physical Electronics Ind., 1979.

Martin Marietta Aerospace will implement the C/P data base into the PWB Manufacturing Facility at Ocala, Florida. All Martin Marietta programs involving PWBs/PWAs will be affected.

2 Characterize various fluxes, both rosin-based and water-soluble, using the chromatograph. Build up a master chromatogram for each kind of flux.

3 Interface the chromatograph into the C/P system.

4 Simplify the sample handling procedure. This can be done by constructing special hardware interfaces (PWAs) to simulate the ICP-5000 Autosampler keyboard. This will place the ICP-5000 Autosamplers directly under control of the minicomputer.

5 Optimize the metallic element detection. This will involve investigating the torch signal to noise ratio and optimizing the signal. Improved standards for the C/P system will also be sought.

6 The Extraction Tank/Pumping unit will also be completely integrated into the C/P system and brought under the control of the minicomputer. This will also require a special hardware interface (PWA) and relays.

Phase IV Establish C/P Data Base

1 Design the C/P data base. This will involve examining the data content and from that defining the corresponding data structure. Software decision points will be determined and a functional specification created for the data base. Field service data will also be incorporated into the data base.

2 The C/P data base will then be proved out. This will include an iteration procedure entailing software modification and revision of the data structure if necessary. The data structure will be set up so direct integration with a yet larger data base encompassing the entire PW manufacturing area can be easily accomplished.

3 Document the entire C/P data base. This documentation will become part of the final technical report (FTR) and include all system designs, flowcharts, software coding, etc. This will be especially relevant for integrating this data base into a larger one.

6.4 THE BENEFITS

The end product of this program will be an implemented data base designed to reduce to a minimum both PW failures in process and latent failures after assembly/conformal coating due to residual surface contamination. This data base will be designed and generated withthe further goal in mind of integrating into a more comprehensive data base covering the entire PW manufacturing area.

3 Using samples drawn from each test lot of PWBs on which a known amount of contaminant has been induced, verify that the induced level is what it is supposed to be. The C/P system can be used for this purpose.

4 Perform the known generic tests on the test PWBs having a fixed amount of contaminant species. These generic tests include:

  a Insulation resistance (IR)

  b Temperature/humidity cycling (vesication)

  c Extract resistivity/conductivity test.

5 All data generated from these tests will be used to build up the C/P data base.

Stage 2

1 Profile key PW manufacturing stages for contaminant species using the C/P system. The key manufacturing stages will be:

  a Drill, deburr, chemical and mechanical clean

  b Electroless plate

  c Apply resist, develop image, electrolytic plate, strip resist

  d Etch image

  e Solder reflow

  f Route to size

  g Mount components

  h Flux/solder.

  Cleaned PWBs will be used as control.

2 Perform the known state-of-the-art for detecting contaminants on PWBs as a comparison with the C/P system.

3 All data generated from these tests will be used to build up the C/P data base.

Phase III Optimize C/P System

1 Procure a chromatograph system to be incorporated into the C/P system. The chromatograph will be carefully chosen for ease of integration into the C/P system.

Phase I Control Manufactured Test Printed Wiring Boards

1 Select the appropriate artwork to generate at least four (4) different component configurations and different line width/line spacings.

2 Manufacture test PWBs. Select eight (8) critical process points after which representative samples of each configuration will be checked for contaminant species using the C/P system. These eight points are:

  a Drill, deburr, chemical and mechanical clean

  b Electroless plate

  c Apply resist, develop image, electrolyte plate, strip resist

  d Etch image

  e Solder reflow

  f Route to size

  g Mount components

  h Flux/solder.

3 Test PWBs will also be used to establish meaningful limits for each contaminant species based on a comparison between the major generic tests such as insulation resistance and temperature/humidity cycling and C/P.

Phase II Test Manufactured Printed Wire Boards and Generate Data

This testing phase will involve two distinct stages (conceptually, not temporally). They are:

Stage 1

1 Establish the baseline cleanliness of the test PWBs. This will be done by controlled cleaning of all test PWBs followed by profiling for remaining contaminant species using the C/P system. Since the C/P system can detect species in the ppb range, it should be very effective for this purpose.

2 Induce a controlled amount of each contaminant species on the surface of representative PWB samples. This can be accomplished using a spray gun technique to apply a fine mist solution of the contaminant species and allowing the solution to dry.

