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INVESTIGATIONS OF A SPARK EMISSION DETECTOR FOR GAS CHROMATOGRAPHIC ANALYSIS

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INVESTIGATIONS OF A SPARK EMISSION DETECTOR FOR GAS CHROMATOGRAPHIC ANALYSIS

By

Sandra Marie Koeplin

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ABSTRACT

INVESTIGATIONS OF A SPARK EMISSION DETECTOR FOR GAS CHROMATOGRAPHIC ANALYSIS

By

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The design, construction and operation of a spark emission gas chromatographic detector is described. The effluent from the chromatographic column is run directly into a spark chamber. The characteristic emission which results from spark excitation is isolated by a monochromator, and the intensity is measured by a photomultiplier tube.

The spark emission detector (SED) is shown to be useful for detection of boron, bromine, carbon, hydrogen, iodine, nitrogen, oxygen, phosphorus, silicon and sulfur with sensitivities in the microgram to nanogram range. The atomic emission lines, used to monitor emission, detection limits and dynamic range for each element investigated are presented. The SED is shown to be reliable to within 2.8% over five chromatographic separations and relatively free from effects due to carbon chain length or bond type. The usefulness of the SED for multielement analysis is demonstrated with several examples. The empirical formulas of several alcohols are determined using the SED. The SED is used to simplify complicated chromatograms obtained with universal detectors by responding to only those compounds containing a particular element, and to separate compounds that cannot be separated by a universal detector. The ability of the SED to uncover peaks hidden by larger interfering peaks is also demonstrated.

The software system design and FORTRAN IV programs for the SED chromatographic system are described. The software package allows for control of a scanning monochromator for multielement analysis and a box-car integrator for time resolved spectroscopy. In addition, raw chromatographic data are obtained, and retention times and areas calculated under software control.

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To Mom and Dad

Carol, John, Rob, Jim and Tom

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CHAPTER I

INTRODUCTION

Gas chromatography has come to be one of the most widely used techniques in the modern analytical laboratory. Although, with the onset of increasingly more complex biological and environmental samples, the job of the chromatographer has become more difficult. The separations obtained are not always clean and easy to interpret; thus, there has been a greater emphasis on improving separation techniques through improved column material, column packing and liquid phase technology. In addition, there has been a move towards improving separation quality through the use of automated control of operating parameters and electronic data handling. Another area of investigation has been involved with new detector technology. The overall effort in chromatography has been towards making complex separations easier to accomplish.

This work deals with an element selective detector to simplify chromatographic separations. Element selective detectors have become very popular due to their ability to ignore all compounds eluting from the column except the compound containing the element of interest. The element selective detector in addition to being

selective, must be reliable, accurate, easy to use and low in cost just like any other chromatographic detector. One further characteristic that would be useful for an element selective detector would be tunability of response for any specific element of interest. This characteristic would eliminate one of the primary inconveniences of many element selective detectors; the need for a different detector for each element of interest. If the detector were tunable, only one detector would be needed to handle all elements of interest.

Since elements emit radiant energy at characteristic wavelengths, the development of a detector involving some sort of emission process would be one approach to a tunable element selective detector. The emission for each element could be monitored by using a monochromator adjusted to the proper wavelength with a photomultiplier tube as the radiation transducer. This work deals with such a chromatographic detector.

The detector to be studied can be called a spark emission detector since the effluent from the gas chromatographic column is run directly into a spark discharge. The characteristic emission which results from spark excitation is isolated by a monochromator, and the intensity is measured by a photomultiplier tube. If the spark detector is used along with a radiation transducer that monitors more than one wavelength, such as a linear

diode array, true simultaneous multielement gas chromatography would be feasible. The primary advantage of this type of system would be the ease with which empirical formulas for the compounds could be determined.

The design, construction and detector characteristics of the spark emission detector are discussed in this work. The ordinary operation and computer control routines are also described. In addition, the tunability, selectivity, reliability and general usefulness of the spark emission detector for gas chromatographic analysis are demonstrated by experimental examples.

CHAPTER II

BACKGROUND

Since gas chromatography can provide both qualitative and quantitative information about the composition of mixtures, it has become one of the most widely used modern analytical techniques. However, with the advent of increasingly more complex biological and environmental samples, the pertinent information from a chromatogram is becoming more difficult to extract. Chromatograms may have not only a large number of peaks, but also overlapping peaks, or large background signals which may obscure many peaks. These things combine to make peak identification very difficult for the chromatographer. Clearly, a means of simplifying the chromatogram would greatly simplify and enhance chromatographic analyses.

Many types of improvements in chromatographic science are available, but this discussion focuses on improving chromatographic analysis through the use of selective detectors, since the more selective the detector, the poorer the chromatographic separation can be. The best detector would be one which conclusively identified the specific compound and the amount of compound eluting from the column. Unfortunately, nothing quite this specific is available. Many methods have

been tried such as using a male gypsy moth to detect the female gypsy moth sex attractant or employing professional "sniffers" to identify the compounds eluting from the chromatographic column. While these methods have merit for qualitative analysis, they are not quantitative and, in addition apply only to a very specific analysis. The completely specific detector that identifies only a single compound requires one detector for each compound of interest. This is impractical due to both cost and storage considerations. This would also be inefficient use of materials since only one detector would be in use for any given analysis and also inefficient use of time due to the necessity of frequent changing of detectors. A better approach would be to develop detectors that respond to a selected class or family of compounds. A better solution still would be a detector which was independently selective for many different classes of compounds.

The introduction of the "element selective" gas chromatographic detector was an attempt to simplify complex chromatograms. The element selective detector, as the name implies is selective for certain elements. Generally, the term "element selective" is reserved for detectors that respond to specific elements other than carbon, such as sulfur, iodine, etc. These detectors reduce complex chromatograms to chromatograms which

contain peaks due to compounds with only the element of interest. There has been an increase in the development of types and applications of various element selective detectors as is apparent from several recent review articles (1-8). This section briefly discusses recent developments in selective detectors for gas chromatography.

A. Ionization Detectors

There are several varieties of ionization type detectors available. The most popular of these is the flame ionization detector (FID). The FID is a universal detector that uses a hydrogen flame to burn the organic compounds and produce ionized molecular fragments. The resulting ions are collected by a pair of electrodes and produce the response signal. Since the FID has proven to be a reliable, sensitive and linear detector, it has served as a model for the class of selective ionization detectors called thermionic detectors. Another popular ionization type detector is the electron capture detector. Recent improvements in thermionic detectors and the electron capture detector are discussed in this section.

1. Thermionic Detectors

The thermionic detector (TID) exists in many physical designs. One basic type of thermionic detector is a

modification of the popular universal FID. It is called an alkali flame ionization detector (AFID) since the design uses a flame and a coated tip, or alkali salt probe to produce an enhanced response for S, P, N, organometallics and halides. Recent studies have investigated new coating materials (9) and tip fabrication (10) techniques. The other basic type of thermionic detector is the flameless version (4,5,11,12) in which the salt container is electrically heated to yield an atomic vapor, and a plasma is used for ion production. The mechanism of the detector response is not well understood. Brazhnikov and Shmidel (13) attempt to explain the mechanism of the response of the TID. They attribute the background current in a Cs coated-tip TID to the thermal ionization of Cs and Cs₂0 formed in an oxygen rich portion of the flame. When P or N containing compounds enter the flame, the combustion products form heavy ions with the Cs ions present in the background, which reduces the concentration of the alkali metal salts in the flame. Since alkali metal salts are active inhibitors of combustion, the decrease in concentration causes an increase in the flame temperature. A higher flame temperature causes more efficient ionization of Cs which in turn causes a change in the monitored current. Other workers have optimized the TID to improve the responses to phosphorous, nitrogen (14,15) and organometallic

compounds (16).

The selectivity of the TID for P to C is about 10^4 , and for N to C, it is about 10^3 . The response is linear over approximately 3 decades in concentration. This detector has absolute detection limits for P, its most sensitive element, on the order of 10^{-12} grams (17). While the TID is not the most selective or the most sensitive detector available, it is being used regularly in the modern analytical laboratory.

2. Electron Capture Detector

The electron capture detector (ECD) is probably one of the most widely used selective detectors (18). It has been improved in recent years from a temperamental device to one that is stable and extremely sensitive for halogenated compounds. This detector consists of a high energy electron source (usually 63 Ni, Sc 3 H₃, 3 H, or 147 Pm) and an electron collector. The electron current decreases as halogenated compounds enter the detector and "capture" electrons.

Recent improvements have extended the linearity and temperature ranges along with the sensitivity. The effects of temperature (19), pressure (20), and voltage (21) on a dc electron capture detector have been investigated. The use of a pulsed mode electron capture detector has been reported (22) and tested for effects

of carrier gas on response (23). New electron sources have also been investigated by several workers (24,25). Dwight and coworkers (24) tested a 55 Fe electron source. Wentworth and coworkers (25) investigated a photoionization source with the Lyman- α resonance line of hydrogen used with triethylamine to produce electrons, which eliminates the conventional radioactive source. The ECD has been coupled to a capillary column to take advantage of the high sensitivity and selectivity of the ECD and the high separation efficiency of capillary columns (26).

The mechanism of the ECD response has been investigated extensively in the last few years (5,27-29). Theoretical studies have attempted to explain the empirical observations that the operational conditions for the coulometric mode, where the number of electrons not collected per unit of time is equal to the number of molecules entering the detector per unit of time, and constant current mode, where the ionization current is kept constant by varying the pulse frequency, are different. In fact, Bros and Page (30) calculate contradictory operating conditions for the two modes. They also explain why the constant current mode gives the best linearity and the coulmetric mode gives the best sensitivity.

With a constant current ECD, a linear range of about 6 orders of magnitude is obtained (5). A reported

sensitivity for CCl_4 is 50 pg (25). This type of sensitivity for halogenated compounds is one of the main advantages for the ECD. A major disadvantage has been the large variation in electron affinity of each compound which results in a separate calibration being required for every compound. However, since the selectivity for halogenated and oxygenated compounds is good, and few other compounds have high electron affinities, the ECD continues to be used routinely, particularly for pesticide analysis (6).

B. Electrochemical Detectors

Three basic electrochemical methods, coulometry, conductometry and potentiometry, have been applied to produce electrochemical detectors. Generally, conductance detectors and coulometric detectors are discussed together since both require either an oxidation or reduction of the organic compounds eluting from the gas chromatographic column.

The microcoulometer has been used for S, N and halogen analyses. The selectivity is very good (31,32); however, the sensitivity has generally been only in the nanogram range (2). Lately, research in the area of electrochemical detectors has emphasized the electrolytic conductivity detector. This may be due to the greater use of the Hall (33) style electrolytic conductivity detector. This is

a smaller, more compact modification of the Coulson coulometric detector that has a linear range of 5 orders of magnitude, sensitivity of 0.1 ng for S, Cl and N and a selectivity for C to S of 10^5 :1 (33). Modifications of the electrolytic conductivity detectors have included temperature control (34), bridge circuitry (35), and solvent venting (36). The mechanism of operation along with numerous applications of this detector are discussed by Pape and coworkers (37).

Electrochemical detectors using various types of electrodes have been described. Methods of detection of carbon monoxide by electrochemical means have been reported by several authors (38, 39). In both these detectors, the CO is electrochemically exidized at a platinum (38) or metallized-membrane electrode (39). The current produced is then proportional to the initial CO concentration. Hydrogen sulfide has also been detected electrochemically by Stetter and coworkers (40) using methods similar to those employed for the determination of CO. Another type of electrochemical detector available is the ion selective electrode. An ion selective electrode has been used to analyze for sulfur compounds. The process consists of conversion of the sulfur compound to hydrogen sulfide which in turn precipitates silver ions from a solution. The monitoring signal is derived from a silver ion selective electrode measuring the decrease in the concentration

of silver ions (41).

C. Optical Emission and Absorption Detectors

Detectors based on an optical response have proven very useful in gas chromatography. These detectors monitor a characteristic line or band emission or absorption by a particular species. This method provides a very selective analysis technique for a variety of elements. These detectors can be divided into those which involve a response to an atomic species such as the microwave plasma emission detector (MPD), atomic absorption and discharge type detectors or those which respond to molecular species such as the flame photometric detector (FPD), molecular fluorescence, chemiluminescence, and ultraviolet detectors. These detectors are discussed briefly in this section.

1. Microwave Plasma Emission Detector

The use of a microwave plasma to excite emission from a gas chromatographic effluent produces a highly selective detector based on atomic emission of the elements of interest. The MPD was primarily a research instrument, until the recent appearance of a MPD from Antek (42) and Applied Chromatography Systems, Ltd. (43). However, the MPD will probably not become as common

as the FPD or AFID since the detector cost is still extremely high. There are many advantages to this detector. The largest purported advantage is the ability to monitor twelve elements simultaneously with this single detector (42,43) while also providing sensitive detection which can be used to determine empirical formulae. The multiple element advantage is not unique to the MPD, but can be obtained with any atomic emission type detector outfitted with a multielement photodetector, probably at a lower cost. The Applied Chromatography Systems, Ltd. MPD is equipped with a direct reader and 12 photomultiplier tubes to allow simultaneous determination of 12 elements.

The microwave plasma gas chromatographic detector has been described by several authors (44,45). This detector has been optimized for ten elements by Van Dalen and coworkers (46). The parameters which were optimized included the pressure, microwave power, observation height and concentration of scavenger gas. With their optimized system, a linear range of 3-4 decades was reported for all ten elements except hydrogen, and detection limits were about 0.1 nanograms.

Various improvements for this detector have been developed. Houpt (47) found that selectivity could be greatly improved by the use of wavelength modulation. Kawaguchi and coworkers (48) found that adding potassium

chloride as an ionization suppressant enhanced the spectral intensities and gave unity slopes for the calibration curves. Serravallo and Risby (49) reported that doping the MPD with oxygen will increase both selectivity and sensitivity. A final improvement involves the construction of a cavity that is cylindrical in shape and allows a stable low pressure helium plasma to be used. This makes use of the better atomization characteristics of the low pressure helium plasma over the atmospheric argon plasma (50). A mechanism for the response of the MPD is discussed by several authors (48,49), although it is still not clearly understood.

2. Atomic Absorption Detectors

The increase in the use of element selective detectors has led to a search for a single detector selective for many elements. Atomic absorption spectroscopy fits this description well. If atomic lines are observed, the selectivity should only be limited by the elements that the source can excite, thus creating a selective detector that is useful for many elements. The main disadvantage to this technique is that it is limited to a single element at any point in time due to the line source limitations. Both flame and non-flame atomic absorption units have been adopted as gas chromatographic detectors (51-55). A flameless gas chromatographic

atomic absorption detector (NFGCAA), constructed by coupling the gas chromatograph to the AA unit by a simple tube connector, has been described by several authors (51,52). Segar (52) with an unoptimized system reported a sensitivity of 10^{-8} gPb for tetra-alkyl lead compounds, while Parris and coworkers (51) described a system able to determine nanogram levels of astantine, selenium and tin.

The flame GC-AA units (FGCAA) were constructed by Wolf (54) by tapping a hole into the center side of a burner head and directly attaching the column to it. Chau and coworkers (55) connected the column and AA by attaching the burner nebulizer tip to the column and also inserting an all glass liner into the burner chamber to eliminate adsorption of the compounds on the burner walls. Absolute detection limits with these units have been reported as 1 ng for Cr (53,54) and 0.1 ng for Pb.

3. Discharge Emission Detectors

Another useful type of multielement selective detector is the arc, spark or glow discharge. Recent papers have described the use of both spark and glow discharges as gas chromatographic detectors. Lantz (8) reported a spark emission detector that obtained sensitivities in the nanogram range for most elements studied. He reported detection of C, P, Si, B, O, S, N and H. The work

presented in this thesis is a new design of the detector described by Lantz. Two papers have recently been published (56,57) which discuss the use of the helium glow discharge emission detector. Feldman and Batistoni (56) describe a simple to construct, inexpensive glow discharge detector. It can detect halogens, S, P, C and metals in column effluents in the nanogram range. A background correction system was used to enhance selectivity and sensitivity. The detector described by Rezchikov and coworkers (57) was used to detect hydrogen and water in gases down to 1×10^{-5} % of the total solution.

4. Molecular Emission Detectors

Chemiluminescence has proven to be a useful tool in the detection of gas chromatographic effluents. The popular FPD operates by the detection of the molecular emission produced from the mixture of column effluent and the mixture of oxygen, air and hydrogen burned inside a shielded jet. A photomultiplier tube and appropriate filters provide the detection system. The FPD is most commonly used to analyze for phosphorus or sulfur containing compounds, but it has also been used for boron (6), nitrogen (6), chlorine (58) and tin (59) containing compounds.

Various instrumental improvements to the FPD have been described to eliminate the problems associated

with its use. Hasinski (60) designed a two section burner head that eliminates extinguishing of the flame during passage of the solvent peak. Instrumental changes have included a detector which premixes hydrogen and column effluent (61), movement of the detector inside the gas chromatographic oven (62), a new geometric arrangement to improve selectivity (63) and a two flame system, the first flame to decompose samples and the second flame to excite emission (64). Flow optimization was also discussed (65) and it was found that flow rates for all gases drastically effect the sensitivity. These authors also recommended that the use of air with the FPD be discon-Several authors combined the FPD with capillary tinued. columns to analyze for both phosphorous containing (66) and sulfur containing (67) compounds.

One of the most serious problems with the FPD, has been related to the detection of sulfur containing compounds. Since S_2 is the emitting species in this case, the response is roughly proportional to the square of the compound concentration. The fact that the response is not always a square relationship has been the subject of several papers. It has been suggested that flow rates (65,68) cause the varying proportionality.

The FPD is a sensitive, selective and easy to use detector. The sensitivity for P is 5×10^{-13} gP/sec, for S it is 5×10^{-11} gS/sec, and the selectivity with

respect to hydrocarbon emission is $5 \times 10^5 \text{ gC/gP}$ and 10^3-10^6 gC/gS (64). The detector has functioned well with only minor modifications; although careful flow rate control will enhance sensitivity further.

A further modification of the FPD has produced a class specific detector that measures the chemiluminescence generated when ozone reacts with compounds emerging from a gas chromatographic column (69). The selectivity of this detector is derived from the reactivity of ozone with varying compounds. It has been demonstrated that it is selective for olefins (69), aromatics (70), saturated hydrocarbons (70), thiopenes (70) and nitrosoamines (71). The thermal and flow properties have been improved (71) by reducing chamber volume and changing the chamber geometry. The sensitivity of this detector is from micrograms to nanograms depending on the compound.

5. Molecular Fluorescence Detector

Molecular fluorescence gas chromatographic detection has also been attempted as a means of selective detection. Several authors have described a spectrophotofluorimeter detector (SPFD) (72-74). Winefordner and coworkers (72) have described a SPFD which uses a flow through gass cell and silicon-intensifier-target (SIT) camera tube mounted at the exit of the emission monochromator. This system, however, provided sensitivities about three to five times

lower than a normal photomultiplier tube with a linear range from 50-900 ng for anthracene. One advantage of this system is the immediate subtraction of the background signal to enhance selectivity. Mulik and coworkers (73) described a system which used a heated transfer line to flow sample past the monochromator and photomultiplier tube for detection. They reported a sensitivity of 50 nanograms for benzopyrene. Cooney and Winefordner (74) investigated instrumental effects on detection limits by the SPFD. They found that improved detection could be obtained by using sources with an intense UV output and a low stray light level.

6. Ultraviolet Detector

While the coupling of an ultraviolet spectrometer and a gas chromatograph has been done, it has been a rarely used detection system. The recent concern about carcinogenic nitrosoamines in many commercial products has prompted the development of methods for quantitative determination of the amount present in a given product. The most recent use of the GC-UV detector (GCUV) has been as a method for the determination of nitrosoamines (75). Although at present this detector is not widely used due to its limited applicability and low sensitivity, it has the potential for further use as a selective gas chromatographic detector.

D. Miscellaneous Detectors

In addition to all of the classes of gas chromatographic detectors that have been discussed previously, there still remain detectors that do not fall into any of these classes. These detectors involve more specialized detection methods such as IR, NMR, or optoaccoustic spectroscopy, piezoelectric crystal sorption, radiochemical methods, and gas chromatography-mass spectrometry. These detection methods will be briefly discussed in this section.

1. IR and NMR Detectors

Infrared and proton NMR spectroscopic instruments have become common in many chemical laboratories; however, their usefulness for analyzing mixtures has been somewhat limited. The combination of a gas chromatograph to either of these instruments can provide selective detection. The gas chromatography/infrared systems that have been used have ranged from simple modifications of commercial modules (76-79), to more complex systems such as Fourier Transform IR detection (80-81) and multiwavelength IR detection (82-83). NMR has also been used as a detector for gas chromatography (84-85). GC-NMR can also provide good qualitative information about complex mixtures.
2. Mass Spectrometer and Plasma Detectors

A mass spectrometer (MS) coupled to a GC has proven to be invaluable in the analysis of many types of complex mixtures. The GCMS has undergone many modifications, but they will not be discussed in this review since it is thoroughly reviewed by Cram and Risby (7).

Recent improvements in GCMS have involved more complex data acquisition and analysis through the use of microcomputers and stored spectral data (86-87). The MS remains the most selective and overall sensitive detection system available today.

Various other multimode detectors which emulate the GCMS in terms of sensitivity and selectivity have been developed. The plasma chromatograph described by Cohen and Karasek (88) is one such detector. The plasma chromatograph is an ion detector that can also provide qualitative information about column effluents (89). However, Bird and Keller (90) have investigated the vapor concentration dependence and concluded that plasma chromatography at present seems inferior to other conventional detectors even though the high sensitivity seems attractive.

