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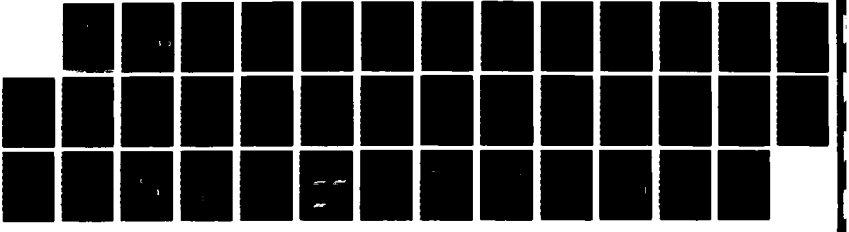

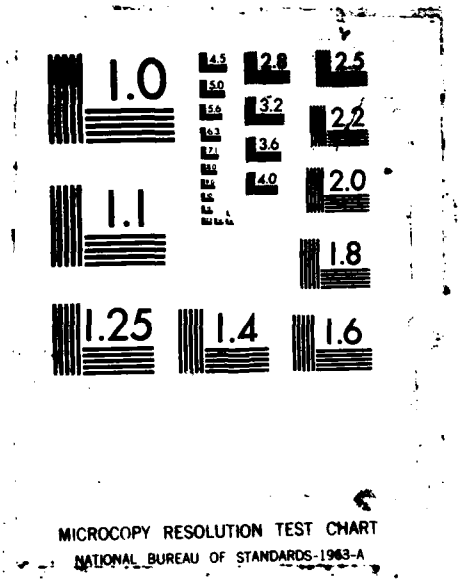
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The use of automatic laboratory techniques is rapdily increasing. Significant changes are occurring both in how tasks are accomplished and in which tasks are practical and cost effective. While the automation of a given task does not inherently dictate the use of some form of computer, the greater system flexibility achieved through software control, coupled with the recent drastic reduction in computer hardware costs, have already made this approach to automation extremely popular.

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20. Abstract (continued)

The vast proliferation of computational hardware does not solve all of the problems in laboratory automation--FAR FROM IT. Two major problem areas arise, development of suitable function systems to conduct the desired chemistry and development of the proper software. Today in many cases workers have resorted to mimicking human manipulation of samples through the use of robotics. While this approach is viable for some situations, it is far from optimal for many other applications.

Laboratory automation today often involves the use of instruments designed to perform a specific task (i.e., sample preparation and analysis) on a high work load. However, there is a trend toward increasing flexibility through multi-task capability. This concept can be implemented through several means. One example would be an instrument which is configured in such a manner that it can or does obtain a wide range of data. Software quickly sifts through the results and displays the requested information to the user. This approach allows a great deal of flexibility since different information can be obtained merely by changing the software. Additionally, the presence of possible interferences, unusual results on species not requested, and even overall system performance can be constantly monitored and presented to the user.

Many of these concepts will be considered while describing a new generation of intelligent atomic spectroscopic instrumentation. The ultimate goal is an automated system capable of accepting any type of sample and performing any analysis such that all desired information would be obtained. Ideally, following analysis, the sample would be returned unharmed. Such a highly flexible, nondestructive instrument is "science fiction" today, but much more limited systems are not out of the question based upon present technology.

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CONCEPTS FOR IMPROVED AUTOMATED LABORATORY PRODUCTIVITY

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Abstract

The use of automated laboratory techniques is rapidly increasing. Significant changes are occurring both in how tasks are accomplished and in which tasks are practical and cost effective. While the automation of a given task does not inherently dictate the use of some form of computer, the greater system flexibility achieved through software control, coupled with the recent drastic reduction in computer hardware costs, have already made this approach to automation extremely popular.

The vast proliferation of computational hardware does not solve all of the problems in laboratory automation--FAR FROM IT. Two major problem areas arise, development of suitable function systems to conduct the desired chemistry and development of the proper software. Today in many cases workers have resorted to mimicking human manipulation of samples through the use of robotics. While this approach is viable for some situations, it is far from optimal for many other applications.

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Introduction

As analytical chemists we are interested in qualitative analysis, composition, quantitative analysis--how much is really there, and, in many cases, speciation--how those various components are combined. The tool that all of us as analytical chemists really dream about having available is what I refer to in concept as the Mark I Magic Analyzer. In this case, the Mark I magic analyzer will accept any sample whatever it might be. We merely tell the Mark I what we would like to know about the sample, and the Mark I performs that analysis while even telling us other interesting and important aspects of that particular sample's composition. Finally, the Mark I would return our sample.

Clearly such technology is not available today. However, some of the concepts in the Mark I certainly can be applied when we consider automation and future automation in our own laboratories. We would like to have the ability to handle samples with little or no sample preparation, or the ability to perform sample preparation automatically in a manner transparent to the user. Figure 1 shows some of these concepts: automatic sampling, automatic sample preparation if required, automated analysis, automated data reduction, and, finally, data presentation, data correlation, and trend pattern analysis. Notice that there is feedback from all of these different steps to the control step. Additionally, we can learn from the trend-pattern analysis, allowing the automated system to actually get smarter as time progresses.

Recently there has been a proliferation in the concept of using robotics to merely replace humans, that is, to have the robot actually go

through all the steps of an analysis that would have been done conventionally with human beings. In some cases this is appropriate; in other cases it would be far better to look over the whole situation, and possibly approach the analysis with robotic and/or other systems in a totally different manner than one would with human lab technicians.

I would like to consider two approaches to the problem of laboratory automation through the use of improved sample handling and with more intelligent instrumentation. In both cases, atomic spectroscopy will be the technology that will be utilized to gain insight into the sample composition. While far from the desired capabilities of the Mark I magic analyzer, atomic spectroscopy does provide in-depth knowledge of elemental composition of the sample. We will be considering flames, DC, and inductively coupled plasmas for actually analyzing samples. Until recently, most samples were analyzed in the liquid form and converted to an aerosol which was introduced into either the flame or the plasma with Bernoulli principle or cross capillary types of nebulizers. In both cases, the sample passes through a rather small capillary that limits the nebulizer in handling highly viscous materials, materials that have very high levels of suspended solids, or even samples with very high levels of dissolved solids, since the end of the capillary can become encrusted by salt crystals and the rate of nebulization altered.

New Technology to Minimize Sample Preparation

Several years ago, my research group first introduced the Babington geometry nebulizer to atomic spectroscopy (1,2) and explored a variety of configurations for such systems (3). At that time we demonstrated the

ability to nebulize motor oils, all the way from SAE 5 W to 90 W transmission grease, condensed milk, whole blood, hydraulic fluid, urine, orange juice, pineapple syrup, and even tomato sauce with absolutely no sample preparation and no problems associated with nebulizer clogging (2). We had a great deal of fun showing a slide depicting spooning tomato sauce into the nebulizer and a nice red cloud issuing from a burner base. We also demonstrated that Babington principle nebulizers had essentially the same sensitivities for conventional aqueous samples at low salt concentrations, etc., while still being able to handle these very difficult types of samples (2). (Table 1)

Babington principle nebulizers were found to provide reliable analysis for such complex and difficult samples as condensed milk, grapefruit juice, blood, etc., showing that the same answers were obtainable directly with the Babington that were observed with conventional acid digestion procedures. We also established that in most analyses the results reflected analysis of the entire sample matrix and not just the supernatant. However, in the case of the tomato sauce, where very large fibrous materials are present, the data indicated that a transport problem caused the results to correlate closely with those obtained from acid digestion of the supernatant. Considering the geometry that was being employed at that time, this was not surprising.