11 Aluminum, Al

12 Iron, Fe

13 Magnesium, Mg

14 Nickel, Ni

15 Gold, Au.

The purpose of the IC is to detect and quantify (profile) the following species:

1 Fluoride, F^-

2 Chloride, Cl^-

3 Sulfate, SO_4^{2-}

4 Phosphate, PO_4^{3-}

5 Bromide, Br^-

6 Mitrate, NO_3^-

7 Nitrite, NO_2^-.

6.2 THE SOLUTION

Design and construct a C/P data base for future comparisons and establishing true statistical confidence limits for each contaminant species. Meaningful cutoff limits for each contaminant species will be established and verified. This data base shall be so constructed so that it can be interfaced with one yet larger more comprehensive encompassing the entire PW manufacturing area. It is expected that the C/P data base will lead to the elimination of generic testing. Future PW field reliability will be statistically predictable within prescribed confidence limits.

6.3 THE APPROACH

The approach will consist of several distinctive phases, some of which will occur concomitantly.

f. HGA-500 Graphite Furnace

g. Graphite Furnace Control Unit

h. AS-40 Autosampler (for furnace) + Control unit

i. AS-50 Autosampler (for torch) + Control Unit

j. PR-80 Printer (line printer)

2 One (1) ion chromatograph (IC) (Dionex AutoIon^{TM} System 12 Analyzer). This can be considered a quasi-subsystem since it can be decomposed into subunits. It is not, however, under the immediate control of its own microprocessor as the ICP-5000 is.

a. IC Autosampler

b. Computing Integrator (Spectra Physics Model SP 4100).

3 Minicomputer (Digital Electronic Corp. MINC-11, a PDP-11/03) with hardware modules for running laboratory equipment.

a. VDU

b. Keyboard

c. Disks (floppy).

The purpose of the ICP-5000 subsystem is to detect and quantify (profile) the following metallic and quasi-metallic elements:

1 Lead, Pb

2 Tin, Sn

3 Copper, Cu

4 Calcium, Ca

5 Sodium, Na

6 Potassium, K

7 Chromium, Cr

8 Zinc, Zn

9 Palladium, Pd

10 Silicon, Si

6.0 FINAL RECOMMENDATIONS: ESTABLISHMENT OF A CONTAMINANT PROFILING DATA BASE FOR PRINTED WIRING BOARDS AND ASSEMBLIES

To completely eliminate generic testing and to establish contaminant profiling on a sound footing, a contaminant profiling data base should be established.

6.1 THE PROBLEM

Contaminant profiling (C/P) truly represents a quantum leap in the state-of-the-art in detecting and quantifying printed wiring (PW) surface contamination. It permits identification of individual contaminant species and the quantification of the level of each species. Current methodologies are generic only and do not permit this. The quantity of each contaminant species can be expressed either in parts-per-billion (ppb) or in micrograms per square centimeter of PW surface ($\mu g/cm^2$). However, what is required is to link the presence and amount of each species on the PW surface to PW degradation. A rigorous testing and evaluation schedule in which the contribution to degradation and the concominant threshold limits of each contaminant species must be established for different PW configurations, packaging densities, and component types. The data generated from this testing and evaluation phase can then be used to build a data base for C/P.

To gain some perspective into the present system, it is appropriate to discuss its main features. Several of the contaminant profiling (C/P) system components can be regarded as systems in their own rights since they can be further decomposed or broken down into a number of distinct subcomponents. Since the C/P system minicomputer is the best computer for the entire C/P system, the other components are, properly speaking, subsystems. These are:

<u>1</u> One (1) inductively-coupled plasma (ICP) spectrophotometer (Perkin-Elmer ICP-5000). The ICP-5000 is a true C/P subsystem since it can be decomposed into distinct subunits.

  a. Model 5000 Spectrophotometer

  b. ICP Source (torch)

  c. Optical Interface between a. and b.

  d. RF Power Supply

  e. Data Station (6800 microcomputer)

    1. Video display unit (VDU)

    2. Keyboard

    3. Disks (floppy)

To compute the cost savings, we assume that 35 percent of the projected total yearly losses are due to residual surface contamination and that the C/P system as it now stands will aid in cutting this figure by 60 percent. This gives a Δ of $1,011,702.

The contaminant profiling system cost $460,000. This amounts to $46,000 over a ten year period. Therefore, the projected total yearly loss due to residual contamination must be modified by this figure. The corrected figure becomes:

Δ = $965,702.

This figure is used to calculate the savings expected per PWA using the C/P system.

