Final Technical Report

AEC COO-2058-4

MOLECULAR STRUCTURE STUDIES:

A GAS PHASE ELECTRON DIFFRACTION UNIT EMPLOYING COUNTING TECHNIQUES

June 1, 1969 through August 31, 1972

INSTITUTION: The University of Toledo, Toledo, Ohio 43606

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ABSTRACT

Construction of an electron diffraction apparatus of unique design, employing electron counting techniques, was undertaken. The apparatus is to be competitive with photographic diffraction units in terms of sample required, and it is hoped that it will be superior in versatility and in freedom from a number of sources of uncertainty. The automated character of the unit will make possible precision not easily obtainable otherwise, and will open opportunities for the study of diffraction on transient species. Data acquisition techniques developed may be adaptable to studies of other scattering phenomena, and to other multiple-source counting problems.

During the contract period the instrument chamber, vacuum system, counting electronics and logic, electron optics, and detection system were designed. Construction was completed on all but the detection system and final details of a mechanical drive. Work on this apparatus is to continue under sponsorship by the National Science Foundation.

This report concerns a program to develop an apparatus of unique design for gas phase electron diffraction. The apparatus is to employ particle counting rather than the conventional combination of rotating sector, photographic plate, and precision microphotometer. The design is to be competitive with the photographic method in terms of the quantity of sample required, and superior in versatility and precision. Until now, the only counting-type gas electron diffraction units required sample in gallon quantities. This is obviously unsuitable for structural studies on most new, interesting molecules. As mentioned, the design should be adaptable to gas-phase x-ray and neutron diffraction as well. Certain of the data-acquisition techniques may be adaptable to studies of other scattering phenomena, and to other multiple-source counting problems.

PERSONNEL:

Principal Investigators:

Dr. H. Bradford Thompson served as Principal Investigator during the period of this contract, and devoted 50% of his time to the program during the three years and four summers.

Dr. E. Jean Jacob joined the program as a postdoctoral research associate in January, 1971, and was named Co-Investigator (with AEC approval) upon being appointed Assistant Professor at the University of Toledo in September, 1971. She served in this capacity through August, 1972, and devoted full time to this program during her period as research associate, January to August, 1971, and also for two months during the summer of 1972.

Other Personnel:

Mr. Gregory Fehn, a master's degree student, worked on this project for approximately 15 months through the fall of 1970, developing data-acquisition software and studying data-checking and monitoring methods. Several undergraduate students have been of considerable assistance: Mr. William Kint worked on servomechanism and computer-programming problems; Miss Christine McLaughlin and Miss Carol Frank helped with computer program assembly and the wiring of the minicomputer interface; Mr. Jack Riggs studied sample injection problems and other problems during the summer of 1972; and Mr. Douglas Bliss has taken on assignments in electrical and electronic design and wiring, and in testing and modification of the vacuum and electron-optics system.

Consultants:

Dr. L.S. Bartell of the University of Michigan served as a consultant on electron diffraction techniques and as a general source of advice and encouragement. Dr. Jimmie G. Edwards of this department contributed expertise on vacuum technology and on sample nozzle design. Professor Donald Ewing of the Department of Electrical Engineering has advised in that area.

We also gratefully acknowledge the advice and counsel of Professor Kozo Kuchitzu, who made several valuable comments during a two-day visit during the summer of 1970.

THE DESIGN OF THE DIFFRACTION UNIT

General Specifications

A 40 kv electron beam is used, the power supply regulated to within 0.03%, allowing wavelength control to within 0.015%. The gas inlet system is jacketed to permit temperature control and to allow study of species at elevated temperatures. The diameter of the pump port equals the diameter of the diffraction chamber to allow the fastest possible removal of the sample gas. This is essential if a continuous jet is to be used. In other respects the diffraction unit is much like other units now in use. See Figure 1.

Detector System

The heart of the detector assembly is a system of slits above Bendix Spiraltron particle detectors. Each slit is 0.2mm or less across, and so shaped as to admit the electrons diffracted at a given angle. This feature is essential if a scintillator system is to compete with photographic recording. At high diffraction angles, using samples of a gram or less, a short slit would collect so few electrons that statistical fluctuations are unacceptable. The photographic process appears to give data consistent to about .0003 (relative). Any scintillator system must collect at least 10^7 counts at each angle to improve on this precision. This requires that at high scattering angles the slits represent several degrees of arc.

The slits are arranged on the top of a piston, the axis of which is the path of the undiffracted electron beam. See Figures 2 and 3. The inner slits are both shorter and narrower than the outer slits. This is fortunate, since at small angles the pattern contains rapidly fluctuating components (with respect to angle) which must be measured to obtain information about the longer interatomic distances. A separate stationary detector consists of a Spiraltron with its own amplifier mounted within a shielded chamber and fastened to the wall of the diffraction chamber. This detector is at a much higher angle than the detector slit, and will be used (1) to monitor the diffraction for large changes symptomatic of experiment breakdown, and (2) to provide a reference count against which the count at each physical position and slit can be compared.

Advantages

One of the limitations on electron diffraction today is the uncertainty resulting from the interaction of at least three factors: sector shape uncertainties, nonlinearities in photographic emulsions and photometer techniques, and imperfect atomic scattering factors for both elastic and inelastic scattering. Proper corrections for any one of these factors might be made if the others could be eliminated or reduced. Data from the present unit should suffer only from the scattering factor error.

The Toledo unit will give digitized data immediately, thus saving time and labor. In addition, checks on the data can be made while the experiment is in progress.

The proper combination of temperature and pressure, electron current, etc. can be found rapidly, without waiting for development of plates, and without using up sample on trial exposures.

