FR-1203-101

NASA CR-
147492

FINAL REPORT

ADVANCED PROTOTYPE AUTOMATED IODINE MONITOR SYSTEM

Contract NAS9-14761

Data Item 2

January, 1976

Prepared for:

National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Beckman® INSTRUMENTS, INC.
ADVANCED TECHNOLOGY OPERATIONS
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CONTENTS

1.0 BACKGROUND

The technique of detecting and measuring parts-per-million concentrations of aqueous iodine by direct spectrophotometric means has had an interesting history dating from the early feasibility study to the present sophisticated prototype Automated Iodine Monitoring/Controller System (AIMS). This final report discusses the latest development in the history which includes these prior efforts:

- Demonstration of Feasibility: Contract NAS9-11879. This program culminated in a simple, manually operated iodine colorimeter.
- Design for an Automated System: Contract NAS9-12769. This design provided for both measuring (monitoring) and controlling iodine in a potable water system.
- A Prototype AIMS: Contract NAS9-13479. This instrument was based on the design of the preceding effort.
- AIMS-A Further Development: Contract NAS9-14298. This program was directed toward the design, fabrication, and test of a system configuration suitable for spacecraft use.

The present effort (NAS9-14761) has been directed primarily toward reducing the power requirement and the weight of the AIMS developed under the previous program. Other objectives of the program included determining the maximum concentration of iodine that can be dissolved in 1) an alcohol solution, and 2) an aqueous potassium iodide solution. Also discussed in this report are the effects of a no flow condition on iodine measurements and the effect of pH on spectrophotometric iodine determinations.

2.0 OPERATING PRINCIPLE

Although the operating principles of AIMS have been discussed in previous reports it may not be amiss, for the sake of comprehensiveness, to restate them in this Final Report.

The AIMS measures aqueous iodine on the basis of the iodine spectroscopy illustrated in FIGURE 2.0-1. Aqueous iodine exhibits an absorbtion band in the 460 -nm region and, for iodine-potassium iodide (I_2-KI) solutions an isosbestic point is found at 466 nm where variations in the KI content do not change the absorption value for a given iodine concentration.

Light transmitted at 466 nm will vary in intensity with the aqueous iodine concentration; but iodine does not absorb in the 600-700-nm region, and so light transmitted at this wavelength can be used as a reference signal against which to ratio the variable signal at 466 nm.

Light maintained at a fixed brightness at the source passes through a 25-mm water filled cell (a continuous sample from the main stream) and is focused onto two detectors via a beam splitter. The beam splitter transmits part of the incident beam through a 466-nm interference filter to the sample detector (a photodiode) and the portion reflected passes through a 631-nm filter to the reference detector (another photodiode). The ratio of the two signals is proportional to the iodine level in the flow-through Sample Cell. The electronically processed signals are used to drive a meter readout, a recorder, and a control signal for an automated iodine addition system.

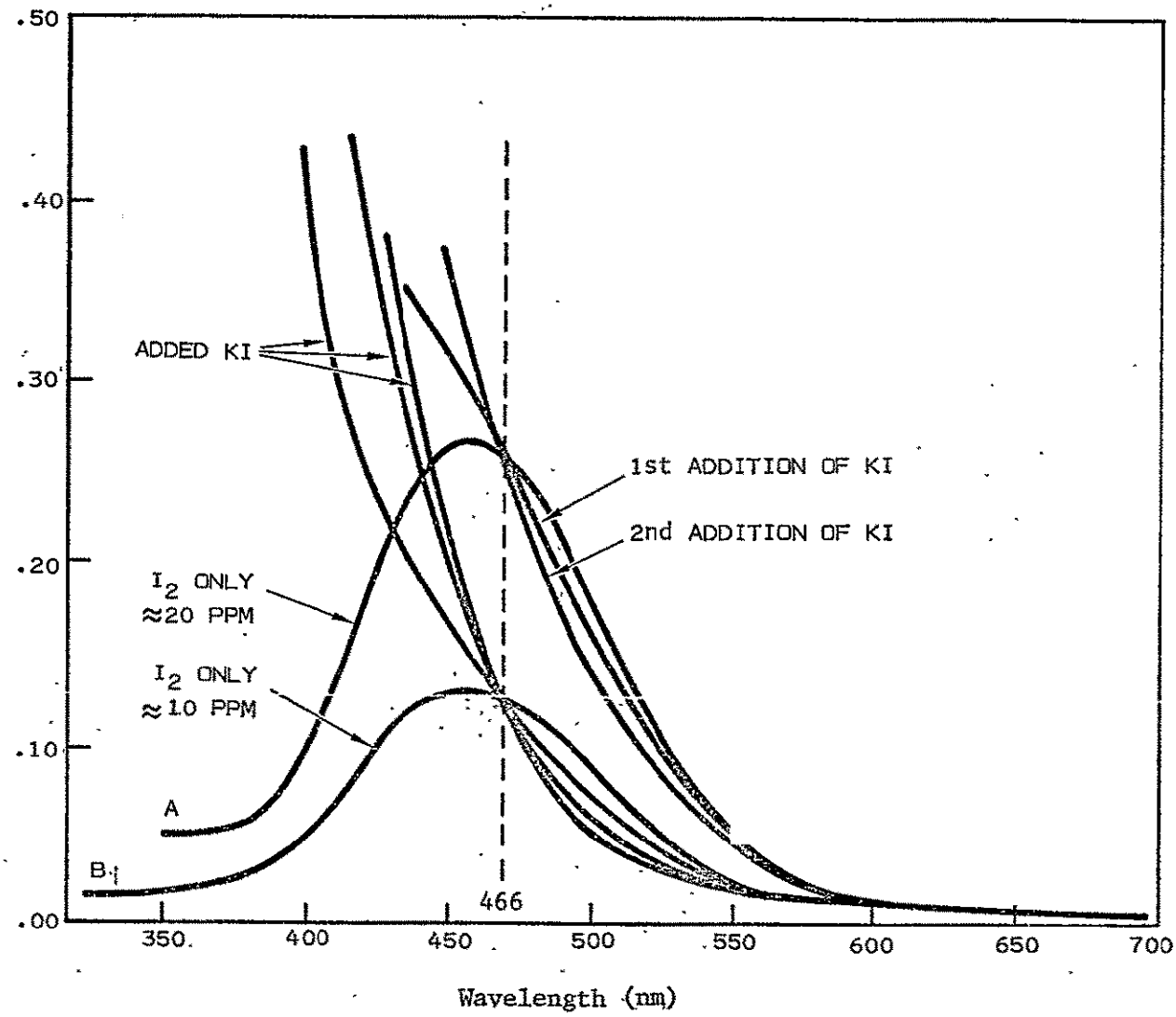

Figure 2.0-1 Measuring Aqueous Iodine at the Isosbestic Point. Curves A and B show the absorption spectrum of aqueous iodine at two different concentrations. The other curves show how this spectrum is altered with the addition of potassium iodine (KI) to the iodine solutions. Note the crossover point, at 466 nm, where the absorption is identical for a given concentration of iodine. This point is named the "isosbestic point."

3.0 MODIFIED AIMS

The two major design goals of the program just completed were to reduce the steady-state power requirement to 6 watts (for the monitor) and to reduce the weight and volume of the monitor. We met these goals by selecting a source using much less power than the previous one and by shortening the Sample Cell pathlength. These two major modifications required redesign, fabrication, and extensive testing in order to verify that the new source still provided sufficient light throughput and that the reduced pathlength still provided adequate sensitivity to meet the original specifications. No repackaging was undertaken as the previous housing could be adapted to the modified components, and housing weight reduction could be demonstrated by analysis since the proposed changes would not adversely affect system performance.

3.1 Source

The previous AIMS lamp (GE 1855) and its circuitry consumed 8 watts. Since this accounted for most of the power required by the monitor we made a search for an equally suitable source, but one using less power.

We found an excellent replacement, a lamp not only requiring less power but also one with features that made it a distinct improvement over the former source. The new lamp is No. 905-10546, manufactured by Baldwin Electronics of Little Rock, Arkansas. It is rated at 4 V drawing only 0.310 A, thus consuming only 1.24 W. Since we are using the same transformer as before there is additional power dissipation which brings the actual wattage to 3.5.

Low power is not the only advantage accruing from the use of this lamp. It shows an improved light pattern, a more even distribution of light which reduces the optical train alignment problem. The lamp filament is rather short, as are the support wires, and this lessens the possibility of filament

movement. This is important, as even minute filament movements can create an appreciable offset in the signal.

Since the Baldwin lamp operates at a lower filament temperature (1900K) than the GE lamp (*ca* 2300K) we were at first concerned that relatively less light in the 466 nm region would be available. Our tests revealed, though, that even when operating the lamp below its nominal voltage (3.8 V instead of 4.0 V) we had sufficient radiant throughput at this wavelength. As partial compensation for the reduced "blue signal" the lower filament temperature reduces the thermal effects on the signal, especially when the AIMS is operated in the no flow mode.

The life rating of the lamp is 5000 hours at 4 Vdc. Since we operate the lamp at about 3.9 V we may expect a somewhat extended life. Interestingly, the literature reports that tungsten lamps have a longer life when operated on ac instead of dc. Baldwin reports 10,000 hours for this lamp when operated on ac.

The filament structure in the Baldwin lamp is precisely aligned with three locating holes in the mounting flange which is an integral part of the lamp base. This feature makes it possible to replace the lamp without realignment problems.

We obtained a set of six lamps to evaluate. Among other things, we were interested in how the Lamp Regulator Circuit would respond to each lamp. Here are the initial filament voltages associated with each lamp:

Lamp No.	Lamp Volts
33845	3.913
33770	3.965
34852	3.829
34797	3.958
45516	3.875
34939	3.991

That these voltages show little spread, and that none shows an initial voltage exceeding 4 V, suggests that each lamp should perform equally well in the AIMS.

In addition to noting the lamp voltages we also found that only minor adjustments in the "balance" (between the "red and blue" signals) and zero pots were required in order to make each lamp give a correct signal reading for a known iodine concentration in the cell solution.

3.2 Short Cell

Reducing the pathlength of the flow-through Sample Cell from 50 mm to 25 mm represents a direct savings in volume and weight for this component (see "Weight Reduction," Section 5). Since the length of the optical train establishes the limit of one dimension of the housing a shortening of the cell permits a substantial reduction of housing weight and volume, a savings of more importance than that obtained simply by reducing the cell dimensions. It was, therefore, of great interest to us to determine whether the inherent loss of sensitivity resulting from the short pathlength would render this approach to weight savings impractical.

After adjusting the electronics to compensate for the sensitivity loss we found, to our satisfaction, that the initial tests indicated the new cell would perform well within the original specifications.

The completed test results (Appendix A) confirmed this impression and they suggest it may be feasible to reduce even more the pathlength and still retain adequate sensitivity.

The short cell is fabricated of aluminum with black anodize finish (FIGURE 3.2.1). We have learned recently that aluminum, even anodized, may be unacceptable because of potential corrosion effects (electrolytic processes within the system). Our cell can be made of stainless steel, if

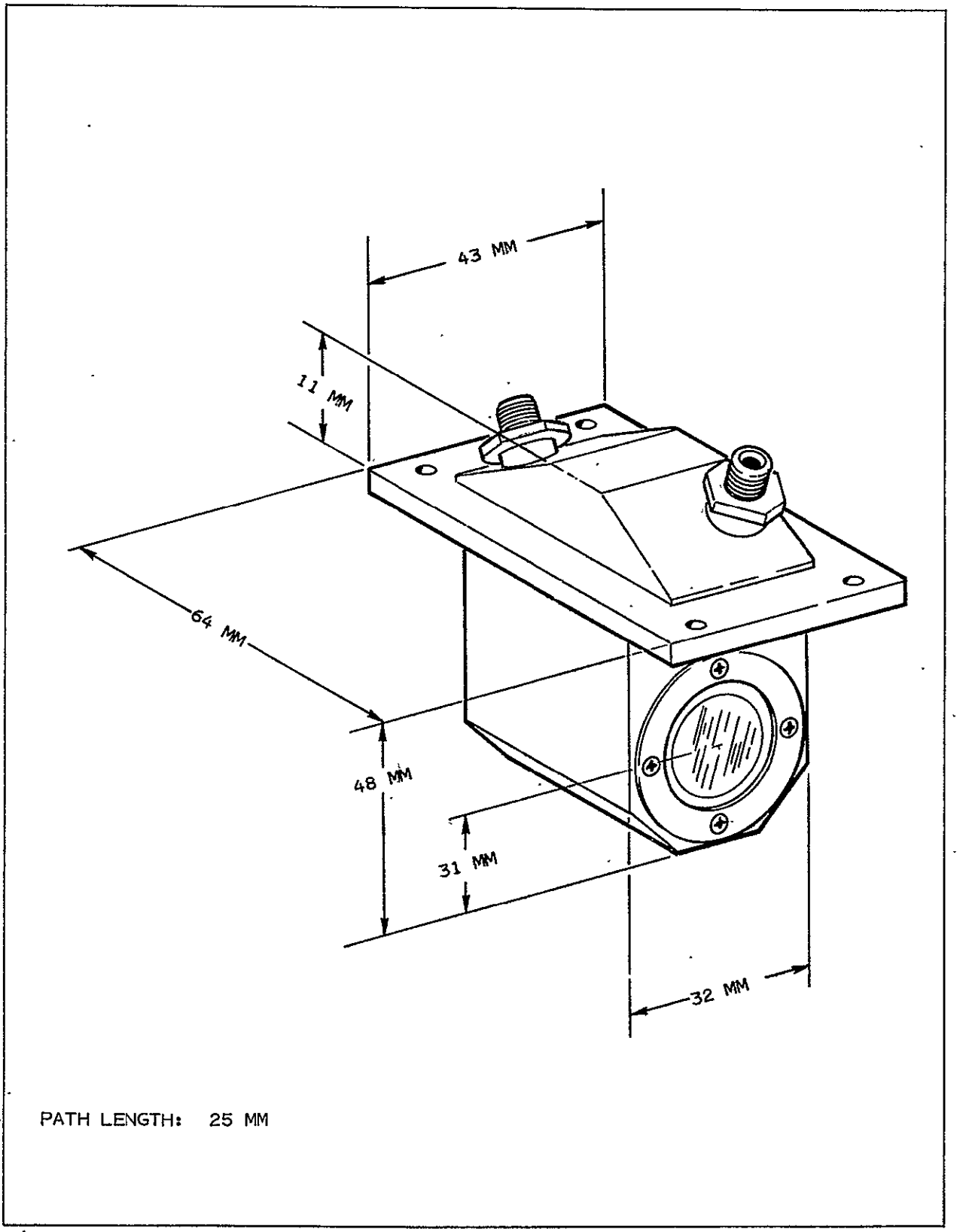

Figure 3.2-1. The New Cell

required, and this would have no impact on its optical performance; its weight would be increased, however.

3.3 Optical Bench

The optical system, composed of the Lamp Housing, Sample Cell, and Detector Housing arranged in-line, has been mounted on an aluminum plate 165 x 35.6 x 6.4 mm (6.5" x 1.4" x 0.25") constituting an "Optical Bench." These components are positively located by pins and secured by screws. An opening to receive the optical bench was cut in the top of the Monitor Housing. A rubber gasket provides a seal between the metal surfaces. The Sample Cell has an O-ring seal to the optical bench. Thus, the Sample Cell can be easily removed from the optical assembly for inspection and the optical bench, with or without the cell in place, can be removed readily when it becomes necessary to replace the lamp.

For a future design we believe it will be feasible to make the lamp housing, the detector housing, and the optical bench out of one piece of material, not as separate pieces. This would ensure a fixed position; the unit would weigh less, and it would occupy less volume than the present optical system.

3.4 Electronics

It was necessary to increase the gain of the "red and blue" amplifiers by a factor of ten in order to use the Baldwin 4-V lamp. Minor changes in the feedback resistors were again required when the 25-mm cell was installed. Because of the lower light output it was also necessary to raise the gain and offset of the amplifier in the Lamp Regulation System.

The rate of change of the lamp intensity as a function of lamp voltage was measured and a plot of the data is given in FIGURE 3.4-1. Note that the curve is nearly linear over the change of interest (3.9 to 4.2 V).

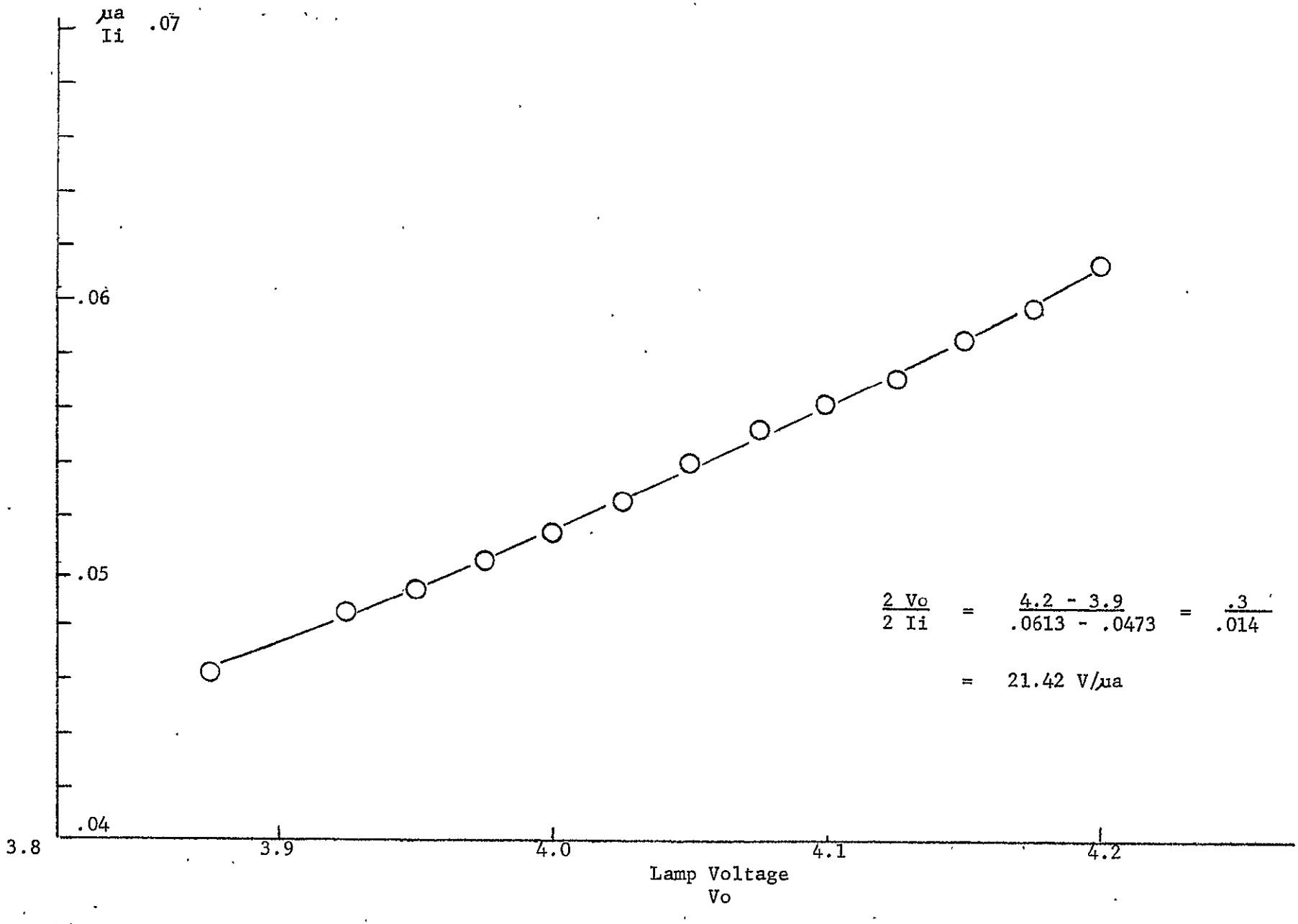

Figure 3.4-1. Change in Source Intensity with Voltage

The noise level in the previous system was determined to be 15 $\pm$5 mV for 0-8 ppm I_2 in the cell (50 mm). We found no change for the present 25-mm system.

The circuitry is essentially the same as that used in the previous AIMS except for the necessary changes in the feedback resistors noted above. FIGURE 3.4-2 is a block diagram of the electronics. Briefly, the signals from the red amplifier (631 nm) and the blue amplifier (466 nm), the reference and sample signals respectively, are applied to the input of an electrical divider. The divider's output is proportional to the quotient of the blue signal divided by the red signal (Reference: Drawing No. 674562). This output is presented through a variable resistor to the current summing inverting input of an amplifier. Adjustment of the variable resistor provides any required span changes. Additional electronic elements provide for zero adjusts and balance. Further amplification of the signal drives a meter and an optical recorder.

The iodine addition circuitry is identical to that used previously and will not be reviewed here as it is discussed in FR-118-101 (August 1975).