3. Piezoelectric Sorption Detector

The piezoelectric sorption detector has been used primarily as a universal detector for gas chromatography,

but recent applications have reported its use as a selective detector for ammonia (91) and sulfur dioxide (92). The effects of temperature (92) and selective coatings have also been discussed (93). The mechanism for the functioning of this detector has been discussed by King (94). This detector has not achieved wide usage, but it seems to have particular applications in the analysis of air pollutants.

4. Other Detectors

There are other gas chromatographic detectors available which have not achieved the popularity of the detectors already described. These detectors are not less useful, but simply less well known or more specific in their operation. Radiochemical detectors are used for the detection of radioactive labelled compounds (95-98). A recent article by Kreuzer (99) described an optoaccoustic detector for gas chromatography. While this is similar to GC-IR, since an IR laser is used, the detection system is quite different. Kreuzer reports that the optoaccoustic detector has a poor selectivity.

E. Summary

The widespread use of gas chromatography has produced a need for methods to simplify the increasingly complex

samples that the chromatographer is called upon to analyze. The selective detector provides a method for simplifying chromatograms of complex mixtures. However, as can be seen from the number of detectors presented in the previous sections, the decision as to which detector is best for any particular application is a difficult one. The decision must include considerations such as: elements of interest, sensitivity, linear range, ease of operation and maintenance, cost and availability. There is presently no single detector which is the best in all of these categories, so the most important considerations must be weighed most heavily.

One of the most important considerations in choosing a specific detector is the decision of which element or elements it is selective for, although, this is not the only factor. For example, the TID, MPD, FPD, conductometric detector and coulometric detector can all be used to detect nitrogen. The TID is more sensitive than some of the others, but more subject to instrumental parameter variations. The conductometric and coulometric detectors are not very sensitive and limited in the number of other elements they can detect. The MPD, on the other hand can easily detect many elements, but it is very expensive. At present the only solution to a very complex problem is to use a combination of several detectors, which is clearly undesirable. The design, construction

and modifications of the Spark Emission Detector (SED) were undertaken in an effort to provide the chromatographer a further, albeit not perfect, alternative for element selective detection.

CHAPTER III

Spark Characteristics

The SED has been shown to be a useful gas chromatographic detector (8,100). However, it was felt that several changes to the previous spark chamber designs would produce a more effective detector. This chapter discusses the specific physical design changes along with the electrical characteristics of the new SED. Spectra of the continum emission variation with time are also included.

A. Design Considerations

An ideal gas chromatographic detector must be sensitive, linear in response over a wide concentration range, free from structural effects, compact and easy to maintain. The SED is designed to meet all these criteria. The previous spark designs of Zynger (101) and Lantz (8) both employed a single gap coaxial spark chamber powered by a Xenon Corporation nanopulser power supply. Both Zynger and Lantz introduced samples into the spark chamber through a teflon tube mounted at 90° to the coaxial line. While these previous designs proved useful, it was felt that several changes would provide a better gas chromatographic detector. The most recent design of the

miniature, nanosecond spark chamber is discussed in this section.

1. Double Gap Design

The SED maintains a coaxial geometry. The coaxial design is employed to produce a high power spark of nanosecond duration with efficient energy transfer. Since the coaxial spark has been shown to be useful as a gas chromatographic detector, the coaxial capacitor spark design serves as the basic pattern for further modification.

The spark used by Lantz used a single gap with the column effluent carried into the spark perpendicular to the spark channel. There are two basic problems with this system: 1) the spark breakdown is affected by anything which enters the spark channel, and 2) the spark channel is destabilized by gas entering from the side. Several methods to correct each of these problems are available.

Spark breakdown can be controlled by using an auxiliary spark gap (102-103). The auxiliary gap is usually a stationary gap in series with the analytical gap or a mechanical rotary spark gap. Either type of control spark gap can improve control of the breakdown voltage since the control gap is normally maintained in a constant environment. While this system is easily adopted, the major drawback is that the energy is dissipated in two separate spark gaps instead of being used exclusively in the analytical gap. Several workers have used electronic triggers, such as thyratrons, instead of an auxiliary gap (103-105). These triggers control the time of discharge reliably regardless of the experimental conditions. However, these systems are expensive, limited in repetition rate and have pulse widths on the order of microseconds.

Since it was desirable to use the high power, nanosecond spark, an auxiliary gap was added to the spark. The thyratron was not used since the spark pulse width would have been increased beyond nanoseconds. The auxiliary gap was incorporated into the spark chamber in a manner designed to maintain the coaxial geometry.

2. Power Supply

The spark can be operated in two modes (106). The first mode is operation with overvoltage which was employed by previous workers (8,101). With this type of operation, the power supply pulses at a constant rate and provides a very reproducible discharge. The repetition rate of spark formation is dependent on the charging rate of the power supply and, in the case of the Xenon Corp. nanopulser used by Zynger and Lantz, 1 kHz is about the maximum possible. The second mode is the free-running

mode where the spark breakdown voltage is equal to the initial charging voltage. Using a high voltage power supply with a free-running spark, the spark repetition rate can be increased to near 10 kHz. This makes faster data acquisition possible, which is highly desirable for multielement gas chromatographic detection.

The most recent SED design employs a Spellman Corporation high voltage DC power supply model #UHR10P100. This power supply supplies 0-10 kV DC and 0-10 mA. A 1 M Ω 100 watt carbon film, current-limiting resistor is placed in series with the DC power supply. The connections to the spark chamber are made through high voltage amphenol connectors and RG/8U cable.

3. Spatial Stability

Since the spark is a transient phenomenon, the spark channel must continually re-form. Since each new channel forms under different conditions, the spark may wander from the place of the previous discharge. This spark wander or positional instability causes optical noise which degrades the signal-to-noise ratio. Spark stability is affected by several factors such as electrode geometry, spark environment and gas flow.

Methods to stabilize spark sources have been described by several authors. Walters and Goldstein (107) suggest that a stable spark should: 1) be unidirectional,

but not overdamped, 2) have gas introduced in a laminar manner, flowing from anode towards cathode and 3) utilize needle like electrodes. Other workers have improved spark stability by flowing gas through the electrodes or by using a sheath surrounding the discharge.

In an attempt to stabilize the nanosecond spark used in this work, the following features were incorporated. Needle-like thoriated tungsten electrodes were used for both the analytical and control gap. A sheath gas surrounded the analytical gap. The gaseous column effluents flowed along the electrodes from anode to cathode. The control gap was isolated and maintained in a pure argon atmosphere.

B. Spark Chamber Construction

A diagram of the spark chamber is shown in Figure 1. The chamber includes three separable components: 1) the capacitor, 2) the auxiliary or control gap and 3) the analytical gap. The three physically separable components facilitate easy maintenance and adjustment. The design incorporates the coaxial geometry for low inductance, a double gap system for breakdown voltage control and axial gas flow injection for spatial stability. The salient features of each of these components are discussed independently in this section.



Figure 1. Diagram of spark chamber construction.

1. Capacitor Construction

The capacitor is constructed of a cylindrical, aluminum bar surrounded by 0.002" Teflon tape (Cadillac Plastics, Detroit, MI) as the dielectric. The Teflon tape is coated with an adhesive backing for ease of attachment to the aluminum bar.

Since the SED is housed within the gas chromatographic oven, Teflon was chosen as the dielectric because it is thermally stable to approximately 250°C (108). Other dielectric materials such as high molecular weight (HMW) polyethylene are not as thermally stable. HMW polyethylene is only stable to about 120°C (108). Teflon tape, as opposed to a machined Teflon jacket, is used to obtain the thinnest dielectric possible since the capacitance increases with decreasing dielectric thickness. The dielectric is then surrounded by a copper tube to complete the capacitor. The entire spark chamber is encompassed by a brass housing to reduce r.f. interference.

Electrical connection from the high voltage D.C. power supply to the capacitor is made through a high voltage amphenol connector threaded into the top of the aluminum bar. Ground connection is made through the extension of the copper tube down to the outer brass housing.

2. Auxiliary or Control Gap Construction

The control gap is located in the mid-section of the spark chamber. The chamber consists of a bored out Teflon tube with holes for the electrodes through the center and a swagelock fitting attached to one end for gas introduction. The electrode gap distance can be varied to a maximum of 6 mm with this chamber. Removable quartz windows are installed to transmit light from the spark to the optical trigger discussed in the next chapter. An argon atmosphere is maintained by the flow of gas through the stainless steel swagelock fitting. The gas exit port is equipped with a long tube to prevent oxygen diffusion into the control chamber.

3. Analytical Gap Construction

The analytical gap portion of the spark chamber was the most difficult to construct compactly. The analytical gap section is the lower portion of the spark chamber shown in Figure 1. This section incorporates a Teflon cone to direct carrier gas and sample along the electrode as well as a sheath gas for stability. An enlarged diagram of this section is shown in Figure 1. The sample and carrier gas enter the Teflon chamber through a stainless steel swagelock fitting and are then directed through a machined Teflon cone down along the thoriated tungsten

electrode. The sheath gas flows into the Teflon chamber from the side opposite the sample through a stainless steel swagelock fitting and is directed through the series of holes located around the electrodes.

The top electrode of the analytical gap also serves as the bottom electrode for the control gap. It is mounted in a Teflon holder and held with a set screw. This electrode is easily replaced with electrodes of different lengths when different gap lengths are required. The bottom electrode of the analytical gap is mounted in a piece of brass held at ground potential. The brass mount can be adjusted with the large threaded knob to obtain different analytical gap lengths.

The analytical gap and control gap can be viewed through one inch holes drilled into the brass outer chamber. The holes are threaded so that optical components like lenses can be inserted and held in place by screw in holders. The light emitted from the analytical gap is focused by a 1" focal length lens mounted in a brass plate. This plate is set into tracks in the spark housing and held in place by 2 set screws. This configuration allows the lens to be moved along the spark channel.

4. Spark Gap Measurement

The spark gap distance has a significant effect on the power of the spark (109) and must be carefully

controlled. The gap distances for both the control and analytical gap are measured with the use of a comparator, reticle and lens combination. The comparator with the reticle attached (Edmund Scientific, Barrington, N. J.) is placed into a threaded cylindrical lens holder which contains an adjustable lens attached to a threaded hole on the spark housing. The lens allows focusing of the spark gap image onto the reticle face. This configuration provides accurate measurement of the gap distance to within 0.1 mm.

C. Electrical Characteristics

1. General Circuit Description

A simplified circuit diagram of the nanosecond spark is illustrated in Figure 2. The spark is considered to be the electrical discharge which results when a condenser is discharged. Therefore, the spark chamber can be considered to be a coaxial line capacitor C_L which is in parallel with the high voltage power supply. The capacitor is charged through a 1 M Ω current limiting resistor and the inductance of the coaxial line L_L . When the capacitor reaches the breakdown voltage of the control gap G_C , the current then follows the imaginary path through R_C , L_C , R_A and L_A . The bridging resistor R_B shunts the current until the resistance of the





analytical gap is less than the resistance of the bridging resistor (typically 11 M Ω). When $R_A < R_B$, the analytical gap breaks down, causing the analytical gap to become conducting. When the gap conducts, analyte material in the gap is atomized and exited. Subsequently, electromagnetic radiation characteristic of the element is emitted. Illustrations of the current waveforms are shown in a later section.

2. Capacitance Measurements

The capacitance of a particular spark is directly related to the power of the spark. The two spark capacitors used in this work have capacitances of 150 pF and 300 pF. The transmission cable used has a capacitance of 29.5 pF/ft for a total line capacitance of 190 pF and 350 pF respectively. The capacitance was determined by comparison with precision capacitors in an RC circuit pulsed by a Wavetek pulse generator. The capacitance can be increased by using a longer capacitor or a thinner dielectric as can be seen by Equation (1) for the capacitance of a coaxial line (110):

$$C = \frac{2\pi\varepsilon_{o}Kl_{L}}{ln((a+t_{D})/a)}$$
(1)

where ϵ_0 is the permittivity, K is the dielectric constant, l_{I_i} is the length of the aluminum bar, a is the radius of

the aluminum bar and t_D is the thickness of the dielectric. However, when increasing the capacitance, care must be taken to insure that the proper LRC ratio is maintained since neither an overdamped nor oscillating spark will provide as efficient a power transfer as a critically or near critically damped spark.

D. Spark Current Measurements

The spark is a transient phenomenon which results from the rapid discharge of a capacitor through a resistance. The current waveform during the discharge can be useful in determining overall spark characteristics. Therefore, current-related waveforms for various spark conditions were obtained by measuring the voltage drop across a small wire. The resulting waveform was displayed and stored with a fast sampling, storage oscilloscope. The data were later digitized, and a current-time curve was generated from the differential equation which describes the current response. The measurement procedure and results are discussed briefly in the following sections.

1. Current Waveform Production

The spark current was measured by placing a small nichrome wire in series with the two spark gaps. The voltage drop across the resistance wire was attenuated

with a resistor-attenuator network that was impedance matched to the input of a sampling, storage oscilloscope (564, 3T2, 3S1). A voltage versus time waveform is obtained from this procedure. The data are then digitized to produce a waveform like the one shown in Figure 3.

The relationship between the voltage versus time data and current-time data is shown by the following differential equation:

$$E(t) = L \frac{di}{dt} + iR + \frac{Q}{C}$$
 (2)

A modified Runge Kutte routine (111,112) based on these data was used to solve the differential equation for current. However, this is not an easy problem since the accuracy of the results depends upon the accuracy of the resistance, inductance and capacitance values of the small wire.

The wire probe was attached to both the bottom electrode of the second gap and ground potential by a set screw connection into the brass mount that holds the electrode in place and the brass outer housing, respectively. The resistance of the wire and connectors was determined by attaching a large current source and measuring the voltage drop. The resistance was determined to be 0.0792 Ω . The capacitance of the wire was estimated to be \approx 1 pF based on normal values of capacitance for



Figure 3. An example of digitized oscilloscope voltage vs time data.

small wires (113). The inductance was estimated to be on the order of 1 to 10 nH from literature values for the inductance of Nichrome wire and brass (114,115). An average of 5 nH was used for the current calculation.

The current calculations were made through the use of the modified Runge Kutte routine (SKRUKU) listed in Appendix A. As it turns out, the single most important factor in the determination of actual current values is the inductance. Since the inductance is not known accurately, the absolute current values obtained may be significantly in error. However, the current values relative to one another are useful in assessing changes in spark characteristics as various parameters are changed.

2. Current Characteristics of the Spark

The effect of varying operating parameters were studied with the use of the current waveforms. Figure 4 illustrates the dependence of the current on the analyte carrier gas. It can be seen that the use of argon instead of helium produces a higher current spark of a longer duration. Emission in argon is also more intense than in helium.

Figure 5 illustrates the effect of supply voltage on current. A lower supply voltage gives a higher maximum current. It was also found that operating at the lowest







Figure 5. Current dependence on DC supply voltage.





supply voltage needed to maintain a stable spark provided the most intense emission.

Figure 6 shows the effect of gap length on the current of a spark with no bridging resistor. The effect of the control gap is illustrated in Figures 6a and 6b. The control gap in 6a is 4.0 mm and in 6b it is 3.0 mm. The sum of the control gap and analytical gaps in both cases is 6.0 mm. Even though the total gap length is the same, the current profiles differ from one another. Decreasing the control gap causes a corresponding decrease in the current as can be seen by a comparison of Figures 6a and 6b. Decreasing the control gap length while maintaining the analytical gap length constant (Figures 6a and 6c) also results in current suppression. The effect of decreasing the analytical gap length can be seen in Figures 6b and 6c. Decreasing the analytical gap also causes a decrease in the current maximum; however, the effect is not as great as that which arises from a change in the control gap length.

Using the bridging resistor, it was found that a large upper gap and a small lower gap produced the most intense emission. This may be due to the control gap acting as a DC gap which increases in power with increasing gap length and the analytical gap acting as an overvolted gap which increases in power with decreasing gap length (109).



Figure 6. Current dependence on gap length.

E. Argon Background Emission

The time-resolved spectra obtained from unscrubbed argon gas are shown in Figures 7a-c. These spectra were generated from the raw emission data by a series of FOR-TRAN IV programs called by SKSPEC (Appendix A). Each digitized data point is the average of 1000 sparks. All data are scaled to compensate for the variable integration windows so that direct comparisons between the figures can be made.

There are several prominent spectral features common to Figures 7a, 7b and 7c. The atomic lines are primarily due to atomic emission by argon and carbon impurities in the tank argon. The band emission is due to hydroxyl bands, the second positive nitrogen band emission and possibly oxygen emission (116,117). These bands also arise due to contamination of the tank argon. The spectral lines and bands are present in different intensities depending upon the time of observation after spark initiation.

Spectrum 7a represents the emission spectrum integrated from 0.5 μ s to 2.0 μ s after spark initiation as indicated by a photodiode-Darlington trigger. During this time period, primarily atomic emission lines are present with only a small amount of molecular emission. Later in time, Figure 7b the argon and carbon emission lines, in addition to the band emission, increase in



Figure 7. Time resolved spectra of argon background emission.

intensity as the spark begins to cool. Still later in time, Figure 7c, from 5.0 μs to 2.0 μs after spark initiation, there is only a small amount of band emission remaining.

In order to maintain the optimum signal-to-noise ratio, it is necessary to adjust the time window of observation. Comparing the carbon emission intensity at the 2478.6Å atomic emission line between the three spectra shown in Figure 7, it can be seen that the carbon emission is greatest from 2.0 μ s to 5.0 μ s. From 5.0 μ s to 20.0 μ s the background emission has died down considerably; however, the signal has also died down. The maximum signal-to-noise ratio for carbon can then be obtained by choosing an integration window from 2.0 μ s to 5.0 μ s. Further examples of the application of time resolved spectroscopy to spark data acquisition are given in Chapter VI.

CHAPTER IV

INSTRUMENTATION

The usefulness of element selective gas chromatographic detectors can be seen by the proliferation of such detectors as discussed in Chapter II. This dissertation deals with the characterization of a spark emission chromatographic detector; however, this detector is useless without the necessary supporting equipment. This chapter discusses all aspects of this detector system except the detector itself since Chapter III provided an extensive discussion of the spark detector itself. The chromatographic equipment, optics, supporting electronics and computer interfacing needed for control and data acquisition are discussed.

A. Overview of the SED System

A block diagram of the entire gas chromatographic SED system is shown in Figure 8. The gaseous column effluents enter the spark chamber where they are atomized and excited. The radiation emitted is then dispersed with a monochromator and transduced to the electrical domain with a photomultiplier tube (PMT). Simultaneously, an optical trigger is fired to start the timing electronics. The timing electronics controls the length of time that





the signal from the PMT is integrated, in addition to allowing for observations to be made an adjustable time after the spark has fired. The integrate analog signal is converted to a digital signal with the use of an analog to digital convertor (ADC). This signal is then analyzed and stored by a PDP 8/e computer equipped with 16K of core memory, an extended arithmetic element and real time clock. The following section briefly discusses each major component of the SED electronic supporting system.

B. Chromatographic Components

The gas chromatographic oven used in this work was built at Michigan State University. The oven consists of a large insulated box, a squirrel cage fan and a series of heating coils. The power to the heating coils can be controlled by a Variac to maintain the oven at the desired constant temperature. The oven contains coiled tubing along the walls to allow all gases to reach thermal equilibrium. "On-column" injection is employed. The column is coiled inside the oven and attached directly to the spark detector which is also mounted inside the oven. The detector is mounted along the inner side wall of the oven and secured in place by a circular mount (Figure 9). Electrical connection from the high voltage power supply to the SED is made through a hole cut in the top of the gas chromatographic oven. Emission from the



Figure 9. Photograph of the SED inside the chromatographic oven.

detector is viewed through a hole cut in the side of the oven. The optical trigger is also attached through a hole drilled in the side of the oven. The trigger and optical connections are discussed in more detail in later sections of this chapter.

The heart of any gas chromatographic system involves the column and mobile phases. The columns that were used varied depending on the separation desired. A discussion of the specific column used is included later with specific parameters of the separation. All injections were made with Hamilton series 7000 syringes to insure that all of the analyte had been removed from the needle. In addition, all needles were cleaned by insertion into a heated syringe cleaner. This cleaner is constructed from an injection septum and a brass tube surrounded by heating tape, which is electrically heated. A vacuum is drawn on this assembly during the cleaning process to aid in the removal of any contamination left in the syringe.

The mobile phase used most often in this work was argon gas. While helium provides a very stable spark, the emission is very low and difficult to detect. The tank argon was passed through a series of purifying tubes separated from each other by glass wool or glass frits. The purifying tubes were filled with a 5A molecular sieve to remove small hydrocarbons and water, ascarite to

remove carbon dioxide, activated charcoal for removal of hydrocarbons and BASF catalyst for removal of oxygen.

The flow rate of the mobile phase was measured by using a bubble flow meter at the detector exit port. The flow rate through the control gap was found to be critical in the control of the spark. For this reason, it was necessary to regulate this flow rate closely. A Gilmont F9160-11 needle valve and rotameter combination was used for this purpose. The sheath gas flow rate for the SED was controlled by a Gilmont F-13 flow meter and Delmar valve combination.

C. Spectrometer

The light emitted from the atoms excited in the spark is collimated by a lens situated so that the spark gap is at its focal point. The light is then directed through a brass light pipe and into the entrance slits of a GCA McPherson EU-701/E monochromator with a EU-700-56 programmable filter attachment. A brass tube aligns the spark gap with the other components along the optical rail. An RCA 1P28 photomultiplier tube (PMT) housed in a GCA McPherson EU-701-30 PMT module serves as the radiation transducer. The PMT is kept off for most of the time by keeping the voltage between dynodes 2 and 3 at 5 volts. The PMT is then turned on by applying a voltage of 150 volts to dynode 3, which causes the full gain to be available again. This sequence is triggered by a signal from the supporting electronics and takes approximately 300 ns to accomplish. This circuit is discussed further in Zynger's thesis (101). The analog signal from the PMT is then the input of the gated integrator discussed in the next section.

