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# ON-LINE URANIUM DETERMINATION USING REMOTE FIBER FLUORIMETRY

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## INTRODUCTION AND SUMMARY

Remote Fiber Fluorimetry (RFF) is being developed at Savannah River Laboratory for the on-line determination of uranium in plant process streams. A prototype system suitable for plant use has been designed and is being built. RFF (Figure 1) has four major components: a laser, an optical fiber, an optrode, and a detector.

Essentially, an optical fiber carries laser radiation from a laser to a process sampling point. An optrode (the optical analog of an electrode) couples the laser light into a sample solution. Fluorescence from the sample is collected by the optrode and goes back through the same fiber to a detector.

Figure 2 shows a cross-section of one of the chemical separations buildings at the Savannah River Plant. Chemical separations are carried out in the "hot" and "warm" canyons. Because the process solutions are very radioactive (especially in the "hot" canyon), all operations are performed remotely. Samples are

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aspirated to a sample aisle where they are collected and sent to a control laboratory for analysis. The present system is a time-consuming and manpower-intensive process.

Using an RFF system, the analysis can be made both simpler and safer. The laser and detector are placed at a convenient remote location, such as the control room. Optical fibers run from the laser to either the sample aisle or process tanks. Multiplexing makes it possible to analyze several different sampling positions with one laser and detector.

The incentives (Figure 3) for demonstrating this technology include reduced analysis time and decreased sample load for the laboratory. Since RFF is a remote on-line technique, sample handling is avoided. Analysis time is 5 minutes (versus the 4-hour minimum needed now). The control laboratory has a decreased sample load. Finally, RFF could easily be incorporated into a large-scale process control system.

**DISCUSSION**

The properties of optical fibers give RFF many advantages (Figure 4). The fibers are inexpensive, typically costing less than $1.00/meter, and they come in any length needed to do the job (1 cm to 1 km). Like coaxial cables they are flexible and have commercially available connectors. Special tools are readily available for fiber polishing and cleaving, and fibers can be terminated in the field in a few minutes. Finally, quartz fibers are radiation resistant, making them well suited for installation in radioactive environments.

Laser systems make RFF systems practical for fluorescence measurements at long distances. Lasers (Figure 5) are directional light sources which efficiently couple light to the fiberoptic cable. Lasers also provide a wide choice of wavelengths, which greatly increases the flexibility of RFF.

Optrodes (Figure 6) couple the light to the analyte. For many types of analyses they can be made analyte specific. In addition, some optrodes can be designed for hostile environments. At Lawrence Livermore National Laboratory (Figure 7), Tomas Hirschfeld has designed optrodes to measure temperature, pressure, pH, and concentration of analytes.

A multiplexer (Figure 8) designed and built at Savannah River Laboratory makes it possible to monitor up to 100 different sample positions, with only one laser and detector.

Most of the work at Savannah River has been with uranium. Figure 9 shows a uranyl absorption spectrum in 0.5M $HNO_3$ with absorption bands appearing at 325nm and 416nm. We excite the uranyl ion at 416nm. Since the optical fiber transmits best in the IR with decreasing transmission towards the blue, this is a good compromise between fiber transmission and uranyl absorption.

Figure 10 shows the DCR-11 laser system from Spectra-Physics, which is designed for plant environments. The laser is air-cooled and totally computer controllable. The 416nm laser light is generated by Stimulated Raman Scattering from the third harmonic of the Nd:YAG laser (Figure 11). This system generates the 416nm laser

light passively, with the only active elements being the flashlamps. The flashlamps should last for several months with routine use, and are easily replaced when needed.

The characteristic uranyl ion fluorescence is shown in Figure 12. This fluorescence spectrum was taken with a $10^{-3}$M uranyl solution in 0.5M $HNO_3$. Detection is made (Figure 13) with an EG & G/PAR OMA III gated intensified photodiode array attached to a spectrograph. The entire detection system is small, and acquires the spectrum in 0.1 seconds.

Figure 14 shows that a calibration curve can be generated. In this figure we have plotted uranyl ion concentration versus fluorescence intesity at 513nm. The concentration range is from 0.2 to 10 gm/liter, bracketing the range of concentrations expected to be seen in the plant streams targeted for RFF analyses (2-7 gm/liter).

Quenching is a major problem with using fluorescence as an analytical technique because it causes a decrease in the uranyl fluorescence intensity. Table 1 shows the effects of fluorescence quenching. Fluorescence was measured over several days from nine different uranyl solutions in phosphoric acid and averaged 7750 cps. 1-5 drops of a strong quencher solution (1 gm/liter $FeCl_3$) were added to each of these samples. Column 2 shows that the resulting fluorescence intensity dropped dramatically. The only difference in the two columns is the quenching.

Figure 15 shows two fluorescence decay curves. In each case the fluorescence intensity was monitored at various times. The top

curve shows the single exponential decay seen from the uranyl ion in $H_3PO_4$. The lower curve shows the fluorescence decay from the same uranyl solution with 2 drops of $FeCl_3$ solution added. In this case, quenching causes the fluorescence signal to decay more rapidly. Figure 16 shows plots of the log of the fluorescence intensity versus time. The plots show that the curves are single exponential decays. Lifetimes can be calculated from the slopes of each line.

For the uranyl ion without quenching, the lifetime is 197 microseconds. Conversely, the quenched solution has a lifetime of 97 microseconds. Quenching in phosphoric acid is greater than in nitric acid, due to the longer lifetime in the phosphoric acid. Any quenching correction which works for phosphoric acid solutions will work for nitric acid solutions.

