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A NEW CELL FOR RAPID ANODIC STRIPPING ANALYSIS A USER-INTERACTIVE COMPUTER PROGRAM FOR THE ANALYSIS OF ANODIC STRIPPING DATA

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A NEW CELL FOR RAPID ANODIC STRIPPING ANALYSIS\*

A User-Interactive Computer Program for the Analysis of Anodic Stripping Data

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BRIEF

This report presents major improvements in cell design to decrease the analysis time, in electrode selection and pretreatment to increase the stability of the paraffin impregnated graphite electrodes employed, in instrumentation, data processing, and in reagent purification.

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ABSTRACT

Reported is a cell designed specifically for high speed anodic stripping analysis. Lead, for example, is determined at the 1-ppb level within 10 min and with a precision of 5%. This time includes aliquoting, sparging, amalgam accumulation, scanning, and cell cleaning. In operation, the solution is forced into a thin film configuration 1-mm thick by rotating the cell, then sparged with nitrogen within 75 sec. The cell is stopped rotating; the solution returns to the floor of the cell; and, the amalgam accumulation step is effected within 7 min or less. A high-speed stirrer of new design is employed. A step and hold voltage ramp is used for the stripping scan. The stripping current is digitized directly employing the bipolar digipotentiogrator and the digital data are distributed in time in a pulse height analyzer operated in the multi-channel scaling mode. The stored data are transferred onto magnetic tape and are processed with a user interactive computer program which requires a CDC-6600 computer equipped with a TV-console, a teletype, and light pen accessories.

Two methods of purifying KCl supporting electrolytes are offered. One method employs the crystal adsorption phenomenon. The other uses an aluminum/mercury amalgam exchange in which electroinactive aluminum ions are exchanged for trace electroreducible ions.

## INTRODUCTION

The entire effort described here is directed first to the determination of lead and cadmium, and later to other metals amenable to stripping analysis, in ocean, bay, and river waters. This effort is but a small part of a large, nascent, environmental study capability being developed at LBL.

We were first attracted to the anodic stripping technique because of its reported high sensitivity for lead and cadmium coupled with the fact that no sample preparation or prior concentration was necessary. However, a review of the literature revealed that much improvement in the current methodology would be needed to decrease the time expended per analysis and thus to make the method attractive for the analysis of large numbers of samples. This report presents major improvements in cell design to decrease the analysis time, in electrode selection and pretreatment to improve the stability of electrode, in instrumentation, in data processing, and in reagent purification. The improvements suggested are based on experience gained in making over 1,000 scans.

Reported for the first time is a cell designed specifically for high speed anodic stripping analysis. Lead, for example, can be determined at less than the 1-ppb level within 10 minute total analysis time. This time includes aliquoting the sample, sparging the solution, accumulating the amalgam, the stripping scan, and finally cell cleaning. Such rapid analysis is made possible through the application of the highly successful technique previously employed to sparge the rotated mercury (1) and rotated platinum cells (2). The presented cell is a cylinder which is closed at the bottom, partially open at the top, and is mounted on a turntable rotated at 1,800 rpm in the apparatus previously described (1). This device is kinematically mounted on a platform

to which a rack and pinion equipped stand is attached. Mounted on the vertically moveable portion of this stand is the electrode assembly which includes the reference, auxiliary, and working electrodes, a stirrer of new design and a second 1,800 rpm motor to drive it, and a nitrogen inlet tube. This assembly can be lowered into or raised out of the cell at will.

In operation, the sample (only 15 ml are required) and a measured amount of mercuric ion are aliquoted into the cell, and the cell is started rotating. Centrifugal force causes the solution to lie in a thin film on the wall of the cylinder where it is sparged of oxygen within less than 75 sec. After sparging, the cell is stopped rotating and the sample solution returns to the floor of the cylinder. At this point, the stirrer motor is started and the amalgam accumulation step begins. Although the stirrer is operated at 1,800 rpm, thus stirring the solution very efficiently, no gas bubbles are drawn into the solution. The total analysis time required is about two thirds that employed to sparge a conventional cell of oxygen.

A comparison of the paraffin impregnated, mercury plated, graphite electrode (3) with the glassy carbon (4) and mercury coated nickel electrodes (5) is made. Reasons for the selections of the graphite electrode are given and pretreatment schedules are discussed. Co-deposition of mercury and sample constituents is recommended.

The digipotentiogrator previously described (6,7) is employed to control cell potential. This device is capable of a digital resolution of 0.5 MHz and a precision of 0.01%. The digital stripping signal generated with a step and hold voltage ramp is stored in a pulse height analyzer operated in the multichannel scaling mode. The data storage is time synchronized with the stepping of the

ramp. The stored data are transferred onto magnetic tape for data processing with a large, user-interactive, program written for the Control Data 6600 Computer.

Two methods for purifying reagent grade KCl are offered; one involves recrystallization; the other, amalgam exchange of electroducible impurities for aluminum ions.

#### EXPERIMENTAL

Instrumentation, Reagents, and Materials. The digital instrumentation used was described previously (6,7,8). The user-interactive computer program employed in processing and stripping data requires a computer in the Control Data 6600 class plus a television console with light pen and teletype accessories.

All water used was purified in the following manner. It was first singly distilled, passed through a 5-foot mixed-bed ion-exchange column, then fed into a quartz still. The distillate was collected in a well leached 4-gallon polyethylene carboy for storage prior to use.

A Beckman #39270 saturated calomel electrode was used as reference.

Saturated KCl solutions, purified of trace heavy metals as detailed below, were used as stock solutions for supporting electrolyte solutions and, in 1:1 dilutions, for filling the reference salt-bridge.

Spectrographic rods 12 inches in length and 1/8 inch in diameter, obtained from the National Carbon Company, were used to prepare the paraffin impregnated graphite electrodes. Ceresin, a "sticky" paraffin, was used for the impregnation. High purity nickel rod and strips of glassy carbon (Beckwith Carbon Company) were also employed in making electrodes. The construction details of these electrodes are given below.



Nitrogen of the same purity described previously (1) was employed in this effort. It was saturated with water prior to admitting it to the cell by passing it through a 3-stage scrubber to prevent sample evaporation and to minimize cell temperature fluctuations.

A 100- $\mu$ l aliquot of Masero Laboratory's high purity mercury metal was dissolved in dilute nitric acid. After dissolution the solution was evaporated to incipient crystallization to drive off excess acid and then, after being cooled, made to volume in 100 ml. This stock solution containing 13.4 mg  $\text{Hg}^{2+}$ /ml was used to prepare, by dilution, the working solutions employed.

Stock solutions of other cations used were prepared by dissolving the required reagent grade materials in appropriate acids, after evaporation of the excess acid, they were made to volume. Working solutions were prepared by dilution.

Purification of Potassium Chloride. Potassium chloride supporting electrolyte and salt-bridge filling solutions were purified of trace metals as follows. Sufficient water was added to 1-kg of reagent grade KCl crystals to dissolve 950g at room temperature ( $\sim 23^{\circ}\text{C}$ ). This was effected by magnetically stirring the mixture overnight in an HCl leached, new, Pyrex beaker covered with Parafilm. The following day, the saturated KCl solution was carefully decanted into a second leached beaker and the crystals remaining in the first container discarded. The decantate was covered with a raised watch-glass, then heated on a hot-plate to evaporate the water. When an estimated 20% of the solution remained, the crystals and supernate were transferred to a sintered-glass filter funnel and the supernate removed with vacuum filtration. The crystals were

then washed with small portions of ice-cold water, and transferred to a dry container for storage.

Preparation of the Electrodes. The graphite rods were impregnated by immersing them in molten ceresin contained in a large test-tube suspended in a boiling water bath. A vacuum was maintained over the melt to promote the rapid outgassing of the graphite. Although the outgassing was generally complete within 15 min, the vacuum impregnation treatment was continued for one half hour after the disappearance of gas bubble activity. Such rapid outgassing portends the production of good electrodes. Occasionally rods will be obtained which give up their adsorbed gasses only very slowly. One lot continued outgassing slowly for 3 days. The poor reproducibility and high background current characteristics of these electrodes rendered them useless.

After impregnation, the rods are withdrawn from the melt and, after being cooled, are stored in a dust free container prior to their being fashioned into electrodes. The rods are broken as needed into pieces 10-mm long, finely threaded, then screwed into the Lucite electrode holder described below. An assembled electrode is potted by dipping the end of the electrode containing the graphite rod into molten ceresin. After solidification, the potted graphite rod is rubbed against #200 emery cloth to bare the end of the electrode. This is followed with rubbing against #600 emery cloth. Finally, the resulting scrobiculate surface is polished to mirror smoothness by rubbing it against Whatman #541 filter paper. Other binder-free paper should serve as well. After washing with water, the electrode is ready for mounting in the electrodes assembly.

Strips of glassy carbon 1/8 inch wide were sawn using a diamond wheel, from a disc 6 inches in diameter and 1/8 inch thick. These strips were cut to 10 mm lengths. The resulting baguets were polished on all sides with diamond dust then cemented with epoxy resin into Lucite electrode holders similar to the one described below. The exposed glassy carbon end of an electrode was washed with water just prior to its use.

Nickel rod, 1/8 inch in diameter and 10 mm long, was finely threaded then screwed into the Lucite electrode holder described below. The nickel and holder was unitized by dipping into a Lucite glue. After being dried, the exposed end of the rod was polished by rubbing against #600 emery cloth. The electrode was anodized then cathodized as described for platinum in a proceeding paper (1), then thrust into mercury metal. The nickel surface will be immediately wetted with mercury. Excess mercury is removed, using a polyethylene spitzer connected through a filter flask to a vacuum line. If the electrode lies in disuse for some time it will be necessary to repeat the treatment just described.

