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AEC RESEARCH and DEVELOPMENT REPORT

AN IN-CELL RECORDING OPTICAL SPECTROMETER

U. L. UPSON
E. J. WHEELWRIGHT

MARCH, 1967

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AN IN-CELL RECORDING OPTICAL SPECTROMETER

By

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E. J. Wheelwright

Fission Product Chemistry
Chemistry Department

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U. L. Upson
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INTRODUCTION

In some radiochemical processes, optical photometry can provide process information not obtainable by other means. This report describes the application of spectrophotometry to studies involving kilogram-scale separation of Pm-147 from process wastes.

In most hot-cell chemical processes, the radioisotopes in the various process streams and vessels can be identified and measured by their characteristic gamma spectra. Thus, the in-cell multichannel gamma spectrometer is perhaps our most valuable tool in radiochemical process control, and is now used extensively in operations carried out remotely in high-level facilities.[1] In such operations as the separation of fission product rare earths, however, some of the important nuclides either are inactive or have activities difficult to detect or evaluate under process conditions.

Am-241 and Pm-147 have gamma activities of low energy and relatively low abundance. Samarium and neodymium, which bracket promethium an ion exchange elution sequence, are not radioactive. However, all these elements have intense and complex light absorption spectra, and are conveniently identified by spectrophotometry.[2]

SUMMARY

A programmed recording spectrophotometer, operating in the visible light region, has been built and installed in a "hot" cell of the Pacific Northwest Laboratories' High-Level Radiochemical Facility, and has proved to be an extremely useful analytical and control instrument in the recovery by ion exchange of Pm-147 and Am-241 from separations plant wastes.

Detection levels for americium, promethium and neodymium are below 1% (<0.0003M), but sensitivity to samarium (which fortunately is not critical) is less certain, owing to variable interference (below 490 mμ) from stainless steel corrosion products in the feed and in the eluant.

---

[a] *Paper was presented at the Tenth Conference on Analytical Chemistry in Nuclear Technology at Gatlinburg, Tennessee, September 27-29, 1966.*

Single-beam design was chosen because it requires a minimum of optical and mechanical components in the high radiation field and potentially corrosive atmosphere inside the cell. Only the tungsten lamp, sample compartment, and sealing window are inside the cell, and these all are remotely replaceable. Intermediate optics are mounted in a bayonet assembly inserted (from outside) into a through-the-wall stepped pipe which provides optical alignment and which contains offset gamma shielding. The monochromator assembly (including slit drive, shutter, and phototube) is mounted on the outside end of the pipe. The power supplies, control and programming chasses, and recorder are installed in a cabinet which can be remote from the optical instrumentation.

Scanning is performed automatically on either of two in-cell flow samples, normally against an air-path reference. Adjustable limits on the scan range permit automatic repetitive scanning of any selected wavelength range, either at timed intervals or in continuous succession. The significant absorption peaks at any given stage in the process can be scanned at 5-min to 2-hr intervals, or the instrument can be set to "ride" on a given peak, and thus to record the growth or decline of that component in the process stream.

The instrument has proved to be a valuable addition to the technology of remote analysis.

RARE EARTH ABSORPTION SPECTRA

The absorption spectra of samarium, promethium and neodymium (obtained *in vitro*) are shown in Figure 1.[2,3] Although there is a wide range of absorption peaks in each of these spectra, the process streams were found to have quite high and variable baselines at both ends of the spectrum

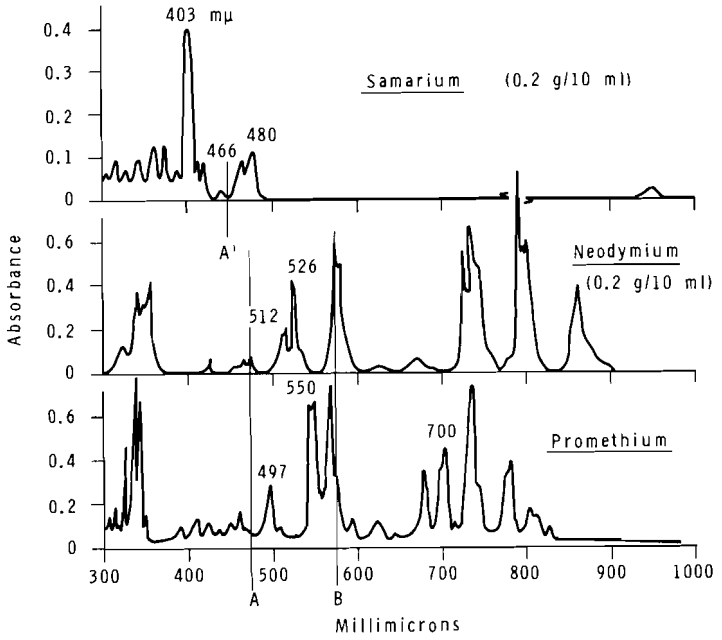

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FIGURE 1. Rare Earth Spectra