Other observations made when analyzing motor oil indicated that when the viscosity of the motor oil increased over approximately SAE 25 W, the actual sample flow across the nebulizer changed. Past this point the viscosity of the standards had to be matched to that of the unknown to insure valid results. While this seems to be a trivial matter, in practice it is a significant limitation since even though a known viscosity oil can be put into a particular engine, the viscosity after a length of time of engine

operation can be quite different. Fuel dilution can decrease the viscosity, sludge formation can increase the viscosity. Therefore, to actually make valid analysis a viscosity measurement was necessary to allow matching of the standards with the unknown. Subsequent studies (4,5) demonstrated that if the nebulizer tip is heated to approximately 70°C, the emission intensities for SAE 20 W, 30 W, 40 W, and 50 W Pennzoil motor oil all converged. Additionally, the sensitivity of the system was increased by approximately an order of magnitude. (Figure 2)

Figure 3 shows the divergence in intensities for a variety of spiked oils from that obtained with 30 W Pennzoil. A greater deviation is observed between various different brands of SAE 30 W motor oil than in fact between the SAE 20, 30, 40, and 50 W Pennzoil, indicating that viscosity is not the major cause of deviation but that other factors in the composition of the oil such as antioxidants, additives, etc., contribute as well. These studies indicated the Babington principle nebulizer's capabilities for analyzing dissolved metals in oils.

But what about real world samples? Real world samples also contain particulates of sizes below the cutoff of the filtration system in the particular engine. As in the case of the tomato sauce, where the large particulates tended to settle out, these relatively heavy metal particles, particularly with the lower flowrates associated with the sample injection in an ICP, can be selectively removed in the spray chamber preventing them from being introduced into the plasma discharge. Analysis of real samples actually showed that in the conventional configuration the results tended to be low. This led to the investigation of inverted plasma configuration, originally used by Reed (6) in the first inductively coupled plasma system where powder and gas were introduced to grow crystals. Subsequently,

Greenfield (7) used a similar configuration for the first analytical studies in an ICP. In later studies the plasma was turned "right side up" and operated in the mode that we normally do today.

A comparison of the results obtained with direct injection ICP, solvent dilution atomic absorption, where the sample was diluted 10 to 1 in MIBK, the inverted ICP, and finally a conventional acid digestion ashed atomic absorption analysis, which we will consider is the actual correct value for the following series of studies, is shown in Table 2. Data from the analysis of several samples by total digestion atomic absorption and then direct injection ICP are shown in Table 3. While this problem could have been automated using robotics to carry out conventional digestion procedures, the inverted ICP equipped with a heated Babington principle nebulizer provides a much simpler approach allowing a sample to be drawn out of a running engine, taken directly to the system, and run in a few minutes' time. Clearly this indicates a route to improve automation and sample throughput by rethinking the method of analysis, incorporating new technology, and, in this case, totally eliminating the sample preparation steps.

Utilizing Information Provided by a Technique

Another case of improved automation involves better utilization of the information actually available from an analytical technique. Again, we will focus on atomic emission spectroscopy, where for any given element there can be a large number of emission lines. Those who have experienced the pain and drudgery of using photographic emulsions also readily appreciate the tremendous amount of spectral information this technique actually provides. Unfortunately, quantitization using photographic emulsions is extremely laborious and generally somewhat limited in accuracy. Two alternative

approaches are commercially available for actually measuring this information. One involves slew scan type of readout where one wavelength at a time is observed. This has a rather major disadvantage because plasma, nebulizers, and readout systems are never totally stable. Also the time involved can be substantial if one wants to look at several lines for each element. The second approach is the direct reader or polychromator, which places a series of slits and photomultiplier tubes on the focal plane. This popular technique suffers from a number of rather significant limitations. It is very expensive, large and bulky--not generally considered a portable type of instrument. Each of the slits and photomultiplier tubes requires alignment to a specific line. This can represent a substantial amount of initial setup time and can require periodic realignment. By far the most serious limitation of the direct reader is the very limited amount of spectral data observed since one photomultiplier is required per line observed.

What is really needed is some type of electronic readout which will measure the photon flux at all wavelengths simultaneously, that is, an electronic equivalent of a photographic emulsion. This has been dreamed of for years and a wide variety of researchers have expended considerable effort investigating a variety of "camera devices," including vidicons, intensified target vidicons, plumbicons, orthicons, image dissectors, photodiode arrays, and a variety of other imaging devices (8,9). The "camera techniques" previously explored have suffered from one or more problems including poor dynamic range, insufficient spectral range, poor reproducibility between detector elements, crosstalk between elements--blooming, smearing, etc., insufficient number of resolution elements, poor

sensitivity (QE), high dark and/or read current, inability to provide integration of photon flux, inability to randomly access detector elements, high cost per detector element, and poor reliability.

Astronomers have also been faced with the problems associated with photographic emulsions. And, in fact, modern astronomy is carried out to a great degree with a variety of new high technology, solid state imaging devices, including Charge Coupled Devices (CCDs) and Charge Injection Devices (CIDs) (10). Since the emphasis in astronomy is generally on extremely low light detection, charge coupled devices are widely utilized (11,12). However, atomic spectroscopy has an unusual condition not often encountered by astronomers. In atomic emission spectroscopy, it is necessary to be able to detect parts per billion of a particular component, while also being able to quantify very high levels of a component without having problems associated with blooming or smearing from lines associated with major constituents in the sample. This necessitates an extremely large dynamic range.

Out of all of the charge transfer devices available today, the charge injection device has the unique capability to read out a given detector element either destructively or nondestructively. Since the charge injection device, unlike the photomultiplier tube, has no internal gain, considerable gain must be added by outside amplifiers. Unfortunately, associated with all amplifiers is a certain degree of noise principally from the very first stage of the amplifier, which is amplified by the entire gain of the amplifier string. Richard Aikens and coworkers (13) at Kitt Peak National Laboratories demonstrated the improved signal to noise ratio inherent by summing a number of nondestructive readouts from the charge

injection device. Since the noise from the video preamplifier is essentially white, summation of multiple nondestructive readouts can eliminate this component. Unfortunately, CIDs are not configured in the ideal geometry. The ideal geometry of approximately one half meter long, the ability to be curved along the focal plane, with individual detector elements 10 microns wide by a couple millimeters tall, is not practical using today's technology. In fact, these devices range from approximately 8 mm X 8 mm containing 1.64×10^4 detector elements to 6.56 mm X 8.78 mm containing over 3.6×10^5 elements. Hardly the desired geometry for incorporation into a conventional direct reading spectrometer.

Since these devices are XY devices, some approach must be pursued which will utilize this format. One choice would be that of an echelle grating spectrometer similar to those manufactured by Beckman Instruments, Leeman Laboratories, etc. In the case of the Beckman echelle spectrometer, on an area 10.2 X 12.6 cm, one actually generates the equivalent of a linear focal plane that would be approximately 10 meters long, achieving high resolution with a quite respectable degree of total light throughput. Unfortunately, 10.2 cm X 12.6 cm is a far cry from the actual size of the devices in question. Previous investigators have faced similar problems with the use of other types of XY detectors. Harry Pardue et al. (14) studied a vidicon detection system on a modified Spectrametrics Beckman echelle spectrometer, where a Cassegrain telescope was used as an image reducer. Figure 4 shows one approach using an echelle grating in conjunction with a first order grating to sort out the orders vertically, a Cassegrain imaging reducing system reduces the image to provide a focal plane suitable for use with the charge injection device detector.

Clearly there are a number of tradeoffs in design of an echelle spectrometer system for use with one of the charge injection device detectors. These include wavelength coverage, resolution and light throughput. Unlike electron beam types of readout systems such as the vidicon, these solid state devices are directly digitally addressable. Therefore, with a properly designed stabilized optical system, extremely accurate background subtractions can be readily performed. Figure 5A depicts a small portion of three orders. One might guess that the very large peak is in fact a signal due to analyte, however, when the background is observed (Figure 5B), the large peak is confirmed to be analyte, while the medium peak just to the right, was in fact due to the background. Subsequently, when these two are subtracted, Figure 5C shows the simplied spectra, clearly indicating that the large peak was sample, but also showing a number of smaller peaks clearly vastly above the signal to noise background readily usable for chemical analysis.