Cell and Electrode Assembly Construction. The cell is constructed in the following manner. The wall of the cell is machined to the desired outside diameter from Lucite rod-stock then center bored to expose the interior. The inside is machined out leaving a lip at the top 7-mm smaller than the inside diameter. This lip serves as a solution retainer when the cell is rotated. The internal cylinder dimensions are 39-mm in diameter and 54-mm in length. After cleaning the cell in the manner previously described (1), it is attached with three screws to a copper turntable dimensionally identical to the one described in a previous paper, and mounted in the motor driver apparatus (1). The cell

is designed to give a film of solution ~ 1-mm thick upon rotating and thus requires 15-ml of solution.

The cell and drive apparatus is kinematically positioned on a base to which a stand is attached. See Figure 1. The vertically movable portion of the stand, equipped with a rack and pinion drive, serves as a support for the electrode assembly, stirrer, stirrer motor, and the nitrogen inlet tube. Figure 2 shows the spacial relations of the various probes with respect to one another. All glass probes were Desiccated to make them hydrophobic. The electrode assembly is situated concentrically with respect to the cell so it can be raised or lowered out of or into the cell at will. In its raised position, it permits aliquoting the sample into the cell, in its lowered position it serves as a cell cover. The base and stand are constructed from aluminum plate and the electrode assembly from Lucite plastic.

A packet of detailed drawings of this equipment will be sent upon request.

Stirrer Construction. A piece of Pyrex cane 5-mm o.d. is melted on one end to form a ball 13-mm in diameter. After being cooled, four grooves are cut into the ball, using a carbide wheel, at an angle of  $30^\circ$  with the ball stem. These grooves must follow the spherical surface at a constant depth and be symmetrical about the equatorial plane of the ball for a distance of  $45^\circ$  of the surface. A groove depth of 2-mm will suffice. After cutting the cane to the required length, the stirrer is fire-polished to eliminate the jagged edges of the grooves. After Desiccating, it is ready for use. Again see Figure 2.

In operation, the direction of the stirrer rotation must be such that the solution is forced downward.

Recommended Procedure. When the graphite electrode is securely mounted in the electrode assembly for the first time, polish it with several strips of Whatman #541 filter paper by pulling the paper back and forth across the exposed graphite surface. Use heavy pressure. This operation rounds off the sharp edge of the tip. Follow this with a light polishing using a soft tissue paper. It is now ready for use.

Aliquot 1-ml of a mercury solution containing 27  $\mu\text{g/ml}$  into the cell. Aliquot 15 ml of the water sample then, if the sample is of fresh water, 250- $\mu\text{l}$  of saturated KCl. Rack the electrode assembly down into the cell. Switch the cell motor on. Sparge the thin solution film with nitrogen at a flow rate of 3L/min or more. After 75-sec, turn the cell motor off and let it coast to a stop. The solution should drain clearly from the wall of the cylinder. If it does not, the cell must be cleaned again as described above. Switch the ball stirrer on. Impose a potential of -1.000 V vs. SCE on the cell and accumulate the amalgam for 7 minutes. Stop the stirrer 5-sec before the initiation of the scan. Scan from -1.000 V to +0.350 V in steps of 7.5 mV while simultaneously storing the digital data in the analyzer. If the sample characteristics are unknown, use a time dwell of 1-sec per channel and observe the current-time decay pattern for each potential step on the oscilloscope. It will do no harm to reduce the time dwell employed in the second scan if the solution conductivity is great enough to permit it. See the discussion below. Upon terminating the scan, transfer the data onto magnetic tape then rack the

electrode assembly up clear of the cell. Wash the probes with water. Buff the electrode lightly with a tissue paper. Suck the spent sample solution out of the cell employing a plastic spitzer connected through a filter flask to a vacuum line. Wash the cell out twice with water then aliquot first the mercury and next a second portion of the sample as described above. Add a sufficient quantity of the elements of interest to double the peak heights in an aliquot of 250- $\mu$ l or less. Proceed with this "spiked" sample as was just described above starting with the sparging step.

At the conclusion of the second scan, the electrode is polished with a strip of filter paper employing sufficient pressure to make a faint black mark on the paper followed by a light buffing with tissue paper. The electrode is now ready for the next analysis.

The calculations of the results are effected in this laboratory with a large computer in the manner outlined below. Since this a somewhat esoteric way of treating the data, it should suffice to say that any legitimate numerical or graphical means may be used to arrive at the analytical function of choice -- i.e., peak height or area -- used for the calculations of the results.

If it is desirable to make more than one standard addition in determining the sample concentration buff only with tissue paper between additions.

#### RESULTS AND DISCUSSION

The inherent high sensitivity of the anodic stripping method is well known; it has, in fact, been called "one of the most powerful electrochemical approaches to trace analysis" (9). Despite this accolade, the method as it now

exists suffers from one or more of the shortcomings listed in the introduction. Our solutions to these difficulties are detailed below.

The most time consuming step in the conventional anodic stripping method is the 15 or more minutes required to sparge a conventional cell of oxygen. In contrast, the presented methodology requires less than 75 sec owing to the incorporation of the highly successful technique developed and reported previously (1,2). In practice, the cell is rotated at 1,800 rpm; the sample solution is forced into a thin film lying on the wall of the cylinder; and, the sample is sparged with nitrogen at a minimum rate of 3L/min. Scans of the supporting electrolyte, employing a hanging mercury drop electrode and taken after 15 sec intervals of sparging indicates slightly more than 60-sec are required to free the cell of oxygen. These results are comparable with those obtained previously in the rotated coulometry cells. A large surface area to solution volume ratio is very conducive to high sparging rates.

The manner of stirring is one of the most important considerations in the design of an efficient cell but seemingly one of the least well studied. Poor stirrer design is reflected in the needless expenditure of time to accumulate the stripping amalgam. Sensitivity is usually compromised. Scores of examples exist in which the workers used nothing more imaginative than a magnetic stirring bar. When employing a paddle or magnetic bar stirrer, efficient stirring becomes progressively more difficult as the sample volume stirred becomes even smaller. At high rates of stirrer rotation, a vortex forms and frothing of the solution eventually follows. Vortex formation and frothing are detrimental in stripping studies because they can interrupt or insulate one or more of the electrical cell leads resulting in a loss of cell potential control.

Frothing is especially troublesome because one or more small bubbles can attach themselves undetected to the working electrode during the amalgam accumulation step thus partially shielding it from the solution. Unexplainably low results are then obtained. In contrast, the presented stirrer will not draw bubbles into the sample provided the solution level covers the ball.

The efficiency of the ball stirrer cannot be compared directly to the commonly used paddle or magnetic bar variety owing to the aforementioned difficulties; however, it has been used in pool type, controlled-potential, mercury coulometry cells with an efficiency some 10 to 20% greater than that obtainable with a rotated disc stirrer having the same diameter as the ball. The disc stirrer will not froth the solution stirred hence the comparison.

All working electrodes discussed below are situated parallel to the floor of the cell and, at the same time, in the strong downward flow of the stirred solution. This orientation prevents the attachment of any adventitious bubbles to the electrode surface and permits the in situ co-deposition of the mercury and sample without the collection of hydrogen bubbles initially formed at the electrode because of initially poor hydrogen over voltage characteristic.

To form a basis for understanding the selection of the electrode type recommended, it is necessary to explore some of the principles underlying the stripping method.

The anodic stripping technique can be viewed as a very efficient electrochemical extraction in which the electroreducible substance is first concentrated in the mercury phase to a level much greater than it exists in solution. To optimize the ratio of the stripping signal to background current,



it is desirable, therefore, to keep the ratio of the mercury volume to solution volume small. On the other hand, viewing the stripping technique as a coulometric process, the time rate of accumulation of the amalgam (time efficiency of extraction at a constant stirring efficiency) improves as the electrode area to solution volume ratio becomes large. The mercury volume employed, however, is necessarily large. These two underlying principles are, from a practical standpoint, inimical; thus, any proposed stripping electrode represents a compromise between some acceptable level of sensitivity and the time one is willing to spend accumulating the amalgam.

One of the first electrodes used was a hanging mercury drop (10,11). This electrode was not entirely satisfactory for analytical work because the rather large mercury volume employed resulted in prolonged amalgam accumulation times, necessitating the use of large sample volumes. Scan rates which were consistent with good sensitivity gave poor resolution. To reduce the mercury volume employed and thus to circumvent the aforementioned difficulties, several thin mercury film-type electrodes were offered (5,12,13,14). These electrodes differed only in the metal substrates used. As expected, the difficulties cited for the hanging mercury drop electrode were ameliorated, however, the amalgam appeared to alloy with the metal substrates of these film electrodes (12). Some investigators found poor reproducibility (12).

In an attempt to overcome the problems associated with the substrates, Matson and co-workers developed a mercury plated, paraffin impregnated, graphite electrode (3). This, in our opinion, is probably the best electrode ever developed for stripping analysis, however, we differ with them on several experimental points. The previous workers recommended using a "good grade of paraffin".

Paraffin denotes a large group of hydrocarbons which differ in melting ranges and physical characteristics. Paraffin acceptable for electrode impregnation will not crystalize on being cooling and will tenaciously cling to a glass rod after solidification. If it fails to meet these tests, it will be unsatisfactory. It will have a poor adherence quality and crack and separate from the substrate upon solidification. Ceresin has these favorable characteristics and is thus recommended.

If the electrode surface is left unpolished, as suggested by our predecessors, the stripping peak heights obtained on the same solution will initially decrease for several successive owing to the sloughing off of the rough surface grains eventually resulting in a smooth surface. The graphite thus appears to electropolish just as does metals on potential cycling. The progress of this electrode area reduction has been observed upon microscopic examinations made between runs. A final polishing step against a binder free paper renders the electrode immediately useful.