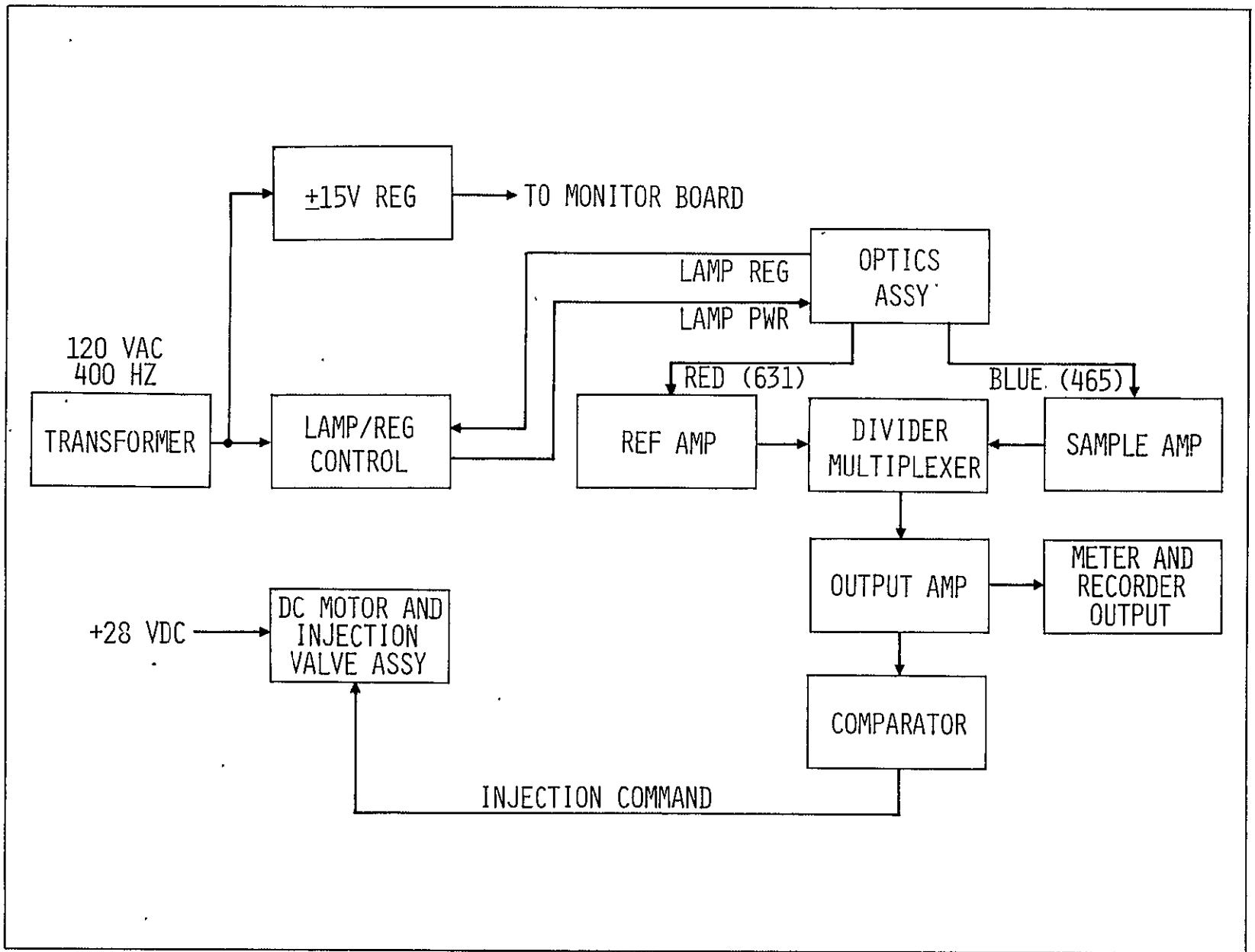

Figure 3.4-2. Electronic Block Diagram

4.0 TEST SETUP

The same Test Setup designed and built for the previous program was used for carrying out all the experimental and formal test procedures discussed in the present effort. Since the work was, however, performed in a different location this time, some minor changes were made. The schematic of FIGURE 4.0-1 is correct in all details as to the layout of the Test Setup. The photographic presentation of FIGURE 4.0-2 is correct except that the monitor shows the 50-mm flow-through Sample Cell instead of the new 25-mm Cell shown elsewhere in this report.

This setup incorporated a mockup of essential features of the Shuttle potable water system. There is a 3.05 m (10') length of 6.4 mm (1/4") stainless steel tubing between the monitor and the large water tank. We could conveniently disconnect the monitor from the tank and make connections to glass flasks for special tests requiring iodine-free solutions.

The Bubble Trap, shown in both figures, could also be readily removed from the system in order to assess its importance in the total system. Its effect is discussed in Appendix A of this report.

No changes were made in the Iodine Addition System and the same iodine storage container (GFE, Hastalloy C) was found to still contain an adequate supply of iodine concentrate under pressure. The iodine content measured the same as before (about 30,000 ppm). Other iodine concentrates, some containing only iodine in alcohol, were also used for special tests. Compressed air, to pressurize the system--a departure from the real case--was again used to verify that the Sample Cell was leakproof under pressure.

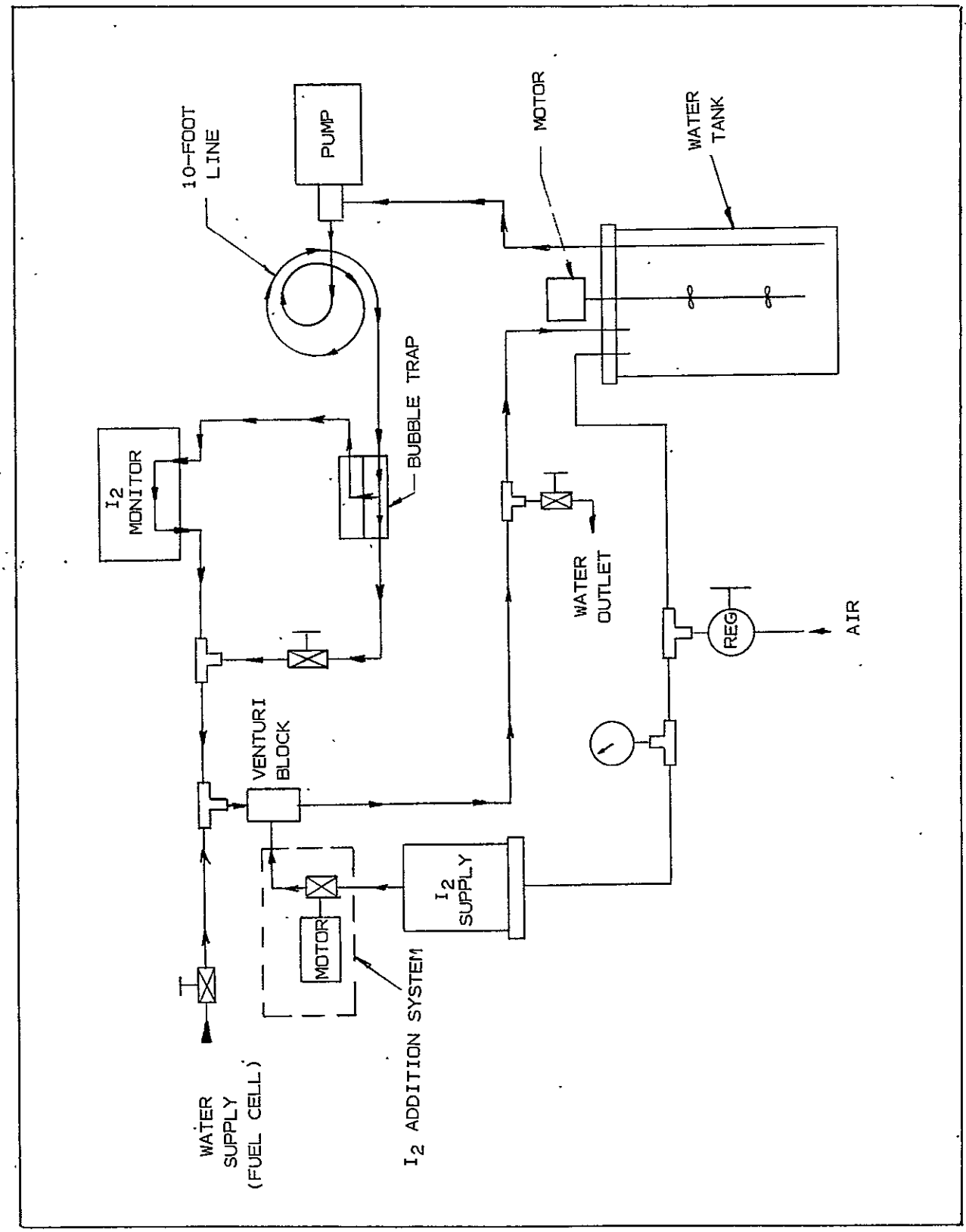

Figure 4.0-1. Test System

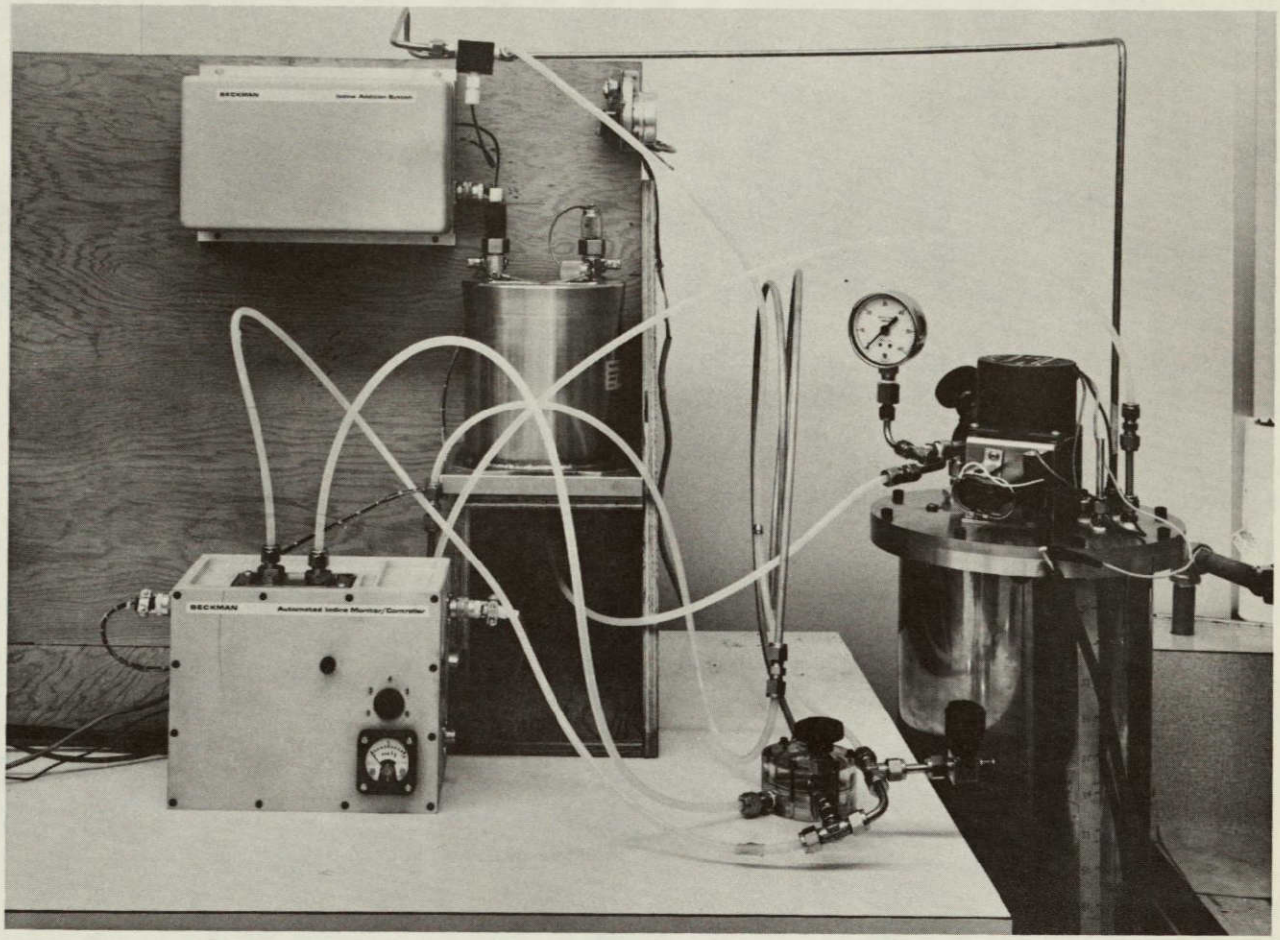

Figure 4.0-2. Testing Configuration

5.0 WEIGHT REDUCTION

How to achieve weight reduction was one of the major objectives of the present program. The AIMS Monitor, constructed under contract NAS9-14298, weighed 4.15 kg (9.17 lb); our goal was to reduce this to 2.54 kg (5.6 lb).

The AIMS housing was fabricated of hogged-out aluminum. The resulting rigidity and great structural strength are, of course, desirable features, but the extra metal (in the ribbing and fillets) to effect them carries an appreciable weight penalty. Since the previous design more than met the strength and rigidity needs, a redesign to meet more realistic requirements would permit a substantial weight savings. One of the greatest savings in weight can be realized by substituting magnesium for the present aluminum. This change alone would achieve a 35% reduction in the housing weight.

The iodine monitors made for the past two programs have consistently demonstrated much more sensitivity than required to meet aqueous iodine determinations. In the interests of weight and volume reduction we realized we could shorten the Sample Cell at the expense of some acceptable loss in sensitivity. We decided to reduce the 50-mm cell length to only 25 mm, a change that would reduce sensitivity by 50%. As the test results in this report amply demonstrate, more than adequate sensitivity remains.

The impact of the shortened cell on a future AIMS design will be very significant: the overall volume and, therefore, the weight of the monitor can be appreciably reduced by perhaps as much as 45%. TABLE 5.1 compares the unmodified AIMS weight elements with the calculated weights for a redesigned version. It was necessary to test and evaluate the reduced cell to verify sensitivity, but the other contemplated changes are simply discussed here as they should have no effect on the performance characteristics of the AIMS.

TABLE 5.1 WEIGHT REDUCTION SUMMARY

	Present Weight of Prototype	
	lb	grams
Sensor Housing	5.3	2400.9
Source Housing Assy	.306	138.7
Detector Housing Assy	.243	110.0
Cell Assy	1.250	566.1
Cover	1.213	549.6
P C Boards	.339	153.4
Rear Cover	.405	183.6
Silicone Rubber Gaskets	.049	22.1
Misc. Hardware	.061	27.5
Total	9.17	4151.9

	Calculated Weight with Weight Savings	
	lb	grams
Sensor Housing	2.91	1318.2
Optics Assy	.774	350.6
Cell Assy	.521	236.0*
Cover	.47	212.9
P C Boards	.339	153.4
Rear Cover	.270	122.3
Silicone Rubber Gaskets	.035	15.9
Misc. Hardware	.035	15.9
Total	5.35	2425.2

*If made of stainless steel to the same design this item will weigh 473 grams.

A breakdown of the weight of some of the components in the Optics and cell assemblies, not given in TABLE 5.1, are presented here.

25 mm cell, empty	132.6 grams		
Cell windows (two)	19.4		
Cell fittings	58.5	210.5 grams	
Optical Bench	138.3		
Lamp	7.2		
Lamp Housing	113.6		
Detector Housing	90.4	349.5	
			560.0 grams

At present the Lamp Housing and the Detector Housing are separate pieces mounted on the Optical Bench. It appears feasible to redesign these components as a one-piece optical assembly on a common base (Optical Bench) and thus further reduce the weight of the Optical Bench. Only the Flowthrough Cell would be removeable. The Optical Bench would, of course, be removable as a unit.

6.0 POWER REDUCTION

In addition to weight reduction, another major objective of our program was power reduction. The monitor component of the previous AIMS required 12 watts steady state. TABLE 6.1 shows how this power was distributed.

TABLE 6.1. FORMER MONITOR POWER PROFILE

Circuit Element	Power (Watts)
Amplifier and Control	1
Regulator	1
Lamp	8
Total (for 85% Transformer Efficiency)	12

Since the light source accounted for most of this power, we made a search for a suitable source using less power.

We were fortunate in finding a source that so well met our requirements as the 4-volt Baldwin lamp. This lamp, consuming only 3.5 watts, is discussed in detail in another section of this report. The energy consumption of the present monitor is given in TABLE 6.2.

TABLE 6.2. POWER PROFILE OF PRESENT MONITOR

Circuit Element	Power (Watts)
Amplifier and Control	1
Regulator	1
Lamp	3.5
Total (85% Transformer Efficiency) (90% Transformer Efficiency)	6.5 6

As seen here, the new source accounts for all of the power reduction. There appear to be no other areas in the circuitry in which power can be reduced. However, total power may be reduced by another 0.5 watt by transformer redesign.

7.0 FLOW ANALYSIS

Since the Monitor can measure the iodine content of the solution in the Sample Cell only, the relevance of the measurement at any moment is dependent on how representative that solution is of the water supply of interest. If an adequate flow rate always exists, and if the round trip time is not unduly long, then the Monitor will give faithful, accurate readings of the iodine level in the water system. If, however, there will be periods of no flow then, depending on several interrelated factors of the entire water system, the monitor reading may not be representative of the iodine level in some water compartment outside of the monitor. Before taking up appropriate response to the flow or no flow condition it is of interest to discuss, briefly, what happens to the iodine level in various water compartments of the Test Setup under the no flow condition.

In one of several no flow experiments, the monitor was connected to a 3-ℓ flask of water containing 8.4 ppm I_2. The water circulating pump was turned off and the iodine content of the solution in the Sample Cell was monitored for the ensuing 14.5 hours. Iodine decay in the cell versus time is plotted in FIGURE 7.0-1. During this no flow period, the iodine concentration in the 3-ℓ flask water supply dropped from 8.4 ppm to 7.2 ppm. Notice that the decay rate in the cell is not linear with time but is more rapid during the first three hours.

In another no flow experiment, the monitor was connected to the tank (38 ℓ) water supply instead of the 3-ℓ flask. The no flow condition was imposed for five hours. The Sample Cell solution was again continuously monitored and hourly samples of the tank solution were also measured for iodine content. The results are plotted in FIGURE 7.0-2. In this case the cell solution dropped only 0.6 ppm in five hours compared to 3.2 ppm in the first five hours of the earlier experiment. The tank solution remained unchanged during

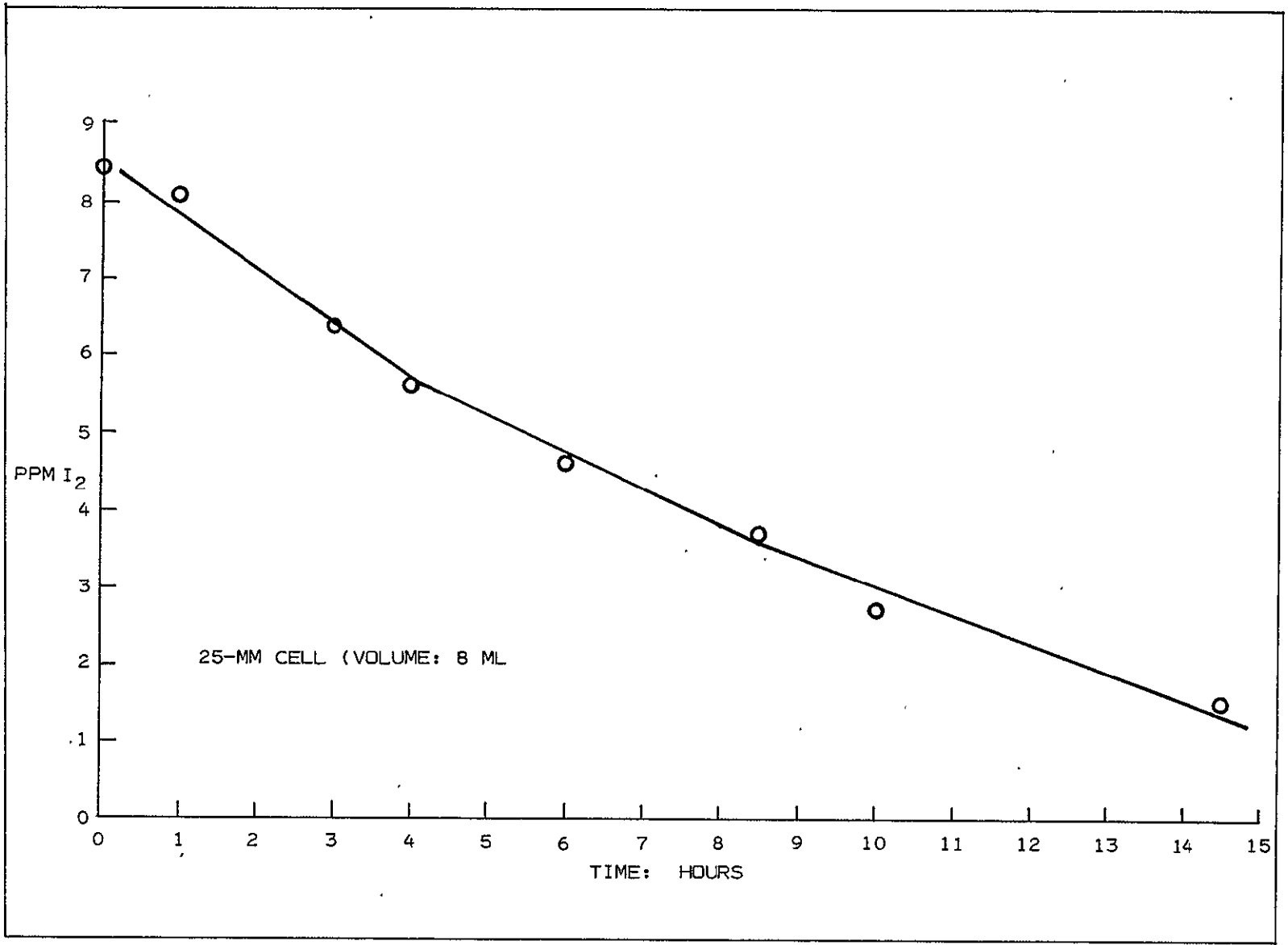

Figure 7:0-1. Iodine Decay in Sample Cell (No Flow Mode)

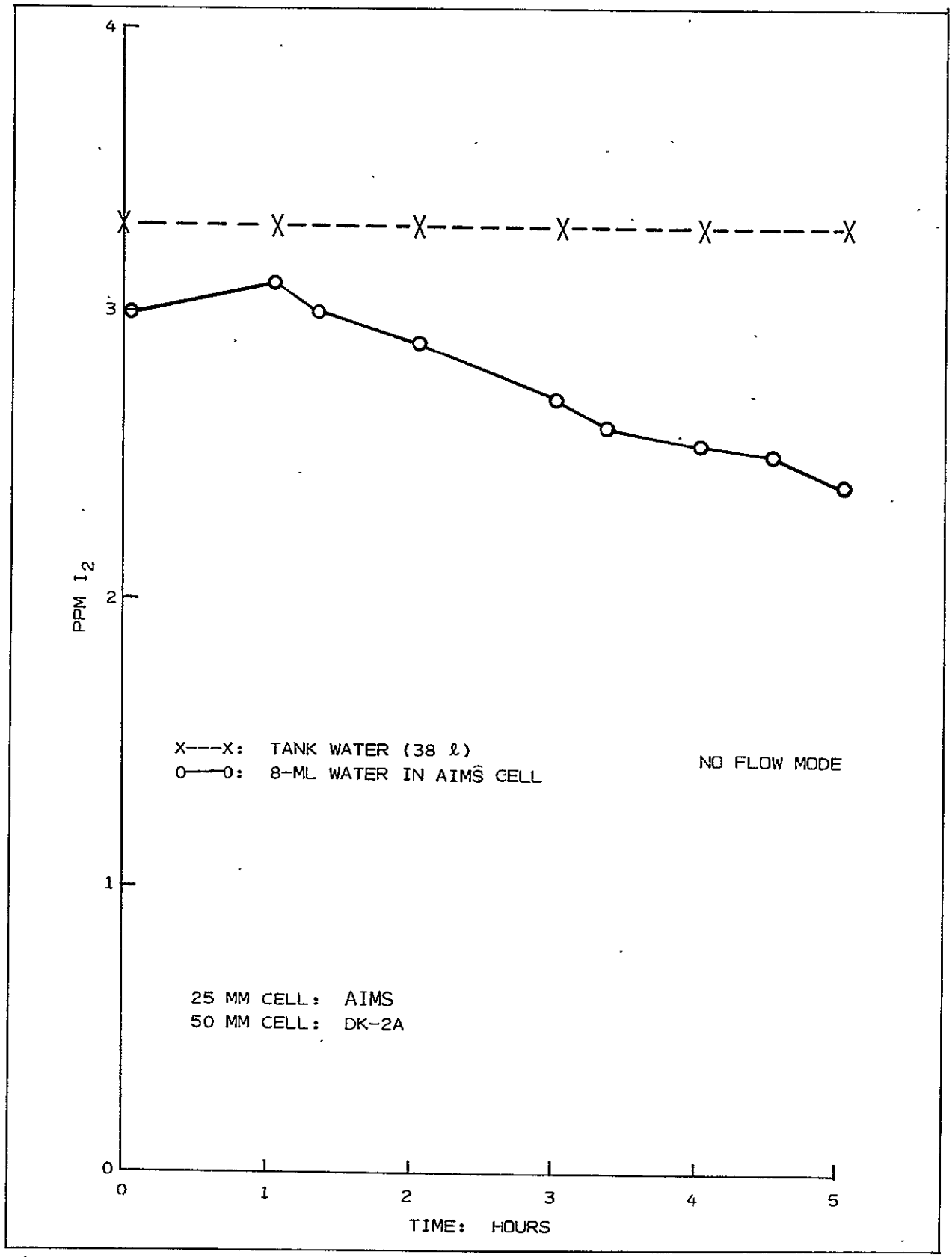

Figure 7.0-2. Iodine Decay in Sample Cell and in Tank--No Flow Mode

the test period. But note that the 3-ℓ flask lost 1.2 ppm in the first five hours. Several no flow experiments have been made during the AIMS programs. They all show that the iodine content of the cell diminishes with time. Frequently, we see a small rise in the readings during the first hour as shown in FIGURE 7.0-2. This occurs with low level iodine solution rather than with high (compare FIGURE 7.0-2 with 7.0-1). Presumably the slight rise is due to thermal effects.

