SECOND QUARTERLY PROGRESS REPORT

June - August, 1959

IN SITU TRACERS PROJECT

U. S. Atomic Energy Commission Office of Isotopes Development Isotope Applications Branch Oscar Bizzell, Chief

AEC Contract AT (11-1)-650

WILLIAM H. JOHNSTON LABORATORIES, INC. Lafayette, Indiana

IN SITU TRACERS II. Quarterly Progress Report

AEC AT (11-1)-650 #6

William H. Johnston Laboratories, Inc.

FOREWORD

This is the second quarterly report prepared under Contract AT (11-1)-650. It covers progress to August 31, 1959.

CONTENTS

Legal Notice					
For	Foreword				
Contents Summary I. Sub-Task A-1 Theoretical Studies A-1.1 Allowable Tracer Concentrations A-1.2 Statistics and Levels of Radiotracer	iv				
Sum	mary		v		
I.	Sub-Task A-1 Theoretical Studies				
	A-1.1 Allowable Tracer Concentrations		1		
	A-1. 2	Statistics and Levels of Radiotracer	3		
и.	Sub-Task A-2 Survey of Potential Applications				
	A-2.1	List of Conferees	6		
	A-2.2	Minutes of Meeting of July 17th	8		
	A-2.3	Suggested Uses of Isotopes in the Paint Industry	12		
ш.	Sub-Task B-1 Low Level Industrial Beta Counting Systems				
	B-1.1	Internal Gas Beta Counter	14		
	B-1.2	Internal Gas Flow Proportional Counter	15		
	B-1.3	Anti-Coincidence Counter	15		
	B-1.4	Shields	17		
	B-1.5	Beta Counter Electronics	20		
IV.	Sub-Task B-2 Industrial Process Gamma Counter				
	B-2.1	Gamma Counter Shield	25		
	B-2.2	Gamma Counter Tank	25		
v.	Sub-Tas	k B-3 Intermittent Low-Level Sampler	28		

SUMMARY

The purpose of this program is to summarize and evaluate the potential usefulness of in situ tracers, design and construct prototypes of large low-level soft beta counters for industrial application, especially of such isotopes as carbon-14 and tritium, and design and construct a prototype of a large low-level liquid scintillation detector for use with process gamma counting.

For the analysis of the problems and potentials of in situ tracers, we chose tracer levels of one per cent of the MPC levels of Part 20 for water effluents to unrestricted areas. Theoretical derivations were made and expressed graphically of the required tracer concentration as a function of instrumental background, efficiency of detector, required statistical reliability; and tracer nuclide. These graphs allow the selection of the necessary tracer concentration for a selected signal error as a function of the instrumental background, volume, and efficiency. The assumed maximum tracer levels are shown for a number of isotopes.

The evaluation of the potential of in situ tracers included a series of formal discussions with members of the National Paint, Varnish and Lacquer Association. Minutes of the July meeting in Buffalo are shown. A list is presented of suggested areas where radioisotopes can be used in the paint industry. This survey is continuing.

The work on the sub-task on the design and construction of low-level soft beta counters consisted of the selection of three types of counters, the construction of several counters; the design and construction of two shields and experiments with water shielding; and the design and construction of associated electronics including a completely transistorized section and the initial. design for a vacuum tube version.

The sub-task on design and construction of a large low-level industrial process gamma counter included the completion of the shield and the construction of the liquid scintillator tank.

Plans were started for an intermittent process stream sampler for cyclic low-level counting, especially of carbon-14 and tritium. Such a device will be useful for studies of air pollution, sewage control, and underground water movements.

I. SUB-TASK A-1 -- THEORETICAL STUDIES

The purpose of this sub-task was to summarize and evaluate the potential usefulness of in situ tracers and provided in-depth technical analysis of procedures and technique. Originally it was planned to develop one or two such examples in detail leading to plans for a plant demonstration. With further study, and as a result of discussion with the Office of Isotopes Development and with industrial engineers, scientists, and managers, it was decided to emphasize instead a more general approach, in which the results of this task could be more useful to industry as a whole and to those industries which are less widely involved now with isotope uses. The reasons for this shift in emphasis are:

- l. The industrial tracer applications which were originally considered for detailed planning on this project were in the petroleum industry. This industry is in the forefront of industrial isotope technology. It is felt that more direct benefit will accrue to the public at large from emphasis in this task on planning for general industrial use, rather than from one or two examples in detail in the petroleum or related industries.
- 2. The discussions with the industrial representatives clearly evidenced interest in general planning and the development of graphs and nomographs for the applications of many radiotracers and the instruments of measurement to a range of industrial process conditions and processes. It was felt that this emphasis on generalized planning would be more valuable than individual calculations only for one or two specific applications, and would stimulate and encourage a more broad industrial response and participation.

A-1.1 - Allowable Tracer. Concentrations

The levels of tracers for in situ tracers were chosen initially as one per cent of the maximum permissible concentrations in water as effluents to unrestricted areas. These values were taken from Table II, Appendix "B", of Part 20 - Standards for Protection Against Radiation. They are shown in Table A-1.1 for some representative isotopes.

PROPOSED MAXIMUM ISOTOPE CONCENTRATIONS
FOR IN SITU TRACERS

(All concentrations are in μ μ curies per liter)

Nuclide	Liquid(a)	Gas(Air) (b)
H³	30,000	500
C14	8,000	100
I ^{1 31}	30	0.4
I ^{1 32}	600	₃₀ (c)
Fe ⁵⁹	60 <u>0</u>	5
Mn 56	1,000	30
P.32	200	2
K ⁴²	3,000	70
Na ²⁴	2,000	40
S ³⁵	600	9
Y 90	200	4
Z ⁶⁵	1,000	4

⁽a) Liquid: Values are 1.0 per cent of MPC Table II, Col. 1, App. "B", Part 20

⁽b) Gas (Air): Values are MPC Table II, Col. 2, Appendix "B", Part 20

⁽c) For insoluble compounds.

A-1.2 -- Statistics and Levels of Radiotracer

Theoretical derivations were made to evaluate the required levels of tracer concentration as a function of instrumental background, efficiency of detector, required statistical reliability, and tracer nuclide. The results of this analysis are summarized for specific cases in Figures 1 and 2. Figure 1 shows the required net sample counting rate in counts per minute as a function of instrumental background counting rates for a required statistical reliability of 3.0 per cent standard deviation of net sample signal, and for three total counting times of one minute, three minutes, and ten minutes. These counting times represent the combined times for the measurement of background and background plus sample, in which the ratio of the former and latter times are chosen to optimize the net signal reliability.