The number of counts taken can be adjusted to the precision desired, the sample available, etc. This is a considerable advantage over the photographic technique, where quick, approximate data is hardly worth obtaining -- by the time exposures are determined and a plate is obtained the time and material used is almost as great as that needed for a set of four or more plates. On the other hand, experiments in which much higher precision is desired will be feasible due to the highly automated nature of the apparatus. The unit can run with minimal attendance for prolonged periods, since the computer can check incoming data for deviations indicating undue drift or experimental failure. The computer controls the drive motor and can be connected to shut off the molecular flow and the electron beam upon beam drift, high chamber pressure, and other undesirable conditions. Thus experiments requiring 10^8 counts at each angle, entailing seven hours of observation would not be prohibitive. The apparatus is equpped with a port and trap for recovery of sample, so that through recycling even higher precision could be obtained over several days.

The entire piston system is moved, so that each slit can serve to measure a range of diffraction pattern. Using 12 slits and a piston motion of 1/5 the minimum met-to-detector distance, it is possible to sweep the range of commonly-used angles.* The piston sweeps this range with a period of five seconds. By accumulating counts at each desired angle on each pass, the effects of drift in the effusion rate and the electron beam intensity can be largely climinated. At an average counting rate of 100 kHz, a typical experiment would require 40 minutes.

To control the switching and gating needed, a small computer (the DEC PDP-8/I) is used. The computer will receive signals indicating the piston position, switch the output of the appropriate detectors into scalers, provide for the gate signals for the scalers, and read and accumulate the scaler outputs. With the versatility provided by the scaler-computer system, it will be possible to read for longer or shorter periods at the various angles, so as to make up for differences in change of scattering angle with piston travel, etc. Fourteen scaler channels are used.

In the center of the piston, a beam trap receives the undiffracted beam. This trap is equipped with four small sensors, spaced around its walls at 90° intervals, so that any drift of the beam from the center of the trap will be sensed as an unbalance in the currents picked up by the sensors. By a feedback circuit to electrostatic deflectors above the diffraction point, the beam can be kept centered automatically.

Computer Interface

The incoming pulses after amplification enter one of 14 prescaling channels, which are located physically near the diffraction unit (Figure 5). An amplifier is used from the output of each scale-of-64 as a line driver for the 20-foot cable from this assembly to the main interface panel, located at the computer (Figure 6).

The Memory Increment feature of the PDP-8/I is used to record the prescaled pulses from the seven channels, essentially simultaneously. In addition, the interface has been equipped with its own timer. These features greatly simplify the software, and remove minor sources of error due to possible dropped counts. This interface is described in detail in Decuscope* Vol. 10, No. 2; we believe it to have applications in a variety of multiple-input counting situations. The worst-case computer time devoted to the recording of counts is less than 5%.

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* Publication of the Digital Equipment Computer Users Society (DECUS).

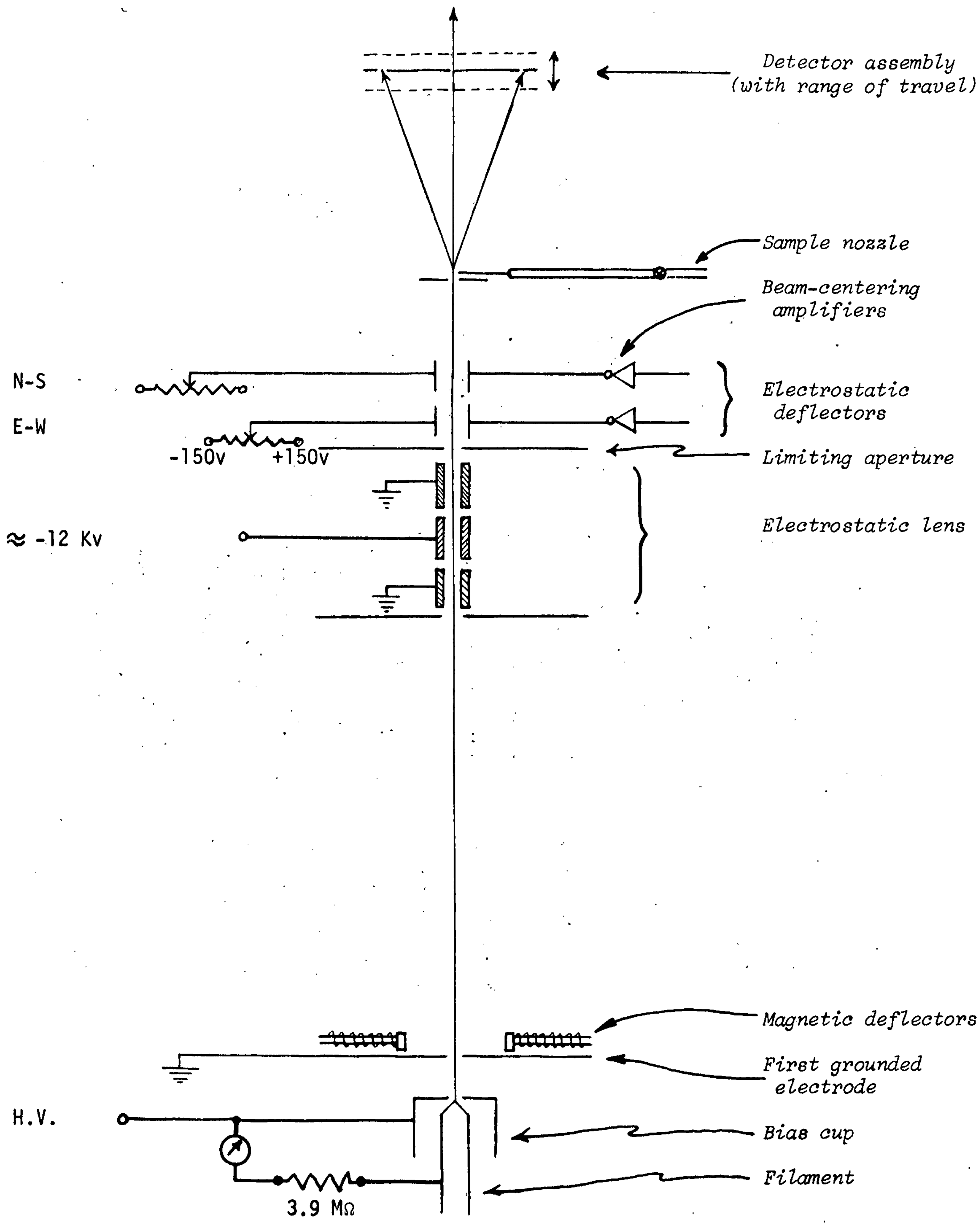
Figure 1. Electron Optics

The vertical scale is reduced by 1:4 throughout. The horizontal scale is also reduced by 1:4 below the first grounded electrode and from the sample nozzle up. Horizontal distances in the central portion are shown 1:1.

