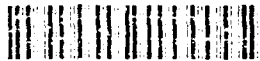


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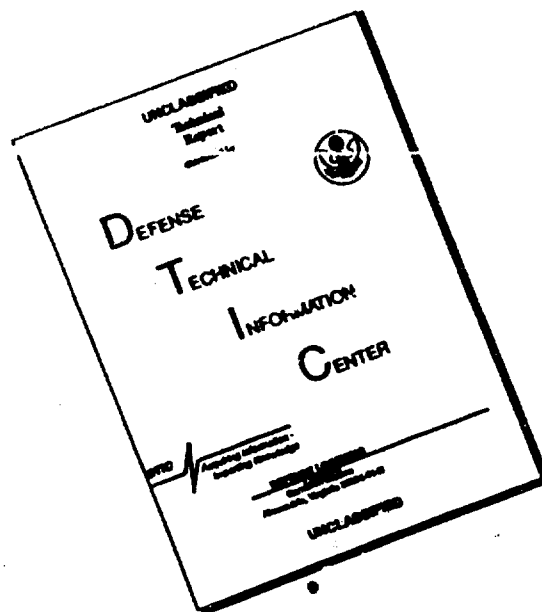


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Report No. B001

NEW METHOD FOR MEASURING TRACE ELEMENTS
IN II-VI SEMICONDUCTING MATERIALS

Final Technical Report

06-JUNE-89

Prepared under Contract Number DAAB07-88-C-F418
for CNVEO, Ft. Belvoir, VA

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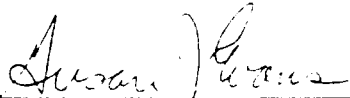

S.J. Evans, President

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1. INTRODUCTION

The electrical and optical properties of II-VI type semiconductor materials are largely controlled by the atomic concentrations of a variety of impurity elements which are present at trace levels in these materials either through deliberate addition or incomplete purification of feedstocks. Knowledge of the true concentration of such trace impurity elements (TIE's) is of vital importance to the preparation of products which will have reproducible, predictable properties. Improving the performance and producibility of high quality MWIR and LWIR IR detector devices fabricated from IIB-VIA compounds and their adjuncts is strongly dependent upon our ability to accurately measure and control the trace level impurity concentrations in these materials. The producers of these materials have clearly presented their need for new measurement methods and systems which will allow them to obtain reliable results at the 10^{14} atom/cm³ (a/cc) level. This is two orders of magnitude below (more sensitive) the existing detection limit of 10^{16} a/cc for most elements in this matrix.

This report covers the investigation of a novel method for determining TIE's in II-VI material via the use of direct Zeeman corrected, graphite furnace, atomic absorption for solid samples (DZAAS). The work is funded under the auspices

of the SBIR, Phase I, Contract Number DAB007-88-C-F418 and was carried out from 01-September-88 to 21-April-89. All research on the DZAAS technique was performed at the VHG LABS, Inc. facilities in Manchester, NH. Sampling and associated labors, as well as alternate technique data, were supplied by Two-Six Incorporated in Saxonburg, PA.

1.1 SCOPE

The aforementioned typical limits of detection are those available for the majority of elements detectable via state-of-the-art technology. In this case the method most widely used is spark source mass spectrometry (SSMS). The problem of insufficient sensitivity is further complicated by the fact that the CdTe matrix (representative compound for II-VI material in this study) has interfering properties for some of the critical TIE's thereby causing decreased sensitivity or in some cases absolutely rendering the element undetectable. This problem has, to this point, hampered the research behind the development of improved IR optical material.

A new analytical tool has recently been developed that combines the advantages of Zeeman corrected, graphite furnace atomic absorption (its extreme selectivity, sensitivity, and

simplicity); with solid sampling capability, i.e., engineered to accommodate milligram size samples thereby getting around the errors associated with sample dissolution such as contamination, sample handling, time, and loss of sensitivity through dilution factors. These characteristics, along with studies performed on equally complex and high purity material, initially supported the hypothesis that this method could, in fact, yield levels of detection in the range of about 10^{15} a/cc. Because of its inherent selectivity this approach should also be capable of determining the TIE's in CdTe without appreciable loss of sensitivity, whereas they are undeterminable or at least determined with extremely poor sensitivity via SSMS due to matrix constituent masking of the element of concern.

1.2 OBJECTIVES

The Phase I program was aimed at answering the following questions:

1. Can solid CdTe be efficiently vaporized at experimental levels of mass?
2. Can the element of interest be physically isolated in the atomization chamber (furnace)?
3. Can the element of interest be spectrally and chemically isolated from the matrix elements?

4. Do the resulting instrumental parameters, necessary to generate a positive response to questions 1 -3, yield sufficient levels of detection?
5. What constitutes acceptable sample preparation?
6. Will the maximum allowable sample size for analysis be adequate in its representation of the whole?
7. What are the figures of merit for the elements of interest in the CdTe matrix?
8. Is the method practical in terms of ease of use, time requirements, calibrating standards and sample preparation?
9. How do the results compare to existing techniques for the determination of Cu, Fe, and In in CdTe?
10. Is there sufficient evidence to continue investigating this approach for additional elements and technique improvements?

1.3 TASKS

A schedule was set up in an effort to expeditiously determine the answers to the previously raised questions. This schedule is graphically represented on Figures 1 and 2. Also listed is the actual performance, on a time basis, with the schedule.

FIGURE 1 - PERFORMANCE SCHEDULE PHASE I

SEP-WK1 SEP-WK2 SEP-WK3 SEP-WK4 OCT-WK1 OCT-WK2 OCT-WK3 OCT-WK4 NOV-WK1 NOV-WK2 NOV-WK3 NOV-WK4 DEC-WK1 DEC-WK2 DEC-WK3 DEC-WK4

TASKS

1. MAT'L BEHAVIOR Vol Studies Cd&Te [*****] []

><

turn temp study

[*****] []

><

2. CALIBRATION

Cu parameters

[*****] []

><

Fe parameters

[*****] []

><

In parameters

[*****] []

><

3. SOLIDS EXP.

(Syn prepped CdTe matrices)

Cu std add study

[*****] []

><

Fe std add study

[*****] []

><

In std add study

[*****] []

><

SEP-WK1 SEP-WK2 SEP-WK3 SEP-WK4 OCT-WK1 OCT-WK2 OCT-WK3 OCT-WK4 NOV-WK1 NOV-WK2 NOV-WK3 NOV-WK4 DEC-WK1 DEC-WK2 DEC-WK3 DEC-WK4

KEY : [****] - contractual timetable
 >.....< - actual timetable

NOTE : A one month extension was granted due to delays in receiving the "Snapshot" samples. This is reflected in the above progress chart.

1.4 CONCLUSIONS

A comprehensive research project was conceived to determine the applicability of a promising new technique to the analysis of heretofore uncharacterizable levels of three critical TIE's, namely copper, iron, and indium, in semiconductor material of the II-VI class. The results, as demonstrated in the following text, clearly indicate that, as a very conservative first approximation, DZAAS will be a mandatory tool for the quantification of TIE's, in high purity semiconductor material, in a complementary fashion with some type of mass spectrometric technique.

This claim is substantiated from the data contained herein. Whereas mass spectrometry yields the best overall detection limits for all trace elements in a simultaneous fashion, isobaric interferences from the CdTe matrix preclude the determination of Fe and deleteriously impact the detection limit for Cu and In. In no case can mass spectrometry achieve even the 10^{17} a/cc level with any confidence, while preliminary data generated in this project using the DZAAS technique was found to reproducibly achieve below 10^{16} a/cc.

1.5 PHASE II OPPORTUNITIES

Based on the data and insight gained from this project several excellent opportunities exist for Phase II research. These topics are dealt with in more detail in Section 6; however, in general the areas seen as beneficial and possessing a high probability of success are:

1. Performance enhancements--modifications to the instrument and the methodology that would yield improvements in figures of merit and increase the range of applicability.
2. Operational streamlining--through automation and application of advanced sample preparation methods, simplify the technique and reduce overall method errors.
3. Increase technique utility--evaluate the range of elements, as well as the range of semiconductor matrices, to which this technique can be applied. Develop sets of well characterized standards for other techniques used in the analysis of semiconductor material. Coordinate with manufacturers doing studies to improve processes through dopant monitoring, trace impurity element surveys, and the benefits of raw material sublimation prior to processing.

2. INSTRUMENTAL TECHNIQUES FOR ULTRATRACE DETERMINATIONS

It is commonly accepted within the elemental analysis community that determinations performed below one ppm of the original material are considered to be ultratrace. The characterization of II-VI materials below about 3×10^{16} a/cc, therefore, must include only those techniques that can perform reliably at ultratrace levels--in the starting material. The last point is extremely important due to the fact that there exist many techniques that state detection limits for Cu, In, and Fe below one ppm; however, for reasons inherent to the particular technique the transference of achievable detection limits in controlled situations can not be made for TIE's in II-VI materials. An example of this would be plasma emission spectroscopy.

Plasma emission is based on the thermal excitation of a sample's constituent atoms and the monitoring of subsequent emitted photons from electronic transitions in a relation of signal intensity to the concentration of known standards. Since all the atoms of the sample are typically excited the instrument must do a good job of isolating all the wavelengths emitted so as to only monitor the intensity of the element of concern's wavelength. Otherwise, false results will occur due to intensity changes from sources

other than the element of concern. The more complex the matrix is, in terms of emission characteristics, the more difficult it is to prevent interferences from occurring. Additionally, whether the excitation source be an inductively coupled (ICP), direct current (DCP), or microwave induced plasma (MIP), the sample typically must be introduced via solubilized or gaseous formats. The typical manufacturers' stated detection limits, in ppm, for the three elements sought in this study are: Cu, 0.002; Fe, 0.005 and In, 0.020.

II-VI material, more specifically CdTe, is a solid material that, one, has a complex emission profile and, two, must be solubilized prior to its introduction to the instrument. Whatever solubilizing method is used the reported detection limit must be multiplied by the final dilution factor to obtain the dissolution procedure's impact on the lower limit value in the solid material. Under optimum circumstances a 5% total dissolved solids approach with CdTe matrices can be used. This results in a twentyfold increase to the detection limit in the solid material. The nonspecific emission emanating from the sample matrix elements has a deleterious effect on the ability to detect an element in that matrix. A 5% solution of CdTe has significant unresolvable emission structure that also deleteriously impacts the overall

detectability of Fe, Cu and In. Previous investigations into the net impact have yielded effects in the 20 to 100 times range on the reported detection limit. Since these factors result in reporting levels of 1 to 10 ppm in the solid material the approach must be rejected due to lack of sensitivity. Moreover, the intention is to find a method, if possible, that minimizes the amount of sample handling because at ultratrace levels contamination from outside sources is a major concern. Certainly, the weighing and subsequent steps involved in sample digestion are undesirable and should be excluded from consideration if at all possible. To this end plasma emission spectroscopy is relegated to the category of nonviable for the determination of TIE's in II-VI material.

There are other viable techniques "on paper" but they are subject to the above pitfalls as well. These would be flame and furnace atomic absorption spectrophotometry (GFAAS and AAS), any electrochemistry approach, ion chromatography and any of the classical wet techniques. Still other considered techniques with the apparent sensitivity such as d.c. arc emission, X-ray fluorescence (energy and wavelength dispersive), and glow discharge emission have shortcomings that prohibit them from performing the task at hand. The one

area that has had some success is the general class of mass spectrometry. Employed as the current technique of choice, mass spectrometry, despite its inherent sensitivity, still has some major drawbacks. It is these problem areas that preclude the determination of some very crucial TIE's in a CdTe matrix and justify the research labors necessary to develop a viable technique. In an effort to understand the reasons behind the limitations of mass spectrometric techniques, thereby rationalizing the need for an adequate replacement, a theoretical background must be set.

2.1 MASS SPECTROMETRY

The technique of elemental analysis via mass spectrometry is very simply described as an instrument having a source for ionizing the sample into an ion beam, a mechanism for inducing a measurable change in the ion beam according to the individual constituents' mass and charge, and a device for detecting the resultant changes in signal. All elemental mass spectrometric techniques measure mass to charge ratios from ion beams containing, in part or as a whole, the sample. They can theoretically measure any element on the periodic chart in one sample run. Additionally, the typical resolution is about one half to one atomic mass unit (amu) for quadrupole systems.

In summary mass spectrometers have as their advantages:

1. High sensitivity for most elements, generally in the nanogram to picogram range.
2. Absolute measurement technique--when using the isotopic dilution method.
3. Complete elemental array analysis--simultaneous-like in approach.

Likewise, as a group, mass spectrometers can be generally qualified as having the following disadvantages:

1. They are expensive (\$250,000 up to \$1,000,000).
2. They require a moderate to high degree of technical expertise to operate.
3. Prone to isobaric interferences from matrix elements.

The main difference distinguishing mass spectrometers for elemental analysis is the way that they get the sample into an ion beam for subsequent isolation; and the means employed in the mass spectrometer for detection of the isolated species. Of the myriad combinations available today, there are three existing approaches that have demonstrated some acceptable performance in semiconductor materials.

Following is a brief summary of the three: spark source, glow discharge, and ICP mass spectrometry.

2.1.1 SPARK SOURCE-MASS SPECTROMETRY

The sample is typically pulverized, mixed with a conductive binder and pressed into a pellet for sparking. Alternatively, the sample can be machined into a pin if the material is conductive and machinable. A spark discharge is applied to the sample and the resulting ablated, ionized species are passed through a variable field magnetic sector for isolation. The detector can either be a photomultiplier tube or a photographic plate with calibrated emulsion.

Unique advantages are:

1. Relative simplicity vis a vis other mass spectrometric techniques.

Unique disadvantages are:

1. Sample requires machining/or can be interfered with from the binder matrix.
2. Equipment not readily available in today's market.