D. Supporting Electronics

The basic design of the supporting electronic system is shown in Figure 10. The design and construction of this system is discussed extensively by my coworker, Gary Seng (118). Thus, only a brief discussion is included here. The schematic diagrams for the entire system are included in Appendix B.

The supporting electronics consists of four main components: 1) a delay scaler, 2) an integrate scaler, 3) an integrator and 4) the computer interface. The interface is discussed in Section F of this chapter. This section describes the operation of the remaining circuitry.

Since the large continuum background signal from the spark decays faster than the analyte emission signal, maximum signal-to-noise ratios for a particular element are obtained some time after the spark has fired. Time resolution allows a signal to be integrated for a specific duration after spark initiation. Time resolution is accomplished in this work through the use of a gated




integrator and hold system. This system allows a delay time and an integrate time to be set for each individual experiment. Once the spark has fired, the circuit delays the preset time and then the signal is integrated for the proper length of time. The integrated signal is then gated to the computer for further processing. A more detailed description of the gated integrator and hold system follows.

The formation of a spark is detected by the optical trigger discussed in Section E of this chapter. The negative going pulse from the trigger starts a series of Schottky counters which count down from a preset delay time. The delay time is the time that must pass after the spark has fired before data are taken. When the delay counters have reached the preset count, a similar series of Schottky counters begins to count clock pulses for the time desired for integration of the analog signal. Both of these scalers can be set by either a PDP 8/e minicomputer or by rotary switches located on the front panel of the MSU built spark electronics box. A 20 MHz crystal oscillator is divided down to a 5 and 10 MHz clock. These are used to pulse, respectively, the front panel delay and integrate circuitry and the computer delay and integrate circuitry. With this circuitry, time resolution of approximately 100 ns is obtained.

The actual analog signal from the PMT is integrated

by a gated integrate and hold circuit that is sequenced by the aforementioned counting sequencer. The signal can then be amplified by factors of 1 to 100 before being sampled by the analog-to-digital converter (ADC) or output to a strip chart recorder.

E. Optical Trigger

Emission data are taken from the spark discharge after the initial background emission has decayed. In order to know the actual time that data are acquired, it is necessary to know the actual time of the spark formation. This problem is a difficult one since the spark is "on" for less than 100 ns, but is repeated at about a 5 kHz rate. The most reasonable solution to this problem was to employ an optical detector of some sort which was triggered from the intense continuum radiation present very early during the discharge.

There were several types of triggers available. A phototransistor, photodiode, photodiode-op amp combination and phototube were all possibilities. A phototransistor provides a good means of detecting a short on time pulse due to its high sensitivity; however, the rather slow response is a definite disadvantage for measurements to be made early in time. The photodiode, on the other hand, provides a very fast response, but a low sensitivity. The photodiode op-amp combination seemed to be

a good solution, except for the high cost and slow response of the commercially available models. A photodiode opamp was designed that incorporated an Motorola MRD 500 combined with a video amplifier as shown in Figure 11a. This combination was not employed since the RF noise from the spark caused problems with the wide bandpass video amplifier. The phototube was also considered since it could provide both a rapid and sensitive response, but due to the bulkiness of the supporting equipment was not utilized.

The two types of trigger systems that are used regularly are shown in Figures 11b and 11c. Figure 11b illustrates a photodiode-darlington circuit which incorporates an MRD 500 photodiode with a typical darlington set-up to provide a clean negative going pulse when an intense spark is provided. This trigger is normally used with a large capacitor or large secondary gap; since with a small capacitor, or lower energy spark, the photodiode tends to produce erratic pulses. A further problem arose due to the RF noise when the trigger circuit was placed physically close to the spark; therefore, the light from the spark is transferred to the trigger circuitry by a lucite light pipe. The advantage of this trigger is that the circuitry can be triggered in less than 100 ns; however, this system was only used for solution work outside the oven since the lucite rod is not thermally stable.







Figure 11. Optical trigger systems for the SED.

The trigger system used for the majority of the work presented in this dissertation is shown in Figure 11c. This circuit uses a Texas Instruments TIL-64 phototransistor and a pull up resistor to provide a negative going pulse when the transistor turns on. This circuit is very sensitive to light emitted from the spark and functions quite reproducibly when placed in close physical proximity to the spark itself. Since the spark resides within the GC oven, and the phototransistor does not function properly above 80 °C, two lenses were used to focus the spark image onto the phototransistor which was mounted on a water cooled plate placed between the inner and outer walls of the oven. This arrangement provides a stable, negative going pulse from +5 V to within +.2 V. The primary problem with this detector is the fall time of typically 1.5 μ s. This then necessitates missing the first 1.5 μ s after the spark has fired. It was found, however, that this was not a significant problem in this work since the best signal-to-noise ratios occur after the high initial continuum emission has died down. An attempt was made to find the phototransistor with the smallest fall time relative to the photodiode. This produced a transistor with a fall time of less than 1 μs , and this one was then used.

F. Interface

The computer used in this work is a PDP 8/e minicomputer with 16K of core memory, an extended arithmetic element and real time clock. The PDP 8/e is equipped with a KA8-E positive I/O Bus interface card (119) which converts the PDP 8/e internal OMNIBUS signals to PDP 8/I and PDP 8/L type bus signals for compatability with PDP 8/I or PDP 8/L peripherals in addition to transferring the internal PDP 8/e OMNIBUS signals to the external bus. The external bus is daisy-chained to the Sykes dual floppy disk, Heath interface buffer box, and a driver-transmitter to pass signals to the equipment in a laboratory on a different floor from the computer.

The interface circuitry built specifically for this work provides the hardware link between the instrument and the computer. Programmed I/O provides the software link. When an octal 6 is indicated in the first digit of a four digit octal code inserted into the assembly language portion of the program, an I/O instruction is indicated. Digits 2 and 3 of the four digit octal code indicate which particular device is to be activated. This is called a device selector. The last digit indicates which IOP will be generated. The combination of the correct device selector and IOP will cause the proper electronic signals to be generated by the interface circuitry to elicit the required response. The interface circuitry for this

instrument was designed to control the various functions of data acquisition, timing, and movement of a GCA Mc-Pherson EU-701E monochromator. The circuit diagrams for the interface are shown in Appendix B. A brief discussion of the interface commands follow.

The analog data are converted to digital data by the ADC which is controlled by an interface instruction set of 3 instructions. These instructions are listed in Table 1. The 6441 command causes the computer to skip the next instruction in the program if the ADC has not finished the conversion of the analog signal to a digital data point and another spark has already fired. This is used to indicate how many sparks have not been used. It also gives an indication of the stability and regularity of the spark. The 6452 command causes the data from the ADC to be gated to the computer. The 6451 command causes the ADC status flag to be cleared. These instructions inserted into the program SKADC (Appendix A) allow for the transfer of data from the experiment to the computer for storage and analysis.

The timing circuitry is set by the rotary switches on the front panel of the supporting electronics cabinet or can be set under computer control through the use of the program SKSET (Appendix A). There are two instructions which control the operation of setting the counters. These instructions are listed in Table 1. TDEL sets the

Table 1. Computer Command Set for the Spark System.

ADC Commands

6441:SKPAD-skip on enabled ADC flag

6451:CLRFT-clear ADC flag

6452:DRIVE-input digital output from ADC to computer

Timing Commands

6442:TDEL-set delay counters

6444:TINT-set integrate counters

Monochromator Commands

6431:STEPS-step the monochromator 6432:UP-enable the direction flag 6434:DOWN-clear the direction flag 6461:ENCOD-skip on positive encoder flag 6464:CLREN-clear the encoder flag proper delay time and TINT sets the proper integrate times.

The monochromator is controlled by an instruction set of 5 commands when only the scan function of the monochromator is used. The five commands are listed in Table The 6431 command causes the monochromator to move one ٦. step in the proper direction. The 6432 command is defined as UP and causes the flip-flop controlling the direction to be enabled indicating a movement to a higher wavelength. The 6434 instruction causes the direction flip-flop to be cleared indicating movement to a lower wavelength. The 6461 instruction is called ENCOD and causes the next instruction in the program to be skipped if the encoder flag has been enabled. The 6464 command clears the encoder flag to allow it to be enabled on the next monochromator step.

CHAPTER V

SOFTWARE

Recent developments in integrated circuit technology have made computers affordable for many everyday applications. The analytical laboratory is no exception to this phenomenon. Many modern instruments are microprocessor or computer controlled to afford the analyst ease in control of mechanical operations, in actual data acquisition and in data analysis. The modern trend in instrumentation is towards total automation accomplished through a complex arrangement of both hardware and software. In many cases, the software greatly enhances the hardware system. This is particularly true of systems in a research laboratory which may undergo complete design changes during the course of the study. One would usually obtain savings in both time and money if the software can be used to implement these modifications.

The spark emission gas chromatographic system generates data at a rapid rate. This requires the use of a fast data analysis and acquisition system. The data acquisition hardware system has been described previously (Chapter IV) and this chapter discusses the software associated with the system, although, it should be noted that when a computer is unavailable, data can be taken with a strip

chart recorder and analyzed in the usual manner. The software system was designed for maximum computer control and minimum human intervention.

A. Choice of a Programming Language

The choice of a computer language is a difficult one since there are many different languages available to the programmer. The most logical way to approach the choice is to decide in the beginning what types of tasks need to be accomplished by the computer and then find a language which can be operated on your specific computer system and which accomplishes these tasks with a minimum of expended energy and resources.

This application required a language which could accomplish both high level tasks, such as data analysis, and low level tasks, such as stepper motor movement. This required a language which accomplished high level tasks with a minimum of assembly language programming and an easy to use assembly language for the other tasks needed. The computer available for this work is a PDP-8E minicomputer with 16K of core memory, an RK05 cartridge disk and dual floppy disks for mass storage. This computer used with an OS/8 operating system allows programming in several languages, but it was felt that a high level language such as FORTRAN II, FORTRAN IV, or BASIC would provide the most flexibility. BASIC, although it is a very popular hobbiest language, was not considered due to the unfamiliarity of the author with the operation of the BASIC compiler and the difficulty in doing I/O in BASIC. That left FOR-TRAN II or FORTRAN IV, FORTRAN II with the SABR assembly language seemed to be an obvious choice since it affords the programmer the opportunity to use standard functions such as natural log and square root without any further programming and yet, still include assembly language code when necessary.

The initial data acquisition programs for the spark emission detector system were written in FORTRAN II/ SABR. The ease of insertion of assembly level code was a distinct advantage. However, with FORTRAN II the user is allowed to open only one device independent file at a time and, for applications such as multielement chromatographic data, more than one file would be desirable. The other commonly touted disadvantages, such as limited integer values and slow multiplication and division due to not using the extended arithmetic element (EAE), can generally be overcome by proper programming. FORTRAN IV on the other hand allows the user to open multiple (up to 4) device independent files simultaneously, uses the EAE, allows integers up to + or - 4096, which is twice as big as FORTRAN II allows, accepts logical variables and uses the overlay structure to expand core space. The main disadvantage of OS/8 FORTRAN IV is the inconvenience associated with inserting assembly language

code into a program. This inconvenience was outweighed by the other advantages, and FORTRAN IV was chosen. Although FORTRAN IV was used in this application, it is not necessarily the best language possible for all applications. The programmer must evaluate his own programming needs and decide for that particular application which language is the best, since one language may accomplish some tasks easier and make other tasks far more difficult.

B. Overview of FORTRAN IV

The OS/8 FORTRAN IV system functions through the use of the FORTRAN IV compiler, RALF assembler, FORTRAN loader and FORTRAN run time system (120). A user's main program and all subprograms are compiled independently by the FORTRAN IV compiler. The compiler translates each FORTRAN statement into Relocatable Assembly Language, Floating-Point or RALF code through the use of a three pass compiler. The RALF output produced is then translated by the RALF assembler into a series of relocatable binary codes for each individual program. The FORTRAN loader then links the individual RALF modules together into a loader image file containing the relocatable main program linked with the relocatable versions of each subprogram. The loader image file is then an executable program with no need for additional assembly or compilation. This loader image file can then be executed at

anytime by using the FORTRAN Run Time System or FRTS. The run-time system allows device independent I/O at run time. The FORTRAN IV system allows easy program revision and rapid execution of programs desired.

C. FORTRAN IV Overlay Structure

The overlay structure operates by maintaining a small main program, all assembly language programs, library subroutines and all common areas in core at all times with all other programs to be used stored on mass storage devices. The main core resident program functions as a controller to call up the other programs as needed. When another program is called by the main program, it is then swapped into core, where it operates and stores any necessary values. After the program has completed its function, the next program called by the main program can then be swapped into the same core position that was occupied by the last program, thus saving the core space that would normally be occupied by all but one of the subprograms called by the main program. This system works most efficiently when subprograms are written to occupy approximately the same amount of space in core, since the most core space needed at run time will be the amount needed by the longest subprogram. It also functions most efficiently when very little is kept in common since all common areas always remain core resident. The overlaying

structure employs maximum core usage to permit operation of very large computer programs on minicomputers.

D. Software System Description

The software for control of the Spark Emission Gas Chromatographic System is written into two main overlay systems. This was necessary since large quantities of data must be stored rapidly. The speed requirements eliminated the possibility of transferring every data point directly to mass storage, and this created a large block of data stored in the common area of core. Since this large block of core was occupied, there was less space left into which other programs could be swapped. The FORTRAN IV plotting package, which is patterned after the DEC plotting package, occupies more core than available when all the common areas and assembly level programs are also core resident. For these reasons, the data acquisition programs and data analysis programs were separated into two main overlay systems: the data acquisition overlay and the data analysis overlay.

E. Data Acquisition Overlay

1. General Description

The design of the data acquisition overlay is shown in Figure 12 Level 0 contains any programs which must always



Figure 12. Data acquisition overlay.

•

remain core resident. These include the main data acquisition program, (SKMNDT), any FORTRAN IV library programs that are needed for program operation (FORLIB), and assembly language programs to control setting delay and integrate times (SKSET), analog to digital conversion (SKADC), real time clock functions (CLOCK), movement of the monochromator (SKUP,SKDOWN) and ringing of the bell (SKBELL). Level 0 also contains all areas designated as common. In this series of routines, all emission intensity data taken from the Spark System are temporarily stored in common and later transferred to a mass storage device. This was done to accommodate the time restrictions on taking multiple element data in real time.

Level 0 can make calls to and receive calls from any other level, but levels other than 0 can only call programs below them and in the same vertical overlay. Since level 0 is always maintained core resident, the programs it holds were purposely held as small as possible. For this reason when it was found that the encoder on the monochromator could not be used to control movement under the slew option, the slew programs were removed from the overlay.

The first vertical overlay shown in Figure 12 is called SKPARM which allows one to set all experimental parameters for any programs needed in a gas chromatographic run. The second overlay SKLNFD is used to find the maximum

emission line intensity for each element of interest and also controls the actual operation of the monochromator. The third overlay scheme is called SKDATA since it actually controls the transfer of analog information to the computer. The final overlay called SKSTOR stores the data obtained for each individual element in the proper file for later analysis.

A flow diagram for the data taking portion of the Chromatographic programs is shown in Figure 13. The flow diagram illustrates the basic order of functions throughout this overlay.

This series of programs is normally put into a LOAD module which can then be executed by the FORTRAN run-time system (FRTS). This load module is stored on a mass storage device and can be called and executed anytime by the run time system. The load module for this set of programs can be generated by compiling each program to get a relocatable file and then typing the following series of commands at the computer terminal:

```
.R LOAD
*SKMNDT.LD,SKMNDT.MP SKMNDT, CLOCK, SKSET, SKADC, SKUP/C
*SKDOWN,SKBELL/O
*<SKDATA
*<SKLNFD
*<SKSTOR
*<SKSTOR
*<SKSEDA,SKSCNR
*<SKORD, SKSNAD/O
*
```

The load module can also be created by typing the



Figure 13. Flow diagram of data acquisition overlay.

BATCH stream command from the keyboard:

SUBMIT SYS: SKMNDT

Once the load module has been created, it can be executed at any time by the following commands to the FORTRAN run time system:

. I	R FRTS		
¥	SKMNDT.	LD	
¥	SKOUT1.	DA	/5
¥	SKOUT2.	DA	16
¥	SKOUT3.	DA	/7
¥	SKOUT4.	DA	/8
¥	\$		

This sequence executes the data acquisition portion of the control routines and assigns the data to be output and permanently stored in SKOUT files on the device specified as the default device (DSK). There may be anywhere from one to four specified output files; the number of output files is dependent on the number of elements one is trying to look at simultaneously. In the case illustrated, the data for each of four elements would be stored in four independent files for later analysis. This device independent I/O feature of FORTRAN IV allows the user an easy way of looking at selected portions of data. In this case the file containing only element one can be viewed, regardless of the other elements.

The data acquisition overlay is controlled by the main program SKMNDT (Appendix A). This program consists

of a series of calls to the subprograms listed in level one. The subprograms of level one will be discussed briefly in the following section.

2. Parameter Input Overlay.

Each individual vertical overlay is a series of programs written to fulfill a particular function. The first of the overlays contains only one program since the program SKPARM calls no other subprograms. This subroutine can be called by inserting the command:

CALL SKPARM (NEL,CAL,DELY,AINT,TMINUT, ELMNT,HEADR)

into a program. This program queries the operator at the beginning of a chromatogram for all operating parameters and then transfers these values to other subprograms through the main program. Program SKPARM asks for the number of elements to be looked at (NEL), the symbols for these elements (ELMNT), the present location of the monochromator (CAL), the desired delay time for each element of interest (DELY), the desired integrate time for each element of interest, (AINT) the amount of time in minutes to take chromatographic data (TMINUT) and the title of the experiment with experimental conditions (HEADR). The inclusion of this program allows the analyst to set all experimental variables initially and then be free until the end of the chromatogram to prepare solutions or other samples while the computer monitors the progress of the current chromatographic separation.

3. Line Finding Overlay

The second overlay in the data acquisition section is involved with the control and movement of a GCA McPherson EU-701 monochromator. The program in level one of this overlay called SKLNFD makes calls to three other FORTRAN programs beneath it in the overlay. The subroutine SKLNFD can be called by inserting:

CALL SKLNFD (NEL, CAL, ELMNT, NGO)

into the main program. This program uses the number of elements (NEL), the present wavelength of the monochromator (CAL), the array of symbols of the elements to be looked at (ELMNT) obtained from the subroutine SKPARM to perform the calculations necessary. For each element that the user specifies, SKLNFD moves near to the strongest line, and then begins slowly scanning while taking emission data until the wavelength of maximum emission is found. Once the maximum emission line for each element is found, the elements are ordered from smallest wavelength to highest wavelength, and the wavelength separation between elements found. The separation needed to move from one element to the next is stored in an array called NGO which is returned to the main program. SKLNFD completes the operation by moving to the location of the element with the smallest wavelength in anticipation for the beginning of the data acquisition functions.

The main program in the line finding overlay (SKLNFD) makes calls to several other FORTRAN subprograms; SKSCNR, SKSNAD, SKORD and several assembly level programs: SKSCUP, SKDOWN, SKSET, SKADC. These other programs complete specific operations upon command and will be discussed briefly.

The subprogram SKSCNR is a FORTRAN program which controls actual movement of the GCA McPherson EU-701 monochromator. SKSCNR is called from SKLNFD by the command:

CALL SCNR (ISTEP, IDIR)

ISTEP is the number of steps calculated for movement of the monochromator from the present position to the position of the element of interest and IDIR is the direction it must move. SKSCNR checks if ISTEP is greater than 4096 and if it is, divides ISTEP by 4096 as many times as possible and returns the remainder. A call is then made to the RALPH routine, SKUP or SKDOWN, depending on the direction of the desired movement. The calls to these programs are made by inserting one of these commands:

CALL SKUP(STEP,CAL,CALZR) CALL SKDOWN(STEP,CAL,CALZR) STEP is the remainder of steps after dividing by 4096. CAL is the number of 4096 loops to be done, and CALZR is an indicator of whether the number of steps is greater or less than 4096.

The programs SKUP and SKDOWN allow the monochromator to scan at approximately 200 Hertz. The scan rate is not regular since the encoder pulses are irregular and subject to a great deal of noise. Even after hardware modifications, as discussed earlier, special programming features were needed. It was found that occasionally the encoder would not produce a pulse. This happened most often on initial start up. The program was designed to wait 16 ms in addition to the initial 5 ms wait and then direct the monochromator to step again until an encoder pulse was detected. This method was reproducible to within ±0.1 A, generally. The monochromator controller made by GCA McPherson also periodically misses one step and then catches up. This is probably due to the method of operation of the encoder itself. At this point it should be mentioned that using the computer clock without the encoder gave results within ± 0.3 Å, but since the initial plan was to control both slew and scan functions, extra time was spent trying to interface the monochromator correctly.

Since the initial plan was that the monochromator move rapidly from one wavelength to the next wavelength,

the slew function was also investigated. The slew functions can be run with the programs SKSLEW and SLWTO (Appendix A), but the movement is always inaccurate. Once the slew motors were directed to step, if they had been up to full speed, they continued to move 15-20 steps $(1.5-2 \text{ \AA})$ before actually stopping. At less than full speed, due to short slew durations, the movement after being directed to stop was less. The problems with the slew function probably arise due to the inability of the electronics to keep count of the rapidly occurring encoder pulses. For the slew portion to operate properly, a hardware as opposed to a software counting system is needed. The slew function on the monochromator is not being used at the present time because with the continuous movement from one wavelength to the next and with only software counting available, the great amount of error in the wavelength setting would quickly give erroneous results.