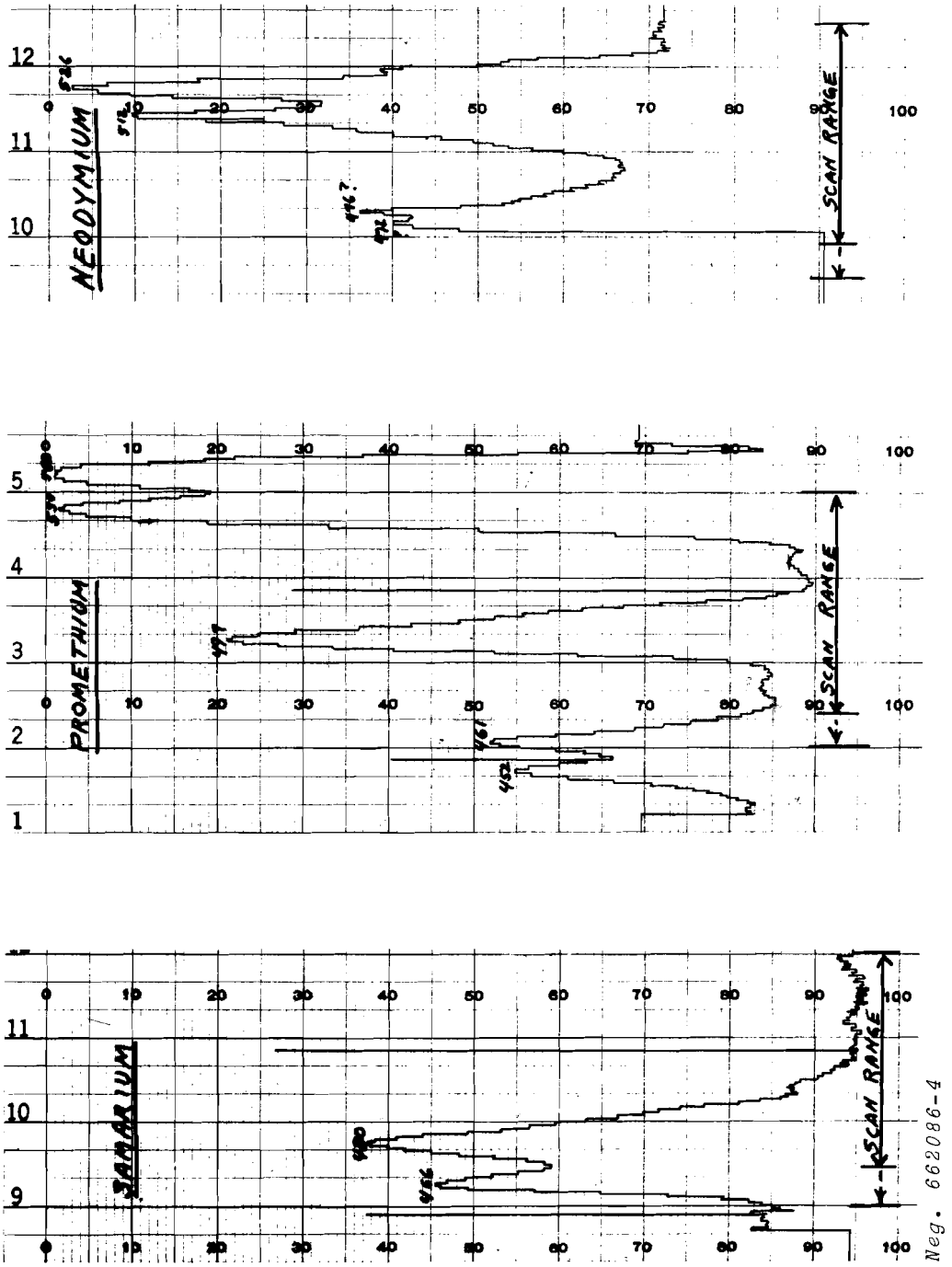

FIGURE 2. In-Cell Sample Spectra

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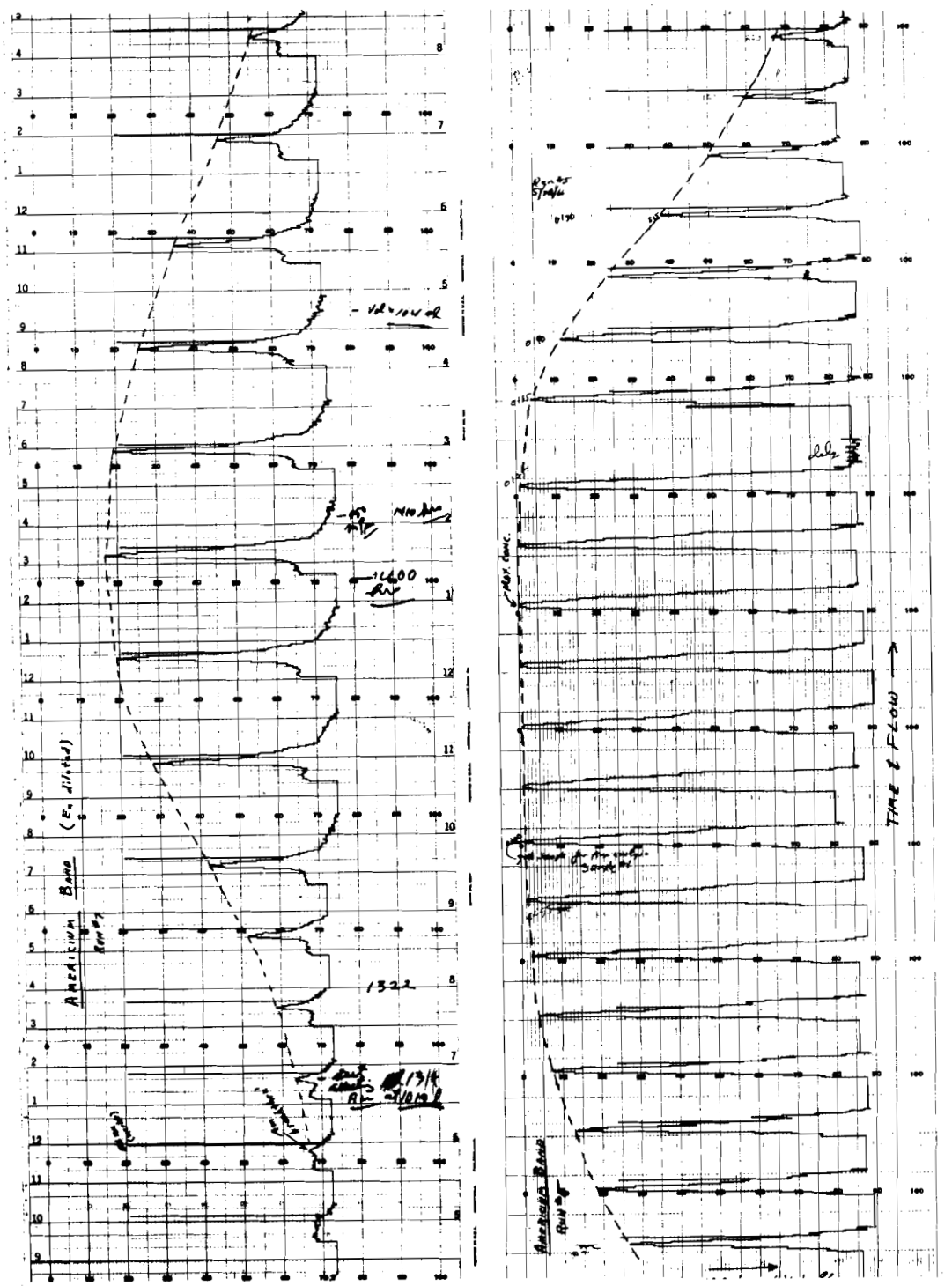

FIGURE 3. Americium Scans

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(especially the blue end) due to corrosion products and degraded organic material. In fact, if the complexant (DTPA)* stands overnight in a stainless steel sample cell, it will turn "black" in the region below ∿450 mμ. Fortunately, however, there are satisfactory absorption peaks within the wavelength range 450 to 600 mμ, for which the baseline is fairly low and constant, expecially in the later stages of the process. Spectra within this range for substantially pure samarium, promethium and neodymium, obtained on in-cell process flow samples, are shown in Figure 2.

AMERICIUM SEPARATION

Separation of americium from the feed mixture is not a primary aim of our program, but it is easily obtained as a by-product, in mixture with europium. It elutes with (and just ahead of) europium, from which it can later be separated, and is easily followed on the optical spectrometer. Figure 3 shows actual process scans of the americium peak at about 508 mμ, for two runs of different americium concentration. The optical spectrometer is essential to this separation since europium has a multipeak gamma spectrum which obscures the 60 keV americium gamma peak, but has no optical absorption above ∿400 mμ.

PROCESS EVALUATION

In the ion-exchange separation of the fission product rare earths and associated elements, gamma-active europium is followed by stable samarium in elution sequence, prior to elution of the promethium product. In elution by DTPA, yttrium elutes between samarium and promethium, and is undetectable by either gamma or optical spectrometry. Thus, it appears as a "hole" or dilution in the changing optical spectrum. This is evident in the upper left hand scans of Figure 4. These scans, taken from the actual process records, also show the growth of promethium (bottom) and the breakthrough of neodymium at the end of the promethium band (upper right). Figure 5 shows the neodymium breakthrough at an earlier stage of another run, the growth of neodymium (bottom), and the final tail-off of promethium (upper right). Decisions as to when to add (or drop) successive columns, and whether to collect or discard final effluents, are based on these optical scans and upon supporting gamma spectrum data.