While the current trend in charge injection device technology is toward a larger number of total detector elements, unfortunately, there is also a trend toward reducing the actual size of the wafer and hence greatly reducing the total area of each detector element. This necessitates even more stringent optical designs. Current devices under investigation include the CID17 and CID20. The CID17 is composed of 248 rows and 388 columns. Each detector element is 23 μ X 27 μ. The CID20 employs 488 rows by 388 columns with each detector element being 11 μ X 27 μ.

To fully appreciate the capabilities of the charge injection devices, one must refer to the quantum efficiencies available in current state-of-the-art photomultiplier tubes, where quantum efficiencies above 10 percent and certainly above 20 percent are extremely rare. In contrast to the

photomultiplier tubes, the charge injection devices such as the CID 17 and 20 have quantum efficiencies approaching 50% ranging from 7% at 200 nm, 13% at 225 nm, to 18% at 800 nm. When this is coupled with the fact that the devices have essentially zero dark current when properly operated, one realizes that this is a truly remarkable detector.

The charge injection device's unique capability to mix both destructive and nondestructive readouts gives the atomic spectroscopist another very powerful capability, that is, to be able to vary the integration time from one wavelength to another dependent on the actual the amount of light observed at each wavelength. Hence it is possible to integrate very intense lines for short periods of time until good signal to noise ratios are obtained, and while the system is still in its linear dynamic range, measure those very intense lines. Subsequently, those intense wavelengths can be destructively read out while integration continues on wavelengths associated with very weak emission lines. The net result is that strong lines are integrated for a short period of time, while weak lines are integrated for extended periods of time allowing good signal to noise ratios to be obtained in both cases without problems associated with overloading the device. This method requires that nondestructive reads be truly nondestructive. The signals observed from rereading four different lines at the rate of one readout per second for eight hours is shown in Figure 6. One approach for implementing variable integration time detection is shown in Figure 7. In this example, there is a combination of a read window, which is 13 detector elements wide by 3 detector elements tall, and an examination window, which is the center array of 3 by 3 detector elements, where the actual emission line falls. The 3 by 5 adjacent areas are used for background subtraction as shown in Figure 8. An actual example of the iron 297.32 nm line is shown

in Figure 9. For the purposes of determining appropriate integration times, it is only necessary to look at the detector elements associated with examination window. Finally, when the signal present in the examination window is of sufficient intensity to allow good signal to noise ratio, the entire array associated with the read window is recorded so that appropriate background correction techniques can be applied. Since these devices have essentially zero dark current when properly operated, the ultimate detection limit is limited merely by the background and drift characteristics of the source being studied and the full charge capacity of a given detector element.

The detection limits, defined as twice the standard deviation of the blank, observed with the CID 17, DC plasma, University of Arizona echelle system versus those published in the literature for the Beckman DC plasma echelle spectrometer are presented in Table 4. It should be noted that the detection limits in the charge injection device system were actually run under one set of conditions for all elements concerned and not optimized from element to element. When comparing the observed detection limits with those obtained from the commercial literature, one sees that certainly the system is very much in the ball park, sometimes beating out and in most cases at least tying, those available from the commercial system. Additionally, dynamic ranges for the charge injection device system extend to well over 10,000 parts per million, one to two orders of magnitude better than those available from the commercial instrument. Additionally, the system is able to perform in very complex matrix systems as shown in Table 5. Note that the detection limits are degraded only slightly for iron, not at all for chromium, and a factor of 10 for calcium and nickel. This is

quite minimal when one considers the complex line structure presented by an element such as gadolinium at such a high concentration.

The overall block diagram of the system is shown in Figure 10. As mentioned previously, when properly operated, charge injection devices have essentially zero dark current. This means that the devices must be maintained at or near liquid nitrogen temperature, necessitating a liquid nitrogen dewar system. The overall instrument is controlled by a Motorola 68,000 base processor hosted in a multibus configuration with a special camera controller developed by Photometrics Ltd. (Tucson, AZ). This camera controller uses 2901 bit slice bipolar processors operated in a pipeline mode to achieve the necessary high speed control of the array detector.

Realization of an Intelligent Spectrometer

Now that we have covered an overview of the spectrometer system, let us go back and ask a few simple questions regarding the analysis of our individual samples.

(1) Do we want an answer, or do we want a valid analysis? This a non-trivial question. All of us realize that many modern day instruments only provide a number and not necessarily a valid analysis.

(2) Do we always analyze very similar samples, or do we get a widely varying number of samples, regarding matrix, the elements of interest, etc.?

(3) Do we have unlimited time to analyze each sample? Unfortunately, time is money.

To achieve a valid analysis using current technology requires a combination of the following:

Initially we must analyze the sample to determine the potential matrix effects, then we must select the appropriate wavelengths for each analyte species. We must validate the procedure using synthetic or NBS standards in as similar a matrix as possible. Next we actually analyze the sample. Note that we had to analyze the sample to find out what type of matrix was present, so that later we could actually analyze the sample in a valid manner. Finally we must check by analyzing the sample by various other techniques and/or the use of standard additions, etc.

This entire process can be greatly simplified by properly employing the capabilities of the previously discussed spectrometer. In fact, with this spectrometer's capabilities, we are able, for the first time, to realize a truly intelligent instrument that can make intelligent decisions on the sample as it is actually being analyzed. What do we mean by intelligent instrumentation? Webster defines intelligence as "the ability to learn or understand or to deal with new or trying situations." In the role of the modern chemical laboratory, an intelligent instrument should have the ability to reason and apply logic at a level normally associated with the human mind. Through proper utilization of the charge injection device echelle spectrometer capabilities, it is possible to observe rapidly and nondestructively the entire emission spectrum of a particular sample during early stages of the analysis (milliseconds). This provides the data necessary for the instrument to make intelligent decisions choosing the following parameters:

(A) Which wavelengths are appropriate for use with this particular sample based on the observed concentrations of each analyte? The observed concentrations of other potentially interfering analytes? The effects of the host matrix, solvent, etc.

(B) Which readout modes are most suitable? How many detector elements are to be read for each wavelength for signal and background correction?

(C) Which data reduction modes will be employed? We have a wide variety of data for doing sloped baseline corrections, etc.

(D) Which diagnostic procedures are desirable? We may want to monitor the argon emission from the plasma at several different wavelengths indicating change in actual plasma excitation conditions. We may want to monitor hydrogen emission associated with the solvent; this would give us information concerning drifts and changes in the nebulizer. We may want to observe carbon emission; this can tell us if the solvent has been changed in a particular sample from aqueous to organic solvent material. If aqueous solutions were used for standardization, the nebulizer will change the nebulization rate and we would have an invalid analysis.

During analysis the system chooses the optimum integration time for each analytical wavelength, remembering that there might be quite a number of analytical wavelengths for each element sought, collects the appropriate background data for each analytical wavelength, and monitors the various diagnostic parameters. Following the analysis, the system reduces and presents the data, compares results obtained for each element at each wavelength employed for that element, and using this can estimate the accuracy and precision for each element. Additionally, the system notes any unusual circumstances, i.e., the example of an organic solvent suddenly substituted for an aqueous set of solutions when the standardization had been done with aqueous standards.

Conclusion

Two rather different concepts have been presented in the hope that they serve as good examples of how new technology can be employed to improve laboratory productivity. Automation of conventional procedures is not always the most appropriate mechanism to achieve optimal results. In the case of oil analysis, new nebulization approaches completely sidestep the need for sample preparation eliminating a whole series of complex, intricate procedures. While these procedures could certainly be automated through the use of robotics, why bother?

