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### Author

Clem, Ray G.

### Publication Date

1972-12-01

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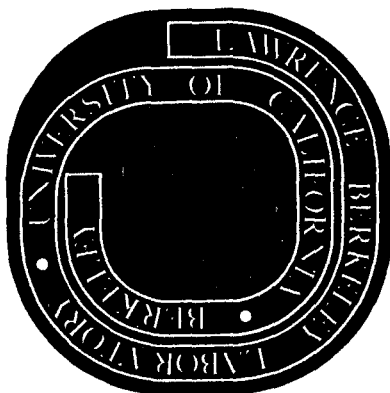
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## A NEW CELL FOR RAPID ANODIC STRIPPING ANALYSIS\*

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

Ray G. Clem, Gerry Litton, and Lawrence D. Ornelas

Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

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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. Metals amenable to this technique are determined at the 1-ppb level or less within 10 min total analysis time and with a precision of 5%. The cell, which is closed at the bottom and partially open at the top, is rotated at a high rate, thus forcing the sample solution into a thin film which is then sparged of oxygen within 75 sec prior to the analysis. A stirrer of new design and rotated at 1800 rpm is employed to assure the rapid accumulation of the amalgam. Recommendations for the kinds of waxes suitable for the impregnation of the graphite electrodes employed is given.

A step and hold voltage ramp is used in stripping the amalgam and the resulting digitally recorded data are transferred onto magnetic tape for processing with a user interactive program written for the CDC-6600 computer.

Two methods for purifying reagent grade KCl are offered. One involves recrystallization; the other, amalgam exchange of electroreducible impurities for aluminum 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 coastal, bay, and river waters. This effort is but a small part of a large, but 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 nearly 3,000 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 as required.

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.

The presented cell does not have sufficient sensitivity to be useful in the determination of Pb and Cd in deep or mid-ocean water samples. A proposed cell capable of detecting these elements at the parts-per-trillion level is briefly mentioned at the end of this report.

A comparison of the paraffin impregnated, mercury plated, graphite electrode (3,4) with the glassy carbon (5) and mercury coated nickel electrodes (6) 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 (7,8) 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 electroreducible impurities for aluminum ions.

#### EXPERIMENTAL

Instrumentation, Reagents, and Materials. The digital instrumentation used was described previously (7,8,9). The user-interactive computer program employed in processing the 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. Chevron Refined Wax 154/156 AMP micro-crystalline wax, unrefined ceresin wax, and Sonneborn Multiwax 180M were 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. After being cooled, it was made to volume in 100 ml. This stock solution containing 13.4 mg Hg<sup>2+</sup>/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 the various molten waxes contained in large test-tubes suspended in a boiling water bath. A vacuum was maintained over the respective melts 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 the appropriate molten wax. Upon 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 electrode assembly.

Strips of glassy carbon  $1/8$  inch wide were sawed 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 protruding end of the rod was exposed and polished with #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  $\sim 1$ -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 as required. 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. The electrode must be positioned just above the stirrer ball and in the strong downward flow of sample solution.

Aliquot 1-ml of a mercury solution containing 27  $\mu\text{g/ml}$  into the cell. Direct nitrogen into the cell at a rate of 5L/min or more during this operation. Aliquot 15 ml of the water sample then, if the sample is of fresh water, 250- $\mu\text{l}$  of purified 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 5L/min or more. After 75-sec, turn the cell motor off and let it coast to a stop. Reduce the nitrogen flow-rate to  $\sim 2\text{L/min}$  to maintain an oxygen-free environment above the solution. The solution should drain cleanly 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. Add a sufficient quantity of the elements of interest to double the peak heights in an aliquot of 250- $\mu\text{l}$  or less. Proceed with this "spiked" sample as was just described above starting with the sparging step.

At the conclusion of the analysis, 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.

Suck the spent sample solution out of the cell employing a plastic spitzer connected through a filter flask to a vacuum line. Thoroughly wash the cell with water and remove the wash water in the same way the spent sample was removed. Aliquot the next sample.

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 peak area used for the calculations of the results.

#### 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" (10). Despite this accolade, the method as it now exists suffers from one or more shortcomings. These problems and our solutions to them 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 recommended 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. The sample is sparged with nitrogen at a minimum rate of 5L/min. The decay of the oxygen current in the cell is measured after each 15-sec interval of sparging

with a DME held at  $-0.800$  V vs. SCE serving as a surrogate for the stripping electrode. The results are shown in Figure 3. Although the data indicate a sparging time of 2 min or more are required, in actual practice considerable sparging takes place during the aliquoting step, so generally no more than 75 sec are required to reduce the oxygen current to the background level.

The decrease in the initial current with increasing KCl concentrations reflects the salting out of oxygen with increasing ionic strength. And, to a lesser extent, an increase in solution viscosity. The noticeable and reproducible convexness of the saturated KCl curve is probably the result of the absorption of water by the KCl from the water saturated nitrogen used for sparging. After sparging, a low nitrogen flow-rate of 1 to 2 L/min is adequate to prevent the ingress of oxygen into the cell since the dead-volume to flow-rate ratio is small.

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 ever 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 may 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, then becomes 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 (6,13,14,15). 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 (13). Some investigators found poor reproducibility (13).

In an attempt to overcome the problems associated with substrates, Matson and co-workers developed a mercury plated, paraffin impregnated, graphite electrode (3,4). This, in our opinion, is probably the best electrode ever offered for stripping analysis, however, we differ with them on several experimental points.

The previous workers recommended using a "good grade of paraffin". We can state unequivocally that no casual relation exists between the paraffin used and the results obtained. Matson's thesis work (4) subsequent to the initial disclosure (3) seems to bear out this conclusion in part. He used several impregnating materials: Gulf brand imbedding waxes, and polyethylene. He concluded the higher the boiling point of the wax the longer the electrodes will function. It appears that most of his work was performed employing 58°C Gulfwax, imbedding wax. Impregnation of the graphite with polyethylene under vacuum and near the decomposition temperature of the polymer gave electrodes initially comparable in performance to his recommended wax; however, they tended to develop cracks in the graphite-polyethylene interface resulting in the seepage of solution into the electrode. This seepage caused the electrodes to fail.

In our studies, we have attempted to determine the initial acceptability and long term stability of the various waxes investigated. Both of these features appear to be critically dependent upon the degree of order within the wax. If an electrode is used immediately after impregnation, virtually any wax will do. Electrodes impregnated with an essentially 100% crystalline wax such as the Chevron microcrystalline wax, however, will fail within a few hours owing to the cracking and the separating of the wax from the graphite substrate. This finding, in conjunction with Matson's report concerning polyethylene, indicates highly crystalline hydrocarbons are, in general, not acceptable as impregnation substances.

The higher the "amorphous" content of the wax, the greater will be the long term stability of the electrode. This effect seems to be ascribable to an

increasing delay in the final ordering of the crystalline phase of the wax. The Sonneborn wax which contains typically 40% non-crystalline substances was used to produce electrodes which were stable for more than one month. Upon failure, however, every subsequent electrode fashioned from the same rod of initially good material failed within a few scans. Electrodes made with unrefined ceresin function well for a week or more, but suffer from water permeability as discussed in more detail below.

Qualitative changes in the physical characteristics of the waxes tested were noted in time after solidifying from their respective melts. These observations may form a basis for screening new waxes for acceptability without the actual and laborious testing of each one separately.

Microcrystalline wax becomes hard almost to the point of being brittle and the presence of the crystalline phase soon becomes apparent upon solidification.

Unrefined ceresin wax is soft and flows easily under pressure several hours after being cooled. Sites of crystal growth appear in a day or so and slowly spread through the mass over a period of a week or more.

The Sonneborn wax is the slowest to harden. Its surface remains soft, sticky, and oily to the touch for days after solidification. No visual evidence of crystallization appears after a month of standing even though by this time the electrodes initially prepared from the melt have begun to fail.

Experiments are underway in which a mineral oil base is used to make a series of waxes containing a known amount of crystalline hydrocarbon. These results will be reported in the future.

In this work, the best results were obtained with the Sonneborn wax; however, at this juncture, there is no guarantee that other investigators will

be as successful. Waxes are the by-products products of petroleum refining, and as such, their compositions change from one production run to the next depending upon the availability and price of various feedstocks and upon the kind and quantity of various additives added. Phenol substituted with long chain hydrocarbons, for example, is commonly added to the extent of a few tenths percent to waxes to increase their molten state stability to air oxidation.