Detection levels for promethium and neodymium are below 1% (<0.0003M), using their most intense absorption peaks within the scan range--at 550 and 526 mμ, respectively. Because of the higher and more variable baseline below ∿490 mμ, samarium evaluation is somewhat less precise. Fortunately this information is less critical.

The 497 mμ Pm peak is used for product concentration evaluation after substantial breakthrough, since tne readout on the present in-cell spectrophotometer is in "percent transmission," and thus the weaker peaks yield more sensitive data at the higher concentrations. Conversion from percent transmission to concentration is quickly obtained

(diethylene-triamine-pentaacetic acid)

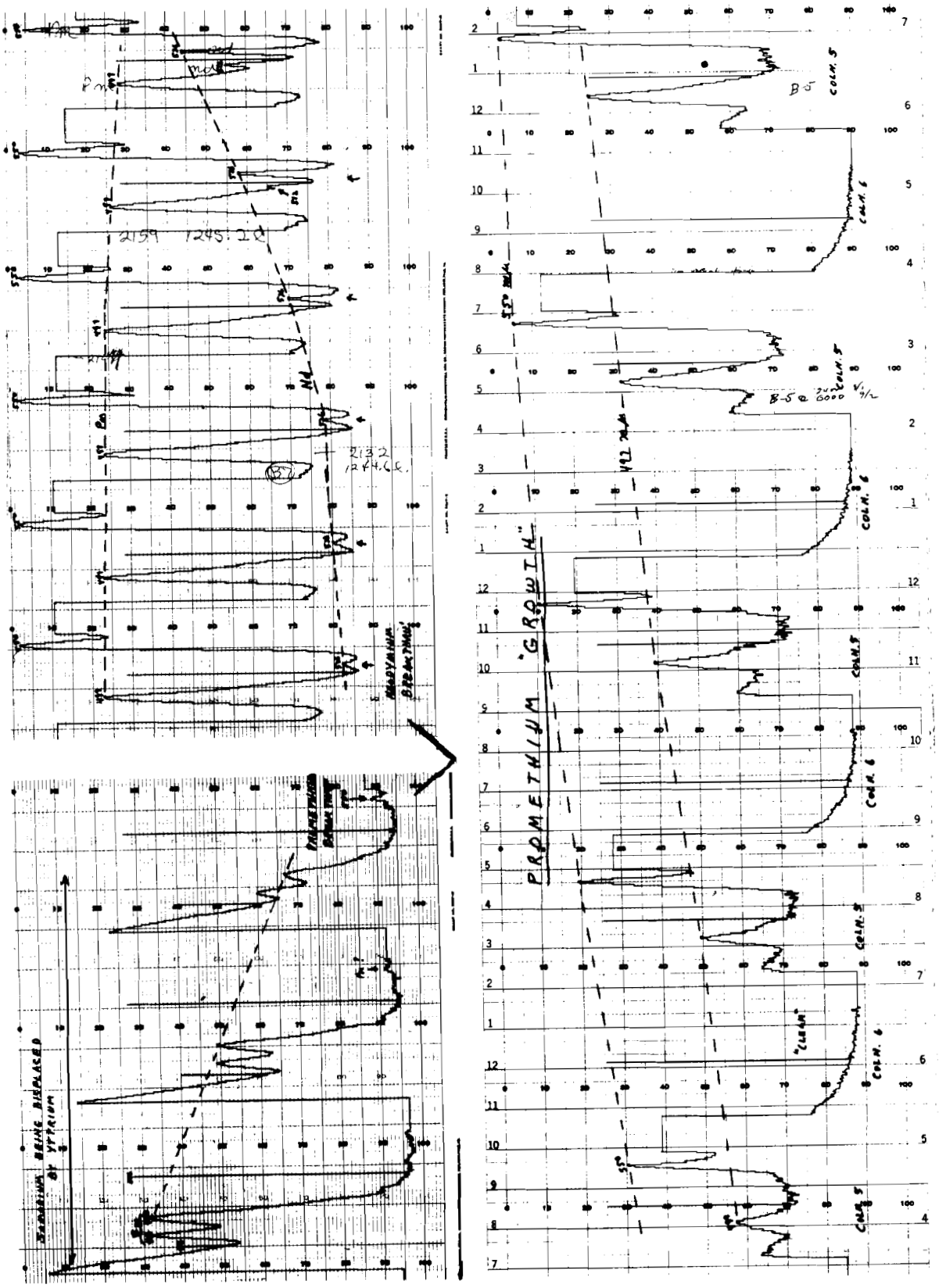

FIGURE 4. Promethium Scans

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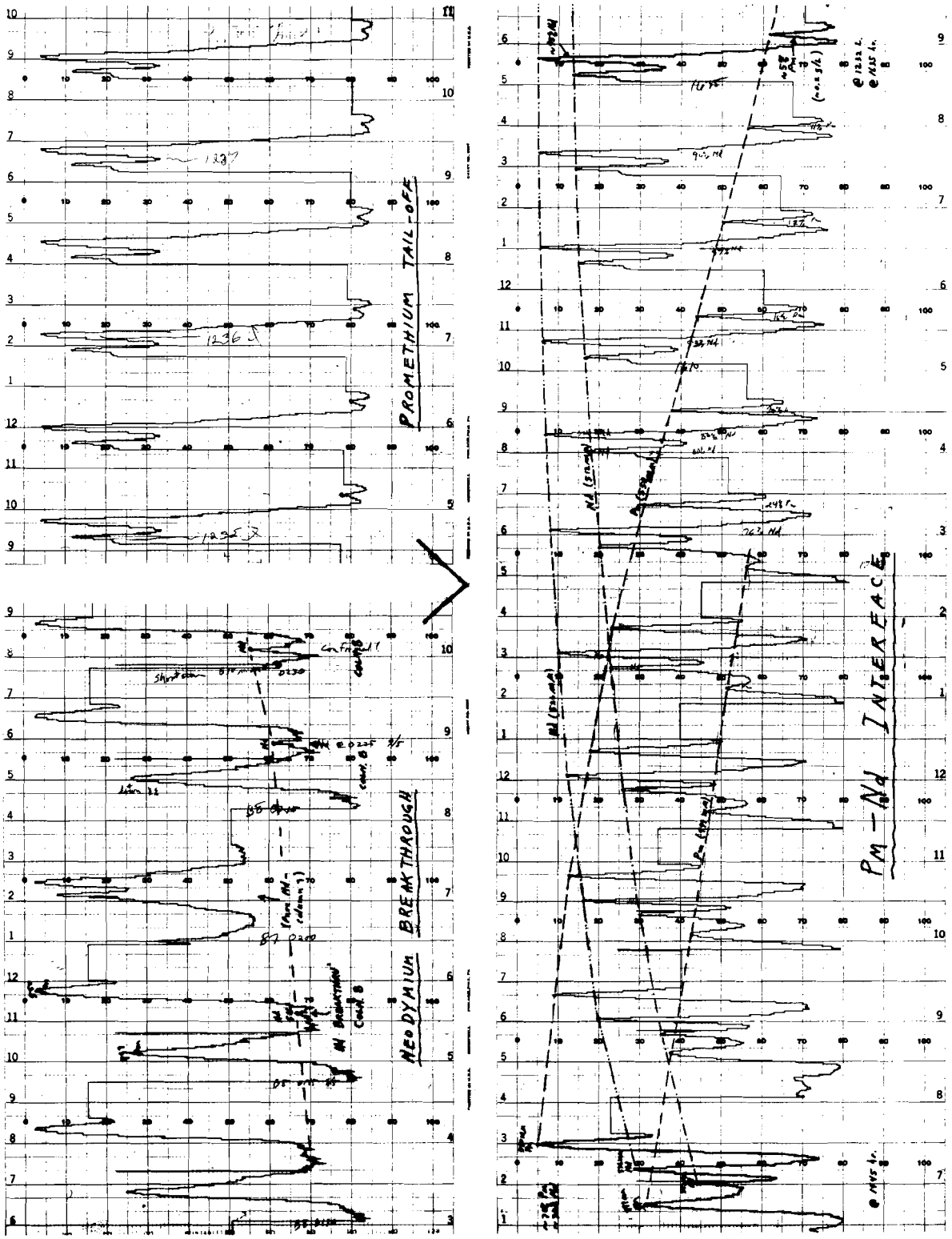