Bulk iodine solutions exposed to light and air show a gradual loss of iodine. Our big water tank (used in the Test Setup) when full, or nearly so, showed only a very slow iodine decay. As shown in FIGURE 7.0-2, there was no measurable loss of five hours. Indeed, it required 37 days for the iodine concentration to drop from 6.2 to 3.3 ppm, an average drop of 0.078 ppm/day. The monitor, in the no flow mode, may show 0.1 ppm loss/hour.

Ambient temperature and the initial iodine concentration, whether high or low, also seem to influence the iodine decay rate. As would be expected, the higher the ambient temperature the faster the iodine leaves the solution, and the higher the iodine content the faster the decay. In the two examples given, the 8.4-ppm I_2 solution decayed faster than the 3.0-ppm I_2 solution.

What these experiments clearly show is that in the no flow mode the monitor will show a much faster iodine decay than is occurring in the water supply outside the monitor. The longer the no flow period the greater will be the error between the monitor reading and the true iodine concentration of the water supply. But, as FIGURE 7.0-2 suggests, the no flow condition could prevail for several hours before the Iodine Addition System (as used in AIMS) would be triggered.

We see, then, that if the no flow condition is of short duration (a few hours) there will be no undesirable impact on the iodine control system. Prolonged no flow would cause unnecessary iodine additions. These additions

would be injected into a non-moving stream where the iodine would only slowly diffuse. This process would continue until circulation was resumed.

To prevent unnecessary iodine additions during a no flow period, the monitor would have to be disabled. A feedback circuit could turn the AIMS on or off as required.

If prolonged no flow periods are to be typical of the water system then a circulating pump could be added to ensure flow at all times. This solution to the problem would, however, add potential problems of its own: added weight, increased power, additional failure modes.

If there is always a flow of water from the fuel cells to the storage tank but no flow periodically through the monitor, then a possible solution to this situation would be to disable the monitor during the no flow period and add iodine to the incoming untreated water on a timed basis.

8.0 IODINE CONCENTRATES

A wide range of iodine concentrates has been used during the course of the aqueous iodine measurement programs. In our early efforts we used iodine dissolved in ethanol and diluted with water to the desired iodine concentration. Later, we were requested to omit the alcohol and to use aqueous iodine-potassium iodide solutions. For the recent AIMS programs we used iodine (I_2) - potassium iodide (KI) concentrates containing 30,000 ppm I_2 and 150,000 ppm KI. This also happens to be the iodine concentration of the solution in the Iodine Concentrate Tank used in the Test Setup.

An expressed interest in higher iodine concentrations (for the purpose of reducing the container volume) led us to investigate maximum practical concentrations for both types of solution: iodine in alcohol, and iodine-potassium iodide in water. The alcohol solution was prepared by making a saturated solution of iodine in ethanol (at room temperature). The I_2-KI formulation was made by adding iodine crystals--until no more would dissolve--to a saturated solution of potassium iodide. The two preparations showed interesting differences.

We were able to read 217,000 ppm I_2 for the iodine-ethanol preparation. This high concentration may not be feasible, however, to use where it is to be injected through a small orifice into water. An aqueous solution of iodine is saturated at 250 ppm I_2 (20°C); hence injecting a solution nearly 1000 times more concentrated into water causes an immediate formation of solid iodine aggregates. The water surrounding those aggregates becomes quickly iodine saturated as they start to dissolve. If, then, there is no mechanical mixing, the iodine aggregates will stop dissolving until the localized concentrations become diluted (by diffusion) below the saturation point.

We have observed this concentrate enter water as a black, smoky rope, rapidly moving about and dispersing as the alcohol carrier goes into solution. The water immediately turns yellow-brown but tiny particles of the precipitated

iodine collect on the walls and bottom of the container and only slowly dissolve if there is enough iodine free water moving across them.

Iodine-potassium iodide aqueous solutions can be made much more concentrated than the iodine-ethanol ones. Ours measured 540,000 ppm I_2. The ratio of KI to I_2 in this solution was 1.8; thus a water supply treated to contain 10 ppm I_2 would also contain 18 ppm KI. This solution is so viscous and syrupy (41% KI, 22.75% I_2) that it produces a long thread when injected into water. This formation does not immediately disperse or diffuse unless there is mechanical mixing present. Indeed, if the concentrate is delivered to the bottom of a beaker of water it lies spread there and only very slowly diffuses upward over a period of several days. This means that, without energetic mixing action, the local concentration of iodine could be quite high for an appreciable time. Until further diluted, the local concentration might produce metallic corrosion even with some types of stainless steel.

An advantage of the 540,000 ppm I_2 concentrate is, of course, that a suitable container would need be only 6% the volume of the present one to hold an equivalent amount of iodine.

9.0 RECOMMENDATIONS

The present AIMS, with its reduced power and shortened sample pathlength, has again demonstrated more than adequate sensitivity, excellent stability, repeatability, and capability to perform in a satisfactory manner in simulated spacecraft environmental conditions. In some tests it has surpassed the achievements of its successful predecessor which had the advantages of more light and longer pathlength.

Since the major objectives of power and weight reduction were implemented only to the extent of using a lower power source and a shortened sample cell housed in the previous envelope, it is suggested that these two tested and proved features be incorporated in an appropriate housing designed to minimize weight and volume. It appears that it will be feasible to fabricate a one-piece optical bench with a built-in detector and lamp housing, thus further reducing weight and volume. Efforts to reduce the sample pathlength even further should be undertaken to determine what the minimum pathlength can safely be.

The orientation test results indicate that improvements are needed in perhaps optical alignment or optical bench rigidity to reduce the offsets now seen. The one-piece optical bench and a diffusion element in front of the source may be a remedy for this problem.

In view of the dramatic effects of pH changes on the apparent iodine concentration of solutions, it is suggested that further studies be made of pH effects on both aqueous iodine and aqueous iodine-potassium iodide solutions.

APPENDIX A

SHUTTLE PROTOTYPE AUTOMATED IODINE MONITOR/CONTROLLER SYSTEM

TEST REPORT

1.0 INTRODUCTION

The Test Plan executed under Contract NAS9-14298 was designed to demonstrate the capability of AIMS to monitor and control the iodine level in a potable water system having the characteristics of the Shuttle System. Final Report FR-1188-101 (August 1975) documents the test results of that program. Under Contract NAS9-14761 two important modifications were made in the AIMS: a lamp using substantially less power was substituted for the former source, and the light path through the Sample Cell was reduced from 50 mm to 25 mm. We made these changes in order to meet a request for lower power and reduced weight for the AIMS. Since these modifications present the possibility of system degradation with respect to sensitivity, accuracy, and precision a Test Plan was developed for the double purpose of assessing the effects of these modifications and again verifying the operation of AIMS with respect to Shuttle requirements.

The Test Plan was performed in a laboratory setting essentially the same as that used for the previous work. The setup, simulating the relevant features of the Space Shuttle potable water supply system, is illustrated schematically in FIGURE 1 and photographically in FIGURE 2. This setup can be readily adjusted to alter flow rates, pressures, water volumes, and iodine concentrations. A variable speed pump controls the flow rate from zero to more than 800 ml/min. System pressure can be varied from zero to 234.4 kPa (34 psig) as illustrated in FIGURE 1.

The Test Plan, documented in IR-1203-102, included tests to evaluate the following:

Test Plan Paragraph	Title
2.1.1	Sensitivity to Changes in Iodine Concentration
2.1.2	Iodine Control
2.1.3	Baseline Hysteresis

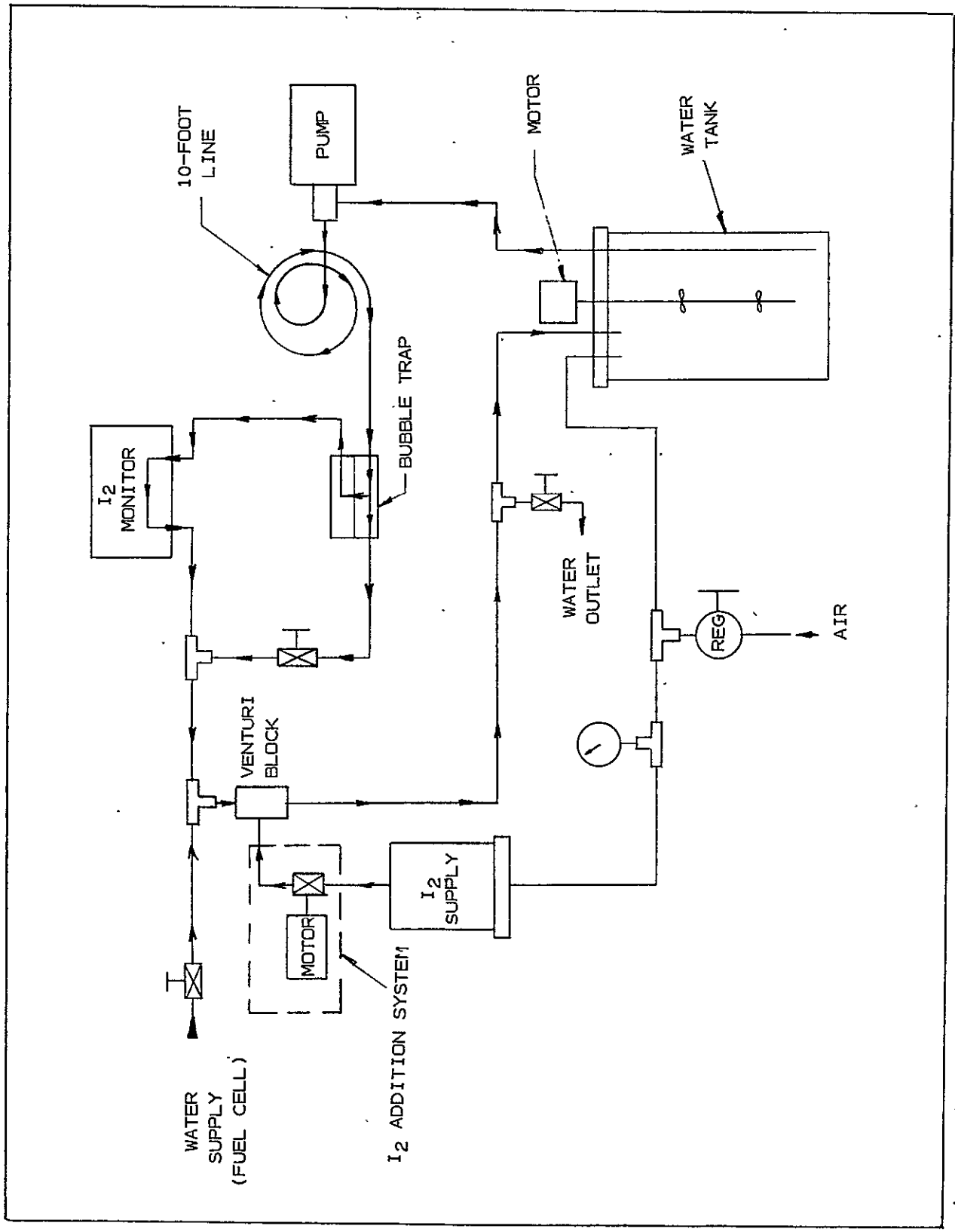

Figure A-1. Test System

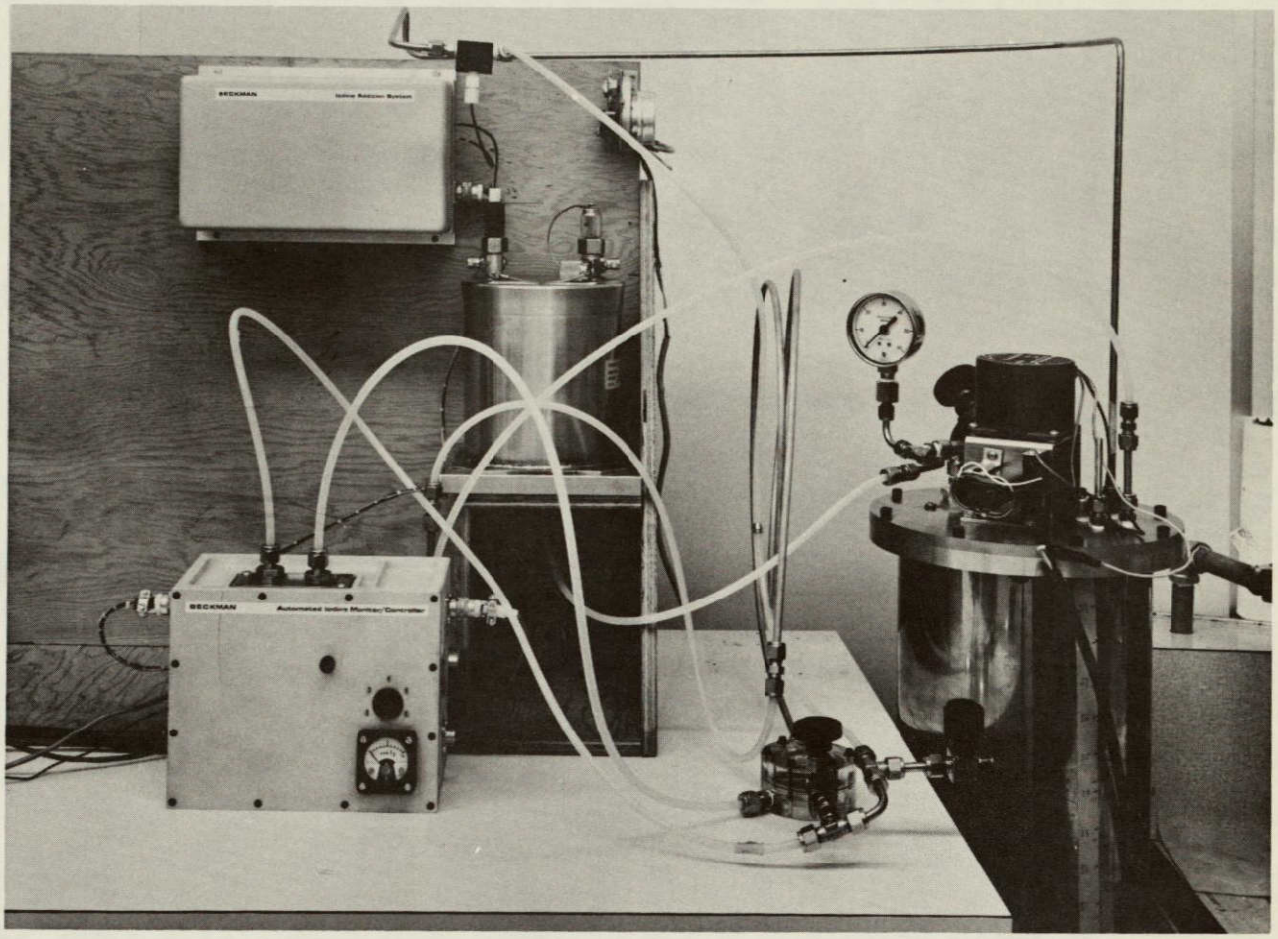

Figure A-2. Test Configuration

2.1.4 Pressure (on sample cell)

2.1.5 Variable Flow Rates

2.2 Trace Interferences

2.2.1.3 Accuracy and Repeatability in the Presence of Varying Amounts of Potassium Iodide

2.3 Baseline Stability

2.4 Requirement for Bubble Elimination

2.5 Instrument Orientation

2.0 TEST RESULTS

Test 2.1.1 — Sensitivity to Change in Iodine Concentration

Sensitivity at low iodine levels was determined by connecting the Monitor to a three-liter flask of deionized water, adding iodine concentrate in 10-µℓ increments, and noting the delta change in the output signal as registered on a digital voltmeter and strip chart recorder. The water volume in the flask was adjusted so that the total water in the system equaled three liters. Microliter pipettes were used to add iodine to the water. The water contained no iodine at the start of the tests.

The addition of 10 µℓ of iodine concentrate (30,000 ppm) changed the signal by +94 mV. A second addition made a change of 96 mV; a third, of 100 mV. Each of these voltage changes represents approximately 0.1 ppm I_2. Using the known values for the volume of the system, the iodine concentration, and the amount of iodine added, the calculated iodine/addition was 0.1 ppm.

The recorder strip chart trace showed one chart division offset for each iodine addition (10 divisions = 1 ppm). This was somewhat more than twice the noise level at that time.

Sensitivity to iodine changes was checked in the same manner at the 2- and 4-ppm levels where 10 µℓ of iodine concentrate added to the water supply again produced 100 mV changes. Addition of approximately 5 µℓ iodine concentrate made a 35-mV change. The resulting offset was clearly visible on the chart but the ΔmV was less than anticipated.

Finally, at the 8.5-ppm level the 10 μℓ iodine addition again made the 100 mV signal change.

These test results indicate that the AIMS will accurately measure differences of 0.1 ppm I_2 over the entire working range and will detect changes of less than 0.05 ppm I_2.

Test 2.1.2 — Iodine Control

The objectives of this test were to verify the level switch functions, the operation of the iodine addition system, and the capability of the system to control and monitor the preset iodine levels through 24-hour intervals. The complete test setup was used and monitoring was continuous. The DK-2A Spectrophotometer provided reference measurements.

Control at 2 ppm: The water in the 38-ℓ tank contained no iodine at the start of this test. A series of 12 automatic iodine injections, made at 10-minute intervals, brought the iodine level to 2.4 ppm. The DK Spectrophotometer measured the iodine content of the tank water as 2.3 ppm I_2. Twenty-four hours later the AIMS read 2.3 ppm which agreed with the DK measurement. Thus the system lost 0.1 ppm in 24 hours. During this time no iodine was added: only if the level had dropped to 2.0 ppm would the addition system have been activated. We believe that additions were not called for because the tank was very nearly full and this decreases the loss of iodine to air (as apparently happened during the previous program).

Control at 3 ppm: At the end of 24 hours at the 2-ppm level, the monitor was switched to operate at 3 ppm. This time only 5 injections over a 50-minute period were required to bring the tank iodine level to 3.3 ppm. The DK Spectrophotometer confirmed this, giving the same measurements. At the end of 24 hours we were faced with an anomaly — the AIMS read 3.6 ppm as did the DK. Since the recorder record showed no subsequent iodine additions, we can only explain the 0.3 ppm *increase* by assuming that some iodine had leaked into the system by way of the valve or had diffused into the water line in the venturi section. The iodine addition system valve

is somewhat worn from extensive use in the previous program and this may account for the slight rise in the tank iodine level. Since the addition system was not under test in this program, we decided to continue with the iodine control test.

Control at 4 ppm: Since the iodine level was now at 3.6 ppm it required only 4 additions to bring the level to 4.3 ppm. The DK read 4.2 ppm.

Control at 5 ppm: After 24 hours the control was set to 5 ppm. Five additions brought the iodine concentration to 5.4 ppm. At this point the DK read 5.2 ppm.

Control at 6 ppm: Set to control at 6 ppm, 5 additions were required to raise the iodine level to this concentration. Both the AIMS and the DK read 6.2 ppm and this value remained constant over the 24-hour interval.

After this test the tank was left for the next 37 days. An iodine determination showed that the level had dropped from 6.2 ppm I_2 to 3.3 ppm. This represents an average loss of 0.08 ppm/day.

These test results show that the AIMS iodine addition system works properly in the modified system and, in addition, that the AIMS iodine readings show excellent agreement with the referee instrument measurements.

Test 2.1.3 — Baseline Hysteresis

This test followed the week-long accuracy tests during which iodinated water was present in the Sample Cell at all times. By connecting the monitor to a zero iodine water supply we measured any zero offset acquired during this time. Our zero reading before the iodine control tests was set at +0.276 volt. After those tests (5 days) zero read +0.286 volt. This rose to +0.483 volt. At this point the water was changed as iodine residual in the plumbing system could have appeared in the solution to some extent and to bias the system zero determination. The reading immediately fell to +0.392 volts. This and subsequent readings at various times are shown following:

Volts	Hours
+0.392	0
.468	1
.576	2
.665	3
.750	5
.800	7
.800	12
.900	16
.900	18

The "red and blue" signals at this point suggested that there was "something" in the water. The "red and blue" signals at the start of the test and at the 18-hour point were:

	Start	18 Hours
Red	10.100	10.045
Blue	10.032	9.911

The change in the blue signal does indicate the presence of some iodine.

A sample of the water showed iodine present to the extent of approximately 0.4 ppm. When the water was changed the previous 0.900-V reading fell to 0.432 V. This is nearly the same reading as at the start. Apparently iodine was still leaking into the stream. At the end of 24 hours the 0.432 V had risen again to 0.500 V.