2.1.2 GLOW DISCHARGE-MASS SPECTROMETRY

The sample, machined in the shape of a pin, is the cathode for a d.c. voltage circuit. Operated at controlled voltage and current, atoms are sputtered off the sample surface from a low pressure inert gas stream. The collisional interaction between the sputtered atoms and the gas stream is sufficient

to effectively ionize the sample atoms. Ions exiting the source are sent through a double focussing mass spectrometer, separated via controlled alterations in the strength of the magnetic and electrostatic fields, and detected via the use of a Faraday cup for strong signals and a Daly detector for weak signals.

Unique advantages:

1. Direct determination of the entire sample matrix.
2. No sample dissolution.

Unique disadvantages:

1. Preferential sputtering rates exist for the elements.
2. Small sampling area.
3. Most costly of the three techniques.
4. Machining of sample required.

2.1.3 INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Developed initially as a source for atomic emission purposes, it was soon discovered that the near 100% ionization efficiency characteristic would make it a useful tool for ionizing solutions or gases prior to presentation to a mass spectrometer. The one initial drawback was that ICP's operate at atmospheric pressures and temperatures of 7,000 to 10,000 degrees Kelvin. This was overcome through clever design and

engineering of a skimming device that "cores" the tail plume of the plasma, in an axial fashion, and quickly shoots the ionized stream into an evacuated chamber for presentation to the mass/charge separator--which as of this report has exclusively been a quadrupole design--and signals are detected via an electron multiplier.

Unique advantages:

1. Utilizes synthetic standards.
2. Least costly of the available mass spectrometric techniques.

Unique disadvantages:

1. Sample dissolution required.
2. Total dissolved solids acceptable are about 0.1%, yielding an instant loss of three orders of magnitude sensitivity in the original sample.
3. Plasma gas and solution media interferences.

2.2 ATOMIC ABSORPTION SPECTROPHOTOMETRY

The theory underlying atomic absorption spectrophotometry (AAS) is that electrons of a specific atom have allowable elevated states of energy to which they can be raised. Each element and each electron in that element has a specific energy diagram that dictates how large and how many the allowable energy transitions are. Energies imparted to an atom's electrons can only be those that the electron can accept. Therefore unique to each atom is the pattern of energy levels that it can absorb. In essence, an atomic fingerprint. Modern atomic absorption goes beyond this, however, by recognizing that if discrete energy, of acceptable quantity to the sought element, can be directed towards ground state (relaxed) atoms of the element then the task of measuring the amount of energy absorbed is rather simple. This being true, then the description of a modern AAS instrument is basically stated. There has to be a source capable of generating energies of discrete quantities. Typically, some sort of discharge lamp, with the element that is being sought as the discharging medium, is employed as the line (quantum energy level) source. Next there has to be a device for generating atoms in their ground state--flames and furnaces are the norm--this being the actual absorption cell. Finally, there must be a way of measuring the amount of

energy emanating from the source and the subsequent drop in transmission from the absorbing atoms present in the absorption cell. Usually one would like to monitor the amount of absorption taking place at the designated line by nonatomic species. This "background absorption" can be easily measured and most AAS instruments today have a mechanism for doing just that.

AAS instruments are relative measuring tools and accordingly must be calibrated if they are to do their job. The calibration of any AAS unit follows the classic rules for transmission of energy by a medium. The concentration of directly absorbing species within that medium can be determined, following Beer's Law, by the amount of decrease in the original transmission. It is abiding by Beer's Law that gives us the capability to add known amounts of an element, within a predetermined range, and plot the ratio of concentration against the loss of transmission (or absorbance). By this calibration any absorbance recorded during an experiment can be related to a concentration.

As previously mentioned the atomization cell in today's instruments is typically either flame or furnace. A flame atomizer works strictly with solutions or gases. The sample

is nebulized and introduced to the flame for subsequent generation of ground state atoms via thermal energy mechanisms. The furnace accomplishes the same feat by electrothermally heating the sample to a point where only atomic species exist for the element of concern. Roughly speaking the temperatures for both are in the 2000 - 3000 degree Kelvin range.

For either of the two cell designs, several points can be made. One, the more specified energy that can be introduced into the absorption cell per atom, the more likely that the atom will absorb. Two, the more ground state atoms that are present in the optical path of the line source, the more likely that the energy will be absorbed. The proof is beyond the scope of this report but suffice it to say that proportionately very few atoms ever interact with line source energies in an AA analysis. This being said, furnace techniques are more sensitive than flame techniques just for that reason--they get more atom/energy interactions to occur. For identical line source energies the furnace gets more atoms in the optical path per unit time than the flame. This is so true that furnace AA's are typically three orders of magnitude more sensitive than flame AA's. The order of detection limits for furnace techniques are in the range that

make them potentially viable for the analysis of semiconductor materials (picogram to nanogram, absolute). Unfortunately, as with previously mentioned techniques, instruments heretofore available only work effectively on solubilized samples.

2.2.1 DIRECT ZEEMAN CORRECTED GRAPHITE FURNACE AA FOR SOLIDS

The limiting parameter that has made furnaces unacceptable as atomizers for solid materials is not, as one might expect, the dissociating energy available within the furnace itself. Actually, the 3000 degrees K is quite sufficient to vaporize most solid materials in existence. What does impact the success of this approach is the spatial considerations. The average size furnace tube is small enough that the large number of atoms generated in a rapidly heated environment are forced out the ends of the tube and thereby spend very little time in the optical path of the absorption cell. As stated above this is one of the critical factors affecting sensitivity in an AA experiment. However, simply increasing the size of the furnace tube is not the answer, as the correction scheme of choice for GFAA is indirect Zeeman (refer to Appendix I for a detailed description of the Zeeman effect and how it is used to correct for nonanalyte absorption). The problem with using indirect Zeeman is that a

absorption). The problem with using indirect Zeeman is that a powerful magnetic field (8,000 to 10,000 gauss) must be present within the absorption cell. This requires a large magnet around the furnace. The larger the distance from the magnet poles to the center of the cell, the larger the field strength of the magnet must be. Thus for economic reasons it is not practical to build a furnace capable of handling milligram size solid samples when using indirect Zeeman correction. Indirect Zeeman was preferred because, other than the magnet, all that was necessary to add was a polarizer to the existing furnace AA.

To overcome the problem several clever engineering developments were applied to realize an instrument that is effectively capable of AA analysis of solids. First, the correction scheme used was that of direct Zeeman. By placing the magnetic field around the line source the furnace was now free and clear to be as large as necessary. Of course, this now required a new way of generating excitation energy, and it required some way of oscillating the effect so as to obtain background information during the inherent transiency of a furnace analysis signal. This was ultimately all accomplished in a creatively simple fashion in the design of the DZAAS unit. The theory and design of the DZAAS unit is

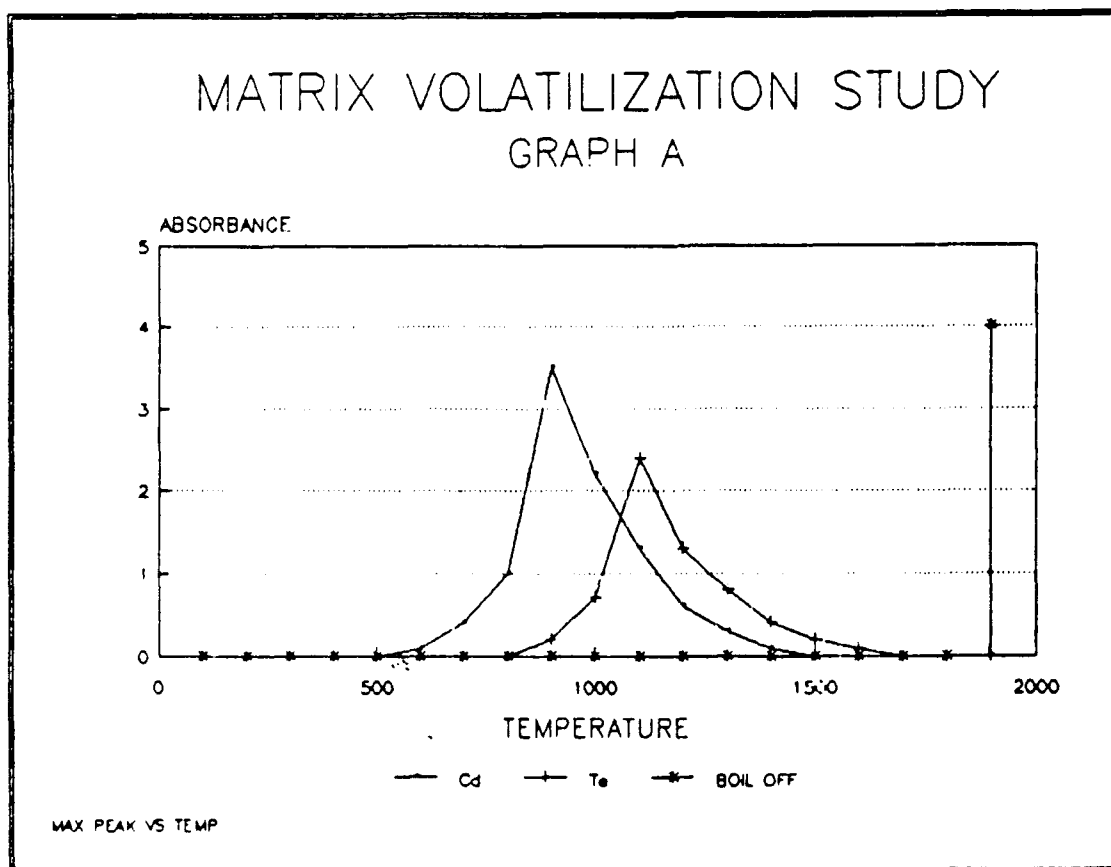
3. DISCUSSION AND RESULTS

The following details the experimentation that occurred during this project. The sequence established by the questions put forth in the objectives section is maintained and all results are directed towards responding to those questions raised therein.

3.1 MATRIX VOLATILIZATION

Studies were performed to evaluate the behavior of the CdTe matrix in the absorption cell. The first study entailed monitoring weak Cd and Te lines to detect at what temperatures boil off began and at what minimum temperature these elements could be effectively driven out of the optical path. The results are shown in **Graph A**. It should be mentioned here that the instrument has a three part furnace temperature setting program. That is, in standard configuration the furnace Phase I temperature is set for the time and temperature that is necessary to dry any liquid within the furnace without driving off any of the analyte. The second stage of the furnace program is Phase II (commonly referred to as the ash stage). This temperature is set to preferentially drive off any of the matrix or render it noninterfering in the final stage of the furnace ramp. The last temperature setting is the one that is used to

volatilize the analyte itself, in such a manner to yield the longest residence time in the absorption cell. This data signified that the CdTe material would begin to boil off prior to the elements of interest. This was an important first finding for it meant that a large number of atoms from the matrix would probably be out of the optical path before the atoms of the analytes were volatilized. The observed temperature of boil off for Cd and Te was about 900 and 1100 degrees C respectively. The maximum temperature requisite to drive off the entire matrix was empirically determined to be about 1900 degrees C.

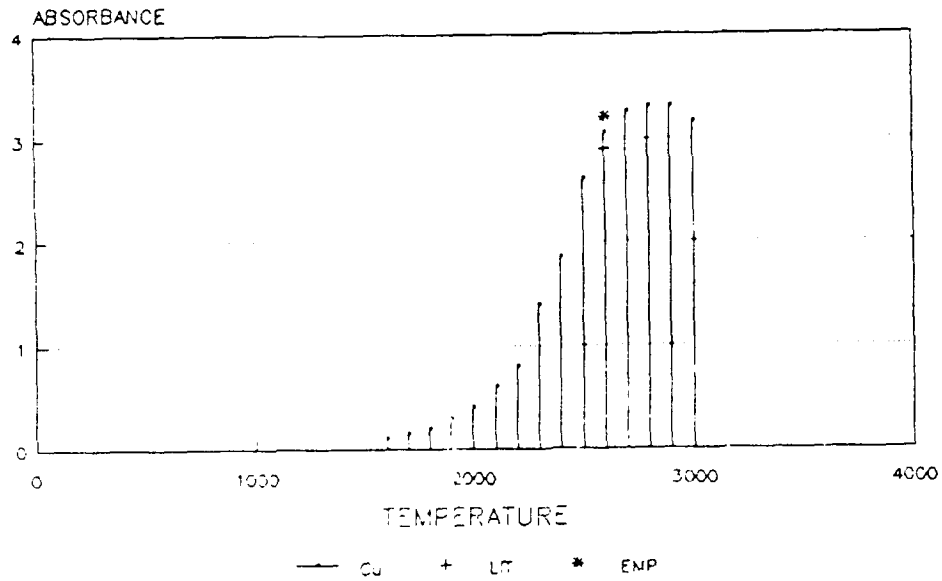


3.2 ANALYTE VOLATILIZATION

Analyte volatilization studies were performed by monitoring the most sensitive line for each of the elements of concern and running the furnace through iterative ramping cycles with 50 degree C increases or decreases in the Phase III temperature. The ideal temperature being sought was that which generated a clean symmetric absorption peak at the lowest temperature possible. Documented findings for this technique in simple aqueous matrices were verified, compared to the data from the matrix volatilization studies and a theoretical best atomization temperature calculated. About this theoretical starting point the 50 degree iterative cycles were run on samples of CdTe containing spiked impurities. Graphically the data obtained for each of the elements is shown in **Graphs B - D**. Visually the lowest possible temperature manifests itself as the peak that is about 90% of the maximum amplitude generated by the highest peak height. The values for Cu, Fe, and In were found to be 2600, 2800 and 2200 degrees C respectively.