The electron gun consists of a bent-tungsten filament (RCA electron microscope filament) surrounded by a bias cup. The system is self-biased by the voltage drop across the bias resistor. The filament is heated by a d.c. current of about 3 amps. In operation the filament current is increased until the gun current (on meter shown) ceases to rise, then is set a value slightly above this, on the gun current "plateau." The high voltage H.V. is set at 40 Kv plus the calculated drop across the bias resistor. The gun is, of course, negative with respect to ground.

The magnetic deflectors consist of four soft iron poles, each wound with #18 magnet wire and set into a soft iron cylinder. These deflectors are used to aim the beam into the input aperture of the electrostatic lens. The lens consists of three stainless steel hollow cylinders. The upper and lower cylinder are grounded; the center one is connected to a variable 20 Kv supply; focus occurs at about 12 Kv. The electrostatic deflector voltages are set manually on one plate of each pair; the other plate is set from a signal obtained from the split beam trap (see text). The sample nozzle is a square-end stainless steel hypodermic needle with an inside diameter of about .02 cm. Details of the detector assembly are shown in Figures 2 and 3.

The vacuum system is divided into two portions by the aperture just above the sample nozzle. The upper ("main") chamber is evacuated by a 6" diffusion pump and liquid nitrogen trap. The lower ("gun") chamber is evacuated by a 2" pump; sample can get into this chamber only through the small aperture. In this way, aperture scattering is minimized; since the beam, after passing the limiting aperture, is not diffused by stray gas.

