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ABSTRACT

This paper describes equipment and techniques used in the tritium laboratory at the Australian Atomic Energy Commission Research Establishment for the determination of low level activities of tritium in water samples. Samples are enriched by electrolysis in sixteen glass cells connected in series. An enrichment of about 25 times and an enrichment factor of about 0.85 are obtained. A calibrated ampere-hour meter in series with a precision shunt measures the weight of water electrolysed and a preset counter is used to shut off the current when 20 g of electrolyte remains in each cell. After distillation the enriched samples are counted in Teflon vials using emulsion liquid scintillation techniques.

The accuracy of measurements is discussed and applied to routine measurements. The overall standard deviation for samples having an activity greater than 5 'tritium units' is less than 10%.

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ACCURACY; EFFICIENCY; ELECTROLYSIS; ERRORS; ISOTOPE SEPARATION; MEASURING METHODS; TRITIUM; WATER

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1. INTRODUCTION

The tritium laboratory at the Australian Atomic Energy Commission Research Establishment, Lucas Heights, NSW, has been operational since 1971. The method currently used for low level tritium measurement is enrichment of the water sample by electrolysis [Allen et al. 1966; Hughes & Holmes 1971; Metson 1969] followed by emulsion liquid scintillation counting of the enriched sample [Sauzay & Schell 1972]. A very small amount of tritium is released into the atmosphere at Lucas Heights in the operation of the reactor HIFAR. The concentration is trivial in relation to potential health hazards but is nevertheless sufficient to cause errors in analysis of environmental water samples. Because of this a unit [Calf et al. 1973] has been installed to maintain the tritium in the atmospheric moisture in the laboratory at the same level as that in Sydney tap water (approximately 60 pCi ℓ^{-1}).

Tritium has a half-life of 12.36 ± 0.03 years [Jacobs 1968] and decays by the emission of a β particle with a maximum energy of 18 keV and an average energy of 5.7 keV. Some useful relationships are given in Table 1.

Tritium is produced in the atmosphere by the interaction of cosmic ray produced particles with the nuclei of atmospheric gases, principally by proton and neutron induced reactions [Allen et al. 1966]. Tritium exists initially in the stratosphere and troposphere as gas, and is oxidised and gradually transported into the lower troposphere to reach the Earth's surface as tritiated water in rainwater, snow and atmospheric moisture.

The annual 'natural' production of tritium is about 4 million curies and, since its half-life is short, the total amount of natural tritium in the biosphere has been estimated at about 3.5×10^7 curies [Schell et al. 1973]. This is equivalent to 3-4 tritium atoms for every 10^{18} hydrogen atoms and it is convenient to express tritium levels in relation to the number of hydrogen atoms in the sample. The term tritium unit (TU) is commonly used to denote the number of tritium atoms per 10^{18} atoms of hydrogen. Thus 1 kg of water with an activity of 1 TU contains 3.24 pCi of tritium.

Since 1954, the tritium content of the atmosphere has increased greatly owing to thermonuclear explosions which yield 1.9×10^7 Ci of tritium per megaton of fusion [Schell et al. 1973]. Thus, weapons testing injected artificially into the atmosphere quantities of tritium greatly in excess of those naturally present before the atmospheric test ban treaty became effective in 1963.

The amount of tritium present in a reservoir at any given time is dependent on the input and outflow. The outflow is governed by rates of removal and decay. In the atmosphere the removal rate (halftime) by precipitation is about one year [Schell et al. 1970].

Environmental tritium is of particular value as a tracer for groundwater of short turnover time. For all hydrological studies, based on the measurement of environmental tritium in groundwater, reference must be made to the basic data obtained from a precipitation survey. These data provide the fundamental information of the variation, both with respect to geographic location and time.

2. ELECTROLYTIC ENRICHMENT OF WATER

2.1 Electrolytic Cell Design

The electrolytic cell (Figure 1) has been designed so that sample enrichment by electrolysis from 600 g to 20 g can be carried out in a single step. The cell is closed by a polypropylene cap and a gas tight joint is provided by a Neoprene 'O' ring. Carry over of spray droplets by evolved hydrogen and oxygen is reduced by a Teflon baffle. The evolved gases pass via a polythene tube to a bubbler filled with silicone oil which keeps the cell at a slight positive pressure to avoid possible contamination from the laboratory atmosphere. The gas from each cell is finally discharged in separate lines into the atmosphere above the building. There have been no explosions since this system was installed two years ago.

2.2 Electrodes

The two anodes (Figure 1) are fabricated from nickel sheet 0.10 cm thick and are 30.5 cm long and 4.4 cm wide, with a smaller section 5.6 cm by 1.3 cm at the base where the last 20 g of sample is confined to the smaller part of the cell. The cathode is made from high purity iron sheet 0.25 cm thick, and has the same dimensions as the anodes. The electrodes are silver soldered to copper rods which pass through the cap. The electrode spacing is maintained accurately at 3 mm by four Teflon spacers. The electrodes are assembled by fixing an anode on each side of the cathode with a nickel rivet which passes through the Teflon spacer.

After being degreased, the electrodes are treated in a solution of Marshall's Bright Dip [Marshall 1952] and then conditioned by operating for 200 hours at 10 amperes. The reproducibility of the electrodes in an electrolysis run is then checked before assaying samples. This configuration of electrodes gives a high value for the electrolysis separation factor β with good reproducibility (see Section 4.2).

2.3 Electrolyte

All environmental water samples with the exception of rainwater are distilled before electrolysis. The sample is made alkaline by the addition of 0.67% w/w A.R. sodium peroxide which prevents corrosion of the electrodes during the electrolytic enrichment.

2.4 Electrolysis

The electrolysis is carried out in a refrigerated bath containing 10% ethylene glycol/water solution controlled at -1 to 0°C. These conditions reduce vapour losses from the electrolyte. Sixteen cells are connected in series (Figure 2) to a rectified a.c. supply (AAEC 20 A current regulated supply type 491, (Figures 3 and 4) which produces 80 V d.c. smoothed to reduce ripple to 35 mV r.m.s. The initial current is 10 A which produces a current density of 120 mA cm^{-2} when the electrolyte weight is 600 g. As the electrolysis proceeds the level of the electrolyte in the cell is reduced. The current is manually reduced to 3 A during the 210 hours required to reach 20 g, so that the current density does not exceed 200 mA cm^{-2}.