It is important to be alert to the symptoms of electrode failure. The manifestations of failure are probably as numerous and as varied as the number of waxes one might test. Microcrystalline wax electrodes exhibit high background currents and poor stripping peak definition upon failure. Bare graphite electrodes behave similarly. Ceresin wax electrodes, at the onset of failure, often yield cathodic indentations near the stripping peak potential of copper. See Figure 4. Once this phenomenon appears, anodization of the electrode increases the indentation current depth and potential width. The sensitivity of elements yielding peaks at potentials more negative than the indentation suffers. They also become more prone to imbibe sample solution as they become older. Sonneborn wax electrodes fail suddenly and completely. Figure 5 shows a stripping polarogram made with such an electrode and Figure 6 is a photomicrograph of the electrode surface. Apparently most of the exposed graphite particles are sloughed off the active surface. The cell resistance also increases suddenly upon failure.

Electrodes made with Sonneborn wax can be kept serviceable indefinitely provided they are buffed often to expose new surface as described in the recommended procedure. Failure of a microcrystalline wax electrode, on the other hand, is permanent and cannot be reversed by buffing.

The behavior of the ceresin wax electrode is remarkably similar to that reported by Florence for the glassy carbon electrode (5). Both electrodes are insensitive to zinc--even when this element is present at the 200 ppb level. The presence of just a mono-layer of hydrocarbon adsorbed onto the plated mercury, in the case of the ceresin electrode, could account for this behavior. An adsorbed layer, incidentally, could also account for the notably flat background current behavior characteristic of all hydrocarbon impregnated electrodes tested thus far. See Figure 7.

Further similarities exist. Florence found, upon using a polished glassy carbon electrode, that the peak heights of the elements of interest obtained on the first scan were somewhat lower than the peak heights observed on successive scans in the same solution. He thus recommended a pre-analysis, amalgam accumulation/stripping cycle prior to the actual analysis to "condition the electrode". This effect is almost certainly the result of the gradual ingression of sample solution into his electrode. Similar results are found with aged ceresin electrodes. They are slowly wetted with the sample solution upon standing as evidenced by the change in the contact angle solution droplets make with the surface in time, and by the gradual loss in reflectivity of the polished surface. Treatment of ceresin electrodes with a surface active agent endows them with a chemical memory.

As was noted above for ceresin, a glassy carbon electrode, if anodized for some time at +1.0 V vs. SCE will yield spurious peaks and indentations when subsequently used for stripping analysis. Simply wiping away the surface haze or film which forms on anodization fails to eliminate the erratic behavior. The proper functioning can be restored only by extensive repolishing with

diamond dust. There appears to be no basis for selecting glassy carbon over graphite. Glassy carbon is rather expensive.

Problems with the aforementioned impregnation waxes aside, the primary difference between the methodology recommended by Matson (3,4) and that proposed here hinges upon the problem of electrode stability. Matson initially claimed that an electrode once plated with mercury was stable indefinitely provided the mercury was not stripped off (3). This initial conclusion was apparently based upon experience gained in analyzing a relatively small number of samples. We confirmed, as he did subsequent to his initial effort (4), that the stripping response deteriorates with time after the initial plating. The background current level increases and the peak height decreases with time upon continued use. Several factors, each individually or in combination, result in this deterioration of the sensitivity and reproducibility of a "permanently" plated electrode.

Thus, Matson found that a plated electrode immersed in a 10-ml sample solution stirred at 350 rpm with a magnetic stirrer exhibited stability for 4 to 5 days. At stirring rates of 500 to 600 rpm electrode failure came in only 1 to 2 days of use. Traces of  $S_2O_8^{=}$  remaining after oxidation of organic matter in water samples hastened electrode failure. The presence of particulate matter or sediment in water samples caused deterioration in less than 4 to 5 hours of use under his recommended conditions through mechanical abrasion of the surface. The stability decreased with the number of transfers of the electrode from cell to cell or upon repeated rinsing or inadvertant rubbing of the surface. Even under optimum conditions of stirring (bubbling nitrogen through the cell at a rate of 0.17 L/min) and supporting electrolyte, the electrode could be employed

for only 3 to 4 days using the peak current height, or for 6 days using the peak area as the analytical function. If the electrode was used at potential values sufficiently negative to cause hydrogen gas evolution, the stability was dramatically decreased. Analysis for zinc in slightly acidic medium necessitated constant refurbishing of the mercury cover.

The amount of mercury plated onto a graphite electrode also had an effect on its stability. At a surface loading of  $5 \times 10^{-7}$  moles Hg/cm<sup>2</sup> or below, Matson found little effect on the stability of the electrode. Above  $10^{-6}$  moles Hg/cm<sup>2</sup>, however, the stability began to decrease. Very heavy coatings of mercury caused the electrode to fail at times ranging from 30 minutes to 3 hours. Failure of the electrode was assignable to the coalescing of mercury droplets between adjacent conducting sites on the electrode.

The previous worker offered direct visual evidence of the differences between a properly operating electrode and one that had failed through electron photomicrographs of collodion replicas of the active surfaces. He was able to correlate his photographic evidence with electrochemical data. A new and properly working electrode loaded with  $1.5 \times 10^{-7}$  moles Hg/cm<sup>2</sup> was coated with drops of mercury ranging in size from 0.02 to 0.25  $\mu$  in diameter (0.15  $\mu$  average) and were distributed over 65 to 75% of the total exposed surface. After the electrode had been used repeatedly to the point of failure, another examination was made. Coalescing of the initially micron-sized drops to drops approaching one fiftieth to one tenth the size of conventional hanging mercury drops appeared to be the physical cause of failure. Baring of the graphite sites upon coalescence of the mercury was the suggested cause of the high residual currents. The peak tailing and peak broadening effects were the result of an increase in the mercury thickness.

It was in view of the rather precarious stability of the permanently plated electrode that we opted to investigate the in situ codeposition of mercury and sample. The success of this approach depends upon two factors, both of which are easily controlled. They are: the spacial relation of the stirrer to the electrode, and the amount of mercuric ions added.

The electrode should be positioned just above the stirrer ball and in the strong downward flow of the solution as recommended. Positioning the electrode at the equator of the ball stirrer and about 1-mm from it results in poor sensitivity and resolution and in high background currents. The strong turbulence in this region of the cell must be dislodging the mercury as rapidly as it is being plated.

The amount of mercuric ion added should not be less than 15  $\mu\text{g}$  nor much more than 30  $\mu\text{g}$  in the recommended 15 ml sample volume. Use of much less mercury than 15  $\mu\text{g}$  results in incomplete electrode coverage and in high background currents. Use of more mercury than 30  $\mu\text{g}$  results in the deterioration of the reproducibility. The reproducibility, discussed in more detail below, is about 5% in the recommended range but only 20 to 30% at the 135  $\mu\text{g}$  level of mercury. Apparently there is some critical drop size above which the mercury is swept off the electrode. At the suggested mercury levels, however, no problems are encountered when the amalgam accumulation times selected are between 7 and 20 minutes.

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 (6) 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 (17,18). 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 8. 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 by more than one data channel.

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 or through calculations based upon the estimated thickness of the mercury film (6).

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 9. 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 10 is a schematic of the overall job flow and Figure 11 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 or names of the element represented by the peak or peaks is/are 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 digipotentiogator. See Figure 12. 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 13. 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 (19,20) as well as from the amalgam electrodes used in this work.

TVPIT was written to take advantage of the on-line interactive facilities at LBL. Therefore, it might not be directly suited for use at other installations. Government-funded institutions may, however, make use of the LBL Computer Center facilities either in person or via remote terminals. The latter may take the form of either a complete remote batch terminal, or a teletype, acoustic-coupler telephone hookup. Interested parties are invited to contact the authors for further information.

No simple statement regarding reproducibility can be made. Reproducibility is a function of the age of the electrode and the nature of the sample as was previously discussed. Under ideal laboratory conditions employing a new electrode and analyzing lead in a supporting electrolyte solution composed of reagent grade salt and quartz distilled water, a precision of 0.25% is obtained at the 4-ppb level. Under similar conditions but using an old electrode which requires frequent buffing, a precision of 5% is obtained. In the analysis of unfiltered natural water samples, however, a precision if better than 5% is seldom attained--even when using a new electrode. Since this degree of reproducibility is attained for Pb at the 1-ppb level and also at the 10-ppb level for spiked

samples, the results must depend upon the sediment/electrode abrasion effect discussed by Matson (4). Similar results are obtained 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 requires its use. The precision obtainable for peak pairs depends upon the degree of overlap, 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 (21). Controlled potential coulometry, while effective, is slow and requires batch-wise treatment of rather small portions of solution (22). 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 study made many years ago by workers employing radio-tracers produced from the decay of radium sources (23,24). A general conclusion of these workers, as stated by Sandell (25), 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 (25), 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 are introduced.