The program SKSNAD provides the actual "line finding" of the overlay. This program is called by:

CALL SNADC (ISTEP, IDIR, WAVEL, ELEMENT)

This program uses SKSCTO to move the monochromator, in addition to SKSET and SKADC which will be discussed with the next overlay. SKSNAD slowly moves the monochromator while taking emission data. Once the vicinity near the strongest line has been scanned, the data are evaluated,

and the strongest emission wavelength for that particular element is stored and returned to SKLNFD as a single element in an array called ELMENT.

The other program called by SKLNFD is SKORD and can be called by:

CALL SKORD (NEL, ELMENT)

SKORD simply orders all the elements of interest from the lowest wavelength to the highest. This is done to allow for the most efficient movement of the monochromator during data taking since it will move continuously forward while taking data and then do a single reverse move to get back to the starting element.

4. Analog to Digital Acquisition Overlay

The data taking overlay consists of a main program called SKDATA which makes calls to two FORTRAN programs (SKSEDA,SKSCNR) and five RALPH programs (SKSET, SKADC, SKUP, SKDOWN, SKBELL).

SKDATA can be called by inserting:

CALL SKDATA (NEL, DELY, AINT, TMINUT, NGO, ITHRU)

into the main program. The number of elements (NEL), the array of delay times (DELY), the array of integrate times (AINT), the total time in minutes to take data (TMINUT), and the array of the number of steps to go between elements (NGO) are passed to SKDATA from the main program, and SKDATA returns the total number of data points that were taken (ITHRU). SKDATA controls timing for the data taking operation in addition to actual operation of the analog-to-digital convertor (ADC). SKDATA adjusts the length of time between data points depending on the number of elements to be scanned. This program also arranges for the movement of the monochromator to the proper wavelength for each element of interest.

SKDATA makes calls to SKSCNR and SKSCTO to move the monochromator. These programs were previously discussed in Section 3 of this chapter and will not be covered again. Calls are also made to SKSEDA, SKADC and SKSET. SKSEDA is a FORTRAN IV routine which controls calls to the assembly level routines, SKADC and SKSET. This series of three programs make up the actual data taking module of this system.

The program SKSEDA serves as the main program in the data taking module. It can be called by inserting:

CALL SKSEDA (TI, DELAY, AINTG, ITHRU)

into another calling program. The argument TI serves as a time counter and directs that data points be taken after the monochromator has moved to the correct position for a given element. The arguments DELAY and AINTG are the delay and integrate times for the particular element that is being observed, and the argument ITHRU keeps track of the number of data points that have been done. The program SKSEDA first arranges for the delay and integrate times to be set by the computer by:

CALL SETIT (DELAY, AINTG)

SETIT uses two operational definitions TDEL (6442) and TINT (6444) to set the delay time and integrate time. The prope values to be set are passed to the assembly language program SETIT from SKSEDA and the proper times are set when the computer implements the proper operational definition.

After the times have been set, the time is checked with:

CALL TIME (SEC)

This call checks the time from the computer real time clock and returns the time elapsed from the last call CLTIME (X) in seconds. CALL CLTIME (X) essentially sets the clock at zero seconds; this is done in the program SKMNDT and serves as the official beginning of the chromatogram. Once the monochromator has stopped moving and the proper amount of time has passed, a data point is taken by inserting:

CALL ADC (ARRAY, NUMAV, NUMDP, MISS)

The program SKADC is a modified version of a program

written by Johnson (121). The arguments NUMAV and NUMDP are passed to SKADC from SKSEDA. NUMAV represents the number of sparks that are averaged to be called one data point and NUMDP represents the number of data points one wishes to take. In a typical chromatogram, NUMAV would be about 1000 and NUMDP would be one. NUMAV equal to 1000 was chosen to insure the following: 1) there would be a statistical sampling of sparks, 2), the time had not changed significantly over the course of data collection and 3) there would be enough time to move the monochromator setting to the next wavelength. The arguments ARRAY and MISS are returned from SKADC to the FORTRAN IV routine SKSEDA. ARRAY contains the array of data values that were taken for the entire chromatogram. These values are stored in FIELD1 common section of core memory for later retrieval. The MISS parameter returns the number of times that the spark fired, but the ADC was not ready to take data. The program SKADC uses three operational definitions: SKPAD (6441), DRIVE (6452) and CLRFG (6451). SKPAD is used to check if the spark has fired, but the ADC was not ready to accept data. DRIVE is used to drive data into the accumulator and CLREFG clears the ADC status flag. This program proved to be very versatile since it allows easy averaging and storage of data points.

5. Data Storage Overlay

The data storage overlay consists of a single program entitled SKSTOR. SKSTOR is a FORTRAN program which separates all intensity data taken into the proper files, transfers correct time data and annotates the files with appropriate identifying remarks. This file can be called by inserting:

CALL SKSTOR (NEL, ITHRU, HEADR, ELMNT, DELY, AINT)

into a calling routine. The argument NEL is the number of elements looked at, ITHRU is the total number of data points stored in COMMON, HEADR is the experiment title, ELMNT is an array containing the symbols of the element being looked at and finally, DELY and AINT are arrays containing the delay and integrate time for each element. After SKSTOR has been executed, there exists NEL files on the disk. Each file contains all pertinent information about a given element. These files are formatted for later evaluation by SKMNAN. After the storage of all data from the current shromatogram, a program to ring the computer terminal bell is called from the main program. The command CALL SKBELL causes the bell to sound to call the operator back to the terminal in preparation for either data analysis or further data acquisition.

F. Data Analysis Overlay

1. General Description

The analysis portion of the chromatographic system is accomplished by a second main overlay system. The design of this system is shown in Figure 14. Level Ø of this overlay contains only the main analysis program, FORTRAN library programs (FORLIB) and any common values. The first overlay of this system is SKSMTH which smooths the data for plotting purposes. The second overlay is SKTPLT which plots all data on a Tektronix 4006-1 graphics terminal. This overlay includes provisions for the user to interact with the cursor on the plotting surface. The third overlay finds the area of all peaks of the chromatogram, and the fourth overlay lists the areas of all the peaks in addition to any other relevant information about that particular chromatogram. This system provides the user with a convenient method of area determination and report production.

A flow diagram of the entire data analysis software package is shown in Figure 15. This diagram illustrates the basic movement through the system.

The series of programs in the data analysis package is normally put into a load module or core image file which can be executed at any time by the FORTRAN run-time system. The load module for this set of programs can be







Figure 15. Flow diagram of data analysis overlay.

generated by compiling each individual program and then typing the following series of commands on the computer terminal.

```
.R LOAD

*<SKMNAN. LD, SKMNAN.MP SKMNAN /0

*<SKTPLT

*<SKSMTH

*<SKAREA

*<SKLIST /0

*<SKTPOS, SKTAXS, SKTPL, SKTPNT /0

* $
```

The load module can also be created by typing the BATCH stream command:

SUBMIT SYS : SKMNDT

Once the load module has been created, it can be executed with the following commands:

```
.R FRTS
*<SKMNAN. LD
*<SKIN. DA /5
*<SKOUT. DA /6
* $
```

The sequence executes the data analysis portion of the control routines. The input file SKIN.DA is read from a mass storage device, and the final calculated data are permanently stored in a file called SKOUT.DA. This produces full chromatographic analysis for each element independently.

The data analysis overlay is controlled by the main program called SKMNDA (Appendix A). This program consists primarily of calls to various subroutines in level 1. These subroutines are discussed briefly in the following section. The main program also arranges that the data file be read from the mass storage device. The data are stored in a position in common and other pertinent information is made available to the main program for later use by other subroutines in the overlay.

2. Data Smooth Overlay

The first vertical overlay in this series of programs deals with smoothing the raw data for plotting purposes. This program is entitled SKSMTH and can be called by inserting

CALL SKSMTH (ITHRU)

into the calling program. The argument ITHRU is the total number of points contained in the file being analyzed. The smoothing routine is suited for a 5, 9 or 15 point least squares smooth-over all the experimental data. This smoothing routine is based on work by Savitzky and Golay (122). A Savitzky-Golay smooth requires the averaging of points on either side of the point to be smoothed. Since chromatographic data files may be up to 1500 points in length, storing all 1500 raw data points and 1500 smoothed data points was impossible. Since it was necessary to have enough raw data points available to smooth a particular point, the space limitation required a unique solution to this problem.

The smoothing routine involves the use of a "running smooth". The "running smooth" required the use of a second array of only 15 points instead of a second array equivalent in length to the first array. This is because the Savitzky-Golay smooth requires, in the case of a 15 point smooth, seven unsmoothed data points on either side of the point to be smoothed. This means that not all points, specifically the first and last seven, can be smoothed. For the case of a 15 point smooth, this program operates by storing the first seven points in a second array and using these values to find the smoothed values for the next eight points. A problem arises since the unsmoothed data points in addition to the smoothed points are needed. The first seven points are then written into the first seven positions of the original array. The next seven smoothed values are then written into the first seven positions of the second array. On the next time through the first seven smoothed values are written into the original array, and the new smoothed values are moved from the last seven . to the first seven positions of the second array. This switch allows the original data values to be used for any points needed and when they are no longer of use to be written over by smoothed values. This switching continues through to the last seven points which are simply
stored unsmoothed in the original array. At the end of the smoothing routine, an array of smoothed data points is located where the unsmoothed had previously been. The original data have not been lost since they were previously stored on a mass storage device, and the user can now use the smoothed data for plotting purposes, but does not have to store another file of smoothed data unless it is needed. The user has the option of picking the smooth best suited to maintaining peak integrity while providing the most noise free chromatograms for plotting.

3. Plotting and Interactive Overlay

The second vertical overlay consists of a main FORTRAN IV program entitled SKTPLT which makes calls to four other FORTRAN IV routines that control the plotting functions of the Tektronix 4006-1 plotting terminal. The plotting and interactive overlay can be called by inserting:

CALL SKTPLT (NPEAK, ITHRU, NEL, TMIN)

into the calling routine. The argument NPEAK is the total number of peaks to be integrated and is passed from the plotting package to the area determining routine. The arguments ITHRU, NEL and TMIN are passed to the plotting routine from the data acquisition overlay by way of SKMNAN. These arguments represent respectively, the total number of data points in the file, the number of elements that were looked at during that run and the time of taking of the first data point for this specific data set.

This program functions by first plotting every fifth point of the entire data array and informs the user of the maximum and minimum intensity and time values. The user then has the option of expanding to full screen any given portion of the chromatogram by simply stating the initial and final points to plot. This expansion then puts the user into the interactive mode. The interactive mode allows the user direct control of the cursor on the Tektronix screen. The controls available to the user are:

CARRIAGE RETURN	Move l step Set for reverse direction
'F'	Set for forward direction
'S'	Stop and go back to main program
' A '	Add the next number typed to the
	initial time and plot that point
' N '	Do another expansion
'P'	Type total number of peaks to integrate
'1''21'	Set as a permanent index

While in the interactive mode, the user can step from point to point and decide on where the peak begins and ends in addition to determining retention time for the peak. These positions are then stored by using the permanent indices, for example index 1 would be the beginning of peak one, index 2 would be the retention time for peak one and index 3 would be the end of peak one, etc. After the user has completed expanding each section in addition to assigning indices, 'P' would be hit on the

keyboard and the user enters the total number of peaks to integrate. This then transfers the indices and data to the area determination program.

This program uses a FORTRAN IV plotting package developed by Joseph (123) from Digital Equipment Corp. plotting routines. The subroutines used are SKTAXS, to plot the axes; SKTPOS, to enter labels within the axes to maintain the largest plotting field possible; SKTPNT, to scale data to fit within the plotting surface; and SKTPL, to actually plot data.

4. Area Determination Overlay

The area determination overlay consists of a single FORTRAN IV program called SKAREA. SKAREA is called from the main routine by inserting:

CALL SKAREA (NPEAK, RESULT, RETIME, NEL, TIMIN, XCOUN)

into the calling routine. The arguments passed to SKAREA are the number of peaks to integrate (NPEAK), the number of elements evaluated during that particular run (NEL), the time of the first data point (TMIN) and the frequency in seconds for data taking (XCOUN). SKAREA returns an array which contains the area of each individual peak (RESULT) and an array which contains the retention time for each individual peak (RETIME).

The area of each individual peak is determined by

first matching the real unsmoothed data points with the corresponding indices. The intensity values are added and multiplied by the time interval for the area determination. Base line correction is accomplished by subtracting the area of the trapezoid formed under the curve. The retention time for each peak is determined by using the computer real time clock with the corresponding index determined for the maximum peak intensity.

5. Report Generation Overlay

The final output of the gas chromatographic data is produced on a line printer in the form shown in Figure 16, and also stored on a permanent file on a mass storage device. The program that accomplishes this is called by inserting:

CALL SKLIST, (NPEAK, RESULT, RETIME, HEADR, EL, DELY, AINT, XCOUN, TMIN, ITHRU)

The arguments are all passed to SKLIST from other portions of the data taking or data analysis routines and have been discussed previously.

After this series of programs has been completed for each element in the chromatogram, the area and retention time for each peak are stored and can later be compared to replicate runs with SKEROR. METHANOL, NITROMETHANE AND CHLOROFORM ON PORAPAK Q 50 ml/min, 150 c isothermal

MICROSEC		
1.8	(W I W)	
INTEGRATION TIME=	RETENTION TIME	2 2 9 4 3 2 4 3 2
Ø.1 MICROSEC	PEAK AREA	26. 32 25. 22 26. 82
C DELAY TIME=	FEAK NUMBER	ન ભ ભ

Figure 16. Sample output from SKLIST.

G. Error Analysis Overlay

This overlay consists of a single independent program (SKEROR). The flow diagram is shown in Figure 17. The function of this program is to read three replicate gas chromatograms and return the average area and relative standard deviation in addition to the average retention time and relative standard deviation. These values are then listed on a file in the format shown in Figure 18 as the complete analysis for a given element. This program can be executed by the following series of commands:

.R LOAD
* SKEROR.LD, SKEROR.MP<SKEROR
* \$
.R FRTS
* SKEROR.LD
*SKIN1.DA /5
* SKIN2.DA /6
* SKIN3.DA /7
* SKOUT.DA</8
* \$</pre>

The final report is stored in the file called SKOUT and SKIN1, SKIN2, and SKIN3 are the input chromatograms to be analyzed.

The three overlays, data acquisition, data analysis and error analysis serve as a series of modules used for control and analysis of any chromatographic data taken. While this is not a completely automated system, it does function as an efficient means for acquiring and analyzing the large amount of data generated by a spark fired at about 4000 Hertz.



Figure 17. Flow diagram of error analysis overlay.

METHANOL,	IN	rkom	IE T H	ANE	AND	CHLOROFO	КM
82-60-5							
CARBOWAX,	150	ۍ	NO	CARE	NO:	LINE	

PEAK NUMBER	FEA	К АКЕА	RETENTI	ON TIMECMIN)
*************	*********			*******
	26	ଅ ମ		2.4
त्त	25	. 44		4
	25	. 78		4
ĤVG	25, 85	ĝ. 44	의 4	G. G
**************	***********			***********
	5	2		1è. ë
ŝ	21	9 4 .		18.8
	25	. 60		1ĕ. 8
AVG	24.17	2.78	1.ë. ë	6. G
***************	***********	******	******	**********
	26	. 82		1.9.8
m	25	. 72		19.0
	22	. 91		19. B
AVG	26.82	1.09	19. Å	6. 6

Figure 18. Sample output from SKEROR.

CHAPTER VI

THE SPARK AS A SELECTIVE G.C. DETECTOR

The miniature nanosecond spark has proven to be a sensitive method for the determination of various elements (124,125). The work of Lantz (8) has shown that the miniature nanosecond spark is a viable detector for gas chromatographic column effluents. The emphasis of this work was to design a stabilized SED which maintained a constant breakdown voltage, regardless of the column effluent entering the spark gap. The design and characteristics of the SED have been previously discussed (Chapter III). This chapter deals with the characteristics of the spark in operation as a chromatographic detector. The maximum time of emission, detection limit and linearity of each element that can be detected by the SED is discussed in this chapter.

A. Overview of SED Performance

The SED used in this work is an emission type detector. The column effluent enters the spark gap where it is atomized and excited. The optical emission from a particular element is monitored with the PMT and data acquisition instrumentation described previously (Chapter IV). A summary of the elements which are investigated

in this work are given in Table 2. The wavelength of the atomic emission line at which the maximum emission signalto-noise ratio is obtained for each element is also listed in Table 2. These elements were investigated because of their chromatographic significance; however, these are not the only elements that can be observed. The work of Zynger (101,124,125) and Seng (118) show the feasibility of detection of various metals. Thus, the SED should also be useful for the chromatographic detection of various organometallic compounds.

The detection limit and dynamic range for each element listed in Table 2 are discussed in subsequent portions of this dissertation. The detection limit for each element was determined by preparing a series of solutions differing by factors of ten in concentration, injecting 1 ul of each solution in the series and monitoring the signal until the signal was not greater than two times the noise. The concentration in grams that produced the final signal was divided by the average peak width for that peak in seconds, as determined by the average of 5 injections, to produce the detection limit in grams/second. The detection limit is reported in this manner since the sample is not introduced as an impulse function, but rather is spread out over a period of time. The solutions used in detection limit and linearity studies are given in Table 3. The reagents

Element	Wavelength(Å)	
Boron	2497.7	
Bromine	4477.8	
Carbon	2478.6	
Hydrogen	4861.3	
Iodine	2062.4	
Nitrogen	4110.0	
Oxygen	7771.9	
Phosphorus	2535.7	
Silicon	2516.1	
Sulfur	2168.9	

Table 2. Wavelengths of Elements Detected with SED.

Element	Compound	Solvent
Boron	ether borofluoride	cci4
Bromine	ethyl bromide	CH ₃ NO ₂
Carbon	n-propanol	H ₂ 0
Hydrogen	n-heptane	CCl4
Iodine	iodomethane	CH ₃ NO ₂
Nitrogen	acetonitrile	DMSO
Oxygen	n-propanol	n-propanol
Phosphorus	triethylphosphite	DMSO
Silicon	tetramethyl silane	Benzene
Sulfur	carbon disulfide	Benzene

Table	3.	Solutions	used for	determination	of	detection
		limit and	linear r	ange.		

are AR grade and used in most cases without further purification.

Typical operating parameters for routine use of the SED are given in Table 4. These conditions provide the most stable spark. The effects of changes in parameters can be seen visually by changes in spark wander, or heard by variations in the audible signal produced by spark firing. Changes can also be seen by variations in emission signal reproducibility and intensity.

B. Effects of Gas Flow Rates on the SED

The SED requires three separate gas flows: control gas, column mobile phase and sheath gas. The control gas is used to maintain a pure argon atmosphere. Accurate adjustment of the control gas is required since improper adjustment will extinguish the spark entirely or cause erratic firing. The control gas can also be used to adjust the firing frequency, by as much as 20%, with faster flow rates producing slower firing rates. The sheath gas is used to contain the spark channel and prevent spark channel movement due to convection within the spark chamber. Over the range 0.8 ℓ/min to 2.5 ℓ/min , the sheath gas visibly stabilizes the spark. At higher flow rates, the spark does not always form between the electrodes, but instead jump around in the chamber due to the large amount of argon present.

DC Volts	4 kV
DC Amps	2.8 mA
Flow Rates	
Control	200 ml/min
Sample	25-50 ml/min
Sheath	l l/min
Gap Distances	
Control	4.6 mm
Analytical	2.0 mm
Monochromator Slit Width	75 µm
Temperatures	
Injection Port	variable
Column	variable

Table 4. Typical Operating Parameters of the SED.

The analytical gas flow rate can be adjusted from 10 ml/min to 0.9 l/min to give a stable spark. However, maximum signal-to-noise ratios for the Porapak Q column are obtained above 45 ml/min. The Van Deemter plot for a Porapak Q column obtained with the SED is shown in Figure 19. This illustrates that the flow requirements for the SED are compatable with the requirements for efficient separations.

C. SED Reproducibility and Stability

A good detector must yield reproducible results from one injection to the next. Figure 20 is an illustration of the typical precision obtainable for 5 consecutive 0.1 μ l injections of carbon disulfide monitored at the carbon 2478.6Å atomic emission line. The variation in both peak height and peak area is less than 2.8%.

Another necessary quality of a good detector is signal stability over long time periods. Figure 21 illustrates the overall stability of the SED. Each point on Figure 21 represents an average of 3 0.1 μ l injections of nitromethane monitored at the carbon 2478.6Å emission line. As can be seen, there is little deviation over the 160 minute time period. In order to test stability under the worst possible conditions, and also hasten the electrode coating process, the chromatographic column was replaced with an empty column and a series of five



Figure 19. VanNeemter plot for a Foranak Q column.



Figure 19. VanNeemter plot for a Foranak Q column.



Figure 20. An example of SED reproducibility.



Figure 21. Signal stability with the SED.

0.1 μ l injections for 2 different compounds was made. The average of these runs for 5 different times is displayed in Figure 22. In between each of these averages, approximately 5 μ l of different compounds were also injected. As the electrodes became coated with carbon deposits, the signals for both nitromethane and acetone decreased; however, the ratio of the two compounds to each other remained relatively constant. In a typical analysis in which an internal standard is employed, the spark should perform well regardless of the condition of the electrodes.