Using a matrix lifetime technique (Hieftje and Haugen)[1], it was possible to compensate for the effects of quenching. Figure 17 shows how this is done. The quenched solution's fluorescence intensity is measured along with its fluorescence lifetime. The lifetime of an unquenched uranyl solution is constant over our concentration range. By multiplying the fluorescence intensity of the quenched solution by a lifetime normative factor, we are able to calculate what the fluorescence intensity would be if no quenching were taking place.

The right column in Table 1 shows the calculated fluorescence intensity using the matrix lifetime correction. As you can see, we were able to compensate for quenching to within the experimental error of our measurement. Using this technique we can determine what the fluorescence intensity of a solution would be if quenching were not taking place, even if we do not know the quenchers or their concentrations.

As part of a demonstration program, we have installed optical fibers between my laboratory and an analyzer demonstration facility (Figure 18). This facility is an exact duplication of the sampling system used in the canyon facilities I described earlier. In this facility we were able to solve engineering problems encountered in moving from a laboratory system to a plant system.

Figure 18 shows the uranium optrode used. Experiments were run inside a process tank and inside a sampler, which demonstrated that uranium could be monitored. The optical fiber runs a distance of 165 meters to my laboratory, where the laser and detector are located. The final slide (Figure 19) shows a calibration curve generated by an optrode inside the process tank at the Analyzer and Control Demonstration Facility.

**CONCLUSION**

I have described how Remote Fiber Fluorimetry (RFF) may be used to determine uranium concentration remotely and how RFF was tested in our analyzer test facility. We have designed and are building a prototype RFF system which will be closely evaluated

this fall. Pending the successful completion of this analysis, the RFF system will be installed in one of the separations buildings at SRP next year.

**REFERENCES**

1. G. M. Hieftje and G. R. Haugen, Analytica Chimica Acta, 123 (1981) 255-261.

TABLE 1

Quenching Effect and Correction

| $10^{-3}$ M $UO_2^{++}$ (cps) | + 1-5 DROPS $FeCl_3$ | QUENCHING CORRECTED |
|---|---|---|
| 7900 | 3800 | 7720 |
| 7730 | 3900 | 7370 |
| 7680 | 2020 | 7380 |
| 8000 | 2750 | 7180 |
| 7500 | 3000 | 7470 |
| 7730 | 2700 | 7050 |
| 7800 | 3400 | 7450 |
| 7700 | 4300 | 7360 |
| 7700 | 2700 | 7790 |
| AVG = 7750 ±140 | | AVG = 7420 ±230 |