The previous workers indicated that an electrode once plated with mercury at  $-200$  mV vs. SCE was reuseable indefinitely provided the plate was not stripped off. It was our experience that an electrode prepared in this way gradually lost sensitivity on each succeeding scan of the same solution as measured by a decrease in lead peak height. Also, the background current increased on succeeding scans. Co-deposition of the mercury and sample circumvents these problems.

At a fixed amalgam accumulation time, the peak height of an indicator ion, such as lead, should increase with increasing mercury concentrations until all the electroactive sites on the electrode are covered with mercury.

This was confirmed. When the mercury concentration was increased from 0.5 to 9 ppm in a series of studies in 0.067M KCl, the lead peak increased up to a mercury concentration of 4 ppm, but the reproducibility deteriorated from 5% at the 1-2 ppm level to 20-30% at the 9 ppm level.

Previous investigators suggested that poor reproducibility obtained in chronopotentiometric studies was due to the ragged penetration of solution into the graphite electrode with time and recommended treating the surface with a wetting agent prior to use (15). In the present application, since the electrode was polished to restore its initial condition after each scan, it seems more likely that ragged penetration of the plated mercury into the electrode was occurring. The sample solution does appear to wet the electrode on long standing. The contact angle the solution makes with the electrode is considerably reduced after the electrode has been immersed for some time. Polishing or buffing the electrode between scans maintains a high contact angle.

Beads of mercury metal, reported previously (3), were not visible on the electrode surface even under a magnification of 230X. Mercury was, nevertheless, present on the electrode because a mercury peak was obtained when the electrode was returned to the cell and stripped. From the foregoing studies, it is recommended that only sufficient mercury be added to make the solution analyzed 1- to 2-ppm on final dilution. Also, the scan should be terminated at a potential sufficiently positive to assure the stripping of the plated mercury. In view of the penetration of solution into the electrode, it is further suggested that the electrode assembly be racked out of the cell and the electrode washed, dried and polished immediately after each scan or at day's end. The electrode must never be treated with a wetting agent, for the electrode is then endowed with a chemical memory. This is very undesirable for stripping work.

To complete the study, it is necessary to report some artifacts observed using the graphite and glassy carbon electrodes and also to compare these electrodes with the mercury-nickel substrate electrode.

Anodic stripping has been used periodically for some three years prior to the sustained effort reported here for the trace analysis of reagent grade chemicals and solutions of the transuranium elements for lead. During this time, electrodes were fashioned from several lots of graphite rods. In addition to the variable impregnability of the rods with ceresin noted above, some of the electrodes exhibited a cathodic going indentation at  $-0.2$  V vs. SCE provided they were not resurfaced between each scan as suggested in the recommended procedure. This indentation appeared after the electrode was used some 10 to 20 times. Prior to the appearance of this anomaly, a steady increase in the signals of the sample constituents was observed for the graphite electrode just as was described previously for the glassy carbon electrode. See Table II, Reference 4. At the first appearance of the anomaly, a decrease in sample sensitivity was noted. See Figure 3.

A new electrode fashioned from a lot having a propensity for this behavior could similarly be induced to exhibit the cathodic indentation if it were anodized at  $+1.0$  V vs. SCE prior to its use. The cathodic indentation increased in depth and width with increasing anodization time. Any peaks which might otherwise have appeared within the indentation region were obliterated and peaks located at more negative potentials than the indentation were much reduced in height. The nature of this indentation was not known. Normal behavior could be restored by simply re-surfacing the electrode.

The glassy carbon electrode (4) was similarly investigated. The haze or film, presumed to be mercury by the previous worker, formed on the glassy

electrode used in this study upon potential cycling. The film was easily removed by wiping the electrode with tissue paper. Subjecting this electrode to a potential of +1.0 V vs. SCE for 15 min, however, resulted in a heavy coating which, while to the eye appeared to be removed on wiping, was still electrochemically present. Many spurious peaks and indentations were observed when this oxidized electrode was subsequently used for stripping analysis. The electrode could be returned to its normal behavior only by extensive re-polishing of the surface with diamond dust. Whether this behavior is universal is not known. Glassy carbon from only a single source was available for this work. There appears, however, to be no basis for selecting glassy carbon over graphite for electrode material. Glassy carbon is very expensive.

A comparison of the graphite electrode with the mercury-nickel substrate electrode gave further evidence that electroreduction of the mercury and sample constituents was occurring inside the graphite electrode. See Figure 4. The final current rise which signals the stripping of the mercury film on the nickel substrate begins at  $\sim -0.2$  V vs. SCE in the chloride solution employed. The stripping of mercury from the graphite electrode does not begin until  $> 0.0$  V vs. SCE. If the mercury were plated onto the graphite surface in more than a mono-layer, the stripping behavior should be the same as for the nickel substrate electrode. The fact that the final current rise is delayed some 200 to 300 mV further suggests that the mercury resides inside the electrode and possibly behind or inside of a membrane since it does not appear to "see" the high chloride concentration which exists in the bulk of the solution.

Another important difference exists. Zinc is readily determined with the mercury-nickel electrode but not with the graphite electrode. The latter

electrode is insensitive to zinc at levels as high as 200 ppb in a KCl supporting electrolyte. This lack of sensitivity has been noted by two previous workers (4,11). If, as might be inferred from the evidence given, the graphite electrode functions as an ion-selective membrane to the exclusion of zinc ions, and if these properties could be altered at will, other important uses for the graphite electrode would follow immediately. A search for these surface functional groups will be made with ESCA.

Just as was found by Florence (4), the peak heights obtained on the first scan of the same solution are somewhat lower than the peak heights observed on successive scans. He prefers to employ the same sample aliquot for recording the sample response and the sample plus standard addition response. This preference is probably based upon the 10 to 15 min sparging time required for his cell. He thus employs a pre-analysis amalgam accumulation-stripping cycle prior to the actual analysis to "condition the electrode". It appears that this conditioning is more related to the adjustment of the oxidation states of the mercury ions than to the conditioning of the electrode. If the sample solution is first shaken with mercury metal prior to running, the conditioning step will be unnecessary. Implementation of this finding will speed up the analyses for those who do not have the rapid sparging capability afforded by the rotated cell. The foregoing is the reason the taking of a new sample for each scan is suggested in the recommended procedure.

A simple dc voltage ramp is generally selected to effect amalgam stripping. It is well known that stripping peak height, hence sensitivity, is related either directly (5) to the scan rate when employing a thin film electrode or to the square root of the scan rate when using a hanging mercury

drop electrode (16,17). The former electrode is preferable for analytical work since the background potential charging component is approximately linear over the potential range used in stripping analysis. Conventional methodology, therefore, requires that rather fast stripping scans be employed to increase the method sensitivity. Unfortunately, loss of resolution for adjacent peaks occurs at very high scan rates owing to tailing because the electrode never reaches equilibrium (limited reversibility) until the end of the scan. Potential location of the current peak can also be shifted to more anodic potentials at high scan rates. Peak tailing complicates the interpretation of the background current making the measurement of the peak heights uncertain.

The presented approach employs a potential step and hold ramp, thus allowing the stripping scan to be treated as a collection of discrete coulometric events. The potential step height selected is generally a compromise between sensitivity and resolution. The greater the potential increment, the greater will be the sensitivity; however, the resolution will be diminished. The hold time selected is that which permits the largest faradaic and capacitive current spikes encountered in the scan to exponentially decay to the background level. See Figure 5. The decay times encountered are short since the thin film electrodes are preferred for this work.

In practice, a hold period of from 0.2 to 0.8 sec is employed for each 7.5 mV potential step. The exact time interval selected depends upon such factors as the water salinity, hence conductivity, and upon the concentration level of the most concentrated element determined, mercury excluded. Allowing sufficient time to pass after each potential step assures the virtual attainment of equilibrium at the electrode thus considerably simplifying the programming

task of extrapolating the background beneath the peak. Furthermore, the highest resolution for the potential increment selected is attained under these conditions and the peak location does not shift.

Considering the foregoing, it might be argued that there is no difference in the results obtained using a dc ramp over those obtained using a step and hold ramp provided both ramps scan the same potential interval in the same time interval. An equal degree of reversibility would be obtained. This is true. If, however, a time twice as long as that necessary for reversibility were employed, the peak heights obtained with a step and hold ramp would remain the same because the same potential step height is retained whereas the results, as measured by the peak heights for the dc ramp would be lowered by a factor of two. This difference is not trivial. The presented approach permits the operator to make a decision as to how long a time dwell interval is needed by observing the current decay after each potential step on the oscilloscope display. Employing a dc ramp, the operator must decide upon the proper scan velocity through trial and error.

The stripping peaks in a single sample can vary by a factor of 100 or more in height. Analog signal recording would require separate scans for each peak varying by a factor of ten or less. Furthermore, unless the peak sought is near the open circuit potential of the cell (W.E. vs. SCE), the recorder offset must be carefully adjusted. Once the stripping signal is recorded in analog fashion, no further data processing is possible. The measurement of the peak height is subjective because the extrapolated background current beneath the peak is almost never a simple linear function.

The high digital resolution and the 0.01% precision, which the system employed is capable, coupled with the digital storage of the stripping signal,



obviates the need for rerunning samples containing elements differing by factors of ten in peak height. Any portion of the stored sweep can be expanded to full scale after the fact for visual inspection using the analyzer display system. See Figure 6. And, since the stored data can be transferred onto magnetic tape, further data processing with a computer is possible.

TVFIT, the program developed to deal with anodic stripping spectra, is a user interactive package of routines which may be operated in either of the two LBL Control Data 6600 computers. The basic operations performed include background current fitting under single or convoluted double peaks, generation of calibration curves from a series of standard spectra, the determination of the concentration of an unknown sample from previously generated calibration curves, and the deconvolution of overlapping peaks. At present, the program can treat 256-channel spectra containing single or double peaks. It could easily be expanded to meet other requirements in the anodic stripping program of study or modified to treat peak spectral data generated with other kinds of instruments which will be introduced into the ecology program. Figure 7 is a schematic of the overall job flow and Figure 8 is a flow diagram of the program.