To summarize, our zero rose only 0.010 V at the beginning of the Hysteresis Test but continued to rise due, apparently, to some iodine contamination to 0.900 V. A change in the water reduced this to 0.500 V. If this value is taken as the new zero, then the change amounts to 0.500 V-0.276 V = 0.224 V, and this is equivalent to approximately 0.2 ppm.

Although scheduled to run only 24 hours, this test was continued another 69 hours, with substantially the same results: a rise in the signal equivalent to about 0.8 ppm followed by an immediate fall to only 0.3 ppm when the water was changed.

Finally, the iodine addition section of the water circuit was bypassed, thus eliminating the possibility of iodine diffusing into the stream. The signal changes with time during the following 24-hour interval are given below:

Signal Volts	Time Hours
0.636	0
.583	1
.491	4
.517	5
.550	8
.530	13
.520	16
.510	20
.500	24

Note that here there is only a small negative change amounting to 0.136 V, equivalent to 0.14 ppm.

Test 2.1.4 — Pressure Test

The purpose of this test is to ascertain the structural integrity of the flow-through cell. This was done by applying compressed air to the water-filled cell at 234.4 kPa (34 psig) and subsequently examining it for leaks.

NASA-JSC informed us that the water system pressure is 55.2 to 117.2 kPa (8 to 17 psig) and tests should be conducted at twice maximum pressure. We performed this test twice at 234.4 kPa (34 psig) and holding for one minute. There was no evidence of leakage.

Test 2.1.5 — Flow Rate

This test examines the effect of variable flow rates on the measurement of a constant iodine level, with zero flow included as a special case. The Variac in the test setup was used to vary the pump speed and hence the flow rate.

At the beginning of the test the flow rate was approximately 80 ml/min. The iodine concentration was 3.0 ppm. For the next several minutes the flow rate was varied according to the following schedule. Adjacent columns show the output voltage and equivalent ppm I_2.

Flow Rate ml/min	Volts	ppm I_2
80	3.280	3.0
480	3.260	3.0
720	3.250	3.0
900	3.250	3.0
240	3.222	2.9
180	3.222	2.9

During the zero flow test (pump off) the iodine concentration in the Sample Cell was continuously monitored and periodic iodine determinations of the tank water were made. The results are tabulated below:

Time		Signal		Tank Water DK-2A
Hours	Min	Volts	ppm I_2	ppm I_2
0	0	3.230	3.0	3.3
1	0	3.402	3.1	3.3
1	20	3.295	3.0	3.3
2	0	3.165	2.0	3.3
3	0	2.925	2.7	3.3
3	20	2.869	2.6	3.3
4	0	2.783	2.55	3.3
4	30	2.750	2.5	3.3
5	0	2.674	2.4	3.3

The slight rise during the first hour of zero flow rate (3.0 to 3.1 ppm) has been observed each time the monitor has been operated at zero flow rate. However, the rise was much higher in the previous system, rising to 1 ppm in three hours. We believe this is a thermal effect and thus we would expect it to be less with the much cooler source now used.

Test 2.2 — Assess Effects of Trace Interferences

This test was designed to assess the effect of nickel, chromium, and ferric ions on the accuracy of the iodine measurement. Although potassium iodide is a normal constituent of the iodine concentrate, the effect of KI on the apparent iodine reading was also determined.

Solutions containing 0.1, 1.0, and 10 ppm of the ions were individually checked in the monitor for zero offset. Next, 100 µℓ of iodine concentrate was added to the one-liter water supply used in these tests. The resulting measurement was then compared to a one-liter solution containing only water and 100 µℓ of the iodine concentrate. Repeated measurements of the latter solution measured 2.6 ppm on the AIMS and 2.5 ppm on the DK-2A. TABLE 1 presents the results of these tests. The interference column in this table represents the difference between the AIMS reading and the 2.6-ppm iodine solution.

TABLE I. TRACE INTERFERENCES

Interferring Ion	Concentration ppm	AIMS ppm	DK-2A ppm	Interference ppm
Ni^{+2}	0.1	2.6	2.5	0.0
Ni^{+2}	1.0	2.6	2.5	0.0
Ni^{+2}	10.0	2.4	2.6	-0.2
C^{+3}	0.1	2.6	2.5	0.0
C^{+3}	1.0	2.6	2.6	0.0
C^{+3}	10.0	2.6	2.6	0.0
Fe^{+3}	0.1	2.7	2.9	+0.1
Fe^{+3}	1.0	3.7	4.3	+1.1
Fe^{+3}	3.0	6.3	7.0	+3.7
Fe^{+3}	10.0	offscale, not measured		

Potassium iodide (KI) was added, crystal by crystal, to an aqueous iodine solution containing 6.35 ppm I_2 (DK-2A:6.5 ppm). KI was added until its concentration in the solution reached 134 ppm. The effects on the iodine reading are tabulated below:

Iodine		Potassium Iodide
AIMS ppm	DK-2A ppm	ppm
6.35	6.5	0
6.35	6.5	5
6.4	6.5	12
6.5	6.5	29
6.5	6.5	69
6.55	6.5	134

Theoretically, if the AIMS were operating precisely at the isosbestic point there should have been no change in the iodine readings as the KI concentration was raised. The DK-2A readings were made, of course, at the isosbestic point. The blue filter in the AIMS passes light at not quite the isosbestic point. This error, coupled with the very high sensitivity of the monitor, could account for the slight rise in the AIMS signal with increasing iodide levels in the solution.

Test 2.3 — Stability

This test was designed primarily to reveal variations or drifting in the baseline signal occurring with time. Deionized water (no iodine) was circulated through the monitor for 212 hours. During this period the output signal was recorded continuously. Additional data regarding lamp, reference, and signal voltages were collected from time to time. Ambient temperature and humidity data were also recorded continuously. The test results are presented in TABLE II. Only the significant changes are tabulated for the baseline signal, as the complete record is too voluminous for inclusion in this report.

The tabulated data show that all the zero deviations appear as negative voltages ranging from -0.10 to -0.60 volt. This range of 0.5 volt represents 0.5 ppm equivalent. If, however, zero had been set in the middle of their range, the variation would have corresponded to 0.25 ppm equivalent.

The lamp voltage shows no significant change. The 0.006 V spread reflects the effect of ambient temperature cycling where the higher the ambient temperature, the lower the lamp voltage, and vice versa.

TABLE II. BASELINE READINGS

Date (1975)	Time	Signal -V	Lamp V	Red -V	Blue -V
October 25	8:00 P	.10			
	10:00	.15			
	11:00	.20			

TABLE II. BASELINE READINGS (Continued)

Date (1975)	Time	Signal -V	Lamp V	Red -V	Blue -V
October 26	2:00 A	.25			
	4:00	.30			
	9:00	.35			
	11:00	.40			
	11:00 P	.40			
	MN	.37			
October 27	3:00 A	.38			
	4:00	.40			
	6:00	.38	4.068	10.507	10.515
	8:30	.34	4.067		
	2:00 P	.42	4.069		
	3:00	.41	4.069	10.516	10.514
	7:00	.45			
	10:00	.50			
	MN	.55			
October 28	7:00 A	.56	4.071	10.509	10.527
	11:00	.48	4.069	10.474	10.475
	Noon	.43	4.068		
	2:00 P	.43			
	4:00	.50	4.070	10.478	10.479
	8:00	.55			
	10:00	.58			
	MN	.60			
October 29	7:00 A	.56	4.072	10.466	10.474
	10:00	.49	4.070	10.443	10.439
	11:00	.42	4.069		
	1:00 P	.40	4.069	10.427	10.412
	3:00	.30	4.067	10.400	10.370
	4:00	.29	4.068	10.402	10.372
	6:00	.30			
	9:00	.40			
October 30	1:00 A	.45			
	4:00	.50			
	5:00	.45			
	8:00	.40	4.071	10.411	10.397
	9:00	.37	4.070		
	11:00	.30	4.069		
	2:00 P	.34	4.070	10.391	10.363
	4:00	.31	4.070		
	6:00	.25			
	7:00	.20			
	8:00	.25			
	9:00	.30			

TABLE II. BASELINE READINGS (Continued)

Date (1975)	Time	Signal -V	Lamp V	Red -V	Blue -V
October 31	2:00 A	.38			
	3:00	.40			
	5:00	.35			
	6:00	.30			
	7:00	.35			
	10:00	.32	4.071	10.365	10.333
	11:00	.26			
	2:00 P	.29	4.071		
	4:00	.32	4.072	10.362	10.326
	7:00	.43			
	10:00	.45			
	MN	.39			
November 1	1:00 A	.38			
	2:00	.39			
	3:00	.40			
	4:00	.42			
	5:00	.39			
	6:00	.38			
	7:00	.35			
	8:00	.33	4.072	10.342	10.309
	9:00 A	.28	4.072		
	10:00	.30			
	3:00 P	.33			
	4:00	.40			
	6:00	.45			
	8:00	.40			
	10:00	.35			
November 2	2:00 A	.30			
	3:00	.23			
	5:00	.15			
	6:00	.10			
	10:00	.10			
	11:00	.12			
	Noon	.20			
	2:00 P	.27	4.073	10.302	10.257
	4:00	.35			
	5:00	.40			
	MN	.40			
November 3	1:00 A	.35			
	3:00	.25			
	6:00	.20			
	8:00	.25	4.072	10.275	10.226

Total: 212 Hours

Test 2.4 — Requirement for a Bubble Eliminator

The AIMS Setup has always included a simple bubble eliminator because past experience showed that air bubbles (generally present in the system) passing through the monitor or remaining in the sample cell, caused noise spikes in the output signal. Test 2.4 was performed to re-examine the requirement for a bubble eliminator. This component was the same as that used in the previous program.

In one of two tests the bubble eliminator was removed and the signal remained quiet for the next 12 hours, followed by a 3-hour period showing one percent noise. During the following 3 hours the signal was again quiet.

In the second test noise developed one hour after the bubble eliminator was removed and continued for the next 10 hours. FIGURE 3 is a tracing of a representative section of the chart recording made during this period. The cyclic pattern was apparently generated by an air bubble rotating about in the sample cell. The bubble eventually escaped and the signal then remained quiet during the succeeding fifty hours. The test was stopped at that point. Other tests were made which showed periods of no noise followed by short intervals of noise spikes.

These tests show that in order to ensure a quiet signal it is necessary to use bubble-free water in a completely water filled system and to prevent air from entering the system. In our setup this is not easy to do.

If air does infiltrate the system, the resulting noise is of two species: single spikes punctuating an otherwise quiet signal, or continuous noise of varying amplitude as shown in Figure 3. Isolated spikes appear to be related to single small bubbles that enter the cell and immediately pass on through. Continuous noise appears to originate from clusters of air bubbles that tend to remain in the cell for long periods of time.

It should be noted that our bubble eliminator did not need cleaning, and presented no problems during the entire test period of several weeks.

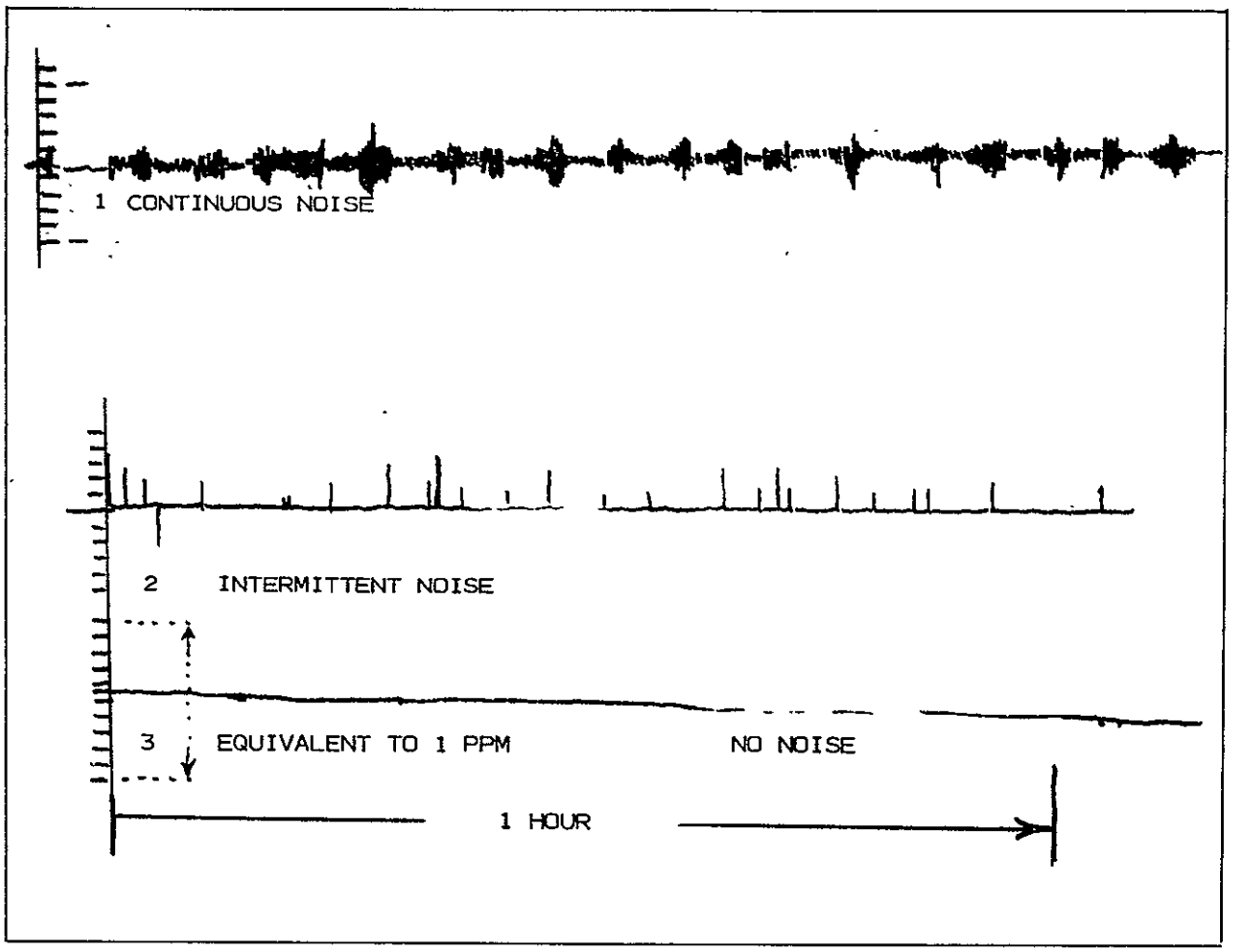

Figure 3. Samples of Performance in the Absence of the "Bubble Eliminator"

Test 2.5 — Orientation Tests

When we changed the AIMS lamp, but prior to shortening the sample cell, we made some orientation tests hoping to see less offsets than was the case when the old lamp was used. In some monitor positions that lamp was apparently responsible for causing signal offsets equivalent to nearly 2 ppm. After making only the lamp change, the offsets were reduced to no more than 0.3 ppm (equivalent).

The second major modification to the monitor was shortening the Sample Cell and this required an increase in amplifier gain in order to preserve the full-scale range of 0 to 10 ppm. Under these conditions, however, the monitor again exhibited increased delta volt changes when put through the orientation test. These changes are given below:

Orientation Test

Position 1	to	Position 2	Position 1 Signal	Position 2 Volts	ΔV
Upright		Face	-.120	.376	+.496
Face		Left End	.692	1.338	+.645
Left End		Right End	1.489	1.226	-.263
Right End		Upside Down	1.271	2.408	+1.137
Upside Down		Back	2.404	2.044	-.360
Back		Upright	1.873	.362	-1.511

We believe these increased offsets are primarily caused by the higher amplification factor of the present circuit. It should be possible, however, to introduce a diffusion element in an improved prototype instrument which would render the active surfaces of the detectors less sensitive to light variations arising out of microscopic movements of the lamp filament.

It is also possible that there are unrelieved stresses between the modified monitor housing and the optical bench plate. These stresses may vary as the housing position is changed, thus introducing minute changes in the optical alignment. Again, the increased amplifier gain would augment the resulting offsets. Data supporting this posibility were provided by operating the optical bench outside of the housing. The offsets were reduced to about one-half their previous values.

APPENDIX B

EXPERIMENTS TO DETERMINE THE EFFECT OF ALTERED pH ON THE DIRECT-SPECTROPHOTOMETRICALLY DETERMINED CONCENTRATION OF AQUEOUS IODINE

1.0 INTRODUCTION

The effect of pH on the spectrophotometrically determined (apparent) concentration of iodine in aqueous solution was investigated. It was found that, with very dilute iodine solutions (5 and 9 parts per million), with or without added potassium iodide, addition of HCl to decrease the pH caused a slight reduction in apparent ppm, but still within acceptable limits. Addition of NaOH to increase the pH caused a drastic reduction in the apparent ppm of iodine above pH 7 for all but one solution. The exceptional solution contained *ca* 9 ppm iodine plus potassium iodide. The rapid reduction of apparent ppm iodine in this solution did not occur until the pH was increased above pH 8.

The results definitely revealed that a minute quantity of added hydroxyl ions to a dilute "neutral" iodine solution casues a drastic reduction in the value of apparent concentration of iodine in solution as determined spectrophotometrically at 465 nm. A study of the pertinent reactions revealed that the added hydroxyl ions cause a stoichiometric conversion of the aqueous iodine to iodate ions which, in solution, do not absorb at 465 nm.

It was also found that the presence in solution of potassium iodide slightly raised the pH at which the apparent ppm of iodine plunged upon addition of hydroxyl ions when compared to an iodine solution of the same concentration but without potassium iodide.

2.0 MATERIALS AND METHODS

All spectrophotometric measurements were made with a Beckman DK-2A Ratio Recording Spectrophotometer in transmission mode with 10.000 cm pathlength cells over the range 350 to 700 nanometers against a water blank.

Degerminations of iodine concentration in parts per million were made by obtaining the percent transmission at 465 nanometers, converting to absorbance at that wavelength, then obtaining the concentration in parts per million from the appropriate standard curve (FIGURE 1).

All pH measurements were made with a Beckman Century SS-1 pH meter equipped with a Beckman #39301 pH glass electrode and a Beckman #39402 reference electrode. The pH meter was standardized with buffers of known pH prior to making any pH measurements.

All reagents used were analytical grade. To decrease the pH of an iodine solution, 1 N HCl was used; to increase the pH, 1 N NaOH was used.

Four different iodine solutions were tested. Two solutions contained approximately 9 mg iodine in 1.0 liter of water. One of these "9 ppm" iodine solutions also contained potassium iodide, the amount added being three times the weight of added iodine. Therefore, one solution contained *ca* "9 ppm" iodine and the other contained *ca* "9 ppm" iodine plus *ca* "27 ppm" potassium iodide. Two other solutions contained approximately 5 mg iodine in 1.0 liter of water. As above, one of these "5 ppm" solutions also contained potassium iodide, the amount added being three times the weight of added iodine.

Each solution was prepared immediately before testing and then divided into two 500-ml aliquots. To one aliquot was added HCl to determine the effect of lowered pH on the spectrophotometric determination of ppm iodine and to the other aliquot was added NaOH to determine the effect of increased pH. While the first aliquot was being tested, the second was kept covered and in darkness. (During all tests, room lighting was kept to a minimum).

Figure 1. Standard Curves for Direct Spectrophotometric Determination of Aqueous Iodine

Before acid or base was added to a 500 ml aliquot of iodine solution, the percent transmission at 465 nm was measured. The pH was also obtained and was found to be variable, mostly within the range pH 6 to pH 7. This range was termed the "neutral" range. Upon addition of acid or base, the pH readings tended to become quite steady, especially toward the extremes of the span over which they were obtained, from pH 3.0 to pH 9.5.

3.0 RESULTS

The results of these pH tests are shown in FIGURE 2 as a plot of spectrophotometrically determined ppm iodine at 465 nm versus solution pH. The graph shows the "neutral" range, pH 6 to pH 7, referred to above. Note that the highest apparent ppm iodine values for each solution lie within this range. These values were also closest to the theoretical values based on the exact amount of solid I_2 added to the solution when they were being prepared. The graph shows quite clearly that, especially for solutions containing *only* iodine, solution pH values greater than pH7, *obtained via addition of hydroxyl ions*, cause the spectrophotometrically determined ppm iodine readings to decrease rapidly. Only the solution containing "9 ppm" iodine *plus* KI appeared to maintain a relatively stable high reading of apparent ppm iodine to pH8.

The maximum and minimum apparent ppm iodine values within the NASA-specified pH range for potable water of pH6 to pH8, the differences between these values and the percent decrease of apparent ppm for each solution tested are tabulated in TABLE I Note that the percent drop of apparent ppm iodine over this range was greater for the two solutions containing no KI, relative to the two solutions of the same concentration, respectively, which did contain KI. Between the two solutions containing no KI, the "5 ppm" solution experienced the more severe reduction in apparent ppm iodine. The same was true for the other two solutions which did contain KI. These results indicate that (a) the reaction between hydroxyl ions and aqueous iodine is stoichiometric and (b) the formation of triiodide complex due to an excess of iodide ions, as in the solutions containing KI, has a slightly inhibitory action on the quite favorable disproportionation of I_2 due to hydroxyl ions.