In use, Figure 1, or a similar figure, is chosen according to the desired statistical reliability of the process to be studied or controlled. Next, the desired frequency of measurement indicates a counting time per measurement which selects an appropriate curve on this figure. Finally, the background counting rate of the instrument under consideration allows the selection from the graph of the necessary net sample signal for such a measurement.

Figure 2 shows the relationship of the net sample signal and detector volume to the required tracer concentration for a given detector efficiency. On this graph, a number of common radiotracers are shown at the tracer concentration corresponding to the values of Table A-1.1. These concentrations are given for initial release and are not adjusted for radioactive decay. In use, the required sample signal obtained from Figure 1 is divided by the detector volume. By the use of the level chosen by the selected radiotracer, the necessary tracer concentration in the process stream is read from the appropriate efficiency curve for the detector.

In addition to the one per cent of maximum permissible concentrations of Part 20, several isotopes in Figure 2 are shown at the maximum permissible concentration in air to unrestricted areas. These levels could apply to gas process streams in which exhaust to the air occurs.

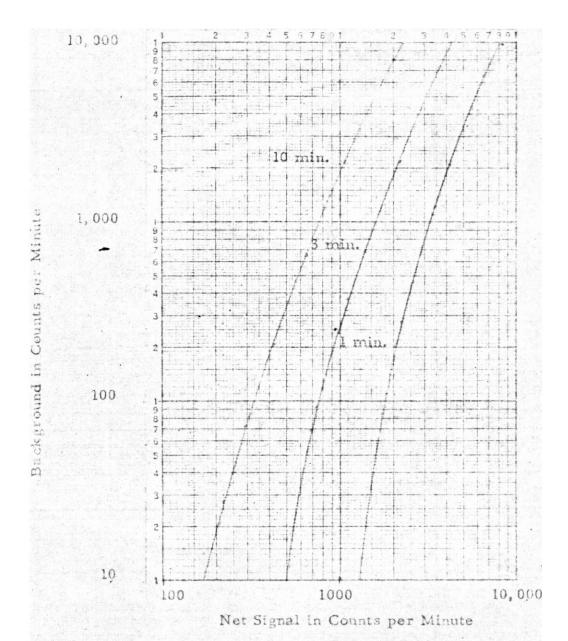


Figure 1: Net signal or sample count versus background for three total counting times (sample + background and background) for 3.0 per cent standard deviation is net signal.

Fig. 2: Net signal divided by detector volume versus tracer concentration as a function of detector efficiency; one per cent of Part 20 MPC values, Table II of "B", are shown. See Table A-1.1.

II. SUB-TASK A-2 -- SURVEY OF POTENTIAL APPLICATIONS

The purpose of this sub-task was to survey potential individual applications. Conferences were held with members of the Scientific Committee and of the Radioisotope Sub-Committee of the National Paint, Varnish and Lacquer Association in a survey of the paint industry, with emphasis on the use of tracers in process research and control.

A-2.1 - List of Conferees

During this period, arrangements were made for discussions with the conferees shown in Table A-2.1. Conferences were held with the people shown, with the exception of the last five people. Arrangements have been made for meetings with these people. The discussions, which were most helpful, were held at Buffalo, New York, Lafayette, Indiana, and Chicago, Illinois.

Table A-2.1

CONFERENCES WITH THE

NATIONAL PAINT, VARNISH, AND LACQUER ASSOCIATION

ON

RADIOISOTOPE APPLICATIONS AND IN SITU TRACERS

AEC AT-(11-1)-650 #6

Neil B. Garlock, NPVLA

Charles E. Loucks, NPVLA

W. H. Lutz, Pratt and Lambert

William Ringel, Pratt and Lambert

- A. E. Van Wirt, Imperial Paper and Color Corporation
- A. F. Kingsley, Spencer Kellogg and Sons, Inc.
- H. M. Schroeder, Spencer Kellogg and Sons, Inc.
- R. L. Terrill, Spencer Kellogg and Sons, Inc.

Francis Scofield, NPVLA

John C. Weaver, Sherwin - Williams Co.

G. G. Schurr, Sherwin - Williams Co.

James A. Arvin, Sherwin - Williams Co.

Stanley Gajownik, Sherwin - Williams Co.

Richard More, Sherwin - Williams Co.

A. F. Bohnert, Enterprise Paint Mfg. Co.

Mark W. Westgate, Gardner Laboratory, Inc.

Royal A. Brown, Egyptian Lacquer Mfg. Co.

Nils Bolin, Egyptian Lacquer Mfg. Co.

T. A. Thorson, Minnesota Paints, Inc.

A-2.2 - Minutes of Meeting of July 17th

The minutes of the meeting of the Radioisotope Sub-Committee of the NPVLA in Buffalo on July 17th were written by Mr. Neil B. Garlock, Chief Chemist of the NPVLA. These minutes are reproduced in part below. The minutes of the subsequent meetings in Lafayette and in Chicago are not yet ready for distribution.

MINUTES OF NPVLA SCIENTIFIC COMMITTEE RADIOISOTOPE SUBCOMMITTEE MEETING BUFFALO, JULY 17, 1959

Present: Mr. Neil B. Garlock, NPVLA; Dr. W. H. Johnston, WHJ Laboratories, Inc.; Mr. W. H. Lutz, Mr. W. G. Ringle, Pratt and Lambert; Mr. A. E. Van Wirt, Imperial Paper and Color Corporation; Dr. A. F. Kingsley, Mr. H. M. Schroeder, Mr. R. L. Terrill, Spencer Kellogg and Sons, Inc.

Dr. William Johnston outlined some AEC activities in field; AEC is spending money in 3 categories: (1) isotope training - perhaps only 20 Ph. D's graduating per year who are directly specializing, (2) radiation technology - application to processing, etc., and (3) isotope development. Office of Industrial Development is doing latter through contracts: Purdue in pharmaceuticals, MIT in soap and detergents. William H. Johnston Laboratories, Inc. contract aims at development of new instruments and techniques, integrating these into a recommended program for tracer applications.

Dr. Johnston said that it was not enough for a research group to know isotopes; they must know an industry and its problems hence the approach via groups such as ours representing trade and industry associations. They are looking for practical research problems, and will carry out surveys, attempting to recommend and develop potential applications. They wish to visit paint plants and laboratories in the course of the study.