ANALYTE VOLATILIZATION — Cu

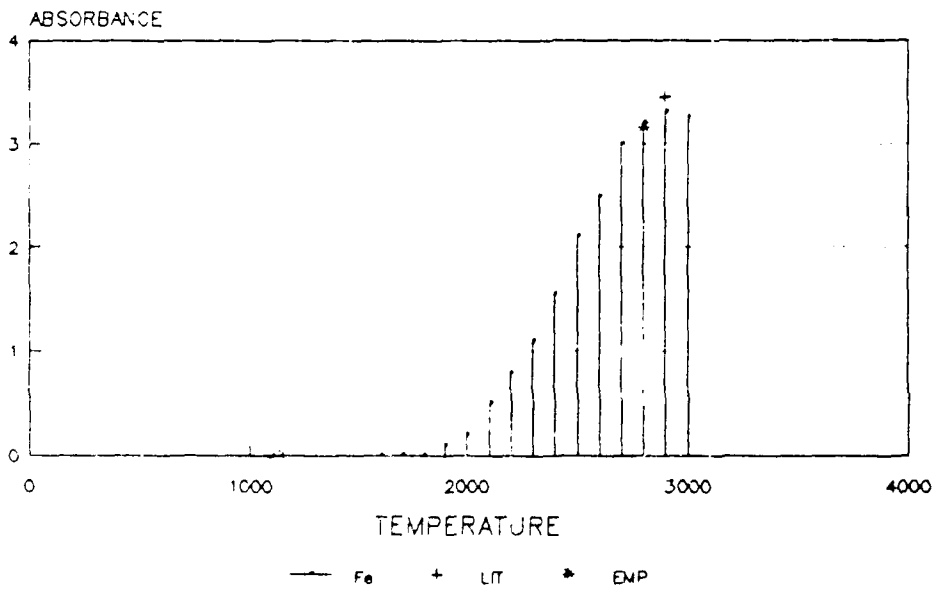
GRAPH B



PEAK AREA VS TEMP

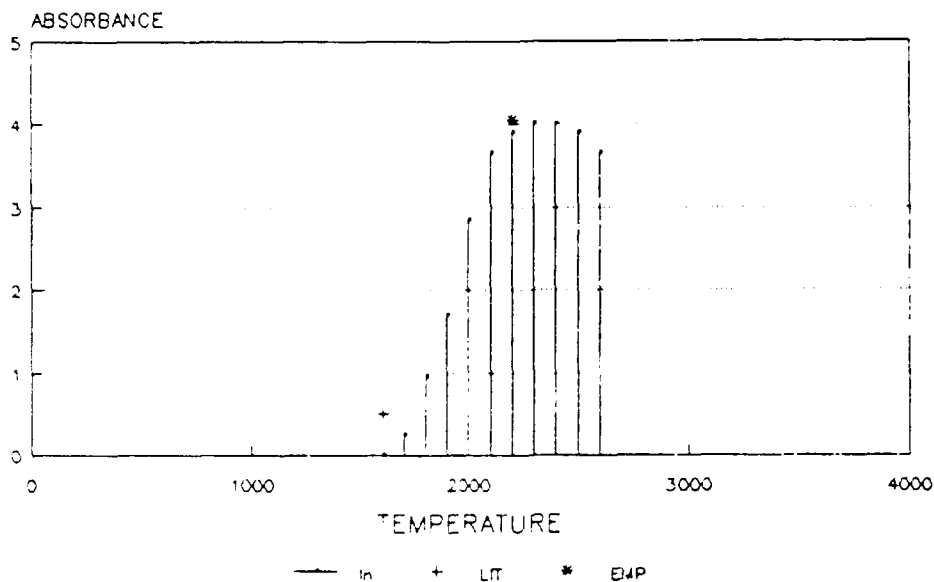
ANALYTE VOLATILIZATION — Fe

GRAPH C



PEAK AREA VS TEMP

ANALYTE VOLATILIZATION — In GRAPH D

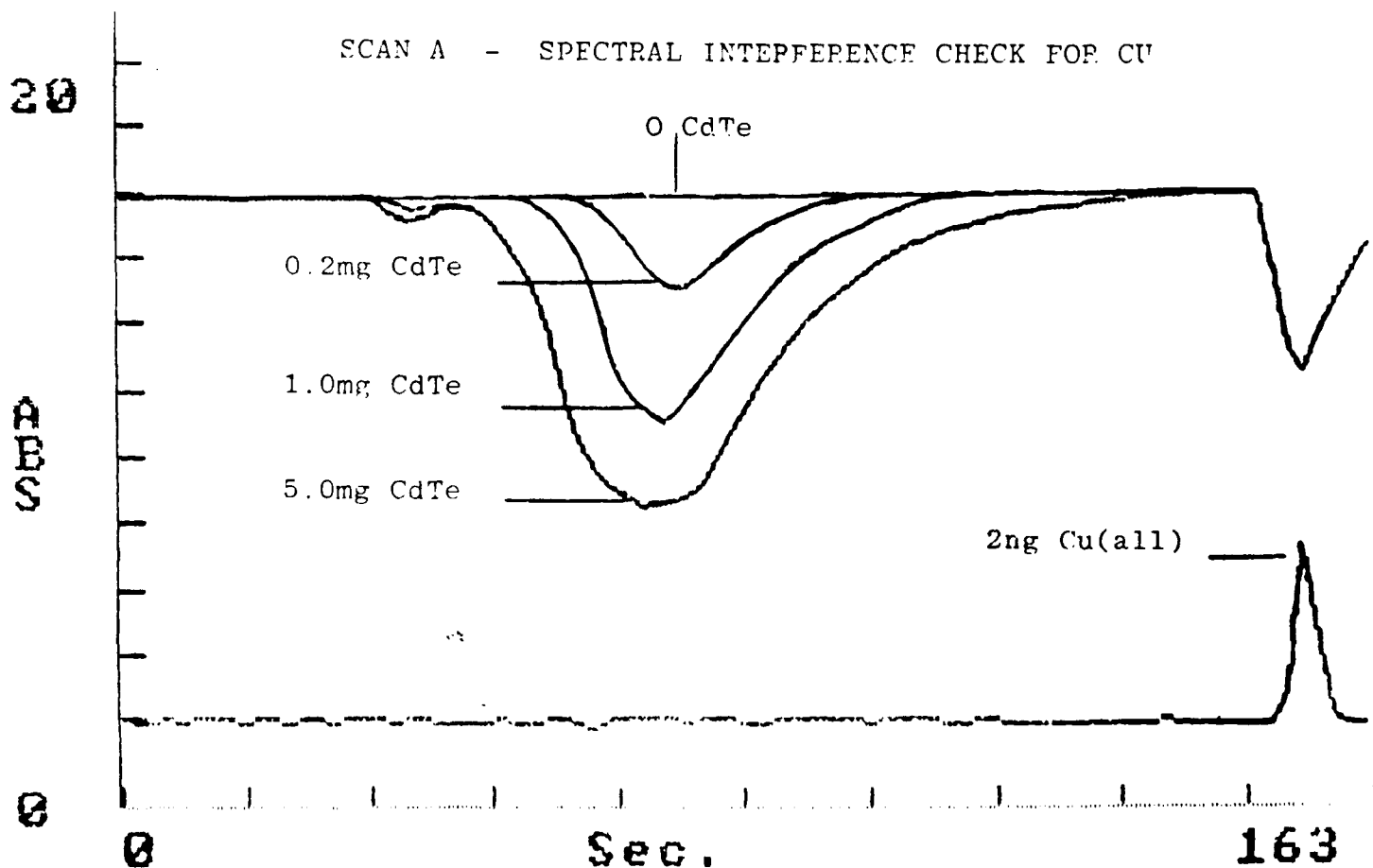


PEAK AREA VS TEMP

3.3 INTERFERENCES

The fact that previous studies have indicated that the elements of interest will volatilize from the CdTe matrix does not necessarily mean that the matrix will not interfere with the formation of ground state atoms, nor cause spectral interferences in the form of uncorrectable nonanalyte absorption. There are numerous, but theoretically less probable, ways that the matrix could cause problems with the successful completion of the experiment. However, by addressing the two specific issues mentioned the likelihood for success is high.

Spectral interferences, or lack thereof, can be determined via peak profiling of each of the elements of concern. By holding the level of concentration constant for the analyte and then adding matrix constituents in a single variable fashion the change in peak profile or total absorption profile would indicate an interference. The total absorbance profiles did change, in varying degrees, as indicated in the SCANS A - C. However, there was no change in the peak area value for each of the elements, thereby lending credibility to the power of the direct Zeeman correction scheme.



20

SCAN B - SPECTRAL INTERFERENCE CHECK FOR FE

SPS

0.2mg CdTe
1.0mg CdTe
5.0mg CdTe

2ng Fe/0 CdTe

2ng Fe/1mg CdTe

0

0

Sec.

87

20

SCAN C - SPECTRAL INTERFERENCE CHECK FOR IN

SPS

0 CdTe

0.2mg CdTe

1.0mg CdTe

5.0mg CdTe

2ng In(all)

0

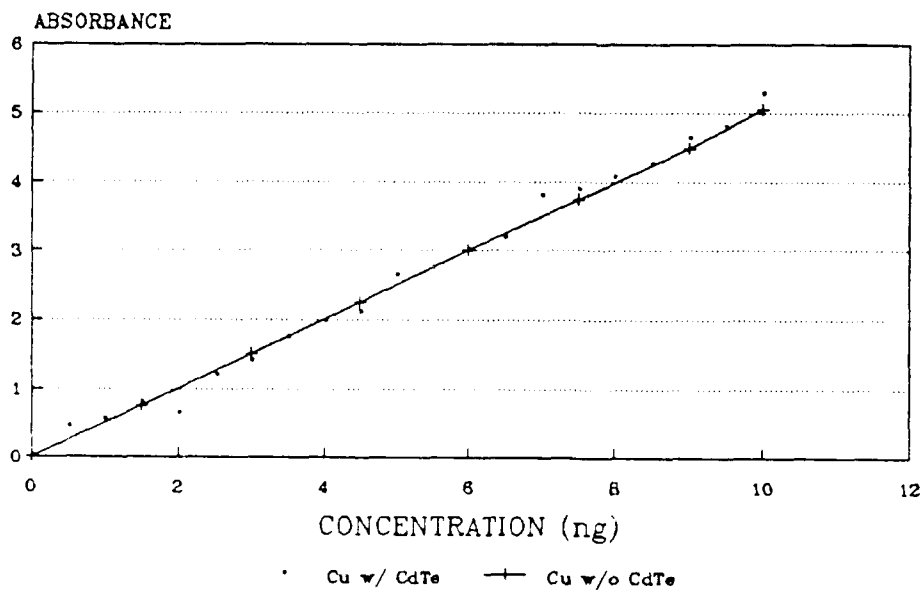
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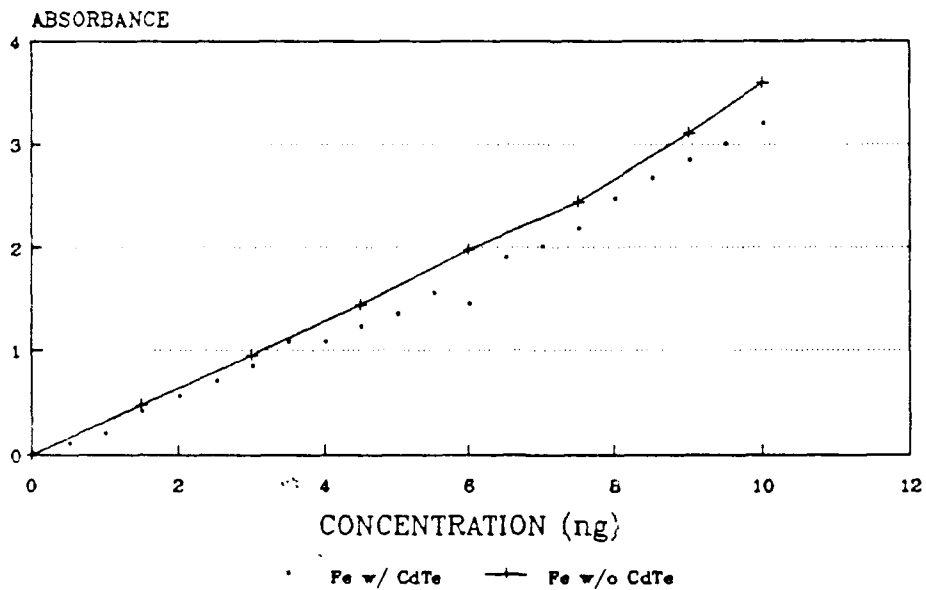
The easiest way to monitor the effects, if any, on ground state atom formation was to establish the curve of growth for each of the elements in a manner free from the matrix elements. Thus, simple aqueous single element solutions of Cu, Fe, and In were independently analyzed and the peak areas and heights recorded. The matrix elements were added in increasing amounts to a midrange value concentration of the specific element being investigated and the net signal plotted against the matrix free value. **Graphs E - G** demonstrate that the curves for Cu and In are in excellent agreement and that slight shifting of the Fe plot exists. For the level of accuracy required the deviation in the Fe calibration curve (about 5%) was considered to be insignificant at this point. The effect is apparently due to the delayed liberation of ground state atoms from the CdTe matrix.