D. Time Resolution Studies for Elements of Interest

The data acquisition system for the SED allows for time resolution of the analyte emission signal. This was incorporated into the data acquisition system since in a spark discharge, the background emission disappears before analyte lines become well defined (126). Thus, if the time window of observation can be chosen to include the time window of maximum emission for the analyte and minimum emission for the background, maximum signalto-noise ratios can be obtained. If the maximum emission for the analyte occurs during intense background emission, the maximum signal-to-noise ratio occurs later in time since the background emission falls off more rapidly than analyte emission. The electronic timing circuitry used



in this work provides a delay after spark initiation and then controls integration for a preset time. This system is described extensively by Seng (118). Since the discharge is a transient phenomenon, there are continual changes in spark characteristics with time. Zynger (101,125) has shown that various elements have different time windows for maximum signal-to-noise ratios. For this reason, the best time window for each element was determined. These values are listed in Table 5.

Each of these values were obtained by observing the emission signal obtained for a variety of delay times and . a constant integrate time for a particular element.

Graphs of relative emission intensity for P and C vs delay time are shown in Figures 23 and 24 and are representative of the procedure followed for each element. The delay times reported are relative to spark initiation indicated by the phototransistor trigger. The best integration time for each element is found by holding the delay time constant at the optimum value and varying the integration time to obtain the maximum signal-tonoise ratio. A representative plot of P signal intensity vs integration time is shown in Figure 25.

Observation of the elements early in time generally produced the maximum signal-to-noise ratio. Integrating for too long a time period was not generally advantageous because the bulk of the emission signal is of a short

Element	Delay Time (µs)	Integrate Time (µs)
Boron	0.1	1.0
Bromine	0.1	0.5
Carbon	0.2	1.0
Hydrogen	0.1	0.4
Iodine	0.1	0.4
Nitrogen	0.1	1.0
Oxygen	0.3	1.0
Phosphorus	0.1	0.6
Silicon	0.1	1.0
Sulfur	0.2	1.0

Table 5. Optimum Delay and Integration Times.





Figure 24. A graph of signal intensity vs. delay time.



Figure 24. A graph of signal intensity vs. delay time.





duration leaving only the background emission. The delay and integration times listed in Table 5 were used for all further studies presented.

E. Carbon Response

1. Detection Limit and Dynamic Range

The primary advantage of the SED is its potential for selective detection. However, simultaneous universal detection is also useful. The carbon response of the SED provides a universal response similar to a FID or thermal conductivity detector (TCD) response. The SED carbon response is limited to a detection limit of l.l x 10^{-8} gC s^{-1} due to the background carbon signal in the argon carrier gas. The detection limit can be reduced by using 99.9999% pure argon, but this would exclude the SED from routine laboratory use due to the expense involved. The SED does not compare to other universal detectors for carbon detection since most other universal detectors use helium carrier gas which has less carbon contamination. However, the SED does compare favorably with other emission type selective detectors which are also used for carbon detection.

2. Structural Effects

The proposed mechanism of response of the SED is via complete decomposition of molecules to atoms (atomization), excitation of the atoms and emission of radiation from atoms produced by compounds entering the spark channel. For this to be true, a compound with only one carbon should give a signal one sixth as big as a six carbon compound regardless of the structure of the compounds. A variety of compounds with different types of structures were investigated for structural effects with respect to carbon. The results are shown in Table 6.

In general, there seem to be few carbon structure effects. The chain length or bond type seem to have little effect on the response except in the cases of carbon tetrachloride, chloroform, chlorobenzene, m-fluorotoluene and carbon disulfide. The low response for chlorobenzene and fluorotoluene may be due to the added stability of the benzene ring. The enhanced response due to compounds with high carbon/chlorine ratios may be due to the electron capturing ability of the chlorine atoms changing the plasma characteristics. Effects similar to these were obtained by Winsor and Denton (127) using an inductively coupled plasma (ICP) for detection of organic compounds.

Compound	Response
nitromethane	100*
methanol	97
carbon tetrachloride	164
carbon disulfide	118
acetonitrile	99
chloroform	152
formic acid	93
bromethane	100
acetone	107
2-propanol	90
2-propyn-l-ol	92
isobutyl alcohol	92
pentane	101
hexane	104
cyclohexanone	100
benzene	91
chlorobenzene	81
m-fluorotoluene	78

Table 6. Response of Carbon Containing Compounds at Carbon 2478.6A Emission Line.

 $\overset{\textbf{*}}{\textbf{l}}$ µg of carbon from nitromethane produces a response of 100.

F. Selective Detection Capabilities

Since the SED is an emission type detector, selective detection is obtained by monitoring a specific atomic emission line for the element of interest. This section reports the detection limit and dynamic range for several elements of chromatographic importance. In most cases reported, the dynamic range is limited by the amount of compound that can enter the spark before it is extinguished.

All data presented in the following sections were obtained by averaging areas obtained from three replicate chromatograms of the mixtures listed in Table 2.

1. Boron

Chromatographic analysis for boron in mixtures has not been a common method of analysis due to the lack of boron specific detectors and the small need for this type of analysis. However, with recent investigations of boron analogs of various amino acids, boron chromatographic analysis may become a useful technique. The investigations of Spielvogel (128) and coworkers on laboratory mice have shown that various boron analogs of some amino acids can be used as anticancer, antiarthritic and cholesterol lowering agents. Boron derivatives of various compounds (129-131) are also becoming more widely used. For these reasons, the boron analysis capability of the SED should

prove useful.

Boron was detected with the SED at 2497.7Å B(I) line with a 0.1 μ s delay time and a 1.0 μ s integration time. This gave a detection limit of 3.0 x 10⁻⁹ g B/s and a linear dynamic range of 3 orders of magnitude.

2. Halogens

Detection of halogens with the SED is limited to bromine at the 4477.8Å Br(I) line and iodine at the 2062.4Å I(I) emission line. Chlorine and fluorine emission are not observed since there are no emission lines in the 2000Å-9000Å range that have excitation energies less than approximately 14 eV (132). It was empirically found that this was the maximum energy that can be excited with the SED. Both bromine and iodine emission lines are observed early in time. However, the sensitivity of the SED is much greater for iodine than for bromine. The detection limit for iodine was 4.2×10^{-7} g I/s and the detection limit for bromine was 1.7×10^{-5} g Br/s. The bromine calibration curve was linear over a 2 decade concentration range and iodine over a 3 decade concentration range. A calibration curve for iodomethane in nitromethane observed at the iodine line is shown in Figure 26.





3. Hydrogen

The ability to analyze for hydrogen is of primary importance since most organic compounds contain hydrogen. Thus, it is important in empirical formula determination. The SED has the most sensitive response to the H(I) emission line at 4861.3Å. Hydrogen was observed with a 0.1 µs delay time and a 0.4 µs integration time. The detection limit for hydrogen was 2.6 x 10⁻⁶ g H/s and the dynamic range was 100.

4. Nitrogen

Selective analysis for nitrogen is useful in applications such as environmental analysis for nitrogen containing compounds like ammonia or nitrous oxides, pharmaceutical analyses for various barbituates and amino acid analysis. The SED is used for N analysis by monitoring the 4110.0Å N(I) emission line with a 0.1 s delay time and a 1.0 μ s integration time. The detection limit for N was 5.0 x 10⁻⁷ g N/s with a dynamic range of 100.

5. Oxygen

The detection of oxygen with the SED requires the use of a red sensitive PMT (R666) in order to detect emission from the O(I) emission line at 7771.9Å. The R666 PMT is less sensitive than the 1P28 by a factor of

about 40 which requires further amplification of the already weak oxygen signal. Oxygen was monitored with a delay time of 0.3 μ s and an integration time of 1.0 μ s. The SED detection limit for oxygen is 2.6 x 10⁻⁶ g 0/s with linear range of 100.

6. Phosphorus

Selective analysis for phosphorus is most useful for simplifying the complicated chromatograms obtained for organophosphate insecticides. Phosphorus emission from the SED is monitored at the P(I) 2535.7Å emission line and is the most sensitive element that the SED is useful for. A working curve for triethylphosphite in DMSO observed at the phosphorus line is shown in Figure 27. A linear range of 1 x 10^4 and a detection limit of 1 x 10^{-10} g P/s were obtained.

7. Silicon

Selective analysis for silicon is useful due to the ease of formation of silyl derivatives. Silicon detection can provide a less complicated chromatogram than that obtained with a universal detector. Silicon emission was monitored at the 2516.1Å Si(I) line. As can be seen from the calibration curve for silicon shown in Figure 28, the SED is linear over 4 orders of magnitude












for silicon. The detection limie was 6.6 x 10^{-7} g Si/s.

8. Sulfur

Sulfur analysis is useful for amino acid analysis since it can provide an easy separation between sulfur containing and non-sulfur containing amino acids. It can also be useful for simplifying complicated chromatograms obtained from various pesticide mixtures. The S(I) 2168.9Å line was used to monitor sulfur emission. The detection limit was 2.5 x 10^{-8} g S/s and the dynamic range was 1 x 10^2 .

9. Summary

The SED is chromatographically useful for at least 10 different elements. The detection limits for each of these elements are summarized in Table 7. The SED cannot compete with the FID for carbon detection or the ECD for chlorine analysis. However, it does compare favorably with detection limits obtained with other emission type detectors such as the MPD or inductively coupled plasma. The multielement advantage of this detector, however, may serve to offset lower detection limits.

Element	Detection Limit (g s ⁻¹)
Boron	3.0×10^{-9}
Bromine	1.7×10^{-5}
Carbon	1.1 x 10 ⁻⁸
Hydrogen	2.6 x 10^{-6}
Iodine	4.2×10^{-7}
Nitrogen	5.0 x 10^{-7}
Oxygen	2.6 x 10^{-6}
Phosphorus	1.0×10^{-10}
Silicon	6.6 x 10^{-9}
Sulfur	2.5×10^{-8}

Table 7. Detection Limits With the SED.

CHAPTER VII

MULTIELEMENT STUDIES

The SED is a versatile and sensitive detector for gas chromatography. However, it's greatest asset is the possibility for simultaneous multielement analysis. The SED can provide the capability of empirical formula determinations without the problems and expense associated with a gas chromatograph-mass spectrometer. This chapter discusses types of multielement detectors available in addition to examples of the SED as it is used for multielement detection.

A. Multielement Detectors

Several methods have been employed or suggested to accomplish multielement atomic emission measurements. Several review articles are available which contain extensive discussions of these methods (133-135). Multielement detectors can be classified into two basic varieties: 1) mechanical scanning and 2) array. The mechanical scanning methods involve mechanical movement of a grating or mirror past a stationary detector. Rapid scanning monochromators, programmable monochromators and filter wheels are of this type. This arrangement provides sensitive detection since the radiation transducer most often

employed is a PMT. The primary limitation involves the time necessary for scanning the required wavelength range. The second variety of multielement detectors includes various array type detectors. These systems are basically a series of discrete detectors each corresponding to a particular wavelength range. PMT arrays provide very sensitive detection, but are limited in resolution to a single wavelength per tube. Other types of arrays such as linear diode arrays or vidicon tubes are limited in resolution to the number of elements in the array and for this reason are generally applicable over a small wave-length range. In addition, they are limited in sensitivity relative to a PMT. However, these types of detectors do have the advantage of providing true simultaneous multielement or multiwavelength detection.

Each individual application that requires multielement analysis must be individually evaluated as to the type of detector needed. Sensitivity, wavelength range, resolution, the time required and cost must be significant factors in any decision. In this application a programmable monochromator was used for multielement analysis since it provides a wide wavelength range and the greatest sensitivity; however, the slow scan rate is a significant disadvantage.

B. Examples of Multielement Capabilities of the SED

It has been shown that the SED is a promising method for GC detection. This chapter demonstrates the most lucrative characteristic of the SED - the multielement capability. Several representative experimental examples are shown to demonstrate this ability.

1. Separation of TMS, Carbon Disulfide and Benzene

The separation of TMS, carbon disulfide and benzene with an SED detector is illustrated in Figure 29. The carbon response shown in Figure 29a is the same type of chromatogram obtained with a TCD. As can be seen, the carbon chromatogram contains only two peaks; however, the first peak has a shoulder indicating incomplete separation. Different chromatographic conditions can be employed to improve the separation or the SED can be used to separate the peaks. This can be seen in Figures 29b, 29c. and 29d with silicon, sulfur or hydrogen detection respectively. It can be seen that the first peak is a combination of TMS which elutes at 1 minute and carbon disulfide which elutes at 1.4 minutes. The final peak is due to the benzene. The sulfur and hydrogen modes are less sensitive than the carbon mode, producing a noiser, but nonetheless useful signal.



Figure 29. Separation of THS, carbon disulfide and benzene.

2. Separation of Methanol, 1-Propanol and 1-Butanol

An illustration of the separation of methanol, 1propanol and 1-butanol is illustrated in Figure 30 Figure 30a is the carbon signal, Figure 30b is the hydrogen signal and Figure 30c the oxygen signal obtained with the SED. Due to the low sensitivity of the SED for oxygen, a high gain is needed, producing a noisier signal when compared to the carbon signal. The mixture in Figure 30 consists of an equimolar concentration of each of the compounds. The areas for each of the three peaks are determined by averaging three replicate chromatograms and then computing the empirical formulas using methanol as an internal standard. The empirical formulas determined are listed in Table 8. From this example it can be seen that the SED is especially useful for the determination of empirical formulas of unknown compounds.

3. Separation of Ethyl Bromide, Iodomethane and Nitromethane

The chromatographic separation of ethyl bromide, iodomethane and nitromethane is listed in Figures 31a-f, in the carbon, iodine, bromine, hydrogen, oxygen and nitrogen modes respectively. The carbon chromatogram indicates only two peaks. However, upon examining the bromine and iodine chromatograms, it can be seen that the peaks



Figure 30. Separation of methanol, 1-propanol, and 1butanol.

Peak Number	С	Relative Areas H	0	Empirical Formula
1*	1.0	4.0	1.0	сн ₄ о
2	3.1	8.0	0.95	с ₃ н ₈ о
3	4.0	10.1	1.2	C ₄ H ₁₀ O

Table 8. Empirical Formula Determination with the SED.

* Methanol (Peak 1) served as the internal standard.



Figure 31. Separation of ethyl bromide, methyl iodide and nitromethane.

representing iodine and bromine containing compounds overlap. This example illustrates the usefulness of the SED for especially complicated chromatographic problems. It is highly probable that there will be many interfering peaks in a given chromatogram and the use of selective detection for many elements can uncover hidden peaks and give information as to the identity of the compound itself through the determination of the empirical formula.

4. Summary

The three chromatograms shown earlier in this section serve as examples of the advantages of the SED as a gas chromatographic detector. The SED can serve to simplify chromatographic techniques by separating compounds with the detector as opposed to the column or operating conditions, simplify chromatograms to only those compounds containing a particular element, eliminate large interfering peaks and provide empirical formulas to aid in compound identification. It can be seen that the SED can be a valuable gas chromatographic detector.

CHAPTER VIII

COMMENTARY

The overall usefulness of the SED as a gas chromatographic detector has been demonstrated in this work. The SED can be used to monitor compounds of ten nonmetallic elements with sensitivities in the microgram to nanogram range. It serves as one of the few chromatographic detectors suitable for selective determination of B and Si containing compounds. The SED is in most cases not affected by carbon chain length or bond type. However, with the present design of the SED there are some structural effects and an improvement in the sensitivity for most elements would definitely make the SED even more attractive.

The double gap design of the SED is a reasonable way to obtain controlled spark of nanosecond duration since electronically triggered spark gaps generally are of a longer duration. An increase in the power attainable by the spark would probably allow higher excitation energies and improve atomization capabilities. This would serve to improve sensitivity and reduce some structural effects. Several methods can be employed to increase the power attained by the spark. The first method would require increased size of the capacitor to allow greater charge

build-up before breakdown. However, since the dielectric is already as thin as possible, the length of the capacitor would have to be increased, which would destroy some of the compactness of the present SED design. Another method involves allowing a greater separation of the control gap; this may cause the capacitor dielectric to breakdown sooner causing an increase in the need for maintenance and repair. Another alternative is to run a different gas such as nitrogen or air in the control gap. Either of these gases would have a greater breakdown potential than This alternative may also cause early capacitor argon. breakdown in addition to requiring a larger DC power supply than is presently used. A final alternative would be to use a hefty pulsed power supply to create an overvolted spark.

Incorporation of source correction into the SED system would enhance SED response. Any source correction employed would need to be fast enough to allow correction of every spark. The source correction system described by Gall (136) which employs a pelicle beam splitter with dual channel integration would be a possible system. Since the SED system electronics have several sophisticated and expensive timing circuits to allow for variable delay and integrate times, dual channel electronics would make the SED rather expensive for routine use. However, the timing circuitry can be reduced by using the same delay and

integration times for all elements with only a small loss of signal and a large cost savings. The source corrected system would improve the precision of the SED.

The use of a programmable monochromator for simultaneous multielement chromatographic analysis is not the optimal system due to the time needed to slew between wavelengths of interest. The most practical system for routine use would employ an array of PMT's at the wavelengths of all elements of interest. If there were only a few close lying elements of interest, a silicon intensified target Vidicon tube may be of use. Maximum advantage of the multielement system can be obtained by incorporating a microcomputer or a system of microcomputers to inject samples automatically adjust chromatographic parameters, analyze data and finally, compute empirical formulas or through use of libraries of chromatograms, report the actual compounds separated.

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APPENDICES

APPENDIX A

Selected Program Listings

C	
C PROGRAM NAME: SKSPEC. F4	
C	
DIMENSION HEADR(11)	
DIMENSION XDATA(1000), TDATA(2), ARRAY(1), WL(1(WEITE(4,64))00)
60 FORMAT(' ENTER HEADING')	
$\frac{READ(4,70)}{EADR}$	
WRITE(5,70) HEADR	
WRITE(0,40)	
READ(4,50)CAL	
50 FORMAT(F10.2)	
BO FORMAT(' INITIAL WL OF SCAN(F)='.\$)	
READ(4,50) START	
WRITE(0,100) 100 FORMAT(' FINAL WI. OF SCAN=(F)'.8)	
READ(4,50)FINAL	
WRITE(0,110) 110 FORMAT(' # OF STEPS RETWEEN POINTS=(1)'. ()	
READ(4, 120) ISTEP	
129 FORMAT(16)	
139 FORMAT(' # OF DATA POINTS=(I)',\$)	
READ(4, 120) NUMAV	
141 FORMAT(' FIRST DELAY TIME=(F)',\$)	
READ(4,50) DLY1	
142 FORMAT(' FIRST INTEGRATE TIME=(F)', \$)	
READ(4,50)AINTE1	
143 FORMAT(' SECOND DELAY TIME=(F)',\$)	
READ(4,50)DLY2	
144 FORMAT(' SECOND INTEGRATE TIME=(F)',8)	
READ(4,50) AINTE2	
IF(STEPN .LT. 0) ISTAR= INT(STEPN5)	
IF(STEPN .GT. 0) ISTAR= INT(STEPN+.5)	
510 IDIR=0	
CALL SCNR(ISTAR, IDIR)	
529 IDIR= 1	
CALL SCNR(ISTAR, IDIR)	
539 FIGU=(FINAL-START)/.1 NUMDP=1	
IF(FIGO .LT. θ .) IIGO=INT(FIGO5)	
IF(FIGU .GT. U.)IIGO=INT(FIGO+.5) IGO=IABS(IIGO/ISTEP)	
IF(FINAL-START) 540, 550, 560	
569 IDIR= 1 CO TO 20	
540 IDIR=0	
29 WRITE(5,129) IGO FSTEP=FLOAT(ISTEP)/10.	