Projected Total Yearly Loss - Residual Contamination (Average):

DS (double-sided)	$ 52,044
FC (flexible circuit)	538,807
ML (multilayer)	612,838
RF (rigid-flex)	482,481
TOTAL	$1,686,170

Projected Total Yearly Loss - Residual Contamination (Average) Using the C/P System:

DS (double-sided)	$ 20,818	
FC (flexible circuit)	215,523	
ML (multilayer)	245,135	
RF (rigid-flex)	$ 192,992	
TOTAL	$ 674,468	= $1,011,702

Projected Total Yearly Cost (Average) not using C/P System:	$16,046,980
Projected Total Yearly Cost (Average) using C/P System:	$15,081,278
DIFFERENCE:	$ 965,702

Average cost of a PWA using the C/P System = $76.444 ($15,081,278/197,285)

Δ using C/P System = $4.895/PWA ($81.339 - 76.444)

5.0 COST/BENEFIT ANALYSIS

A cost/benefit analysis shows it is economically advantageous to use the Contaminant Profiling System.

One of the chief purposes for developing the contaminant profiling (C/P) system was to lower the overall cost of producing printed wiring assemblies (PWAs). It is appropriate to compute the cost savings (Δ) for each PWA produced.

To compute the cost savings for each PWA produced, yield factors and normal production allowance factor obtained from Martin Marietta Aerospace's Ocala Facility were used. Since the C/P system is estimated to have a working life of ten years, production costs and the number of PWAs produced were averaged over a ten year period. The baseline figures to obtain the averages were this year's production figures coupled with a projected linear growth pattern of 20 percent per year.

Projected Total Yearly Loss (Average):

DS (double-sided)	$ 148,698
FC (flexible circuit)	1,539,448
ML (multilayer)	1,750,966
RF (rigid-flex)	1,378,518
TOTAL	$4,817,630

Projected Total Yearly Cost (Average):

DS (double-sided)	$ 495,296
FC (flexible circuit)	5,127,734
ML (multilayer)	5,832,266
RF (rigid-flex)	$4,591,684
TOTAL	$16,046,980

Projected Total Number of PWAs Produced (Average):

DS (double-sided)	86,806
FC (flexible circuit)	23,674
ML (multilayer)	78,914
RF (rigid-flex)	7,891
TOTAL	197,285

Average cost of a PWA = $ 81.339 ($16,046,980/ 197,285)

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              SUBROUTINE HEARIC(IUNIT,IFLAG,HEARS)
              BYTE HEARS(83)
              CALL CLRSTR(HEARS)
              INDEX=1
        1     IFLAG=MTIN(IUNIT,HEARS(INDEX))
              IF(IFLAG.GT.0.AND.INDEX.EQ.1)RETURN
              IF(IFLAG.GT.0)GO TO 1
              IF(.NOT.(HEARS(INDEX).EQ.10.AND.INDEX.EQ.1))GO TO 50
              IFLAG=1
              HEARS(1)=0
              RETURN
        50    IF(HEARS(INDEX).NE.13)GO TO 2
              HEARS(INDEX)=0
              RETURN
        2     IF(INDEX.GT.82)RETURN
              INDEX=INDEX+1
              GO TO 1
              END
```

```
0054          IF(HOLD1.EQ.1)RETURN
0056          IF(INSTR(1).NE.'R'.OR.INSTR(2).NE.'E')RETURN
0058          CALL MOVCUR(9,46)
0059          CALL ATTRIB(0)
0060          TYPE 1008
0061    1008  FORMAT('+ACTIVE   ')
0062          CALL MOVCUR(24,1)
0063          SEQ(5)='11
0064          SEQ(6)='103
0065          SEQ(7)='110
0066          SEQ(8)=ISEQN1
0067          SEQ(9)=ISEQN2
0068          OPEN(UNIT=8,NAME=SEQ,TYPE='NEW',CARRIAGECONTROL='LIST')
0069          CALL MOVCUR(13,6)
0070          CALL ERASEL(0)
0071          CALL MOVCUR(24,1)
0072          TYPE 1003
0073    1003  FORMAT(' The IC is ready for operation.'/' Set IC to AUTO and
             1 press START.'/)
0074          IPOS=2
0075          RETURN
0076    200   CALL HEARIC(1,HOLD1,INSTR)
0077          IF(HOLD1.NE.0)RETURN
0079          IF(INSTR(1).NE.'D'.OR.INSTR(2).NE.'A')GO TO 210
0081          REPLY='G'
0082          CALL MTPRNT(1,REPLY)
0083          GO TO 200
0084    210   IF(INSTR(1).EQ.'E'.AND.INSTR(2).EQ.'N')GO TO 299
0086          WRITE(8,1005)INSTR
0087    1005  FORMAT(83A1)
0088          RETURN
0089    299   CLOSE(UNIT=8)
0090          IER=MTDTCH(1)
0091          IPOS=3
0092          CALL MOVCUR(9,46)
0093          TYPE 1010
0094    1010  FORMAT('+FINISHED   ')
0095          CALL MOVCUR(24,1)
0096          RETURN
0097    300   RETURN
0098          END
```