Similarly, sodium chloride can be effectively purified in the same manner as KCl.

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  $23^\circ C$ . 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

Future reports will concern electrodes, cells, and instrumentation. Electrode stability is of pressing concern now. Research is continuing in this area, and hopefully, production of an electrode having much longer term stability than that reported here will be possible.

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.

In field work, container contamination of water samples is an ever present problem which becomes progressively worse as the time lapse between sampling and analysis increases. The sheer weight and bulk of the water samples limit, to a large extent, the number of samples one might take on an outing, especially if the distances between the sampling site and the transportation are great. These difficulties are the result of inadequate field instrumentation. It would be far better to analyze the samples on site. A preliminary engineering study indicates it is possible to build a field instrument weighing less than 25 lbs. Such instrument would include a digipotentiogator, a step and hold voltage ramp, a system timer, a miniature strip chart recorder to record and view the resulting data on site, and a cassette recorder to simultaneously record the digital data. One channel could be reserved to record voice descriptions of the sample. The digitally recorded data could be processed in the laboratory with the computer program just described. Off-site recording, therefore, need not compromise precision. The rotated cell and requisite equipment would be operated from a rechargeable battery pack. The nitrogen required for sparging

could be supplied by controlled thermal decomposition of ammonium nitrite. The instrumentation could also be employed for field spectrometric or potentiometric measurements with very little modification.

#### ACKNOWLEDGEMENTS

We thank Dr. E. K. Hyde and Dr. E. H. Huffman for their past support and Dr. J. M. Hollander for his recent support. Thanks also go to Dr. R. C. Fox of Chevron Research's Wax Department in Richmond, California for his interest and for supplying test samples used in this study. We are also indebted to Dr. D. K. Roe of Portland State University, Oregon, for his helpful suggestions.

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\* Work performed under the auspices of the U. S. Atomic Energy Commission.

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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 impregnated graphite electrode, the reference salt-bridge, and the sample port.

Fig. 3. Cell Sparge Behavior with Time.

Fig. 4. The Cathodic Indentation.

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

lower trace: The cathodic indentation.

Fig. 5. The Sonneborn Wax Electrode at Failure and After Repolishing.

upper trace: Anodic stripping polarogram taken at the point of failure. Shower of points at the beginning and end of trace is the result of display fold-over owing to the high background current.

lower trace: A scan of the same solution with the failed electrode after buffing the surface. Note that the background current is much lower.

Fig. 6. Photomicrograph (230X) of the electrode used to obtain the upper trace in Figure 5. The surface is almost devoid of graphite sites.

Fig. 7. A Comparison of the Graphite Electrode and Mercury-Nickel Substrate Electrode.

upper trace: The mercury-nickel substrate electrode response.

lower trace: The 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 and the notably flatter  
background response.

Fig. 8. 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. 9. 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,  $\sim 10$  ppb Cu,  $\sim 4$  ppb Cd, and  
27 ppm Hg. Total volume is 16 ml.

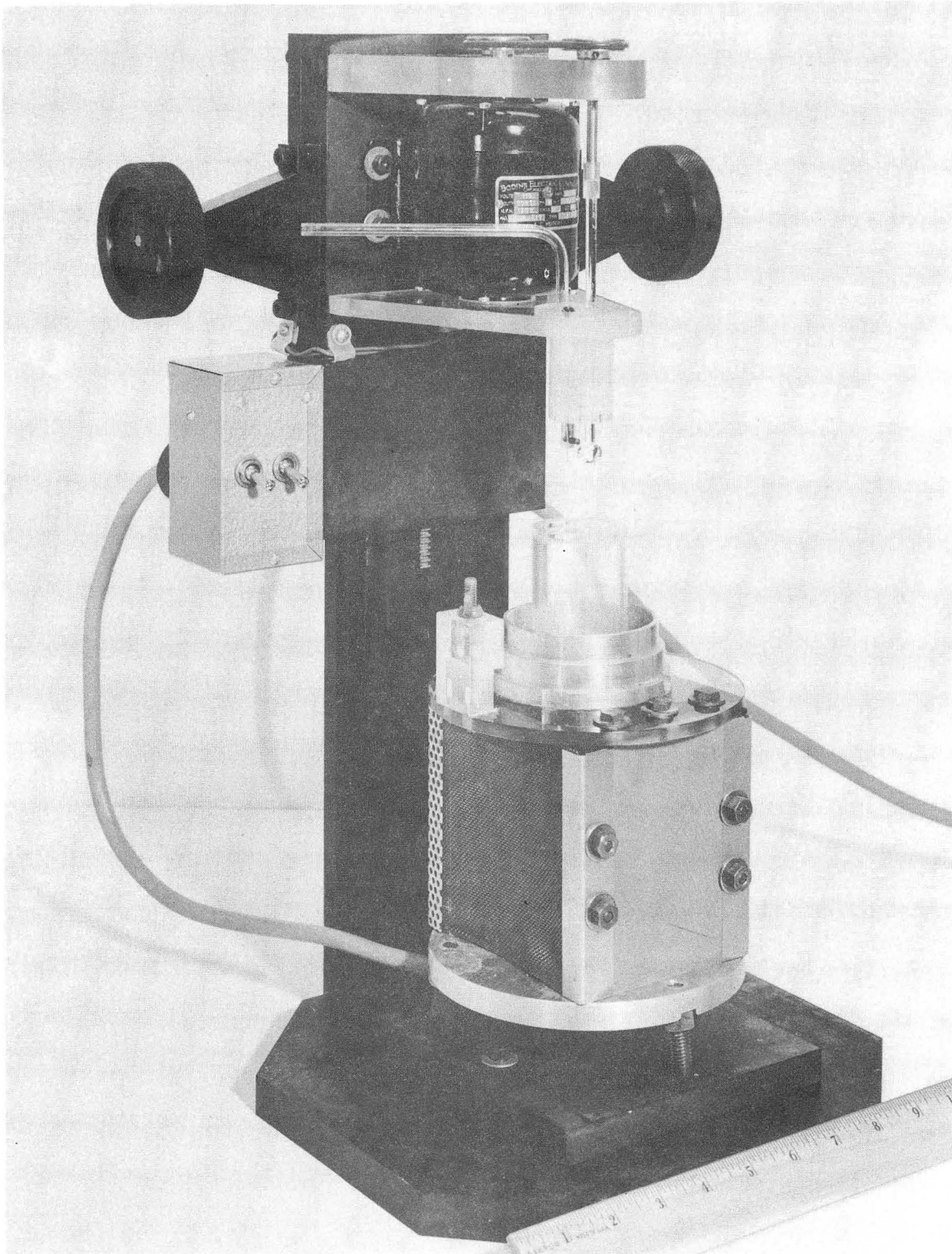
Conditions: See conditions for Figure 7.

Fig. 10. Schematic of the Overall Job Flow.

Fig. 11. Flow Diagram of the Stripping Analysis Program.