INTERFERENCE STUDY - Cu CAL GRAPH E



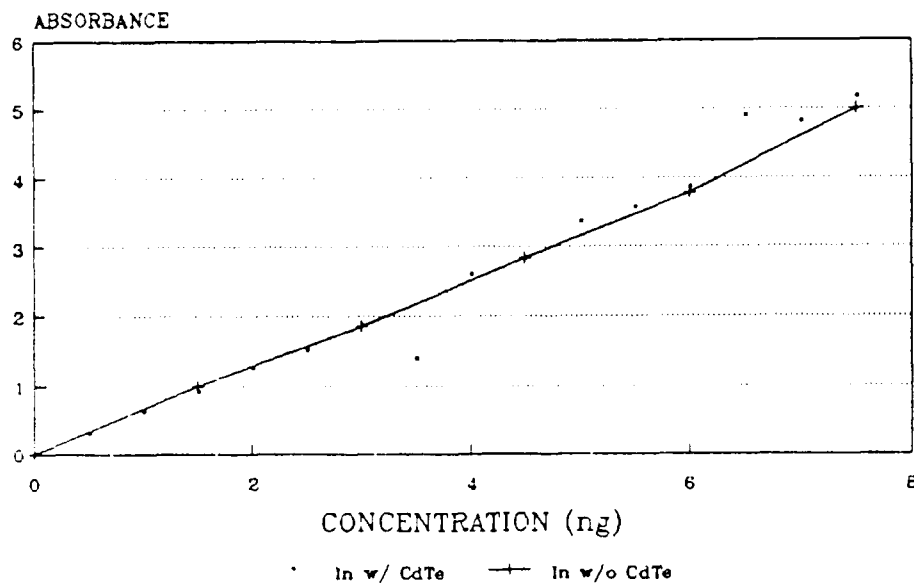
324.8 nm

INTERFERENCE STUDY - Fe CAL GRAPH F



248.3 nm

INTERFERENCE STUDY - In CAL GRAPH G



3.4 SAMPLE PREPARATION

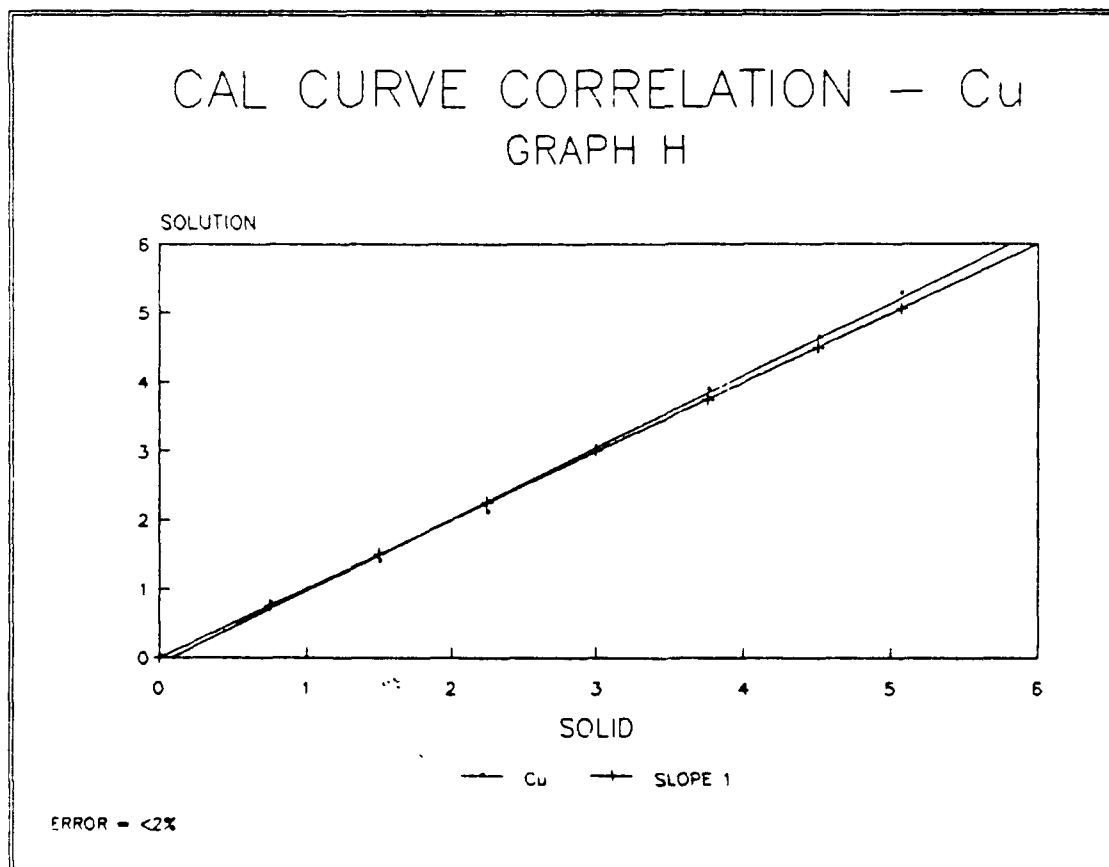
The object of this study was one of the key issues being addressed. Any technique cannot be considered viable if the time, material, potential for contamination, labor, facilities requirements, technical expertise or degree of difficulty were sufficiently impacting enough to override any of the other benefits provided by the proposed approach. The basic hypotheses being tested is that assuming sample homogeneity at the 0.1 to 1.0 milligram level (an assumption that is to be tested later in this program), that the sample can be pulverized to an average particle size distribution of

about 0.1 milligram using a sapphire mortar and pestle. The sample would be double wrapped in preleached plastic and placed inside a poly bag prior to pulverization. In this manner the sample, once taken from the ingot and cleaned, would not be exposed to a potentially contaminating environment until subsampled for analysis with a teflon spatula. The proof of effectiveness is experimentally designed to be derived from other test data. That is, no specific test will be undertaken to verify sample preparation validity, but rather homogeneity tests, detection limit tests, reproducibility tests, and data comparisons with other methods will be monitored for errors attributable to sample preparation. Accordingly, if errors are seen then a revised program will be enabled whereby prior to analysis sample fragments will be acid etched to remove contamination.

3.5 CALIBRATION

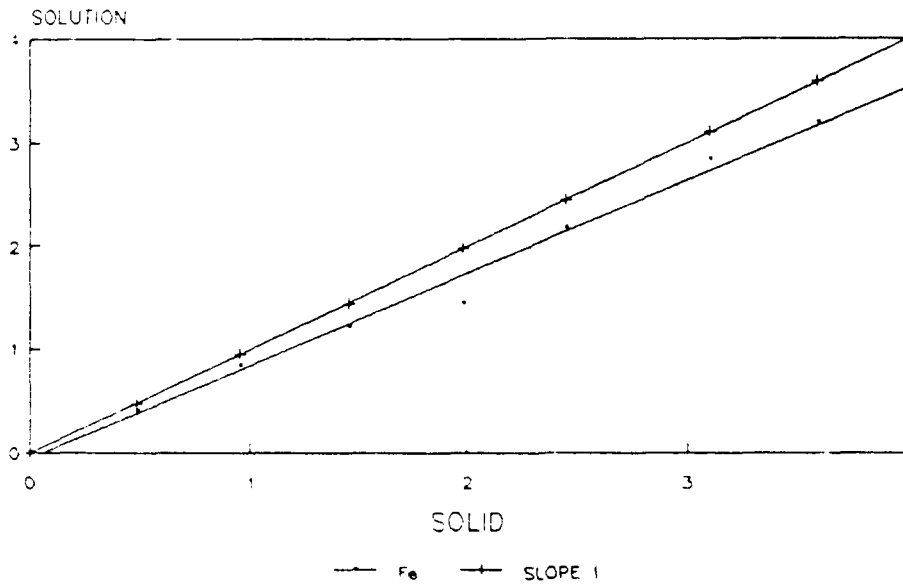
The difficulty encountered with most new techniques and/or new material characterization is that, because the tool is based upon a relative measurement scheme, the lack of reference material for calibrating purposes is insurmountable. In search of the ultimate "black box" where the device used is an absolute approach, the next best thing would be a device that calibrates on simple aqueous solutions

of the element being determined. The DZAAS approach has this as a potential benefit. The test designed for this evaluation was to establish a curve of growth for each of the elements and then correlate that data against a curve of growth derived from high purity CdTe material with synthetically added amounts of the specified element. Good correlation would indicate that all subsequent research could be done with aqueous calibration. Poor correlation would require that synthetically prepared standards be used. Correlation plots for this test are given in Graphs H - J and they show good agreement across the board.



CAL CURVE CORRELATION - Fe

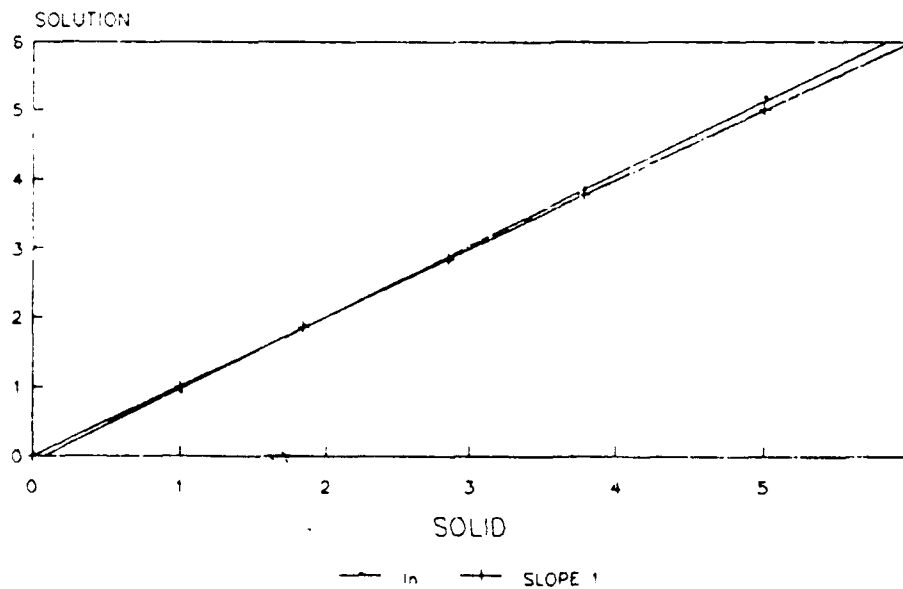
GRAPH I



ERROR = -10%

CAL CURVE CORRELATION - In

GRAPH J



ERROR = <2%

3.6 DETECTION LIMITS

Incorporated as part of this overall project was participation in a round robin analysis of raw material Cd and Te, manufactured CdTe, and sublimed CdTe from the same lot. Elements of concern were spiked into a crystal grown from the same starting materials and tip, center and heel samples taken. These were supplied by Two-Six, Inc., Saxonburg, PA and are henceforth referred to as "Snapshot" samples. The sublimed material was expected to be of the highest purity, and the method of standard additions--used due its ability to mathematically obviate the matrix contribution--verified that the levels of Cu, Fe and In were sufficiently low to use as a blank for the detection limit study. The determination of detection limits was described as the ability to detect a finite small signal over and above the noise of the background. The IUPAC convention of three times the standard deviation of the background was employed. By analyzing the sublimed material at least ten times, rejecting any statistical fliers, determining the standard deviation on the group and factoring by three, the detection limits were derived. The data and resulting values are given in TABLE A.

TABLE A - DETECTION LIMIT DATA

	Cu	Fe	In
STD ADDN	0.080	0.200	0.040

RUN #1	0.136	0.220	0.005
#2	0.090	0.080	0.082
#3	0.040	0.152	0.009
#4	0.052	0.198	0.013
#5	0.050	0.163	0.098
#6	0.060	0.060	0.092
#7	0.150	0.201	0.020
#8	0.110		0.083
AVERAGE	0.086	0.153	0.050
STD DEV	0.039	0.057	0.039
DET LIMIT (3 X SD)	0.118	0.172	0.117
PPMA	0.224	0.369	0.112

3.7 SAMPLE SIZE AND HOMOGENEITY

This very basic question of sample size limitations of the instrumental technique being representative of the sample as a whole is easily checked through statistical evaluation of repeat runs on a single sample. The test design is that the standard deviation (sd) obtained on a series of sample runs should agree with sd's obtained on known reference material containing the same concentration level of the element being tested. All parameters should be maintained constant, including the sample size. Moreover, as a test of reasonability, the three elements studied in this project

should all have similar sd's. The samples for this test will not be blended so as to avoid masking any nonhomogeneity. It is also important to note that for elemental concentrations less than two orders of magnitude above the detection limit that imprecision contributions from the background noise will have some effect. This effect can be modeled and will be corrected out should the data fall below this value. **Table B** data indicates that this is not a concern.

TABLE B - HOMOGENEITY STUDY

	Cu	Fe	In
SNAPSHOT SAMPLE	3.90	4.80	12.52
5034-HEEL	4.59	4.53	10.60
	3.91	2.80	10.67
	4.30	3.40	9.30
	3.30	3.32	9.22
	3.32	4.75	13.99
	4.24	3.99	
AVERAGE	3.94	3.94	11.05
STD DEV	0.45	0.73	1.71

STD REF MAT'L	1) 16.10	2) 8.50	3) 15.50
	10.10	5.40	14.20
	12.00	6.20	12.80
	11.20	9.80	9.50
	13.00	5.10	9.10
	12.70	8.00	14.50
	15.00	9.80	12.00
	15.90	10.83	
AVERAGE	13.35	7.95	12.51
STD DEV	2.17	2.04	2.29

- 1) NBS 1632a COAL, Cert @ 16.5 ppm
- 2) NBS 1568 RICE FLOUR, Cert @ 8.7 ppm
- 3) None available, SPEX graphite std @ 10 ppm - info only

3.8 FIGURES OF MERIT

For this project's purpose figures of merit will be defined for each of the elements, at the analytical wavelength used, as follows:

1. Characteristic mass (sensitivity)
2. Precision
3. Detection limit
4. Rollover
5. Accuracy (spike recoveries)

The purpose of calculating these is twofold: one, to establish criteria from which other analysts can judge the degree of success of their experimental data; and two, to evaluate the confidence and reasonability of the test method, from within the test and against other methods. Refer to **Table C** for the experimental findings and the **Glossary** for detailed formulae on the following.