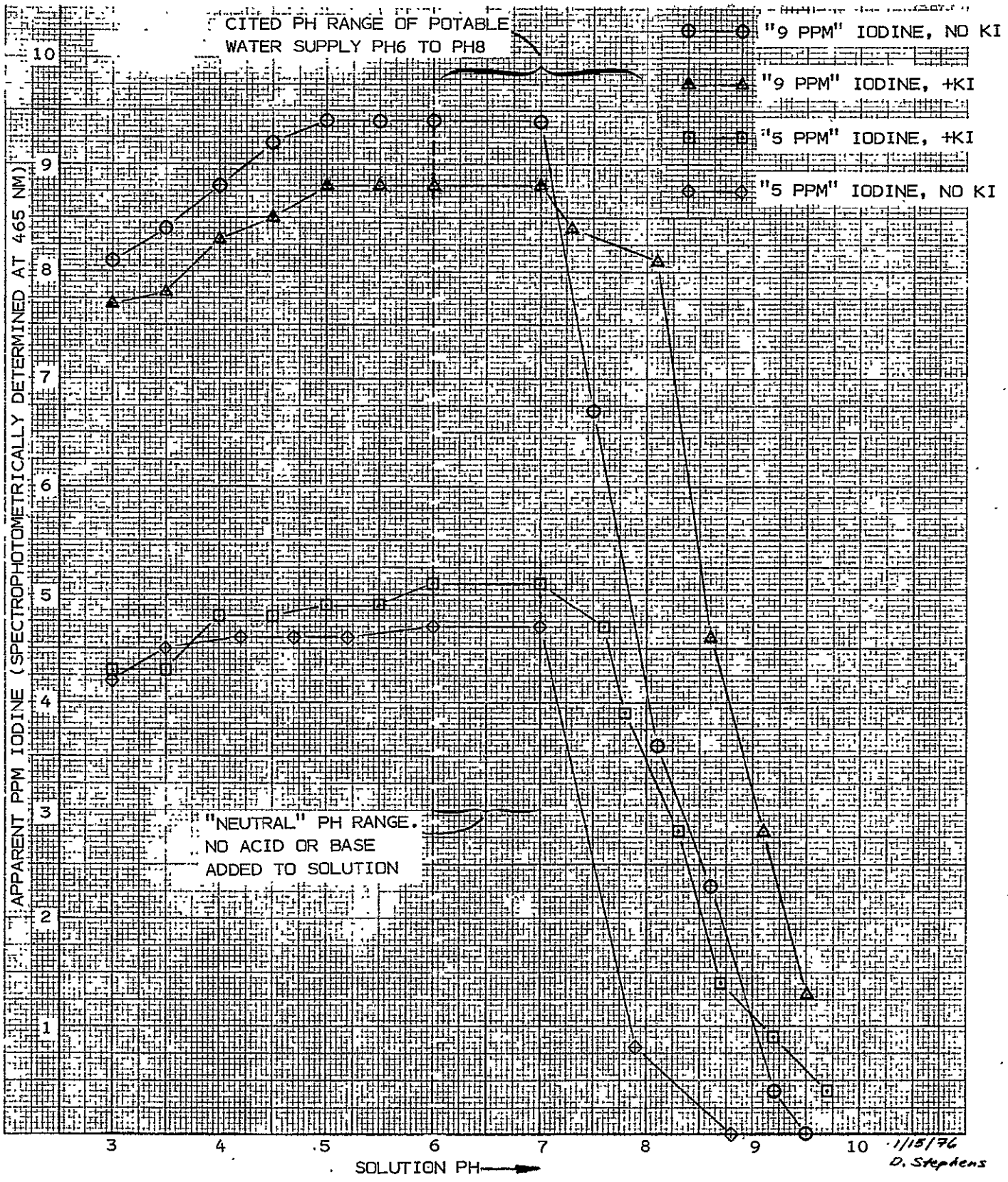

Figure 2. Apparent Concentration of Iodine, Determined by Absorbance of the Solution at 465 nm as a Function of Solution pH. pH adjusted with HCl or NaOH.

TABLE I. DECREASE IN APPARENT PPM IODINE OVER THE RANGE pH 6 TO pH 8

Solution	Maximum ppm Iodine	Minimum ppm Iodine	Decrease in Apparent ppm	% Decrease Relative to Max.
"9 ppm" Iodine no KI	9.4	4.1	5.3	56%
"9 ppm" Iodine + KI	8.8	8.1	0.7	8%
"5 ppm" Iodine + KI	5.1	3.4	1.7	31%
"5 ppm" Iodine no KI	4.7	0.7	4.0	85%

4.0 DISCUSSION OF PERTINENT IODINE CHEMISTRY

Iodine (I_2) is only very slight soluble in water. At 25°C, the maximum concentration of aqueous I_2 attainable in pure water is *ca* 0.001 M which is equivalent to 254 parts per million (ppm).

Aqueous I_2 will undergo hydrolysis, yielding iodide and hypoiodous acid, but to an extremely limited extent as indicated by the equilibrium constant of the reaction:

$$I_2 + H_2O \rightleftharpoons H^+ + H^- + HOI \qquad (R1)$$

$$Keq = 2 \times 10^{-13} \text{ at } 25^\circ C$$

In this reaction, the concentration of HOI has been determined to be 6.4 x 10^{-6} M at 25°C (see 1, below). There is, therefore, a negligible concentration of HOI in an aqueous solution of I_2.

Another hydrolysis reaction which will occur to a very limited extent is the formation of the hydrated iodine cation by the reaction.

$$I_2 + H_2O \rightleftharpoons H_2OI + +I^- \qquad \text{(R2)}$$

$$Keq = 1 \times 10^{-10} \text{ at } 25°C \text{ (see 2, below)}$$

Again, the accumulation of product would be negligible.

The very slow formation of triiodide also occurs in an aqueous solution of I_2.

$$I_2 + I^- \rightleftharpoons I_3^- \qquad \text{(R3)}$$

$$Keq = 1.4 \times 10^{-3} \text{ at } 25°C \text{ (see 3, below)}$$

where either the scant formation of I^- (aq) via the above hydrolysis reactions is presumably the rate determining step or that the slow production of triiodide is due possibly to the presence of trace amounts of contaminants in solution which act as reducing agents.[4]

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[3]Sneed, M.C., J.L. Maynard, and R.C. Brasted, *Comprehensive Inorganic Chemistry,* Vol. 3 Princeton, D. Van Nostrand Co., Inc., 1954

[4]Wolfenden, J.H., *Anal. Chem.*, 29:1098. (1975).

The solubility of I_2 in water is greatly increased by the presence in solution of additional iodide ion, such as from dissolved potassium iodide. The result is the formation of triiodide by reaction R3 where an excess of iodide displaces the equilibrium from the left far to the right. This reaction is important as a means of bringing iodine into aqueous solution. As indicated, however, the reaction is reversible and so free I_2 is always present in solution. (The concentration of I_3^- in aqueous I_2 solutions containing KI is sufficiently high that these solutions should be regarded as $I_2 + I_3^-$ solutions instead of only I_2 solutions.)

Iodine reacts with hydroxide ion in cold alkaline solution to form the hypoiodite ion, IO^- and iodide ion,

$$I_2 + 2\ OH^- \longrightarrow IO^- + I^- + H_2O \qquad \text{(R4)}$$

$$\text{Keq} = 30 \text{ at } 25^oC \ ^{1,5}$$

As can be seen, the equilibrium constant for this reaction is very favorable. This reaction is rapid, even at room temperature. The hypoiodite ion is, however, extremely unstable in alkaline solution and disproportionates rapidly to form iodate ion:

$$3IO^- \longrightarrow IO_3^- + 2I^- \qquad \text{(R5)}$$

$$\text{Keq} = 10^{20} \text{ at } 25^oC \ ^{1,5}$$

The equilibrium constant for the above reaction is extremely favorable. The rate of disproportionation of IO^- is so fast that the formation of IO_3^- is essentially instantaneous. IO^- is undetectable in basic solution.

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[5] Bailar, J.C., Jr., H.C. Emeleus, R. Nyholm, and A.F. Trotman-Dickenson, (ed.), *Comprehensive Inorganic Chemistry*, Vol. 2 Oxford, Perganon Press, Ltd, 1973.

The equilibrium constant for disproportionation of IO_3^- is

$$4IO_3^- \rightleftharpoons I^- + 3IO_4^- \qquad \text{(R6)}$$

$$Keq = 10^{-53} \text{ at } 25^oC \ ^1$$

which makes this reaction negligible. Iodate is also very stable with respect to reactions such as

$$7\ IO_3^- + 9H_2O + 7H^+ \rightleftharpoons I_2 + 5H_5\ IO_6 \qquad \text{(R7)}$$

$$Keq = 10^{-85} \text{ at } 25^oC \ ^5$$

$$4\ IO_3^- + 3OH^- + 3H_2O \rightleftharpoons + 3H_3IO_6^{-2} \qquad \text{(R8)}$$

$$Keq = 10^{-44} \text{ at } 25^oC \ ^5$$

Therefore, irrespective of rate, no disproportionation of IO_3^- occurs.

The overall reaction of I_2 in basic solution is thus given by:

$$3I_2 + 6OH^- \rightleftharpoons 5I^- + IO_3^- + 3H_2O \qquad \text{(R9)}$$

With strong base, the iodine will react stoichiometrically to yield iodate and iodide ions.

The reaction is reversible and on acidification the I_2 is reformed.

If KI is present in solution, reaction R3 will affect reaction R9, pulling it somewhat to the left. Therefore, a slight excess of hydroxyl ions, over that amount necessary if KI was absent, is necessary to shift reaction R9 an equivalent amount to the right.

APPENDIX C

COMPARISON OF A LEUCO CRYSTAL VIOLET METHOD OF DETERMINATION OF AQUEOUS IODINE TO A DIRECT SPECTROPHOTOMETRIC METHOD

1.0 INTRODUCTION

The apparent concentrations of aqueous iodine in parts per million (ppm) in a series of dilute solutions of unknown concentration were determined by both a Direct Spectrophotometric (DS) method and a Leuco Crystal Violet (LCV) method. These determinations were performed in order to ascertain whether or not the results agreed to within the acceptable limit of $\pm$ 1 ppm over the concentration range tested. The data indicated that 1) the agreement between these two methods was well within the above acceptability limit, 2) the correlation between the ppm values obtained by both methods did not appear to be linear *over the range 0 to 8 ppm* but did appear to be essentially linear *over the range 1 to 8 ppm* where the DS method yielded data consistently greater than those yielded by the LUC method by ~0.65 ppm, and 3) the LCU method was about 75 times more sensitive than the DS method over the range 0 to 10 ppm.

2.0 MATERIALS AND METHODS

All Spectrophotometric measurements were made with a Beckman DK-2A Ratio Recording Spectrophotometer in transmission mode. For the Direct Spectrophotometric (DS) method, 5.000 cm pathlength cells were used and the absorbance was measured at 465 naometers. For the Leuco Crystal Violet (LCV) method, 1.000 cm pathlength cells were used and the absorbance was measured at 592 nanometers. A water blank was used for the DS method and a blank containing a mixture of water and the LCV solution in the ratio discussed below was used for the LCV method.

The LCV solution used for the LCV method was Indicator Solution 34-1, cited in Section V of the Final Report (Contract Number NAS9-11861) submitted to NASA MSC, Houston, Texas, by the University of Alabama College of Engineering in March, 1972. The composition of this solution is given below:

9.25 g Leuco Crystal Violet: 4,4'x4" - methylidynetris (N,N-dimethylaniline, Eastman)

6.9 g 85% H_3PO_4

3.6 g H_gCl_2

All reagents used were reagent grade.

The iodine solution was initially made as a 100 ppm stock (100 mg I_2 plus 300 mg KI dissolved in and diluted to 1.0 liter with water). Dilutions of aliquots from this stock solution yielded iodine solutions, the exact concentrations of which were unknown but spanned the range from about 1 ppm to ~8 ppm.

After mixing, the solution were kept in subdued light until analyzed. During the spectrophotometric analysis of any one solution, the DS reading was obtained first with the LCV reading taken immediately thereafter. For the LCV measurements, 25.0 ml of the solution being analyzed was mixed with 5.0 ml of LCV solution and the absorbance at 592 nm was taken immediately thereafter.

Standard curves were used to determine the apparent ppm iodine in the test solutions from the absorbance data. The curves were plotted according to data obtained in prior experiments at Beckman by these methods with known concentrations of aqueous iodine. FIGURE 1 gives the standard curve for the LCV method over the range 0 to 10 apparent ppm iodine. FIGURE 2 gives the standard curve for the DS method over the range 0 to 12 apparent ppm iodine.

3.0 RESULTS

The standard curve in FIGURE 1 yields a slope of 0.195 absorbance units per apparent ppm unit of iodine for the LCV method. The curve in FIGURE 2 yields a slope of 0.0128 absorbance units per apparent ppm unit of iodine for the DS method. If one considers the pathlengths of the cells used in these two methods, 1.000 cm and 5.000 cm, respectively, one finds that, according to

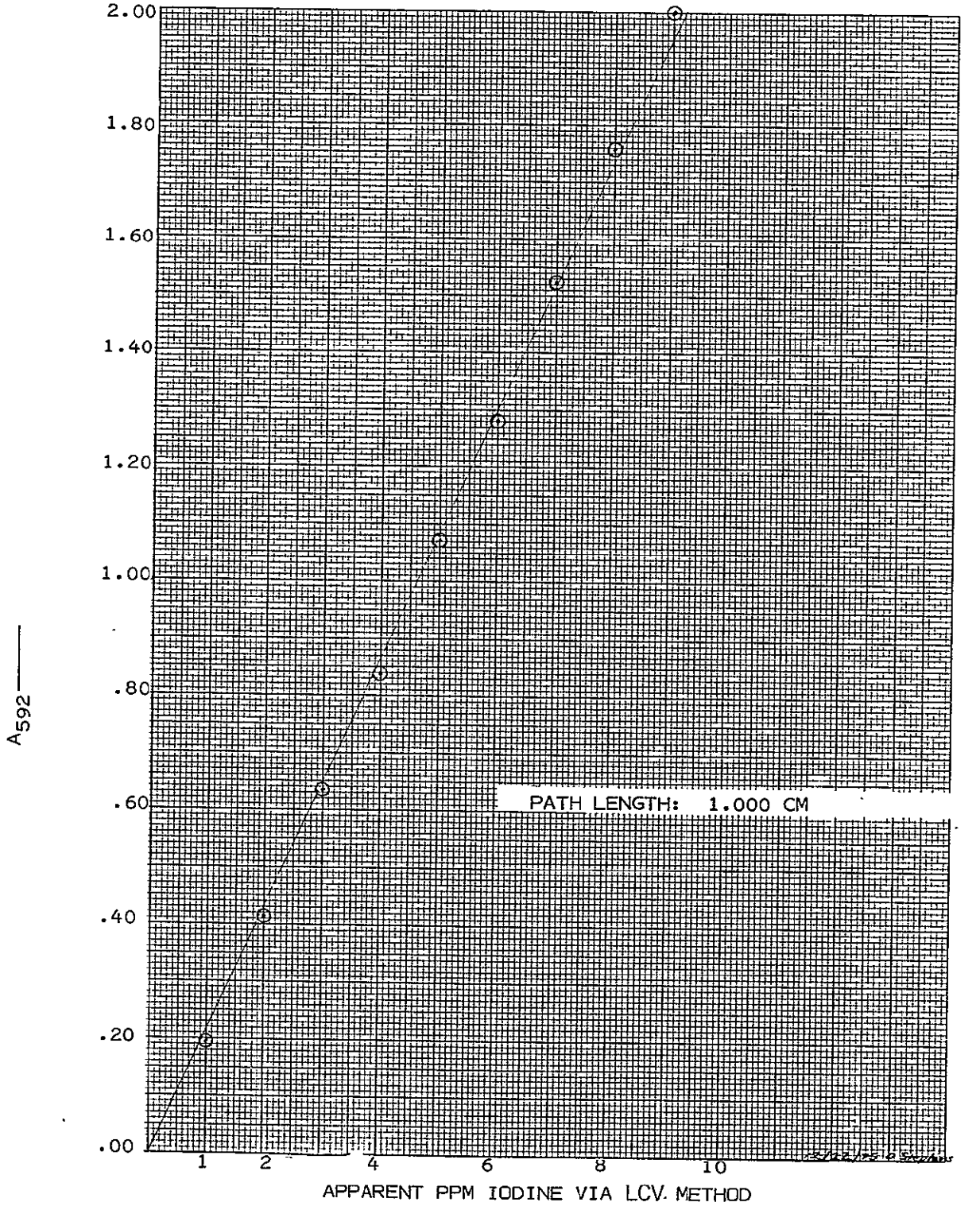


Figure 1. Standard Curve, Ieuco Crystal Violet (LCV) Method of Determination of Aqueous Iodine

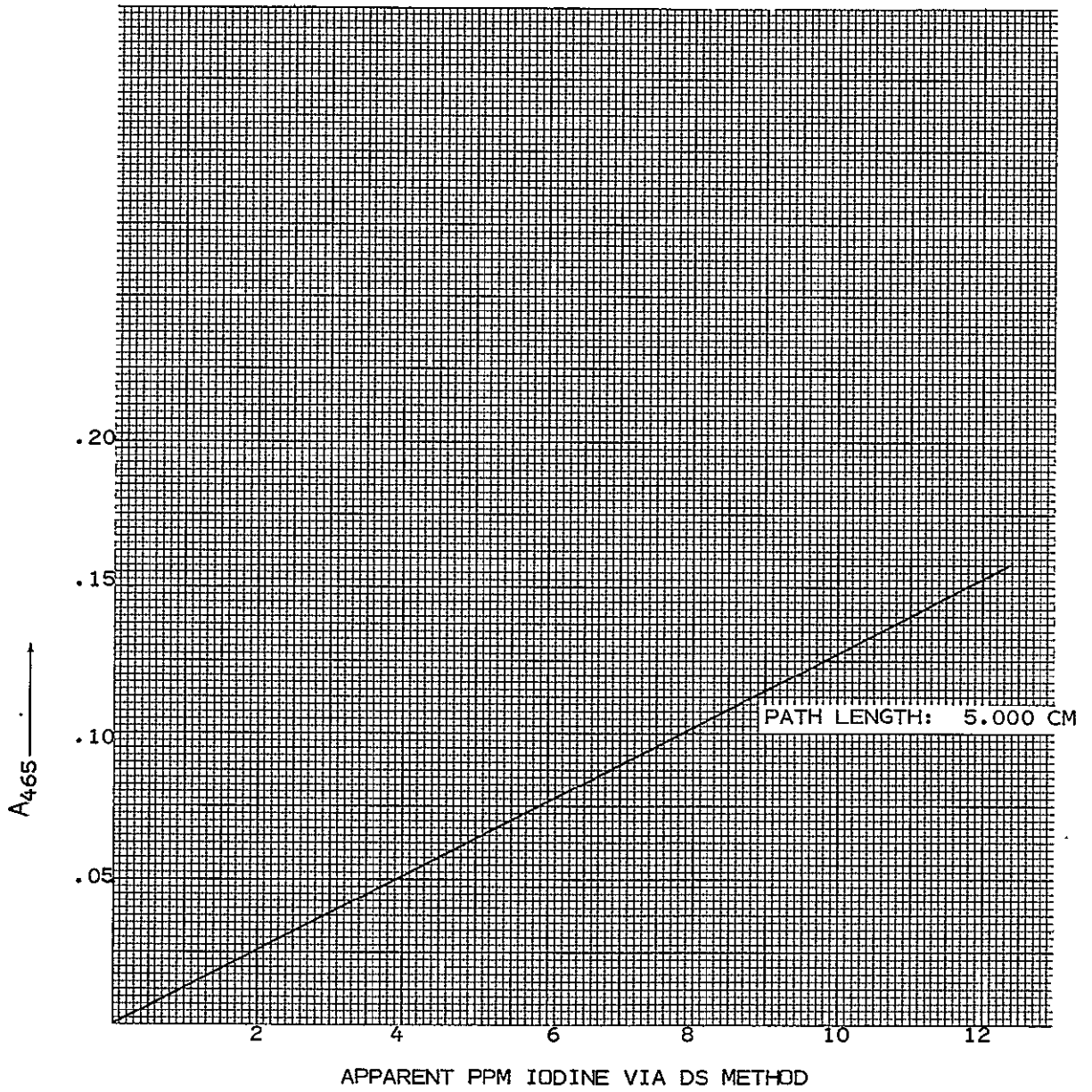


Figure 2. Standard Curve, Direct Spectrophotometric (DS) Method of Determination of Aqueous Iodine

these data, the LCV method is about *75 times more sensitive* than the DS method over the concentration range tested.

For the solutions of unknown concentration within the tested range of 1 to 8 ppm iodine, the apparent concentrations of iodine obtained by both the LCV method and the DS method are plotted one against the other in FIGURE 3. The long dashed line shown is that along which the plotted points *would* be situated if both methods yielded the same values for apparent ppm. As can be seen, the DS method appears to yield data that is consistently about 0.65 ppm greater than that yielded by the LCV method over this range. The solid line connecting the plotted points should intuitively intersect the origin (short dashed line) so apparently the relationship between the data obtained by these two methods is not linear over the range 0 to 8 ppm.

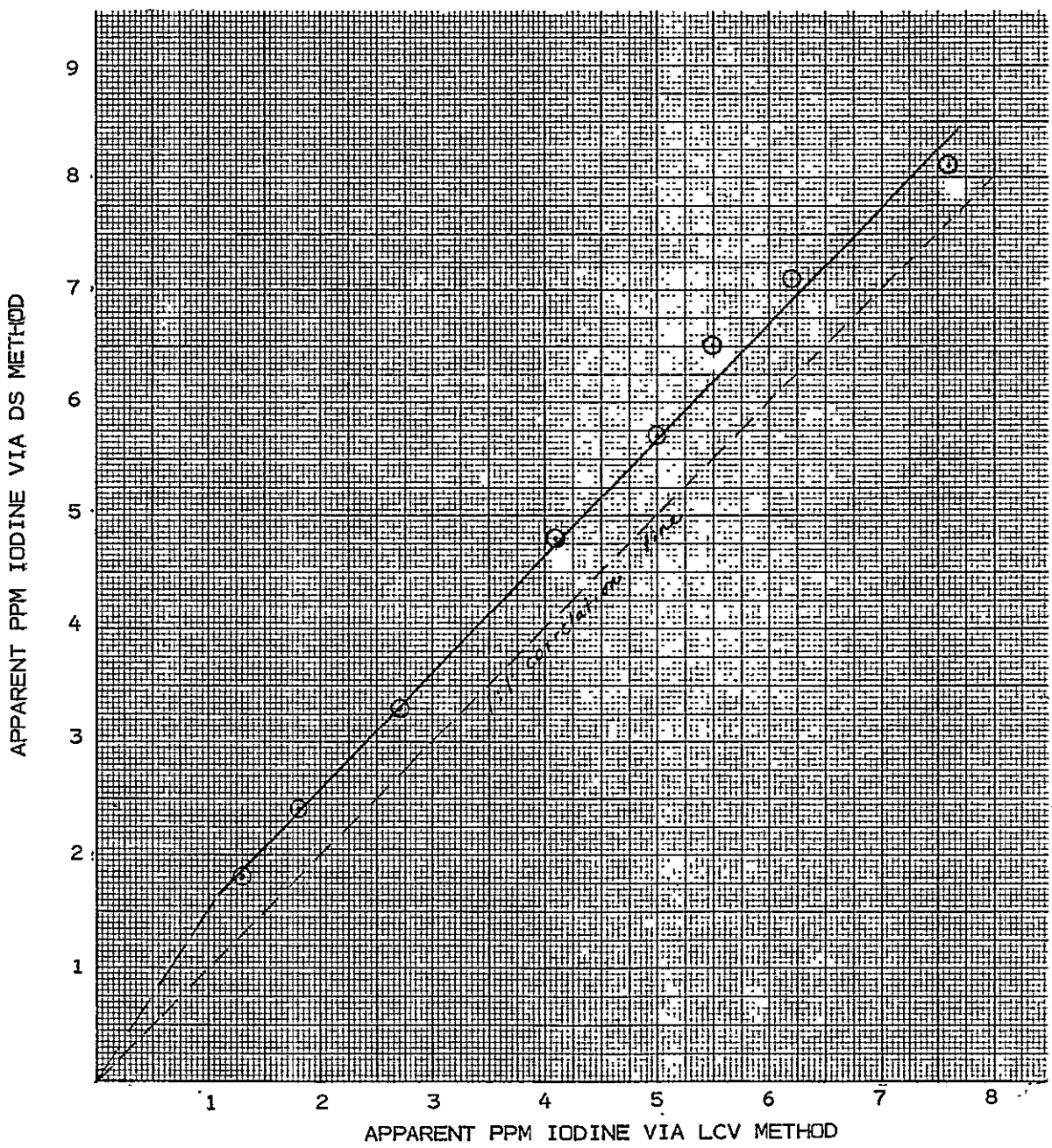


Figure 3. Plot of Apparent ppm of Aqueous Iodine Determined via DS Method Versus the Same Obtained with the LCV Method

APPENDIX D

SHUTTLE PROTOTYPE AUTOMATED MONITORING/CONTROLLER SYSTEM

PRELIMINARY PRIME ITEM DEVELOPMENT SPECIFICATION

1.0 SCOPE

1.1 General

This specification establishes the performance, design, development, and test requirements for the Automated Iodine Monitoring/Controller (AIMS) System hereinafter referred to as the System).