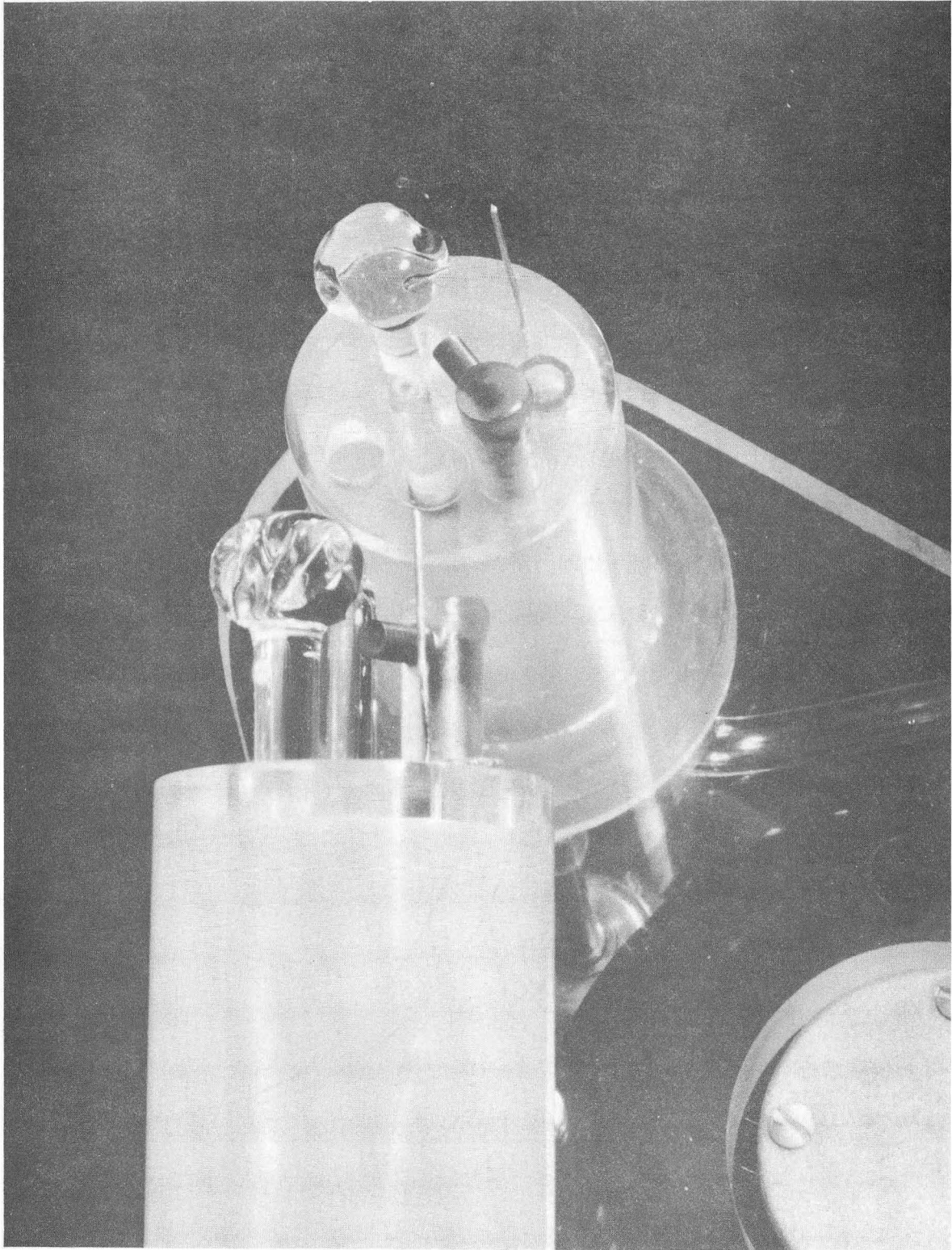
Fig. 12. Computer Display of a Lead Peak and the Calculated Background at the  
1-ppb Level in 0.4M KCl.

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



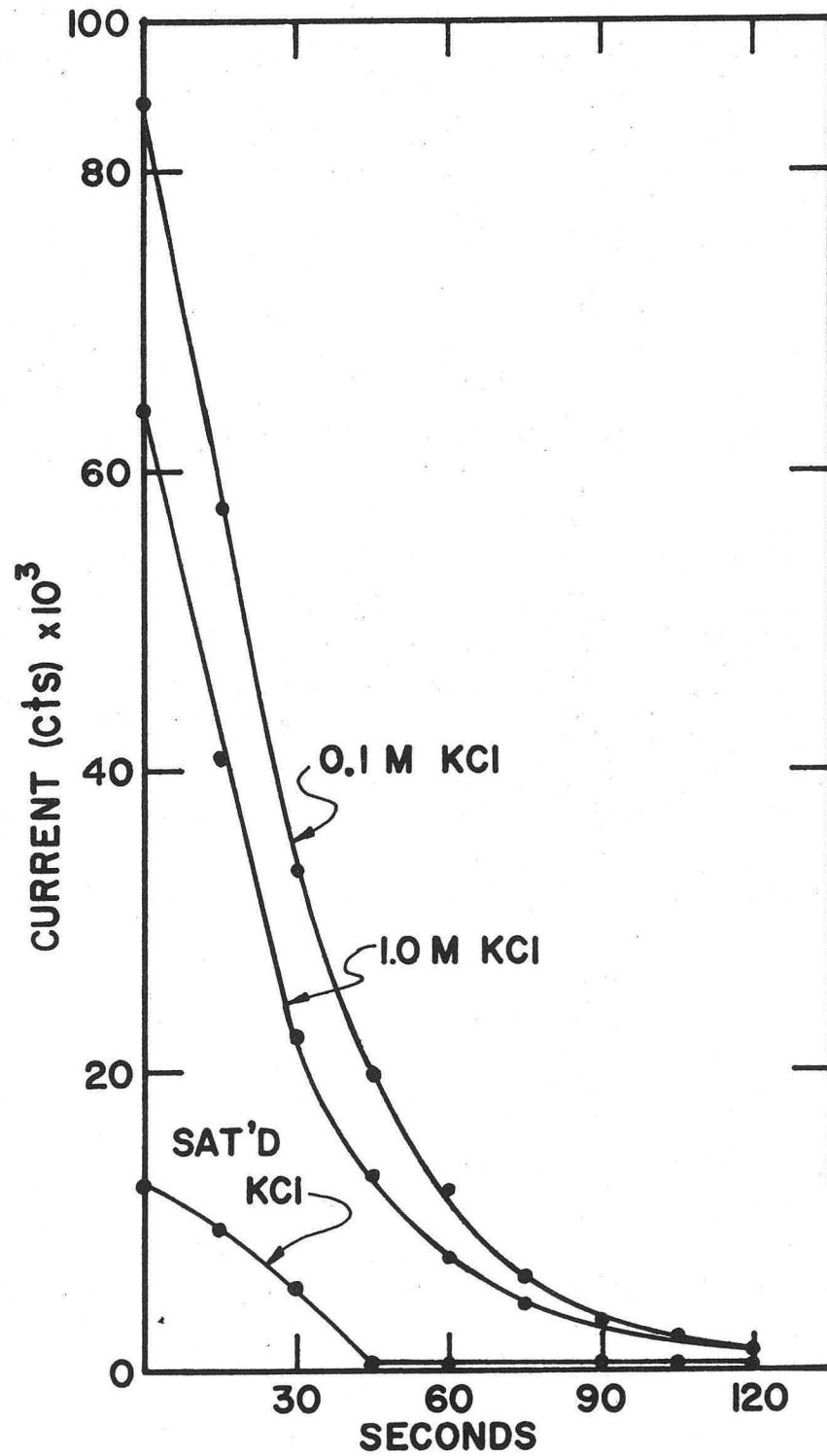
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Fig. 1



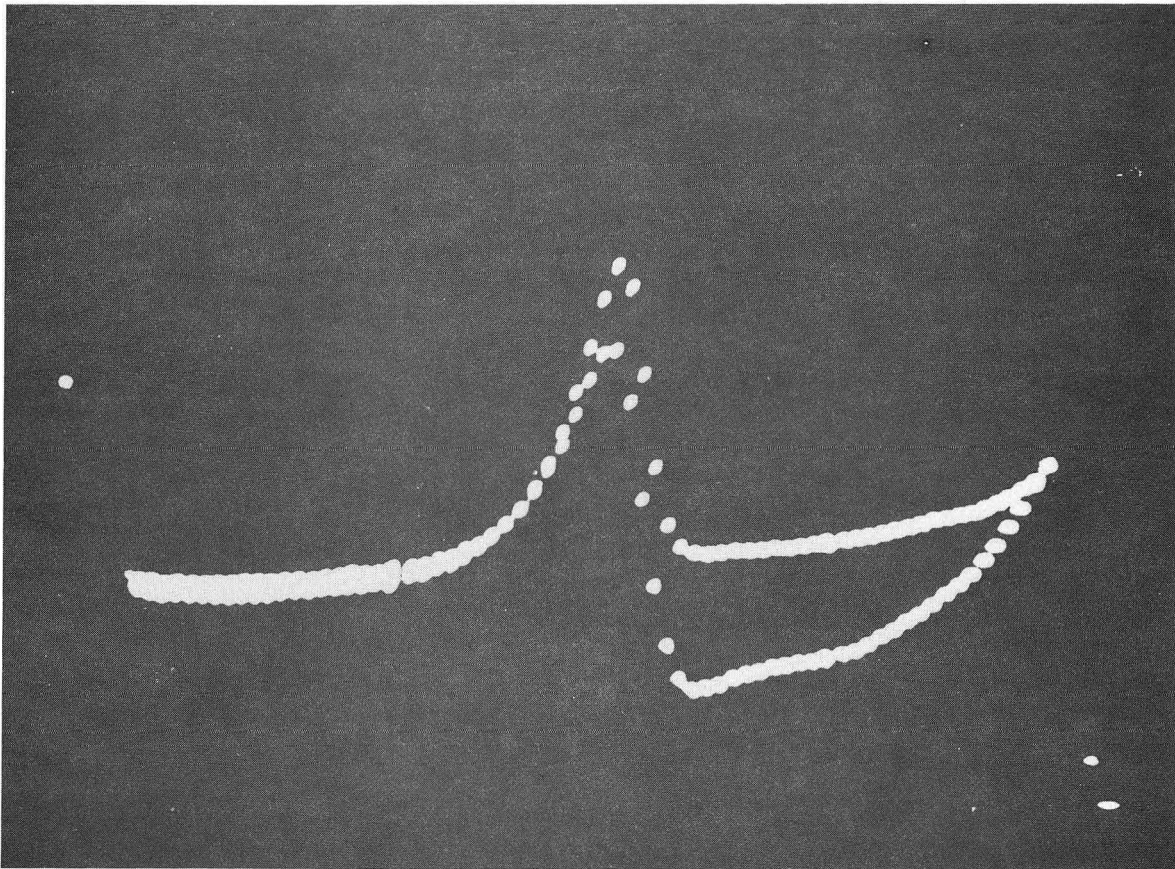
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Fig. 2