A calibrated ampere-hour meter (AAEC current integrator type 479) in series with a 0.0376 ohm precision shunt (Figures 3 and 5) measures the current through the cells and is an approximate measure of the weight of the water electrolysed. A preset counter (AAEC preset counter type 509) is used to shut off current (Figures 3 and 6) when approximately 20 g of electrolyte remains. From Faraday's Law, it can be shown that 1 g of water is electrolysed by 2.978 ampere-hours of current.

Fourteen samples and two tritiated water spikes are connected in series. Each cell is weighed at the beginning and end of the electrolysis. The details of the electrolysis are recorded each day on a log sheet (Figure 7).

On completion of the electrolysis, the sodium hydroxide concentration in the electrolyte is about 20%. This sodium hydroxide contains some tritium from the sample and, to avoid a possible isotope effect, the sodium hydroxide is converted to sodium carbonate by bubbling dry carbon dioxide gas through the sample which is then distilled to dryness. The distillate is then counted.

3. LIQUID SCINTILLATION COUNTING

In low level counting, the samples remain unchanged in the vials for at least one week. Thus, the scintillation mixture must have long term stability and the vials must not be permeable to or interact with the scintillant mixture which would result in a change in background or efficiency.

Also the highest possible efficiency(E) is essential for detecting tritium in the scintillation mixture with the lowest background(B). It has been shown that Teflon vials [Calf 1969, 1971] allow larger figures of merit (E^2/B) ratios to be obtained, and thus are ideal for low level tritium determinations. They are particularly suitable for use in emulsion liquid scintillation counting techniques. No inherent vial background variance was found within the accuracy obtained in a routine counting time of 500 minutes. The average weekly measurement of background over four months using Teflon vials is shown in Figure 8. The long term mean background counting rate is 6.05 counts min^{-1} with a mean efficiency of 18.6%.

In a 25 mℓ Teflon vial, 10 g of distilled enriched sample is mixed with 11 mℓ of Instagel (Packard Instrument Co.), and the vial placed in a Packard 3375 liquid scintillation spectrometer operating at 8°C and with the discriminators set at 045-600 and the amplification at 100%.

Twenty vials are placed within the automatic sample changer in the order: $T, S_{A1}, S_{A2}, S_B, U_1, U_2, U_3, U_4, B_1, U_5, U_6, U_7, U_8, U_9, U_{10}, B_2, U_{11}, U_{12}, U_{13}$ and U_{14}, where T is the tritium standard of known activity prepared from an accurate dilution of the NBS Standard No.4926 (see Section 4.3). S_B, S_{A1} and S_{A2} are the samples of the tritiated water spike before and after enrichment, B_1 and B_2 are background samples, and U_1-U_{14} are the enriched samples.

The vial cycle is 20 min preset time, with the exception of samples T, S_{A1} and S_{A2} where 500,000 preset counts are accumulated in about 10 min. The above set includes all instrument checks for stability, calibration and enrichment factor measurements. The cycling method provides background and efficiency checks and improves long term reproducibility.

All results are processed using a computer program which calculates for each sample total count and time, checks Poisson and Gaussian distribution and rejects readings outside three standard deviations. The program then calculates TU in the sample, correcting for the decay that has occurred between date of sampling and analysis.

4. CALCULATION OF RESULTS

4.1 Enrichment Factor

The enrichment of tritium due to electrolysis is given by the relation [Bigeleisen 1962]:

$$\alpha/\beta = \alpha^{-0\cdot35} \quad ,$$

where α is the electrolysis fractionation factor deuterium to protium and β is the same factor tritium to protium. β is also defined by the relation:

$$\beta = \frac{\text{rate of loss of protium}}{\text{total protium}} \times \frac{\text{total tritium}}{\text{rate of loss of tritium}} \quad .$$

In an electrolytic cell, the amount by which the sample is enriched in tritium is given by

$$\text{enrichment} = T_t/T_o = R\ W_o/W_t \quad ,$$

where T_o is the initial tritium activity, T_t is the final tritium activity, W_o is the initial weight of the sample, W_t is the final weight of the sample, and R is the enrichment factor.

In a single step electrolysis:

$$R = \left(\frac{W_t}{W_o}\right)^{1/\beta} \quad .$$

4.2 Reproducibility of Enrichment Factor

When a set of cells, connected in series and containing equal weights of water and electrolyte, are electrolysed at a constant temperature, the weight lost from each cell, the enrichment factor and β will be found to vary from cell to cell, owing to small differences in each cell. Larger variations may also occur in a single cell from run to run.

The reproducibility of the cells in a single run was checked a number of times and the results from a typical enrichment are shown in Table 2. Each cell contained identical amounts of tritiated water and sodium peroxide.

4.3 Efficiency

The tritiated water standard, from the National Bureau of Standards, Department of Commerce, Washington, D.C. (NBS), had an activity of 0.878×10^4 disintegrations $s^{-1}\ g^{-1}$ on September 3, 1961. The estimated maximum inaccuracy is ± 1%.

An accurate dilution of the standard with tritium free water to give an activity of approximately 6.5 x 10^3 disintegrations min^{-1} g^{-1} was used to determine the counting efficiency of the system.

4.4 Tritium in Sample

TU (in enriched sample) =

$$\frac{[\text{count rate (counts min}^{-1}) - \text{background (counts min}^{-1})] \times 10^5}{\text{weight of sample counted (g)} \times \text{\% efficiency} \times 7.19}$$

$$\text{TU (in sample)} = \frac{\text{TU (in enriched sample)}}{\text{Enrichment}}$$

This activity has to be corrected for the decay of tritium between the date of sampling and analysis.

5. ESTIMATION OF TRITIUM IN STANDARD WATER SAMPLES

The accuracy of the method was checked by assaying a series of samples made by diluting a calibrated tritiated water standard assumed to be 1390 TU ± 3% (10.0 disintegrations min^{-1} g^{-1}) with tritium free water. These dilutions were measured by accurately weighing the water to a maximum error of 0.01% and results are shown in Tables 3 and 4. The results show that tritium can be estimated satisfactorily and that no contamination of tritium free water samples occurs.

6. ERRORS IN RESULTS

6.1 Error in Efficiency

The NBS standard has an estimated maximum inaccuracy of ± 1%, so that when counting errors are considered, a typical efficiency of the counter is 18.64 ± 0.21%, an error of 1.1%.