To initiate a computer run, a 7-track magnetic tape containing the day's recorded spectra is submitted to the computer center. Alternatively, previously run data, stored in the CHIPSTORE library, can be copied onto a disc file for processing. A deck, consisting of only a few cards required to control the job, is read into a card reader attached to the CDC-6411 computer. These card images are retained on an associated disc, until being transferred to a disc attached to one of the 6600 computers. When the job is executed, the 6600 is instructed to fetch the main program and its associated subroutines from the

data cell library. This program, which amounts to several thousand card images, is loaded into core, preprocessed for any changes, and is then executed.

When execution begins, the program is in the calibration mode. The program requests a starting spectrum number via a light-pen message displayed on the TV screen of the VISTA console. The operator responds by teletyping in the requested information. Upon finding the requested spectrum, it is loaded into core and is displayed in its entirety on the TV screen. The user indicates, by means of a light pen, the boundary markers before and after the peak or peak set. These markers designate the points at which he wishes the background fit to begin and end. Only the portion of the spectrum indicated by these markers is displayed full scale on the console screen. If two overlapping peaks are to be treated, the user must, in addition to selecting the boundary markers, indicate the peak channel numbers, again using the light pen. To satisfy the next program request, the name of the element represented by the peak entered via teletype.

For a single peak, the program calculates then displays the least-squares fit of the extrapolated background beneath the peak using the previously designated boundary markers plus three additional channels to the right or left of the right or left marker, respectively. Three additional channels are all that are deemed necessary for the calculation of the background in view of the virtually noise-free spectra obtained using the digipotentiogrator. See Figure 9. The program is allowed to fit up to a third order polynomial if, for example, an inflection point is required for the best fit. Although the same boundary markers are retained for each succeeding spectrum in the calibration series, the polynomial order is free to vary with changing background conditions to produce the best least-squares minimization fit.

The numerically integrated peak area is held in memory after each fit. Upon indicating the termination of a calibration series with a light-pen message, the program then requests a concentration value for each spectrum processed. After supplying this information via teletype, the program calculates, by least-squares, the equation for the linear calibration curve and displays this along with the plot of the equation on the TV-console. The equation intercept is the blank concentration. For each succeeding spectrum called up, the program will now report the peak area and the concentration as measured against the previously calculated calibration curve. Initiation of a new calibration run destroys the old calibration curve.

In principle, the manner of treating two overlapping peaks is similar to that used for single peaks. A calibration series is made, using a set of standards, followed by a non-calibration series, in which the results of the calibration run are employed to determine sample concentrations. In practice, however, there are several complications. Since it is necessary to obtain the area under each peak as though it were by itself, a best fit is made to the pair using a sum of two gaussian functions. Once this is done, the background is subtracted and each peak area calculated by numerically integrating its gaussian. See Figure 10. From this point on, the program simultaneously carries on double calibration runs. Once the calibration curves are established, the program fits gaussians to each sample spectrum, and the two concentrations are calculated from the two calibration curves.

From the foregoing exposition, note that, first, the program is subjective only to the extent that the user is permitted to select boundary markers and to indicate whether the fit is to be made to one or to two peaks. The background

fitting and peak area integration processes are wholly objective. This is an important consideration if unskilled help is enlisted. Second, very little user training is required to execute the program, and third, the spectrum can be processed at a rate exceeding 3,000 per hour with a visual check. In fact, the data processing could be fully automated by by-passing the VISTA routines if experience proves that day-to-day samples from the same source do not vary appreciably with respect to background or peak channel considerations.

Peak area rather than peak height is selected as the analytical function of choice because it is useful for processing stripping data from solid electrodes (18,19) as well as from the amalgam electrodes used in this work.

The reproducibility attainable with the graphite electrode is limited more by the suggested polishing schedules employed than by the instrumentation used. If, for example, the electrode is polished with the filter paper between each scan, a relative standard deviation of 15% is obtained using the recommended standard addition method. This deviation is found for lead at both the 1- and 10-ppb levels. If, on the other hand, the electrode is polished with filter paper, then buffed with tissue paper prior to the first scan, then with tissue paper alone prior to the second scan, the relative standard deviation is only 5% at the 1- and 10-ppb lead levels. If the graphite electrode did not suffer from the drawbacks discussed above and were thus perfectly stable, a precision of 1% or better would be attainable at the 1-ppb level of lead employing a 7 min amalgam accumulation time. Similar results are found for cadmium.

The standard addition technique is recommended in the analysis of natural waters. The introduction of complexing agents from human or industrial sources can affect the stripping peak heights and potential locations just as they can

affect polarographic wave heights and half-wave potential locations. For this reason, development of standard calibration curves in the laboratory employing reagent grade chemicals for use on samples obtained in the field should be discouraged.

Although a program exists to deconvolute overlapping peaks, a situation has never been encountered in natural waters which required its use. The precision obtainable for peak pairs depends upon the degree of over-lap, the relative peak heights, and upon the complexity of the background fit. The calculation of the standard deviation for each peak is complex and is treated in standard texts on statistics.

One of the most difficult problems associated with stripping analysis and one which generally has no simple or unique solution is the purification of the reagent grade chemicals employed as supporting electrolytes. This problem of purity and not the inherent sensitivity of the method is the limiting factor in the efficacy of the procedure. Several solutions to the problem have been proposed, none of which is entirely satisfactory. Ion-exchange is poorly effective because the major cations or anions in a supporting electrolyte solution have some exchange affinity and thus greatly reduce the resin affinity for the offending ions which are typically present at the parts per billion level (20). Controlled potential coulometry, while effective, is slow and requires batch-wise treatment of rather small portions of solution (21). Solvent extraction can be used to advantage, but since the extractant is usually a strong complexing agent employed in excess, one faces the problem of completely removing it after the extraction. Negative blanks owing to the masking of the element determined are more troublesome than the positive ones encountered before the extraction.

The purification procedure recommended for KCl is an adaptation of a crystal adsorption phenomenon observed many years ago by workers employing radio-tracers produced from the decay of radium sources (22,23). A general conclusion of these workers, as stated by Sandell (24), is that if the trace component is a cation, the cation of the predominate crystal phase should have an ionic radius near that of the former. Thus, essentially, all the lead, cadmium, and thallium impurities are adsorbed onto the surface of the excess KCl crystals. The method is much more effective, if the dissolution is carried out at room temperature. Initial dissolution of the crystals with heating followed by prolonged cooling to permit the gradual formation of crystals seems less effective in removing the trace heavy elements, although the same degree of separation should be approached in time. The optimum excess crystalline KCl is 5-10% of the total KCl used (24), however, a much wider range can be tolerated. See Table I. Electroactive substances such as copper and zinc are held in the solvent phase. This is the reason for the evaporation of the saturated KCl solution to a small volume followed by vacuum filtration in the recommended procedure. The filtration step removes much of the copper and zinc. The recovered crystals are purer by a factor of 20 to 30 than the starting material and no foreign substances have been introduced.

Other possible supporting electrolyte salts:  $K_2SO_4$ ,  $NH_4NO_3$ , and  $KNO_3$  were found to contain 257, 144, and 280 ppb lead on a solute basis, respectively. No purification procedures were developed for these salts but, as was illustrated with KCl, one must not assume that recrystallization necessarily gives a purer product.

Amalgam exchange of trace electroactive ions for electroinactive aluminum ions is another method briefly investigated for purification of neutral

or slightly basic supporting electrolyte solutions. A saturated aluminum/mercury amalgam develops a potential of  $-1.535$  V vs. SCE in a saturated KCl medium at  $23^{\circ}\text{C}$ . Shaking such an amalgam with a portion of an unpurified, nitrogen sparged, supporting electrolyte solution adjusts the oxidation state of all redox couples to  $-1.535$  V in a short time since the amalgam breaks up into myriad droplets on being shaken. The solution volume to amalgam (electrode) surface area is therefore very favorable when viewed as a controlled-potential coulometric process. The removal of aluminum hydroxide formed, owing to the slow reaction of the amalgam with water, presents some problems. Centrifugation seems to be the simplest means of removing the precipitate. Although this method is capable of producing solutions containing  $< 1$  ppb lead, it is a batch-wise process relegated to the treatment of small solution volumes which require further manipulation to remove the excess aluminum. For these reasons, it is unattractive as a general procedure, but available if needed.

#### FUTURE WORK

Isotopic dilution mass spectroscopy has long dominated the field of trace analysis at the parts per trillion levels. When one considers the 1-liter and more sample volumes spectroscopists often employ, there is no practical reason why anodic stripping could not be made competitive, provided it too could be modified to deal with large sample volumes. It seems relatively simple to devise a flow-cell which would permit the attainment of such low concentration levels. Such a cell will be reported in the future. It is anticipated that a sample throughput many times greater than the 1 to 3 analyses per day now attainable with mass spectroscopy could be achieved.

Work is now underway to determine available lead and cadmium in soil samples using a hot KCl extraction. Available or free lead ion is the noxious component in soils germane to living systems. Fixed or insoluble lead is not.

It is currently popular to determine lead and other elements in air collected on filter papers by neutron activation or x-ray fluorescence. The success of long-term studies using such a collection scheme depends upon the filter efficiencies being invariant from lot to lot. Determination of the relative efficiencies could easily be accomplished by drawing the filtered air through several bubblers following with the analysis of the bubbler contents for lead.