```
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              SUBROUTINE ION(ISEQN1,ISEQN2,IPOS)
              BYTE INSTR(83),OUTSTR(83),SEQ(14),REPLY,BEGIN(13),END(5)
              DATA SEQ/"104,"131,"61,"72,0,0,0,0,0,"56,"104,"101,"124,0/
              DATA BEGIN/"37,"40,"102,"105,"107,"111,"116,"42,"111,"103,
             1"42,"40,0/
              DATA END/"37,"105,"116,"104,0/
              GO TO (100,200,300,10,50),IPOS
      100     CALL MOVCUR(24,1)
              TYPE 1000
      1000    FORMAT('$Does the SP-4100 require program loading (Y/N    ')
              ACCEPT 1001,REPLY
      1001    FORMAT(A1)
              IF(REPLY.NE.'Y')GO TO 199
              TYPE 1002
      1002    FORMAT(/' Ready to load program into the IC-SP4100.  Restart
             1 SP-4100.'/' On the SP-4100 Keyboard, type BAUD1200:IV=2:
             2!"GO":LOAD"IC"'/)
              IPOS=4
      10      CALL HEARIC(1,HOLD1,INSTR)
              IF(HOLD1.EQ.1)RETURN
              IF(INSTR(1).NE.'G'.OR.INSTR(2).NE.'O')RETURN
              CALL MOVCUR(9,46)
              CALL ATTRIB(0)
              TYPE 1006
      1006    FORMAT('+LOADING      ')
              CALL MOVCUR(13,6)
              CALL ATTRIB(5)
              TYPE 1007
      1007    FORMAT('+Loading BASIC into SP-4100')
              CALL ATTRIB(0)
              CALL MOVCUR(24,1)
              OPEN(UNIT=8,NAME='SY:ICPROG.LST',TYPE='OLD',CARRIAGECONTROL
             1='LIST')
              CALL MTPRNT(1,BEGIN)
      2       CALL CLRSTR(INSTR)
              READ(8,1004,END=4)NCHRS,(INSTR(KOUNT),KOUNT=1,NCHRS)
      1004    FORMAT(Q,83A1)
              CALL MTPRNT(1,INSTR)
              GOTO 2
      4       CALL MTPRNT(1,END)
              CLOSE(UNIT=8)
      205     CALL MOVCUR(13,6)
              CALL ERASEL(0)
              CALL ATTRIB(5)
              TYPE 1009
      1009    FORMAT('+Initializing SP-4100')
              CALL ATTRIB(0)
              CALL MOVCUR(24,0)
              CALL MTPRNT(1,'RUN1')
              GO TO 500
      199     TYPE 1020
      1020    FORMAT(' On the SP-4100 Keyboard, type RUN1'/)
      500     IPOS=5
      50      CALL HEARIC(1,HOLD1,INSTR)
```

APPENDIX 1

A FEW WORDS ABOUT SOLVENTS

The electronics industry still relies heavily on solvents. They are used to degrease printed wiring (PW) panels before processing, and they are frequently used to decontaminate PW assemblies immediately after the flux/soldering operation.

The chief purpose of a solvent after soldering is to remove all residual fluxes, any wax used during the process, and standoff materials (solvent soluble). The materials which the solvent is required to remove can be of quite different chemical nature. Fluxes, especially activated ones, contain polar and ionizable organic molecules as well as nonpolar organics. Further, activated fluxes will contain highly ionizable material in the form of activators such as diethylamine hydrochloride. The action of fluxes can also result in the formation of heavy metal chlorides. For example, the following reaction probably takes place:

$$\mathrm{CuO} \xrightarrow[\text{activator}]{\mathrm{Cl}^-} \mathrm{CuClO} \xrightarrow[\text{activator}]{\mathrm{Cl}^-} \mathrm{CuCl_2}$$

That is, the reaction of flux with activators results in oxychlorides and chlorides. These latter are ionizable.

It is especially important to remove ionic and ionizable residues since their presence on PW will degrade the electronic properties and often lead to corrosion. It has been proposed that the threshold limit for ionic material is 1 microgram of sodium chloride (NaCl) or equivalent per square centimeter of board area, i.e., 1.0 μg NaCl or equivalent/cm^2.[1]