2.0 APPLICABLE DOCUMENTS

2.1 Government Documents

The following documents of the issue in effect on the date of invitation for bid or request for proposal, form a part of this specification to the extent specified herein:

Specifications:	
Federal Military Others	To be determined
Standards	
Drawings	
Other Publications	

2.2 Non-Government Documents

The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

Specifications Standards Drawings Other Publications	To be determined

3.0 REQUIREMENTS

3.1 System Definition

This specification describes one type of water bactericidal system (Iodine Monitoring/Controller System) for use in the Space Shuttle in conjunction with the Shuttle water system (Figure 1). The system includes three individual items:

- Iodine Addition System (For test setup)
- Monitor Assembly
- Iodine Concentrate Tank (For test setup)

Functionally, the system is composed of two subsystems:

- Iodine Monitoring Subsystem, and
- Iodine Controller Subsystem

3.1.1 Missions

The System shall be capable of 720 successful continuous operating hours (minimum).

3.1.2 System Diagrams

Figure 2 is the System Electronic Block Diagram, and Figure 3 is the System Mechanical Block Diagram.

3.1.3 Interface Definition

The System shall meet the following interface requirements.

3.1.3.1 Water Source

The System shall accommodate a supply of water at the rates of 8.8×10^{-4} kg/s (7 pounds/hr, nominal), and 1.5×10^{-3} kg/s (12 pounds/hr, maximum).

3.1.3.2 Water Quality

The System shall be compatible with essentially distilled water with a minimum I_2 demand (0.1 ppm of iodine).

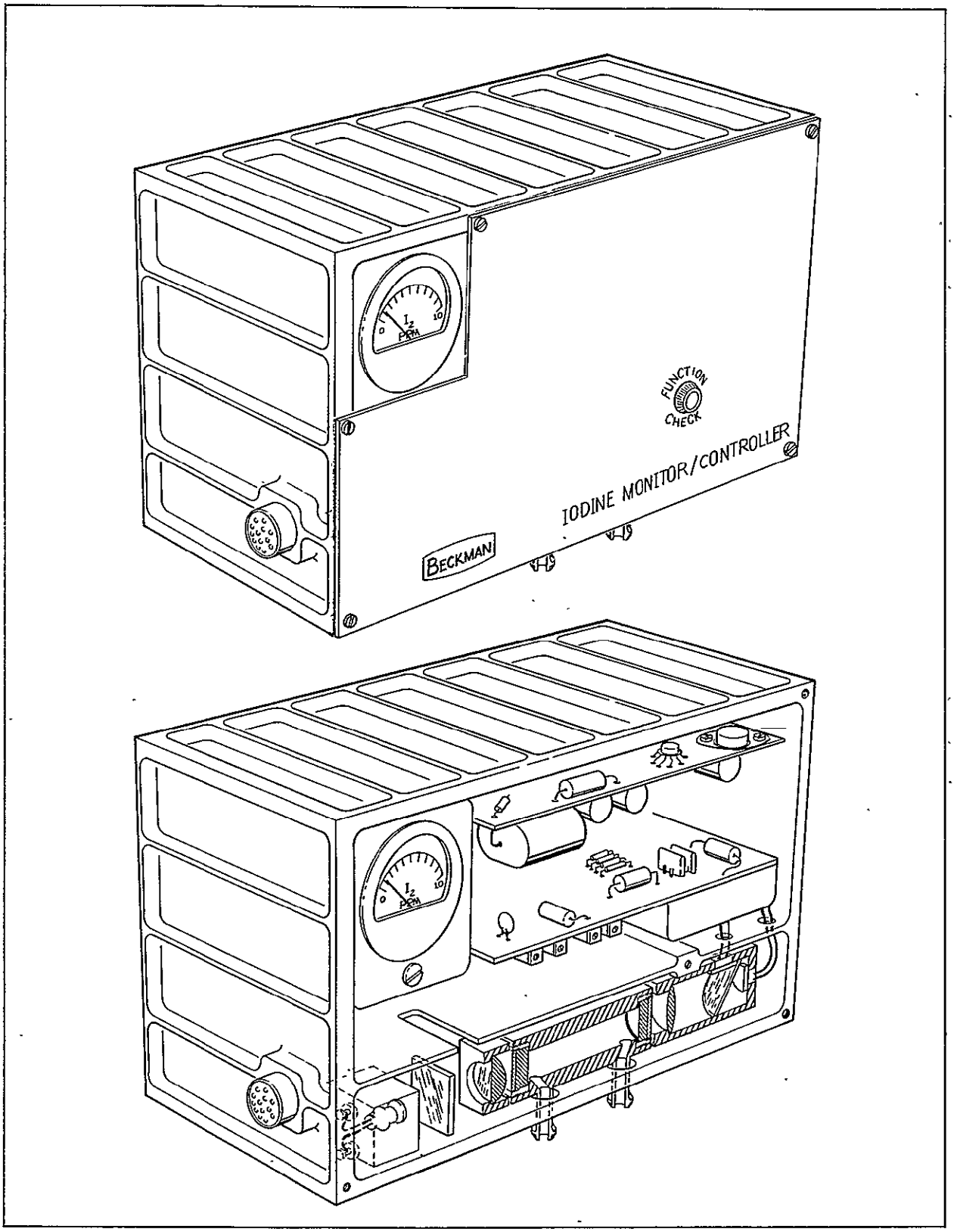


Figure 1. Iodine Monitor/Controller (Preliminary Flight Prototype Status)
A: With Cover; B: Cover Removed

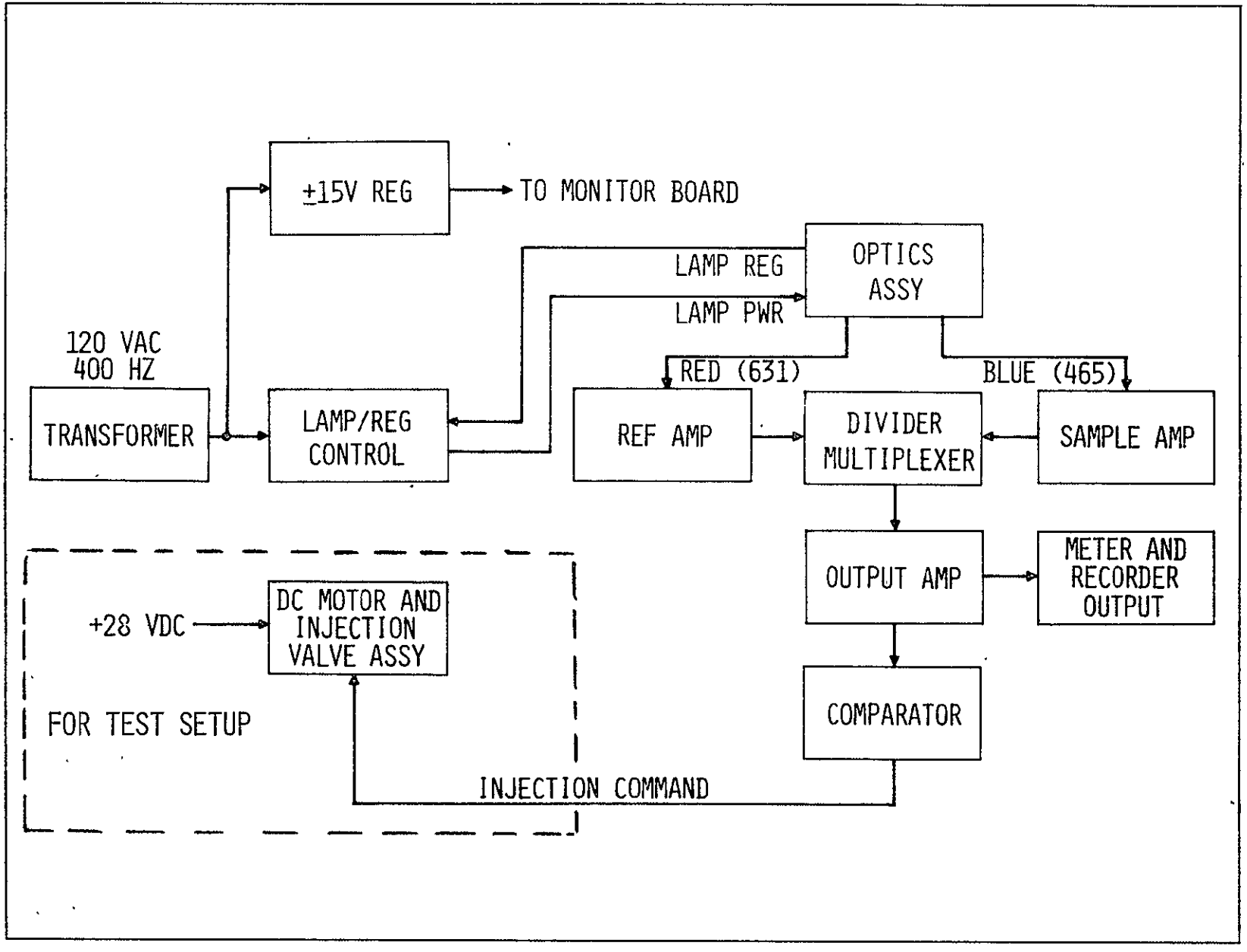


Figure 2. Electronic Block Diagram

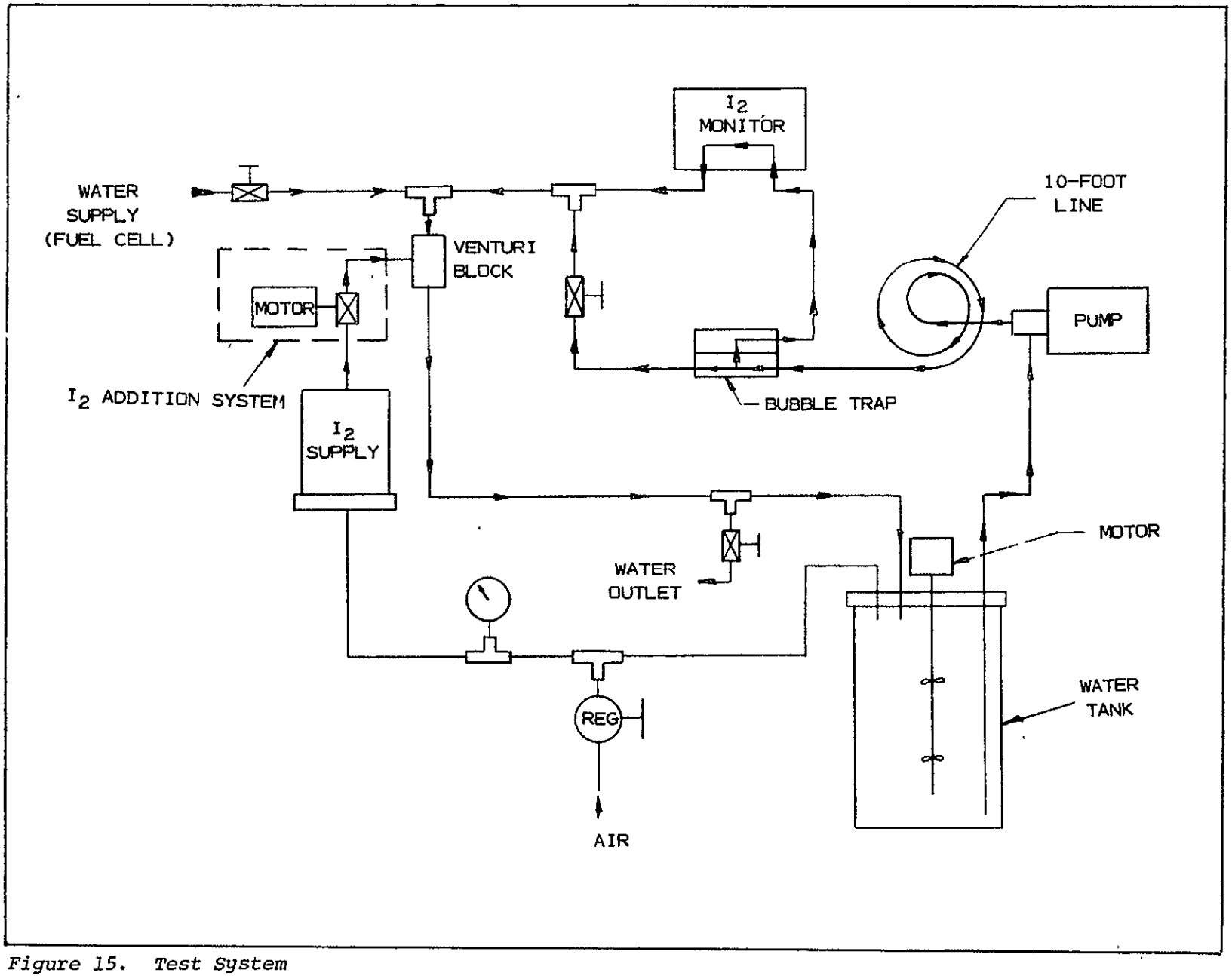


Figure 15. Test System

3.1.3.3 Water Input and Output

The water input and output interfaces shall mate with 6.35 mm (1/4-inch) stainless-steel swagelock fittings.

3.1.3.4 Electrical Power

The System electrical interface shall accommodate 120 Vac, 400 Hz, and 28 Vdc power.

3.1.4 Government-Furnished Equipment

The following equipment to be incorporated into the System design shall be furnished by the Government:

Name	Part No.
• Iodine Storage Container, Skylab	To be determined

3.1.5 Operational and Organizational Concepts

To be determined.

3.2 System Specifications

The Iodine Monitoring/Controller Systems shall meet the following specifications:

a. Iodine Level - The System shall control iodine level between 2 and 6 ppm. The System shall hold the iodine level to within ±1 ppm of desired level.

b. Iodine Level Display - The System shall display the iodine level on a 38-mm (1-1/2 inch) analog meter. The analog meter shall have a range of zero to 10 ppm.

c. Iodine Controller Signal - The Iodine Monitor shall provide a zero- to five-Vdc signal to the Iodine Controller.

d. System Output - The System shall provide an output signal of 100 mV full scale for a recorder.

e. Power Source - The System shall operate from 120 Vac, 400 Hz, and 28 Vdc power.

f. Self Check - System design shall include a functional check device which shall indicate normal system operation.

g. Weight and Volume - Emphasis shall be placed on minimizing System volume and mass. A design goal shall be to achieve a volume of 1443 cm^3 (88 $in.^3$) and a weight of 2 kg (4.5 lb).

h. Optical System Alignment - The Optical System subsystems (optical bench and electronics) shall be positively located, aligned, and locked in place to ensure reliable functioning under varying g forces and in any orientation.

i. Transport and Storage - System design shall enable transport, storage, and handling by a common carrier complying with best-commercial practice.

j. Health and Safety Criteria - Iodine in high concentrations is unpalatable and corrosive. All containers of concentrated iodine, either a part of the System or located in the contractor's facility, launch facility, or on board the Shuttle or Skylab, shall be legibly marked with appropriate caution or warning notices.

3.3 Operational Modes

a. Monitor - Optics and electronics shall continually monitor iodine level for meter readout or recording.

b. Iodine Addition Enable - The System shall compare the iodine level to a predetermined desired iodine level. Iodine level in excess of desired level shall maintain the System in the monitor mode. An iodine level below the desired level shall induce injection of iodine.

c. Iodine Injection - The System shall receive iodine when added to the water supply in response to a low iodine level indication by the Iodine Addition Enable operation mode.

3.4 Minimum Life Expectancy

Minimum System life expectancy shall be equal to the total shelf life, from the time of Government receipt of the item to launch, and the mission duration of 720 continuous operating hours (Paragraph 3.1.1).

3.5 Reliability

The System shall have no single failure points that result in a constant dump sequence.

3.6 Maintainability

To be determined.

3.7 Availability

The System shall be fully available at the start of the mission. All interface connections shall be complete, fluids added, and functional checks performed.

3.8 Environmental Conditions

The system shall meet the following environmental conditions:

- To be determined.

3.9 Design and Construction

Using flight hardware design concepts and choosing appropriate materials, the design shall minimize the volume and weight of the System without reducing the operational characteristics, reliability, or ruggedness of the System. The design shall specify flight-rated components. However, commercial standard parts may be employed where form, fit, and function are not affected.

3.9.1 Iodine Monitoring Subsystem

The Iodine Monitoring Subsystem shall be based on the prototype system developed under NAS9-14298. The design of this portion of the system shall incorporate the following:

a. The optical components, provided with locating pins, shall be positively positioned and locked on an "optical bench" mounted on the base plate of the enclosure.

b. The electronics shall be mounted on printed circuit boards which also will be locked in place as a discrete system. The instrument power shall be in accordance with Paragraph 3.1.3.4.

c. A "Function Check" device shall be included. A selected filter-type design, which can be brought into the light path by turning a knob on the front panel, shall be used. Its effect shall be to cause the meter reading to increase by a known amount (e.g., 4 ppm) and thus will indicate that the Monitor is operating properly.

3.9.2 Iodine Controller Subsystem

The design of this subsystem shall be based on the concept employed in the iodine-addition portion of the prototype system. This subsystem shall incorporate the following:

a. The selectable control range for iodine shall be in accordance with Paragraph 3.2a. Iodine shall be held within the limits specified in Paragraph 3.2a.

b. Technology developed during the Skylab Program and associated with the Skylab Iodine Addition System shall be considered in the design of the Iodine Controller Subsystem. In particular, a reservoir for containing the stock iodine solution along with proven materials shall be considered for incorporation in the design.

3.9.3 Materials and Processes

To be determined.

3.9.4 Electromagnetic Radiation

To be determined.

3.9.5 Nameplates and Product Marking

To be determined.

3.9.6 Workmanship

To be determined.

3.9.7 Interchangeability

Items identified with the same part number shall be interchangeable without having to change, alter, or select the parts to fit.

3.9.8 Safety

The System shall be capable of indicating an excess or deficit of iodine.

3.9.9 Human Performance/Human Engineering

To be determined.

3.10 Documentation

The System shall be identified by detail fabrication drawings, photographic coverage of subassemblies and assemblies, and a System Test Plan and Test Report.

3.11 Logistics

To be determined.

3.11.1 Maintenance

3.11.1.1 Zero Check

The following ground-based checkout shall be performed between missions:

NOTE

Do not turn Monitor off.

a. Close valves at inlet and outlet to Monitor.

b. Disconnect inlet and outlet lines from Monitor flow-through cell.

c. Allow iodine-free water to flow in and out of sample cell to flush cell thoroughly.

d. Note meter reading. It should be zero. If meter reading is off zero, remove four screws holding the sample cell in place. Carefully remove cell and look through all windows to see if air bubbles are present. Remove air bubbles by tilting and jarring the cell.

e. Carefully replace sample cell, making sure its O-ring gasket seats properly. Replace four screws.

f. Recheck zero.

g. If meter reads above zero, remove cell, remove screws holding one window in place, and remove the window.

h. Clean window using detergent, then thoroughly rinse. (The other window can be cleaned without removal.)

i. Replace window, then replace cell (make sure gasket seats properly). Refill cell with iodine-free water (eliminate bubbles as in step d., if necessary).

j. Recheck zero.

k. If zero deviation persists, it will be necessary to reset zero. This is done by removing the front cover of the Monitor, laying it down flat. The zero trimpot is the middle one of the three in the middle of the top circuit board. Carefully turn the zero trimpot adjustment screw slightly (CW or CCW, as required) to obtain a zero indication. The cover can be raised enough to see the meter during this adjustment. Temporarily replace the cover, using one or two screws, and observe the zero for about three minutes. Another small adjustment may be necessary.

NOTE

Do not attempt to check zero over a long time interval with a static sample--circulating water through the cell is required for long-term thermal stability.

l. Complete replacement of front cover.

m. Push "Function Check," Meter should read approximately 5 ppm I_2.

n. Reconnect Monitor to input line only.

o. Connect a temporary drain line to the output of the sample cell.

p. Open input line and allow enough water to flow through the cell to remove all bubbles. Turn input off.

q. Remove temporary output line and reconnect normal output line.

3.11.1.2 Replacement of Lamp

The following steps describe the procedure for changing the source in the Monitor:

a. Turn Monitor off.

b. Remove front cover

c. Disconnect the Microdot cable from the Lamp Housing (Lamp Housing is on right) and also pull lamp terminals out of the cable sockets.

d. Remove screws holding Optical Bench to case.

e. Tilt Optical Bench out of housing by lifting right end.

f. Loosen the three cleats holding the lamp by rotating their screws until cleat flats clear the lamp flange.

g. Pull lamp out of Lamp Housing.

h. Insert new lamp--it will fit only one way on the two locating pins.

i. Tighten the cleat screws so that the cams strike the lamp flange, then turn each screw one more 1/2 turn so that cleat rotates up and over the lamp flange.

j. Reconnect both the lamp terminals and the Microdot connectors.

k. Replace Optical Bench.

l. Replace front cover.

m. Turn Monitor on.

n. After three hours warmup, check zero (Paragraph 3.11.1.1) above.