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LITERATURE CITED

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- (1) R. G. Clem, F. Jakob, D. H. Anderberg, and L. D. Ornelas, *Anal. Chem.*, 43, 1398 (1971).
- (2) R. G. Clem, *ibid.*, p. 1853.
- (3) W. R. Matson, D. K. Roe, and D. E. Carritt, *ibid.*, 37, 1594 (1965).
- (4) T. M. Florence, *J. Electroanal. Chem.*, 27, 273 (1970).
- (5) D. K. Roe and J. E. A. Toni, *Anal. Chem.*, 37, 1503 (1965).
- (6) W. W. Goldsworthy and R. G. Clem, *ibid.*, 1718 (1971).
- (7) W. W. Goldsworthy and R. G. Clem, *ibid.*, in press.
- (8) R. G. Clem and W. W. Goldsworthy, *ibid.*, 918 (1971).
- (9) R. J. Joyce and C. C. Westcott, *Symposium on Trace Char.*, NBS (1966).
- (10) H. Gerischer, *Z. physik. Chem.*, 202, 302 (1953).
- (11) W. Kemula, Z. Kublick, and Z. Galus, *Nature*, 184, 1795 (1959).
- (12) K. W. Gardiner and L. B. Rogers, *Anal. Chem.*, 25, 1393 (1953).
- (13) T. L. Marple and L. B. Rogers, *Anal. Chim. Acta*, 11, 574 (1954).
- (14) R. Neeb, *Z. Anal. Chem.*, 180, 161 (1961).
- (15) P. J. Elving and D. L. Smith, *Anal. Chem.*, 32, 1849 (1960).
- (16) W. H. Reinmuth, *ibid.*, 33, 185 (1961).
- (17) I. Shain and J. Lewinson, *ibid.*, p. 187.
- (18) S. S. Lord, R. C. O'Neill, and L. B. Rogers, *ibid.*, 24, 209 (1952).
- (19) M. M. Nicholson, *ibid.*, 32, 1058 (1960).
- (20) A. Ringbom, "Complexation in Analytical Chemistry", Chapt. 6, Interscience, New York (1963).
- (21) L. Meites, *Anal. Chem.*, 27, 416 (1955).

- (22) H. Kading, Z. physik Chem., A162, 174 (1932).
- (23) O. Hahn, "Applied Radiochemistry", p. 103, Cornell Univ. Press, Ithaca (1936).
- (24) E. B. Sandell, "Colorimetric Determination of Traces of Metals", pp. 30-33, Interscience, New York (1959).

Table I. Effect of Conditions on the Purification of KCl

g KCl/100 ml H <sub>2</sub> O	g KCl undissolved	ppb Pb in supernate <sup>a</sup>
150	120	35
100	70	17
50	20	5.2
35	5	4.0
30	0	130 (Starting Material)
60 <sup>b</sup>	30	28
—	30 <sup>c</sup>	1.7

All samples prepared by stirring 21 hr. at room temp. (~ 23°C).

<sup>a</sup>Calculated on solute KCl basis.

<sup>b</sup>Solution heated to boiling then allowed to cool to room temperature overnight.

<sup>c</sup>Analysis of a sat'd KCl solution prepared in 1965.

## FIGURE CAPTIONS

Fig. 1. The Rotated Apparatus and Electrode Assembly.

Fig. 2. The Electrode Assembly.

Reflected in a mirror positioned beneath the assembly are counter-clockwise: the glass ball stirrer, the platinum counter-electrode, the nitrogen inlet tube, the ceresin impregnated graphite electrode, the reference salt-bridge, and the sample port.

Fig. 3. The Cathodic Indentation.

upper trace: A normal stripping polarogram. The peak is due to the presence of copper.

lower trace: The cathodic indentation.

Fig. 4. A Comparison of the Graphite Electrode and Mercury-Nickel Substrate Electrode.

upper trace: The mercury-nickel substrate electrode response.

lower trace: The ceresin impregnated graphite electrode.

Conditions for both scans: 7 min amalgam accumulation time,  $\Delta E = 7.5$  mV/step,  
 $\Delta t = 0.8$  sec/step.

Solution for both scans: 0.4M KCl containing 27  $\mu$ g Hg/16 ml total sample volume.

Note the much greater sensitivity for the lower trace.

Fig. 5. Current-Time Decay Curves for the Stripping of Pb at the 2-ppb Level.

Solution: 0.4M KCl containing 28  $\mu$ g Hg/16 ml of sample.

Conditions:  $\Delta E = 7.5$  mV/step,  $\Delta t = 0.8$  sec/step,  
analyzer advance rate = 100 channels/sec,  
E start = -600 mV, E stop = -492 mV.

Fig. 6. Digital Display of Anodic Stripping Scans.

Lower trace shows the complete scan. Note the barely discernible peaks of cadmium, lead, and copper and finally the very large mercury peak.

Upper traces are the digitally expanded peaks barely visible on the lower trace.

Solution: 0.4M KCl containing 27 ppb Pb, ~ 10 ppb Cu, ~ 4 ppb Cd, and 27 ppm Hg. Total volume is 16 ml.

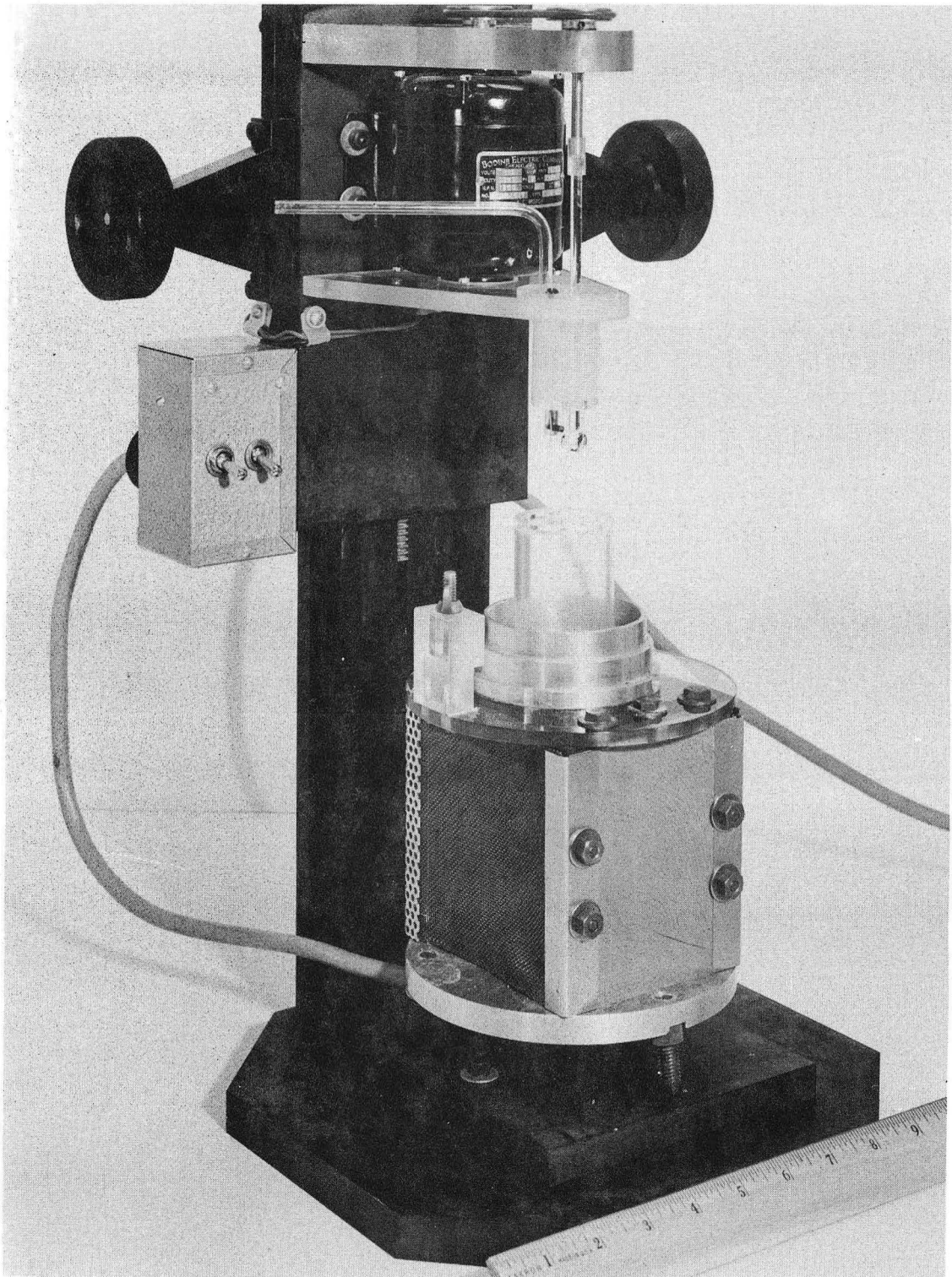
Conditions: See conditions for Figure 4.

Fig. 7. Schematic of the Overall Job Flow.

Fig. 8. Flow Diagram of the Stripping Analysis Program.

Fig. 9. Computer Display of a Lead Peak and the Calculated Background at the 1-ppb Level in 0.4M KCl.

Fig. 10. Computer Display of a Two Peak Fit to Cd and Pb and the Calculated Background Fit at the 13 and 42 ppb Levels, Respectively.