W. H. Lutz told of an instance where his organization had attempted to apply an isotope technique to a problem involving thickness and wear of floor finishes. At the time, they were advised this might be hazardous for those in contact with such finishes.

- Dr. Johnston said that use of in-situ tracers would permit this type of investigation, and hazard would not be a factor.
- Dr. Johnston briefly outlined his personal and company background.
- Mr. Terrill read a list of about 15 suggestions for application of radio-chemistry thought to be of broad interest to the paint industry.
- Dr. Johnston inquired about specific control problems in the manufacture and use of paint. Mr. Lutz listed these as follows:
- (1) Determination of hiding power.
- (2) Drying characteristics.
- (3) Color properties.
- (4) Consistency determination.
- (5) Thickness and integrity of applied films such as can coatings.
- (6) Endpoint of reaction for vehicle preparations.

He did not consider present test me thods for these characteristics to be deficient, nor did the liklihood of applying tracer techniques seem obvious in these fields.

Further discussion lead Mr. Ringle to point out two other areas in which problems did exist:

- (7) Off-standard batches showing trouble with level, sagging or other properties and difficulty of checking role of components in such troubles.
- (8) Presence of critical contaminants such as sometime occurance of seeds of zinc oxide/alkyd resin enamels.

Mr. Van Wirt pointed out that pigmentation work raised questions regarding interfacial phenomena, thus it was often desirable to know what went on in a microscopic area, e.g. in a l mil paint film or even on individual pigment crystals. Dr. Johnston outlined a photomicrograph technique involving point-emission tracks in a sensitized strippable emulsion. The pigment and/or vehicle gives off radiations which are recorded on the film.

In discussing application of tracers to process control, Mr. Terrill said he could easily visualize applications in continuous processes but that batch operations were generally fairly simple to control anyway. Dr. Johnston pointed out that tracers were commercially used in determining when batch mixing of heavy greases was complete, at an economic saving over other methods.

Mr. Lutz pointed out the limitations on the market for equipment inherent in the financial and technical make-up of the paint industry; with 1200 companies in the industry.

Dr. Johnston outlined the five basic applications or radiochemistry:

- (1) Absorption and scattering properties applied in thickness gauges, etc.
- (2) Ionizing action of radiation applied in processing, sterilization, etc. as Co⁶⁰, Cs¹³⁷ or via accelerator e.g. Van der Graff or resonant transformer. KWH cost is very high as compared to thermal activation. More research needed, such application is longer term.
- (3) Birth and decay of isotopes activation analysis.
- (4) Decay rate (1/2 life) radiocarbon dating for geology and archeology; natural tritium, use in hydrology.
- (5) Tracer or tag techniques application as (a) bulk lost pipes, etc.
 (b) physical tagging, (c) chemical molecular or atomic tagging to follow given atom or molecule in reaction. These uses are characterized by extreme sensitivity of detection.

Dr. Johnston stated in reply to an inquiry from Mr. Terrill that "hot lab" techniques are now frequently unnecessary, and some exempt isotopes can be purchased without major restriction. Foodstuffs are not exempt in any case. Maximum permissible concentrations for materials are set by regulation. He stated that an aggressive campaign is needed to inform the public that by no means all of the uses of radioisotopes are hazardous.

In discussing a basis for a future course of action, it was agreed that the Subcommittee would list possible areas for research and process control applications. The NPVLA will set up visits to companies in the paint industry for Dr. Johnston. Dr. Johnston was asked to furnish a list or reference to exempt isotopes and prepare a brief outline of recommended techniques and necessary instruments to permit their use.

The subcommittee members attended a luncheon arranged by Mr. W. H. Lutz of Pratt and Lambert, at the Buffalo Club. During luncheon the question of phthalic anhydride loss from alkyd resins in process was discussed.

Respectfully submitted,

NEIL B. GARLOCK

A-2.3 - Suggested Uses of Isotopes in the Paint Industry

Some of the possible areas where radioisotopes can be used in the paint infinitry were discussed at the meeting in Buffalo, New York on July 17th. These are summarized in Table A-2.3. All of these possible uses were discussed, and the emphasis in our work was placed upon no. 22, the measurement of air pollution from the paint industry, no. 1, accelerated studies of film deterioration, and no. 10, the measurement of film thickness of paints.

Table A-2.3

SOME SUGGESTED AREAS WHERE RADIOISOTOPES CAN BE USED IN THE PAINT INDUSTRY

- 1. Study film deterioration with time, radiation, different atmospheres and accelerated conditions.
- 2. The use of paint as a radiation detector.
- 3. The effect of anti-corrosive pigments and corrosion in general.
- 4. The effect of paint driers.
- 5. Determine the relationships in multicomponent vehicles.
- 6. Solvent release from single and multisolvent systems.
- 7. Catalyst action on catalytic vehicles.
- 8. The action of fungicides in paint films.
- 9. The me chanism of chalking of paint films.
- 10. Film thickness of paints.
- 11. Plasticizer loss and migration in lacquer films.
- 12. Color change in paint films.
- 13. Pigment dispersion and influence of additives.
- 14. Permeability of paint films.
- 15. Complete reaction in resin, pigment and vehicle manufacture.
- 16. Presence of toluene di-isocyanate in urethane coatings.
- 17. Fundamental pigment-vehicle relationships.
- 18. Adhesion of paint films to different substrates.
- 19. Determination of low lead content in paint films.
- 20. Determination of the age of paint films.
- 21. Labeling of paints by brand.
- 22. The part the paint industry plays in air pollution.

HI. SUB-TASK B-1 - LOW LEVEL INDUSTRIAL BETA COUNTING SYSTEMS

The purpose of this sub-task was to design and construct prototypes of large low-level soft beta counters for industrial application, especially of such isotopes as a carbon-14 and tritium. The survey and initial study of this problem led to the selection of three approaches. These were a low-level flow proportional counter and automatic mixer of the process stream gas or vaporized liquid with methane or methane and helium; an internal gas counter for either Geiger or proportional use with automatic cyclic filling of sample and counting gas; a carbon-14 process stream counter in which two techniques are under consideration, either a foil flow device in which the sample volume is separated by a Mylar foil from a Geiger flow detector or a capillary plastic scintillation device.

The design specifications for the counters and the associated electronics emphasized the following conditions:

- 1. Sensitivity and large size of detector.
- 2. Ruggedness of design and construction.
- 3. Reliability and stability of counter and electronics.
- 4. Simplicity of operation.
- 5. Minimum installation and maintenance costs.

B-1.1 - Internal Gas Beta Counter.