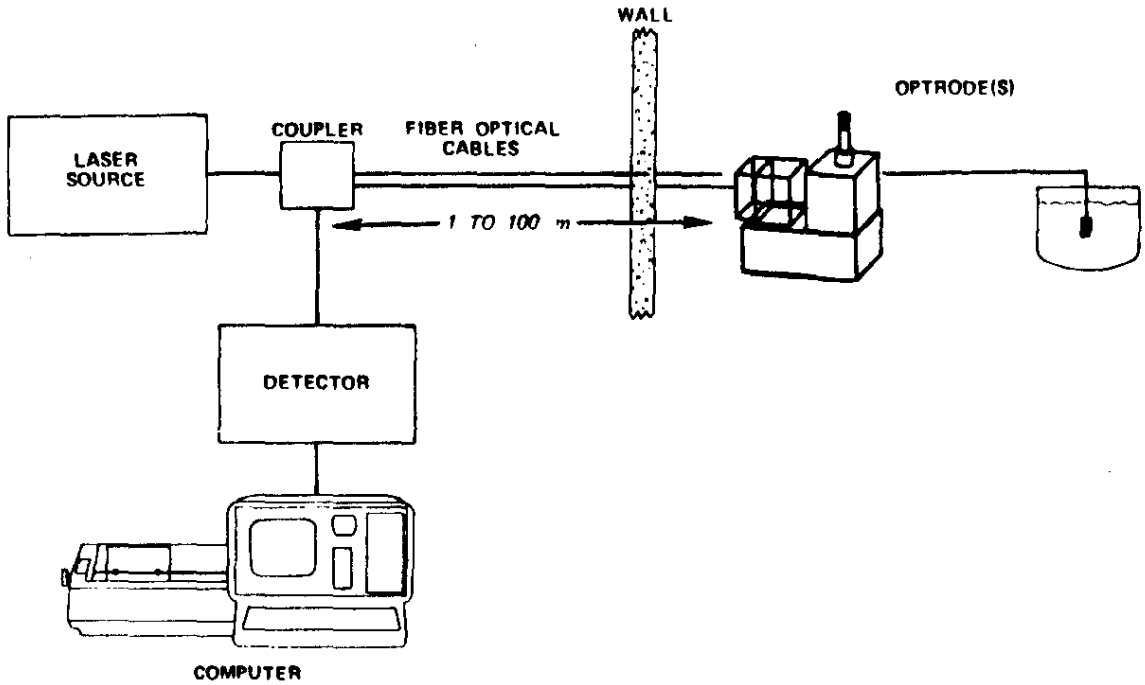


**FIGURE 1. Remote Fiber Fluorimetry (RFF) Components**

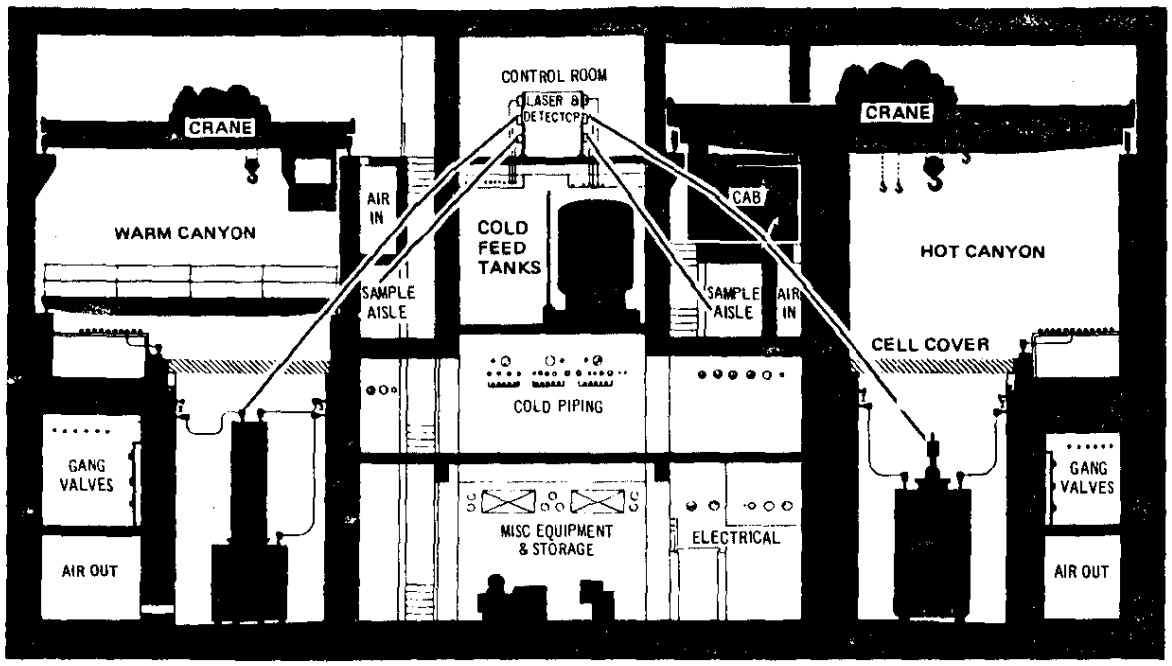


**FIGURE 2. Separations Building Cross Section**

Incentives

- Demonstration of technology
- Speed
- Decreased sample load for Laboratories Department

**FIGURE 3. Incentives for Using Remote Fiber Fluorimetry (RFF)**

Fiber Optics

- Inexpensive
- Lengths -- 1 cm to 10 km
- Like coaxial cables
- Radiation resistant