FIGURE 5. Neodymium Scans

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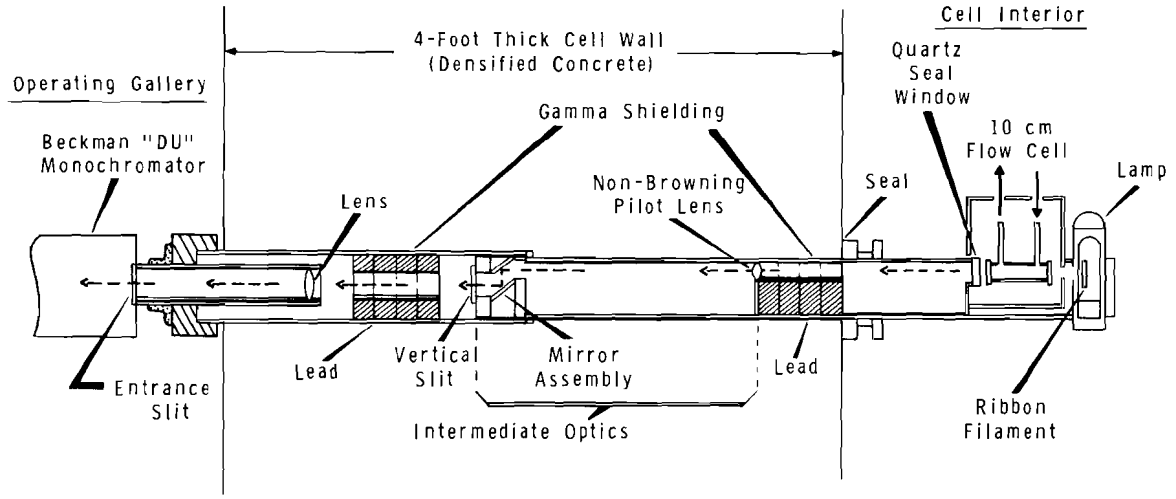
from a straight line graph on semilog paper. For product take-off from the final stage, both gamma and optical analyses give quite satisfactory concentration indications, and each confirms the other during this critical step.

INSTRUMENT DESIGN

Experience in the remote operation of hot-cell processes dictates the utmost in simplicity, durability, and reliability--and very limited space requirements--in in-cell instrumentation; and to our knowledge, no commercially available spectrophotometer adequately meets these criteria. It seemed essential that a minimum of components be located inside the hot cell, and that none of these be critical optical elements. Therefore, an instrument was designed of which only the light source and sample cells (plus an integrity seal window) are located inside the cell. The light beam is brought outside the cell, through gamma shielding off-sets, for spectral analysis. Figure 6 shows the simple design of the optics that permit remote location of the samples and light source.

The light from the tungsten lamp passes through either an air path or the selected sample, and the pilot lens focuses the filament image through the mirror assembly onto the intermediate slit. A second lens focuses the slit image upon the entrance slit of the monochromator. The mechanical design of the assembly is shown in Figure 7. The entire remote optical system is enclosed and supported by a rigid pipe assembly which serves as an optical bench, with the in-cell components cantilevered into the cell.

Figure 8 shows the cantilever section (with sample compartment removed), the bayonet lamp assembly (easily replaced remotely), the



PROFILE VIEW

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FIGURE 6. In-Cell Spectrophotometer