To remove ionic and ionizable residues, especially those contaminating electronic assemblies after the flux/soldering operation, the solvent should preferably be a system composed of several different molecular constituents.[2] For practical purposes an azeotrope is best.

An azeotrope is a mixture of mutually miscible molecular species. Although a mixture, an azeotrope has several properties resembling that of a pure compound. For instance, at constant pressure it will have a constant composition, one of the distinguishing hallmarks of a true compound. Also, at constant pressure it has a definite fixed boiling point, like a pure compound. If the pressure is not changed, it is physically impossible to separate the components of an azeotrope, say by distillation.

For example, at atmospheric pressure (P = 760 mmHg) the binary azeotrope of ethanol (C_2H_5OH) and water has a constant composition by weight of 95.57 percent ethanol and 4.43 percent water and a fixed, definite boiling point of 78.2°C (172.8°F). As long as the pressure is not varied, water cannot be separated from the alcohol in this azeotrope by such physical means as distillation. If one attempts to distill a given amount of this azeotrope, one will find that it boils at 78.2°C and that the distillate possesses the same identical composition to the liquid being distilled and will also boil at exactly the same temperature, like a pure compound. Only if the total pressure to which the azeotrope is subjected is changed can the boiling point and the composition be changed, thus proving that an azeotrope is really not one pure compound but a unique mixture of several different compounds. Normally, during PW manufacturing no attempt is made to manipulate the total pressure of the azeotrope system which is that of ambient. Therefore, under such conditions an azeotrope system should possess a fixed composition and a fixed boiling point. The distillate of such a system should be easily recondensable to the original azeotrope.

But the fact that a solvent system is an azeotrope does not necessarily ensure that it is a good solvent system for PW manufacturing. Recall that the solvent system must be capable of removing different kinds of chemical species, the most important being ionic and ionizable species. The fact that a system is an azeotrope merely ensures constant physical properties. One of the molecular constituents of the azeotrope should be a polar material also capable of exerting hydrogen bonding and possessing a dielectric constant ≥ 20.

It is appropriate to ask at this point: What is a polar solvent? The answer to this question rests upon the definition of "polar." One definition of "polar" is this. Polar material is one whose molecules possess a finite, nonzero, permanent dipole moment. For a molecule to have a permanent dipole moment, it must meet two criteria, viz.:

<u>1</u> It must have polar bonds

<u>2</u> The polar bonds must be distributed asymmetrically throughout the molecule.

Let us consider several examples. A bond will be polar if there exists an unequal distribution of electron density between the two atoms making up the bond, and this will occur if the two atoms differ greatly in their ability to attract electrons. For example, carbon dioxide, CO_2, is composed of two polar bonds which we can represent thus:

$$O \underset{=}{\longleftarrow\!\!\!+} C \underset{=}{+\!\!\!\longrightarrow} O.$$