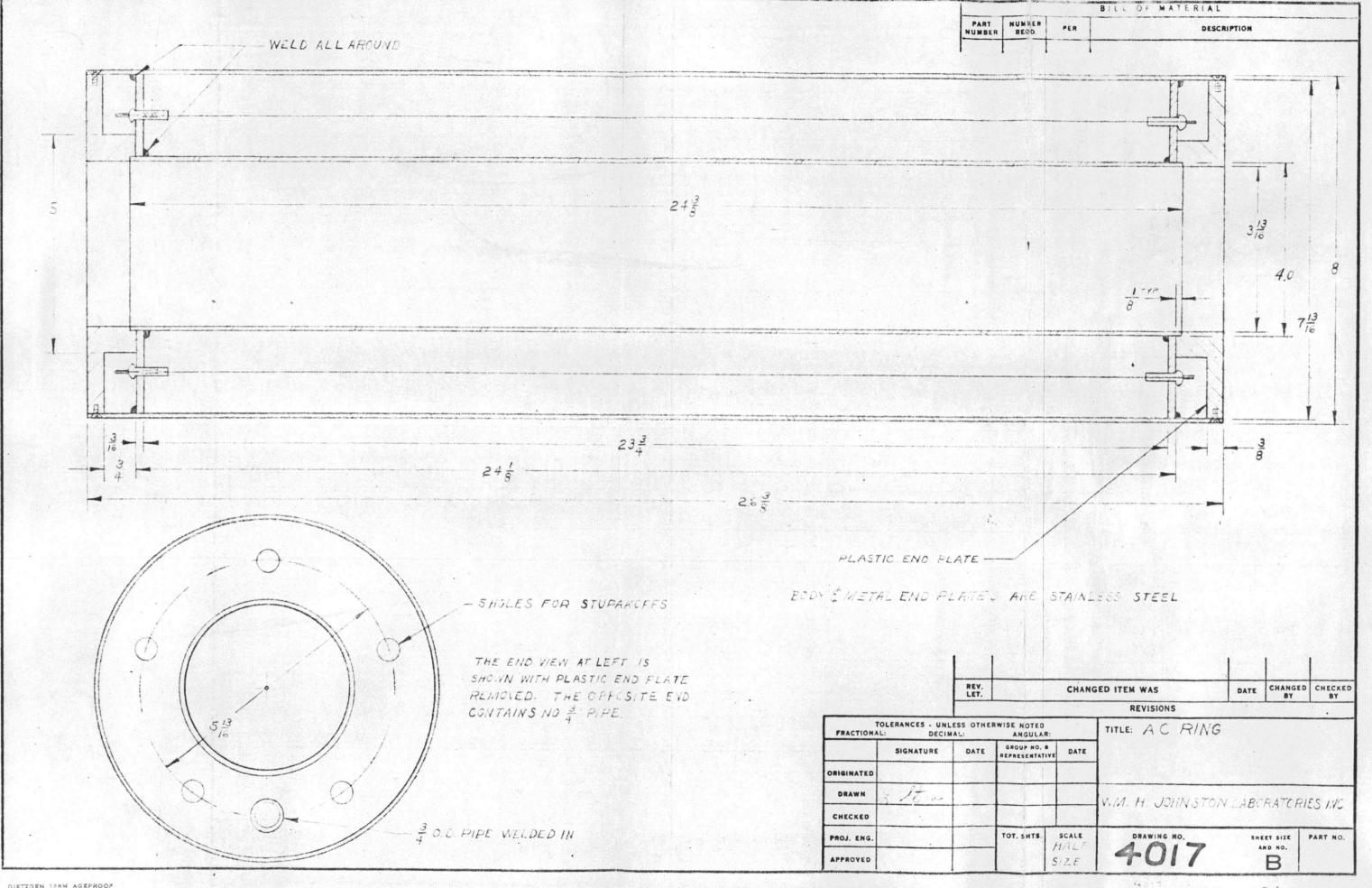
An internal gas counter for Geiger or proportional use was built and tests were begun. It is planned to use this counter with the automatic cyclic control unit. This counter is sensitive to carbon-14 and tritium. It was used for the shield tests described below.

B-1.2 - Internal Gas Flow Proportional Counter

This counter was based upon the work of Wolfgang and Rowland (Richard Wolfgang and F. S. Rowland, Analytical Chemistry, 30, May, 1958, p. 905). Design work was begun on an industrial version of this counter. For many applications, either a gas stream aliquat or a vaporized liquid stream can be introduced directly with counting gas. For other uses, it is proposed that an appropriate gas liquid chronograph be used in conjunction with cyclic sampling of the plant stream.

B-1.3 - Anti-Coincidence Counter

A rugged anti-coincidence counter was built for use with the internal gas and proportional flow beta counters. This unit consisted of stainless steel construction with multiple anodes and a common counting gas. The design is shown in Plate B-1.3.

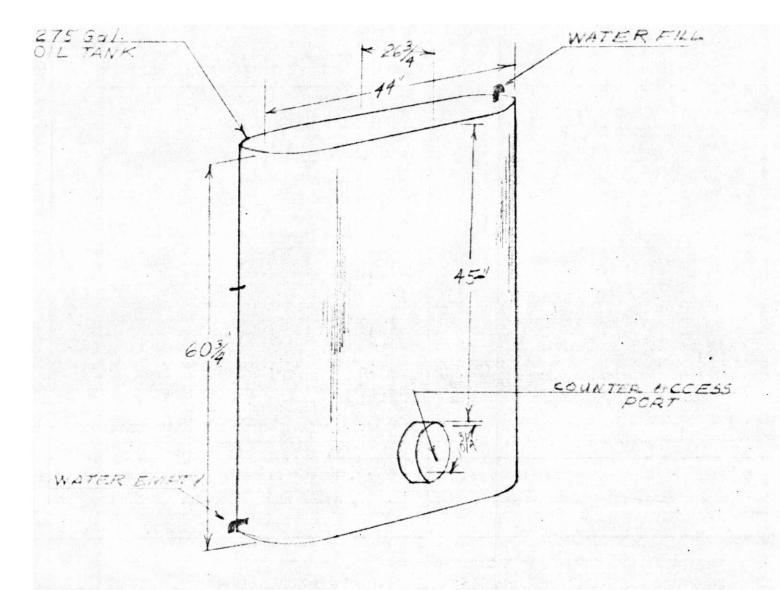


B-1.4 - Shields

An iron shield was constructed providing eight inches of shielding for a cylindrical counter chamber thirty-eight and seven-eighths inches in length and twenty-three inches in diameter. It was found that industry has scrap steel units for extrusion molding which consist of cylinders of various internal and external diameters. By combining these, in appropriate selections, two such cylinders gave a shield of the desired dimensions. Since these units were considered scrap, it was possible to obtain them at scrap iron prices, which amounted to a significant savings.