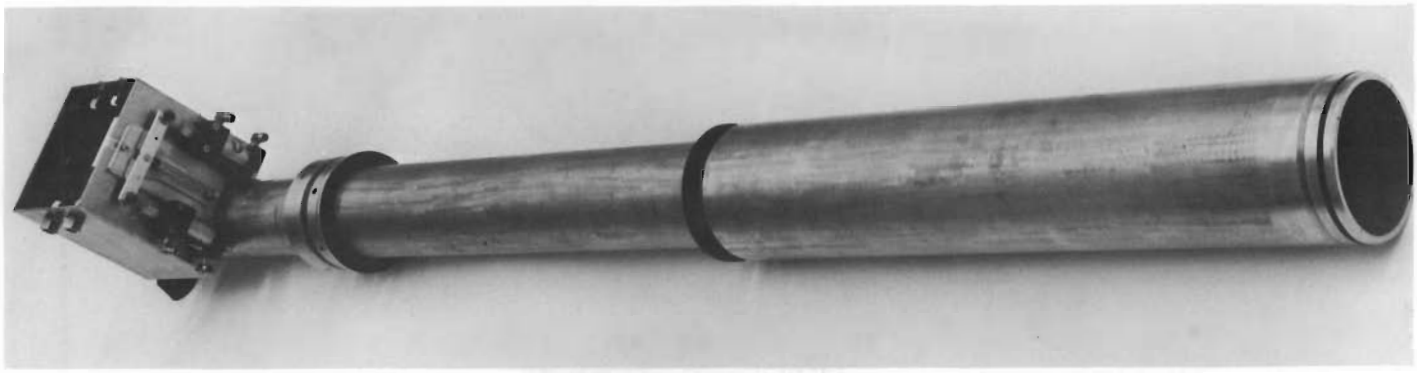

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FIGURE 7. Assembly

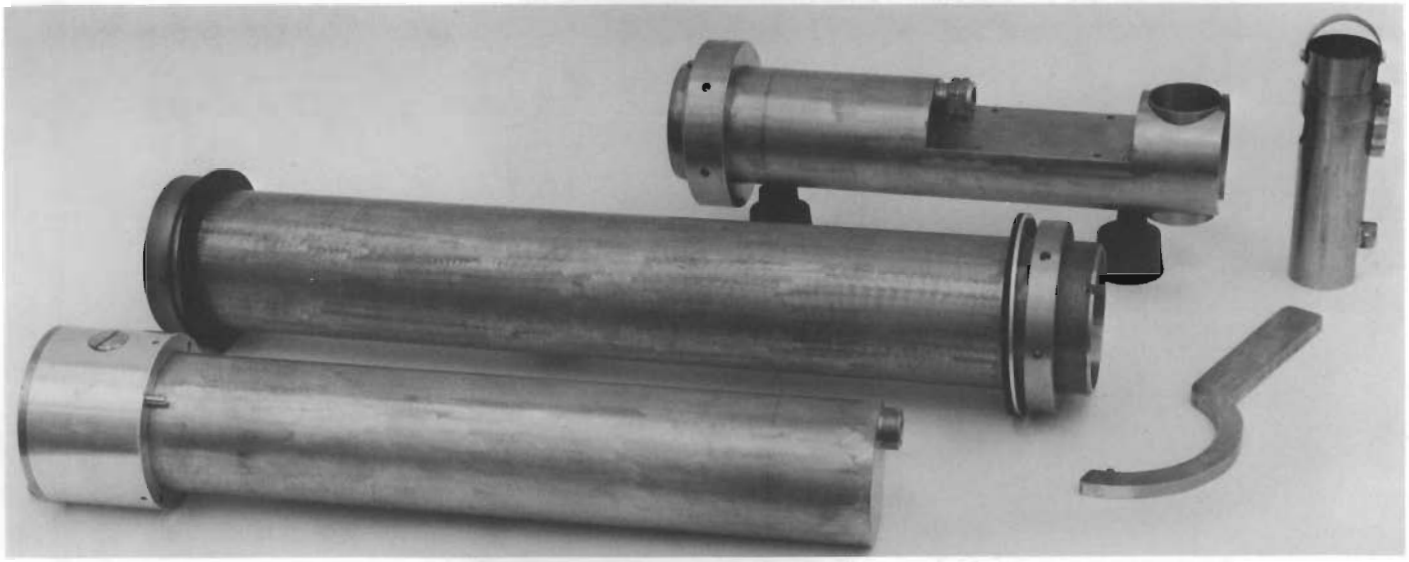

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FIGURE 8. Intermediate Optics (removed)

smaller through-the-wall pipe section (and lock-and-seal parts) and, in the foreground, the intermediate optics section, which is removable from the front face (outside) of the cell. Figure 9 is a photograph of this section partially inserted into the inner pipe section (the injector-blade slit edges are not yet installed). The larger pipe section, shown at the right (Figure 9), brings mechanical alignment through the wall to the external optics.

The sample compartment mounts in the saddle of the cantilevered section and is remotely removable (Figure 10). A separately removable sample cell hanger assembly is designed so that if either of two air cylinders is actuated, one of two flow sample cells is inserted into the light beam, and at no signal from the programmer, a reference air path is in the beam (Figure 11).

The sample cell (Figure 12) consists of a 4-inch length at 3/4 ips stainless

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FIGURE 9. Intermediate Optics (inserted)

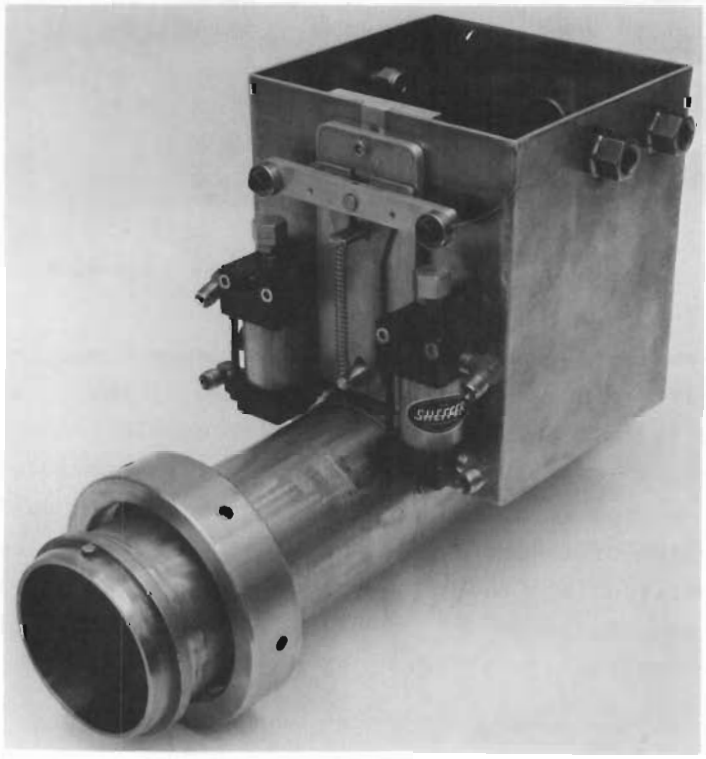

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FIGURE 10. Sample Compartment

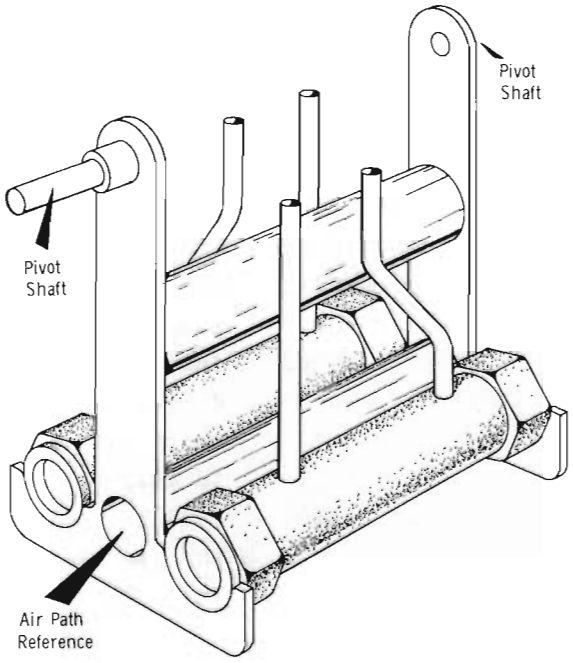

FIGURE 11. Sample Cell Hanger Assembly

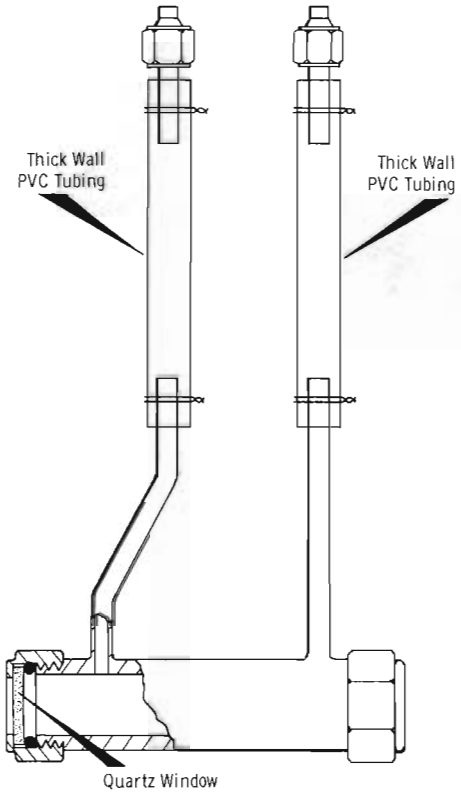

FIGURE 12. Sample Cell

steel pipe with tubing side ports. The 1/4-inch-thick quartz end windows are sealed by neoprene O-rings and modified 3/4-inch Swagelok tube nuts. The cell path length, with O-rings compressed, is 10.0 ± 0.1 cm. The cell is inserted into the process flow through flexible heavy-wall polyvinyl tubing connected to fixed fittings in the cell compartment wall (Figures 10 and 13).