The direction of the arrows gives the direction the electrons are pulled in. Thus between each oxygen atom and the carbon there is a partial separation of charge. But carbon dioxide is a perfectly symmetrical molecule. All three atoms making it up lie along a straight line, and since polar bonds act like vector quantities, the polarity of one bond perfectly cancels that of the other. The result is that carbon dioxide has a zero dipole moment even though it has two polar bonds. The case of carbon tetrafluoride, CF_4, is another interesting example. This molecule has four polar bonds, for the electronegativity (ability to attract electrons) of fluorine is much greater than that of carbon. The molecule, however, possesses perfect tetrahedral symmetry, and it is possible to show that the vector sum of all four polar bonds is again zero. Thus the molecule possesses a zero dipole moment. Water, H_2O, also possesses two polar bonds. But water is an asymmetrical molecule. The two polar bonds do not completely cancel each other. Water has a permanent dipole moment of 1.84×10^{-18} e.s.u. x cm or 1.84 Debyes.

Figure 1. Water has a permanent dipole moment, i.e., unequal electron distribution.

The dipole moment of a molecule is usually measured in the gas phase. In Table 1 are given the dipole moments of some common solvents used in the electronics industry.

Table 1

Substance	Dipole Moment, μ, in Debyes
Water H_2O	1.84
1,1,1-Trichloroethane CCl_3CH_3	1.77
Methylene Chloride CH_2Cl_2	1.54
Methanol CH_3OH	1.70
Ethanol C_2H_5OH	1.69
1-Propanol $CH_3CH_2CH_2OH$	1.68
2-Propanol $CH_3CHOHCH_3$	1.66
1,1,2-Trichloro-2,2,1-trifluoroethane CCl_2FCClF_2	0.98
Perchloroethylene CCl_2CCl_2	0
Carbon tetrafluoride CF_4	0

Besides the dipole moment of a molecule, the dielectric constant is also of great importance. The dielectric constant is a distinguishing characteristic of a bulk amount of material. It can be defined in several ways. Theoretically, the dielectric constant of a material is the ratio of the electric permittivity, ϵ , of the material to the electric permittivity in vacuo ϵ_0, i.e., D (dielectric constant) $=\epsilon/\epsilon_0$.[3] Therefore, D is unitless.

For practical purposes, the dielectric constant is defined as the ratio of the capacitance of a parallel-plate capacitor filled with the dielectric material in question to the capacitance of the capacitor where air is the dielectric.[4] This is possible since D = 1.0000 for a vacuum while D = 1.0006 for air. The dielectric constant is a measure of the ability of a dielectric material to store energy when exposed to an electrostatic field. It is easy to show that the energy density of an electric field for a parallel-plate capacitor with a dielectric filling the space must be D times the energy density of the field in vacuo.[5] See Table 2 for the dielectric constants of some common solvents used in the electronics industry.

Table 2

Substance	Dipole Constant, D, at 25°C
Water H_2O	78.5
Methanol CH_3OH	32.6
Ethanol C_2H_5OH	24.3
1-Propanol $CH_3CH_2CH_2OH$	20.1
2-Propanol $CH_3CHOHCH_3$	18.3
Methylene Chloride CH_2Cl_2	9.1
1,1,1-Trichloroethane CCl_3CH_3	7.5

Table 2 (Continued)

Substance	Dipole Constant, D, at 25°C
Trichloroethylene CCl_2CHCl	3.4 (16°C)
1,1,2-Trichloro-2,2,1-trifluoroethane CCl_2FCClF_2	2.4
Perchloroethylene CCl_2CCl_2	2.2
Carbon tetrafluoride CF_4	1.0 (vapor at 0.5 atm)

Since the dielectric constant is a measure of a material's ability to store electrostatic energy, this also implies that the electrostatic force of attraction between two charged particles will be less in a dielectric material than *in vacuo*. Further, the greater the dielectric constant of the material, *the less* the force, all else being equal. For example, consider the Coulobmic attraction between a sodium ion and a chloride ion at a distance apart of 20 A (2×10^{-7} cm) in:

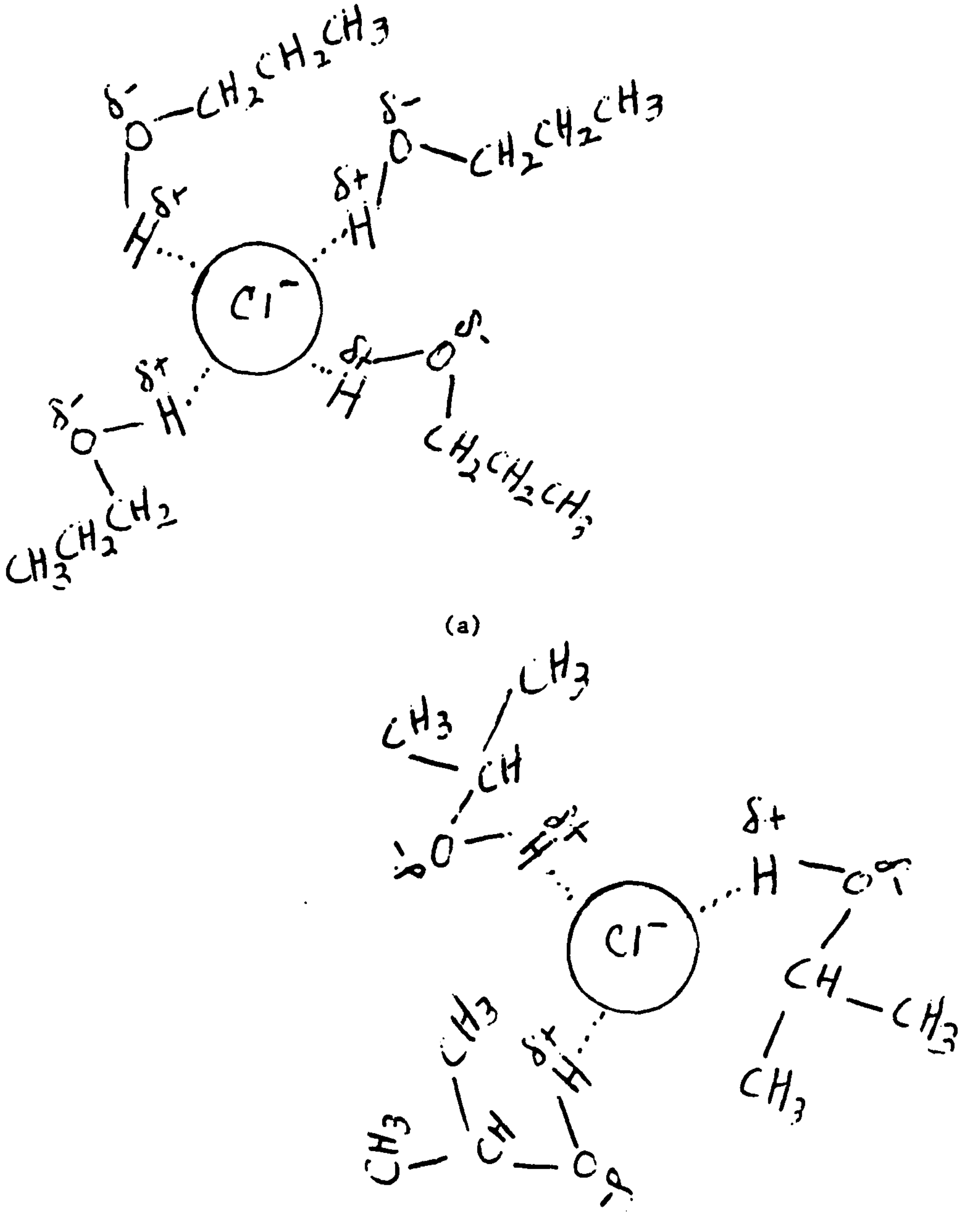
1 1,1,1 trichloroethane
2 ethanol
3 water.