A water shield was constructed for testing the use of water for industrial low-level counting. Such a shield would have the advantage of easier mobility and economies in construction. A 250 gallon commercial home oil tank was used for these tests. Such a tank can be purchased for under \$30.00, and provides a maximum of 45 inches of water shield for a nine inch diameter counter. The water shield and counter port are shown schematically in Plate B-1.4.

Comparison measurements were made on the internal gas counter with helium-butane filling, as shown in Table B-1.4. In the sixth column, the effects are shown of the water shield with open ends to the counter port. These data are not corrected for the difference in length of the iron and the water shields.



WATER SHIELD

PLATE B-1.4 WILLIAM H JOHNSTON LABORATORIES, INC LAFAYETTE, IND.

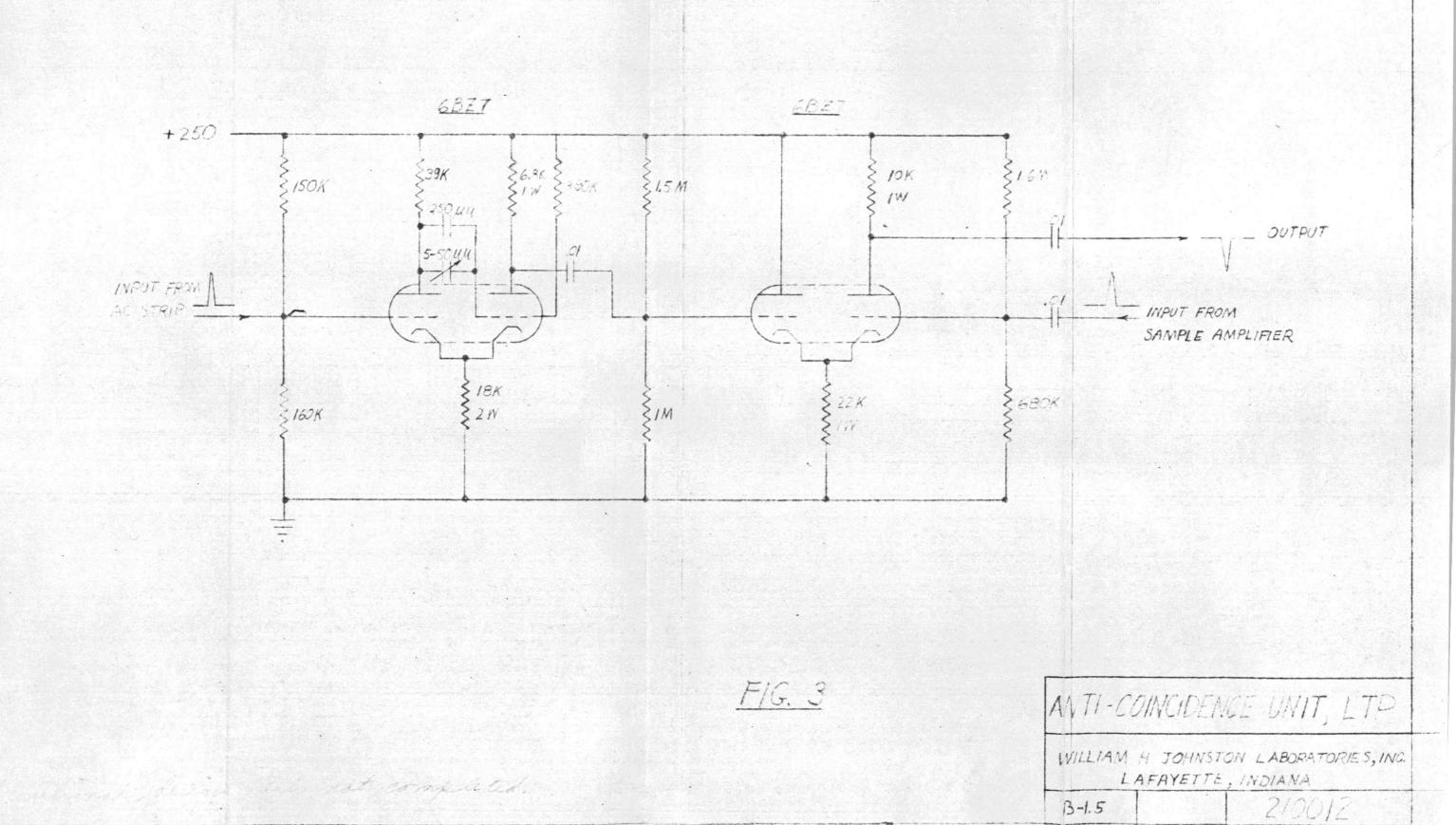
Table B-1.4

COUNTER FILLING	VOLTAGE	PLATEAU LENGTH, V	BACKGROUND UNSHIELDED c/m	BACKGROUND 8" IRON SHIELD c/m	BACKGROUND WATER c/m	BACKGROUND WATER AND 4 IN. STEEL ENDS c/m
1	1375	250	186 <u>+</u> 4.3		117.1 + 2.8	115.6 + 2.8
2	1475	250	214.7 + 2.7	93.2 <u>+</u> 1	127.6 <u>+</u> 2.7	
3	1450	400	201.6 + 2.7	90.8 <u>+</u> 2.4	118.1 + 2	117.3 + 1.4
4	1550	400	207. 7 <u>+</u> 1		120.6 ± 0.8	