6.2 Error in Enrichment and Enrichment Factor R

Taking into account weighing errors and counting errors, typical results for an electrolysis run are:

Count rate of spike S_B before enrichment (T_o)	97.3 ± 0.2 counts min^{-1} g^{-1}	
Count rate of spike S_A after enrichment (T_t)	2884.0 ± 1.1 counts min^{-1} g^{-1}	
Tritium enrichment (T_t/T_o)	29.64 ± 0.06	(0.2%)
Weight concentration due to electrolysis (W_o/W_t)	33.71 ± 0.24	(0.7%)
Enrichment factor (for a single cell)	0.88 ± 0.01	(1.1%)
Enrichment factor R (for any cell related to two spike samples)	0.88 ± 0.02	(2.1%)

The standard deviation in the enrichment procedure is ± 2.1%.

6.3 Error in Results

Using the same approach as Hartley [1972], we can expect the overall standard error of measurements in tritium assays after 500 min counting time to be as shown in Table 5 and Figure 9.

The difference between the estimated and actual tritium activity in a sample (Tables 3 and 4) was normalised by dividing by the theoretical standard error (Figure 9), and the r.m.s. average of these normalised differences was found to be 1.3. This indicates that there is good agreement between the theoretical and practical errors.

7. CONCLUSION

Facilities for the analysis of tritium in environmental water samples have been developed and used for the past four years for tritium determinations at levels below 100 TU. Using two electrolysis units and one liquid scintillation counter, it is possible to estimate eleven water samples per week.

The method described enables routine tritium determinations to be made with an accuracy satisfactory for hydrological investigations.

8. ACKNOWLEDGEMENTS

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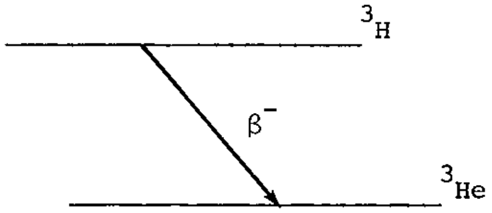
TABLE 1

TRITIUM - USEFUL RELATIONSHIPS

1. Decay

Half-life $T_{H_3} = 12.36 \pm 0.03$ years



β^-: 0.018 MeV ~ 100%

2. Tritiated water

1 kg of water gives 7.19 disintegrations min^{-1} TU^{-1}

1 TU = 3.24×10^{-3} pCi g^{-1}

1 µCi g^{-1} = 3.087×10^{8} TU

1 disintegration min^{-1} g^{-1} = 139.1 TU

TABLE 2

REPRODUCIBILITY OF TRITIUM ENRICHMENT

Cell No.	Initial weight W_o(g)	Final weight W_t(g)	Weight concentration W_o/W_t	Initial tritium activity T_o (counts min^{-1} g^{-1})	Final tritium activity T_t (counts min^{-1} g^{-1})	Enrichment T_t/T_o	Enrichment factor R	β
1	600.0	21.3	28.17	84.4	2056.6	24.37	0.87	24.0
2		19.5	30.77		2245.0	26.60	0.86	22.7
3		20.4	29.41		2177.5	25.80	0.88	26.5
4		20.1	29.85		2210.5	26.19	0.88	26.6
5		20.0	30.00		2130.0	25.24	0.84	19.5
6		20.5	29.27		2105.2	24.94	0.85	20.8
7		20.8	28.85		2086.6	24.72	0.86	22.3
8		19.9	30.15		2154.2	25.52	0.85	21.0
9		20.1	29.85		2107.5	24.97	0.84	19.5
10		20.5	29.27		2077.8	24.62	0.84	19.4
11		20.3	29.56		2119.7	25.11	0.85	20.8
12		20.1	29.85		2118.6	25.10	0.84	19.5
13		20.4	29.41		2105.5	24.95	0.85	20.8
14		19.8	30.30		2165.0	25.65	0.85	21.0
15		19.8	30.30		2115.3	25.06	0.83	18.3
16		20.3	29.56		2098.8	24.87	0.84	19.4
					Mean	25.3 ± 0.6	0.85 ± 0.01	21.4 ± 2.4

TABLE 3

ESTIMATION OF TRITIUM IN STANDARD WATER SAMPLES

No.	Sample	Tritium enrichment	Gross counts $\min^{-1}$	Weight of sample counted	TU found*
1	Tritium free water	25.26	6.43 ± 0.11	9.975	0.0 ± 0.4
2	Tritium free water	25.11	6.33 ± 0.11	10.014	-0.3 ± 0.4
3	2.5 TU	25.55	7.13 ± 0.12	9.969	2.0 ± 0.5
4	2.5 TU	25.11	7.10 ± 0.12	10.000	2.0 ± 0.5
5	5.0 TU	25.55	8.24 ± 0.13	9.995	5.2 ± 0.5
6	5.0 TU	25.26	8.02 ± 0.13	9.966	4.1 ± 0.5
7	10.0 TU	25.56	9.51 ± 0.14	9.951	8.9 ± 0.5
8	10.0 TU	25.26	9.79 ± 0.14	9.941	9.9 ± 0.5
9	20.0 TU	23.95	12.70 ± 0.17	10.000	19.3 ± 0.6
10	20.0 TU	24.06	12.93 ± 0.16	9.958	21.0 ± 0.6

* *The errors shown are 1 σ counting errors.*

The efficiency was 18.84% and the background 6.43 ± 0.08 counts $\min^{-1}$.

TABLE 4

ESTIMATION OF TRITIUM IN STANDARD WATER SAMPLES

No.	Sample	Tritium enrichment	Gross counts min^{-1}	Weight of sample counted	TU found*
1	Tritium free water	27.13	6.47 ± 0.12	9.960	-0.4 ± 0.4
2	Tritium free water	27.13	6.55 ± 0.11	10.012	-0.3 ± 0.4
3	50.0 TU	26.79	25.72 ± 0.22	9.972	51.7 ± 0.7
4	50.0 TU	26.79	25.53 ± 0.22	9.930	51.4 ± 0.7
5	100.0 TU	27.13	44.23 ± 0.29	9.996	100.2 ± 0.9
6	100.0 TU	26.95	44.43 ± 0.30	9.978	101.6 ± 0.9
7	200.0 TU	27.13	76.22 ± 0.38	9.958	186.3 ± 1.1
8	200.0 TU	26.45	80.52 ± 0.40	9.985	202.3 ± 1.2
9	500.0 TU	27.13	199.77 ± 0.62	9.997	514.9 ± 1.7

* *The errors shown are 1 σ counting errors.*

The efficiency was 19.24% and background 6.63 ± 0.08 counts min^{-1}.