A ribbon filament lamp is prealigned in a bayonet assembly which snaps into the far end of the cantilever section (Figure 13). The installed assembly, as viewed through the cell window, is shown in Figure 14. The external components--the monochromator, programming units, power supplies, and recorder--are shown in Figure 15.

OPERATION

Each spectral scan is obtained point-to-point as in manual scanning, but all steps are automatically controlled. A scan programmer originally designed for a different problem has been modified for this application. The single-point program is indicated on the dial on the upper panel of Figure 16. First, a pulse is sent to the monochromator drive unit, advancing the wavelength about 1 mμ, then the recorder servo amplifier compares the detector signal for air-path light intensity with a full-scale reference voltage, and drives a slit-adjust servo motor to obtain a light intensity equivalent to full-scale readout. Then the sample cell is interposed in the light beam, and the recorder circuit is switched into the amplifier input and output to give a pen response of "percent transmission," and the chart drive is momentarily actuated to give a slight incremental chart advance.

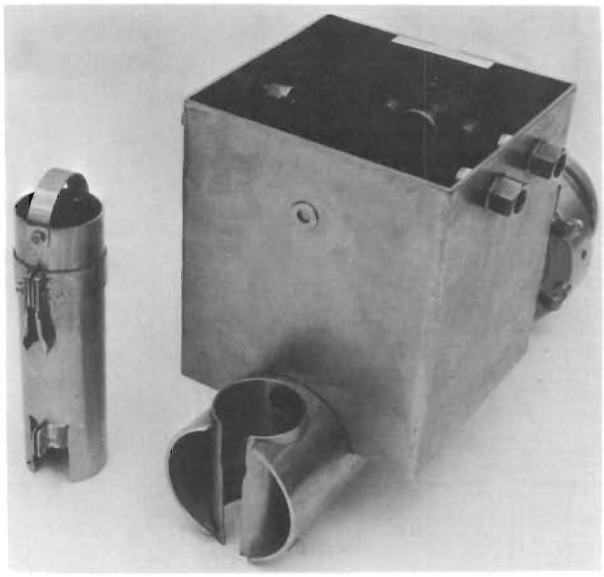

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FIGURE 13. Lamp Assembly

At regular intervals on the monochromator drive gear, an indexing switch is actuated and a pulse is sent to the recorder to yield a wavelength marker pip. The voltage for this signal is derived from a position-indicating potentiometer on the slit-adjustment, so that the end of the pip indicates slit width. Any deviation from the normal slit width for a given wavelength, as indicated by the pip, is a warning of instrument malfunction-e.g., aging lamp, lamp or phototube voltage variation, or instrument misalignment.

The nominal single-point period is 10 sec, giving a plotting rate of 6 points/min, but in the case of substantial slit adjustment or wide pen travel (as on sharp peaks or marker pips), a null-detector circuit

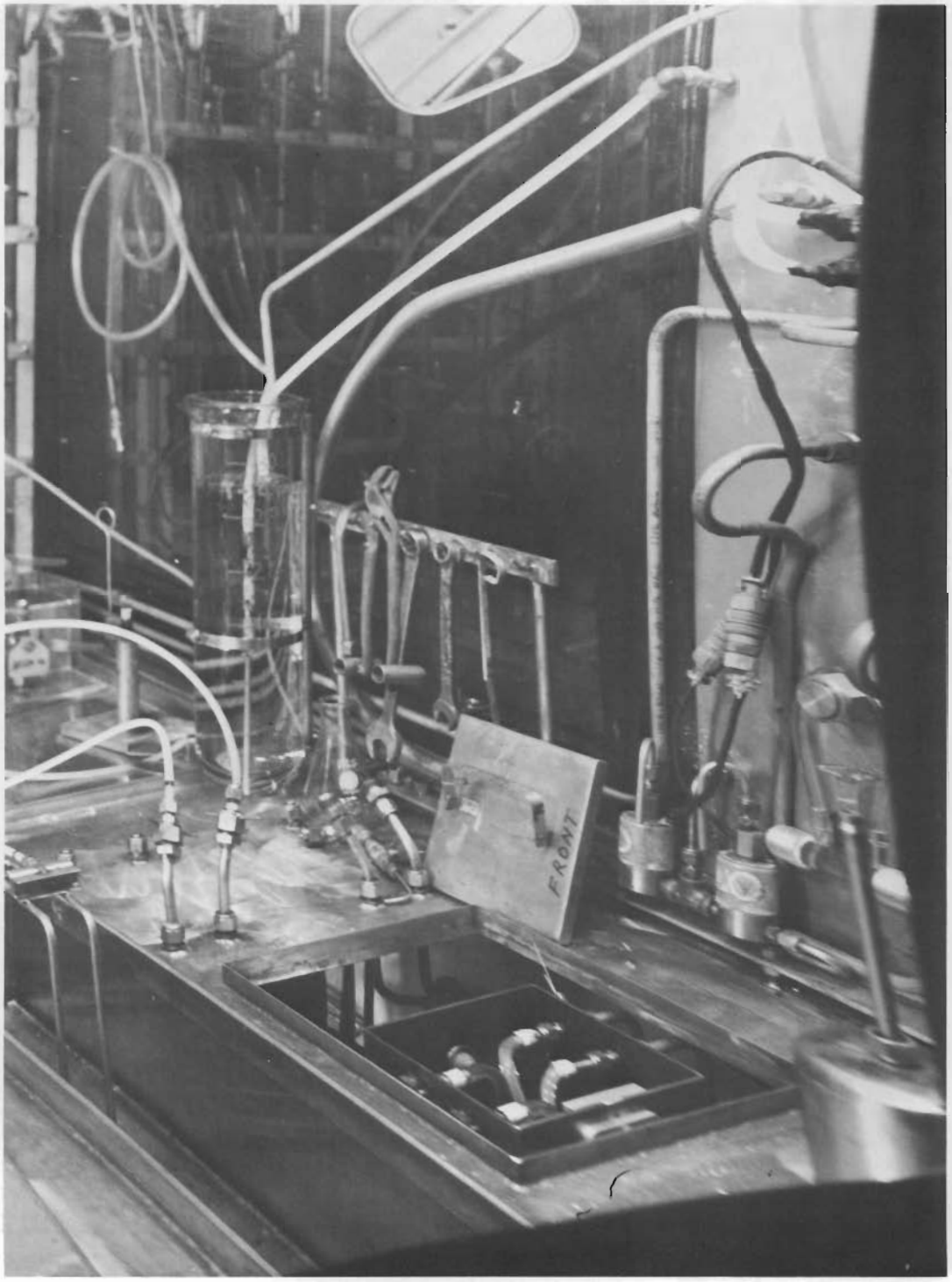

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FIGURE 14. In-Cell Installation