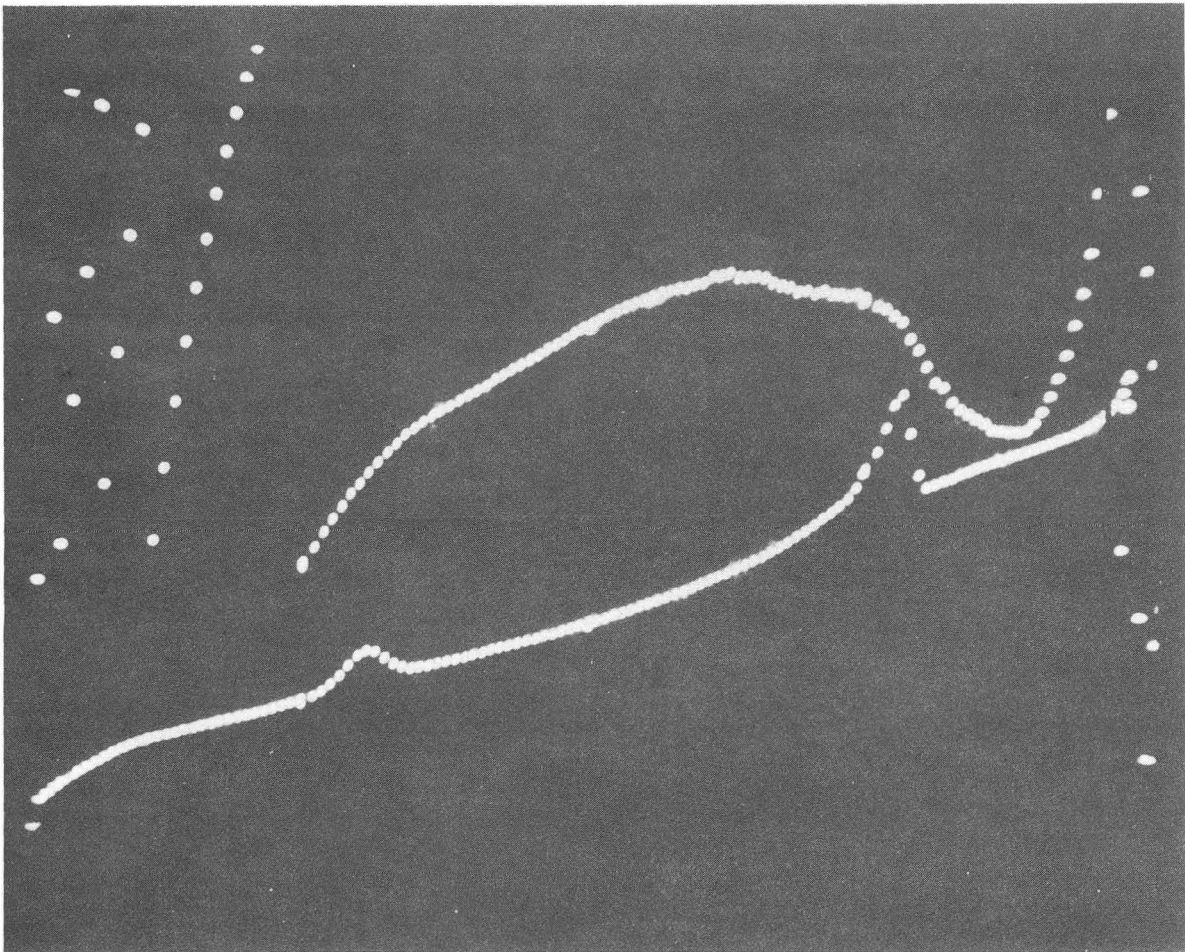
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Fig. 3



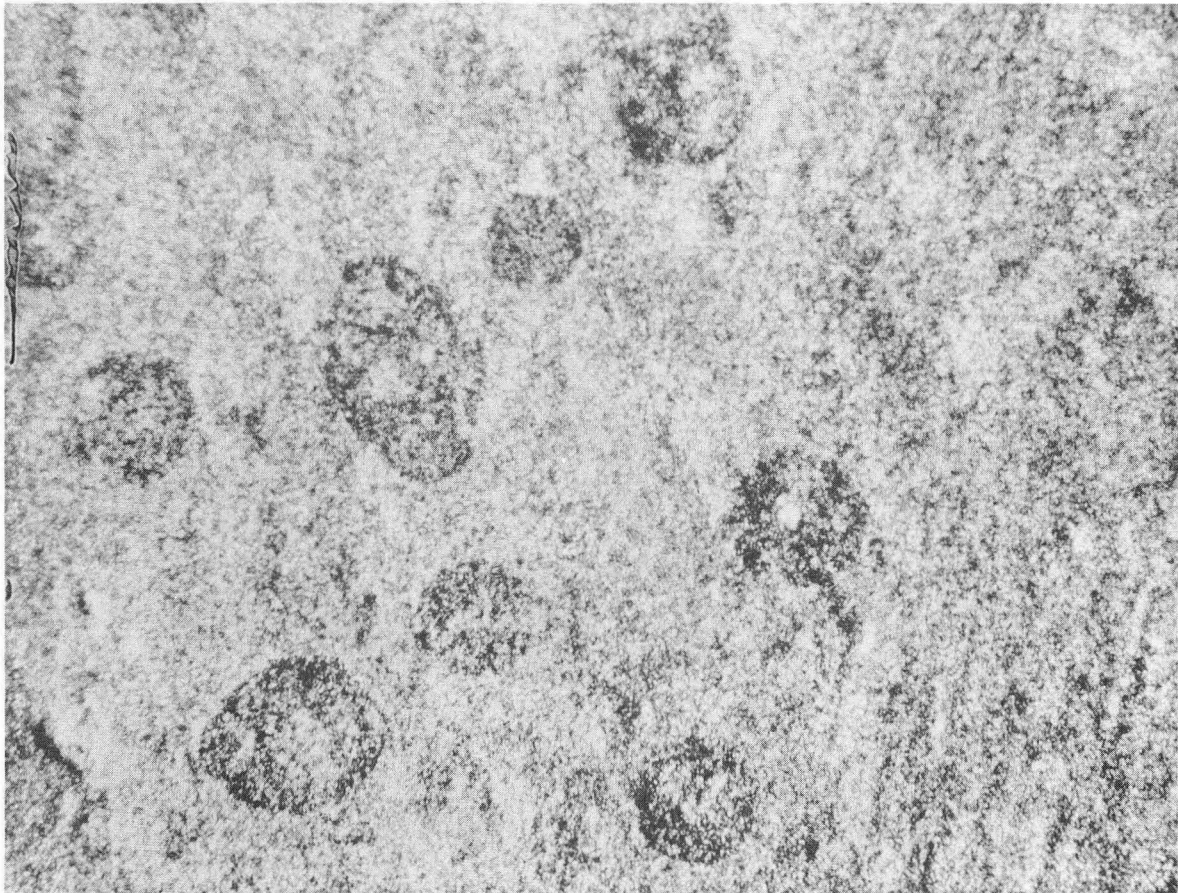
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Fig. 4