The second example illustates how proper utilization of the information content provided by a technique can significantly reduce the amount of labor necessary to achieve reliable valid analysis. This example also points toward, in the view of this author, the next major breakthrough in laboratory automation--intelligent instrumentation, often referred to as artificial intelligence.

Acknowledgments

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Figure Legends

Figure 1. Automated chemical analysis normally involves several steps. Currently numerous different spectroscopic techniques are employed in the analysis step.

Figure 2. Emission intensity as a function of temperature for various grades of Pennzoil HD motor oil, each spiked with 100 $\mu g/g^{-1}$ level Conostan oil soluble Fe standard: (◇): 20 W; (□): 30 W; (▲): 40 W; (⧗): 50 W.

Figure 3. Ratios of emission intensities given by various oils to the intensity measured for Pennzoil 30 W at the same temperature: (◇): Pennzoil 20 W; (□): Penzoil 40 W; (▲): Pennzoil 50 W; (⧗): Ray Lube 30 W; (○): Quaker State 30 W; (■): Valvoline 30 W; (●): Kendall GT-1 40 W.

Figure 4. An optical system employing an echelle grating, first order grating and Cassegrain image reducer to create a two-dimensional focal plane suitable for use with charge injection device detectors.

Figure 5. Plot of a spectrum showing analytical lines with background from the plasma (A), plot of the background from the plasma (B), and background subtracted from the analytical signal (C).

Figure 6. A plot of observed signal for four analytical lines of different intensity read nondestructively at a rate of one read per second for 8 hours. Note that the observed line intensities are not affected by over 2.8×10^5 readouts.

Figure 7. The readout during quantitative analysis involves nondestructively sampling a three-by-three detector "examination" matrix to determine when a selected line has reached the desired intensity, and then reading a three-by-thirteen array multiple times to accurately acquire both the line and background intensity.

Figure 8. A representation of how a "read" window is selected to contain a spectral line and adjacent background.

Figure 9. An actual example of a read window showing the observed intensity for the iron 297.32 line and surrounding background.

Figure 10. A block diagram of the CID-17 camera system used for this work. Array detector sequencing is provided by a Photometrics Ltd. camera controller which receives instructions from a host Motorola 68,000 based computer.

Table Legends

Table 1. Zinc analysis in μg/ml.

Table 2. A comparison of four methods for the determination of iron in a 30 W motor oil sampled from an automobile.

Table 3. A comparison of the results of analysis of four motor oil samples by Direct Injection Inverted ICP and Acid Digestion, followed by Determination by AA.

Table 4. A comparison of detection limits observed with the direct current plasma source and CID spectrometer compared to those obtained with a commercial DCP echelle system showing competitive detection limits.

Table 5. Detection limits observed in a 1000 μg/ml gadolinium matrix demonstrating a maximum of one order of magnitude loss when analyzing a matrix producing a very complex emission pattern.

TABLE 1

Zinc Analysis in µg/ml

Matrix	Babington	Total Digestion*	Centrifuge Supernatant Digested
Condensed Milk	7.5	7.9	1.6
Grapefruit Juice Homogenized	0.39	0.41	0.25
Pineapple Syrup	0.54	0.58	0.56
Hemolyzed Whole Blood	12	13	14
Tomato Sauce	0.62	≈4	0.64
Pickled Beet Juice	0.72	0.81	0.70

*Acid digested samples were run using AA.

TABLE 2

Comparison of Methods for Iron in Lubricating Oil

Method	Concentration Iron µg/ml
Direct Injection Upright ICP	56
Solvent Dilution AA	36
Direct Injection Inverted ICP	117
Ashed AA	106

TABLE 3

Sample	Total Digestion AA(μg/ml)	Direct Injection Inverted ICP (μg/ml)
1	140	141(±22)
2	404(±35)	406(±14)
3	205(±22)	242(±22)
4	106(±15)	117(±15)

TABLE 4

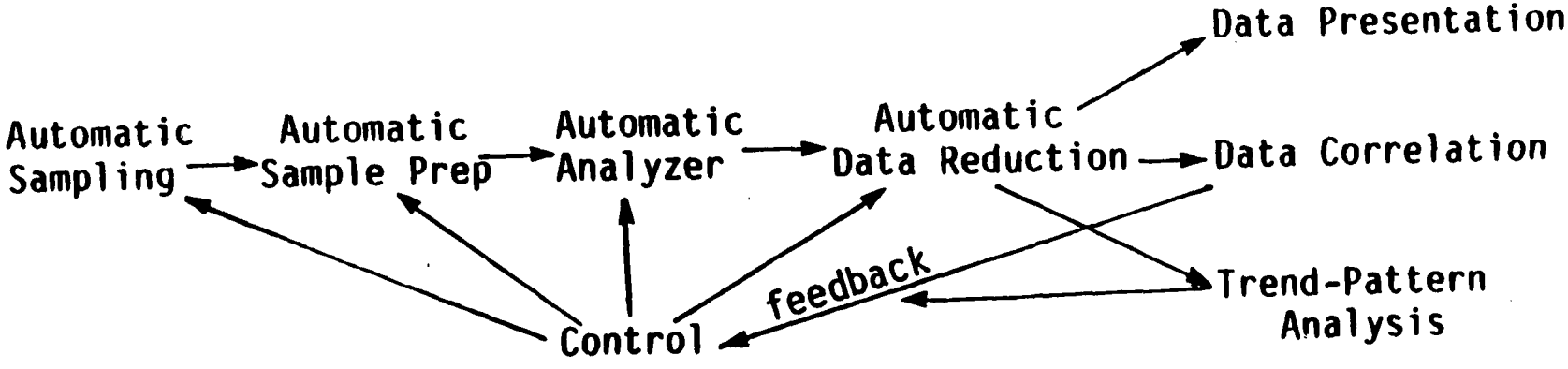
Element	Wavelength	Detection Limit	
		CID17, DC Plasma/ UA Echelle	Beckman DC Plasma/ Echelle
Al	308.22	7	
	394.40	3	
			2 (396.15)
Ca	393.37	1	0.7
	396.85	2	
	422.67	0.4	
Cr	357.87	2	2
	359.35	4	
	360.53	6	
	427.48	4	
	428.97	5	
Cu	324.75	3	2
	327.40	3	2
Fe	358.12	6	
	371.99	1	5
	373.49	3	
	373.71	15	
	386.00	15	
In	303.94	7	20
	325.86	12	
	410.18	2	10
	451.13	2	4
Mn	259.37	5	2
	293.93	2	
	403.08	4	10
	403.31	5	
	403.45	6	
Ni	352.45	7	
			2 (341.48)
Pb	363.96	11	
	405.78	6	20
			10 (368.35)

TABLE 5

Detection Limits for Several Elements

in a 1000 ppm Gadolinium Matrix

Element	Wavelength	Detection Limit
Ca	422.67 nm	3
	396.85	5
	393.7	3
Cr	425.43	2
	427.48	14
Fe	373.49	2
Mg	279.55	.2
	280.27	.4
	285.21	.6
Ni	341.48	70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Automatic Analyzer
Automatic Data Reduction
Data Presentation
Data Correlation
Trend-Pattern Analysis
feedback
Control