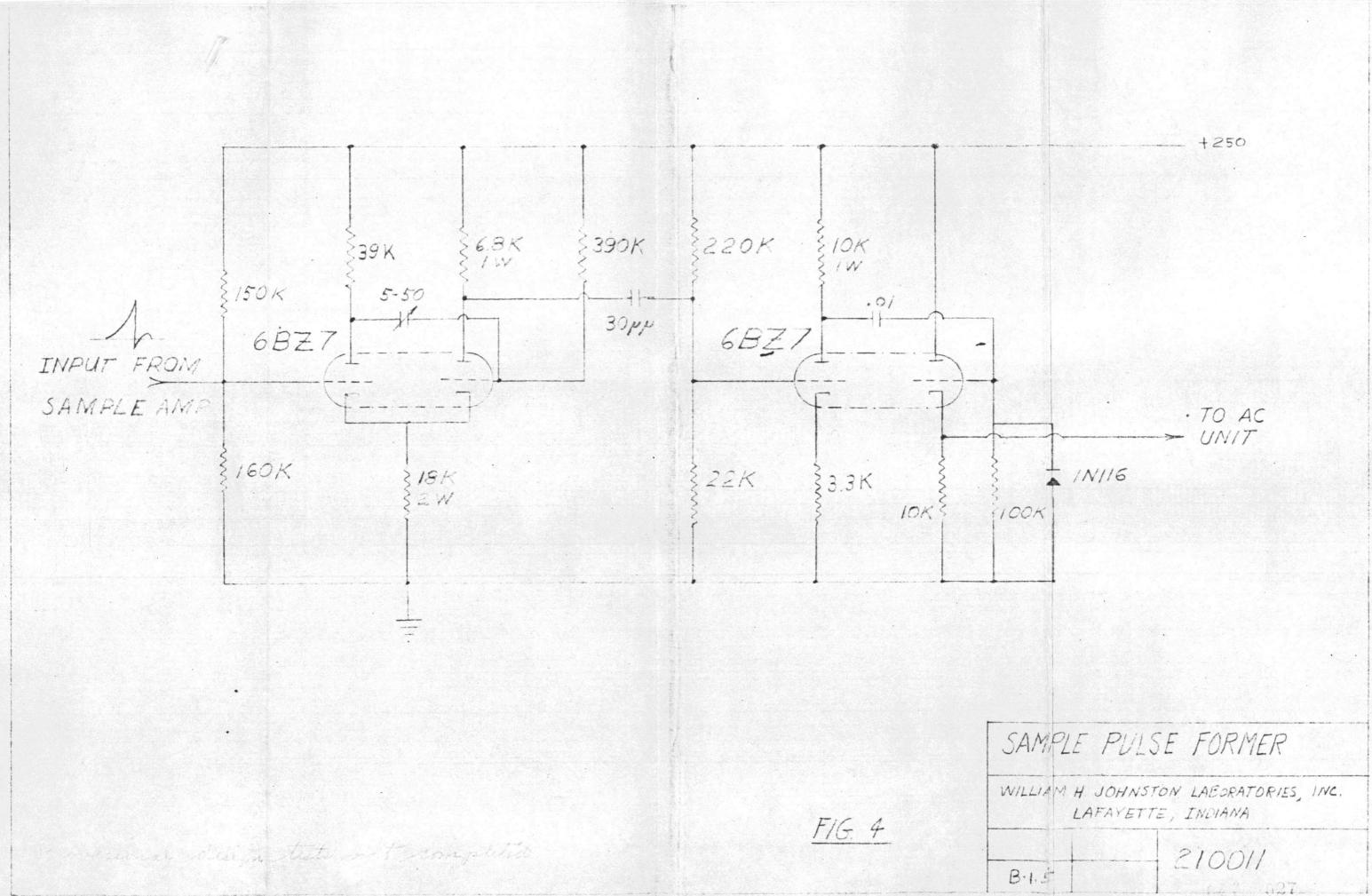
B-1.5 - Beta Counter Electronics

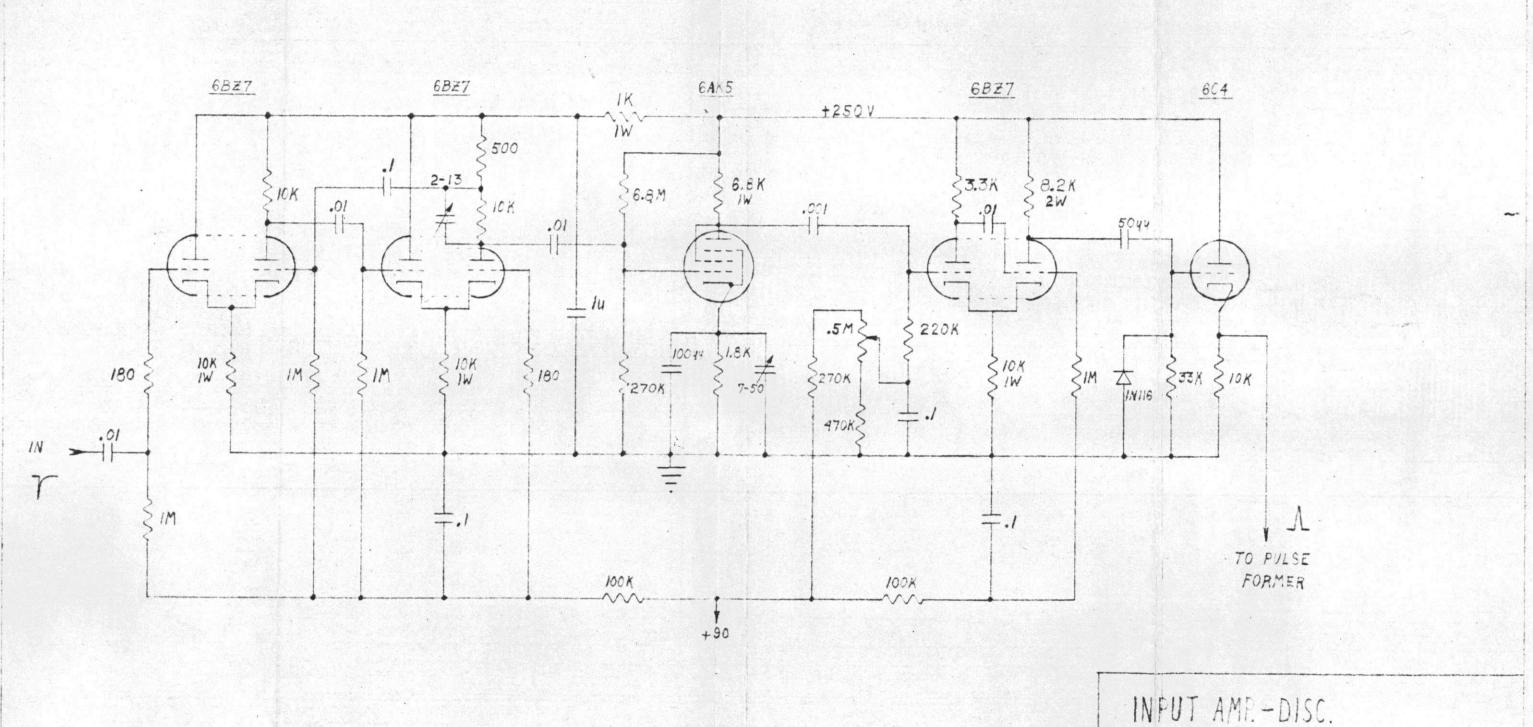
A completely transistorized anti-coincidence circuit was breadboarded for tests of the internal gas counter systems. Designs were made of three transistorized amplifier circuits for tests leading to the proportional counter system electronics.