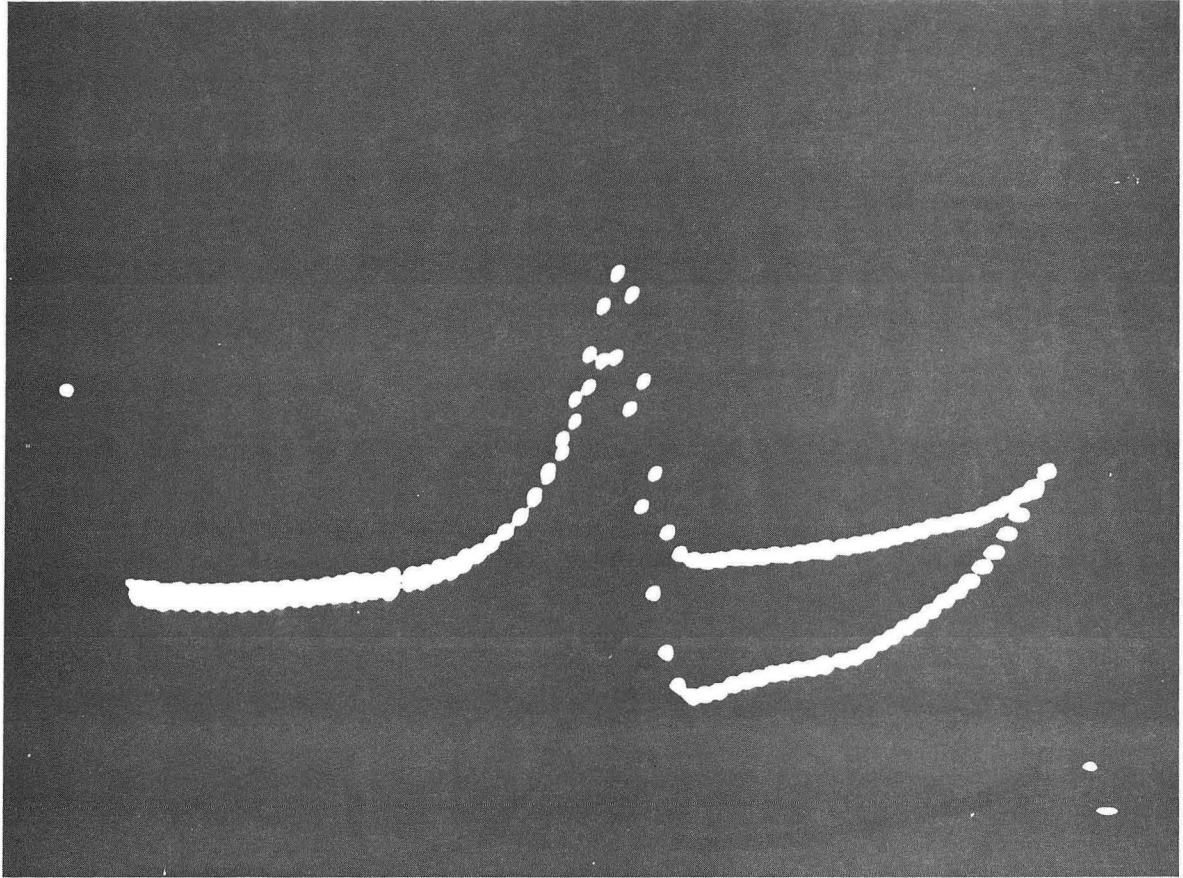


XBB 724-2255

Fig. 1



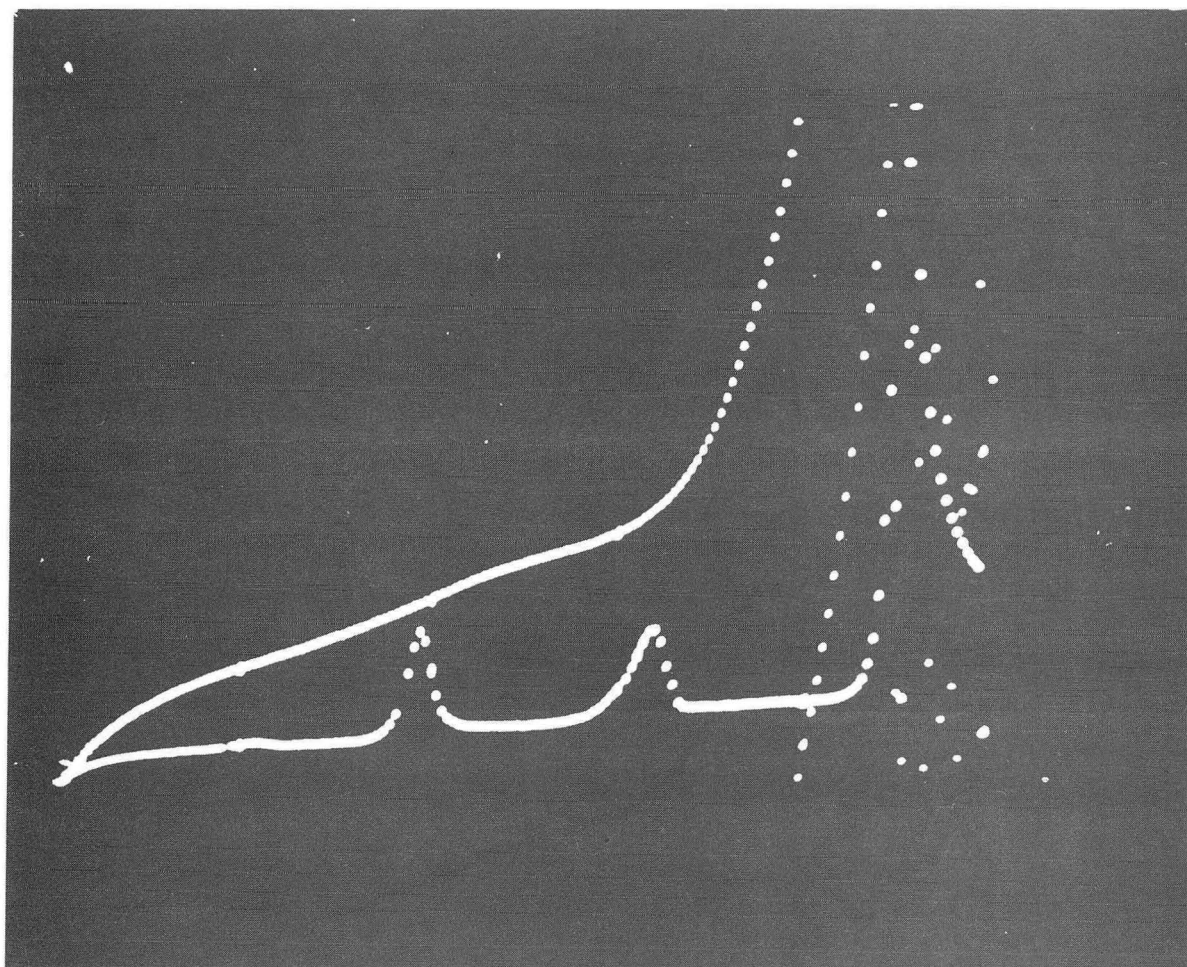
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XBB 726-3240