APPENDIX E

SHUTTLE PROTOTYPE AUTOMATED MONITORING/CONTROLLER SYSTEM

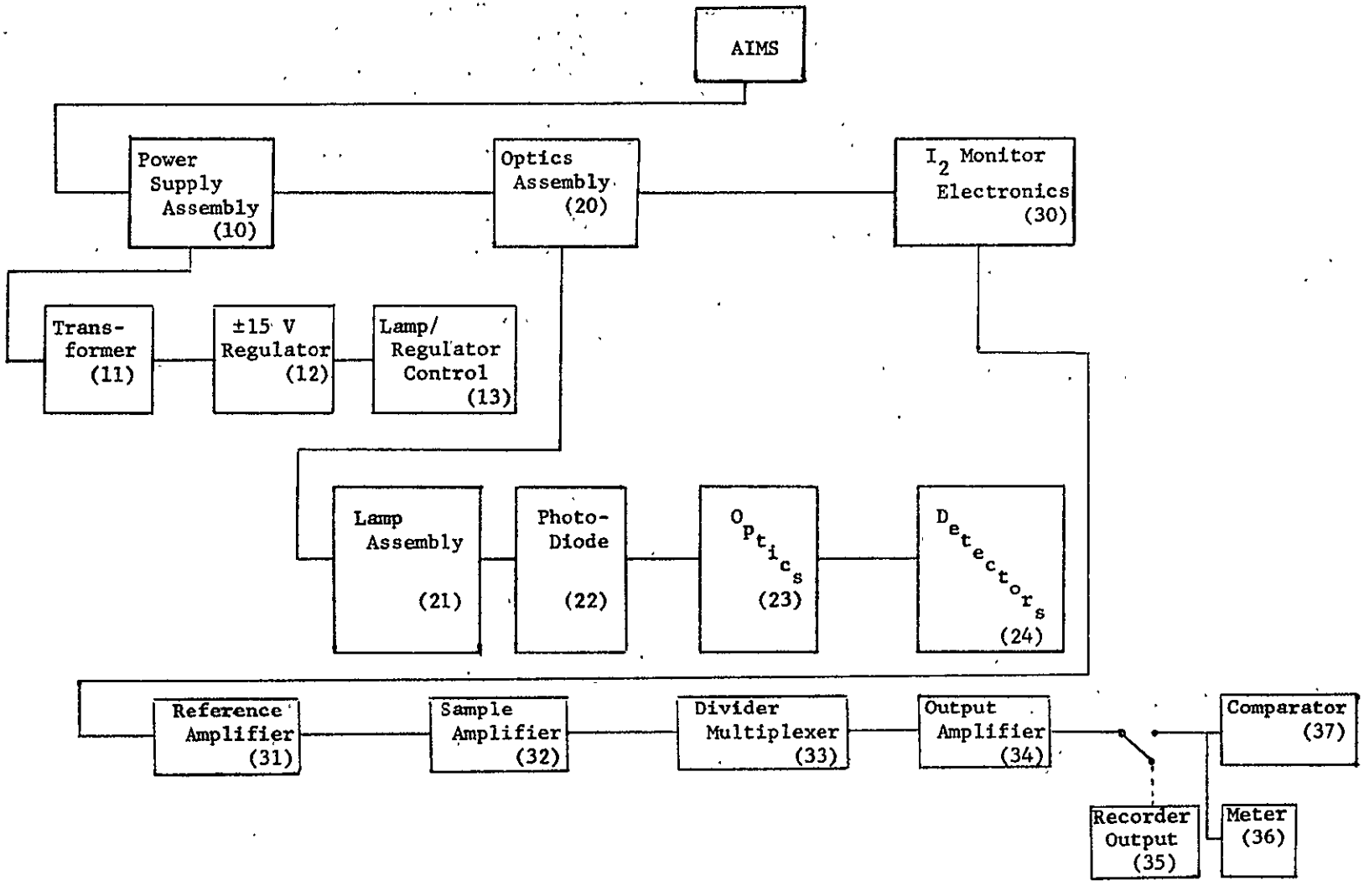
PRELIMINARY FAILURE MODES AND EFFECTS ANALYSIS (FMEA)

This document contains the FMEA for the developmental Automated Iodine Monitoring/Controller System (AIMS). FIGURE 1 is a reliability logic diagram which shows the system is basically a single line without redundancy provisions.

CONCLUSIONS

This FMEA has been conducted on a rather high level due to the preliminary nature of the design. Certain conclusions can be drawn at this stage:

- The mission effect of very-high or very-low meter readings must be defined before design effort is expended to control failures affecting the reading. Consideration should be given to designing a more comprehensive self-check feature.
- Many of the failure modes defined in this report are the result of problems unique to the prototype and test setup. To control these failure modes, it is recommended that subsequent procurements establish criteria for elimination of single failure points and that FMEA of the system be expanded down to the part level in cases where the effect is catastrophic. This will enable more realistic risk assessment.



Notes: 1. Assembly 35 is not operational during flight.
2. Assembly 36 is for indication only during flight.

Figure 1. Reliability Logic Diagram (AIMS)

FAILURE MODES AND EFFECT ANALOG

COMPONENT	FAILURE MODE	FAILURE EFFECT	REMARKS
Power Supply Transformer	No output to ±15V regulator.	I_2 content of water system falls below acceptable level.	Meter reads zero.
	No output to lamp/ regulator control.	Indeterminate.	Blue and red output equal zero but electronics does not recognize 0÷0.
±15V Regulator	Loss of both +15V and -15V power.	I_2 content of water system falls below acceptable level.	Meter reads zero.
	Loss of -15V power.	Meter reads maximum. System will not inject I_2.	
	Loss of +15V power	Meter reads zero. System will not inject I_2.	
	±15V output out of tolerance.	Incorrect meter reading. System may or may not inject I_2.	
Lamp/Regulator Control	Loss of output to lamp.	Indeterminate.	Output of both blue and red channels goes to zero but divider multiplexer does not recognize 0÷0 input.
	Low lamp voltage.	No effect.	
	High lamp voltage.	Decreased lamp life. Possible temperature-related errors.	
Optical Assembly Lamp Assembly	Loss of output.	Indeterminate.	Output of both blue and red channels goes to zero but divider multiplexer does not recognize 0÷0 input.

COMPONENT	FAILURE MODE	FAILURE EFFECT	REMARKS
Photodiode	Loss of output	Decreased lamp life (Lamp/ Regulator drives to maximum output). Possible temperature related errors.	
Optics and Detectors	Loss of red (631nm) output.	I_2 content of water system rises above acceptable level.	
	Loss of blue (465nm) output.	I_2 content of water system falls below acceptable level.	
	Red output increases with respect to blue.	I_2 content of water system falls below acceptable level.	
	Blue output increases with respect to red.	I_2 content of water system rises above acceptable level.	
Iodine Monitor Electronics	Fails to provide I_2 inject command.	I_2 content of water system falls below acceptable level.	
	Constant I_2 inject command.	I_2 content of water system rises above acceptable level.	
	Loss of recorder output or incorrect recorder output.	No effect. Output is used for ground checkout only.	
	Loss of meter output.	Meter indicates zero.	
	Incorrect meter output.	Meter may read high or low.	

APPENDIX F

SHUTTLE PROTOTYPE AUTOMATED MONITORING/CONTROLLER SYSTEM

PRELIMINARY OPERATING AND MAINTENANCE INSTRUCTIONS

1.0 IODINE MONITOR DESCRIPTION

The Monitor houses the optical and electronic systems (FIGURES 1-1 and 1-2). The optical system comprises, in effect, an "optical bench" with the following elements in series:

Lamp Housing. The lamp housing contains a 4-volt tungsten lamp as a source and a filtered (465 nm) photodiode to monitor the light output. A lens on the front of the housing collimates the light into the sample cell entrance window. A Microdot connector on the housing makes internal connections to the light monitoring photodiode. The lamp leads plug directly into jacks on the 4-V supply leads. These leads connect to the PC Board below.

Sample Cell. This is a 25-mm-long, flow-through, anodized aluminum cell with two windows and two 6.4 mm (1/4-inch) water connections. The water inlet is in the end facing the lamp housing. An O-ring on the sample cell establishes a seal between the cell and the optical bench.

Detector Housing. A lens (facing the sample cell exit window) focuses the collimated beam into the housing, where a beam splitter reflects light onto one detector (through a 631-nm filter), and transmits light to a second detector (through a 465-nm filter).

A movable filter actuated by a pushbutton on the front of the monitor (Function Check) can be inserted between the sample cell and the lamp housing to simulate an iodine upscale change of approximately 5 ppm. It serves simply as an indicator of proper functioning.

The electronic system (FIGURE 1-3) lies below the optical bench. It receives and processes the detector signals and performs several functions:

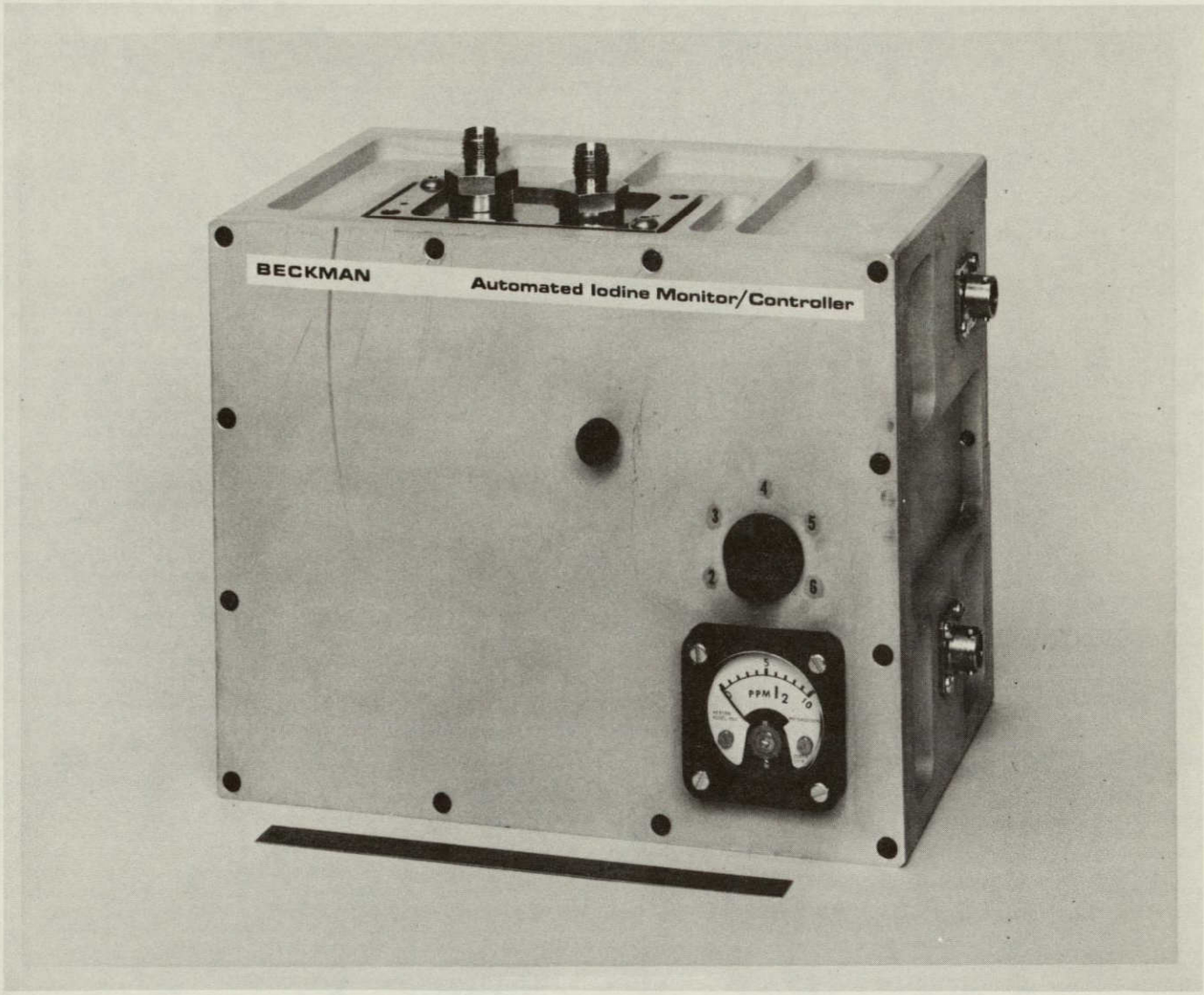


Figure 1-1. AIMS Monitor

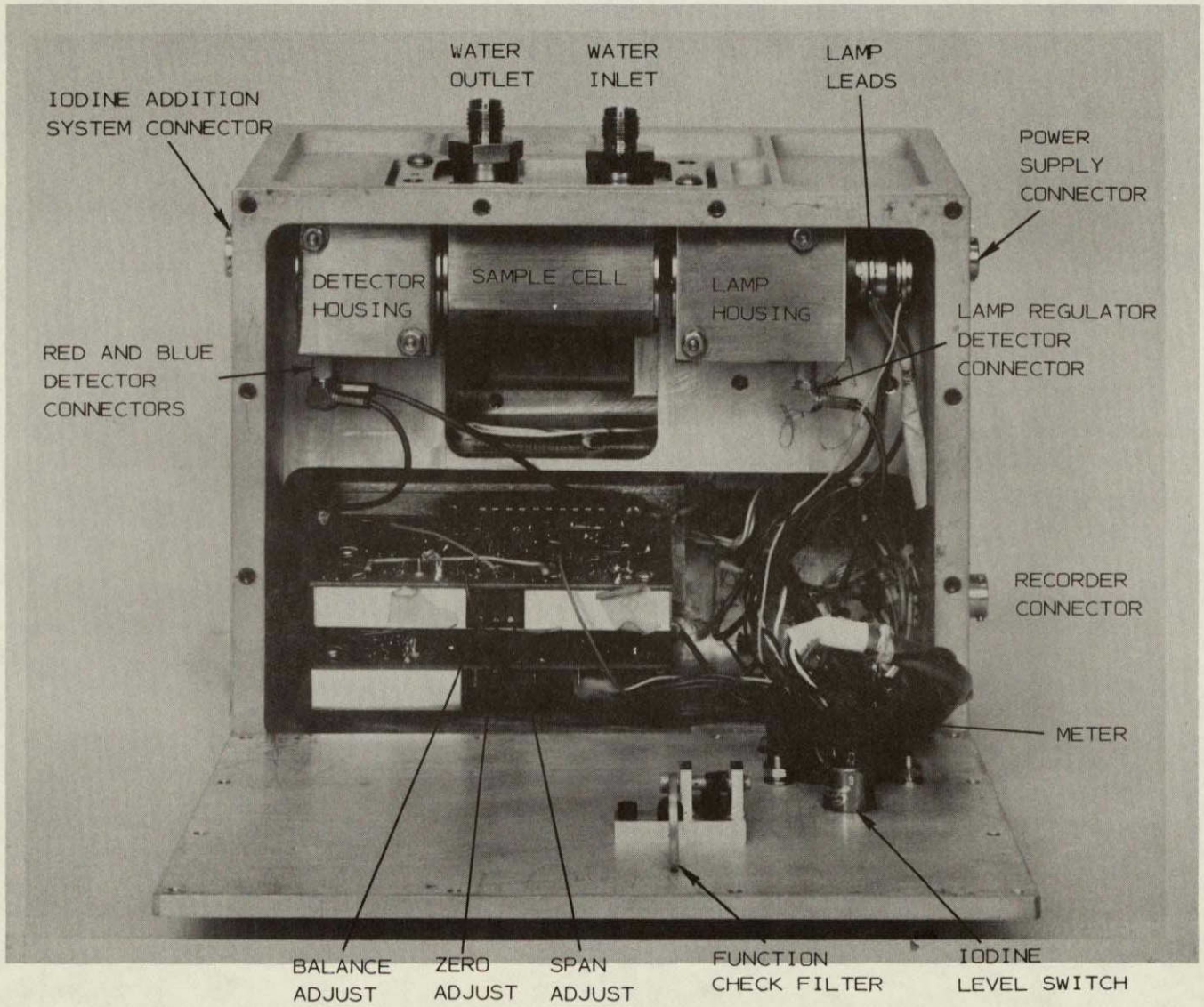


Figure 1-2. AIMS Monitor, Interior View

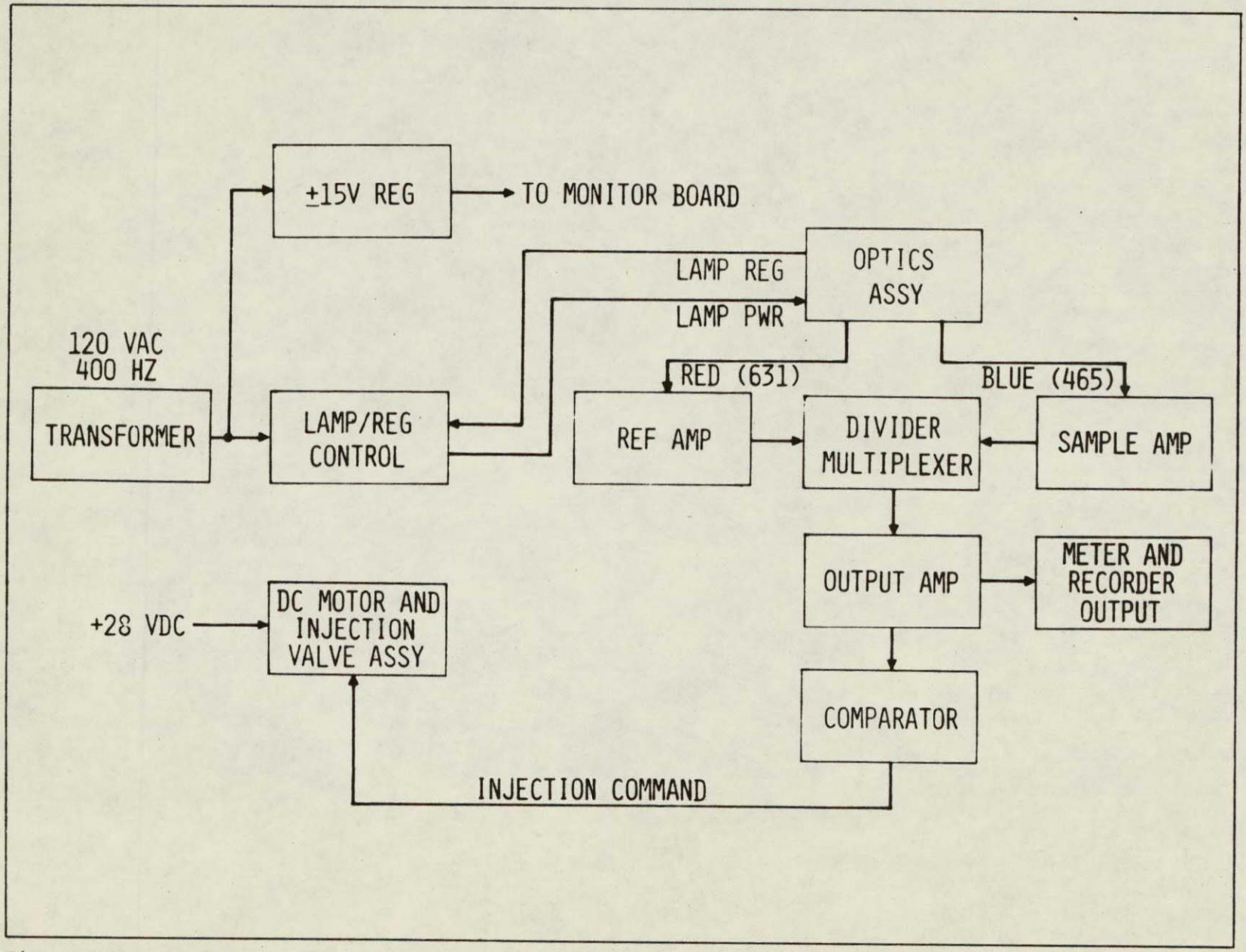


Figure 1-3. Electronic Block Diagram

- Controls the brightness of the source;
- Ratios the 631- and 465-nm signals;
- Presents the processed signal on the readout;
- Provides a signal to the Iodine Addition System.

The blue signal (465 nm) decreases with increasing aqueous iodine; the red signal (631 nm) remains constant. With no iodine in the water the ratio of the two signals is 1, represented on the readout by "zero ppm I_2". The ratio of these two signals varies, then, with changing concentrations of iodine.

1.1 Electrical Connections

The female connector on the power supply cables connects to the top connector on the double connector side of the Monitor. Attach the free ends, as marked, to a 110-Vac, 400-Hz power supply, and to a 16-Vdc supply as indicated by cable labels.

Connect one end of the black, blue, red, and orange cable to the single connector side of the Monitor (as indicated). (Later, the other end will be connected to the Iodine Addition System.)

1.2 Water Lines

See FIGURES 1-4, 1-5, and 1-6 for plumbing layout. Tubing may be 6.4 mm (1/4-inch) Teflon or stainless steel. A 3.05-m (10 ft) section of stainless steel is indicated in FIGURE 1-4 and shown in FIGURE 1-5. The pump is indicated in FIGURE 1-4, but is not visible in FIGURE 1-5 as it is behind the Monitor.