The characteristic mass (m_0) is an important criterion for ensuring the validity of a newly created calibration. In other words, once the m_0 is known then from that point an analyst will be able to immediately determine the reasonability of a generated calibration.

Precision is evaluated using relative standard deviations and poor precision is indicative of either sample nonhomogeneity or instrumental parameters out of control.

Detection limit is covered in section 3.4.

Rollover is basically the upper limit in concentration to which any calibration should be made. It also should be reproducible.

Accuracy is usually defined as the agreement (sometimes using relative bias) between known values from a certified reference material (CRM) and the values obtained from the instrument for that standard. CRM's are not available for impurities in CdTe matrices, thus the method of spiked recoveries will be used. In this case, the spiked concentration will be biased against its reported value. Spikes will be introduced via solution standards of the element of concern.

All the above data is given in **Table C** for the specified wavelengths used in this study.

TABLE C - FIGURES OF MERIT

	Cu	Fe	In
WAVELENGTH (nm)	324.8	248.3	325.6
Mo	20 pg	6 pg	5 pg
ROLLOVER (conc)	9 ng	8 ng	5 ng
DET LIMIT (ppmw)	<0.10	<0.20	<0.01
RSD @ 10xDL	6%	11%	4%
RECOVERY (Rel bias @ 10xDL)	12%	15%	9%

3.9 DATA COMPARISON WITH OTHER TECHNIQUES

The Snapsnot samples round robin testing yields information in terms of not only this technique's success in determining low levels of TIE's in CdTe matrices, but sheds some light on the agreement with known levels of spikes and the correlation of data with other proposed and currently acceptable techniques. Refer to **Table D** for a comparative matrix on common sample analyses. The tabulated data is further elucidated by **Graphs K - M** which clearly indentifies the central focal point of technique agreement as that being generated by DZAAS. Where data is supplied the lack of consensus among mass spectrometer techniques is apparent when one considers that the target value for spiked elements in the tip, center and heel samples were 5-8 ppma for Cu and Fe and 10-15 for In.

TABLE D - DATA COMPARISON BY TECHNIQUE

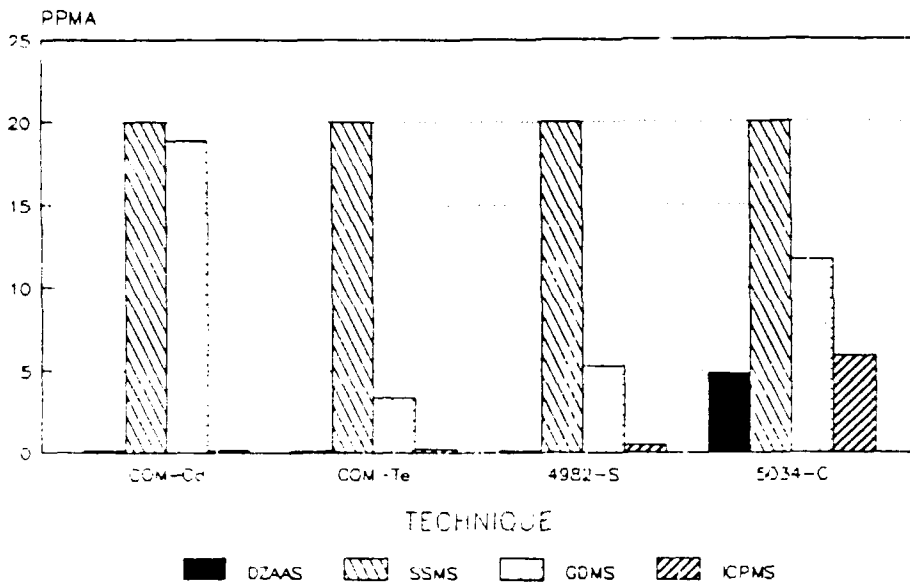
Cu			Fe			In		
LAB	Technique	ppma	LAB	Technique	ppma	LAB	Technique	ppma
LAB 1	DZAAS	<0.2	LAB 1	DZAAS	<8.17	LAB 1	DZAAS	0.14
LAB 2	SSMS	INT	LAB 2	SSMS	INT	LAB 2	SSMS	<0.3
LAB 3	GDMS	<18.9	LAB 3	GDMS	<1.14	LAB 3	GDMS	<220
LAB 4	ICPMS	0.13	LAB 4	ICPMS	<2.43	LAB 4	ICPMS	INT
COM-Cd		EM7037	COM-Cd		EM7037	COM-Cd		EM7037
COM-Te		EM7182	COM-Te		EM7182	COM-Te		EM7182
4982-S		4982	4982-S		4982	4982-S		4982
5034-T		5034-T	5034-T		5034-T	5034-T		5034-T
5034-C		5034-C	5034-C		5034-C	5034-C		5034-C
5034-H		5034-H	5034-H		5034-H	5034-H		5034-H

NOTES : Conversions from ppmw to ppma as follows:
 Cu = 1.89 Fe = 2.15 In = 0.96

LAB 1 VHG LABS, Manchester, NH
 LAB 2 Walters Chemical Consulting, Dayton, OH
 LAB 3 C. Evans & Assoc., Redwood City, CA
 LAB 4 Elemental Research, N. Vancouver, BC

TECHNIQUE COMPARISON - Cu

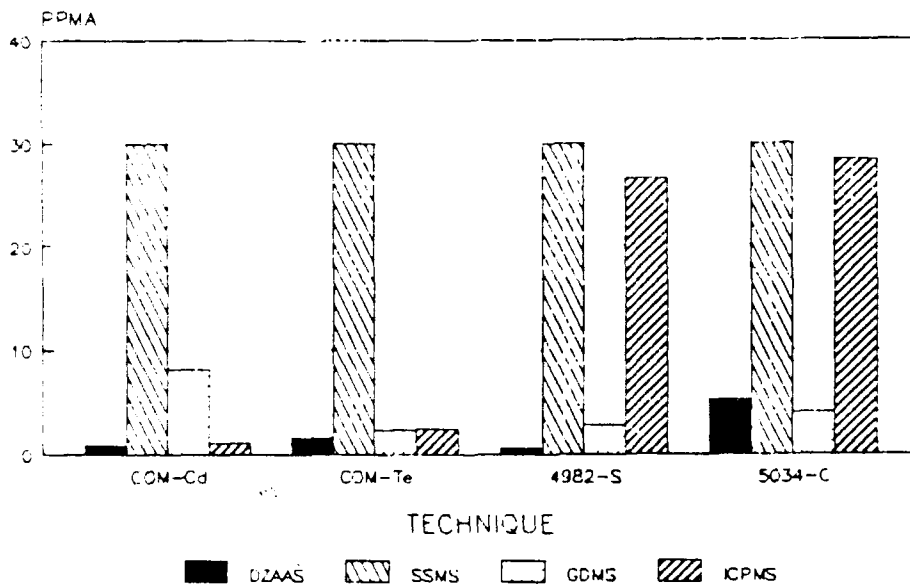
GRAPH K - Cd, Te, & CdTe



SEB DAB007-85-C-F418

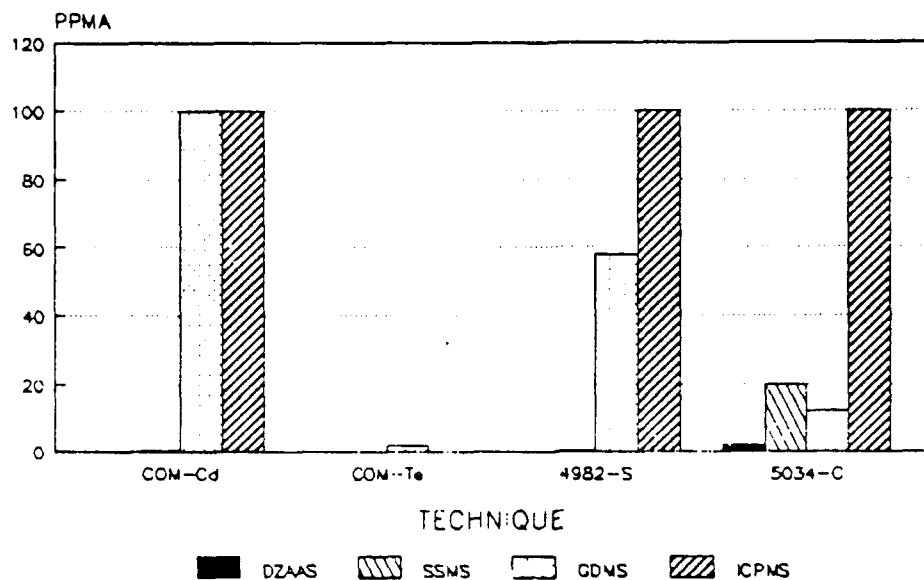
TECHNIQUE COMPARISON - Fe

GRAPH L - Cd, Te, & CdTe



SEB DAB007-88-C-F418

TECHNIQUE COMPARISON — In GRAPH—M Cd, Te, & CdTe



SB/R DAB007-88-C-F418

4. PHASE I CONCLUSIONS

By referring to the questions raised in the objectives section and responding to them through the data gathered, we can now evaluate the degree of success achieved by this research. The conclusions drawn will be directly supported by the data.

Regarding the question of sample and analyte volatilization; and spectral and chemical interferences; it should be clear that if the CdTe samples can be analyzed against an aqueous

calibration, and if spiked recovery data was acceptable, then there remains no doubt that at least for the elements tested that the DZAAS technique is sufficiently powerful to negate matrix effects. This, indeed, has been demonstrated, and beyond direct spectral interference and line source availability, there is reason to believe that this approach will just as effective for other elements.

The question of the achieved detection limits being low enough to warrant immediate acceptance or, at least, further investigation has been clearly responded to in a positive manner. Although the values obtained aren't quite down to the 10^{14} a/cc level there certainly is reason to believe that this feasibility phase of the research project generated low enough detection limits to ensure a high probability that further work in this area will bear fruit. More importantly though, is that the data that this cursory investigation yielded is better than any techniques currently in use. The significance of this statement stands alone in its impact, yet combined with the following facts there is overwhelming evidence in support of continued research.

As for acceptable sample preparation the proposed methodology was completely acceptable for the CdTe and Te samples, no

further treatment will be necessary. The Cd raw material, however, presented a challenge. Cd is much too soft and malleable to be crushed into milligram size fragments. The alternate approach of drilling and acid etching was employed. This proved to be alright for the determination of Cu and In, but for nanogram quantities of Fe there still remained some contamination from the drill bit. It was easy to identify those sample that were contaminated because the Fe value was way beyond the calibration upper limit. These were rejected data points, accordingly, but the subsequent tube cleaning process through repetitive burn outs was an inconvenience.

Sample homogeneity appeared to be adequate to allow milligram size samples to represent the whole. The question that remains for ingot production is where should samples be taken.

The figures of merit have been established under a specified set of parameters. This benchmark will permit continued research to occur with greater facility through goal setting and evaluation of results against previously achieved data. A major finding in this investigation was that the DZAAS technique quite nicely responds to an age old problem. Although many techniques have theoretically promising figures

of merit, the lack of calibration standards has curtailed further evaluation. The ability to successfully analyze complex materials, such as those addressed in this report, with simple aqueous elemental standards cannot be understated.

The information presented herein describes the results obtained on a novel approach to the determination of trace impurity elements in semiconducting material. The technique is extremely practical in terms of its achieved figures of merit and detection limits--especially in light of the fact that other techniques cannot even detect the elements sought in this study. There should be no doubt in anyone's mind that AA instruments (and the same goes for DZAAS) are much simpler and easier to operate than any form of mass spectrometry. It is true that AA techniques are sequential in nature and that much more information can be generated from a mass spectrometer in an equivalent amount of time--but if the data is wrong or unusable what good is celerity? Also it is suggested that DZAAS would be one of the essential tools in the semiconductor industry's analytical laboratory, not the only one. As a complementary technique to mass spectrometry the DZAAS has its own unique niche. At a significantly lower price than mass spectrometry there is cost justification.

It was clear that during this study that several avenues could be pursued to further enhance this technique. There certainly exist more elements and matrices where lower levels of detection are desirable, so the answer to the question of continued investigation is strongly positive. These and other topics are dealt with in more detail in Section 6.

5. SUMMARY

The intent of Phase I projects is to provide sufficient information to warrant continued research on the subject matter. Based on the positive responses obtained in this study it must be concluded that the project was an overwhelming success. Furthermore, the design of the project obviates speculation as to the reproducibility and validity of data and the derived conclusions. For example, the Snapshot samples were run in blind fashion with no previous knowledge of sample concentration nor other technique data. **Table E** contains the data generated on two CNVEO samples and a complete listing of the Snapshot data is given in **Table F**. Post data evaluation, the indication is that the DZAAS method was the only technique to yield both reasonable results and low levels of detection for the suite of elements tested. This uniqueness alone justifies investigating the

opportunities that exist for further improvements and applicability. As it stands this technique should be considered by semiconductor manufacturers as a necessary add to their analytical repertoire.