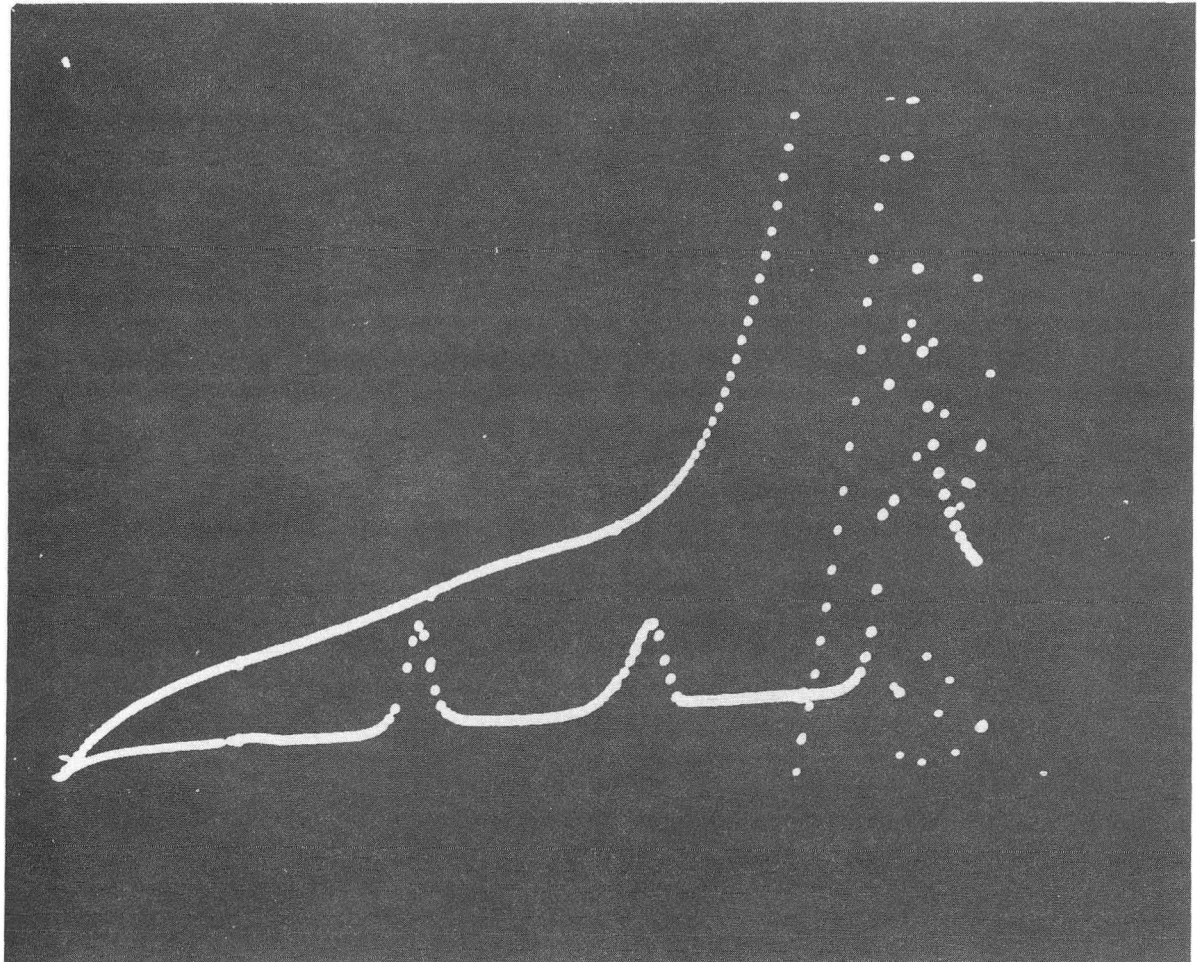
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Fig. 5



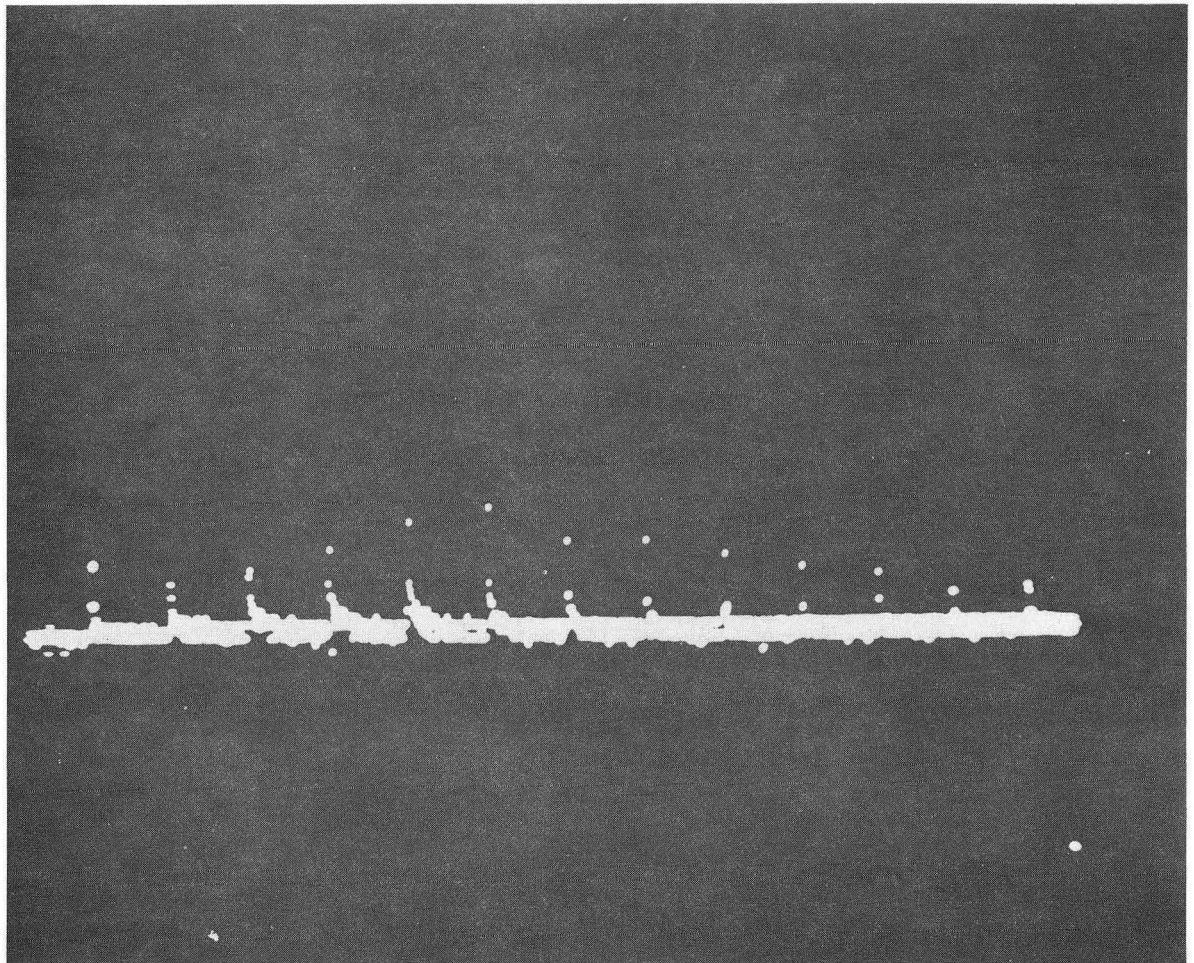
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Fig. 6



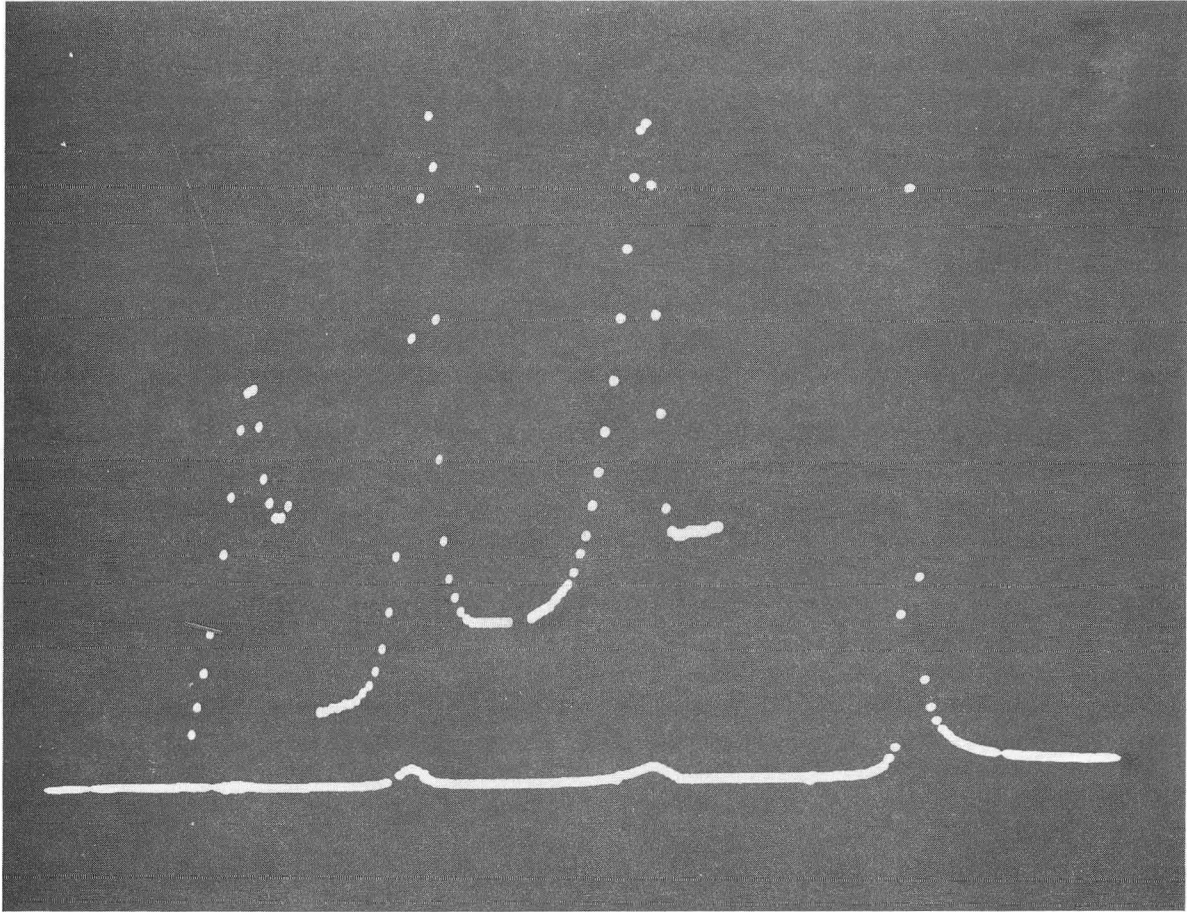
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Fig. 7



