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DETERMINATION OF KEROSENE ENTRAINMENT LOSSES IN THE SOLVENT EXTRACTION OF A LEACH LIQUOR

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DETERMINATION OF KEROSENE ENTRAINMENT LOSSES
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Christian M. Lapointe*

ABSTRACT

The entrainment losses of kerosene in the barren raffinate, in the course of the solvent extraction of uranium from a leach liquor, have been determined by the addition of C^{14} -labelled decane to the circuit. The toluene extract of the raffinate was made the main constituent of a liquid scintillator in which the carbon activity was measured by means of a single channel beta-ray spectrometer. An average value of 33 ppm kerosene was found in the raffinate.

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INTRODUCTION

When evaluating the chemical processing costs of recovery of uranium from leach liquors by the solvent extraction method, the losses of solvent and diluent incurred in the operation of the circuit may be a decisive factor in the adoption of the method for a particular ore in a given location. This loss is inherent to the process, and unavoidable. Its value sets a limit to the economy of the process and, when accurately known, may be used as a basis for comparison of the operation in different plants, where other controllable losses may vary widely.

Two methods are now in common use for the determination of the diluent losses. In the first method, the inventory difference method, the solvent is contacted with a sulphuric acid solution until the steady state solubility loss is reached. Its volume is then measured, and it is cycled in a continuous extraction apparatus against a known volume of leach liquor. The volume of the solvent is measured at the end of the run and, if the amine molality has been determined before and after the cycle, the experiment supplies information on both the amine solubility loss and the total diluent loss, whether they are due to evaporation, to spillage, or to actual entrainment in the barren raffinate going to waste. This is the method currently used in the evaluation of uranium extractants (1).

A second method involves the direct determination of the diluent loss by entrainment in the barren raffinate. So far, the

determination of the kerosene content of the barren raffinate has been done by extracting the hydrocarbons with carbon tetrachloride and measuring the absorption with an infra-red spectrometer.

The availability of C^{14} -labelled decane, a homologue of the major constituents of kerosene, prompted us to tag the kerosene with the radioactive hydrocarbon and to try to follow the destiny of the tracer through the extraction process.

METHOD AND APPARATUS

The Solvent Extraction Apparatus

The solvent extraction continuous testing apparatus used at the Mines Branch has been described elsewhere(2). It consists of a bank of four mixer-settlers in which the leach solution is fed counter-currently to the organic phase, consisting of a 5% solution of the uranium solvent (TIOA, tri-iso-octylamine) in B. A. Jet Kerosene. After contact, the barren raffinate goes to waste. The loaded solvent is contacted with the strip solution in a two-stage mixer-settler, and the high-grade strip goes to precipitation, while the barren solvent is returned to the extraction circuit.

The volume of the organic phase being recycled is approximately twenty litres. Decane was chosen among available C^{14} -labelled hydrocarbons because it is a homologue of the main constituent of kerosene and will have no tendency to distill off preferentially. The amount used, 0.1 mc, was dictated by reasons of economy (C^{14} -decane costs \$400 per mc) and of safety: the extractor was operated

in the open, and, because of evaporation, the C^{14} content of the atmosphere had to be kept to a minimum.

The radioactive decane was diluted up to 100 ml with kerosene, and then distributed in the various compartments of the extractor for more rapid mixing. Actual sampling was started after several days of operation, to ensure a uniform distribution of the tracer and a steady state loss. The usual volume of barren raffinate samples was one litre; in certain cases, two-litre samples were taken, for greater accuracy in the measurements. At the time of sampling, 20 ml of the barren solvent was also taken, to be used as an internal standard.

Preparation of the Scintillator

The most sensitive method for the determination of the soft beta activity of radiocarbon consists in dissolving the active compound in a solvent capable of being used as the main component of a scintillator(3). Toluene was used, for obvious reasons. The one-litre barren raffinate sample was extracted in batches by repeated shaking with 100 ml toluene to which 5 ml inactive kerosene had been added in order to reduce the losses, if any, to the aqueous phase. The two phases were separated in an extraction funnel, and the toluene extract was washed three times with a sulphuric acid solution at pH 1.5. The use of distilled water for washing retards the phase disengagement. The extract was then shaken with a small amount of activated alumina, for drying and clarifying. After decantation, the liquid scintillator was prepared by adding to the toluene extract 0.4 g p-terphenyl and 10 mg

diphenyl-hexatriene(5, 6). When the measurements were to be performed at -70°C , 2,5 - diphenyl-oxazole was used instead of the terphenyl, and 2 % absolute ethyl alcohol was added. This solution remained perfectly clear at -80°C , and the addition of that small amount of alcohol reduced the pulse height by only about 5%.