**FIGURE 4. Advantages of Fiber Optics**

Characteristics of Laser Light

- Intense
- Directional
- Multiple wavelengths

FIGURE 5. Characteristics of Laser Light

Optrodes

- Couple light to analyte
- Analyte specific
- Designed for hostile environments

**FIGURE 6. Characteristics of Optrodes**

Optrodes Measure

- Temperature
- Pressure
- pH
- Concentration

**FIGURE 7. Optrode-Measurable Properties**

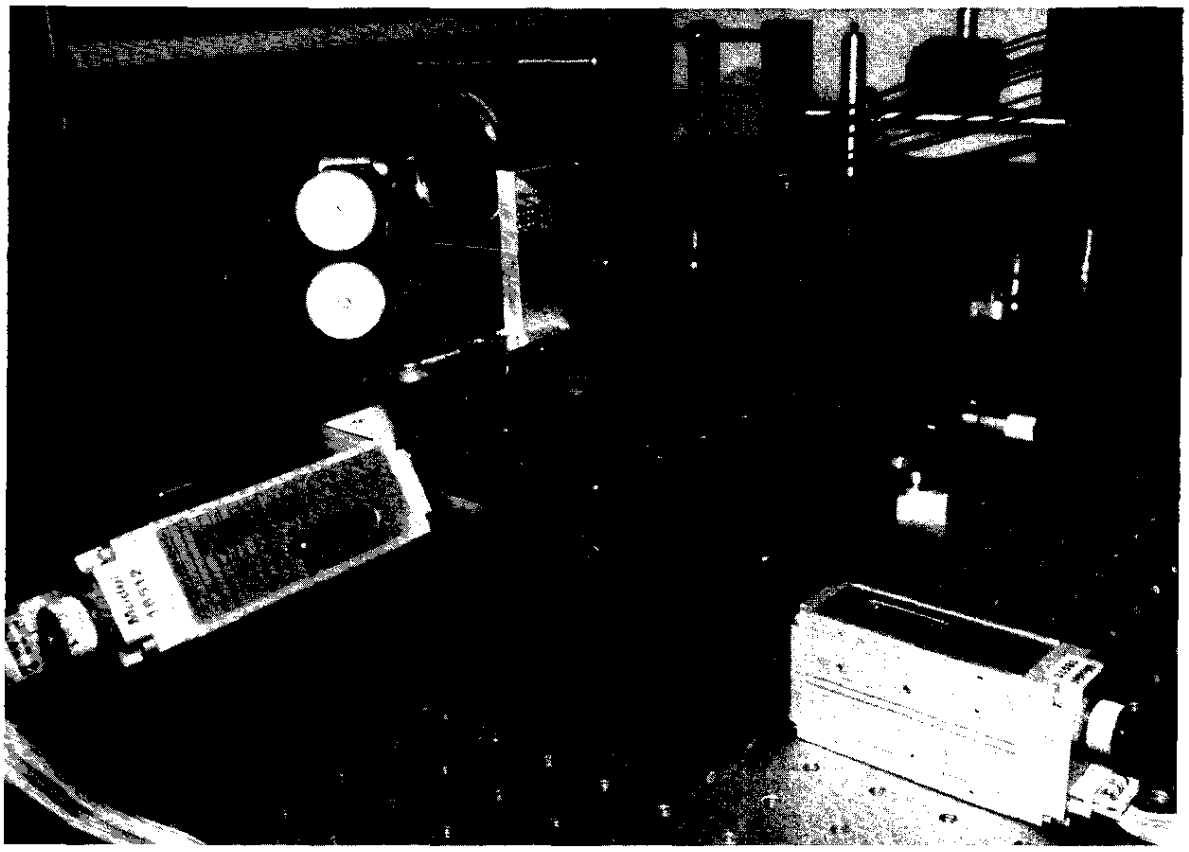

FIGURE 8. Multiplexer

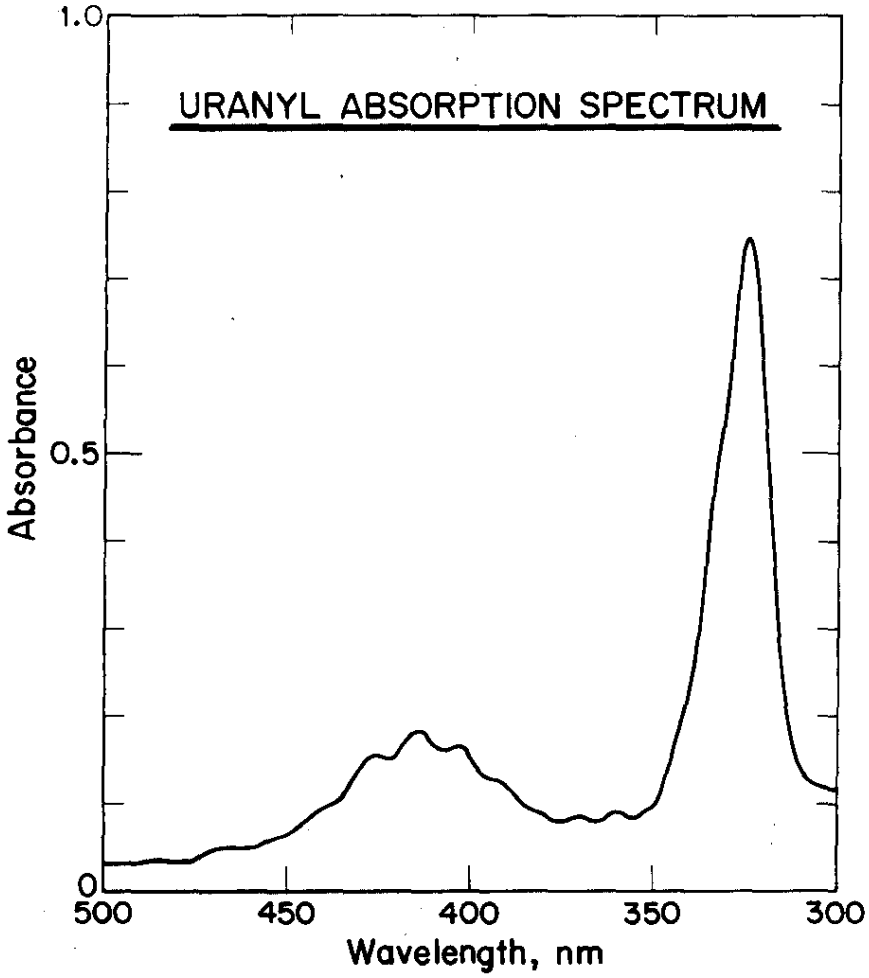


**FIGURE 9. Uranyl Absorption Spectrum in 0.5M $HNO_3$**

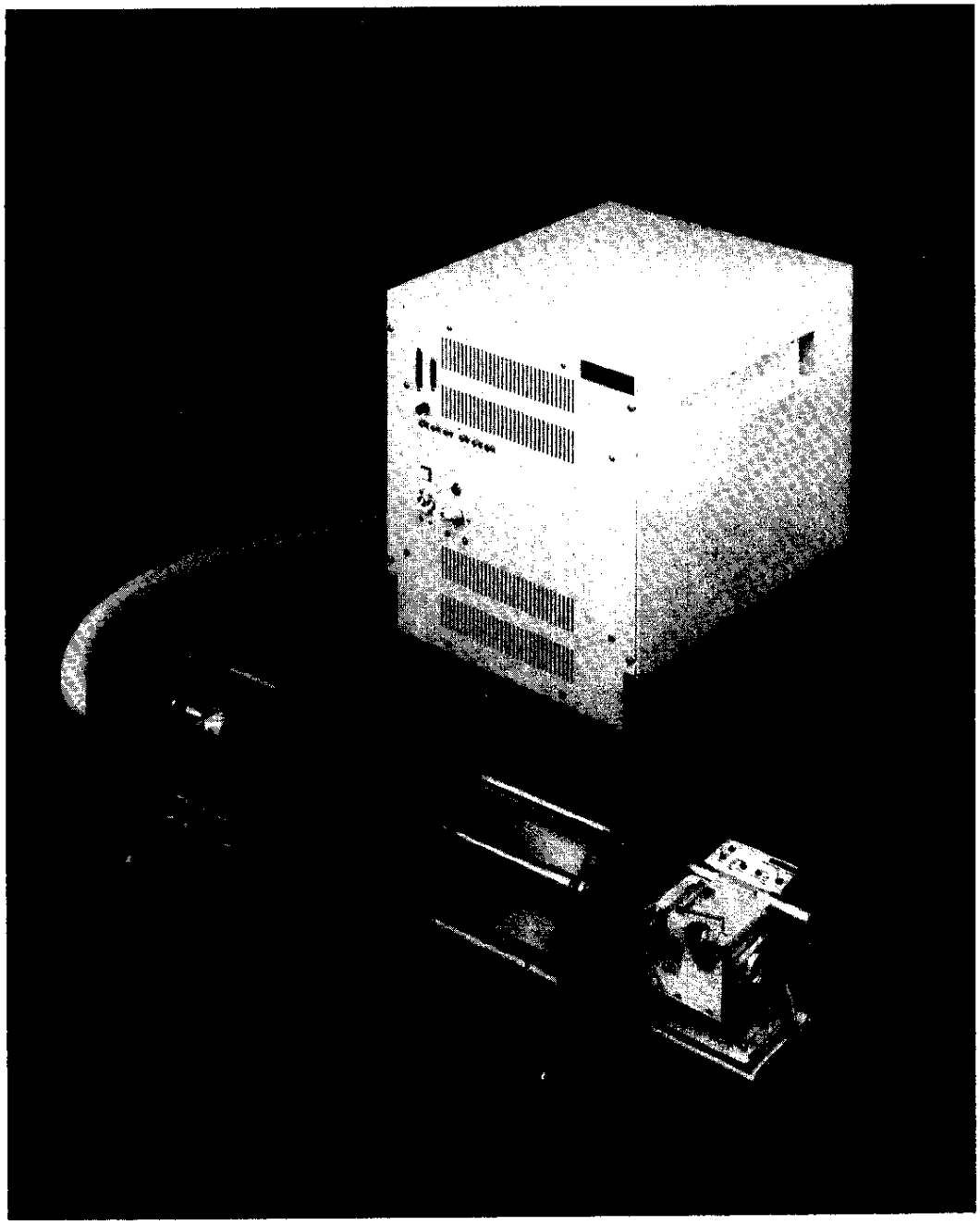

**FIGURE 10. DCR-11 Laser System**

## LASER SYSTEM

**FIGURE 11. 