TABLE 5

COUNTING ERROR AND OVERALL STANDARD ERROR OF TRITIUM MEASUREMENT

TU in sample	1σ counting error (TU)	Overall standard error of measurements (TU)
0.0	± 0.4	± 0.5
1.0	± 0.4	± 0.5
2.5	± 0.4	± 0.5
5.0	± 0.4	± 0.5
10.0	± 0.4	± 0.6
20.0	± 0.5	± 0.7
50.0	± 0.6	± 1.3
100.0	± 0.8	± 2.3

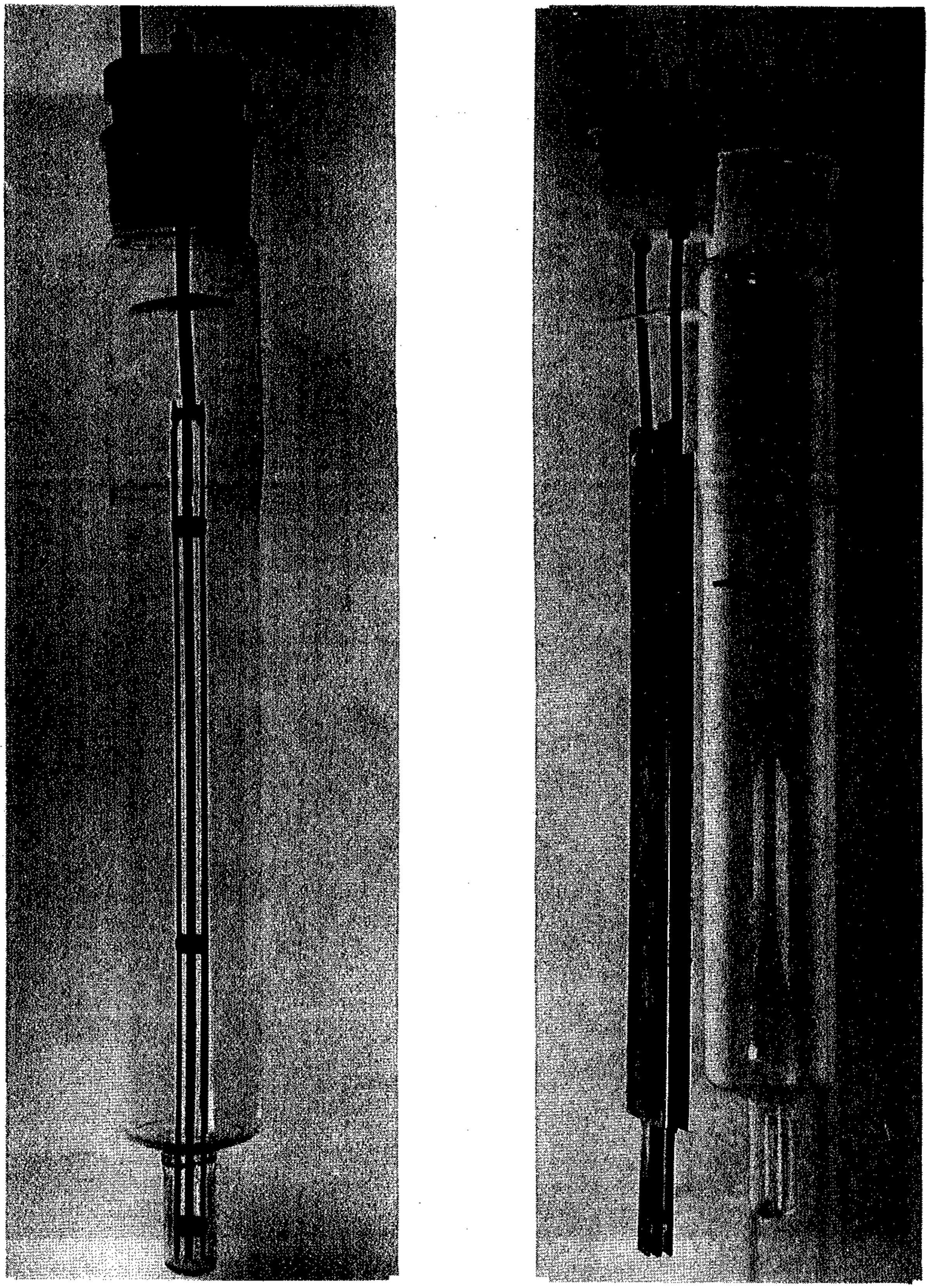


FIGURE 1. ELECTROLYSIS CELLS AND ELECTRODES