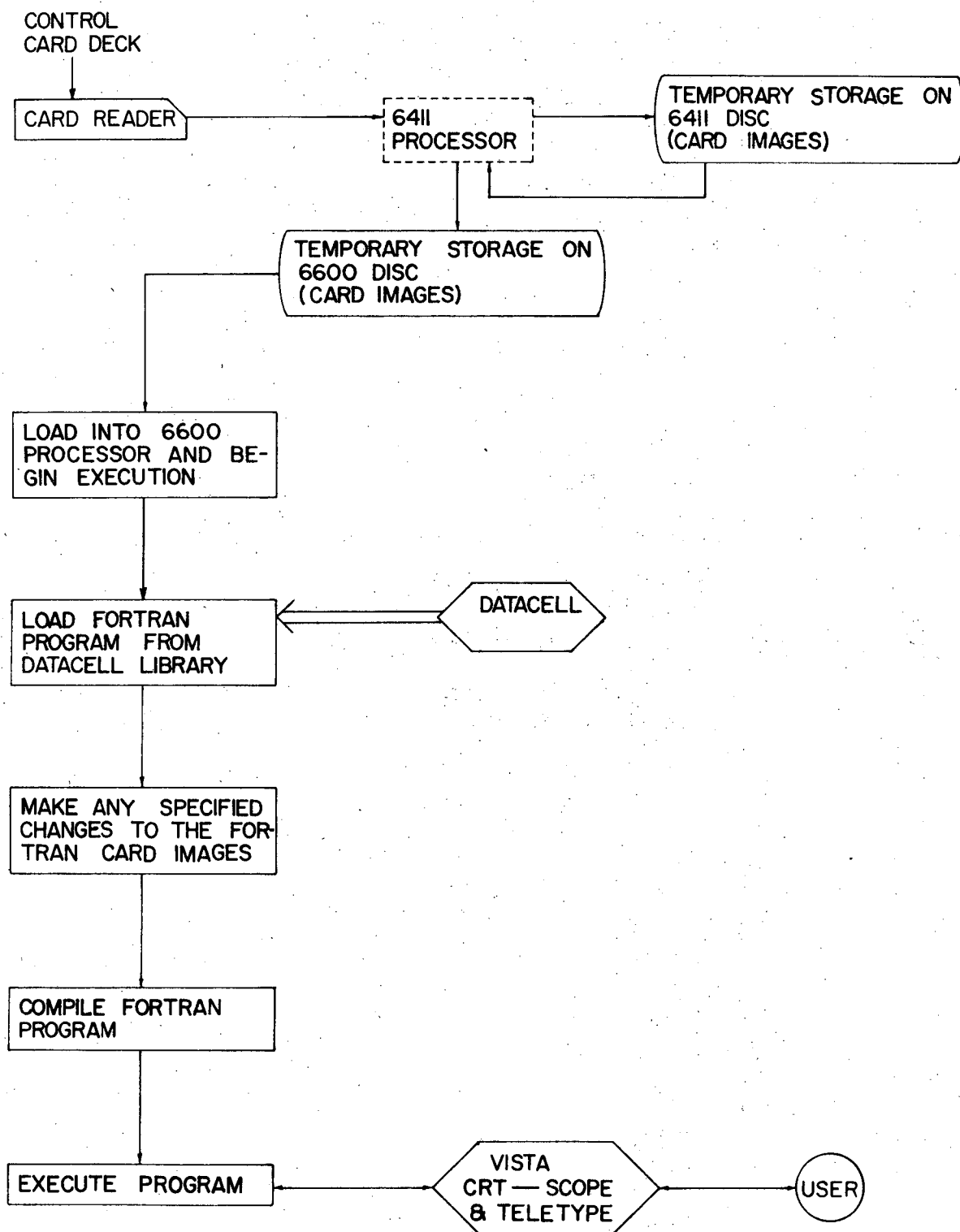
XBB 726-3241

Fig. 8



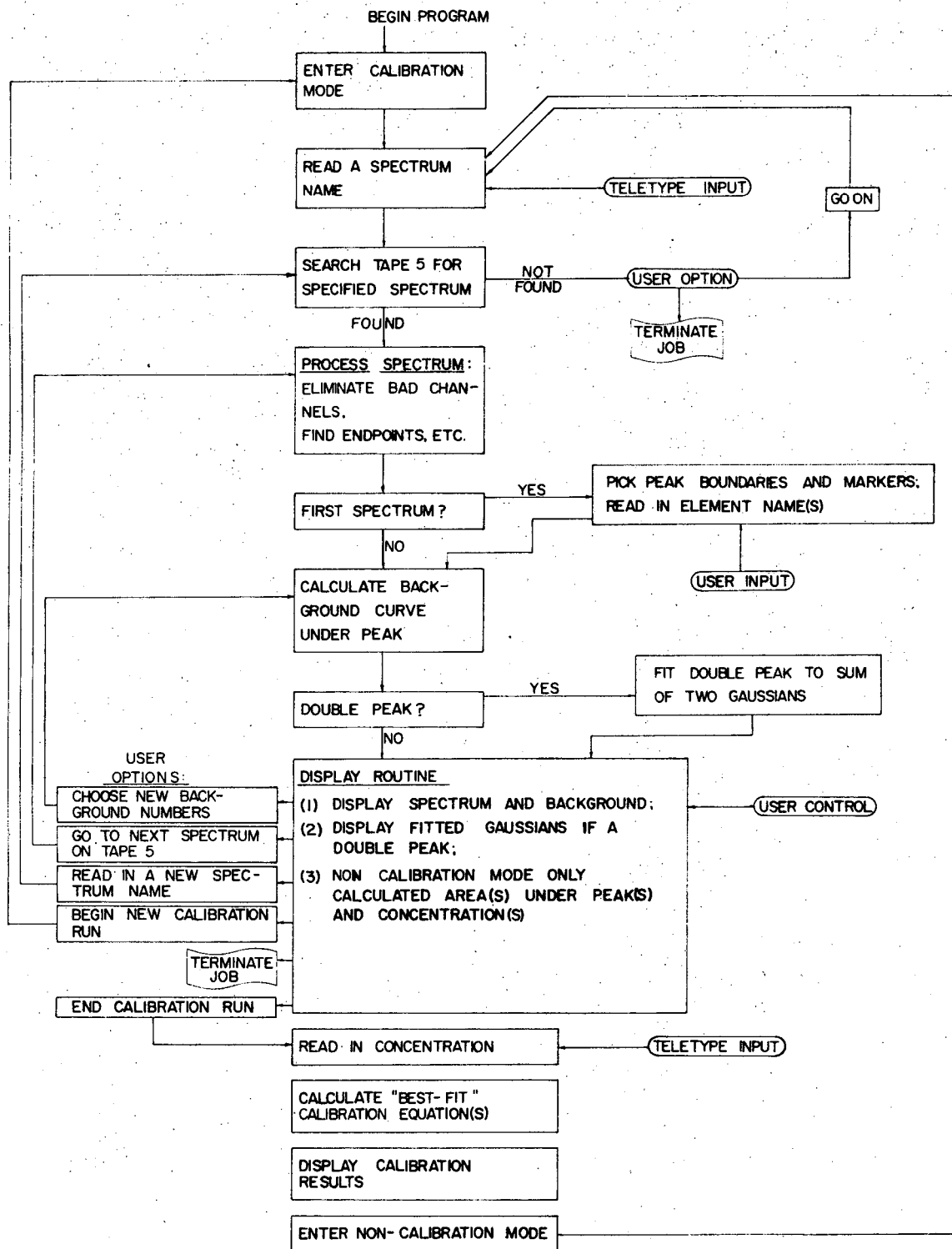
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Fig. 9