	1011NT= 0
10	$\frac{1000100}{100100}$
1.	100-1000 1000 00 10 10
	100-100-1000
	$\begin{array}{c} 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100 \\$
1 2	
19	$\frac{1}{100} = \frac{1}{100} = 1$
	DU DOU I-I,IGUN IE(I EO I)VI(I)-STADT
	$\frac{1}{1} = \frac{1}{2} = \frac{1}$
	IF(I .EQ. I) GO IO 000
	$\frac{1}{1} \frac{1}{1} \frac{1}$
	IF(IDIR .EQ. 0) WL(I)=WL(ILL)=FSILF
	CALL SCAR(ISTEP, IDIR)
699	CALL SETTICULY1, AINTEI)
	CALL ADC(ARRAY, NUMAV, NUMDP, MISS)
	TDATA(1) = ARRAY(1) / FLUAT(NUMAV)
16	FORMAT(G15.B)
	CALL SETIT(DLY2, AINTE2)
	CALL ADC(ARRAY, NUMAV, NUMDP, MISS)
	TDATA(2) = ARRAY(1) / FLOAT(NUMAV)
	XDATA(I) = TDATA(I) - TDATA(2)
580	CONTINUE
	WRITE(5,240)(WL(1),XDATA(1),I=1,IGON)
	IF(IOUNT . EQ. 0) GO TU 601
	DO 581 $J=1, IOUNT$
	DO 582 KK=1,1000
	IF(KK . EQ. 1) WL(KK) = WL(IGON) + FSTEP
	KKL=KK-1
	IF(IDIR . EQ. 1) $WL(KK) = WL(KKL) + FSTEP$
	IF(IDIR .EQ. 0) $WL(KK) = WL(KKL) - FSTEP$
	CALL SCAN(ISTEP, IDIR)
	CALL SETIT(DLY1, AINTE1)
	CALL ADC(ARRAY, NUMAV, NUMDP, MISS)
	TDATA(1) = ARRAY(1) / FLOAT(NUMAV)
	CALL SETIT(DLY2, AINTE2)
	CALL ADC(ARRAY, NUMAV, NUMDP, MISS)
	TDATA(2) = ARRAY(1) / FLOAT(NUMAV)
	XDATA(KK) = TDATA(1) - TDATA(2)
582	CONTINUE
	WRITE(5,240)(WL(I),XDATA(I),I=1,1000)
240	FORMAT(2G15.6)
581	CONTINUE
	GO TO 601
550	WRITE(0,690)
690	FORMAT(' NO MOVEMENT NEEDED')
601	CONTINUE
	END

с с с с с с с с с с	THIS PROGRAM SOLVES THE DIFFERENTIAL EQUATION FOR THE LR CIRCUIT ASSOCIATED WITH CURRENT MEASUREMENTS FOR THE SPARK BY PERFORMING A RUNGE KUTTE ON THE DATA.
0000	PROGRAM NAME: SKRUKU. FT
435	DIMENSION V(100), A(4), B(4), C(4) CONTINUE
26	READ(1,20) FRAME=',A6) Format(' File RAME=',A6) Bead(1,20) NDT
20	FORMAT(' NUMBER OF DATA POINTS(I)=', I2) BEAD(1 32) VOLT
32	FORMAT(' NUMBER OF MILLIVOLTS/DIV(F)=',F8.2)
	VI=(VOLT*8.0E-03/3.35)*19.39 SH=0.05*T1
	R=0.0792 DU=5.0
	DT=(1./DU)*SH CUR=0.0
	Q=0.0 A(1)=0.5
	A(2)=-0.4142136 A(3)=2.4142136
	A(4) = 0.1666667 B(1) = 2.0
	B(2) = 1.0
	B(3)=1.0 B(4)=2.0
	C(1)=0.5 C(2)=-0.4142136
	C(3)=2.4142136
	TMX=FLOAT(NPT-1)*SH
	CALL IOPEN('SYS',FNAME) DO 30 K=1,NPT
28	READ(4,28) AQ, TT, VV $FORMAT(A2,2F6,2)$
20	V(K) = VI * VV
30	CONTINUE
261	READ(1,261)FNM Format(' File NAME For Output=', A6)
	CALL OOPEN('FLP2', FNM)
7	CONTINUE
2	CONTINUE
49	AK=DI*(V(I)-COR*R) FORMAT(E15.7)
	CUR=CUR+A(J)*(AK-B(J)*Q)-C(J)*AK Q=Q+3.*A(J)*(AK-B(J)*Q)-C(J)*AK
1	CONTINUE IS=I
	T=FLOAT(IS)*SH WRITE(4,46)T,CUR
8	IF(T-TMX)7,8,8 CONTINUE
46	FORMAT('RD', 2E15.5)
	GO TO 435
	END

THIS PROGRAM SERVES AS THE MAIN CONTROL FOR ALL S. KOEPLIN DATA TAKING PROGRAMS. IT WILL MOVE THE MONOCHROMATOR, TAKE DATA, AND STORE THE DATA. PROGRAM NAME: SKMNDT.F4 DIMENSION ARRAY(1500), ELMNT(4), HEADR(11) COMMON ARRAY CALL CLOCK(100) CALL SKPARM(NEL, CAL, DELY, AINT, TMINUT, ELMNT, HEADR) 1 CALL SKLNFD(NEL, CAL, ELMNT, NGO) 123 READ(4,22) KEYBD 22 FORMAT(A6) IF(KEYBD .EQ. 'C') GO TO 124 GO TO 135 CALL CLTIME(X) CALL SKDATA(NEL, DELY, AINT, TMINUT, NGO, ITHRU) 124 CALL SKSTOR(NEL, ITHRU, HEADR, ELMNT, DELY, AINT) GO TO 44 WRITE(0,33) FORMAT(' TO START HIT G THEN RETURN') 135 33 GO TO 123 CALL SKBELL 44 END

THIS PROGRAM ALLOWS THE USER OF THE S. KOEPLIN DATA TAKING ROUTINES TO ENTER ALL PERTINENT INFORMATION AT THE BEGINING C C OF A CHROMATOGRAM AND THEN SIGNALS COMPLETION AT THE END. CCCCCCCC PROGRAM NAME: SKPARM. F4 SUBROUTINE SKPARM(NEL, CAL, DELY, AINT, TMINUT, ELMNT, HEADR) DIMENSION ELMNT(4), HEADR(11), DELY(4), AINT(4) Q WRITE(0,10) FORMAT(' HOW MANY ELEMENTS DO YOU WANT TO LOOK AT?', \$) 10 READ(4,15) NEL FORMAT(12) 15 IF(NEL .LT. 4) CO TO 68 WRITE(0,800) 18 CANT DO MORE THAN 4 ELEMENTS') 800 FORMAT(' CO TO 9 DO 25 I=1, NEL 68 WRITE(0,223) FORMAT(' ELEMENT SYMBOL=',\$) 223 READ(4,30) ELMNT(I) WRITE(0,80) ELMNT(1) FORMAT(' DELAY TIME(F) FOR 'A6,' IN MICROSECONDS=' ,\$) 80 READ(4,85) DELAY 85 FORMAT(F8.0) DELY(I) = DELAY*10. WRITE(0,90)ELMNT(1) FORMAT(' INTEGRATE TIME(F) FOR ' A6, 'IN MICROSECONDS=', \$) 90 READ(4,85) AINTG 30 FORMAT(A6) AINT(I)=AINTG*10. 25 CONTINUE WRITE(0,40) FORMAT(' WHAT WL IS MONO AT NOW(F)?=',5) 40 READ(4,50) CAL FORMAT(F10.2) 50 WRITE(0,60) FORMAT(' ENTER HEADING') 60 READ(4, 70) HEADR 70 FORMAT(11A6) WRITE(0,95) FORMAT(' HOW MANY MINUTES DO YOU WANT TO TAKE DATA FOR?=(F)',\$) 95 READ(4,50) TMINUT IF(NEL .GT. 1) GO TO 199 IF(TMINUT .LE. 25.) GO TO 500 WRITE(0,850) FORMAT(' MAX TIME IS 25 MINUTES') 110 850 GO TO 95 100 IF(NEL .GT. 2) GO TO 200 IF(TMINUT .LT.30.) GO TO 500 WRITE(0,860) FORMAT(' MAX TIME IS 30 MINUTES') 860 GO TO 95 IF(NEL .GT. 3) GO TO 300 IF(TMINUT .LT. 45.) GO TO 500 200 WRITE(0,870) FORMAT(' MAX TIME IS 45 MINUTES') 870 GO TO 95 IF(TMINUT .LT. 50.) GO TO 500 300 WRITE(0,880) FORMAT(' MAX TIME IS 50 MINUTES') 880 GO TO 95 WRITE(0,845) FORMAT(' INJECT- THEN TYPE G RETURN TO START TIMING ',*) 500 845 RETURN END

CCCCCCCCCCCCCCC THIS PROGRAM CONTROLS SCANNING OF THE MONOCHROMATOR AND FINDING OF THE MOST INTENSE LINE FOR A GIVEN ELEMENT. IT CAN FIND A TOTAL OF FOUR ELEMENTS AND PASSES THE LOCATIONS BACK TO THE MAIN PROCRAM. PROGRAM NAME: SKLNFD. F4 SUBROUTINE SKLNFD(NEL, CAL, ELMNT, NGO) DIMENSION ELMENT(4), ELMNT(4), NGO(4) K= 0 103 IDIR=0 DO 88 I=1, NEL IF (ELMNT(I) .EQ. B) WAVEL=2497.2 IF (ELMNT(I) .EQ. CU) WAVEL=3247.5 IF (ELMNT(I) .EQ. P) WAVEL=2535.6 IF (ELMNT(I) .EQ. CAII) WAVEL=3933.6 IF (ELMNT(I) .EQ. CAI) WAVEL=4226.7 IF (ELMNT(I) .EQ. C) WAVEL=2478.6 IF (ELMNT(I) .EQ. AL) WAVEL=3961.5 IF (ELMNT(1) .EQ. MO) WAVEL=3798.3 IF (ELMNT(I) .EQ. SI) WAVEL=2881.6 IF (ELMNT(I) .EQ. I) WAVEL=4110.0 IF (ELMNT(I) .EQ. H) WAVEL=4861.3 IF (ELMNT(I) .EQ. S12) WAVEL=2516.1 30 CONTINUE STEPN=(WAVEL-CAL)/.1 IF(STEPN .LT. 0.) NSTEP= INT(STEPN -.5) IF(STEPN .GT. 0.) NSTEP= INT(STEPN + .5) IF(STEPN .EQ. 0.) NSTEP = 0 IF(NSTEP .LT. 0) IDIR=0 IF(NSTEP .GE. 0) IDIR=1 IF(IDIR .EQ. 1) ISTEP=IABS(NSTEP)+30 IF(IDIR .EQ. 0) ISTEP=IABS(IABS(NSTEP)-30) IF(ISTEP .EQ. 0) GO TO 60 CALL SCNR(ISTEP, IDIR) 60 IDIR=0 ISTEP=60 CALL SNADC(ISTEP . IDIR, WAVEL, ELMT) ELMENT(K) = ELMT CAL= WAVEL-30. CONTINUE 88 IF(NEL .EQ. 1) GO TO 188 CALL SKORD (NEL, ELMENT) 188 TNOWAT= WAVEL-30. STP=(TNOWAT-ELMENT(1))/.1 IF(STP .LT.0.)NSTP=INT(STP-.3) IF(STP.GT.0.)NSTP=INT(STP+.5) IF(STP.EQ.0.)NSTP=0 IF(NSTP.LT.0) IDIR=0 IF(NSTP.GT.0) IDIR=0 IF(NSTP.EQ.0)GO TO 104 CALL SCNR(NSTP, IDIR) DO 20 I=1, NEL IF(I .EQ. NEL)GO TO 10 NGO(I) = IFIX(ELMENT(I+1)-ELMENT(I)) GO TO 20 NGO(1) = IFIX(ELMENT(1) - ELMENT(1)) 10 20 104 CONTINUE

RETURN END

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PROGRAM NAME: SKSNAD. F4 SUBROUTINE SNADC(ISTEP, IDIR, WAVEL, ELMT) DIMENSION ARRAY1(1), STORE(100) NUMAV= 1000 NUMDP=1 DO 50 I=1, ISTEP CALL SCDWN (1.,0.,1.) CALL ADC (ARRAY1, NUMAV, NUMDP, MISS) STORE(I) = ARRAY1(1) CONTINUE PMAX=STORE(1) DO 70 L=I, ISTEP IF(STORE(L) .GT. PMAX) ISTP=L IF(STORE(L) .GT.PMAX) PMAX=STORE(L) CONTINUE TOGO=FLOAT(100-ISTP) ELMT=WAVEL + (TOGO -50.) RETURN END

FOR A PARTICULAR ELEMENT.

THIS PROGRAM PUTS THE ELEMENTS OF INTEREST IN ASCENDING С ORDER TO ALLOW THE MONOCHROMATOR TO MAKE THE MINIMUM NUMBER OF STEPS POSSIBLE. CCCCCCCCCC PROGRAM NAME: SKORD. F4 SUBROUTINE SKORD(N, ELMENT) DIMENSION ELMENT(4) NM=N-1 DO 10 K=1,NM JO= K+ 1 J=JO,N DO 10 IF(ELMENT(K)-ELMENT(J))5, 10, 10 SAVE=ELMENT(K) 5 ELMENT(J) = ELMENT(K) SAVE=ELMENT(J) CONTINUE 10 RETURN END

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THIS PROGRAM SCANS THE MONOCHROMATOR AND TAKES

DATA FROM THE ADC TO FIND THE MAXIMUM EMISSION LINE

0000	THIS PROGRAM ALLOWS FAST SCANNING OF THE GCA MCPHERSON MONOCHROMATOR.
с с с	PROGRAM NAME: SKSCNR. F4
-	SUBROUTINE SCNR(ISTEP,IDIR) CALZR=-1. CALL=0.
10	IF(ISTEP .LE. 4096) CO TO 15 ISTEP=ISTEP -4096 CALL=CALL + 1. GO TO 10
15	IF(CALL .EQ. 0.)CALZR=1. IF(CALL .EQ. 0.)CAL=0. IF(CALL .CT. 0.)CAL=-CALL STEP=FLOAT(-ISTEP) WRITE(0.21)IDIR.STEP.CAL.CALZR
21	FORMAT(16,3F10.2) IF(1DIR .EQ. 1) GO TO 40 IF (1DIR .EQ. 0) GO TO 20
20	CALL SCOWN(STEP, CAL, CALZR) RETURN
40	CALL SCUP(STEP, CAL, CALZR) RETURN END

C C C	THIS PROGRAM CONTROLS THE SLEW FUNCTIONS OF THE MONOCHROMATOR.
	PROGRAM NAME: SKSLW. F4
L	SUBROUTINE SLW(ISTEP,IDIR) CALZR=-1. CALL=0.
10	IF(ISTEP .LE. 4096) GO TO 15 ISTEP=ISTEP -4096 CALL=CALL + 1. GO TO 10
15	IF(CALL .EQ. 0.)CALZR=1. IF (CALL .EQ. 0.) CAL=0. IF (CALL .GT. 0.) CAL = -CALL STEP=FLOAT(-ISTEP) IF(IDIR .EQ. 1) CO TO 40 IF (IDIR .EQ. 0) GO TO 20
20	CALL SLWTO('DOWN', STEP, CAL, CALZR) RETURN
40	CALL SLWTO('UP', STEP, CAL, CALZR) RETURN END

/ THIS PROGRAM SETS DELAY AND INTEGRATION TIMES /////// PROGRAM NAME: SKSET. RA 1 SECT SETIT JA #ST ORC #XR. .+10 TEXT +SETIT+ #RET. SETX #XR SETB **#BASE** .+3 JA **#BASE**, ORG .+6 DELAYT, **/STORE RETURN LOCATIONS** ORG .+3 FINIT, .+3 ORC ORG #BASE+30 FNOP JA FNOP #RET **GOBAK**, 0;0 #ARCS, .+3 ORG .+0011 #TMP, ORG 0001 #LIT. 2000 0000 0002 3000 0000 0003 3000 0000 #LBL=. **#LBL** ORG #RTN. BASE **#BASE** #GOBAK JA STARTD #ST. 0210 #GOBAK, 0 **FSTA** 0200 #XR SETX **#BASE** SETB LDX 0,1 **#BASE FSTA FSTA** #ARCS #BASE, 1+ FLDA% FSTA DELAYT #BASE, 1+ FLDA% /PASS ADDRESS TO 8 MODE CODE FINIT FSTA STARTF 0002,0 LDX LDX 0003,0 #LIT+0000 FLDA /PASS DELAY TIME TO 8 MODE FLDAX DELAYT ALN A **FSTA** DEL8 /PASS INTEGRATE TIME TO 8 MODE FLDA% FINIT ALN 9 **FSTA** INT8 FCLA TRAP4 **#SET8** /GO TO 8 MODE 0004,0 LDX EXTERN #NE JA #RTN LDX 0005,0 EXTERN #NE #RTN JA

1	THIS PRO	DGRAM ACQUIRES	DATA FI	ROM ADC	AND 8	TORES	IT I	IN
/								
/								
/	PROGRAM	NAME: SKADC. RA						
/	0505	470						
	SEUT	AUG FLOAT						
	EXTERN	IPIY						
	JA	#ST						
•XR.	ORG	.+10						
	TEXT	+ADC +						
≠RET,	SETX	≠XR						
	SETB	#BASE						
	JA	.+3						
ADDAV	ORG	. +0						
WIIMAV.	ORG	.+3						
NUMDP.	ORG	.+3						
MISS,	ORG	.+3						
	ORG	#BASE+30						
	FNOP							
	JA	#RET						
CODAR	FNOP							
#GUDAK,	OBC	+3						
AV.	ORG	.+0003						
DP,	ORG	.+0003						
Ι,	ORG	.+0003						
YMISS,	ORG	.+0003						
•THP.	ORG	.+0011						
≠LIT,	0001							
	2000							
	0000							
	3000							
	0000							
	0 003							
	3000							
	0000							
	0000							
	0003							
	#LBL=.							
	ORG	#LBL						
#RIN,	BASE	#BASE						
#9T	JA STARTD	#GUBAK						
-01,	6210							
	FSTA	≠GOBAK, €						
	0200	-						
	SETX	#XR						
	SETB	#BASE						
	LUX Fot	T, I TRASE						
	f 5 i A Fsta	# ARCS						
	FLDAX	#BASE, 1+						
	FSUB	#LIT+0012						
	FSTA	AR	/PAS	S ADDRE	85 TO	BCODE		
	FSTA	ARRAY						
	FLDAS	#BASE, 1+						
	551A F1 Dag	ABASE 1-						
	r luhn	- DROLI IT						

≠G 000 1,	FSTA FLDAX FSTA STARTF LDX LDX LDX FLDA STARTD FSTA JA FNEG ALN FSTA LDX FLDA STARTD FSTA	NUMDP *BASE, 1+ MISS 0002,0 0003,0 0004,0 NUMAV *G0001 FLOAT .+0004 0 AV8 0005,0 NUMDP *G0002	✓CONVERT TO SMODE COMPATIBILITY ✓PASS TO SCODE
<i>-</i> G0002.	STARTF JSR JA JA	FLOAT .+ 0004	
	FNEG ALN FSTA LDX FLDA TRAP4 LDX FLDA FNORM FSTA JSR JA JA FSTA% LDX FLDA FSTA FSTA FSTA	6 DP8 0006,0 *LIT+0000 *ADC 0007,0 XMISS YMISS IFIX .+0004 YMISS MISS 0010,0 *LIT+0000 I NUMDP *DOTMP+0000	<pre>/CONVERT T SCODE VARIABLE /PASS NUMBER DATA POINTS REQUESTED /GO TO SMODE CODE /GET VALUE /CONVERT TO F4 TALK /SAVE THE VALUE</pre>
≠G 000 3,	LDX	9 011, 9	
#30,	FLDA ATX FLDA% FNORM FSTA% FLDA FADD FSTA FSUB JLE LDX EXTERN JA LDX EXTERN JA LDX EXTERN JA	I 7 ARRAY,7 ARRAY,7 I *LIT+0000 I *C0003 0012,0 *NE *RTN 0013,0 *NE *RTN	✓CONVERT ALL VLAUES TO F4
- DO INF,	UNG		

•
1 8 MODE CODE 1 1 DEFINE I/O COMMANDS 1 1 TDEL=6442 TINT=6444 1 111 1 FIELD1 #SET8 Ø IOF CLA CLL ✓GET DELAY TIME ✓INVERT TO COUNT DOWN ✓SET DELAY COUNTERS TAD **DEL8+2** CMA TDEL CLA CLL TAD INT8+2 /GET INTEGRATE TIME CMA /INVERT TO COUNT DOWN TINT CLA CLL ION CDF CIF 0 JMP% *SET8 1 1 // DEFINE RECESARY CONSTANTS 1 1 DEL8. 0000 0000 0000 INT8, 0000 0000 0000 **#ADC 8MODE CODE** 1 DDEFINE I/O COMMANDS 1 /***NOTE CHANGES 7/8/77*** SKPAD=6441 DRIVE=6452 CLRFG=6451 START FO EXECUTABLE CODE 1 FIELD1 #ADC Ø **/SAVE RETURN** CLA /CLEAR AC TAD AR **/PICK UP DATA FIELD** AND N7 /MASK CLL RTL ✓MOVE TO RAL PROPER BITS TAD N6201 **/SKELETON CDF INSTRUCTIONS** DCA .+1 Ø **AS IN LINE CODE** TAD .-1 DCA CCDF SAVE FOR FUTURE REFERENCE **/ELSEWHERE** TAD NPTAV1 DCA NPTAV

	ISZ AR+1	/NECESSARY SO AS NOT TO MISS
	SKP	THE FIRST POINT
	JMS SUB	ZON'T KNO WHY
	ISZ AR+1	
	SKP	
	JMS SUB	
	ISZ AR+1	
	SKP	
	JAS SUB	
	JAP CHECK	
STR,	CLA CLL	
	SKPAD	AND CONTINUE
	JAF .TZ	VTS INC DOINTED
CHECK	SVDAD	/ ILS ING FUINIER /CONVERSION VET2
CHECK,	IMP _1	ZNO WAIT
	DRIVE	VYES GET IT
	CLRFG	CLEAR FLAG
	RAL	SET FOR STRANCE INPUT
	CML	COMPLEMENT MOST SIGNIFICANT BIT
	RAR	/RESTORE TO PROPER POSITION
	CMA	COMPLEMENT AC
	TAD PRAD	ADD PREVOIUS RESULT
	DCA PRAD	SAVE IT
	SZL	/OVERFLOW?
	ISZ MSWRD	YES, INC. MOST SIGN WORD
	JMP .+2	NO, CONTINUE UNABATED
	HLT 107 NDTAN	//ADDEND UVERFLOW?
	ISZ NPIAV	/DURL ILI /No Cet another point
		ACET READY TO STORE A POINT
	TAD N13	/NECESSARY FIR NORMALIZATION
	DCA% AR+1	PUT 13 INTO EXPONET
	ISZ AR+1	MOVE POINTER TO NEXT LOCATION
	SKP	
	JMS SUB	∕GO CHANGE THE DATA FIELD
	TAD MSWRD	∕PICK UP MOST SIGN WORD
	DCA% AR+1	/DEPOSIT WORD 2 FORT VARIABLE
	ISZ AR+1	/INCREMENT POINTER
	SKP	
	JANS SUB	
	TAU PHAU	
	DUAX ARTI	
	ISL ARTI	
	ING SITE	
	CL CLI	
	DCA PRAD	CLEAR STORAGE
	DCA MSWRD	
	TAD NPTAV1	/RESET COUNTER
	DCA NPTAV	
	ISZ NUMDP8	TAKEN NUMBER OF REQUESTED DATA POINTS
	JMP STR	✓NO, GET SOME MORE
		TURN INTERRUPT BACK ON BEFORE EXITING
	CDF CIF 0	/GET SET TO RETURN
	JMP% #ADC	/GO BACK TO RALF