TABLE E - ANALYTICAL RESULTS ON CNVED SAMPLES

SAMPLE	Cu		Fe		In	
	ppmw		ppmw		ppmw	
G-12	0.023		0.177		0.001	
CdZnTe	0.006		0.614		0.009	
	0.031		0.535		0.002	
	0.017		0.627		0.010	
	0.028		0.316		0.000	
	0.010		0.384		0.008	
			0.221			
		a/cc		a/cc		a/cc
	Avg 0.019	1.1	Avg 0.411	24.7	Avg 0.005	0.2
	sd 0.010		sd 0.184		sd 0.005	
	RSD 52%		RSD 45%		RSD 100%	
P190-9	0.022		1.073		0.035	
HgCdTe	0.050		0.593		0.048	
	0.011		0.604		0.015	
	0.011		0.679		0.029	
	0.046		1.174		0.054	
	0.029		0.390		0.037	
	0.018		0.665			
		0.345				
		a/cc		a/cc		a/cc
	Avg 0.027	1.6	Avg 0.690	41.4	Avg 0.036	1.1
	sd 0.016		sd 0.295		sd 0.014	
	RSD 59%		RSD 43%		RSD 38%	

NOTE : All concentrations are derived from peak integration values.
 ppmw = parts per million by mass
 a/cc = 10^{15} atoms per cubic centimeter

TABLE F - DZAAS ANALYSIS OF SNAPSHOT SAMPLES

SAMPLE	Cu		Fe		In				
	ppmw	ppma	ppmw	ppma	ppmw	ppma			
COM-Cd EM7037	Avg <0.1 sd RSD	<0.2	COM-Cd EM7037	Avg 0.423 sd 0.155 RSD 37%	0.91	COM-Cd EM7037	Avg 0.130 sd 0.100 RSD 66%	0.14	
COM-Te EM7182	Avg <0.1 sd RSD	<0.2	COM-Te EM7182	Avg 0.355 sd 0.300 RSD 85%	1.61	COM-Te EM7182	Avg <0.1 sd RSD	<0.1	
4982-S	Avg <0.1 sd RSD	<0.2	4982-S	Avg 0.300 sd 0.225 RSD 75%	0.65	4982-S	Avg <0.1 sd RSD	<0.1	
NOTE: All concentrations are derived from peak integration values	4982	Avg <0.1 sd RSD	<0.2	4982	Avg 0.252 sd 0.212 RSD 84%	0.54	4982	Avg 0.104 sd 0.101 RSD 97%	0.100
5034-T	Avg 1.659 sd 0.234 RSD 14%	3.14	5034-T	Avg 2.758 sd 0.698 RSD 25%	5.93	5034-T	Avg 11.33 sd 1.32 RSD 12%	10.88	
ppmw = parts per million by mass	5034-C	Avg 2.539 sd 0.160 RSD 6%	4.80	5034-C	Avg 2.443 sd 0.148 RSD 6%	5.25	5034-C	Avg 2.421 sd 0.481 RSD 20%	2.32
ppma = parts per million atom basis	5034-H	Avg 3.940 sd 0.451 RSD 11%	7.45	5034-H	Avg 3.944 sd 0.720 RSD 18%	8.48	5034-H	Avg 11.05 sd 1.71 RSD 15%	10.58
SRM 1) Avg sd cert	13.30 2.20 16.5		SRM 2) Avg sd cert	7.95 2.04 8.7		SRM 3) Avg sd cert	1.29 0.36 1.00		
RepStd	Avg 1.01 sd 0.05 known 1.00		RepStd	Avg 0.563 sd 0.002 known 0.50		RepStd	Avg 2.078 sd 0.22 known 2.00		
	1) NBS 1632a Coal			2) NBS 1568 Rice flour			3) SPEX G-Std not SRM		

6. PHASE II OPPORTUNITIES

Through the course of Phase I several new research and development opportunities with high probabilities for success manifested themselves. Listed under the various headings by which they can be segregated, these new hypotheses stand alone, each on its own merit as individual tasks, as having the potential to further enhance the DZAAS technique as the only methodology capable of yielding 10^{14} - 10^{15} a/cc sensitivity in CdTe matrices while continuing to be low cost, easy to operate, and an intrinsic component in the IR optic manufacturing industry's attempt to produce higher quality and lower cost material.

6.1 PERFORMANCE ENHANCEMENTS

6.1.1 Quartz windows mechanically closing during the third phase of the furnace cycle. This would concentrate the atoms during the signal measurement period thereby increasing the signal to noise ratio (better detection limits). It has been demonstrated that the Cd and Te components of the sample do not spectrally interfere--that is, the Zeeman correction scheme works.

6.1.2 Through the use of either optical pyrometry or thermocoupling more critically monitor the various furnace phase temperatures. It was noted during this aspect of our Phase I experiments that temperature settings were crucial to successful set up of the instrument and that the electronic feedback method of reporting furnace temperature did not appear to be highly accurate. Either because of this or indicative of a separate phenomenon it was observed that tube to tube variances in heating efficiencies existed. A more accurate temperature reading would enhance performance.

6.1.3 Develop low frequency (LF) discharge lamps for the trio of elements studied under Phase I. The data contained herein was gathered using a cathodic sputtering discharge device as the primary line source. This is less stable and more difficult to properly set up (technique oriented) than an LF lamp. LF lamps have already been engineered for some of the higher vapor pressure elements and the performance improvement for those elements was significant. A factor of 2 to 5 improvement in signal to background ratios is possible.

6.2 Simplification of Operation

6.2.1 Automate the transfer of sample from the balance to the sample insertion carriage assembly. By doing so one significant area of potential method error (operator bias plus imprecision) would be eliminated. Existing robotics can easily be adapted.

6.2.2 Develop a sample preparation method that minimizes the time, technique and potential for sample contamination yet assuredly yields homogeneous subsamples for analysis.

6.3 Increase Technique Utility

6.3.1 Expand the array of elements that are possible by this technique to include all critical TIE's in CdTe matrices. Perform figure of merit studies for about 20 - 30 elements as specified through a poll of the semiconductor industry and end users. Included in this group, but not limited to, are As, Sb, Ga, Cr, Ni, Li, Na, and P.

6.3.2 Expand the field of sample matrices that can be analyzed by this technique. Choose a fixed set of critical TIE's (about 5) to perform viability tests for alternate detector materials, thin film epitaxial layers, and other substrate materials.

6.3. Several techniques exist that offer potential as analytical tools for physical and chemical testing of II-VI material. One drawback to date has been the lack of well characterized standards for instrument calibration. One such example would be SIMS. The DZAAS technique could be used to accurately determine ultratrace levels and sample homogeneity of specified target elements.

6.3.4 At the current level of performance this technique lends itself to meaningful studies that could be undertaken to improve manufacturing processes. Examples of this are characterization studies of the process from raw material through final product; correlation studies between physical and optical properties and the determined chemistry; element doping for tracing studies; and the effect of sublimation as a purification procedure.

7. REFERENCES

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8. APPENDIX I - ZEEMAN BACKGROUND CORRECTION FOR GFAA

Atomic absorption spectrometry (see Figure I-1) is based on the principle that light of a certain wavelength is absorbed by the atoms of the element to be analysed, as a function of the concentration of the element. If the element is brought into the beam path this absorption on the element spectral line is discernible as a lessening of the light intensity and can be measured with a suitable detector. A disadvantage of this method is the non-specific absorption caused by background effects, which can lead to incorrect measurement results.

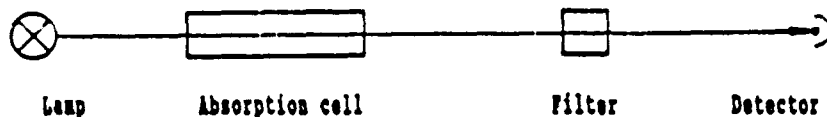


Figure I-1. Diagram of an atomic absorption spectrometer

Background correction subtracts nonatomic absorption signals from the total absorbance signal generated, to give a corrected signal. Background correction is required with furnace work more frequently than with flame work. Furnace samples are not contacted by the reactive species that would be present in a flame, which aids in the breakdown and removal of interferences. Two types of background correction are typically available from manufacturers and are described further in the following sections.

The continuum source background corrector is designed to automatically correct for broad-band nonatomic absorption. A continuum source emits light over a broad spectrum of wavelengths instead of at specific lines. With this system, light from the primary source and the continuum source is passed alternately through the flame or furnace. The element being determined effectively absorbs light only from the primary source, while background absorption affects both beams equally. Therefore, when the ratio of the two beams is measured electronically, the effect of the background absorption is eliminated.

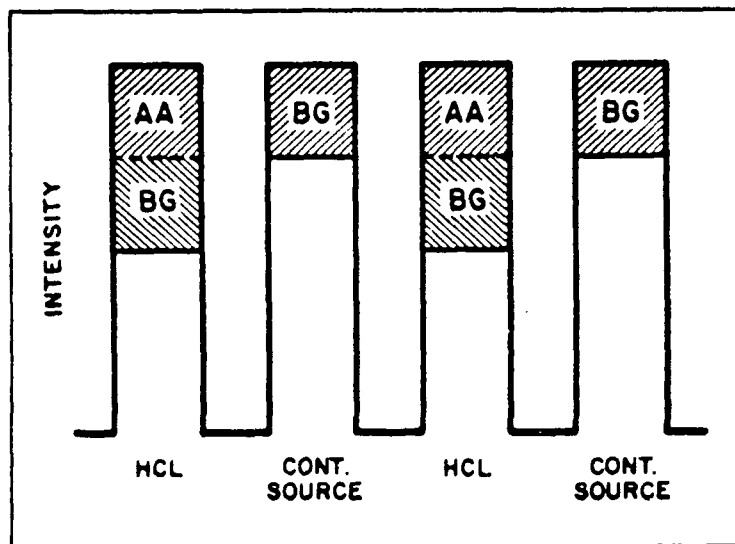


Figure I-2. Continuum Source Background Correction Signals

A deuterium arc lamp background corrector is used for the far UV region and a tungsten-iodide lamp for the near UV and visible regions of the spectrum. The continuum lamp has a finite lifetime and must be replaced periodically. The image of the background corrector source should be coincident with that of the primary source while passing through the center of the graphite tube, for the most accurate correction.

The background source must match the primary source in intensity, as well as pathway. If using a deuterium source background corrector at a wavelength above 300 nm the primary source intensity may have to be reduced (by lowering the lamp current) in order for matching to occur.

Background correction with a continuum radiation source is limited to background absorption that is constant (with wavelength) over the observed spectral range (spectral bandwidth or slit width). When the background absorption changes with wavelength within the observed spectral range, the continuum source background corrector subtracts the average background signal which may not be identical with the actual background absorption on the resonance line. A non-uniform background absorbance may be caused by atomic lines of matrix elements or by a rotational fine structure of molecular spectra. It often can be recognized by the fact that structured background absorption changes with the selected slit width. Structured background frequently causes overcompensation. An example of structured background is seen in the case of the determination of selenium in blood.

At the most sensitive wavelength for selenium, 196.0 nm, several iron emission lines are located within the bandpass. Even though the monitored average background absorption is small ($<0.4 \text{ A}$) in undiluted blood, overcompensation will occur because the average background absorption of the iron lines is different than the actual background absorption exactly at the same selenium wavelength.

For some graphite furnace determinations, continuum source background correctors are adequate. Background correction with a continuum source is limited in many instances, and for those cases the Zeeman background correction system will prove a better choice.

With the Zeeman effect, atomic lines are split into three or more polarized components in a strong magnetic field (Figure I-3). In the simplest case (normal Zeeman pattern) the single pi (π) component remains at the original analyte wavelength. The sigma (σ) components are symmetrically shifted away from the central analyte wavelength (typical separation is 0.01 nm). With more complicated or anomalous Zeeman patterns, both the pi and sigma absorbances are split into several components. In addition, the pi and sigma components are polarized differently. The pi components are linearly polarized in a direction parallel to the magnetic field while the sigma components are polarized in a direction perpendicular to the magnetic field (displayed below the central line in the figure).

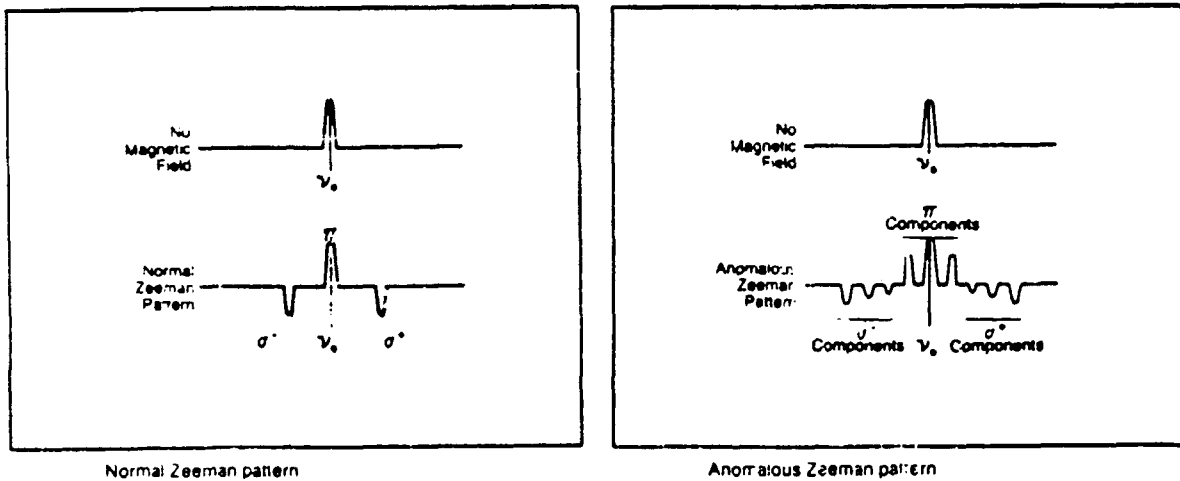


Figure I-3. Zeeman Splitting of an Absorption Line in a Magnetic Field.

Indirect Zeeman correction instruments use a fixed linear polarizer to reject radiation due to the pi components and pass radiation due only to the sigma components. The magnet is operated in an alternating fashion at 60 Hz (or 50). When the magnetic field is off, both sample and background absorbance are measured. When the magnetic field is on (8 kgauss strength), only the background absorbance is measured, since the sigma components are shifted away from the emission line of the light source. Background correction is performed by subtraction of the field-off and field-on measurements, yielding only the atomic absorption signal due to the analyte itself. Figure I-4 shows schematically what is being measured at each instant in time.