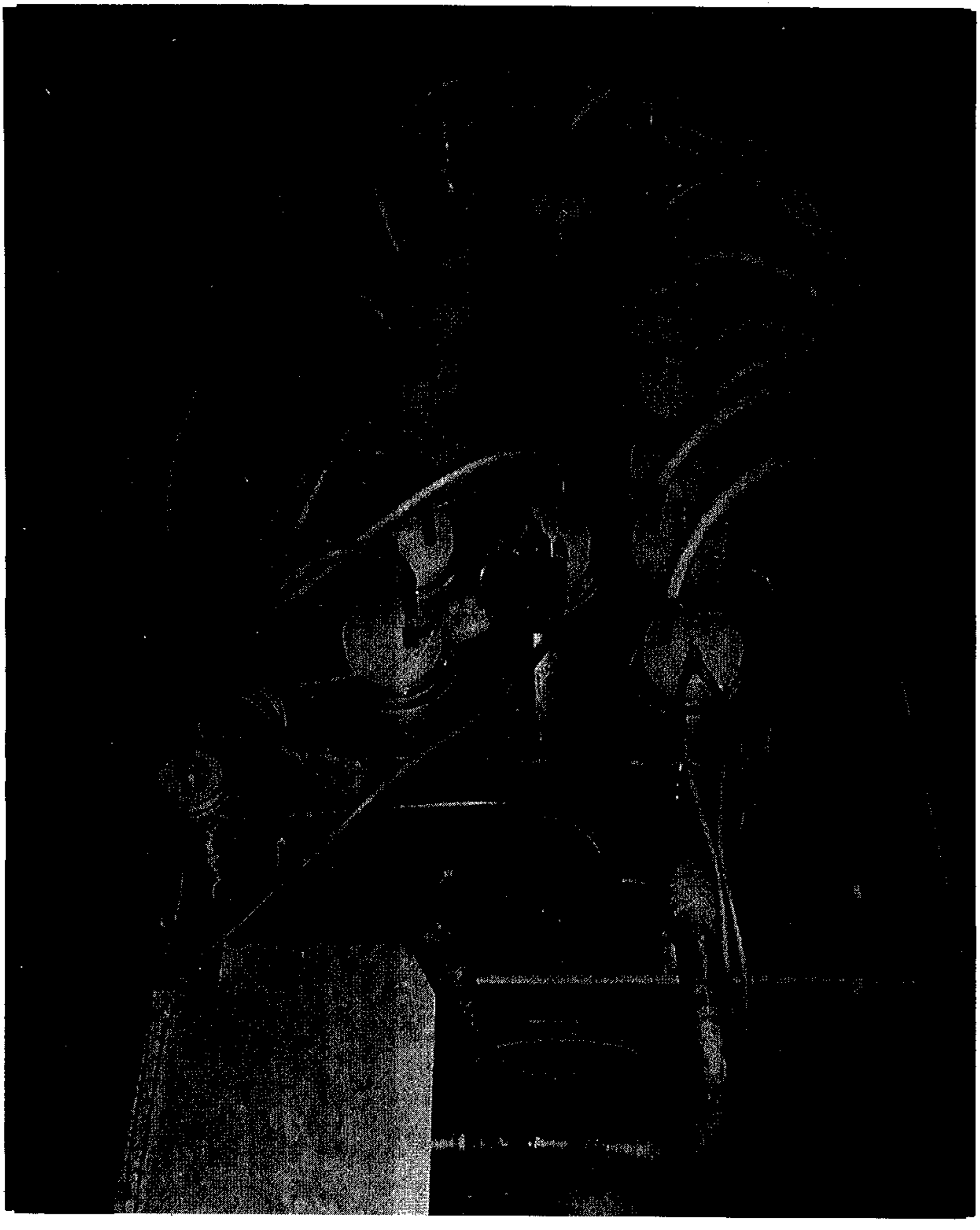


FIGURE 2. SIXTEEN ELECTROLYSIS CELLS CONNECTED IN SERIES IN REFRIGERATED BATH

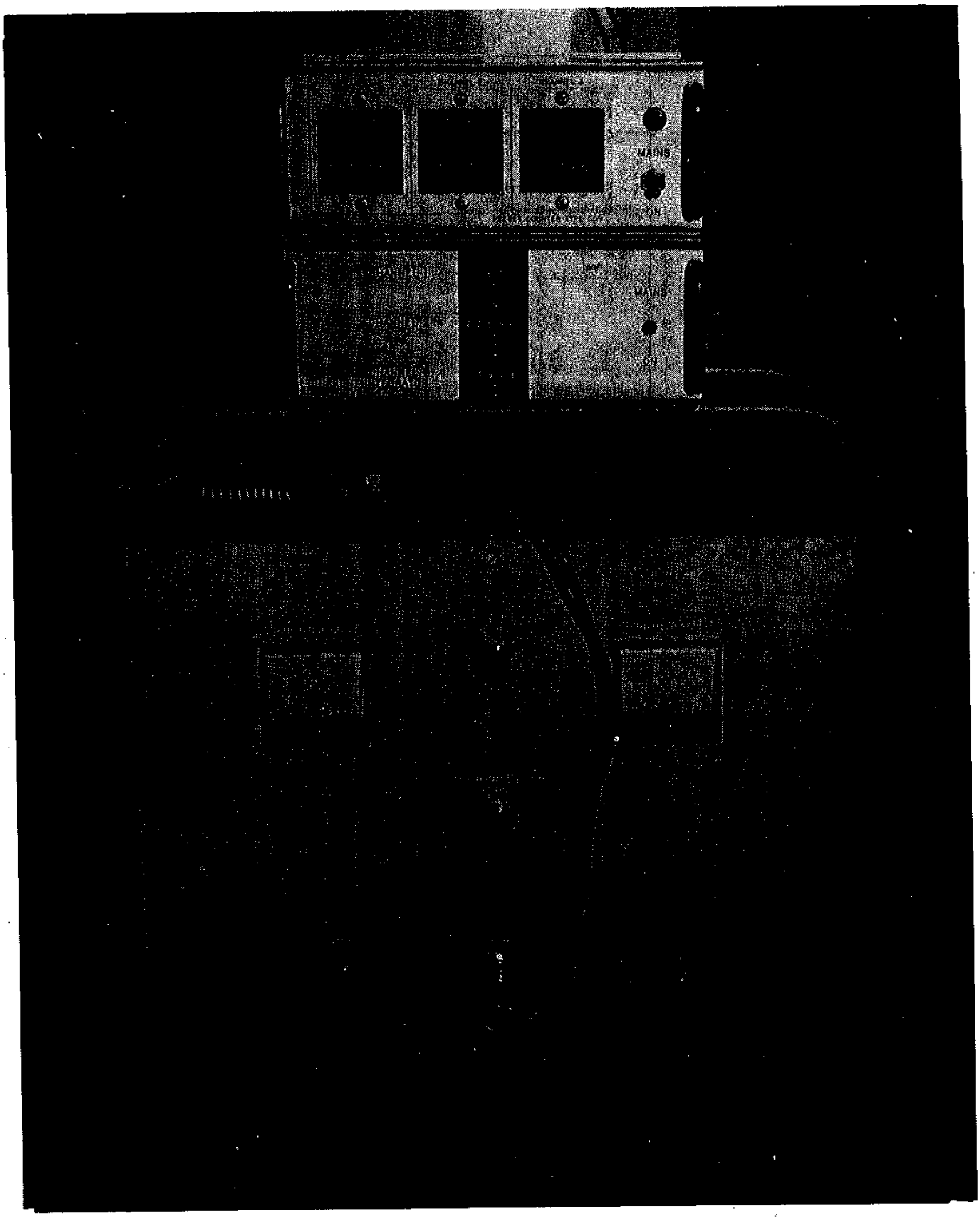
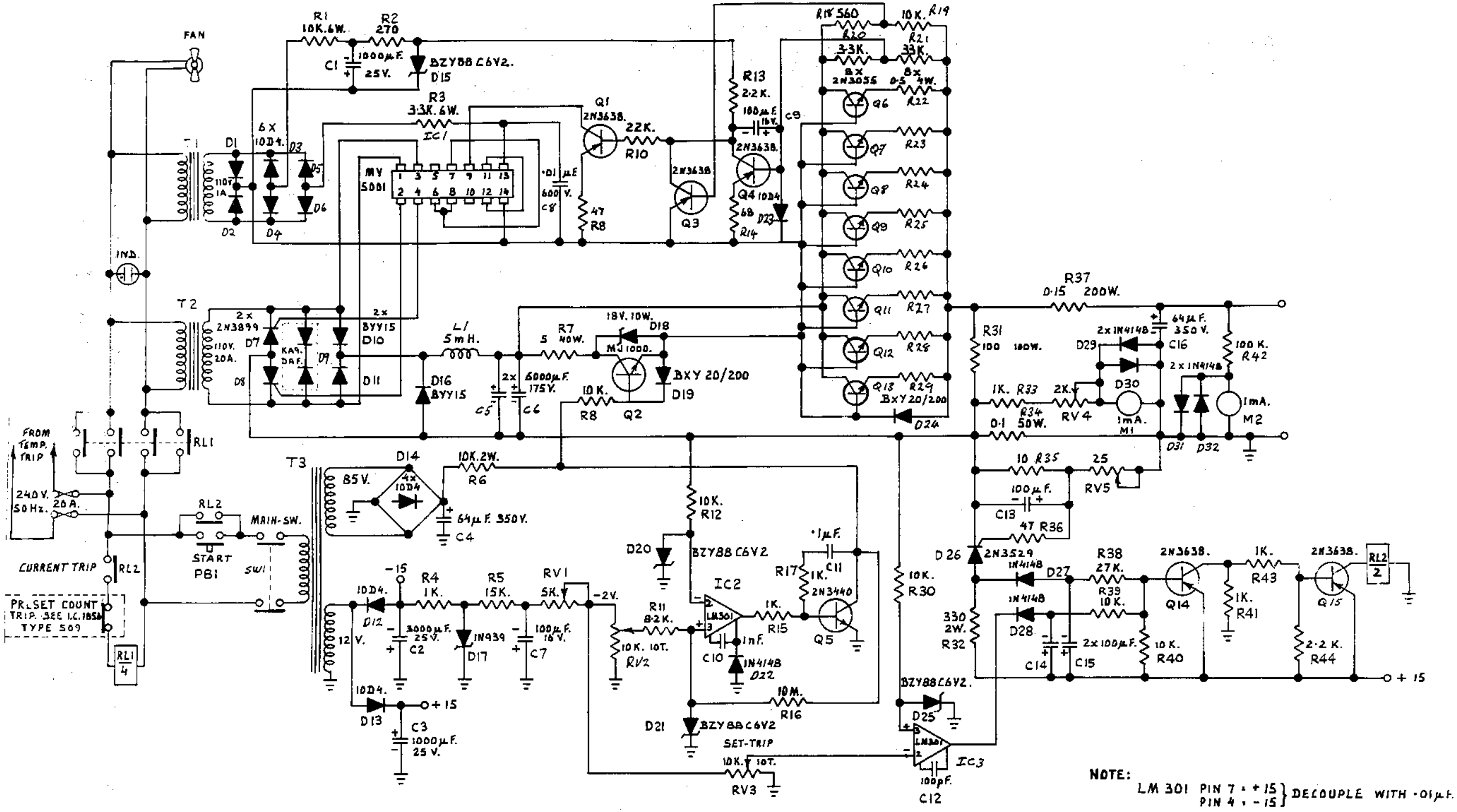