416nm Laser-Light Generation Process**

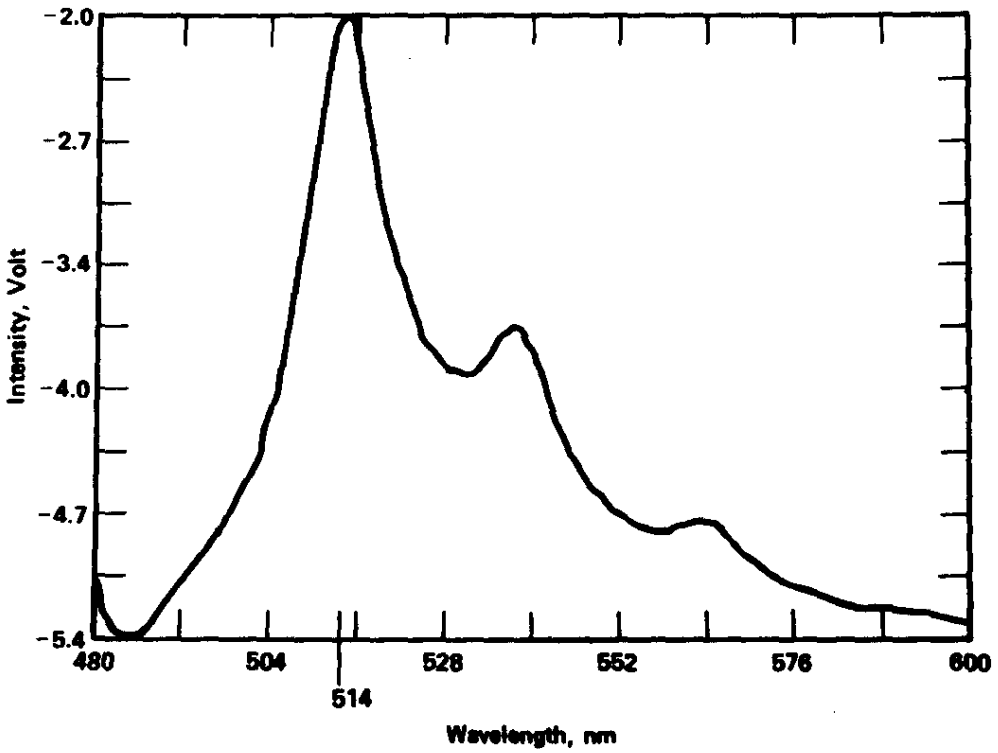


FIGURE 12. Characteristic Uranyl Ion Fluorescence Emission

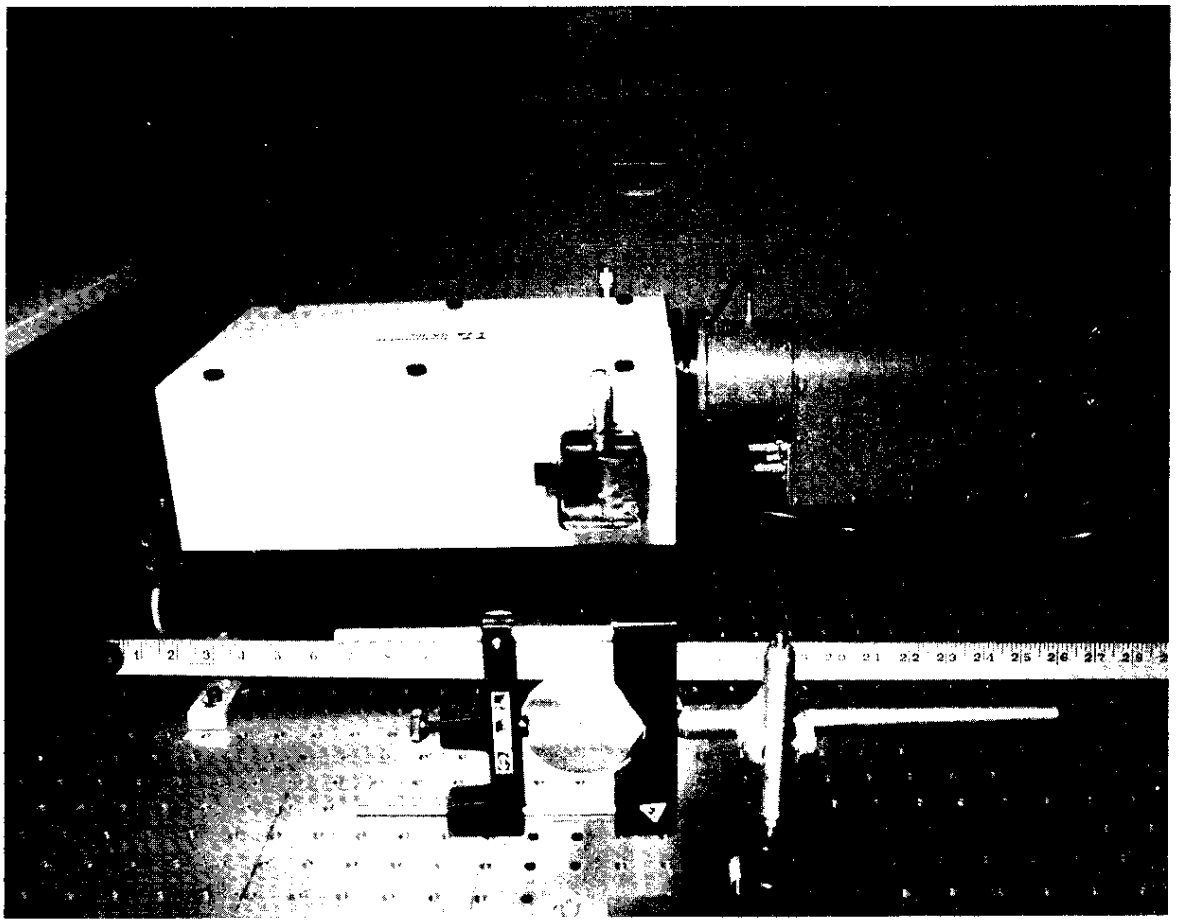

FIGURE 13. Detector and Spectograph

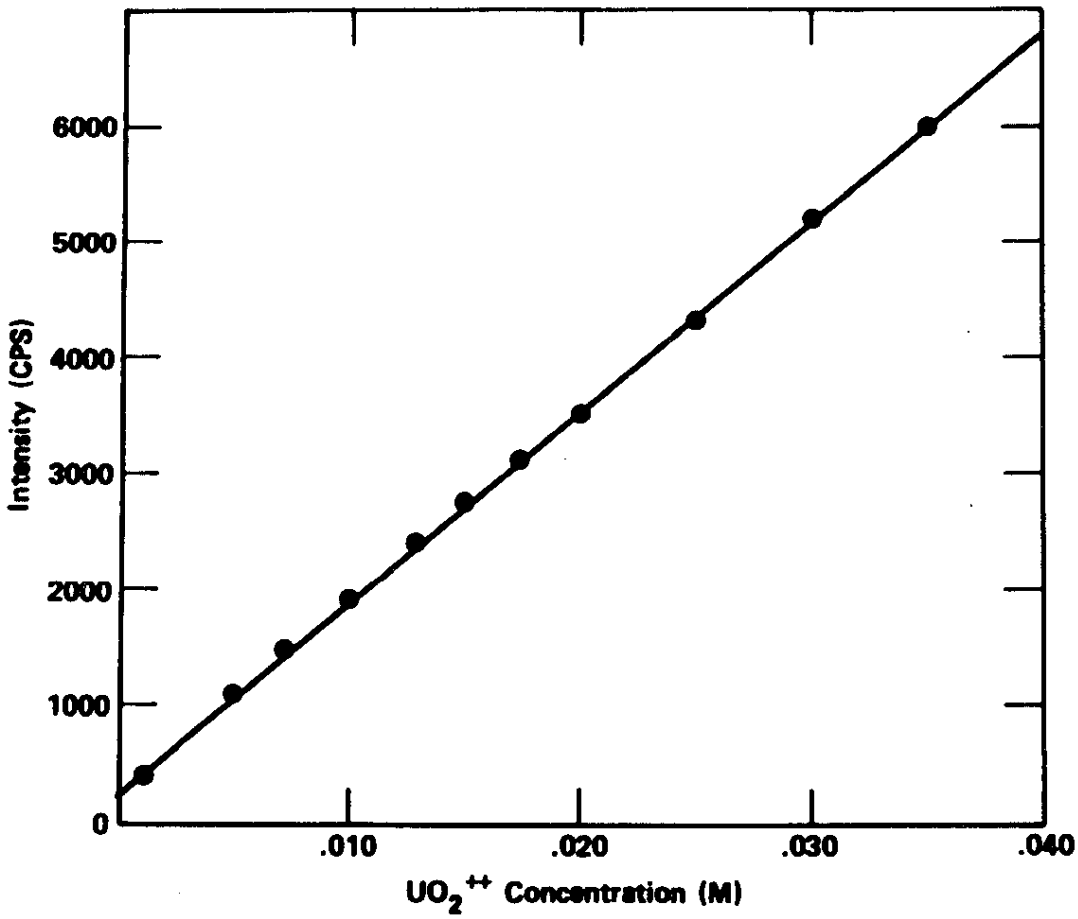


FIGURE 14. Calibration Curve for Uranylion ($UO_2^{++}$)