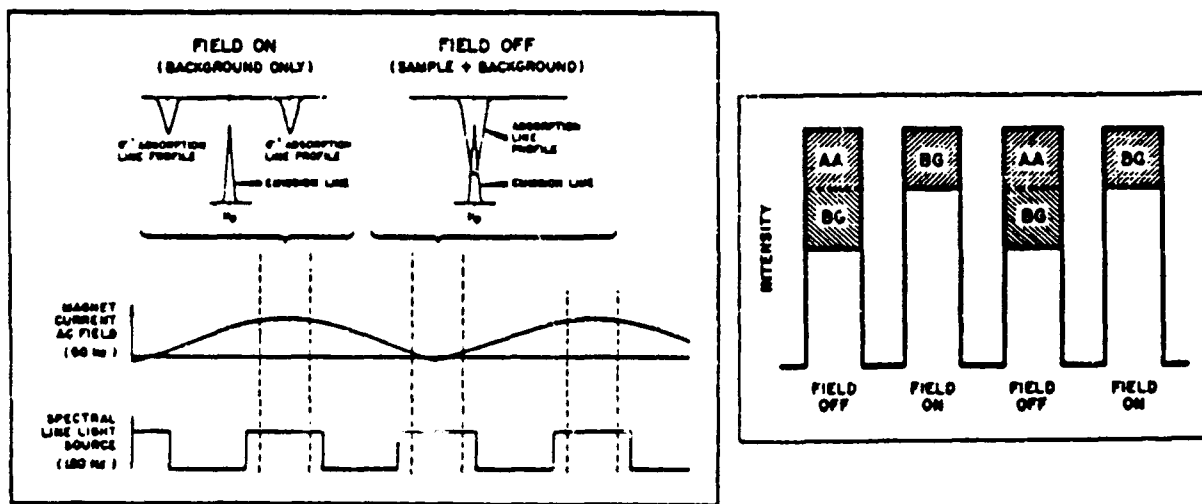


Figure I-4. Background Correction with a Direct Zeeman System.

Zeeman effect background correction makes it possible to compensate for nonspecific absorption up to about 2.0 Å. In addition, it permits correction for continuous background as well as for structured or line background. This technique provides a true double beam system and utilizes exactly the same wavelength and the same narrow profile of the primary emission line for both measurements.

The only disadvantage of using the Zeeman effect for background correction may be a slightly reduced linearity of the calibration curves and a minor loss in sensitivity for some elements. This is, however, more than compensated by the accuracy of the background correction. There is also a significant improvement in the signal-to-noise ratio compared to continuum source background correction, which results in better precision and detection limits for real samples.

In direct Zeeman atomic absorption the lamp is operated in a magnetic field. The absorption signal is compared with the

background signal using appropriate polarization optics and a lock-in amplifier.

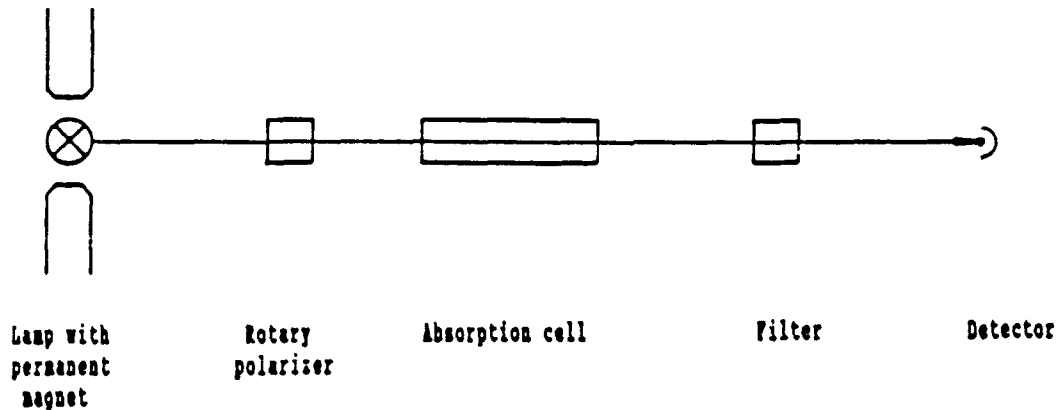


Figure I-5: Diagram of a direct Zeeman atomic absorption spectrometer

The magnetic field splits a resonance line into three components. The π -component can be absorbed both by the elements and by the background, whilst the two σ -components are absorbed only by the background. With the aid of electronic evaluation the actual atomic absorption of the element to be detected can then be determined from the difference with the aid of a lock-in amplifier. The construction and mode of operation of the GRUN SM20 Zeeman atomic absorption spectrometer are shown schematically in Figure I-6.

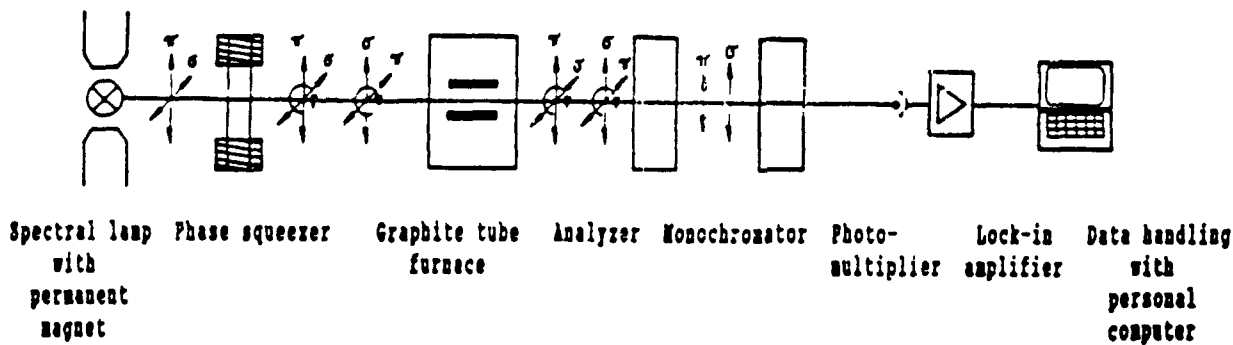


Figure I-6: Diagram of construction and mode of operation of the GRUN SM20.

APPENDIX II - TECHNICAL VIEW OF THE SM20 DZAAS UNIT

II.1 Instrument construction

The GRON SM20 is made up of three functional units

the lamp unit
the furnace unit and
the spectrometer

and incorporates the electronics required for control and evaluation. Figure 1 shows the front view of the GRON SM20. The furnace power unit, which also contains the mains power supply for the atomic absorption spectrometer (AAS) and all peripheral equipment, is not shown.

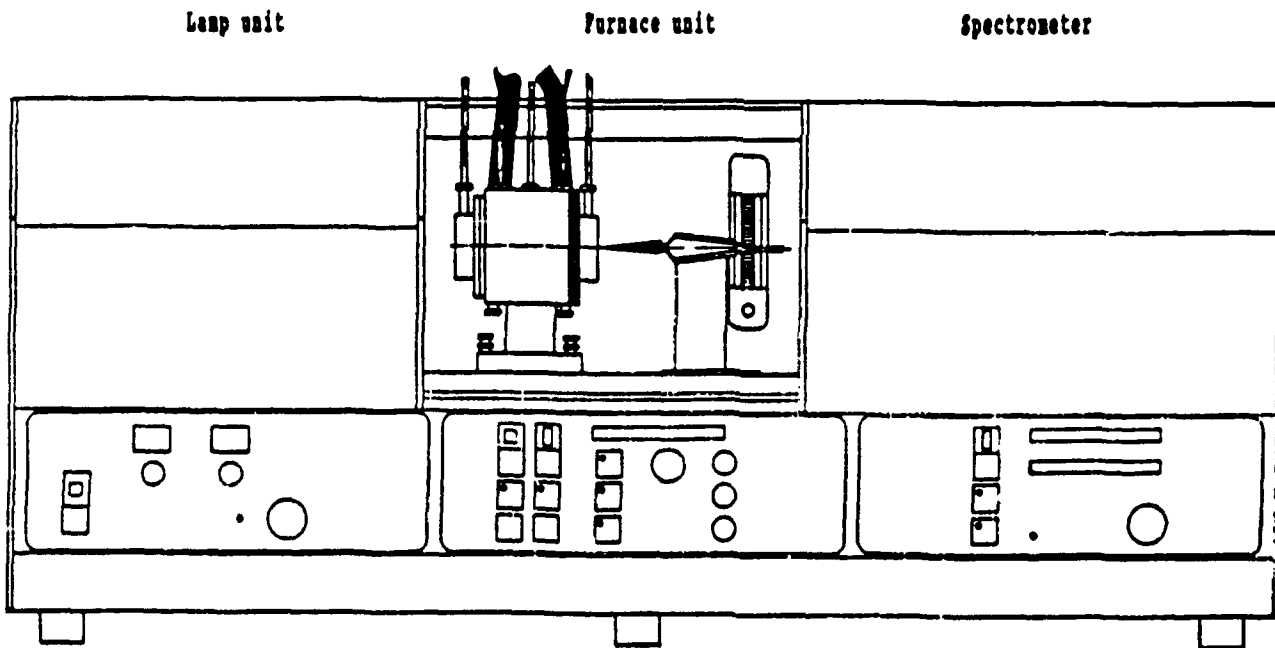
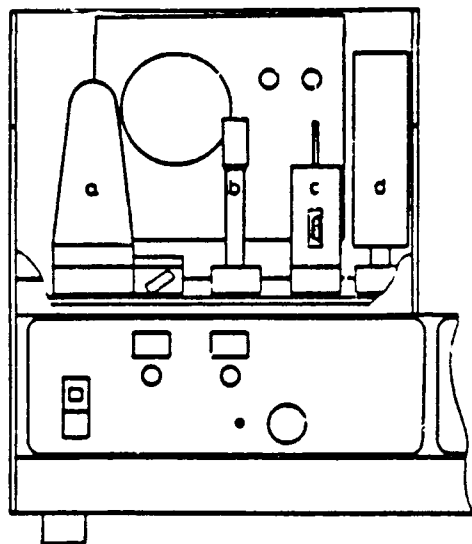


Figure 1: Front view of the GRON SM20

The layout of all components in the beam path on an optical bench of integrated design obviates the need for complex optical and mechanical adjustments. Ergonomic aspects played an important role in the design and layout of the connectors and controls required for operation of the instrument.

The lamp unit contains all the components for generation of the spectral lines and for compensation



- a Permanent magnet with lamp fitting
- b Lens
- c Compensation plate
- d Phase squeezer

Left instrument chamber

Figure 2: Lamp unit

No tools are required for fitting and adjusting the lamps.

Two special types of lamp are available for the GRON SM20: an Electrode Low Frequency Lamp (ELFL) for elements with a high vapor pressure and a Magnetically Concentrated Lamp (MCL) for elements with a low vapor pressure. The connectors for the two types of lamp are different and cannot be confused. When fitting a lamp it is necessary only to ensure that the pole shoes are correctly located on the poles of the magnet.

The furnace unit comprises the graphite tube furnace, the boat carriage and the gas flowmeter and from the user's point of view constitutes the heart of the atomic absorption spectrometer. For this reason it is of uncluttered design and has been made easily accessible in the central section of the instrument.

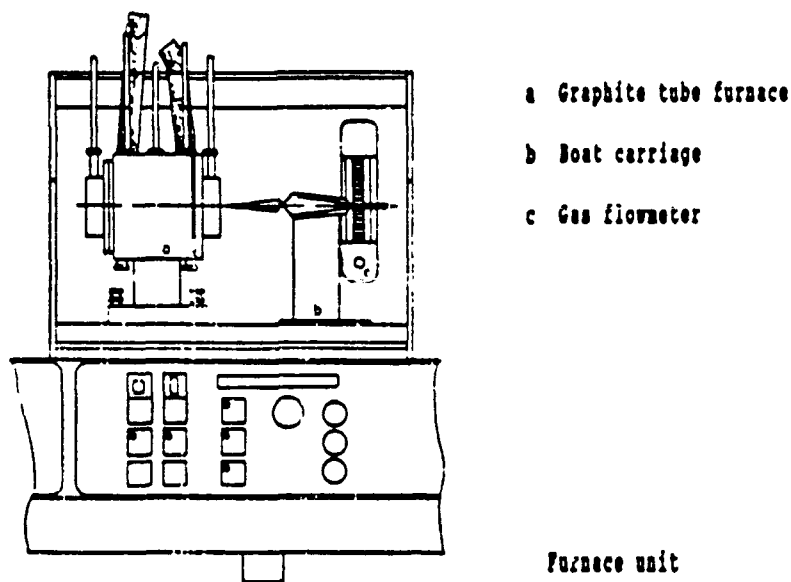
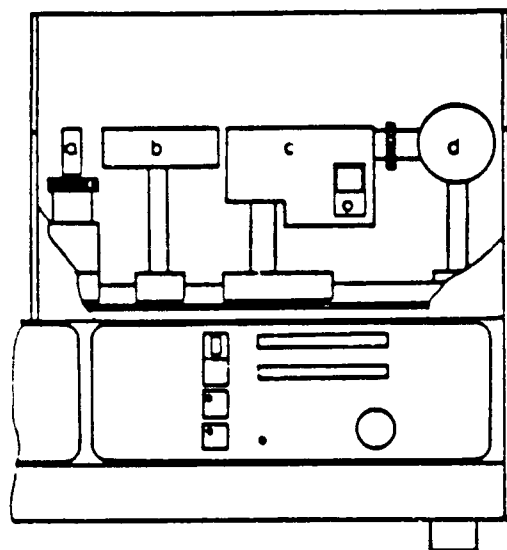


Figure 3: Furnace unit

The graphite tube furnace is provided with quick-release connectors for cooling water and gas and can be replaced by other atomization units with a minimum of effort. The sliding carriage is mounted on ball bearings and is designed to take the special tweezers which permit problem-free insertion of the sample boat into the furnace, without contamination.