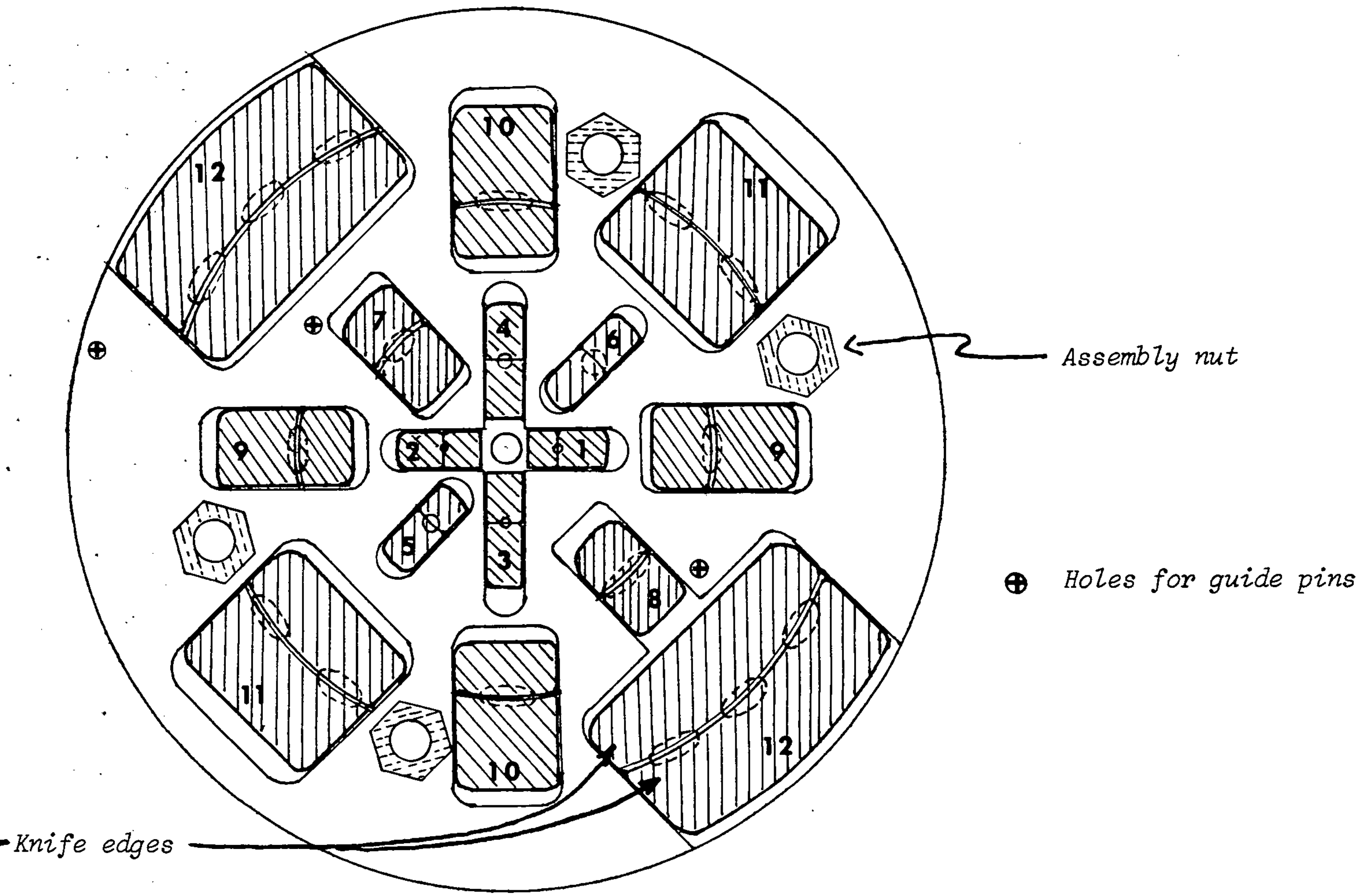


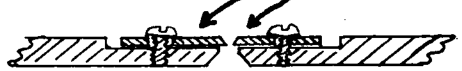
Schematic of Electron Optics

Figure 2. Slit Plate and Knife Edges

This view is as seen looking at the detector mechanism from below. The scale is 1:1. The plate is 1/8" aluminum and the knife edges are stainless steel. This and all other stainless steel in the unit has been tested, and is nonmagnetic. The curved knife edges (5-12) have precision machined edges. The inner four slits have precision ground edges, since the slits are to be narrower and shorter, and uniformity more important. The assembly nuts are on threated rods which hold the plates of the detector assembly together and to the end plate of the moving portion of the apparatus. The three guide-pin holes are used to line up precisely the three plates (see Figure 3) that make up the front end of the detector assembly.

TOP VIEW





Cross section of typical slit

SLIT PLATE AND KNIFE EDGES

Numbers index discreet slit radii.
Center hole contains trap for the
undiffracted beam.

Figure 3. Cross Section of a Typical Detector Slit Assembly

The first plate, with knife edges, is as shown in Figure 2. The third or upper plate contains slits and circular depressions for mounting of the Spiraltrons. The slits in the slit plate are limiting; those in the detector plate are large enough to admit any electron coming from the diffraction point, at any point in the vertical travel of the detector. The upper slits do, however, provide discrimination against electrons scattered from walls or stray molecules.

The 3/8" center plate is a spacer, with passages much larger than either slit. Its main functions are to provide accurate relative spacing of the othertwo plates, and to prevent electrons scattered from the edges of a given slit from entering some other detector. Air-escape channels provide evacuation of the chambers and detectors.

The scale of this drawing is 2:1 for one of the outer detectors.

Cross section of a typical detector channel.

The pointed lines define the angular limits for detection over the range of nozzle-to-slit distances. Note the directional discrimination against delocalized scattering.