Coulomb's law states that the force of attraction (or repulsion) between two charges is: $F = (1/4\pi\epsilon)\, qq'/r^2$ where q and q' denote the magnitude of the charges and r is the distance between them. Since $\epsilon = D\epsilon_0$ we have $F = (1/4\pi D\epsilon_0)qq'/r^2$. *In vacuo* the Coulombic force between a sodium ion and a chloride ion *at a distance* of 20 A is: $F = (1/4\pi\epsilon_0)qq'/r^2 = 5.76 \times 10^{-6}$ dyne. In 1.1,1-trichloroethane this force is $5.76 \times 10^{-6}/7.5 = 7.68 \times 10^{-7}$ dyne. In ethanol it is 2.37×10^{-7} dyne, and in water 0.73×10^{-7} dyne. That is, the force between the two ions in ethanol is about 1/3 of what it is in 1,1,1-trichloroethane and in water it is about 1/10 of what it is in 1,1,1-trichloroethane. A high dielectric constant, then, will ensure that the force of attraction between two ions will be less than what it would be if the dielectric constant were low (D = 1 for vacuum). Further, the fact that a molecule possesses a high dipole moment does not necessarily mean that a bulk amount of its liquid will have a high dielectric constant. The relationship between the two is rather complicated.[6] 1,1,1-Trichloroethane is a case in point. Its dipole moment, 1.77 Debyes, is comparable to that of water, 1.84, but its dielectric constant, 7.5, is quite small compared to that of water, 78.5.

Some solvent chemists consider solvents with a high dielectric constant as "polar" solvents. Solvents with a low dielectric constant are then classified as "nonpolar."[7] The cutoff point for the dielectric constant is generally taken to be 30.[8] Thus, by this definition solvents with a dielectric constant >30 are classified as polar whereas those whose dielectric constant <30 are classified as nonpolar. Going back to Table 2 the only liquids in that table considered polar by this definition are water and methanol. All others would be classified as nonpolar.

This distinction is not as useful as one would think. Many solvent chemists today also distinguish between protic and aprotic solvents.[9] Protic solvents are those that contain hydrogen which can either enter into hydrogen bonding or be donated (Bronsted acid). Many members of this class are also amphiprotic, i.e., they are capable of autoprotolysis. For example, the antoprotolysis of methanol proceeds as follows: $CH_3OH + CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$. Aprotic solvents, although they may contain hydrogen atoms, have no hydrogen atoms which may enter into hydrogen bonding or be donated. Aprotic solvents having high dielectric constants, such as DMF (N,N-dimethylformamide, D = 36.7) are sometimes referred to as dipolar aprotic solvents.

It is instructive to contrast a dipolar aprotic solvent such as DMF (D = 36.7) with a polar protic solvent such as methanol (D = 32.6). Both have about the same dielectric constant. Both reduce the Coulombic attraction between ions, it also solvates the ions. That is, the hydrogen atom on the alcoholic portion of the molecule (-OH) enters into hydrogen bonding with the ions. The ions are then said to be solvated. This hydrogen-bonding interaction between ions and solvent molecules helps to stabilize the ions, tending to prevent ion association and ion pairing within the solvent.[10] For this reason protic solvents with fairly high dielectric constants (D >20) are best in dissolving ionic and ionizable residues left on the PW surface after flux/soldering.



(a)

(b)

Figure 2. (a) Solvation of Cl^- ions by 1-propanol molecules, (b) solvation of Cl^- by 2-propanol molecules. The .... bond denotes a hydrogen bond.

It is important, then, that the solvent system used to remove ionic material on PW and other electronic devices contain a protic component capable of hydrogen bonding. If the first definition of polar is used, i.e., a polar molecule is one possessing a finite, nonzero, permanent dipole moment, then the fact that it is polar alone is not a sufficient condition for removing ionic contaminants, but merely a necessary one. If the second definition of polar is used, i.e., a polar solvent is one whose dielectric constant ≥ 30, then one of the molecular constituents of the azerotrope should be capable of exerting hydrogen bonding (i.e., be protic) and possess a dielectric constant ≥ 20. This latter material will, in general, be very effective in dissolving ionic and ionizable residues left on the PW surface after flux/soldering.