The gas flowmeter indicates the gas flow rate and is used for flow adjustment.

The spectrometer consists of lens, analyzer, monochromator and photomultiplier with an integrated high tension voltage supply and signal preamplification.



- a Lens
- b Analyzer
- c Monochromator
- d Photomultiplier

Right instrument chamber

Figure 4: Spectrometer

The analyzer consists of quartz platelets positioned obliquely in the beam path. The lattice monochromator is fitted with 0.25 nm slit pairs as standard.

The photomultiplier is located in a housing together with the high tension voltage supply and the amplifier.

The electronics are fitted as plug-in modules in the housing of the GRON SM20, behind the control panel. The leads linking the functional units and the controls are therefore short. The electronics contain all drivers, for example for lamp current, lamp heating, phase squeezer, analog voltages for furnace current and photomultiplier and the evaluation units such as the lock-in amplifier, electronic stray light filter and measured signal processing. Automatic balancing of the Zeeman compensation is carried out by an internal microprocessor. In addition, the electronics also provide the signal processing for connection of the personal computer and the X-T recorder. The plug-in technique allows easy replacement of modules and thus enables rapid and simple servicing of the electronics.

1.2 Control panel

The control panel, located below the functional units, is clearly laid out and readily accessible. The controls and displays under each unit relate to the unit directly above. All controls and displays which have to be set or checked only once during one or more analyses, such as the control for the monochromator setting, have deliberately not been incorporated in the control panel. Figure 5 shows the entire control panel.

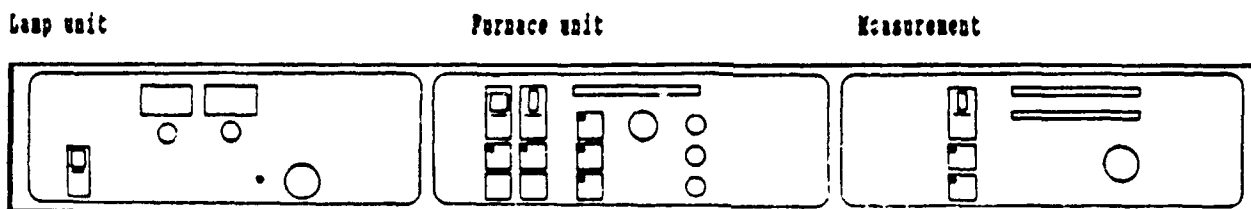


Figure 5: Control panel

The main switch for the GRON SM20 and all peripheral equipment is located on the lamp unit control panel (see Figure 6), together with the controls necessary for the lamp.

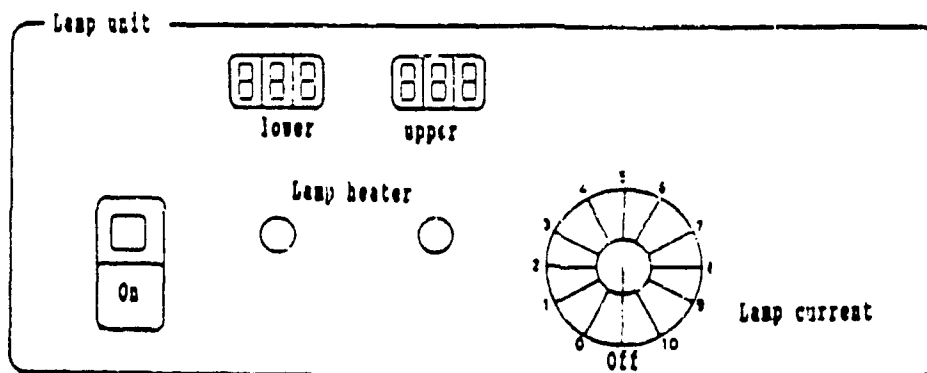


Figure 6: Lamp unit control panel

Main switch:

The atomic absorption spectrometer and, via a remote connection in the furnace current unit, all peripheral equipment connected to the instrument (see Figure 13) are switched on or off at the main switch. The green indicator lamp lights when the equipment is ready for use.

Upper/lower lamp heater:

These two controls are used to set the heaters to the values indicated on the lamp. Digital displays show the settings in Amps.

Lamp current:

This control knob is used to set the lamp current, in scale divisions, to the value indicated on the lamp used. Activation of the lamp current is indicated by the red LED.

The furnace program parameters required for an analysis can be set manually on the furnace unit control panel (see Figure 7).

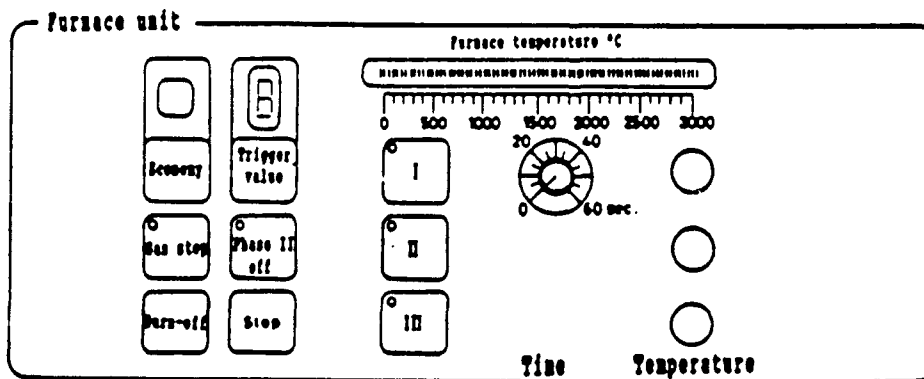


Figure 7: Furnace unit control panel

Economy:

The 'Economy' feature of the GRON SM20 switches off the gas and water supply automatically if there is a break of 20 minutes between measurements. The supplies are switched on again either by starting a new measurement or by pressing the 'Economy' control. The current status is indicated by the light above the control:

green: gas and water supply on
red: gas and water supply off

Burn-off:

When this control is actuated the furnace is brought to maximum temperature for a period set by the manufacturer. This prevents sample to sample contamination.

Trigger value:

The trigger value display is actuated by pressing this control. The correlation between the display and the trigger value is shown in Figure 8.

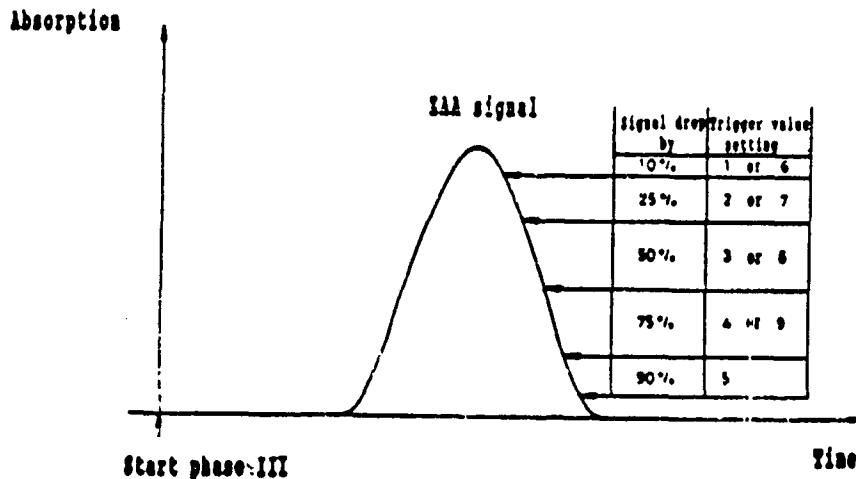


Figure 8: Correlation between trigger values and signal pattern

Phase II (ashing) off:

This feature allows the analysis time to be shortened for matrix-free samples, especially solutions, by cutting out the ashing phase from the the furnace program.

Stop:

A measurement, calibration or analysis can be stopped by actuating this control.

I (drying phase); II (ashing phase); III (atomization phase):

The furnace temperatures for the analysis are set using these controls. The furnace temperature set and reached is shown in degrees Celsius on the "Furnace temperature" bar display (bar scale 0....3000 °C). By pressing the button the furnace is heated to the temperature set with the corresponding control knob. When these buttons are pressed to heat up the furnace the shut-off times or trigger values set are not operative. The furnace is switched off again only when the button used is released.

Time:

This control knob is used to set the time taken for phase I. The scale is in seconds (0....60) and the length of time chosen depends on the amount of sample used.

All displays and controls needed for balancing and optimization of the measuring signal are located on the measurement control panel (see Figure 9).

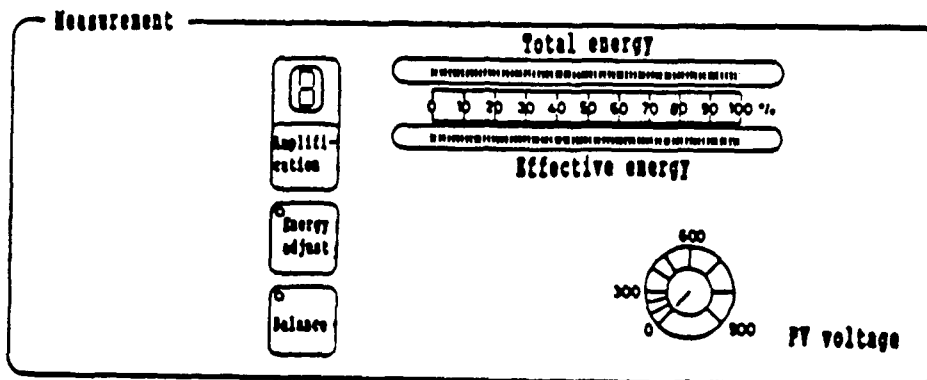


Figure 9: Measurement control panel

Amplification:

This key is used to set the amplification factor (1-8) of the electronic measurement amplifier. The amplification setting is dependent on the sample to be analysed (see Section 4.1).

Balance:

The Zeeman compensation is balanced automatically on pressing this control. The red LED is lit while balancing is in progress. It goes out when balancing is complete.

PV voltage:

The photomultiplier high tension voltage can be manually adjusted between 0 and 900 V using this control knob. This is used to set the effective energy display to 30 %.

The two bar displays show the measurement signals (effective energy, total energy) in percent. The display serves for signal adjustment and signal optimization. All other processing of the measurement signals is conducted via the personal computer connected to the instrument.

The controls for setting the time constant and the wavelength have not yet been mentioned. As these controls are not required during an analysis after instrument setting and signal optimization have been carried out they are located in the instrument and not on the control panel.

The control knob for the time constant (0.3; 0.7; 1.4 sec) is in the lamp section on the back of the instrument housing (see Figure 22). The control knob for the wavelength (190 - 750 nm) is located directly on the monochromator in the spectrometer (see Figure 4).

1.3 Instrument operation - introduction

In simple terms operation can be broken down into three stages:

Signal optimization
Calibration
Analysis.

By way of introduction these are described briefly below. Detailed instructions for the individual stages are given in the next section.

Signal optimization entails both start-up (switching on the instrument) and adjustment of the lamps and setting of the wavelength and the photomultiplier high tension voltage.

Calibration usually involves several measurements on a sample of known element content (reference solution, certified reference material ACRMO). The mathematical correlation between the measurement signal and the element content of the sample is determined from the results (reference curve).

During analysis the element content of the sample is determined from the measurement signal with the aid of the reference curve. The analytical result is obtained by determining the mean value from several parallel measurements on a sample.

10. GLOSSARY

Accuracy: The agreement between the measured mean on a set of results and the known value--sometimes expressed as % relative bias, i.e.,

$$\%RB = \frac{\text{known} - \text{measured}}{\text{known}} \times 100$$

Background: An error in measurement caused by the spurious absorption from nonanalyte species at the same wavelength as the element of interest.

Characteristic Mass: The mass of the analyte that generates a signal of 0.0044 A*s on an integrated basis (sensitivity).

$$m_0 = \frac{(\text{ug of std})(\text{conc of std})(0.0044)}{(\text{Value in A*s})-\text{blank}}$$

Detection Limit: The concentration or mass of an element that yields a signal equal to three times the baseline noise.

External Gas: A gas (Ar or N) used to protect the outside of the furnace tube.

Gauss: A unit of magnetic field strength.
10,000 gauss = 1 tesla.

Graphite Furnace: A device for atomizing a sample to its component ground state atoms for absorption measurement.

Integrated Signal: The area under an absorbance peak profile (Absorbance * second units).

L'vov Platform: The small boat that contains the sample to be atomized.

Peak Signal: The highest value in absorbance units of a peak profile.

Phase I: The initial (drying) phase of the furnace program set by temperature and time parameters.

Phase II: The second (ashing) phase of the furnace program whereby the sample is pretreated to isolate the sample matrix from the element of interest.

Phase III: The final stage of the furnace program where the analyte element is atomized--converted into an elemental state ready for quantitation.

Phase Squeezer: Optical component in the DZAAS instrument that optically rotates the plane of polarization 90 degrees.

Polarizer: The optical component in a Zeeman correction system that isolates the plane polarized light emanating from the line source.

Precision: A term to define the degree of confidence on the mean for a set of data--usually expressed as relative standard deviation, i.e.,

$$RSD = \frac{\sum X^2 - n\bar{X}^2}{n} / \bar{X}$$

Rollover: The maximum absorbance value that can be attained in a Zeeman corrected system's calibration curve.

Temperature Ramp: The controlled rise in furnace temperature between two furnace program phases.

Volatilization: The passing of a solid or liquid to a vapor state.

Zeeman Effect:

The phenomenon of an atomic spectral line being split and spatially offset into its magnetic and electronic components by a magnetic field.