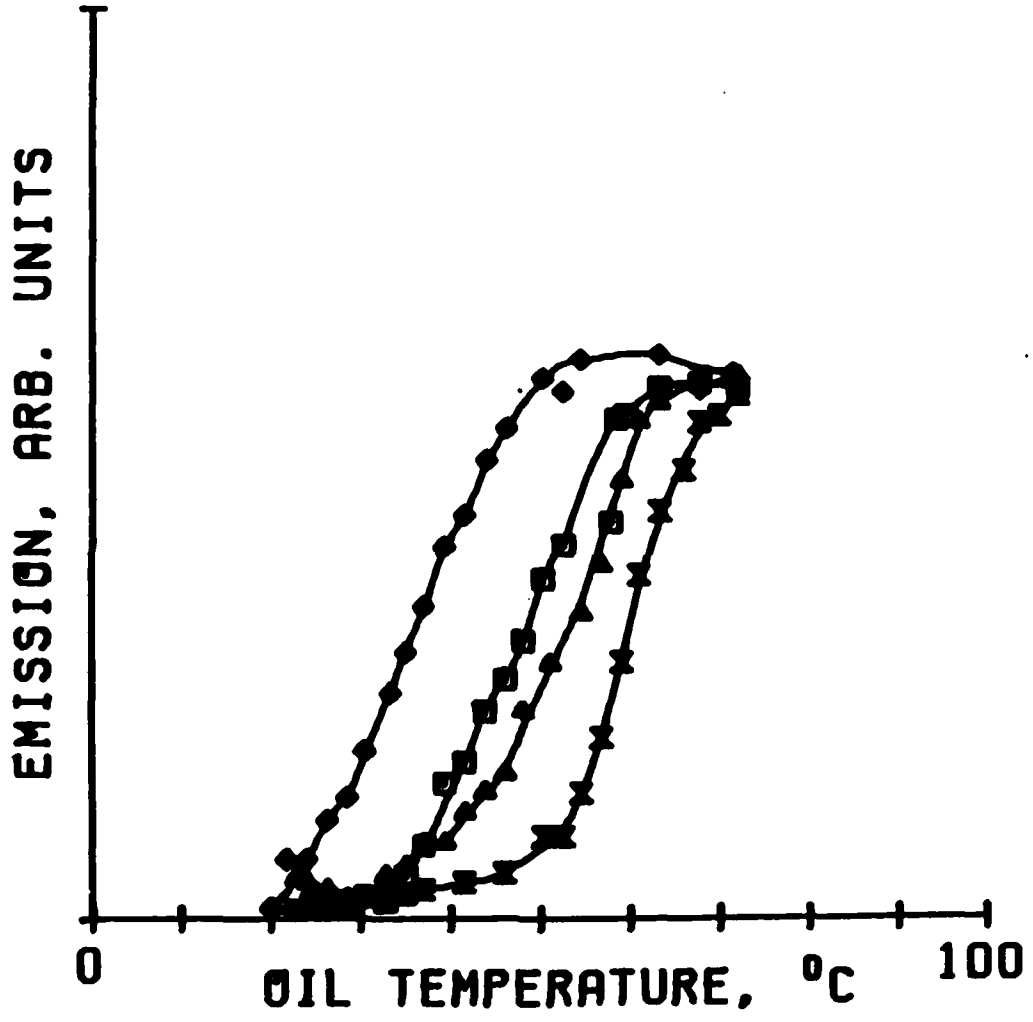
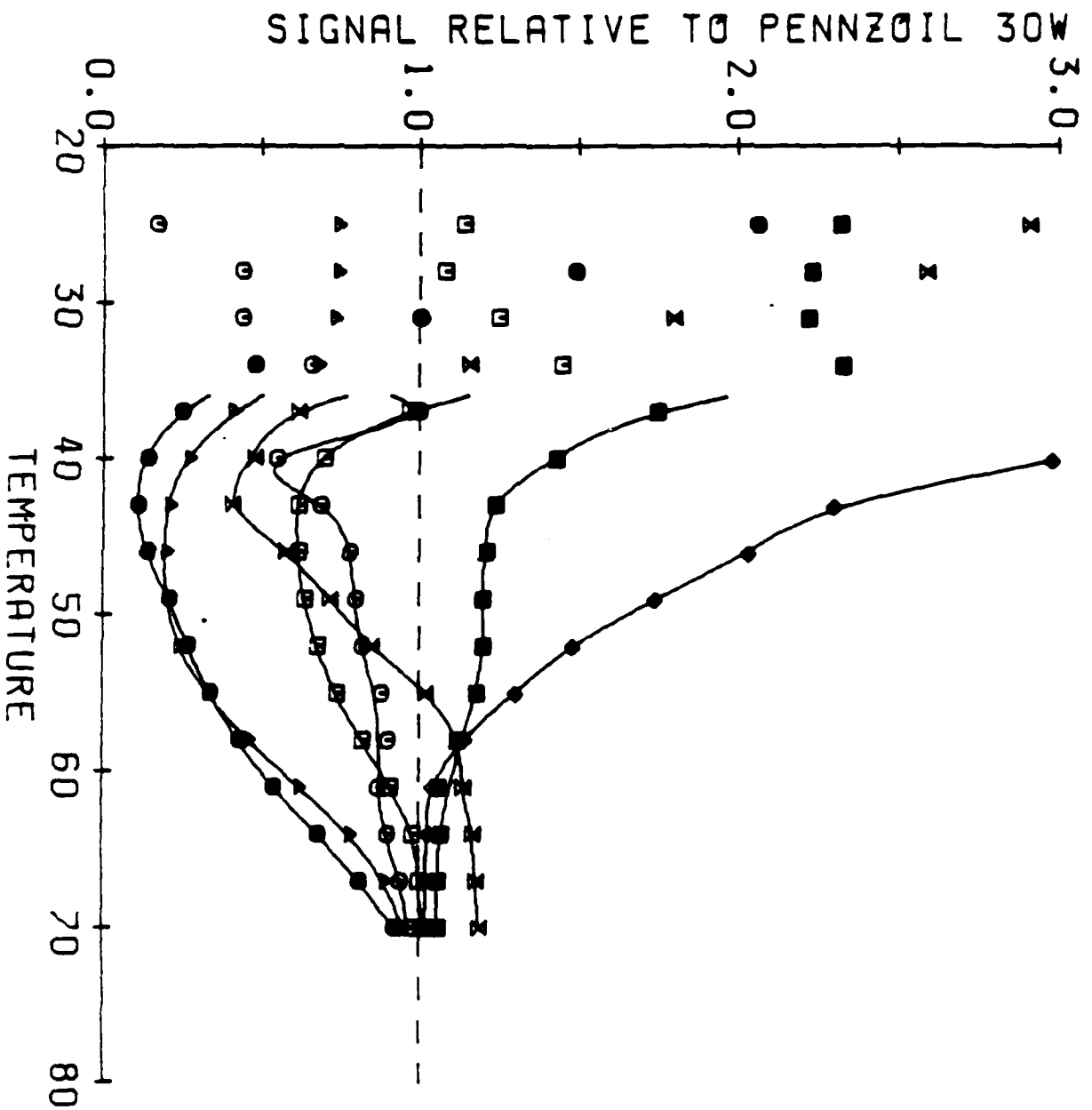


FIGURE 2. EMISSION INTENSITY AS A FUNCTION OF TEMPERATURE FOR VARIOUS GRADES OF PENNZOIL MOTOR OIL.
◆ 20W, ■ 30W, ▲ 40W,
⧗ 50W.