Generally, a lower molecular weight alcohol, such as methanol, ethanol, or one of the proponols, has been chosen as the hydrogen bonding component having a moderately high dielectric constant. Alcohols act primarily through the mechanism of hydrogen bonding in solvating ionic species. Even slight amounts of alcohols will radially alter the extent of association of halide salts in low dielectric solvents.[11] The alcohol molecule interacts with ionic species forming on ion-dipole attraction in which the alcoholic hydrogen plays a distinct role. For halide anions, solvation increases in the order $Cl^{-} > Br^{-} > I^{-}$. Solvation of the cationic species is relatively independent of size. Solvation refers to the surrounding of a solute species such as Cl^{-} by a definite number of solvent (protic) molecules. See Figure 2.

Regarding alcohols, primary alcohols such as methanol, ethanol, and 1-propanol are expected to hydrogen bond more effectively with ionic species than secondary alcohols such as 2-propanol. The diminished hydrogen-bonding ability of 2-propanol will result in less stabilization for the solvent-separated ion pairs in this solvent than in the primary alcohols.[12] That the hydrogen bonding capacity is greater in 1-propanol than in 2-propanol is also evident from a comparison of their boiling points.

	Bp
1-propanol (n-propyl alcohol)	97.2°C (207.0°F)
2-propanol (isopropyl alcohol)	82.3°C (180.1°F)

In this discussion of solvents we saw that solvent systems which were azeotropes offered distinct advantages. Further, for the purposes of removing ionic contaminants one of the components should be a polar species capable of hydrogen bonding.

NOTES

1. See W. Bernard Wargotz, "Quantification of Contaminant Effects Upon Electrical Behavior of Printed Wiring, "*IPC Technical Paper*, September (1977), 13.

2. This paper will deal only with solvent systems. Aqueous cleaning systems will not be addressed.

3. See F. Woodbridge Constant, *Theoretical Physics*, Volume 2 (Reading, MA: Addison-Wesley, 1958), p.251.

4. For a parallel-plate capacitor filled with a dielectric whose dielectric constant = D, the capacitance is $C = \epsilon_0 DA/L$ where A is the plate area and L is the distance between the plates. If air (or better, vacuum) is between the plates, then $C(air) = \epsilon_0 A/L$. Obviously, $C/C(air) = D$.

5. Constant, *Theoretical Physics*, Volume 2, pp. 169 and 256.

6. The relationship is given by

$$[(D-1)/(D+2)](M/d) = \text{constant} + 6093.6\,\mu^2/T$$

where M is the molecular weight of the substance in question, d its density, and T the temperature in degrees Kelvin. See Samual H. Maron and Carl F. Prutton, *Principles of Physical Chemistry*, 4th ed. (New York: Macmillan, 1965), p. 697.

7. See E.J. King, "Acid-base Behavior," Chapter 3 in A.K. Covington and T. Dickinson, eds. *Physical Chemistry of Organic Solvent Systems* (London and New York: Plenum Press, 1973), p. 333.

8. *Ibid*., p. 333.

9. See A.K. Covington and T. Dickinson, "Introduction and Solvent Properties," Chapter 1 in *ibid*., p. 4.

10. See Roger G. Bates, "Medium Effects an pH in Nonaqueous Solvents," Chapter 2 in J.F. Coetzee and Calvin D. Ritchie, eds., *Solute-Solvent Interactions* (New York and London: Marcel Dekker, 1969), pp. 52ff.

11. See R.P. Taylor and I.P. Kuntz, Jr., *J. Am. Chem. Soc.*, *92* (1970), 4816.

12. See Sister Mary A. Matesich, John A. Nadas, and P. Fennell Evans, *J. Phys. Chem.*, *74* (1970), 4572.