The Scintillation Spectrometer

Figure 1 shows the arrangement of the liquid phosphor container, the multiplier phototube and its associated pre-amplifier, and the double-walled aluminum shield used for operation at dry-ice temperature. The phototube, a Dumont type 6292, was especially chosen for stability and low noise level. As will be explained below, argon has to be bubbled through the scintillator in order to sweep out any dissolved oxygen. The figure shows the argon bubbler, containing a 5% solution of kerosene in toluene. This solution saturates the argon and thus minimizes evaporation losses in the scintillator itself. The bubbler also acts as a rough flowmeter for the regulation of argon. After passing through the scintillator, the gas escapes through a small vent at the top of the container, thus maintaining a slight positive pressure over the liquid.

In order to increase the light collection and hence the pulse height, it is customary to coat the outside of the phosphor container with a diffuse reflector, such as alumina or magnesia. Excellent results were obtained here by evaporating aluminum in vacuo on the internal surface of the container. A thin coating of paraffin wax,

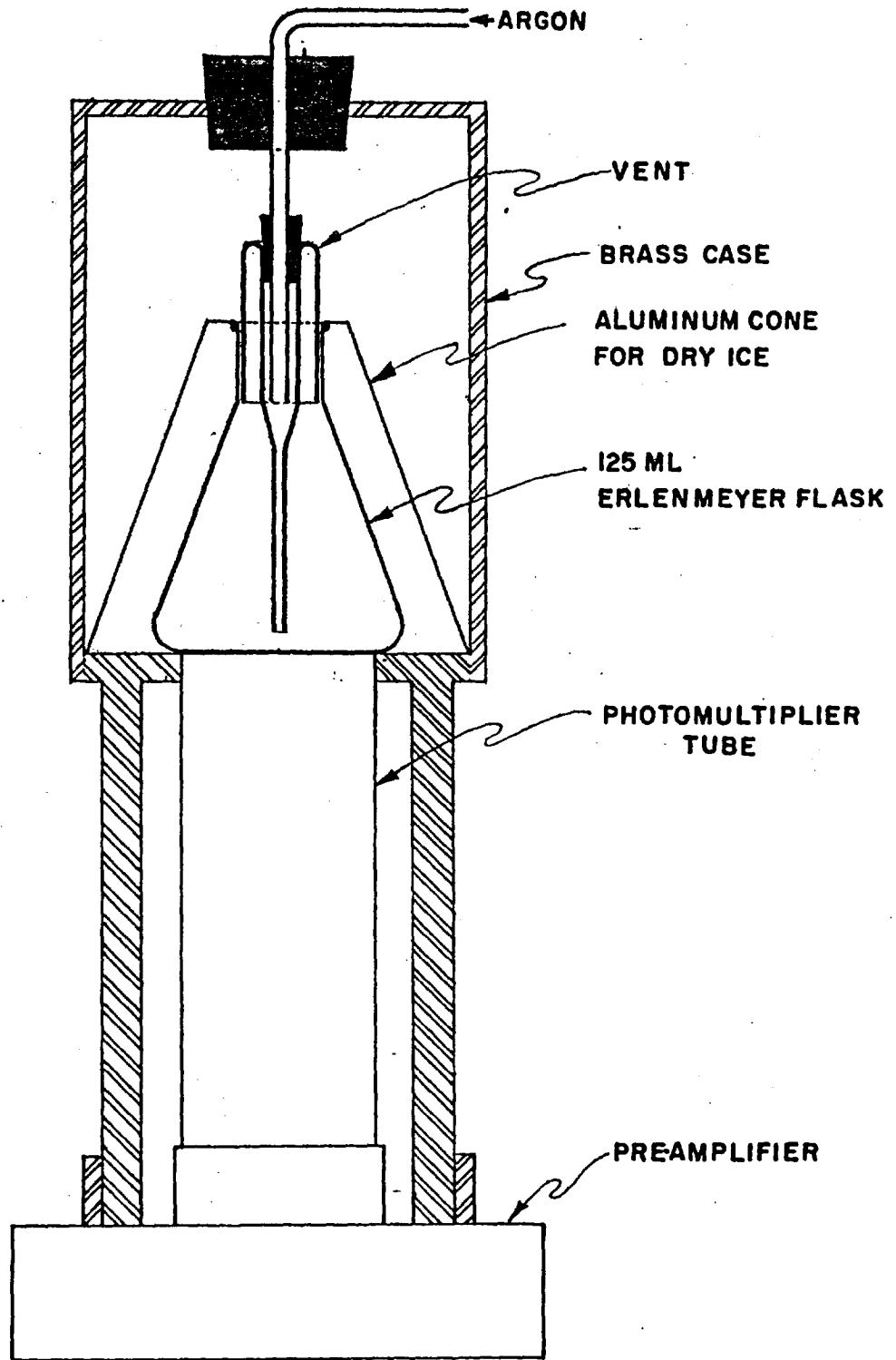


FIG. 1-LIQUID SCINTILLATION DETECTOR.

melted at the bottom of the glass flask, was dissolved after evaporation of the metal, leaving a clear window for coupling to the multiplier phototube. The aluminum coating, being a first surface mirror on a conical surface, approximated the properties of a parabolic mirror and reflected a large fraction of the light onto the photocathode. Comparison with an uncoated container showed that aluminizing increased the light collection by a factor of about 2.

The pulses from the pre-amplifier are fed to a type 1820 Nuclear-Chicago spectrometer. This unit, operating at 750 volts phototube voltage and maximum gain, is highly stable, and the spectrum obtained covers the energy region of zero to approximately 300 kev. The block diagram in Figure 2 shows that the following information can be recorded on the three scalers and on the ratemeter and its associated chart recorder:

- 1 - The integral count for particles of energies greater than 300 kev. This value is used for monitoring the background (scaler 1).
- 2 - The integral count for particles of energies down to near zero (scaler 2).
- 3 - The differential count for particles of energies smaller than 300 kev, in a band (window width) 30 kev wide (scaler 3).
- 4 - The differential or integral count rate corresponding to either scaler 2 or scaler 3 (ratemeter and recorder). This is used for monitoring long counting periods.