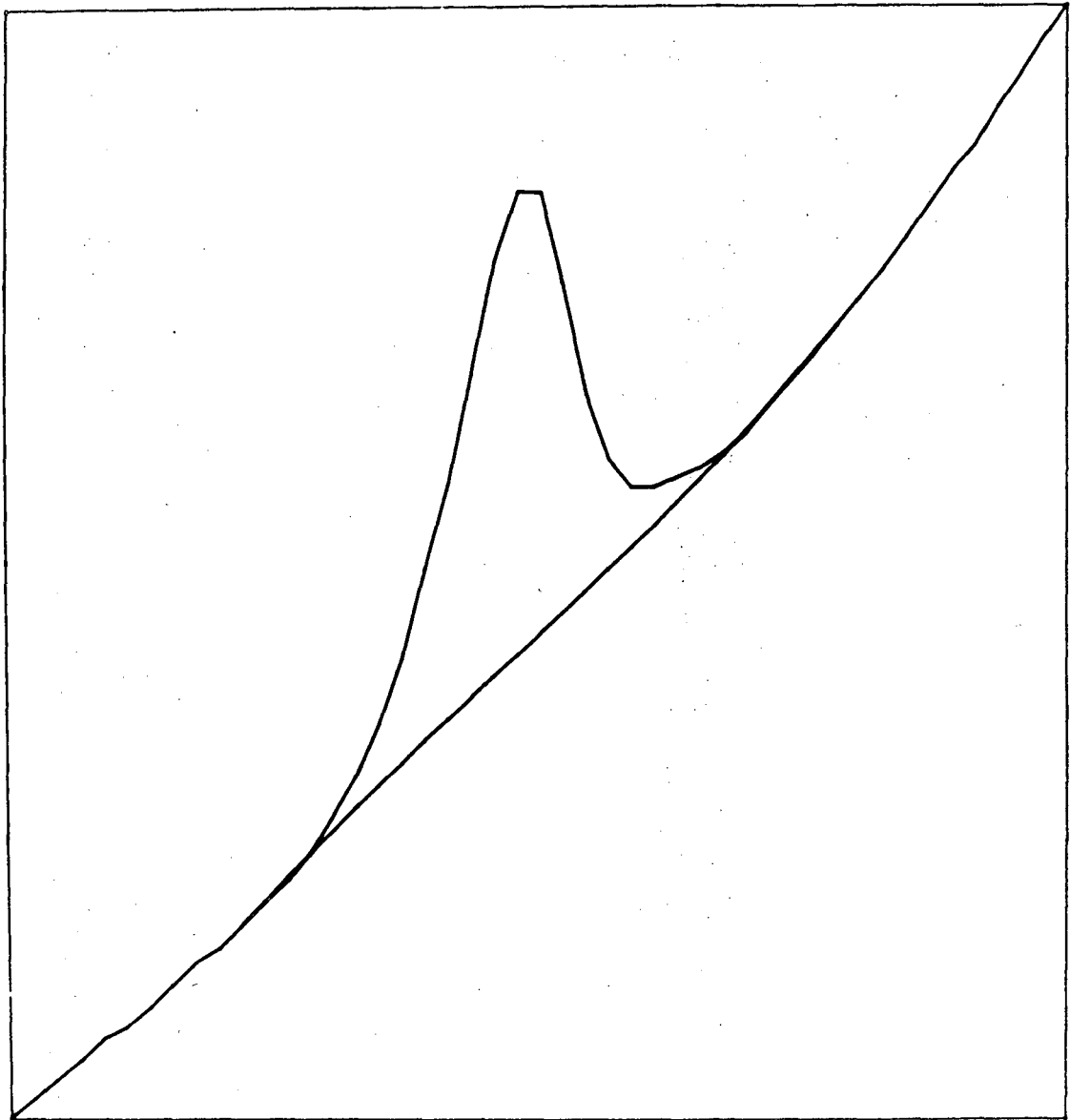
XBL 726-1120

Fig. 10



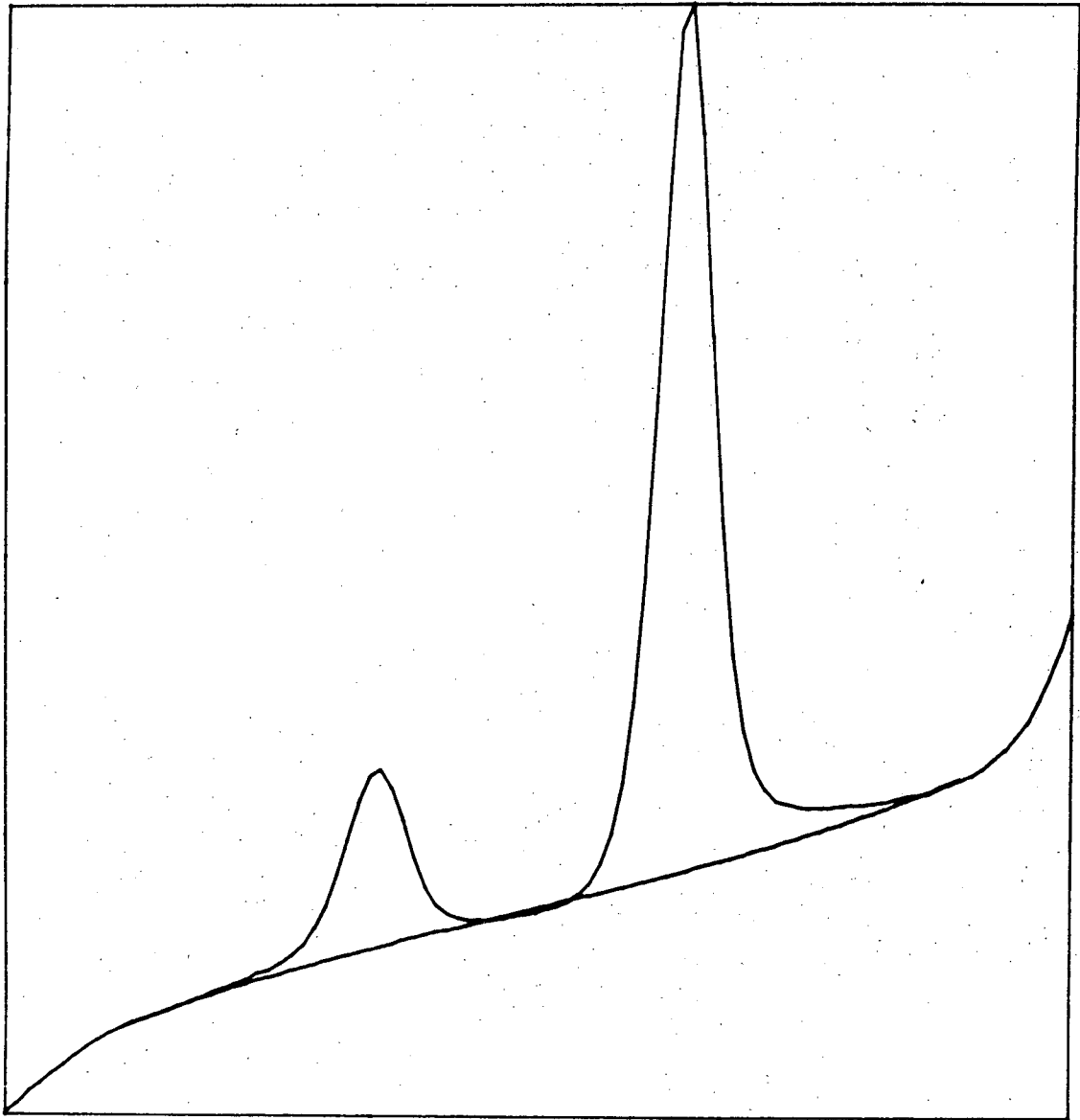
LBL 720-1121

Fig. 11



XBL 726-1065

Fig. 12



XB1 726-1064

Fig. 13

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