SIGNAL RELATIVE TO PENNZOIL 30W
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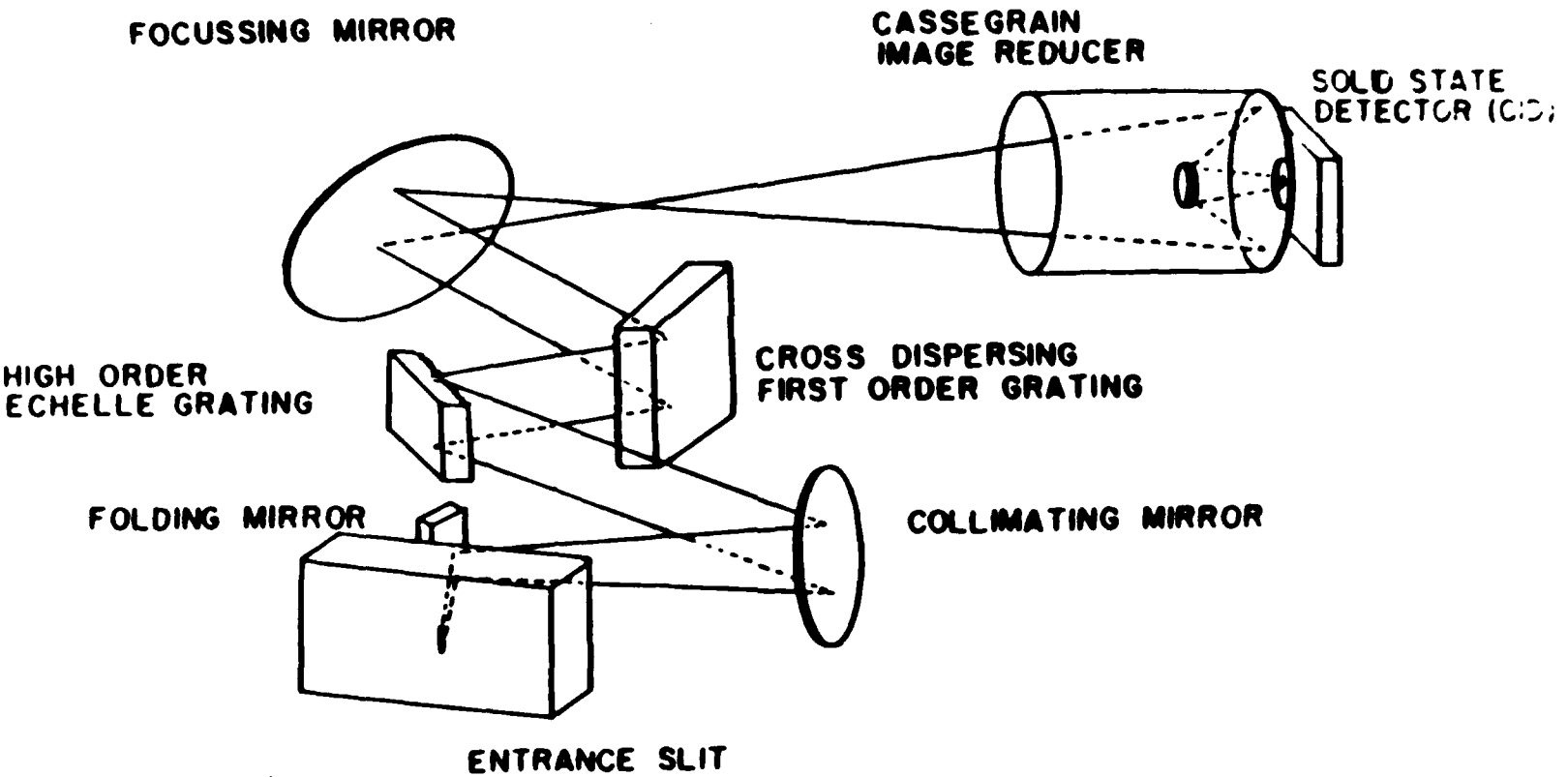
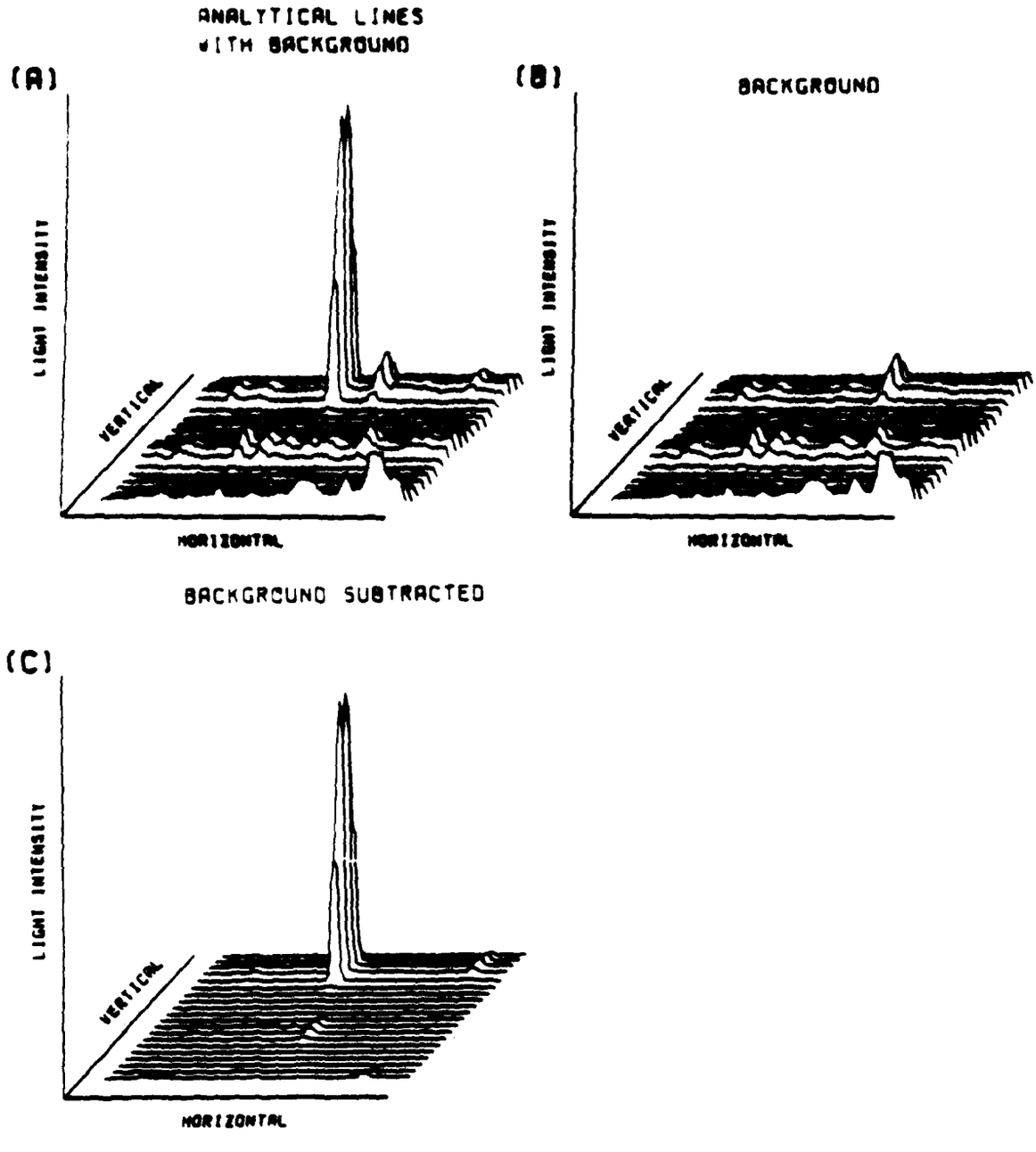