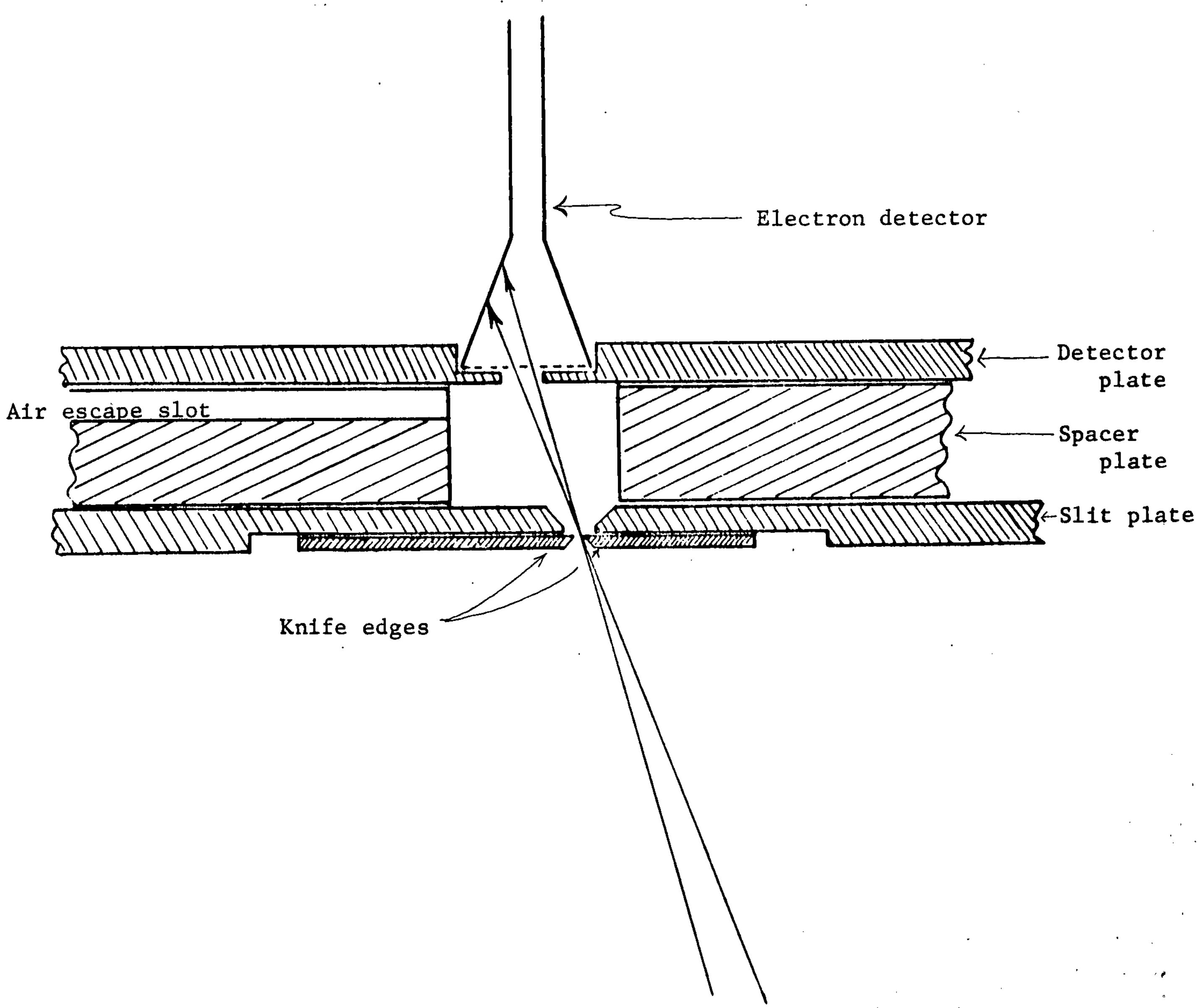
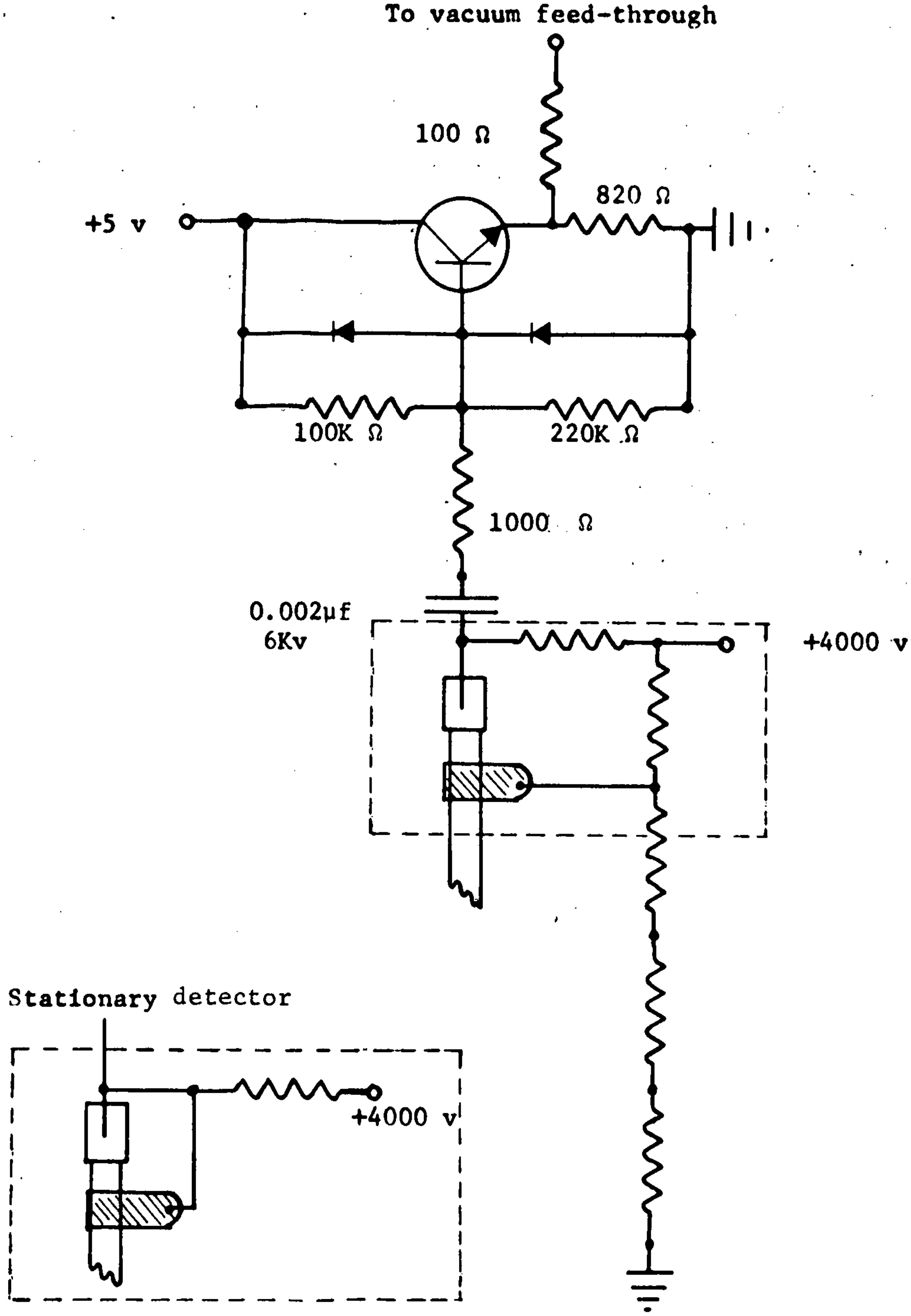


Figure 4. Emitter-follower Current Amplifier for Detector

A simple emitter-follower current is used to match impedence to the vacuum-wall feedthru for each detector. This circuit is mounted on an epoxy-fiberglass etched-circuit panel in the vacuum chamber. The resistance string used to provide the 150v bias needed by the collector cap on the Spiraltron is also shown. This circuit employs a zener diode and capacitor network, so that change in the voltage used does not effect the bias.

The corresponding "tail end" of the stationary detector is also shown. In this case the cap and high voltage tab have been connected together, since maximum gain in this circuit is now crucial. If a fixed fraction of counts in the stationary detector are missed, it will still fulfull its function. This simplification was employed because the spacing within the stationary detector housing is very tight, and there is little room for the string of resistors.