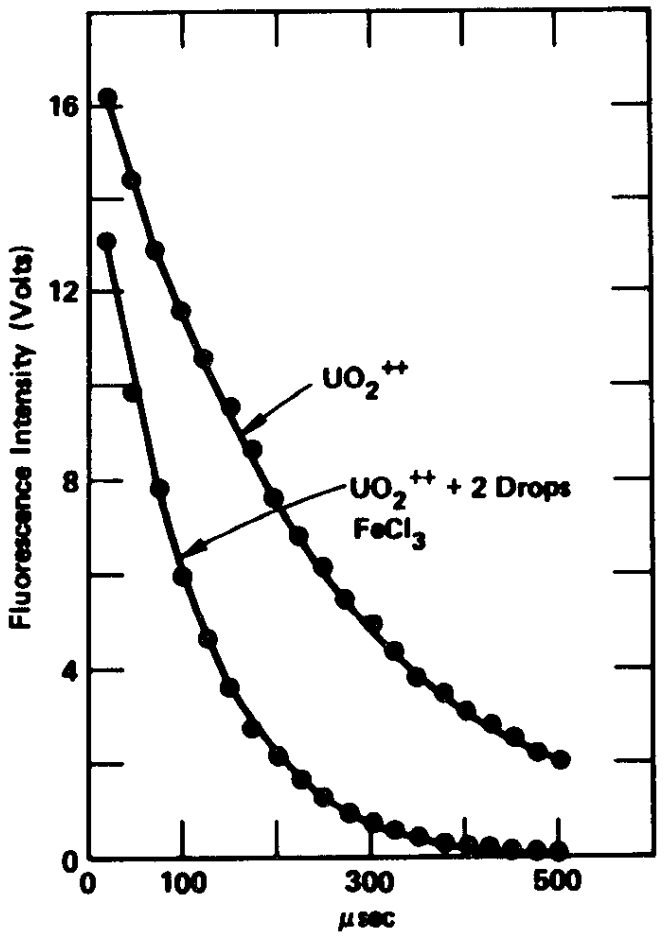


FIGURE 15. Fluorescence Decay Curves

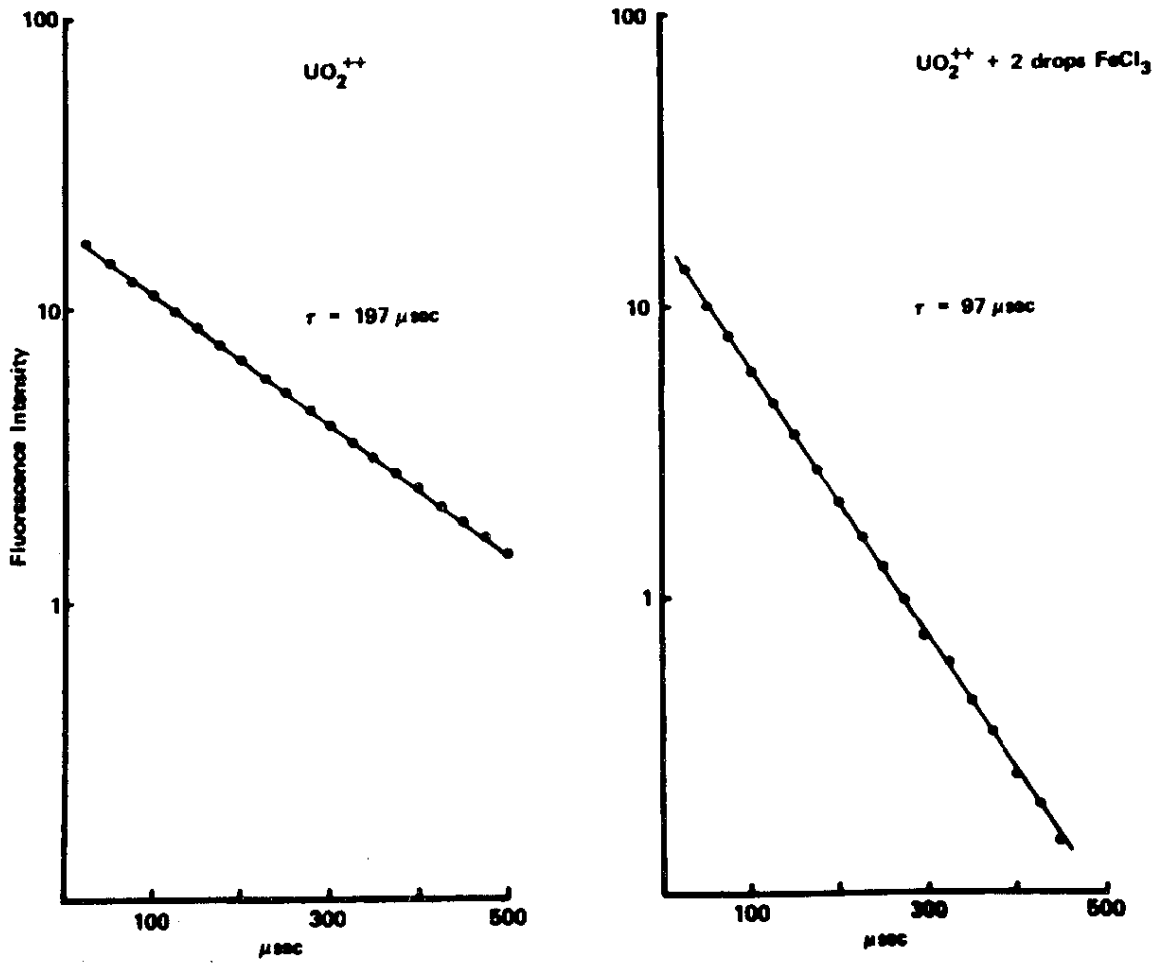


FIGURE 16. Fluorescence Intensity vs. Time

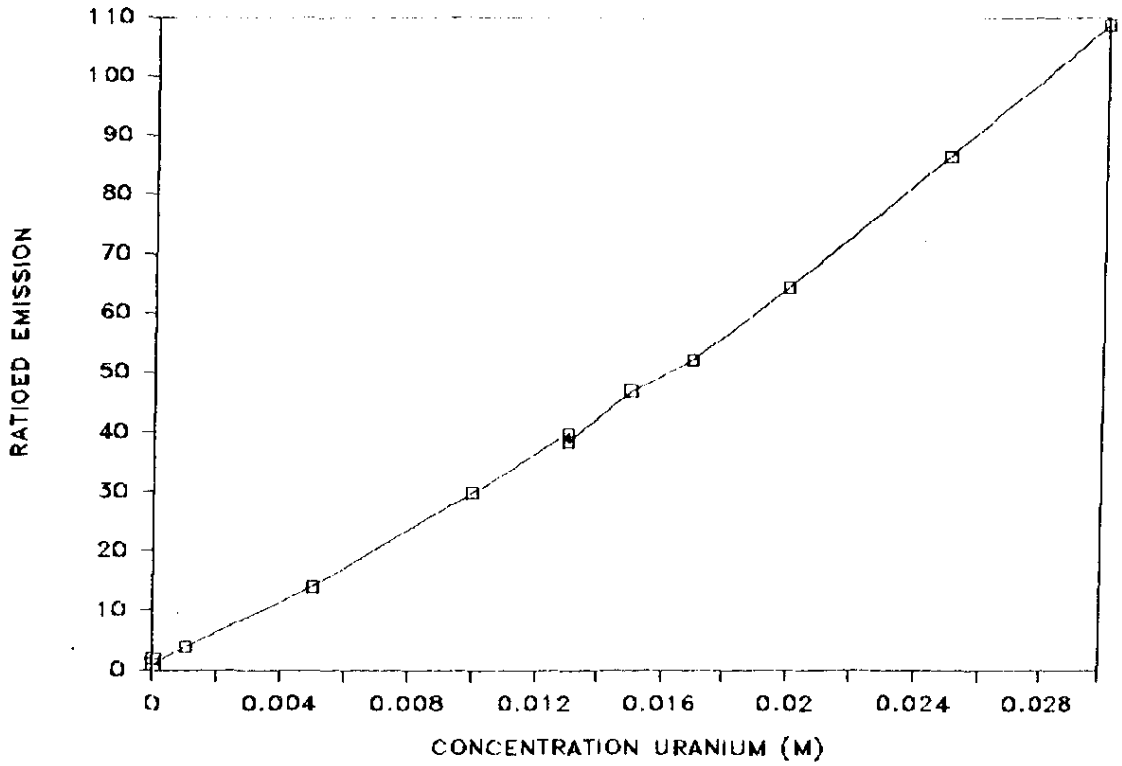


**FIGURE 19. Calibration Curve from Optrode in Process Tank**

Matrix Lifetime Correction