SUB,	0	/SAVE THE RETURN
•	CLA CLL	
	TAD N10	
	TAD CCDF	/INCREMENT THE DATA FIELD
	DCA +1	
CCDF.	0	/SET TO EXECUTE AS IN LINE CODE
	CLA CLL	
	JMPX SUB	
∕DEFINE	THE NECESSAY	CONSTANTS
AR,	0000	
·	0000	
N7.	0007	
N10.	0010	
N6201.	6201	
N13,	0013	
AV8	0000	
-	0000	
NPTAV1.	0000	
NPTAV,	0000	
DP8.	0000	
- •	0000	
NUMDP8.	0000	
XMISS,	0 027	
-	0000	
MISSED,	0000	
PRAD,	0000	
NEWDI	0000	

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/	THIS IS	THE ASSEMBLY LEVEL PRO	GRAM TO CONTROL THE
/	MONOCHR	DMATOR. IT IS DESIGNED	TO FUNCTION WITH THE
/	ELECTRO	NICS BUILT BY G. SENG.	
/			
/			
1			
	PROGRAM	NAME: SKDOWN, RA	
	1100102		
,			
/	SFOT	SCOM	
	SECI		
	JA	*51	
#AR,	UNG		
	TEXI		
≠RET,	SETX	# AR	
	SETB	*BASE	
	JA	.+3	
#BASE ,	ORG	.+6	
STEP,	ORG	.+3	
CAL,	ORG	.+3	
CALZR,	ORC	.+3	
	ORG	#BASE+30	
	FNOP		
	JΛ	#RET	
	FNOP		
#GOBAK.	0:0		
#ABGS.	ORG	.+3	
#TMP	OBC	+0011	
#1.17	0001		
- 511,	2000		
	0000		
	0000		
	2002		
	3000		
	0000		
	0093		
	3000		
	0000		
	#LBL=.		
	ORG	*LBL	
#RTN,	BASE	*BASE	
	JA	#GOBAK	
≠st,	STARTD		
	0210		
	FSTA	#GOBAK,0	
	0200		
	SETX	#XR	
	SETB	#BASE	
	LDX	9,1	
	FSTA	#BASE	
	FSTA	#ARGS	
	FLDA%	#BASE, 1+	
	FSTA	STEP	
	FLDA7	#BASE, 1+	
	FSTA	CAL	
	FLDA%	*BASE. 1+	
	FSTA	CALZR	
	START		
	LDX	9002, 9	
	LDX	0003.0	
	FLDA	#LIT+0000	
	FLDA%	STEP /BEGIN	FIXING F4 ARGUMENTS
	ALN	9	
	FSTA	STP8	
	FLDA%	CAL	
	ALN	0	

FSTA CAL8 FLDA% CALZR ALN A **FSTA** CALZ8 TRAP4 *SCNDN /GO TO SCAN DOWN SECTION LDX 0004.0 EXTERN ≠NE JA #RTN 0005,0 LDX EXTERN #NE JA #RTN DEFINE I/O COMMANDS ENCOD= 646 1 STEPS=6431 DOWN=6434 CLREN=6464 BEGIN EXECUTABLE COMMANDS SECTION TO SCAN DOWN FIELD1 #SCNDN Ø IOF /INTERUPT OFF CLA CLL ISZ CALZD TAD CALZD /SEE IF NEED >4096 STEPS SZA /GO TO EXT1 IF <4096 STEPS JMP EXTI STRT1, CLREN DOWN **/SET DIRECTION DOWN** CLA CLL /SET EXTRA LOOP IN CASE ENCODER TAKES LONG TAD LPB8 DCA LPB /GET READY FOR 5 MSEC WAIT TAD TWAIT DCA WAIT ISZ WAIT JMP .-1 CLA CLL TAD TLOOP WAI1, DCA LOOP STEPS /STEP AB11, ENCOD JMP .+2 JMP .+4 **/CHECK FOR ENCODER FLAG** ISZ LOOP JMP .-4 JMP TD1 ISZ T4096 JMP STRT1 /INCREMENT 4096 LOOP /INCREMENT # OF 4096'S **ISZ CALED** JMP STRT1 /THIS BEGINS SECTION FOR <4096 STEPS EXT1. CLREN /IT WORKS THE SAME WAY AS THE FIRST SECTION DOWN CLA CLL

TAD LPB8

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DEFINE NECESSARY CONSTANTS

WAIT, TWAIT, 0000 3500 0000 STP8, 0000 STP8D, 0000 TLOOP, 3000 LOOP, 0000 LPB8, 7777 LPB, CAL8, 0000 0000 0000 CALED, 0000 CALZ8, 0000 0000 CALZD, 0000 T4096, 0000

DCA LPB TAD TWAIT DCA WAIT ISZ WAIT JNP .-1 CLA CLL TAD TLOOP TO1. DCA LOOP STEPS AB1, ENCOD JMP .+2 JMP .+4 ISZ LOOP JMP .-4 JMP TD11 ISZ STP8D JMP EXT1 JMP ENDI ISZ LPB JMP .+2 TD11, STEPS STEPS SIEFS TAD TLOOP DCA LOOP JMP AB1 ISZ LPB JMP .+2 STPS TD1. STEPS STEPS STEPS TAD TLOOP DCA LOOP JMP AB11 CLREN END1, ION CDF CIF 0 JMP73 #SCNDN

/ / /	THIS IS THE SCAN TO FUNCT	THE NUP FION	RALPE FUNCT WITH	I MAC TION THE	CHINE LI OF THE ELECTR	EVEL 1 MONO ONICS	PROGR CHROM BUIL	AM TO ATOR. T BY (CONTR IT I G. SEN	ol S Des G.	IGNED
/											
/											
	SECT	SCUI	>								
AVB	JA	#ST									
- AR,	TEXT	+501	, 1P +								
•RET.	SETX	#XR	· ·								
	SETB	#BAS	SE								
	JA	.+3									
BASE,	ORG	.+6									
CAL	ORG	.+3									
CALZR.	ORG	.+3									
·	ORG	#BAS	SE+30								
	FNOP		_								
	JA FNOP	#RE1									
COBAK.	r NOF										
ARCS,	ORG	.+3									
#THP,	ORG	.+90)11								
≠LIT,	0001										
	2000										
	0000										
	3000										
	0000										
	0003										
	3000 8000										
	#LBL=.										
	ORG	#LBI	<u> </u>								
•RTN,	BASE	#BAS	E								
TPA	JA Startd	#GUI	JAK								
-91,	0210										
	FSTA	#GOE	BAK,0								
	0200										
	SETA	# AR	.F								
	LDX	0.1									
	FSTA	#BAS	SE								
	FSTA	#ARC	S								
	FLDAX FSTA	# DAS	5E, 1+								
	FLDAZ	#BAS	SE. 1+								
	FSTA	CAL									
	FLDA%	#BAS	SE, 1+								
	FSTA	CALZ	CR .								
	LDX	0002	2.0								
	LDX	0003	9,0								
	FLDA	#LI]	r+0000)							_
	FLDAX	STEF	3		/СН	ANCE	F4 AR	GUMEN	TS TO	RALP	H
	ALN FSTA	STPE	2								
	FLDA%	CAL									
	ALN	0									
	FSTA	CALE	3								
	FLUAX AIN	GALZ	71								
	FSTA	ČAL2	28								
	TRAP4	#SCN	IUP		∕G0	TO S	CAN U	P SEC	TION		
	LDX	0004	1,0								
	EXTERN	#NE	1								
	LDX	0003	5.0								
	EXTERN	#NE									
	JA	#RTN	Ŧ								

DEFINE I/O COMMANDS ENCOD=6461 STEPS=6431 UP=6432 DOWN=6434 CLREN=6464 BEGIN EXECUTABLE COMMANDS SECTION TO SCAN UP FIELD1 *SCNUP 0 IOF /INTERUPT OFF CLA CLL ISZ CALZD /CHECK IF NEED TO MOVE >44

. / / / / / /

111111111

	CLA CLL	CUECE IF HEFT TO MOVE LAGGE STEPS
	TAD CALZD	CHECK IF NEED TO HOVE / 4090 STELS
	SZA	
	JMP EXT2	/IF < 4096 GO TO EXT2
STRT2.	CLREN	CLEAR ENCODER FLAG
211121	UP	SET DIRECTION FLAG UP
	CLA CLL	
	TAD LPB8	/EXTRA LOOP IN CASE ENCODER PULSE TAKES LONG
	DCA LPB	
	TAD TWAIT	
	DCA WAIT	
	ISZ WAIT	✓BEGIN WAITNG ABOUT 5 MSEC
	JMP1	
WAI2,	CLA CLL	
	TAD TLOOP	
	DCA LOOP	
	STEPS	STEP MONO
AB22,	ENCOD	CHECK FOR ENCODER PULLSE
	JMP +2	
	JMP .+4	
	ISZ LUUP	KEEP CHECKING
	1SZ T4096	LINCREMENT 4096 COUNTER
	IMP STRT2	
	ISZ CALED	/INCREMENT # OF 4096 COUNTER
	JMP STRT2	
EXT2.	CLREN	CLEAR ENCODER AND DO AMOUNT < 4096
	UP	IN THE SAME WAY AS ABOVE
	CLA CLL	
	TAD LPB8	
	DCA LPB	
	TAD TWAIT	
	DCA WAIT	
	ISZ WAIT	
	JMP1	
102,	CLA CLL	
	TAD ILOUP	
	DLA LUUF STERS	
A 12 2	BILFS FNCOD	
ADG,		
	187 LOOP	

TD22,	JMP4 JMP TD22 ISZ STP8D JMP EXT2 JMP END2 ISZ LPB JMP .+2 STEPS TAD TWAIT DCA WAIT ISZ WAIT JMP1 STEPS TAD TWAIT ISZ WAIT ISZ WAIT ISZ WAIT JMP1 STEPS TAD TLOOP DCA LOOP	
TD2,	JMP AB2 ISZ LPB JMP .+2 STEPS TAD TWAIT DCA WAIT ISZ WAIT JMP1 STEPS TAD TWAIT DCA WAIT ISZ WAIT JMP1 STFPS	
end2,	TAD TLOOP DCA LOOP JMP AB22 CLREN ION CDF CIF Ø JMP% #SCNUP DEFINE NECESSAR	/INTERUPT ON /GO BACK Y CONSTANTS
WAIT, TWAIT,	00 00 4 100	
STP8,	0000	
GTDOD	0000	
TLOOP.	4000	
LOOP.	0000	
LPB8,	7777	
LPB,	0000	
CAL8,	0000 0000	
CALED.	0000	
CALZ8,	0000	
_	0000	
CALZD,	0000	
T4096,	0000	

167

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THIS IS THE ASSEMBLY LANGUAGE PROGRAM WHICH CONTROLS '; THE MONOCHROMATOR. ///// PROGRAM NAME: SKSLWT. RA 1 SECT SLWTO JA #ST ORG .+10 #XR, TEXT +SLWTO+ #RET, #XR SETX SETB **#BASE** .+3 JA **#BASE**, ORG .+6 ARG, STEP, ORG .+3 ORG .+3 CAL, CALZR, ORG .+3 .+3 ORG #BASE+30 ORC FNOP **#RET** JA FNOP **#GOBAK**, 0;0 #ARGS, ORG .+3 .+0011 #TMP, ORG #LIT. 0001 2000 0000 0002 3000 0000 0003 3000 0000 0417 2716 4040 2520 4040 4040 #LBL=. #LBL ORG **#BASE** #RTN, BASE **#GOBAK** JA STARTD #ST, 0210 #GOBAK, 0 FSTA 0200 SETX #XR **#BASE** SETB LDX 0,1 **#BASE FSTA** FSTA **#ARGS** FLDA% #BASE, 1+ FSTA ARG FLDA% #BASE, 1+ FSTA STEP FLDA7 **#BASE, 1+** FSTA CAL FLDA% #BASE, 1+ FSTA CALZR STARTF 0002,0 LDX LDX 0003,0

	FLDA%	ARG		
	FSUB	#LIT+0011		
	JNE	#G0001		
	FLDA	#LIT+0000		
	FLDA%	STEP /BEGIN	CHANGING F4 ARGUMENTS INT	O RALPH
	ALN	0		
	FSTA	STP8		
	FLDA%	CAL		
	ALN	0		
	FSTA	CAL8		
	FLDA%	CALZR		
	AIN	9		
	FSTA	CALZ8		
	TRAPA		CO TO SLEW DOWN	
#00001	INY	0004 0	CO TO BEEN DOWN	
- 00001,	FIDA	ABC		
	Fein	#1 IT+0014		
	INE	*C0000		
	JNE	# GUUUZ		
	J LUA	-LIITUUUU		DAT DT
	FLUA%	SILT	CHANGE 14 ANGUMENTS TU	NALTI
	ALN	0		
	FSTA	5178		
	FLDA%	CAL		
	ALN	U		
	FSTA	CAL8		
	FLDA%	CALZR		
	ALN	0		
	FSTA	CALZ8		
	TRAP4	#SLUP	∕GO TO SLEW UP	
≠G0002,	LDX	0005, 0		
•	EXTERN	#NE		
	JA	#RTN		
	LDX	0006.0		
	EXTERN	#NE		
	.14	#RTN		
/	UA			
,		NEFIWE ADDERO		
/	FNCOD-4	ALI UTDETS		
	SLUF=04	161		
	SLUN=64			
	CLREN=6	909		
	CLRSW=6	929		
/				
/				
/				
/				
/		8 MODE CODE		
/				
/				
/		SECTION TO SLE	W DOWN	
/				
/				
	FIELD1	#SLDWN		
	0			
	CLA CLL	•		
	ISZ CAL	.ZD	/CHECK IF OVER 4096	
	TAD CAL	.ZD		
	SZA			
	JMP EXT	R2	/JMP IF LESS THAN 4096	
	CLREN			
	SLDN			
	FROD			

-CHECK FOR ENCODER PULSE JMP .-1 ISZ TLOOP JMP .-5 ISZ CALED /COUNT TO 4096 **/INCREMENT NUMBER OF 4096 LOOPS** JMP .-7 EXTR2. /DO THE NUMBER OF STEPS LESS THAN 4096 CLREN SLDN ENCOD JMP .-1 ISZ STPED **CHECK FOR ENCODER PULSE** JMP .-5 CLRSW CDF CIF 0 JMP% #SLDWN 111 1 DEFINE NECESSARY CONSTANTS 1 1 1 STP8, 0000 0000 STPED, 0000 CAL8, 0000 0000 CALED, 0000 CALZ8, 0000 0000 CALZD, 0000 0000 TLOOP, 1 1 1 1 1 SECTION TO SLEW UP . #SLUP,0 /THIS SECTION OPERATES BASICALLY THE SAME AS THE SLEW DOWN SECTION, ONLY THE DIRECTION /FLAG ON THE INTERFACE IS DIFFERENT CLA CLL ISZ CALZD TAD CALZD SZA JMP EXTRI CLREN SLUP ENCOD JMP .-1 ISZ TLOOP JMP .-5 ISZ CALED JMP .-7 CLREN EXTR1. SLUP ENCOD JMP .-1 ISZ STPED JMP .-5 CLRSW CDF CIF 0 JMP% #SLUP

C CCCCCCC	THIS PROGRAM CONTROLS THE ACTUAL DATA ACQUISION FROM THE ADC. IT CAN BE USED FOR UP TO FOUR ELEMENTS. IT WILL SCAN TO THE LINE OF MAXIMUM EMISSION FOUND BY SKLNFD AND THEN PROCEED TO ACQUIRE DATA. PROGRAM NAME: SKDATA.F4
C C C C	
	SUBROUTINE SKDATA(NEL, DELY, AINT, TMINUT, NGO, ITHRU) DIMENSION DELY(4), AINT(4), NGO(4) IDIR=1 TI=1.
	ITHRU=1 TSEC=TMINUT×60.
	IF(NEL .EQ. 1) GO TO 50
15	DO 20 l=1,NEL-1
	ITHRU= ITHRU+ 1
	NGON=NGO(1) DELAY=DELY(1)
	AINTG=AINT(I)
	CALL SCNR(NGON, IDIR)
	TI=TI+1.5
20	CONTINUE
	IDIR=0
	NGON=NGU(NEL) CALL SONB(NGON IDIR)
	IF(NEL . EQ. 2)TI=TI+3.
	IF(NEL .EQ. 3) TI=TI+6.
	IF(NEL .EQ. 4) TI=TI+9.
	GO TO 15
50	DELAY=DELY(1)
	AINTG=AINT(1)
10	LALL SKSEDA(TI, DELAY, AINIG, ITHRU)
	ITHRU= ITHRU+1
	TI=TI+1.
40	GO TO 10 CONTLINE
70	RETURN
	END

THIS PROGRAM STORES ANY CHROMATOGRAPHIC DATA TAKEN C BY SKMNDT.F4. IT WILL STORE DATA FOR UP TO FOUR DIFFERENT ELEMENTS IN SEPARATE FILES UNDER NAMES THAT ARE SPECIFIED AT RUN TIME. THE AMOUNT OF TIME BETWEEN EACH DATA POINT DEPENDS UPON THE NUMBER OF ELEMENTS. IT IS CALCULATED TO Ċ Ċ C Ĉ ALLOW MOVEMENT BY THE GCA MCPERSON MONOCHROMATOR TO CLOSE Č C LYING ELEMENTS. Č C Č C PROGRAM NAME: SKSTOR. F4 С Ē SUBROUTINE SKSTOR(NEL, ITHRU, HEADR, EL, DELY, AINT) DIMENSION ARRAY(1500), HEADR(11) COMMON ARRAY TMIN1=1. TMIN2=2.5 TMIN3=4.0 TMIN4=5.5 IF(NEL .EQ. 1) GO TO 10 IF(NEL .EQ. 2) GO TO 20 IF(NEL .EQ.3) GO TO 30 WRITE(5,200)HEADR WRITE(6,200) HEADR WRITE(7,200) HEADR WRITE(8,200) HEADR WRITE(5,201) ITHRU, NEL, TMIN1 WRITE(6,201) ITHRU, NEL, TMIN2 WRITE(7,201) ITHRU, NEL, TMIN3 WRITE(8,201) ITHRU, NEL, TMIN4 DO 6 I=1, ITHRU, 4 WRITE(5,202) ARRAY(1) WRITE(6,202) ARRAY(I+1) WRITE(7,202) ARRAY(I+2) WRITE(8, 202) ARRAV(1+3) 6 CONTINUE GO TO 98 WRITE(5,200) HEADR 30 WRITE(6,200) HEADR WRITE(7,200) HEADR WRITE(5,201) ITHRU, NEL, TMIN1 WRITE(6,201) ITHRU, NEL, TMIN2 WRITE(7,201) ITHRU, NEL, TMIN3 I=1, ITHRU, 3DO 7 WRITE(5,202) ARRAY(I) WRITE(6,202) ARRAY(I+1) WRITE(7,202) ARRAY(I+2) 7 CONTINUE GO TO 98 WRITE(5,200) HEADR 20 WRITE(6,200) HEADR WRITE(5,201) ITHRU, NEL, TMIN1 WRITE(6,201) ITHRU, NEL, TMIN2 DO 8 I=1, ITHRU, 2 WRITE(5,202) ARRAY(1) WRITE(6,202) ARRAY(1+1) CONTINUE 8 GO TO 98 WRITE(5,200) HEADR 10 WRITE(5,201) ITHRU, NEL, TMIN1 WRITE(5,108)EL, DELY, AINT 108 FORMAT(A6, 2G10.1) WRITE(5,202)(ARRAY(1), I=1, ITHRU) FORMAT(11A6) 200 FORMAT(216,F8.1) 201 202 FORMAT(4G15.8) CONTINUE 98 RETURN

END

THIS PROGRAM CONTROLS THE DATA ANALYSIS PORTION OF THE S. KOEPLIN CHROMATOGRPAHY PROGRAMS. IT ALLOWS FOR READING OF A DATA FILE, SMOOTHING OF DATA, PLOTTING OF THE DATA ON A TEXTRONIX GRAPHICS TERMINAL, INTERACTIVELY DECIDING ON C C CCCCCCC THE PEAK LIMITS, AREA COMPUTATION AND FINAL REPORT GENERATION. Ċ C PROGRAM NAME: SKMNAN, F4 С Č COMMON ARRAY, INDX DIMENSION ARRAY(1500), INDX(21), HEADR(11), TMSEC(1) DIMENSION RETIME(7), HITE(100), TME(100), RESULT(7) READ(5,75) HEADR 75 FORMAT(11A6) 80 FORMAT(216, F8.1) READ(5,60) NDPT, NEL, TMIN ITHRU=NDPT/NEL READ(5,100)EL, DELY, AINT 38 FORMAT(16) DO 586 I=1, ITHRU READ(5,83) ARRAY(I) 586 CONTINUE 85 FORMAT(4G15.8) FORMAT(' TYPE WHICH YOU WANT PLOTTED-SM OR RAW? ', \$) 90 WRITE(0,90) 95 FORMAT(A6) READ(4,95) TYPE IF(TYPE .EQ. 'SM') GO TO 10 IF(TYPE .EQ. 'RAW') GO TO 20 CALL SKSMTH(ITHRU) 10 CALL SKTPLT(NPEAK, ITHRU, NEL, TMIN) IF(TYPE .EQ. 'RAW') GO TO 50 20 **REWIND 5** READ(5,75) HEADR READ(5,80) ITHRU, NEL, TMIN READ(3, 100) EL, DELY, AINT READ(5,85)(ARRAY(I), I=1, ITHRU)CALL SKAREA(NPEAK, RESULT, RETIME, NEL, TMIN, XCOUN) 50 CALL SKLIST (NPEAK, RESULT, RETIME, HEADR, EL, DELY, AINT, XCOUN. C TMIN, ITHRU) 100 FORMAT(A6,2G10.1) END