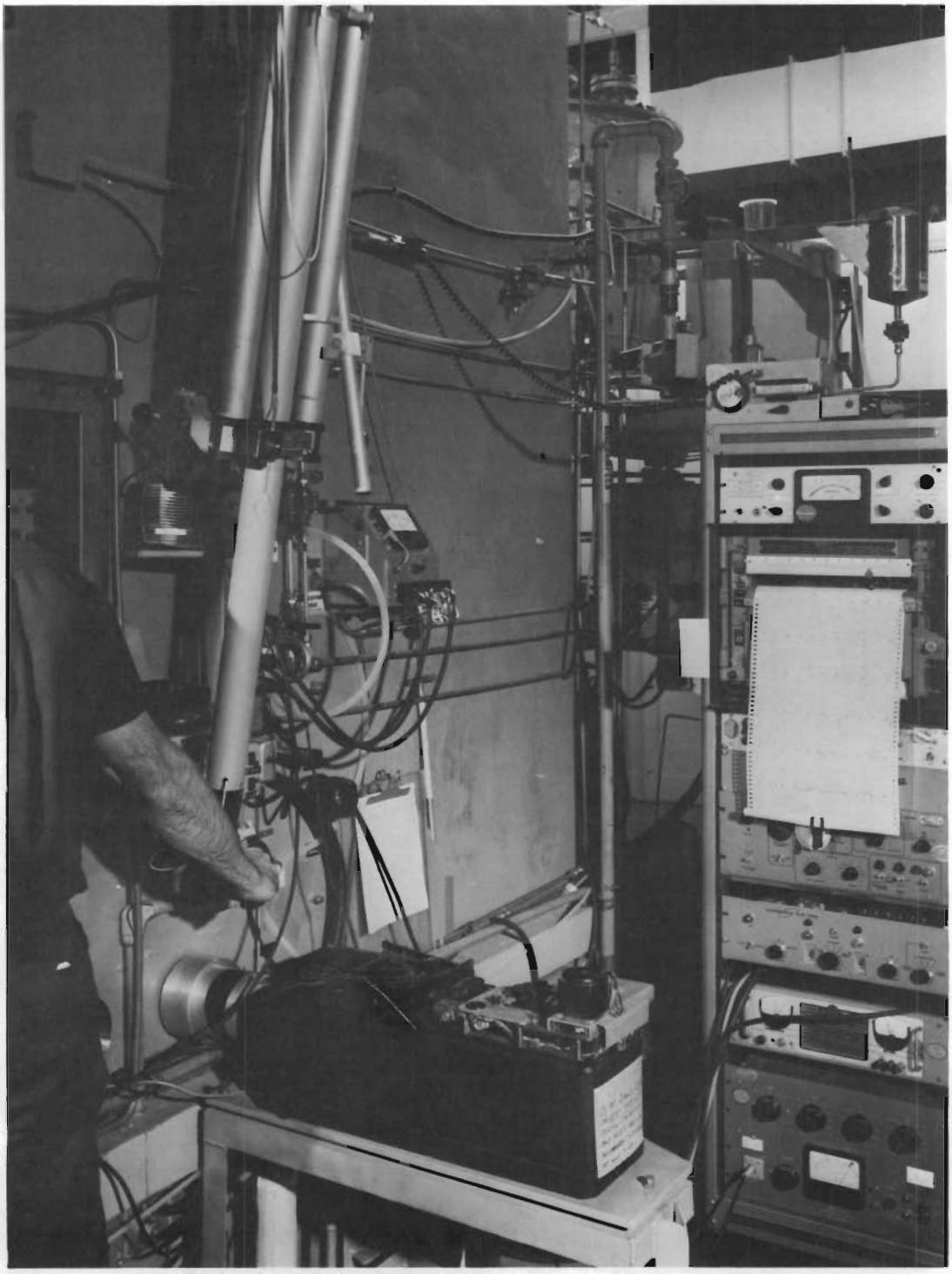

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FIGURE 15. External Components

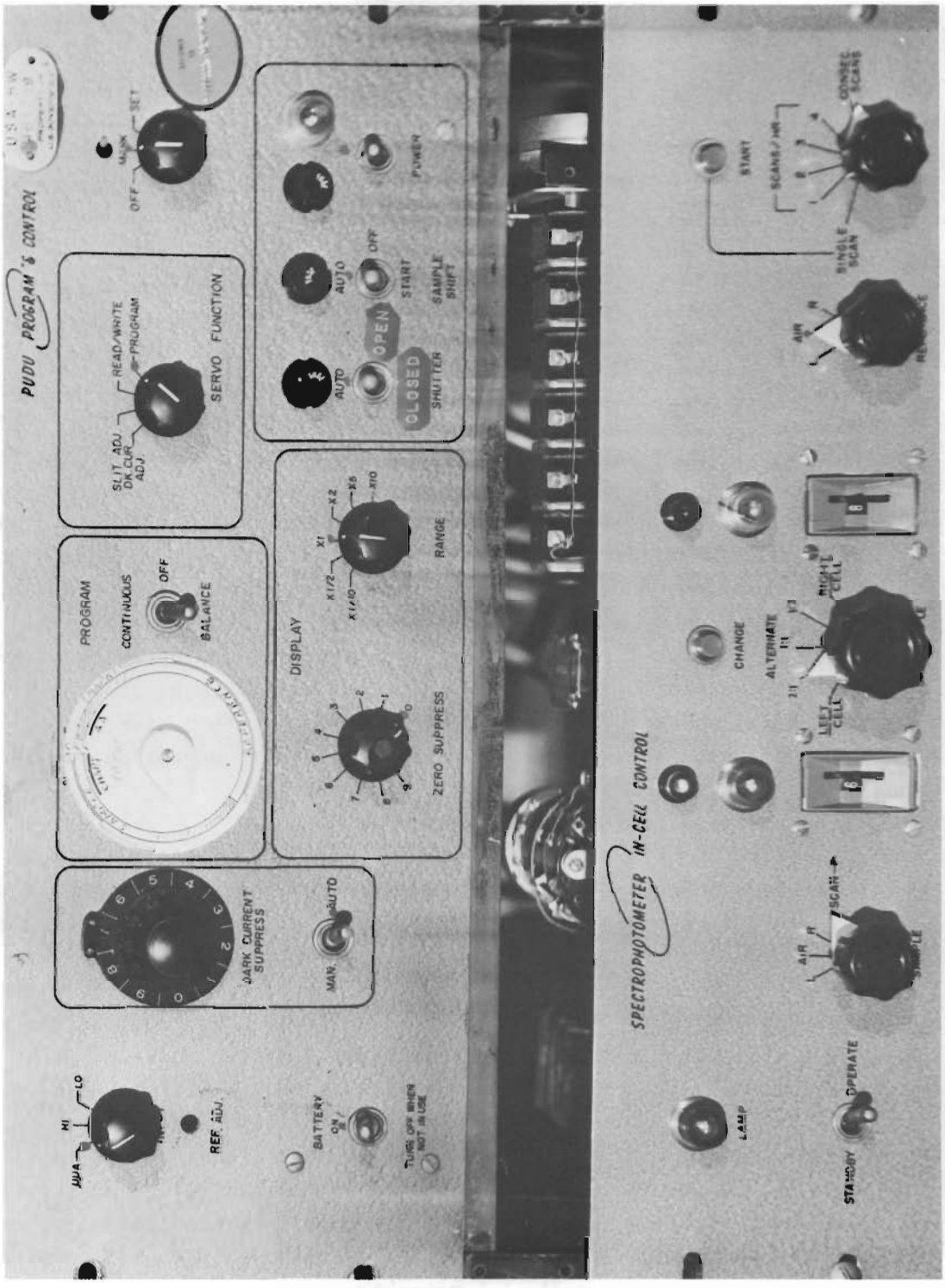

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FIGURE 16. Programming Chassis