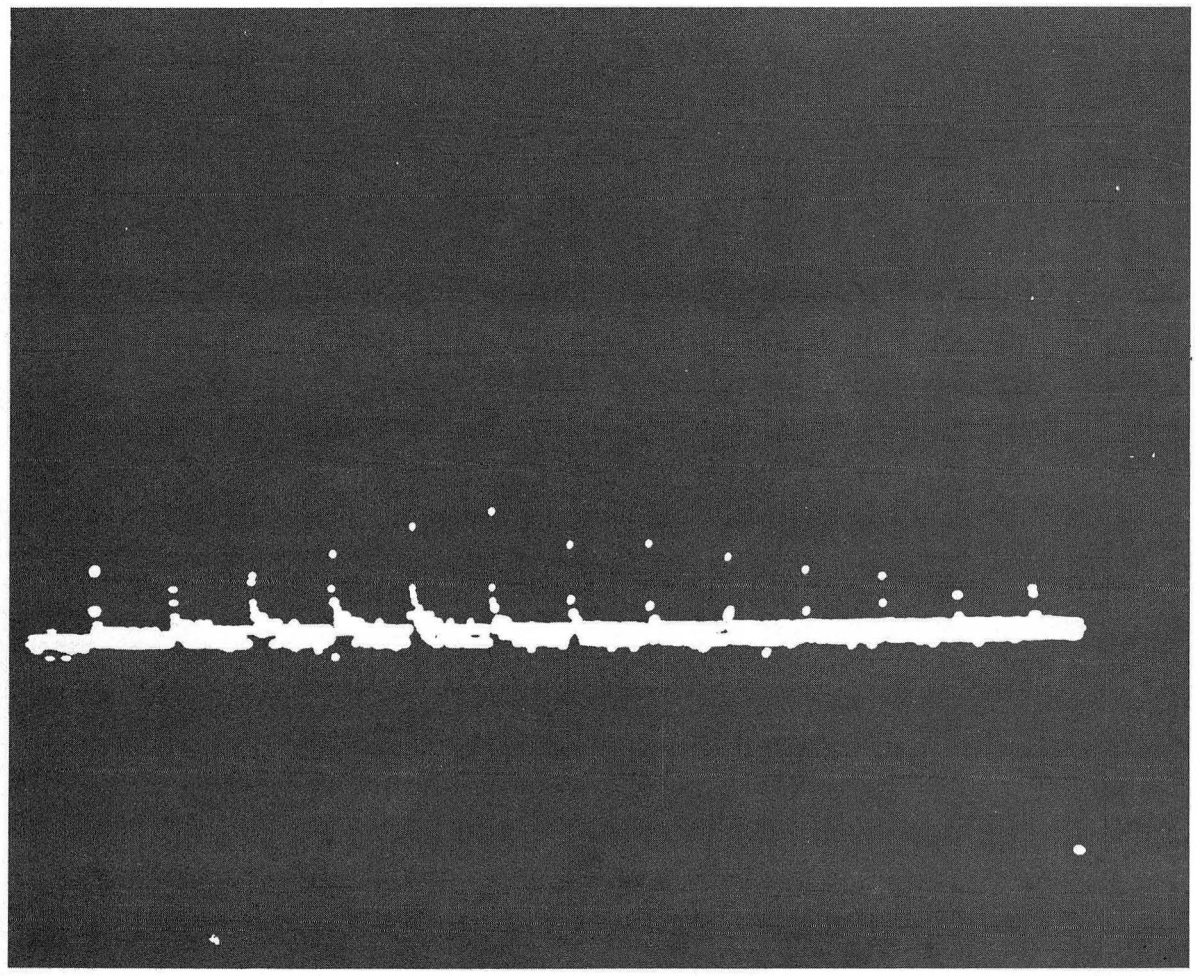
Fig. 3





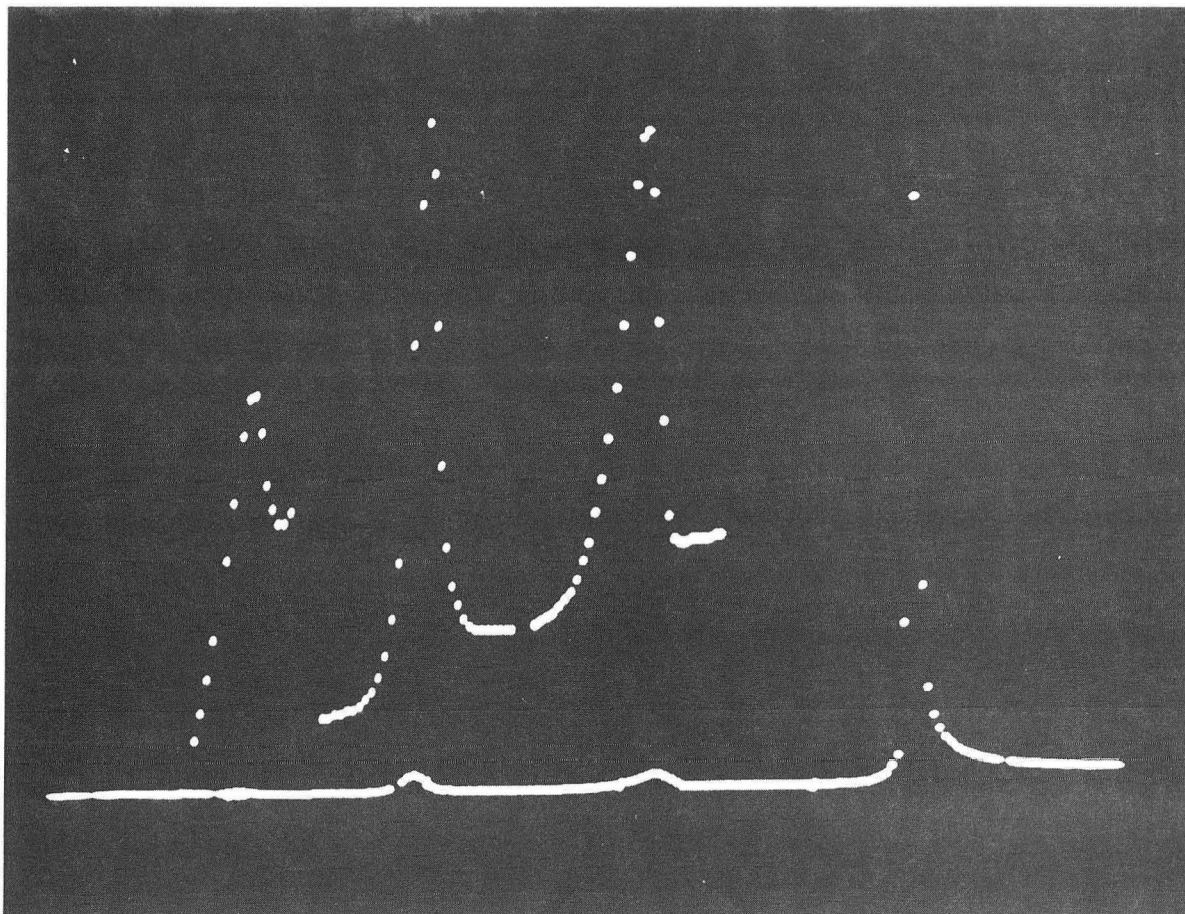
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Fig. 4



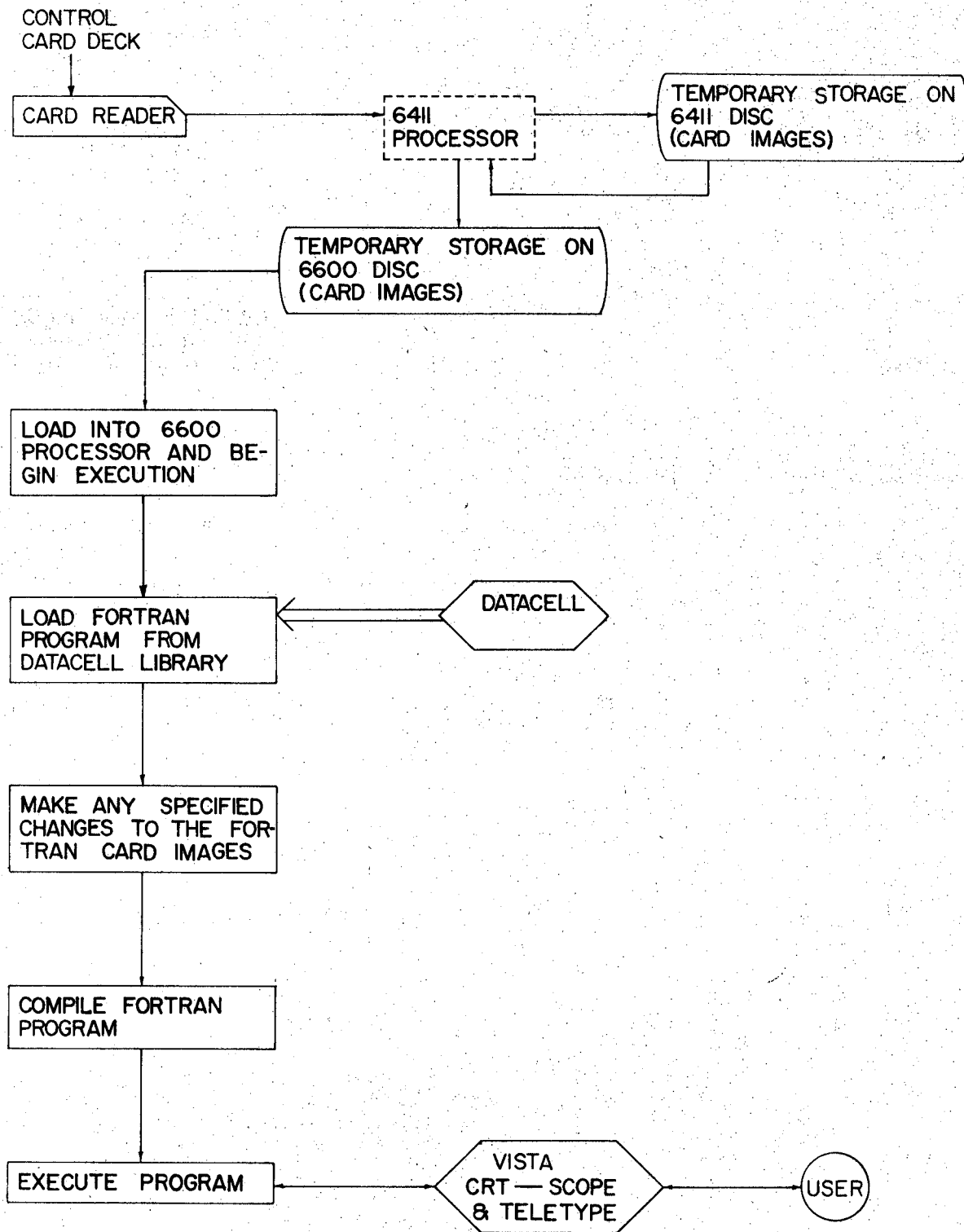
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Fig. 5



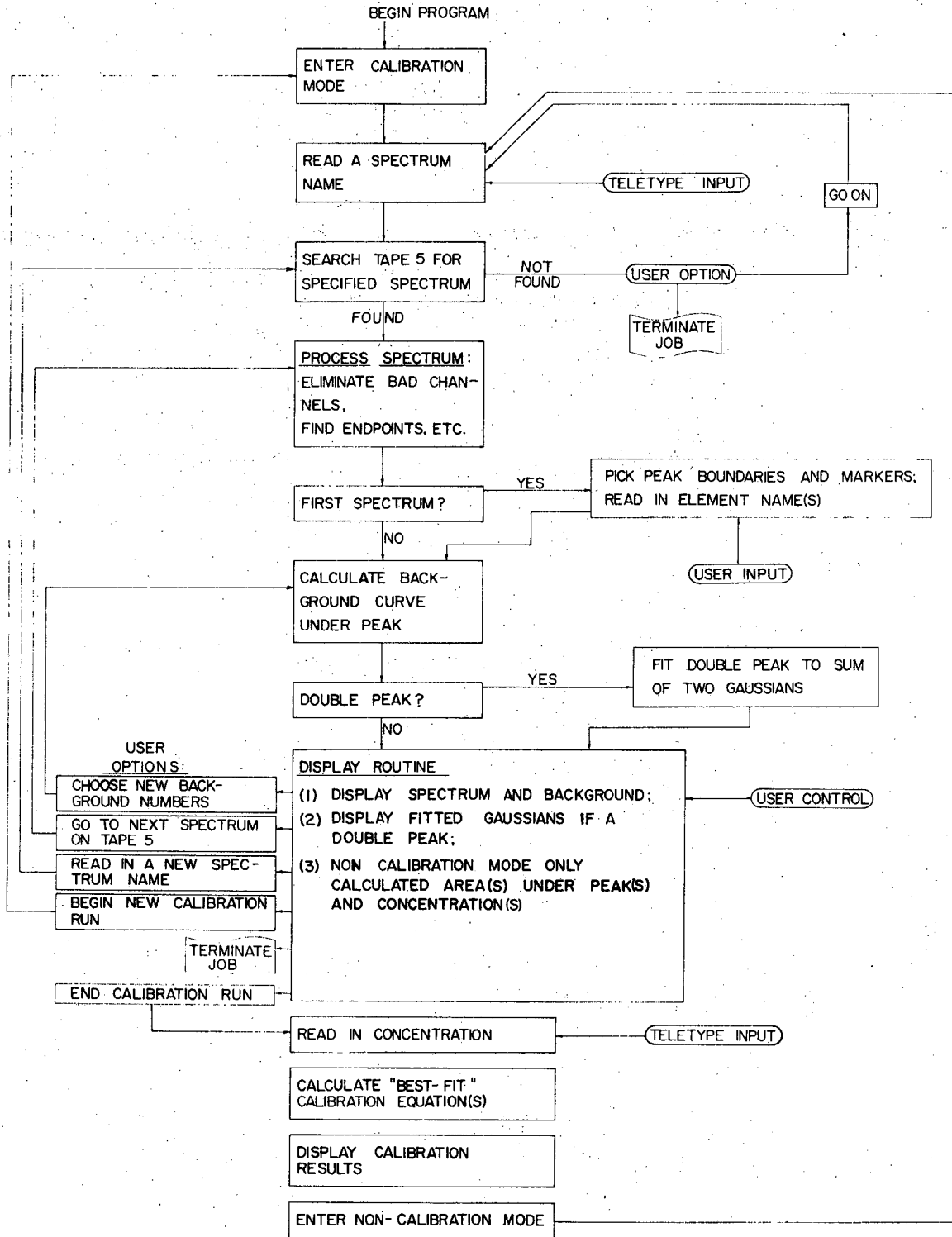
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Fig. 6