$$I_0 = I' (\tau_0/\tau')$$

- Quenched intensity $I' = 3800$ cps
- $\tau_0 = 197\ \mu$ sec
- $\tau' = 97\ \mu$ sec
- $I_0 = 3800\ (197/97) = 7720$ cps

**FIGURE 17. Matrix Correction Technique**

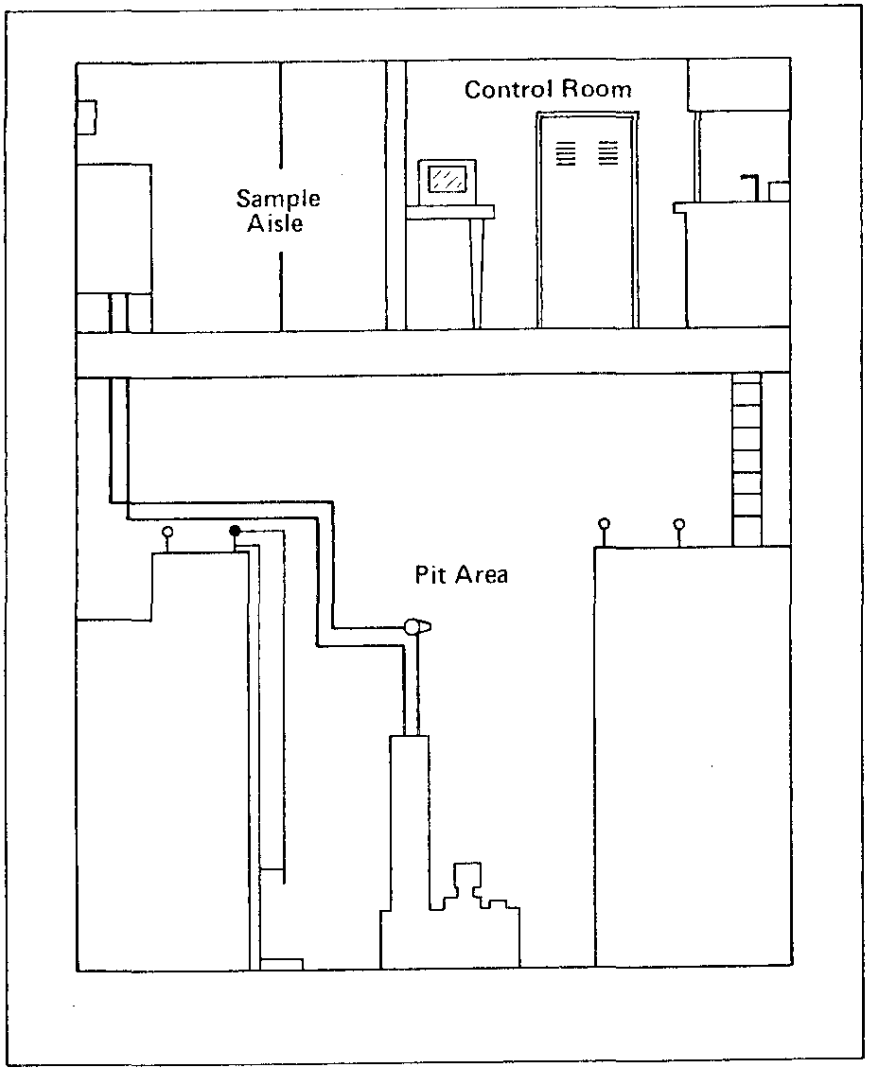


FIGURE 18. Analyzer and Control Demonstration Facility, Cross Section