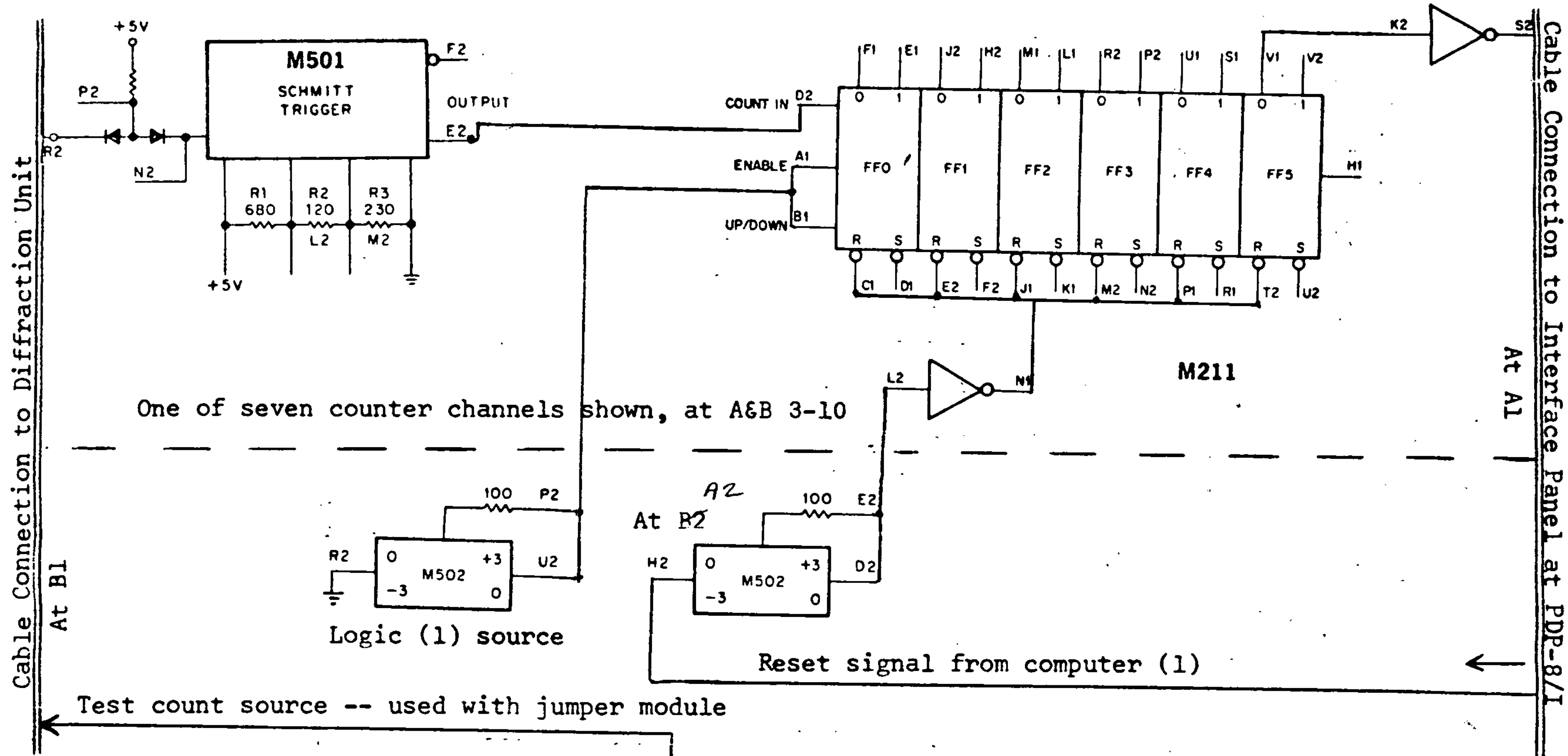


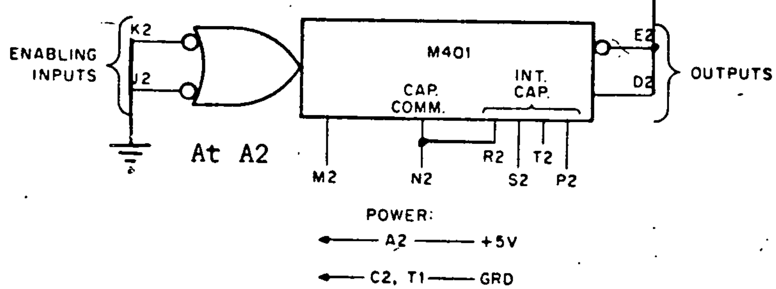
Emitter-follower current amplifier for electron counters

Figure 5. Prescaler Logic Circuit

Individual modules are shown as illustrated in the Digital Equipment Corporation Logic Handbook. The M211 module is a scale-of 64 prescaler. Each counter channel is triggered by a pulse of at least 50 nsec. at the Schmidt Trigger input. The upper and lower threshholdof the trigger can be varied over a small range by setting the voltages at pins L2 and M2. Without alteration, the trigger operates from output pulses from the emitter-follower preamplifiers (Figure 4). The M401 variable clock module is used to create pulses for logic testing. By replacing the cable to the diffraction unit with a module bearing a simple diode-capacitor-resistor network, the clock pulses can be used to create simulated detector pulses, with rapid rise and exponential decay.

The cable to the computer, in addition to transmitting the output pulses, carries a signal to reset each prescaler to zero, and also the -10v supply required by the M502 level adjuster. One half of the M502 is used merely to produce the logical "1" needed to keep the M211's in the enabled, count-up state.





M401 VARIABLE CLOCK

Prescaler Logic Circuit.