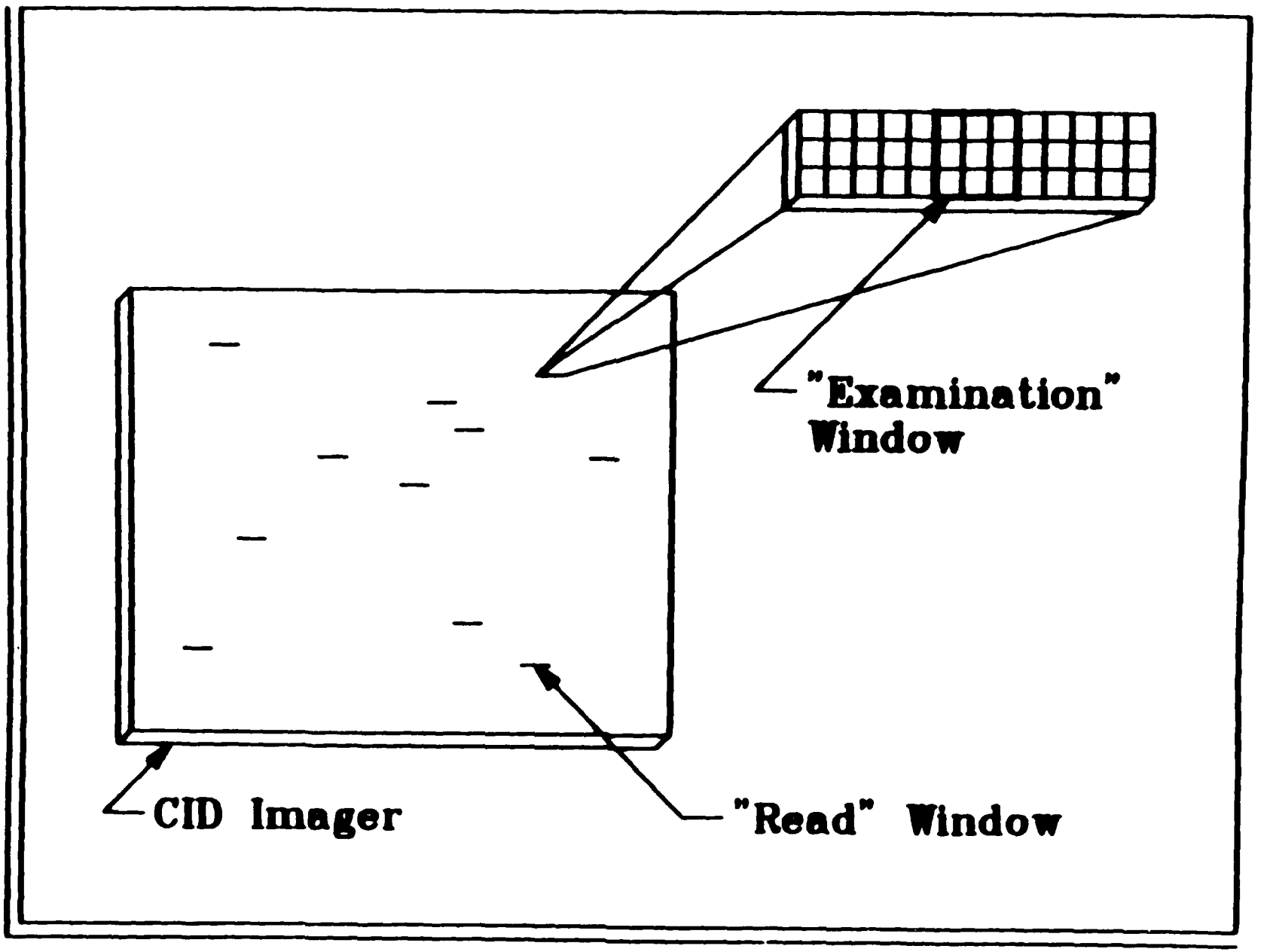
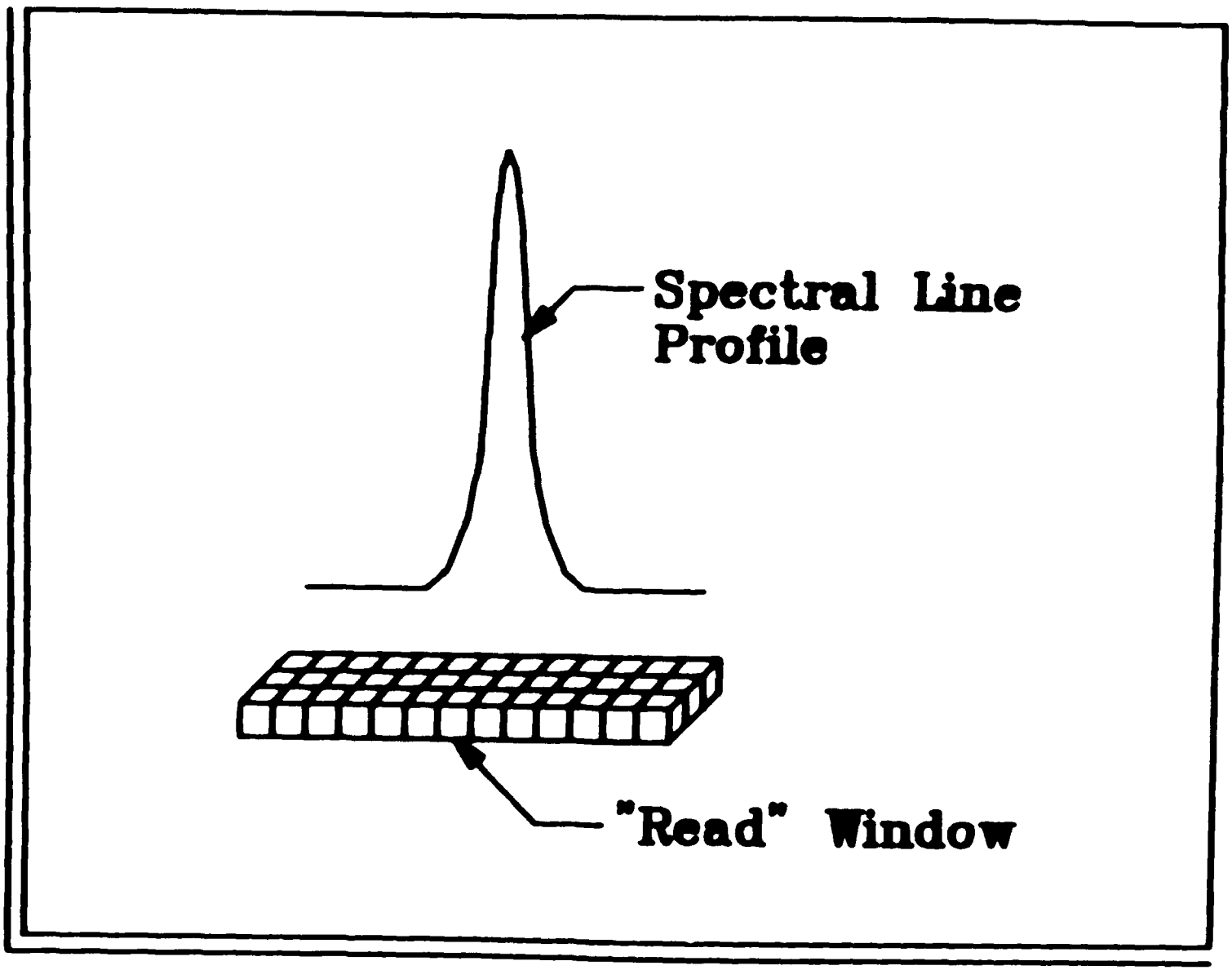
1.0
2.0
3.0
20
30
40
50
60
70
80
TEMPERATURE