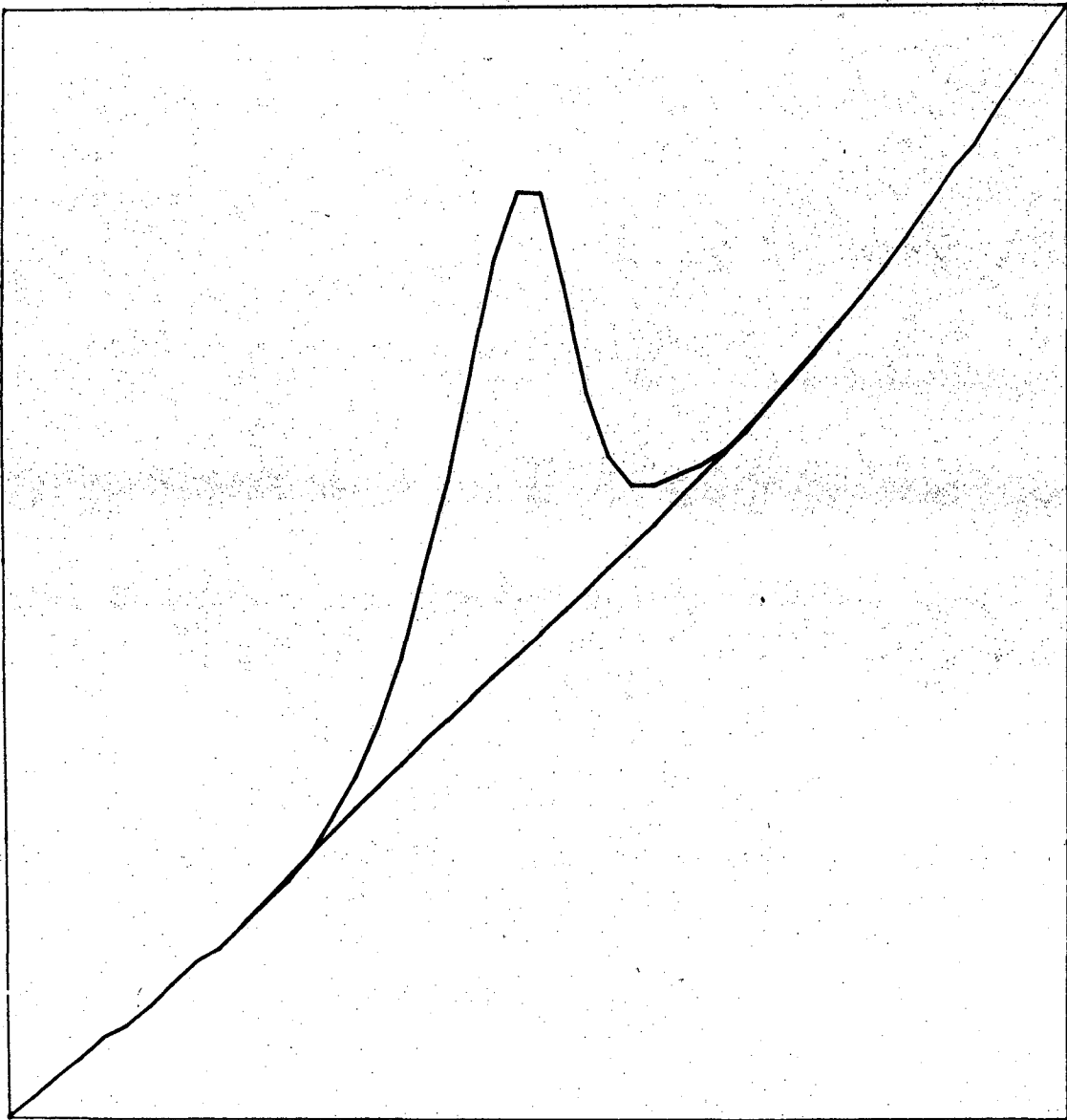
XBL 726-1120

Fig. 7



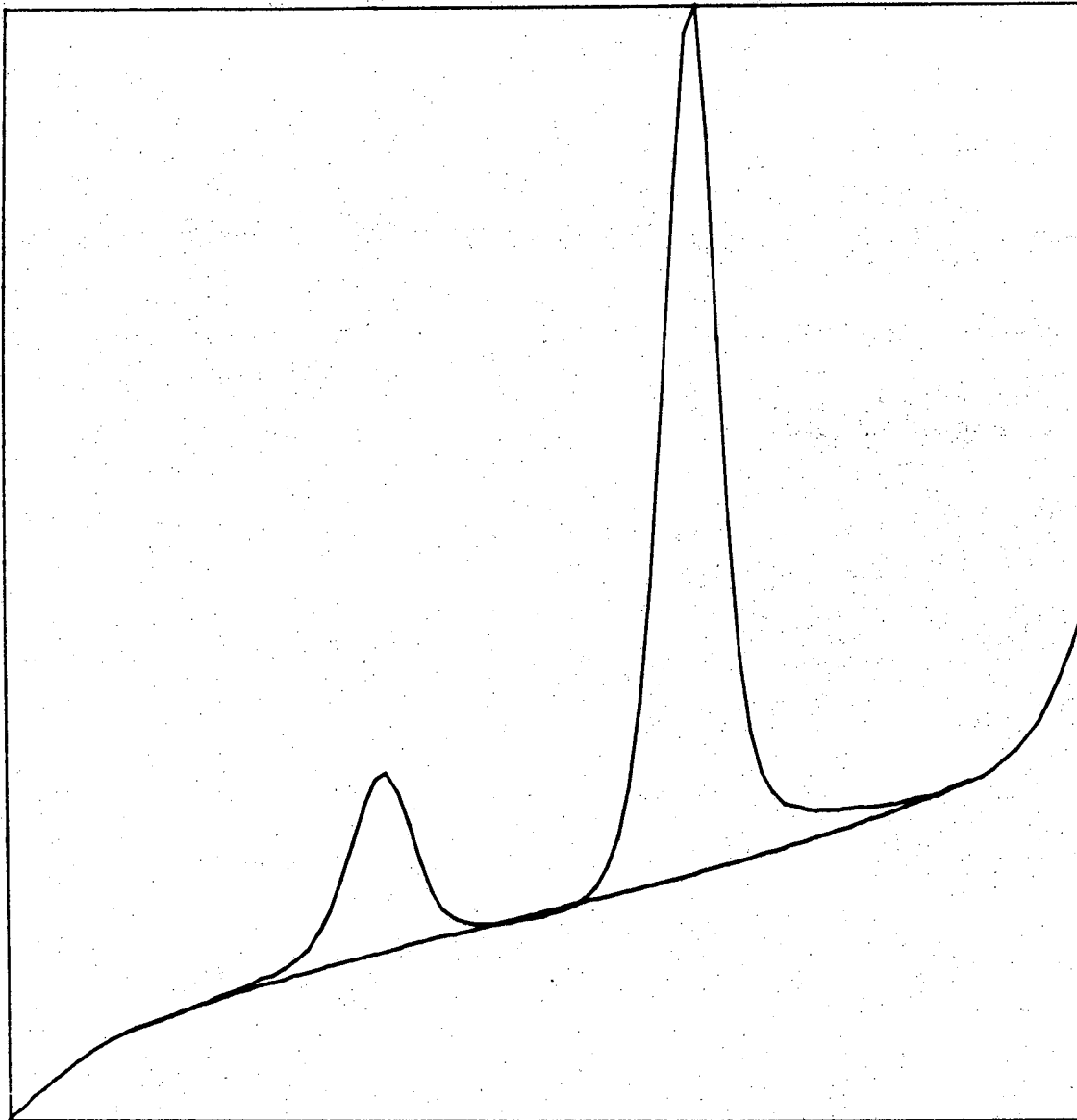
ABL 720-1121

Fig. 8



XBL 726-1065

Fig. 9



XB1 726-1064

Fig. 10

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