1.3 Bubble Trap

A simple bubble trap is used in this system because it is difficult to avoid all bubbles in a ground test system and they disturb the output signal. The trap is connected as shown in FIGURES 1-4 and 1-5. The trap is a plastic chamber divided into two parts by a fine mesh screen supported by a heavier screen. Water passes across the top part carrying any bubbles with it into the return water line. Part of the incoming stream passes through the screens

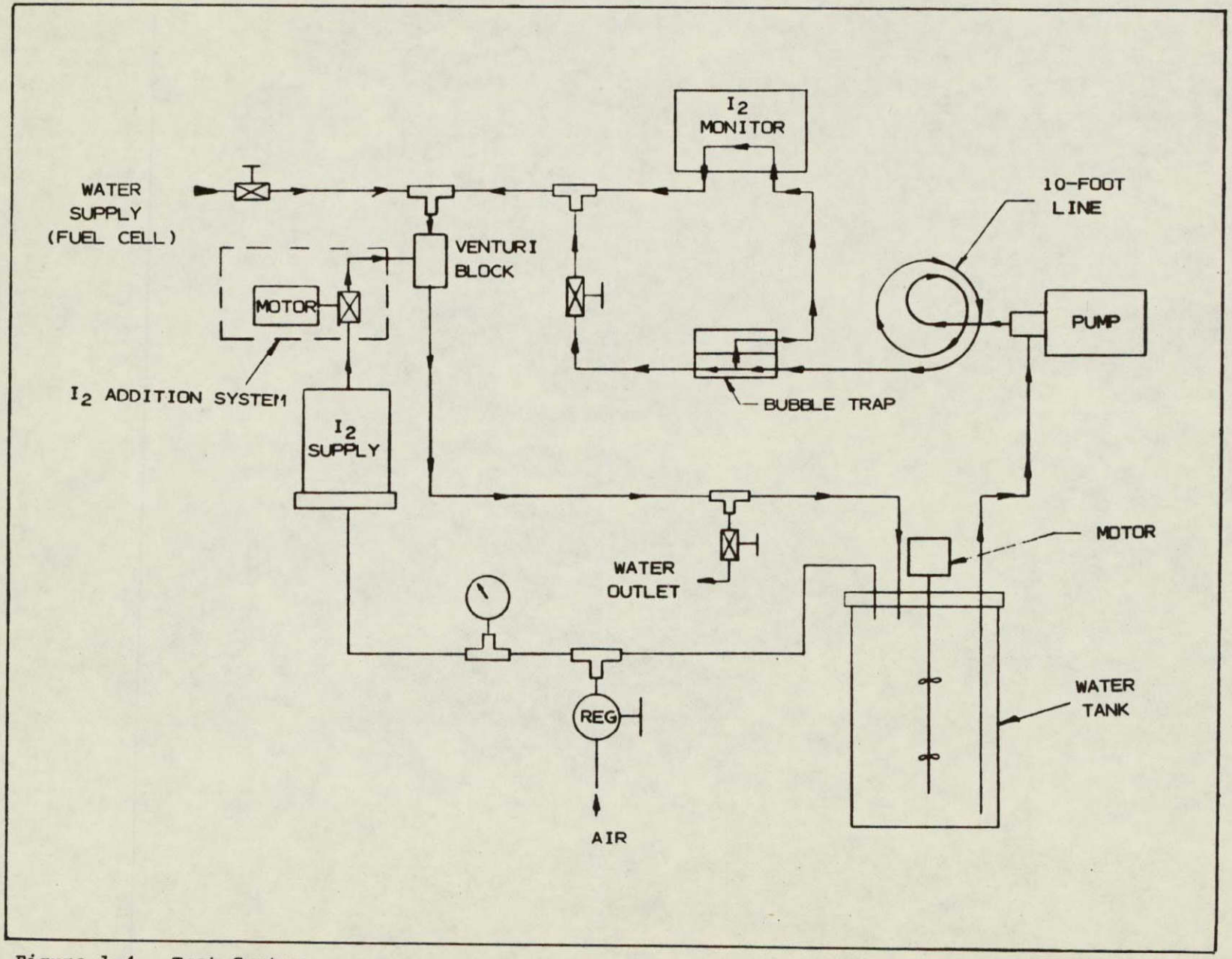


Figure 1-4. Test System

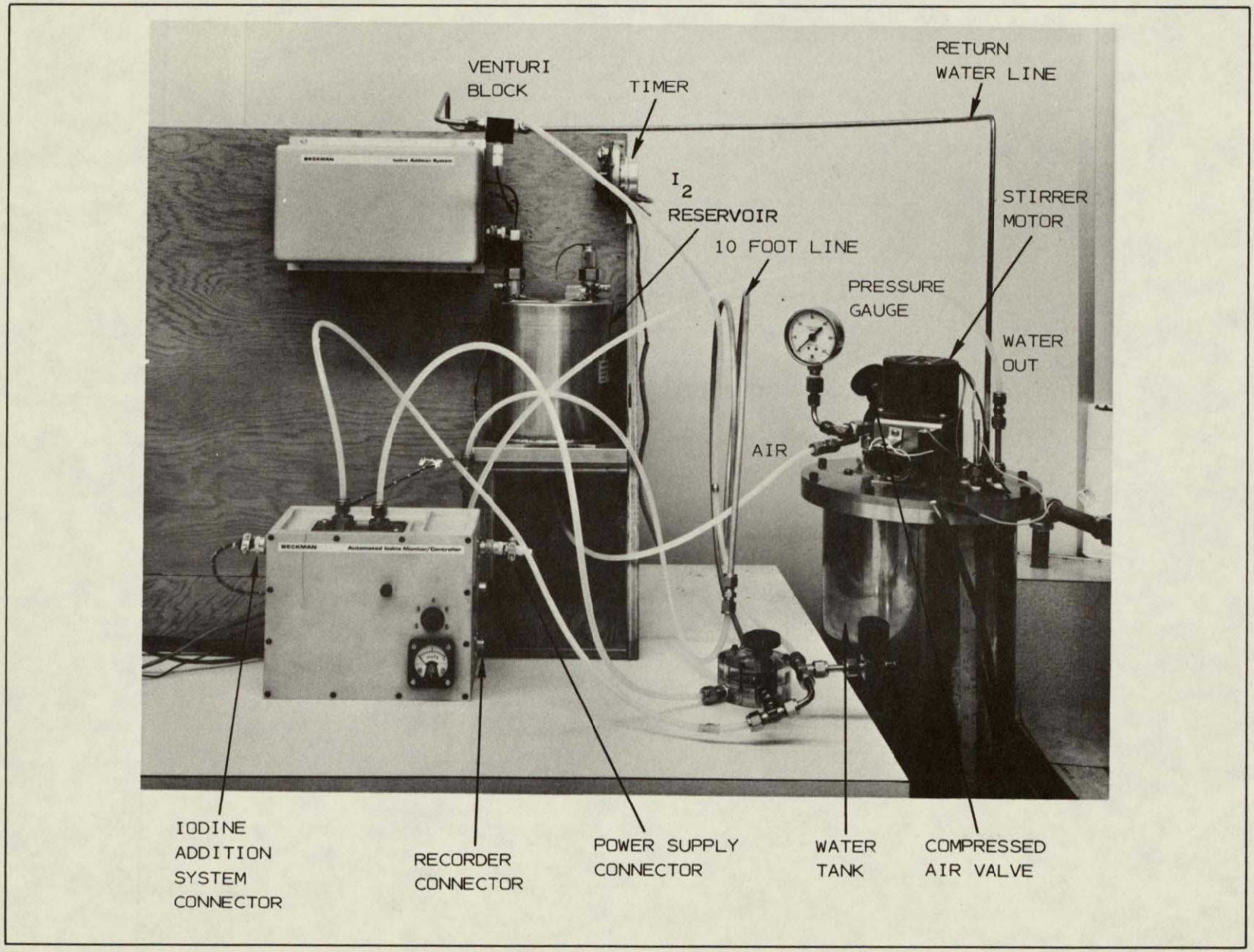


Figure 1-5. System Plumbing

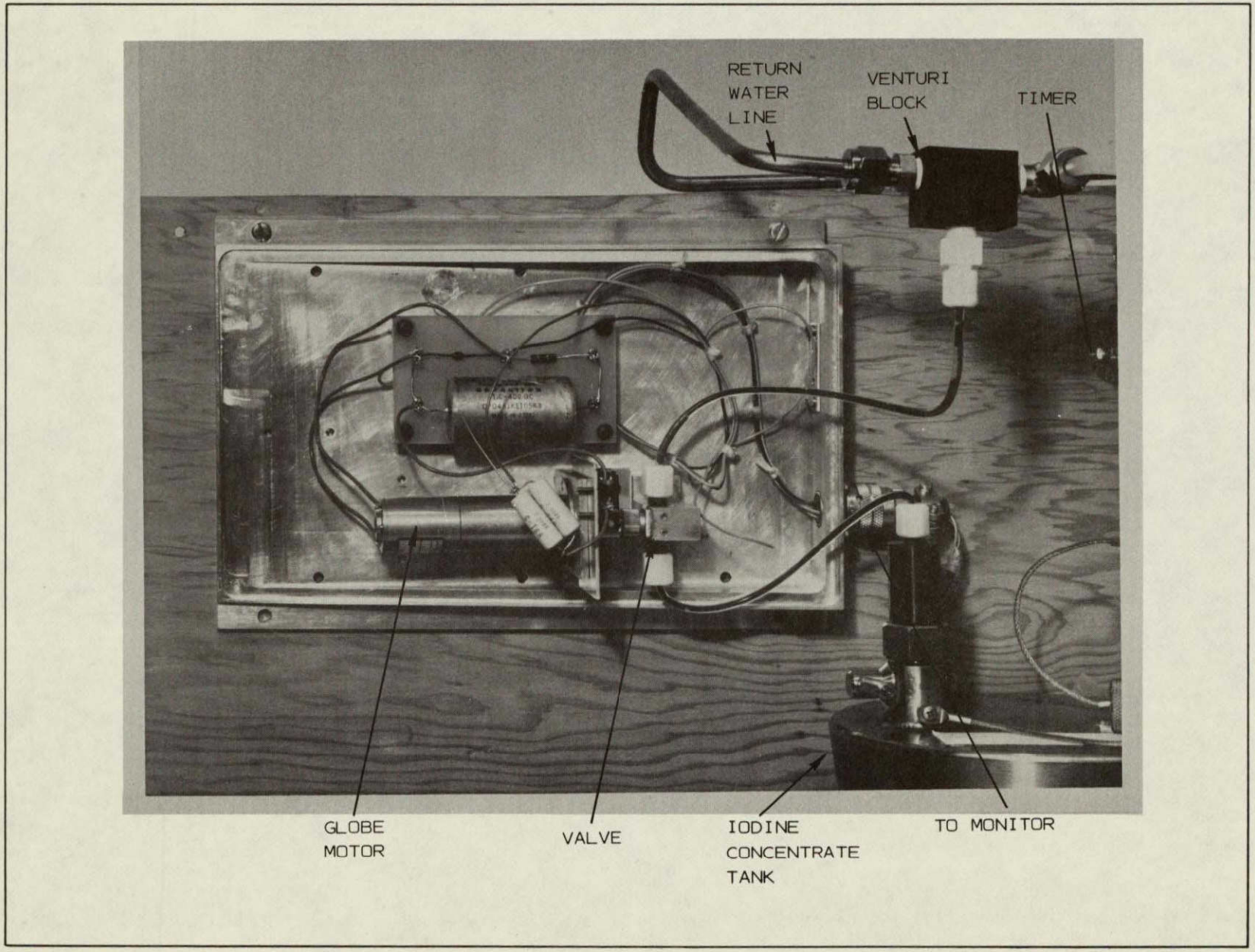


Figure 1-6. Iodine Addition System

and enters the flow-through sample cell in the Monitor. This water is bubble-free. A valve in the output side of the water/bubbler line controls the flow rate through the screens.

1.4 System Pressure Lines

Compressed air is used to vary the pressure for the pressure tests on the Monitor. Air at regulated pressures from 0 to 34-psig (0 to 234.4 kPa) is applied to the top of the water tank and also to the underside of the Iodine Supply Tank. It is applied at these points to maintain a pressure differential across the spring-loaded Iodine Supply Tank. Teflon tubing, 6.4 mm (1/4-inch), is used to connect the air supply to the plate in the bottom of the Iodine Tank.

1.5 Recorder Connection

The recorder cable (male) connects between the Monitor bottom connector (on the two-connector side) and a recorder. Recorder output is set to 100 mVdc, full scale.

1.6 Startup

The inlet and outlet tubes of the sample cell have been connected to the water tank. In order to check the Monitor's zero, it will be necessary to disconnect these water lines from the water tank and place the ends in a large beaker or flask (3ℓ, e.g.) of distilled or deionized water.

Turn the Monitor on. This will be done by turning on the 110-Vac, 400-Hz power supply as the Monitor does not have an on/off switch.

1.6.1 Filling Sample Cell and Bubble Trap

Start pump (for water circulation). Make certain that both the bubble trap and the sample cell are bubble-free. The bubble trap should be checked first. It is important that there be no bubbles in the lower section--the section that provides bubble-free water to the sample cell. Bubbles here can be eliminated by tilting and tapping the bubble trap. Bubbles in the upper section will pass on out, if the valve is opened slightly. Varying the pump speed will facilitate bubble removal. Once the start-up bubbles are removed from the lower section of the trap, no more should appear there during normal operation.

Having eliminated bubbles from the trap, it is next essential to make sure they are not present in the sample cell where they can degrade the signal-to-noise ratio and also cause offsets in the readout.

Remove four screws and carefully remove the sample cell for visual inspection. Keep the pump on and remove any bubbles by tilting, shaking, and tapping the cell. Replace the cell, making certain the O-ring gasket seats properly.

1.6.2 Checking Zero Stability (Plain Water Only)

When the monitor is first turned on there will be an appreciable zero offset in the upscale direction. This offset will slowly decrease over a period of several hours as the system warms up. It is desirable to monitor this drift on a recorder. When a stable reading prevails, note the zero level. It may be necessary to reset the zero. If so, follow the instructions under "Zero Check", Paragraph 4.3, starting with step d.

1.6.3 Function Check

After a stable, accurate zero is obtained, check span by depressing the FUNCTION CHECK button on the front of the Monitor. This action inserts a filter into the colorimeter light path, thus simulating a color change equivalent to 5 ppm I_2, approximately. When FUNCTION CHECK is operated, the meter should read 5 ppm I_2 when the sample cell contains plain water, and it should "add" 5 ppm to the reading of an aqueous iodine solution.

NOTE

In general, the function check will not affect the automatic Iodine Addition System, except under one unique condition. If the function check is performed immediately before the Monitor output signal would have initiated an iodine addition event, then the apparent addition of 5 ppm I_2 (equivalent) will, of course, prevent the addition of iodine to the water supply. Since the Monitor interrogates the iodine status of the water supply once every ten minutes, there would only be a ten-minute delay in making the iodine addition.

1.6.4 Iodine Level Control

The Iodine Level Control is identified by the five-position switch knob located above the meter on the front of the Monitor. When the Monitor is interfaced with the Iodine Addition System this switch can be set to control the iodine level in the water supply at 2, 3, 4, 5, or 6 ppm I_2.

2.0 IODINE ADDITION SYSTEM DESCRIPTION

The Iodine Addition System uses a modified Hamilton Microvalve to permit iodine to flow from the Iodine Concentrate Tank (at 5 psig, or 34 kPa) to the venturi section of the water supply return line. This two-way valve is rotated by a small Globe motor. When the iodine level falls below a preset value, the Monitor sends an ON signal to a microswitch in series with the Monitor and the valve motor. The microswitch is closed for a short period once every ten minutes by a cam on a timer (part of the test setup). The valve motor has a cam that overrides the timer cam, thus ensuring that the motor will stay on for a complete revolution and that the valve will stop in the closed position. The notch in the cam has been adjusted in the present system so that the valve will undergo two complete revolutions. This provides enough iodine (200 $\mu\ell$ at 30,000 ppm) to make a small change in the iodine level in the 39-ℓ tank used in the test setup. If the iodine level in the water system requires no additional iodine, then the addition system remains inactive.

2.1 Iodine Reservoir Interface

Mount the Iodine Reservoir (also known as the Iodine Concentrate Tank) as shown in FIGURE 1-4. A Teflon tube connects one of the two valves on the tank to one end of the Hamilton valve. Since the iodine is under about 34 kPa (5 psig) pressure in the tank, the tank valve is not opened until the complete AIMS has been assembled and checked. A second length of Teflon tubing connects the other side of the Hamilton valve to the venturi block as shown in FIGURES 1-4 and 1-5.

If the AIMS is to be operated in a pressurized mode (air pressure), tubing is connected from the compressed air "Tee" (FIGURE 1-4) to the connection on the plate below the Iodine Reservoir. This will allow the Δp of the reservoir to be preserved under varying system pressures.

2.2 Water Supply Interface

The Iodine Addition System interfaces with the water supply at the venturi block site. The input water from the supply flows through the venturi and picks up concentrated iodine whenever the Addition System valve opens. This stream, carrying the iodine concentrate, is conveyed by 6.4-mm (1/4-inch) stainless-steel tubing to the water tank, where a motor-driven stirrer mixes the iodine with the tank water.

2.3 Electrical Interface

The Iodine Addition System motor is powered by a 16-Vdc supply. When iodine is required by the system, a relay in the Monitor closes. This brings power from the dc supply to a microswitch. Closure of the microswitch by a cam on a ten-minute timer transmits the power to the motor in the Iodine Addition System.

One end of a black, blue, red, and orange cable has already been connected to the Monitor (Paragraph 1.1). The other end is now connected to the connector on the Iodine Addition System.

The timer cord is plugged into a 110-Vac/60-Hz outlet when it is desired to activate the Addition System. (The 16-Vdc power supply leads for the Addition System motor have already been connected per instructions in Paragraph 1.1.) The pump is connected to a Variac (110 Vac/60 Hz) so that the voltage may be varied from 50 to 110 Vac to control the pump speed.

2.4 Pressure Interface

Compressed air is applied to the system through a regulator at 0 to 234.4 kPa (0 to 34 psig). The air is applied simultaneously to the space above the water in the water tank and to the bottom of the Iodine Concentrate Tank.

3.0 OPERATION

3.1 Start-up

At this point, the water lines are still connected to the flask of plain water. They should now be connected to the water tank. When operating in the normal

configuration, make certain that the bottom section of the bubble trap is bubble-free. Occasionally when going from the plain water flask to the Water Tank, the bubble trap may drain to the point that air gets into the bottom section. The bubble trap may be cleared of air bubbles by tilting and tapping it. It will then be necessary to recheck the sample cell to make sure it is bubble-free.

3.2 Check List

Before adding and controlling iodine to the system, check the following:

- All plumbing connections are tight;
- The circulation pump is ON;
- The power supply for the Monitor and the Addition System are ON;
- The timer is ON;
- The recorder, if used, is ON;
- The valve on the bubble trap is open one turn;
- The function check makes a 5-ppm meter response when it is activated.

3.3 Adding and Controlling Iodine

Set the iodine level switch to the desired I_2 level. Open the iodine reservoir valve.

About seven double injections will be required to raise the iodine level by 1 ppm in a 39-ℓ tank of water. Since injections are made at ten-minute intervals, this change will require one hour and ten minutes.

4.0 MAINTENANCE INSTRUCTIONS

4.1 Tools, Support, and Facilities Equipment

No special tools are required to service or set up the AIMS. The screws holding the sample cell and the front cover in place require a 3/32-inch Allen wrench for removal. A very small screwdriver (jeweler's) is required to adjust the zero trimpot. Ordinary wrenches are used to make plumbing connections.

A high input impedance digital multimeter should be used to make electrical measurements.

4.2 Maintenance Schedule

4.2.1 Lamp Replacement

For preventive maintenance, it is recommended that the lamp be replaced every six months.

4.2.2 Bubble Trap

The fine mesh screen in the bubble trap will gradually clog with continued use and finally, if not cleared, will cut off water circulation in the cell. Before this happens the screen will develop a darkened, less transparent color. Also, sudden 100% closure followed by 100% opening of the bypass valve will produce a signal offset when the screen is offering increased impedance to the passage of water.

The bubble trap can be easily removed and disassembled. The screen can be cleaned by scrubbing with a brush and vigorous washing. An excellent cleaning is obtained by using an ultrasonic cleaner.

4.3 Zero Check

Since AIMS-IV is fully automated, no maintenance procedure is specified for a one month's mission. Between missions the following check-out is recommended:

NOTE

Do not turn Monitor off.

a. Close valves at inlet and outlet to Monitor.

b. Disconnect inlet and outlet lines from Monitor flow-through cell.

c. Allow iodine-free water to flow in and out of sample cell to flush cell thoroughly.

d. Note meter reading. It should be zero. If meter reading is off zero, remove four screws holding the sample cell windows to see if air bubbles are present. Remove air bubbles by tilting and jarring the cell.

e. Carefully replace sample cell, making sure its O-ring gasket seats properly. Replace four screws.

f. Recheck zero.

g. If meter reads above zero, remove cell, remove screws holding one window in place, and remove the window.

h. Clean window using detergent, then thoroughly rinse. (The other window can be cleaned without removal.)

i. Replace window, then replace cell (make sure gasket seats properly). Refill cell with iodine-free water (eliminate bubbles as in sec d., if necessary).

j. Recheck zero.

k. If zero deviation persists, it will be necessary to reset zero. This is done by removing the front cover of the Monitor and laying it down flat. Because the Optical Bench is sensitive to ambient light, it must be covered with light-proof cloth before making the zero adjust. Alternatively, a cardboard cover with a hole opposite the trimpots can be readily improvised. The zero trimpot is the middle one of the three in the middle of the top circuit board (FIGURE 1-2). Carefully turn the zero trimpot adjustment screw a little (CW or CCW, as required) to obtain a zero indication. The cover can be raised enough to see the meter during this adjustment. Temporarily replace the cover, using one or two screws, and observe the zero for about three minutes. Another small adjustment may be necessary.

NOTE

Do not attempt to check zero over a long time interval with a static sample--circulating water through the cell is required for long-term thermal stability.

l. Complete replacement of front cover.

m. Push "Function Check". Meter should read approximately 5 ppm I_2.

n. Reconnect Monitor to input line only.

o. Connect a temporary drain line to the output of the sample cell.

p. Open input line and allow enough water to flow through the cell to remove all bubbles. Turn input flow off.

q. Remove temporary output line and reconnect normal output line.

4.4 Changing Lamp

The following steps describe the procedure for changing the source in the Monitor:

a. Turn Monitor off.

b. Remove front cover.

c. Disconnect the Microdot cable from the Lamp Housing (Lamp Housing is on right) and also pull lamp terminals out of the cable sockets.

d. Remove screws holding Optical Bench to case.

e. Tilt Optical Bench out of housing by lifting right end.

f. Loosen the three cleats holding the lamp by rotating their screws until cleat flats clear the lamp flange.

g. Pull lamp out of Lamp Housing.

h. Insert new lamp--it will fit only one way on the two locating pins.

i. Tighten the cleat screws so that the cams strike the lamp flange, then turn each screw one more 1/2 turn so that cleat rotates up and over the lamp flange.

j. Reconnect both the lamp terminals and the Microdot connectors.

k. Replace Optical Bench.

l. Replace front cover.

m. Turn Monitor on.

n. After three hours warmup, check zero (Paragraph 4.3 above).

4.5 Electronic Test Points

Inside the Monitor are five colored, nonterminated leads taped together at their free ends. Four different electronic parameters may be measured by attaching a high impedance voltmeter (0-10 Vdc) to each of four colored wires (black wire is common):

Red: The "red signal" only.

Blue: The "blue signal" only.

Green: The ratio signal (output signal to meter).

White: The lamp voltage.

When the water contains no iodine, the red and blue signals should be approximately equal and measure -8 Vdc. The output signal (green wire) should read approximately zero. The lamp voltage may read between 3.8 and 4.2 Vdc depending on its age and the ambient temperature at the time of measurement. The lamp voltage is nominally 4.0 Vdc. Its actual value depends, however, on the ambient temperature and may range from 3.8 to 4.2 Vdc. As the lamp ages, the voltage will slowly rise but will still fluctuate with temperature.