A vacuum tube variation of the amplifier and anti-coincidence electronics was also designed. This units is shown in Figures 3, 4, 5, and 6. Initial design work was begun on the analog signal device for the low-level beta counters. A preliminary design was made using a Sigma motor to accept the net sample pulses, and to produce one of several analog signals.



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design to prest constitute.

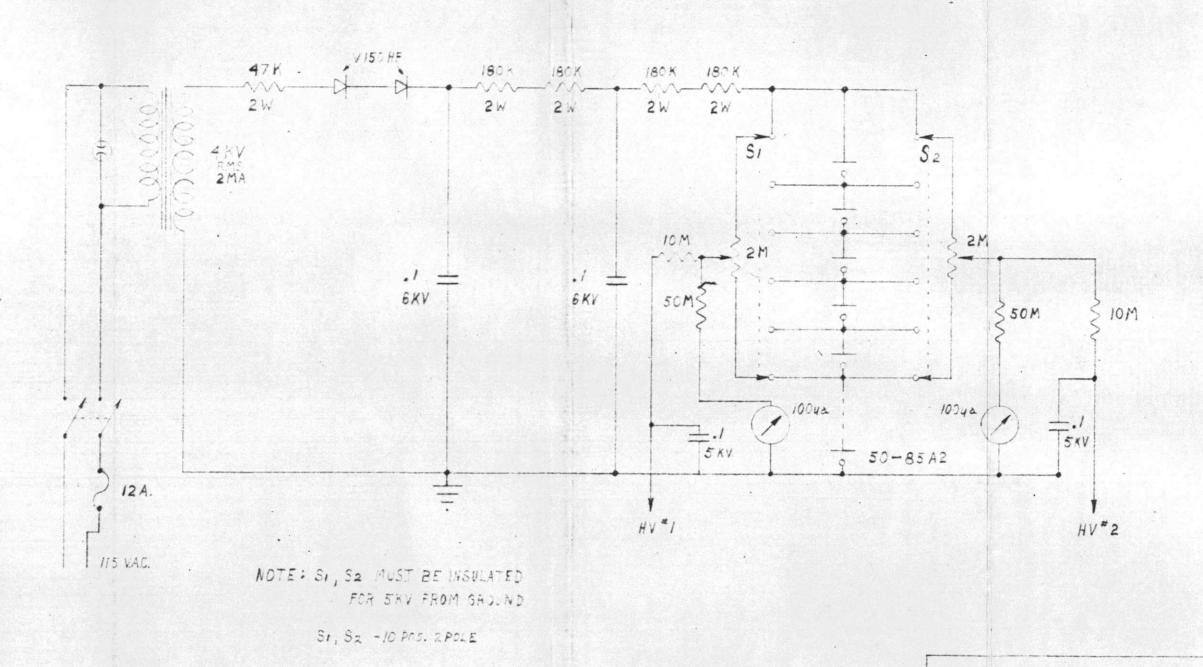
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IV. SUB-TASK B-2 -- INDUSTRIAL PROCESS GAMMA COUNTER

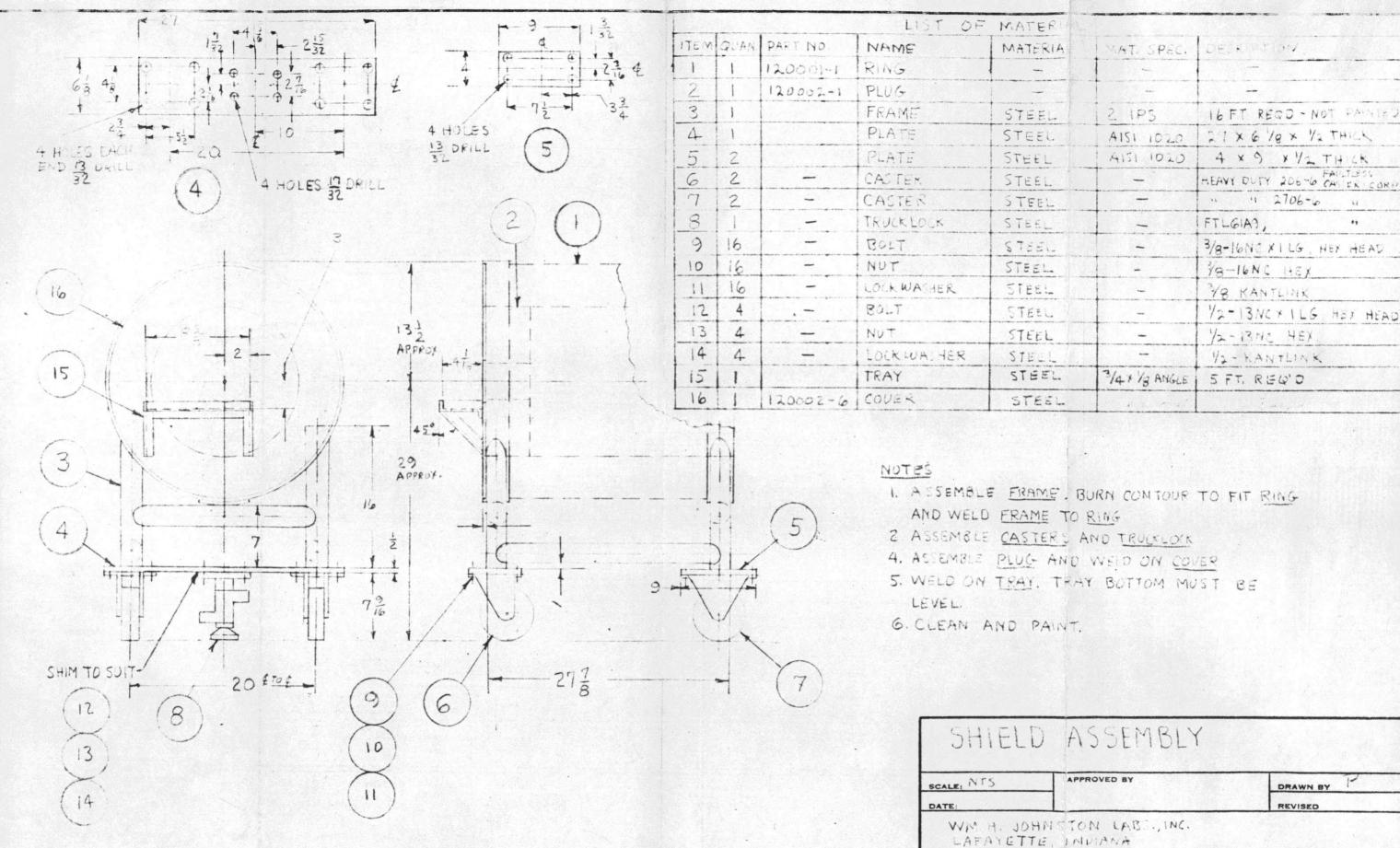
The purpose of this sub-task was the design and construction of a prototype of a large low-level liquid scintillation detector for use with process gamma counting in industrial tanks and pipe systems. A large liquid scintillation counter was partially constructed, consisting of a complete shield and the liquid scintillator tank. This unit was a version of the original Los Alamos small animal counter and was based upon a commercial unit made by Johnston Laboratories, Inc. It was designed for use with either continuous flow of the process stream or with cyclic sampling for longer counting periods.