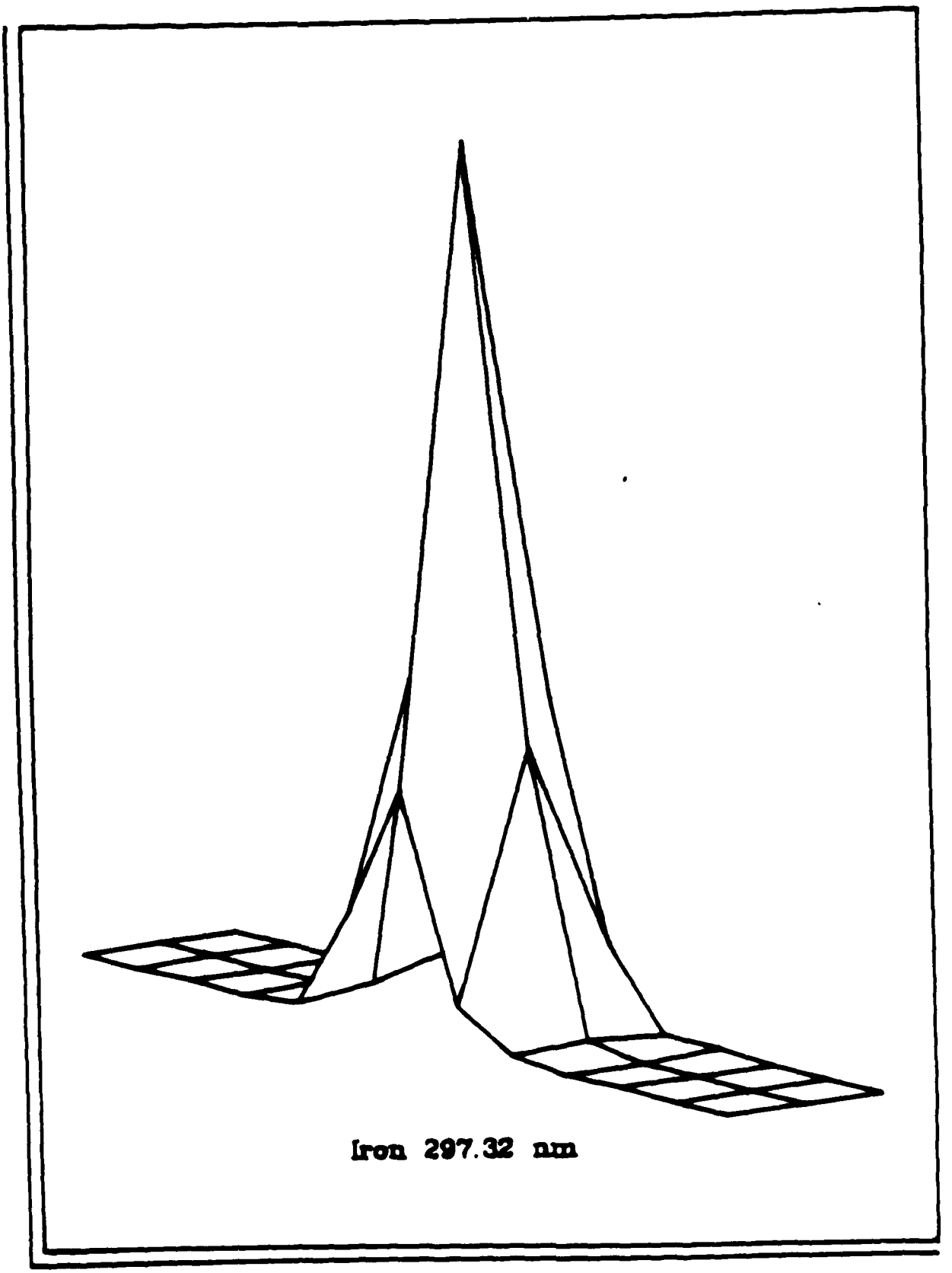

FOCUSSING MIRROR
CASSEGRAIN
IMAGE REDUCER
SOLID STATE
DETECTOR (CID)
HIGH ORDER
ECHELLE GRATING
CROSS DISPERSING
FIRST ORDER GRATING
FOLDING MIRROR
COLLIMATING MIRROR
ENTRANCE SLIT


ANALYTICAL LINES
WITH BACKGROUND
(A)
LIGHT INTENSITY
VERTICAL
HORIZONTAL
(B)
BACKGROUND
LIGHT INTENSITY
VERTICAL
HORIZONTAL
BACKGROUND SUBTRACTED
(C)
LIGHT INTENSITY
VERTICAL
HORIZONTAL

INTENSITY (ADU)
0.00
1000
2000
3000
4000
5000
TIME (HOURS)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

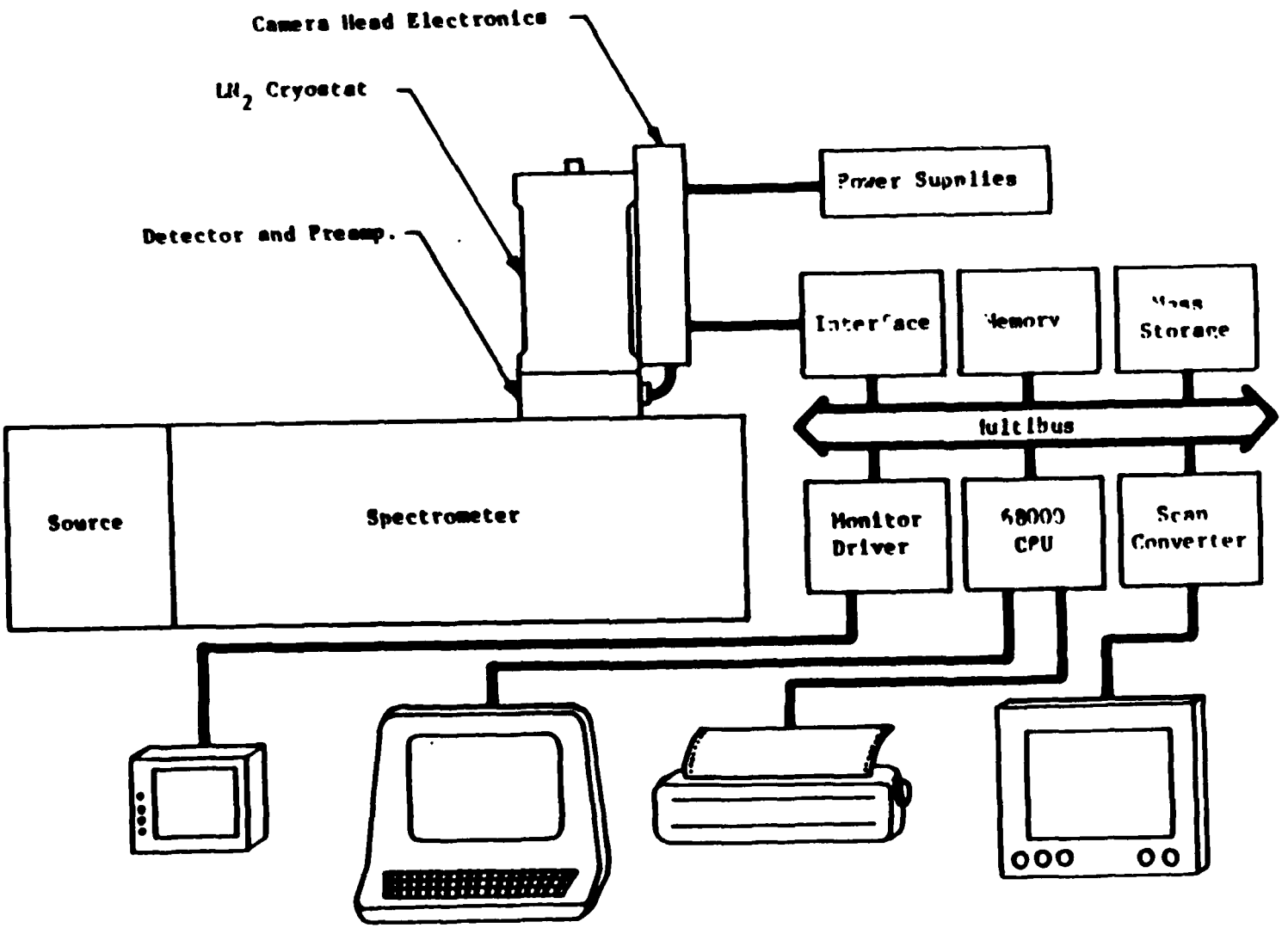

"Examination"
Window
CID Imager
"Read" Window


Spectral Line
Profile
"Read" Window



Iron 297.32 nm

SYSTEM BLOCK DIAGRAM



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