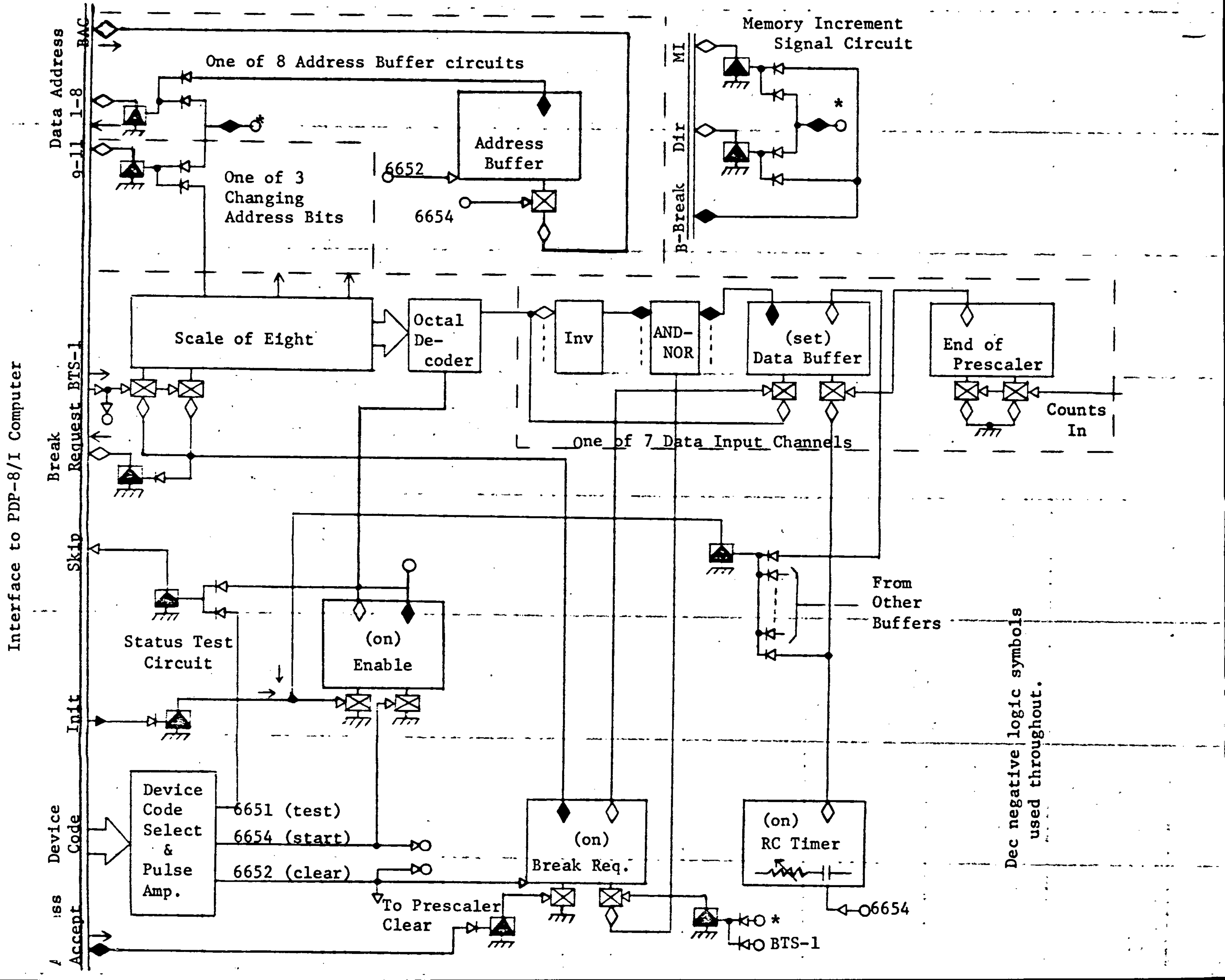
Located near e.d. unit. For test purposes, clock module can simulate test counts if jumper module is used in place of cable from e.d. unit.

Figure 6. Computer Interface

At a given recording position the computer senses a signal through a Schmidt-trigger on a DEC AX08 peripheral and gives a 6656 instruction to the interface with address of the first of 14 storage locations in the AC. This instruction turns on the Enable flip-flop, sets bits 1-7 of the core addresses to be used into the Address Buffer, clears the data buffer on each input channel, starts the timer module and sets each prescaler to 64 (i.e., half-full). This setting of the prescalers provides for "rounding" to the nearest half-count in terms of Data Buffer input. The scale-of-16 triggered by the BTS-1 pulse during each instruction then constantly scans the channels via the octal decoder, and provides bits 8-11 of the data core address. When a Data Buffer is set and the scale-of-16 comes to the matching address, a positive level will occur at the output of the And/Nor module. This permits the next BTS-1 pulse to set the Break-Request flip-flop. This in turn has three results: (1) a break request is sent to the PDP-8/I, (2) the scale-of-16 counter is halted so that the address will not be changed until it is accepted by the computer, and (3) the appropriate Data Buffer is cleared. The Break Request slip-flop is reset by the leading edge of the Address Accept signal from the computer, and the required Memory Increment and Direction signals are obtained by a NAND between the B-Break signal and the interface Enable flip-flop. The scale-of-16 resumes scanning, and can find another count as early as the positive-going BTS-1 change that occurs during the B-Break. On the PDP-8/I this can be within three microseconds.

Entry of data ceases when the timer module returns to the off state. A logical NAND is then performed so that a signal is sent to disable the Enable flag only when the last filled Data Buffer is cleared. Thus prescaled counts cannot enter the buffers after the Timer period, but counts already in the buffers are read.

By this process, prescaled counts from seven channels have been accumulated in seven consecutive addresses. Upon arrival at the next recording position, the computer repeats the process in the preceding two paragraphs, using a new storage address. Incoming counts at 500 kHz, prescaled by a factor of 128, could be counted for one second before overflowing one word of core. The upper limit on the incoming pulse rate is governed by the cycle period of the Scale-of-16. As a worst case, if each Data Buffer required servicing and if each computer instruction were 4.5μsec in length, this cycle period could be as great as $16 \times 4.5 + 14 \times 1.5 = 93$ μsec. At 500kHz prescaled by 128 the average interval between counts would be 256μsec.



Interface to PDP-8/I Computer
Data Address
BAC
1-8
9-11
One of 8 Address Buffer circuits
Address Buffer
6652
6654
One of 3 Changing Address Bits
Memory Increment Signal Circuit
MI
Dir
B-Break
*
Scale of Eight
Octal De-coder
Inv
AND-NOR
(set) Data Buffer
End of Prescaler
Counts In
One of 7 Data Input Channels
Break Request BTS-1
Skip
From Other Buffers
Status Test Circuit
(on) Enable
Init
Device Code
Device Code Select & Pulse Amp.
6651 (test)
6654 (start)
6652 (clear)
To Prescaler Clear
(on) Break Req.
(on) RC Timer
6654
BTS-1
Accept
Dec negative logic symbols used throughout.

PROGRESS TO DATE (Through August, 1972)

Data Acquisition System:

The basic hardware and software for data acquisition, from the discriminator through the prescalers to the computer memory, has been tested, and is ready to use. The computer is a PDP-8/I, and the interface has been constructed using Digital Equipment Corporation modules and accessories. While the logic design follows established practice, its application to the present system has required testing, minor alteration, and statistical analysis. The extensive logic wiring reflects the patient efforts of Miss McLaughlin. The circuitry shown has been tested on all control channels, and on two input channels using a clock module to simulate incoming counts.