FIGURE 3. CURRENT REGULATED SUPPLY TYPE 491, CURRENT INTEGRATOR TYPE 479 AND PRESET COUNTER TYPE 509



NOTE:
LM 301 PIN 7 = +15 } DECOUPLE WITH ·01µF.
PIN 4 = -15 }

FIGURE 4. 20 A CURRENT REGULATED SUPPLY TYPE 491 (AAEC) CIRCUIT

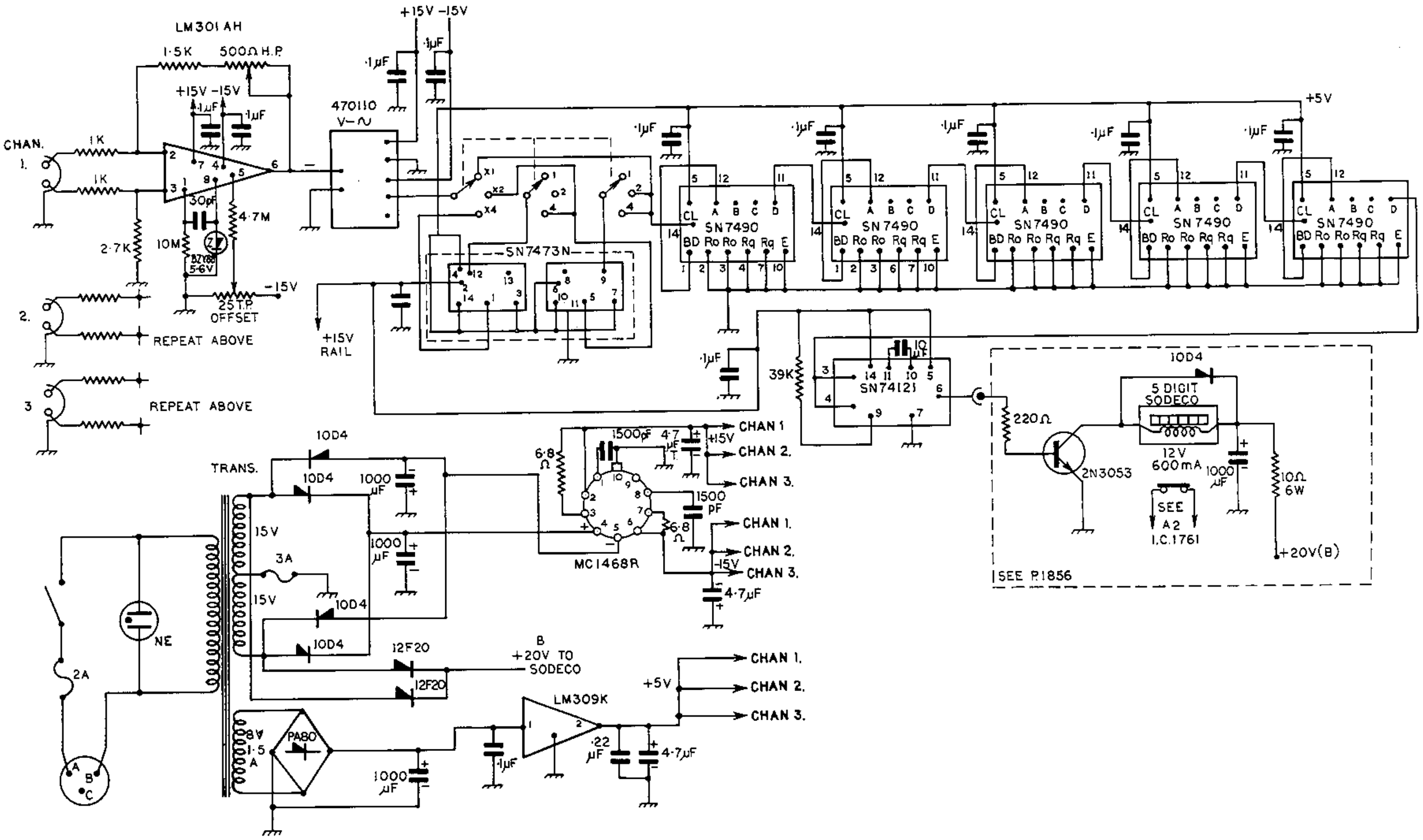
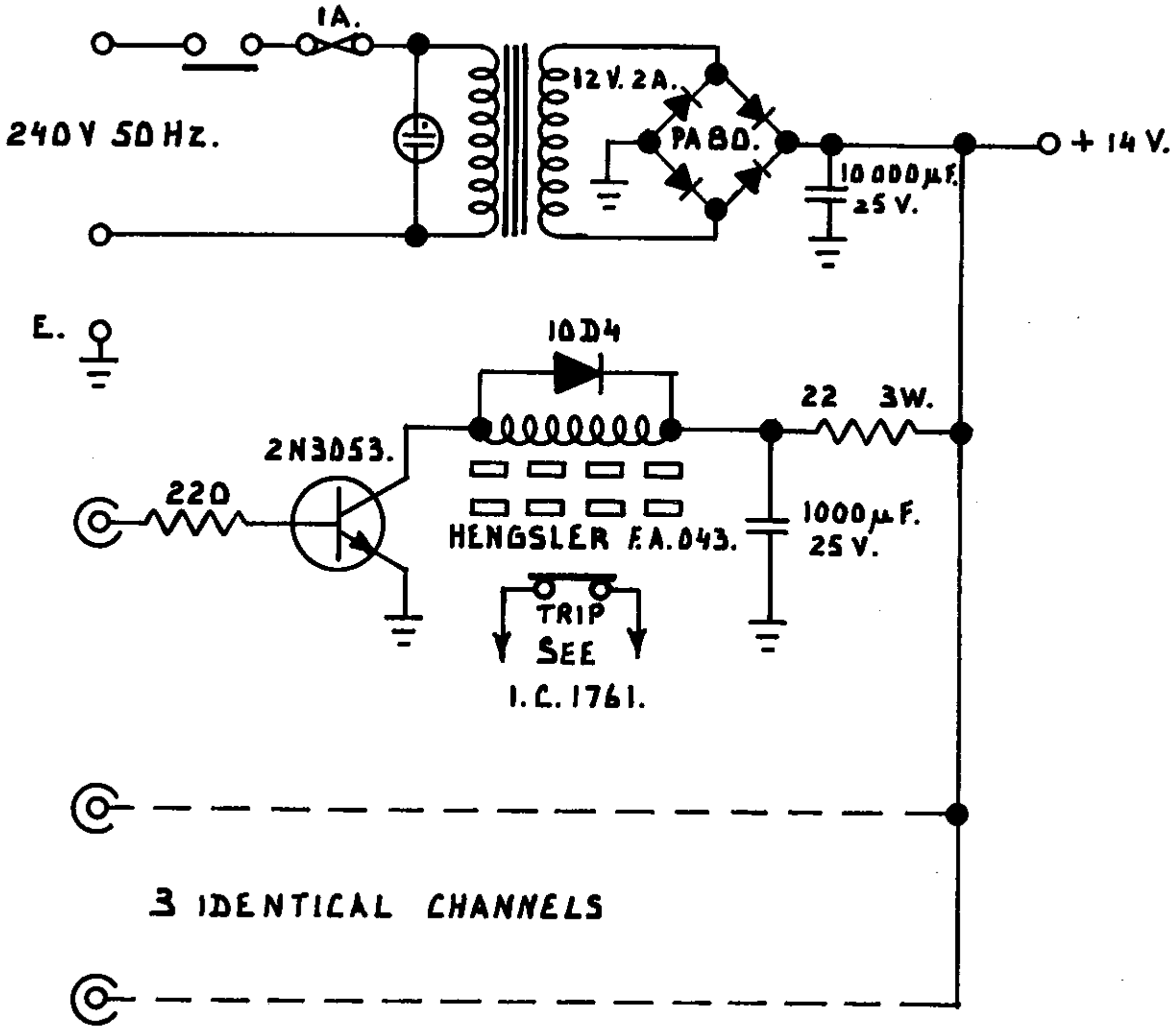


FIGURE 5. THREE-CHANNEL CURRENT INTEGRATOR TYPE 479(AAEC) CIRCUIT



INPUTS FROM PIN 6 OF 74121
OF TYPE 479

FIGURE 6. PRESET TRIPLE COUNTER TYPE 509(AAEC) CIRCUIT FOR CURRENT INTEGRATOR TYPE 479(AAEC)