B-2.1 - Gamma Counter Shield

The shield for the industrial process gamma counter was constructed of iron, as shown in Plate B-2.1. This unit is conveniently mounted on rollers, and contains the liquid scintillator tank.

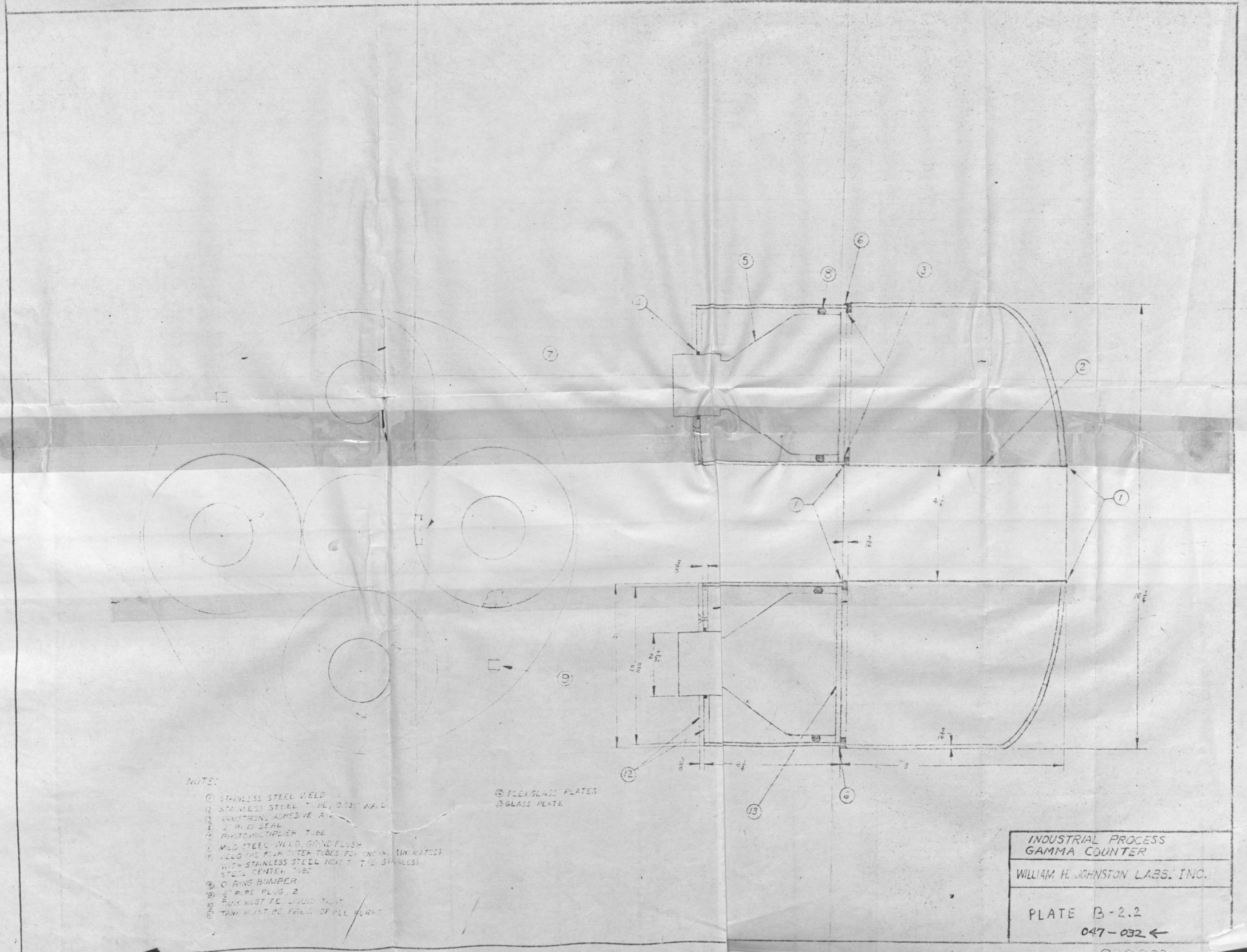
B-2.2 - Gamma Counter Tank

The gamma counter tank was constructed as shown in Plate B-2.2. This tank has four ports for mounting four 5 inch photo-multiplier tubes, and is a version of the small animal counter built by this laboratory for Purdue University in the spring of 1958. This tank will be filled with a liquid scintillator of toluene, PPO, and POPOP. Experiments were done on the possibility of finishing the inner surface of this tank by the use of cadmium plating. This experiment was unsuccessful because of the rapidity of attack by sulfides.



DRAWING NUMBER

HOE



V. SUB-TASK B-3 - INTER MITTENT LOW-LEVEL SAMPLER

The general problem of maintaining extremely low concentrations of tracers in process streams for in situ tracer measurements requires, according to the analysis of Section A-1, counting times which make impractical continuous measurements in all cases. On the other hand, many potential applications of in situ tracers involve measurements of variables which are changing slowly enough to readily accept measurement intervals as long as ten minutes. It was decided, therefore, to design automatic sampling equipment which would provide low-level counting by cyclic measurements from process streams. Such a device would be useful for a large variety of measurements, including the use of tracers in studies of water pollution, air pollution, and underground water movements. The design work has begun on this sub-task.