arrests the program until balance is achieved. If balance cannot be achieved, as for severe misalignment, lamp failure, etc., the program remains stopped until corrected, and the instrument does not yield invalid data.

At the end of the scan of the selected range, the wavelength selector is returned to the lower limit position, and the chart is advanced 1 inch to separate successive scans. During the reset period, any drift in dark current is automatically suppressed to zero.

The lower panel of Figure 16 is a recent functional addition that gives automatic repetitive analysis of either sample cell, or of both cells in a preselected sequence, at a selected frequency. The scan frequency can be varied from 1 to 8 scans/hr, or in succession without between-scan delay, to accommodate the varying needs of the process. This leaves the operators free from the necesssity of continually resetting and restarting scans, yet avoids the superfluous output of continuous analysis during noncritical stages of process operation.

A TRIPLE-WAVELENGTH SPECTROMETER

Initially it was thought that a nonscanning continuous monitor would be the preferred instrument, because it would yield an instantaneous indication and a continuous record of successive rare earths of interest. Accordingly, an instrument was designed and built to measure three wavelengths (403, 526, and 703 mμ) characteristic of samarium, neodymium and promethium, respectively (Figure 17). For one position of a manually operated shutter, the 403 mμ peak of samarium would be compared with the 703 mμ peak of promethium, giving a downscale reading for samarium, an upscale reading for promethium, and a midscale reading for equal concentrations of each. Similarly, following the "heart cut," a shift of the shutter would yield a similar comparison of the promethium and neodymium concentrations. Actually, however, the highly variable baselines encountered in the process streams make this instrument only marginally useful. On the other hand, the scanning spectrophotometer, which had been considered an auxiliary accessory, proved much more sensitive and informative. Visual observation and interpretation of the optical spectra (including baseline variations due to impurities, gassing, degraded resin, etc.) have yielded valuable clues to operation beyond our anticipation.

FUTURE MODIFICATIONS

The monochromator, originally intended as a part-time auxiliary to be substituted for the triple-wavelength instrument, is mounted normal to the cell wall, projecting into the operations gallery, and subject to easy misalignment. This crystal monochromator is being replaced by a grating monochromator which will be mounted on the base plate of the now extinct triple-wavelength device and firmly anchored to the wall. This monochromator also will yield a linear wavelength record which can be correlated with the chart divisions.

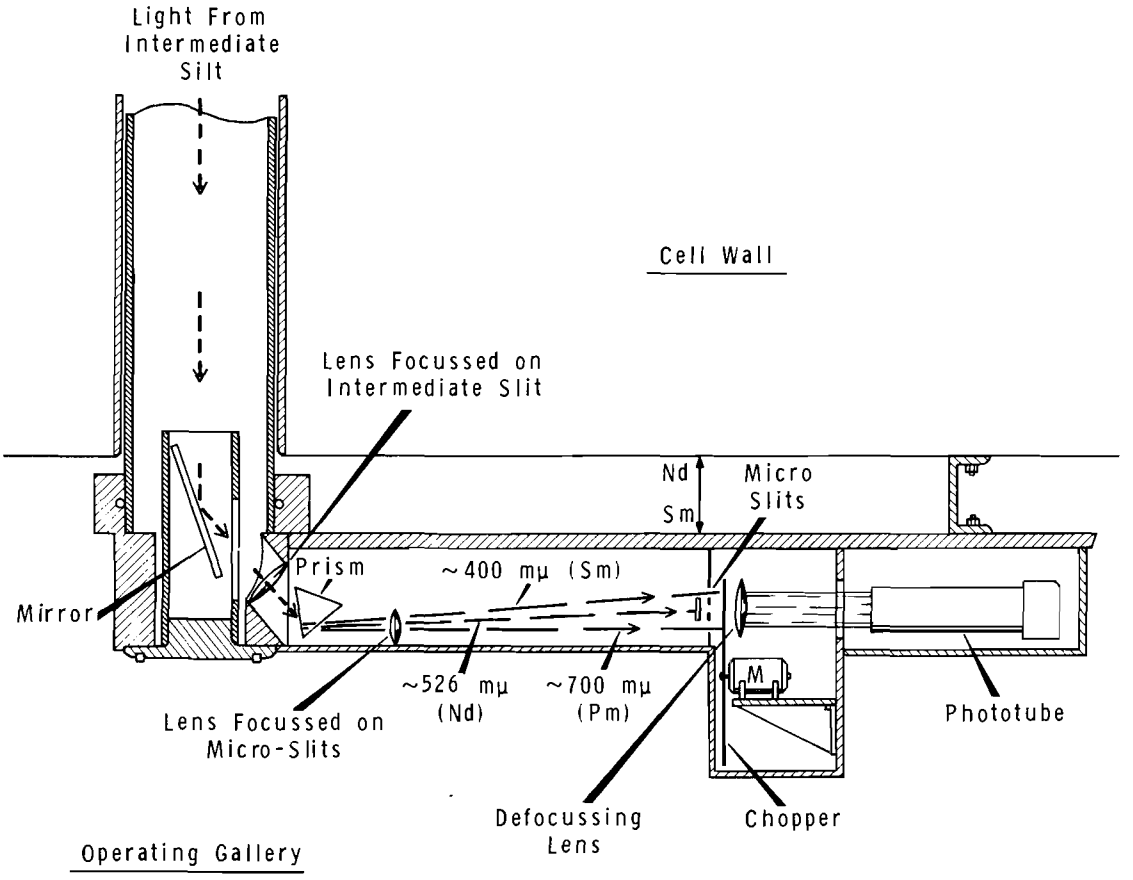

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FIGURE 17. Triple-Wavelength Spectrometer

A position-indicating potentiometer installed on the monochromator drive will make it possible to select the scan limits electrically, rather than by hand-set limit switches. This will permit the selection of different scan limits for the two samples, as well as the selection of fixed preset limits, by rotary switch position. These modifications will make this very useful instrument even more effective.

ACKNOWLEDGEMENTS

Much credit is due to William J. Coleman of our Optical Shop for his advice and help on the design of this instrument; to the shop personnel who prepared and mounted many of the optical components; and to A. W. Madsen, who accurately fabricated the machined parts.

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