DATE ____________

ELECTROLYSIS COMMENCED ____________ HOURS AT ______ AMPS

CELL No	TARE WEIGHT	CELL + SAMPLE	WEIGHT SAMPLE Wo	SAMPLE No	WEIGHT Na_2O_2 ADDED	CHECK WEIGHT	WEIGHT AFTER ELECT.	WEIGHT WATER + Na OH	WEIGHT WATER AFTER ELECT. Wt	Wo/Wt
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										

CALCULATIONS

DATE	HOURS	TIME	AMP	WATER ELECT	WATER LEFT	CORR. WATER LEFT	479 INTEG. READING

CHECK WEIGHING

CELL No	WEIGHT	WEIGHT LESS Na_2O_2	FOUND	CALC

FIGURE 7. DAILY LOG SHEET

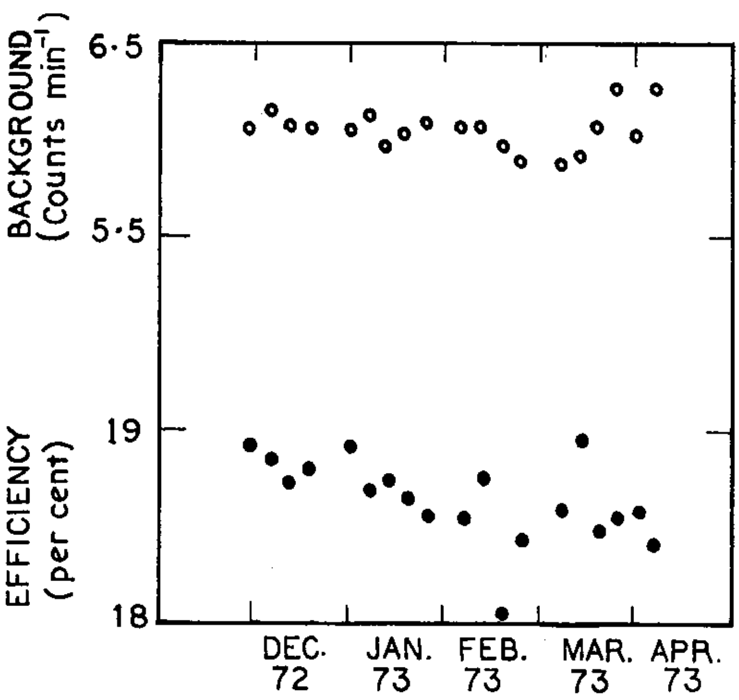


FIGURE 8. BACKGROUND AND EFFICIENCY VARIATIONS

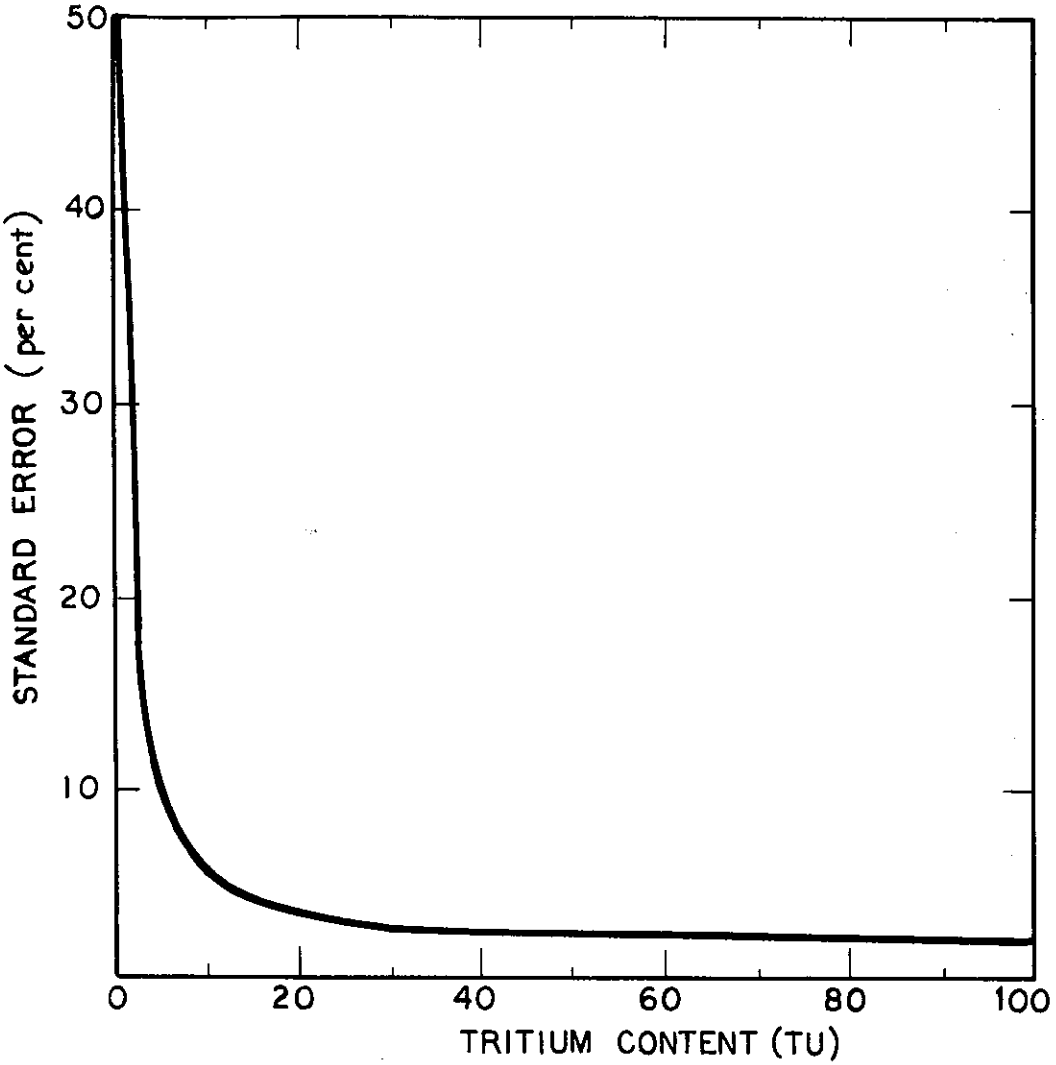


FIGURE 9. STANDARD ERROR OF MEASUREMENT WITH THE PRESENT SYSTEM AT VARIOUS TRITIUM ACTIVITIES