THIS PROGRAM PERFORMS A SAVITZKY AND GOLAY SMOOTH ON С THE DATA SUPPLIED TO IT. IT IS A RUNNIGN SMOOTH THAT ONLY REQUIRES ONE EXTRA ARRAY OF PIFTEEN ELEMENTS IN C CCCCCC ADDITION TO THE DATA ARRAY. PROGRAM NAME: SKSMTH. F4 С C C SUBROUTINE SKSMTH(ITHRU) **COMMON ARRAY** DIMENSION ARRAY(650), X(15) WRITE(0,500) FORMAT(' 5,9, OR 15 POINT SMOOTH? ',5) 500 CONTINUE 499 READ(4,501) ITYP FORMAT(13) 501 IF(ITYP .EQ. 5) GO TO 10 IF(ITYP .EQ. 9) GO TO 20 IF(ITYP .EQ. 15) GO TO 30 WRITE(0,502) FORMAT(' ONLY 5,9,15 POINT SMOOTHS ARE ALLOWED, TYPE NUMBER AND 502 RETURN') 1 GO TO 499 С С CCCC **5 POINT SMOOTH** С 10 ISMPT= ITHRU-4 ICOUN=1 X(1) = ARRAY(1)X(2) = ARRAY(2)JKL=1 X(3) = 17.*(ARRAY(ICOUN+2))+12.*(ARRAY(ICOUN+1)+ARRAY(ICOUN+3)) 11 +-3.*(ARRAY(ICOUN)+ARRAY(ICOUN+4)) 1 IF(ISMPT .EQ. JKL)GO TO 12 JKL=JKL+1 X(4) = 17.*(ARRAY(ICOUN+3))+12.*(ARRAY(ICOUN+2)+ARRAY(ICOUN+4)) +-3.*(ARRAY(ICOUN+1)+ARRAY(ICOUN+5)) 1 JKL=JKL+1 12 ARRAY(ICOUN) = X(1) ARRAY(ICOUN+1) = X(2) X(1) = X(3) / 35. X(2) = X(4) / 35. ICOUN= ICOUN+2 IF(ICOUN .LT. ISMPT) GO TO 11 K= 1 15 DO 13 I=ICOUN, ISMPT+2 ARRAY(1) = X(K)K=K+1 13 CONTINUE RETURN C С C

CCCC 9 POINT SMOOTH С 20 ISMPT= ITHRU-8 ICOUN=1 X(1) = ARRAY(1) X(2) = ARRAY(2)X(3) = ARRAY(3)X(4) = ARRAY(4)JKL=1 21 I0=0 I1=1 12=2 13=3 I4=4 15=5 I6=6 17=7 I8=8 DO 25 I=5,8 X(1)=59.*ARRAY(ICOUN+I4)+54.*(ARRAY(ICOUN+I3)+ARRAY(ICOUN+I5)) +39.*(ARRAY(ICOUN+I2)+ARRAY(ICOUN+I6))+14.*(ARRAY(ICOUN+I1)+ 1 ARRAY(ICOUN+ 17))+-21.*(ARRAY(ICOUN+10)+ARRAY(ICOUN+18)) 1 10=10+1 I 1= I 1+1 I2= I2+1 13=13+1 14=14+1 15 = 15 + 116=16+1 17=17+1 18=18+1 IF(ISMPT .EQ. JKL) GO TO 26 JKL=JKL+1 25 CONTINUE ARRAY(ICOUN) = X(1) 26 ARRAY(ICOUN+1) = X(2) ARRAY(ICOUN+2) = X(3) ARRAY(ICOUN+3) = X(4)X(1) = X(5) / 231. X(2) = X(6) / 231. X(3) = X(7) / 231. X(4) = X(8) / 231. ICOUN= ICOUN+4 IF(ICOUN .LT. ISMPT) GO TO 21 K= 1 DO 27 I=ICOUN, ISMPT+4 $\mathbf{ARRAY(1) = X(K)}$ K= K+ 1 CONTINUE 27 RETURN C С CCCC 15 POINT SMOOTH C 30 ISMPT= ITHRU-14 ICOUN= 1 X(1) = ARRAY(1) X(2) = ANRAY(2) X(3) = ARRAY(3)X(4) = ARRAY(4) X(5) = ARRAY(5) X(6) = ARRAY(6)X(7) = ARRAY(7)

JKL= 1 J0=0 J1=1 J2=2 J3=3 J4=4 J5=5 J6=6 J7=7 J8=8 J9=9

35 36

	J 10= 10
	J11=11
	J12=12
	J 13= 13
	J 1 4 = 1 4
	DO 35 I=8,14
	X(1)=167.*ARRAY(ICOUN+J7)+162.*(ARRAY(ICOUN+J8)+ARRAY(ICOUN+J6))+
1	122.*(ARRAY(ICOUN+J10)+ARRAY(ICOUN+J4))+87.*(ARRAY(ICOUN+J11)
1	+ARRAY(ICOUN+J3))+42.*(ARRAY(ICOUN+J12)+ARRAY(ICOUN+J2))+-13.*
1	(ARRAY(ICOUN+J13)+ARRAY(ICOUN+J1))+-78.*(ARRAY(ICOUN+J14)+ARRAY)
1	(1COUN+J0) + 147.*(ABRAY(1COUN+J9) + ABRAY(1COUN+J5))
-	IO = IO +1
	10=10+1
	J6=J6+1
	J7=J7+1
	J8=J8+1
	J9=J9+1
	J 10= J 10+ 1
	J11=J11+1
	J12=J12+1
	J 13=J 13+1
	J14=J14+1
	IF(ISMPT, EQ. JKL) GO TO 36
	CONTINUE
	ABRAY(ICOIN) = Y(1)
	$\frac{1}{2} \frac{1}{2} \frac{1}$
	$\mathbf{A} \mathbf{D} \mathbf{A} \mathbf{V} \left(\mathbf{I} \mathbf{O} (\mathbf{N} + \mathbf{I}) - \mathbf{V} \left(2 \right) \right)$
	$\frac{\mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A}$
	ARRAI(ICOUNTS) = A(9)
	ARRAY(1000)+4) = X(5)
	$\mathbf{ARRAY}(1\mathbf{C}\mathbf{U}\mathbf{U}\mathbf{N}+5)=\mathbf{X}(6)$
	ARRAY(1C00N+6)=X(7)
	X(1) = X(8) / 1105.
	X(2)=X(9)/1105.
	X(3)=X(10)/1105.
	X(4)=X(11)/1105.
	X(5)=X(12)/1105.
	X(6) = X(13) / 1105.
	X(7) = X(14) / 1105.
	ICOIN=ICOUN+7
	IF (ICOUN, LT. ISMPT) CO TO 31
	DO 40 is icoun isomera?
	LND

40

THIS PROGRAM PLOTS THE DATA PASSED TO IT ON A TEKTRONIX GRAPHICS TERMINAL. THE FIRST PLOT CONSISTS OF A PLOT C С OF EVERY FIFTH POINT AND AFTER THAT THE USER IS ALLOWED TO INTERACTIVELY DEFINE THE POINTS TO BE PLOTED. INDICES CAN BE SET TO DEFINE PEAKS. THIS SET OF PROGRAMS USES THE FORTRAN IV PLOTTING PACKAGE DEVELOPED BY M. JOSEPH. **PROGRAM NAME: SKTPLT. F4** С Ĉ SUBROUTINE SKTPLT(NPEAK, NDPT, NEL, TMIN) COMMON ARRAY, INDX DIMENSION ARRAY(1500), INDX(21) IDIR=0 ITHRU=NDPT/NEL IF(NEL .EQ. 1) XCOUN=1. IF(NEL .EQ. 2) XCOUN=3. IF(NEL .EQ. 3)XCOUN=6. IF(NEL .EQ. 4)XCOUN=9. XMAX=FLOAT(ITHRU+XCOUN) XMIN=TMIN YMIN= ARRAY(1) YMAX= ARRAY(1) DO 101 J=1, ITHRU IF(ARRAY(J) .GT. YMAX) YMAX=ARRAY(J) IF(ARRAY(J) .LT. YMIN) YMIN=ARRAY(J) 101 CONTINUE CALL TPLINT(XMIN, XMAX, YMIN, YMAX, 1, 1) CALL TAXIS(1,0,0) XVAL=XMIN DO 202 K=1, ITHRU, 5 XVAL=XVAL+(5*XCOUN) CALL TPLT(-1, XVAL, ARRAY(K)) CONTINUE 202 CALL TPOSIT(34,60) WRITE(0,301) ITHRU FORMAT(16, 'POINTS BY 5') 301 CALL TPOSIT(0,0) WRITE(0,520) YMAX CALL TPOSIT(32.0) WRITE(0,520) YMIN WRITE(0,510) FORMAT(' INITIAL POINT # TO PLOT=',\$) 510 READ(4,511) IPT 511 FORMAT(16) WRITE(0,512) FORMAT(' FINAL POINT " TO PLOT=',*) 512 READ(4,511) IFPT IF(IFPT-IPT) 59,59,61 WRITE(0,60) FORMAT(' TRY AGAIN') 59 60 **GO TO 1** NU= IFPT-IPT 61 IF(NU .LT. 975) GO TO 62 WRITE(0,63) FORMAT(' CANT DO MORE THAN 975 POINTS') 63 **GO** TO 1 IDIR=0 62 XMAX=(FLOAT(IFPT-1)*XCOUN)+TMIN XMIN=(FLOAT(IPT-1)*XCOUN)+TMIN YMIN=ARRAY(IPT) YMAX= ARRAY(IPT) DO 10 J= IPT, IFPT

IF(ARRAY(J) .GT. YMAX) YMAX=ARRAY(J) IF(ARRAY(J) .LT. YMIN) YMIN=ARRAY(J) 10 CONTINUE CALL TPLINT(XMIN, XMAX, YMIN, YMAX, 1, 1) CALL TAXIS(1,0,0) XVAL=(FLOAT(IPT-1)*XCOUN)+TMIN DO 20 J=IPT, IFPT CALL TPLT(-1, XVAL, ARRAY(J)) XVAL=XVAL+XCOUN 20 CONTINUE CALL TPOSIT(0,0) WRITE(0, 520) YMAX 520 FORMAT(G15.8) CALL TPOSIT(32.0) WRITE(0,520) YMIN CALL TPOSIT(34,2) WRITE(0,511) IPT CALL TPOSIT(34,70) WRITE(0,511) IFPT J= IPT READ(4,591) KEYBD 25 501 FORMAT(A2) IF (KEYBD .EQ. ' ' .AND. IDIR .EQ. 0) J=J+1IF (KEYBD .EQ. ' ' .AND. IDIR .EQ. 1) J=J-1IF (KEYBD .EQ. ' ') GO TO 30 IF(KEYBD .EQ. 'R') IDIR=1 'F') IDIR=0 IF(KEYBD .EQ. 'S') GO TO 100 'A') GO TO 21 IF(KEYBD .EQ. IF(KEYBD .EQ. IF(KEYBD .EQ. 'N') GO TO 1 IF(KEYBD .EQ. 'P')GO TO 99 '1') INDX(1)=J IF(KEYBD .EQ. '2') INDX(2)=J IF(KEYBD .EQ. '3') INDX(3)=J IF(KEYBD .EQ. IF(KEYBD .EQ. '4') INDX(4)=J IF(KEYBD .EQ. '5') INDX(5)=J 141) IF(KEYBD .EQ. '6') INDX(6)=J '7') INDX(7)=J IF(KEYBD .EQ. '8') INDX(8)=J IF(KEYBD .EQ. '9') INDX(9)=J IF(KEYBD .EQ. '10') INDX(10)=J IF(KEYBD .EQ. IF(KEYBD .EQ. IF(KEYBD .EQ. '11') INDX(11)=J '12') INDX(12)=J '13') INDX(13)=J IF(KEYBD .EQ. '14') INDX(14)=J '15') INDX(15)=J IF(KEYBD .EQ. IF(KEYBD .EQ. IF(KEYBD .EQ. '16') INDX(16)=J '17') INDX(17)=J IF(KEYBD .EQ. IF(KEYBD .EQ. '18') INDX(18)=J IF(KEYBD .EQ. '19') INDX(19)=J '18') INDX(18)=J '20') INDX(20) = J '21') INDX(21) = J IF(KEYBD .EQ. IF(KEYBD .EQ. GO TO 25 IF(J.GT. IFPT) J=I IF(J.LT. IPT) J=IPT 30 IFPT) J=IFPT XVAL=FLOAT(J) CALL TPLT(-1, XVAL, ARRAY(J)) GO TO 25 21 READ(4,511) KADD J= IPT+KADD CO TO 30 WRITE(0,515) FORMAT(' TOTAL # OF PEAKS TO INTEGRATE(I)') 99 515 READ(4,518) NPEAK

- 518 FORMAT(13) 100 CONTINUE RETURN
 - RETU END

PROGRAM NAME: SKAREA. F4

PASSED FROM SKTPLT.

SUBROUTINE SKAREA(NPEAK, RESULT, RETIME, NEL, TMIN, XCOUN) COMMON ARRAY, INDX DIMENSION ARRAY(1500), INDX(21) DIMENSION RESULT(7), RETIME(7), HITE(100), THE(100) J=NPEAK*3 NUMB=1 IF(NEL .EQ. 1)XCOUN=1. IF(NEL .EQ. 2)XCOUN=3. IF(NEL .EQ. 3)XCOUN=6. IF(NEL .EQ. 4) XCOUN=9. DO 25 I=1,J,3 KSKP=1 KK= 1 K= INDX(I) K1=INDX(I+1) K2=1NDX(1+2) KD=K2-K TME(1)=(FLOAT(K-1))*XCOUN+TMIN IF(KD.GE. 100) CO TO 88 DO 35 II=K,K2,KSKP 32 HITE(KK) = ARRAY(11) KK= KK+ 1 TME(KK) = TME(KK-1) + XCOUN CONTINUE 35 NPTS=KD/KSKP SUM= 0. DO 20 IG=1.NPTS SUM=SUM+HITE(IG) CONTINUE 20 FSUM=SUM*XCOUN RESULT(NUMB) = KSKP*(FSUM-(FLOAT(NPTS)*.5*(HITE(1)+HITE(NPTS)))) RETIME(NUMB) = ((FLOAT(K1-1) *XCOUN) +TMIN)/60. NUMB= NUMB+1 25 CONTINUE RETURN IF((KD/2) .GE. 100) GO TO 98 88 KSKP=2 GO TO 32 98 IF((KD/3) .GE. 100) GO TO 108 KSKP=3 CO TO 32 108 IF((K/4) .GE. 100) GO TO 118 WRITE(0,113) FORMAT(' PEAK IS TOO WIDE') 118 113 KSKP=10 GO TO 32 RETURN END

THIS PROGRAM FINDS THE AREA OF A PEAK, AND CORRECTS FOR BASELINE DRIFT BY SUBRACTING OUT A TRAPEZOID. THE AREAS ARE FOUND ON THE PEAKS DEFINED BY THE INDICES

		THIS PROCRAM LISTS OUT ALL DATA FROM AN INDIVIDUAL CHROMATOGRAM TAKEN UNDER THE CONTROL OF SKMNDT.F4 ONTO THE LINE PRINTER AND COMPUTER FILE. PROCRAM NAME:SKLIST.F4
Ċ		
		SUBROUTINE SKLIST(NPEAK, RESULT, RETIME, HEADR, EL, DELY, AINT,
	C	XCOUN, TMIN, ITHRU)
		DIMENSION HEADR('1), RESULT(7), RETIME(7), THSEC(1), ARRAY(1500)
		COMMON ARRAY
		WRITE(6, 70) HEADR
		WRITE(0, 100/EL, DELI, AINI UDITE(0, 25) UFADD
		WRITE(3, (3) HEADR
		WRITE(6, 102) NPEAK
70		FORMAT(11A6)
75		FORMAT('', 11A6)
		WRITE(6,80)
80		FORMAT(///, ' PEAK NUMBER', 5X, 'PEAK AREA', 5X, 'RETENTION
	С	TIME(MIN) *,//)
		WRITE(3,80)
		DO 85 K=1,NPEAK
		WRITE(6,90) K, RESULT(K), RETIME(K)
90		FORMAT(3X, 12, 9X, 613, 4, 6X, 610, 2)
08		CONTINUE
100		CONTINUE FORMAT(' ' A6 ' DELAV TIME= ' C10 2 ' INTECRATE TIME= ' C10 2)
102		FORMAT(), AC, DELAT TIME- , OTO. 2, INTEGRATE TIME- , OTO. 2,
		BETHAN
		END

C	THIS PROCEAN FINDS THE AVERACE RETENTION TIME AND ADDA
C C	FOR THOSE INCOMPANY AND AN AND THE AND AND AN AND AND AND AND AND AND AND
	FUR INTE CHANNAIDGRAMES AND REFURIS INESE VALUES ALONG
L A	WITH THE STANDARD DEVIATIONS.
Ľ.	
C	
С	PROGRAM NAME: SKEROR. F4
С	
С	
Č	
5	DIMENSION TITL(11), DAT(11), HEADR(11)
	DIMENSION TAUC(3) THE $1(3)$ THE $2(3)$ THE $2(3)$
	$\mathbf{D} \mathbf{M} \mathbf{E} \mathbf{N} \mathbf{G} \mathbf{O} \mathbf{A} \mathbf{N} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{A} \mathbf{D} \mathbf{E} \mathbf{A} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{A} \mathbf{D} \mathbf{E} \mathbf{A} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{A} \mathbf{D} \mathbf{E} \mathbf{A} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} O$
	DIMENSION AAVG(3), AREA(3), AREA(3), AREAG(3)
	READ(4,280)TITL
28 1	FORMAT(' ENTER TITLE')
28 0	FORMAT(11A6)
	WRITE(0,283)
283	FORMAT(' ENTER DATE')
	READ(4, 280) DAT
	WRITE(0.284)
284	FORMAT(' ENTER COLIMN TYPE FLOW BATE TEMP. FTC. ')
2 07	BEAD A 280 HEAD
000	
202	
	WRITE(3,282) HEADR
	READ(5,280)TIT1
	READ(5, 121) NPEAK
	WRITE(3, 120) NPEAK
	DO 11 I=1, NPEAK
	READ(5,130)AREA1(1), THE 1(1)
	WRITE(3,131)AREA1(I),TME1(I)
11	CONTINUE
	READ(6,280)TIT2
	READ(6, 121) NPEAK
	WEITE(3, 120) NPEAK
	DO 12 I=1.NPEAK
	BEAD(6, 130) ABEA2(1) TME2(1)
	$\mathbf{T}_{\mathbf{T}} = \mathbf{T}_{\mathbf{T}} = $
10	
12	
	$\mathbf{READ}(7, 200) 1110$
	READ(7, 121) NFEAK
	WRITE(3, 120) NPEAK
	DO 13 I=1, NPEAK
	READ(7, 130) AREA3(1), THE3(1)
	WRITE(3, 131) AREA3(1), TME3(1)
13	CONTINUE
120	FORMAT(1H0, 16, ' PEAKS')
121	FORMAT(16)
130	FORMAT(G13.4,G13.4)
191	FORMAT(180, G13, 4, G13, 4)

	DO 25 I=1.NPFAK
	AAVG(I) = (AREA1(I) + AREA2(I) + AREA3(I))/3
	TAVG(I) = (TME1(I) + TME2(I) + TME3(I))/3.
	SQSUM1=(ABEA1(1)-AAVG(1))*(ABEA1(1)-AAVG(1))
	SQSIF(2 = (ABEA2(1) - AAVG(1)) * (ABEA2(1) - AAVG(1))
	SQSIM3 = (AREA3(1) - AAVG(1)) * (AREA3(1) - AAVG(1))
	SUM(1) = (SOBT((SOSUM1+SOSUM2+SOSUM3))/2.)/AAVG(1)
	$T_{2SIIM} = (TME_{1}(1) - TAVG(1)) * (TME_{1}(1) - TAVG(1))$
	$T_{2SUM2} = (TME2(1) - TAVG(1)) * (TME2(1) - TAVG(1))$
	T2SUM3 = (TME3(1) - TAVG(1)) * (TME3(1) - TAVG(1))
	TSUM(1) = (SOBT((T2SUM1+T2SUM2+T2SUM3))/2)/TAVG(1)
25	CONTINUE
	WRITE(8, 280) TITL
	WRITE(8, 280) DAT
	WRITE(8,280) HEADR
	WRITE(8, 240)
	WRITE(8, 169)
240	FORMAT(//' PEAK NUMBER', 12X. 'PEAK AREA', 10X
	C 'RETENTION TIME(MIN)'/)
	DO 26 I=1, NPEAK
150	FORMAT(/4X, 'AVG', 10X, G13.4, ' ', G13.4, 7X, G13.4, 1X, G13.4/)
	WRITE(8,288) AREA1(I), TME1(I)
288	FORMAT(22X,G13.4,16X,G13.4)
	WRITE(8,285) I, AREA2(I), TME2(I)
	WRITE(8,288) AREA3(1), TME3(1)
285	FORMAT(4X, 12, 16X, G13.4, 16X, G13.4)
	WRITE(8,150) AAVG(1), SSUM(1), TAVG(1), TSUM(1)
	WRITE(8,160)
160	FORMAT(' ***********************************
	C*************************************
26	CONTINUE
	END

APPENDIX B

Data Acquisition and Interface Circuits

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The monochromator interface circuit (encoder monitor). Figure B7.