Maintenance software, making it easy to spot and debug problems in the logic, has been developed to test each logical function. This software contains the core of the ultimate data-acquisition system, and can serve this purpose until attention can be diverted to development of more sophisticated programming.

The interface has been designed to use the Memory Increment feature of the PDP-8/I to record the prescaled pulses from the seven channels, essentially simultaneously. In addition, the interface has been equipped with its own timer. This greatly simplifies the software, and removes minor sources of error due to possible dropped counts. This interface is described in detail in a separate report (COO-2058-3); we believe it to have applications in a variety of multiple-input counting situations.

Analysis of the statistical problems involved from prescaling roundoff and other sources has been completed. In the present design, counts are prescaled by 64. Within very wide limits of total count and of dwell-time per position, errors from this source will not be significant.

Mechanical Design:

The vacuum shell has been assembled, complete with the required stands and supports. The axis of the unit is aligned along the local direction of the earth's magnetic field; adjustment has been built into the stands for minor correction of this orientation as required. The major parts of the shell are standard or modified vacuum components, using copper-gasket seals.

The larger of two oil diffusion pumps (a 6" NRC pump) can maintain a vacuum in the closed system below 10^{-7} torr without outgassing or cooling, and below 10^{-8} torr using liquid nitrogen in the trap. Since the pressure is much higher during sample injection, this is deemed an adequate vacuum. Backstreaming of diffusion pump oil under experimental conditions (that is, during injection of sample through the nozzle) made it necessary to place a baffle between the pump and the liquid nitrogen trap. A simple baffle consisting of two semicircles of aluminum sheet, in thermal contact with the walls and so placed as to block direct optical lines from pump to trap, proved sufficient. No trace of pump oil was subsequently found on the cold trap. As a further precaution, however, we changed from silicone pump oil to polyphenyl ehter. Silicone oil was discarded on the advice of Professor Kozo Kuchitzu of the University of Tokyo. Dr. Kuchitzu warns that these oils are so highly insulating that a very thin layer on the inside wall of the apparatus can build up a surface charge having erratic effects on the electron beam. Dr. Edwards suggested polyphenyl ether (Santovac 5, Monsanto Chemical Company), which gives excellent results.

The smaller diffusion pump, which evacuates the gun chamber, proved inadequate, being unable to maintain a pressure lower than 10^{-5} torr under experimental conditions. The air-cooled pump was replaced by a water-cooled pump, which immediately was able to reach 10^{-7} torr, an acceptable level.

The sample-injection system has been testedusing CCl_4, a 0.28 mm square-end hypodermic needle as a nozzle, and a pressure behind the nozzle of about one torr. This approximates a typical flow in the photographic process. Under these conditions, the pump and liquid-nitrogen trap could maintain a pressure of 2×10^{-5} torr, which compares favorably with pressures in photographic units. Prior degassing of the sample is found to be very important if pressures this low are to be achieved during steady flow.

Under these conditions it is difficult to ascertain that pure sample, free of volatile impurities, air from leaks, and contaminants from gaskets and vacuum greases, is entering through the jet. As soon as possible a non-magnetic (quadrupole) mass-spectrometer-type residual gas analyzer is to be attached to the diffraction chamber.

Electron Optics:

The 40-kv supply with rectified 4-volt, 5-ampere filament supply has been completed and tested. The supply is enclosed in a steel mesh cage with a power-cord disconnect attached to the door. The high voltage is measured using a Beckman Instruments 100-kv voltage divider. The electron gun has been constructed and tested. Electron-beam optics, including two sets of beam deflectors and an electrostatic lens, have been constructed and await testing. The optics resemble quite closely those in the electron diffraction unit of Dr. L.S. Bartell at the University of Michigan, except for the use of an electrostatic lens. The divided beam trap, designed to detect and allow correction for beam drift, has also been constructed. Control circuitry for all phases of the optics is complete.

The electron gun originally gave some difficulty -- the high voltage would discharge (arc) every few minutes. A redesigned gun chamber, allowing 3/4" spacing within the vacuum system between the gun a -40 Kv potential and any grounded surface eliminated this annoyance. Apparently the former 3/8" spacing was insufficient.

The self-centering feature of the beam trap, wherein the trap is divided into four mutually insulated segments, and current differentials are fed to two operational amplifiers which apply corrective voltages to the electrostatic detectors, has been tested on a prototype. The final split beam trap, an integral part of the detector assembly, is complete.

Detector System:

Progress in this area has been slowest, since my testing required operational assemblies in all other areas. Two detection systems: (1) scintillator-photomultiplier combinations, and (2) direct electron multiplication, using a device such as the Bendix Spiraltron. Tests at a fixed position indicated that the Bendix Spiraltron multipliers had approximately a 45% efficiency, by comparison with a faraday trap. This may exceed the efficiency of photographic plates, for which little definite data is available. In addition the Spiraltrons were not detectably sensitive to beam direction or position, and led to a simple, compact experimental design. We thereupon decided to use the Spiraltrons.

The detector system using spiraltrons is described in the preceding section. Detector system fabrication is complete, and assembly and testing are in progress. Problems with leaks and mechanical stability under operating conditions have been met as they arose.

CONCLUSION:

Work on the apparatus described herein is continuing under sponsorship by the National Science Foundation. This has turned out to be truly a major undertaking, with numerous unforseen problems, delays, and pitfalls. However, no insuperable obstacles have been encountered, and the research effort has had numerous beneficial side effects for the investigators, for this department and institution, and hopefully for the scientific community. The Investigators wish to express their gratitude to the Atomic Energy Commission and its personnel for their support, encouragement, and understanding during these initial phases. We pledge our continued effort to make this project worthy of that support.