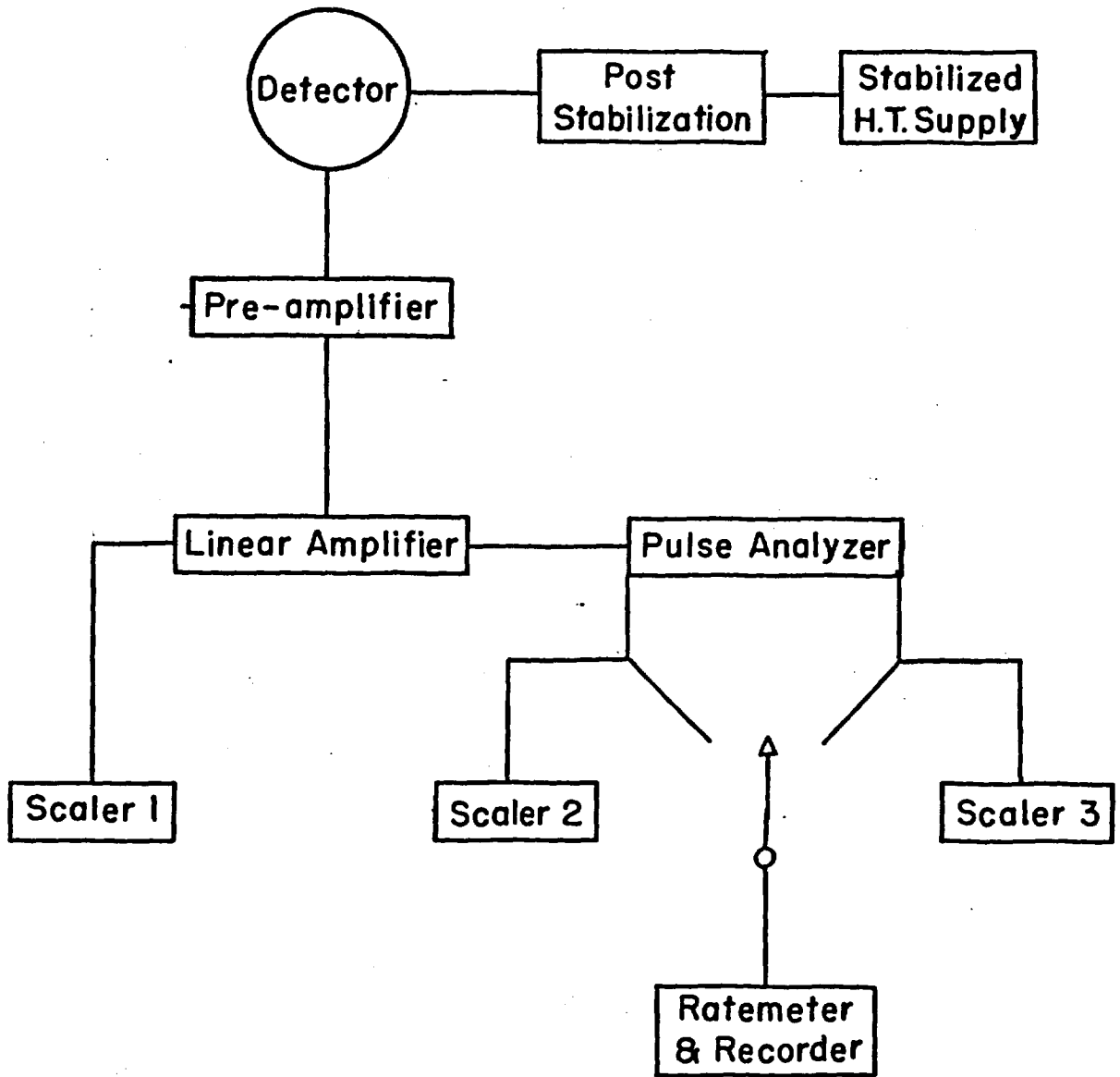


FIG.2-BLOCK DIAGRAM OF COUNTING SYSTEM.

The Technique of Measurement by Internal Calibration

When the radioactive source to be measured is distinct from the detector, it can be compared easily enough with a standard source in order to measure detector sensitivity and background and correct for them. But when it constitutes an integral part of the detector itself, several assumptions have to be made as to sensitivity, background, and calibration. Some of these assumptions can, however, be partly verified, and the reproducibility of the results constitutes the best check of their validity.

a) Constancy of pulse height for a given particle energy.

For a particle of given energy, the amplitude of the pulse obtained at the output of the multiplier phototube can be used to define the sensitivity. The pulse height varies with the voltage on the tube, the temperature, and the composition of the phosphor. In this study, the high voltage and the temperature were maintained constant, and the uniformity of the phosphors was ensured by careful mixing and aliquoting of the solid components. The remaining variable was the amount of pulse-quenching agents dissolved in the toluene during the extraction of the barren raffinate.

Besides extracting from the raffinate the trace of kerosene to be measured, with its tagged decane, the toluene will extract at least two quenching agents: some water, and most of the amine dissolved or entrained. Shaking the toluene extract with activated alumina was found to remove the water without appreciable removal

of the tracer. The quenching effect of up to 200 ppm amine was measured and found to be small (Figure 3). Correction is made for this effect by comparing the activity of a Cs^{137} standard source as obtained with the phosphor containing the amine with the activity obtained with a pure phosphor.

The important quenching agent present in the phosphor is dissolved oxygen. At sea level, toluene will absorb about 0.05 g/l of oxygen from the atmosphere. With the detector geometry used throughout this work, the integral counting rate for energies greater than 300 keV with an air-saturated phosphor is only half that obtained with an oxygen-free phosphor (Figure 4).

Of the various methods proposed for controlling the pulse-height quenching due to oxygen, it was found here that the simplest and most effective was the continuous bubbling of toluene-saturated argon through the scintillator, under a slight pressure. This ensures complete removal of oxygen and facilitates the calculation of corrections for quenching by other agents.

b) Constancy of the shape of the background curve.

When the C^{14} tracer is dissolved in the phosphor, background measurements can be performed only at energies greater than 150 keV, and a coefficient of regression has to be used to correct for the background under the C^{14} activity. This assumes that the background varies linearly in both regions of the spectrum, that is, that the shape of the background curve remains constant. This was

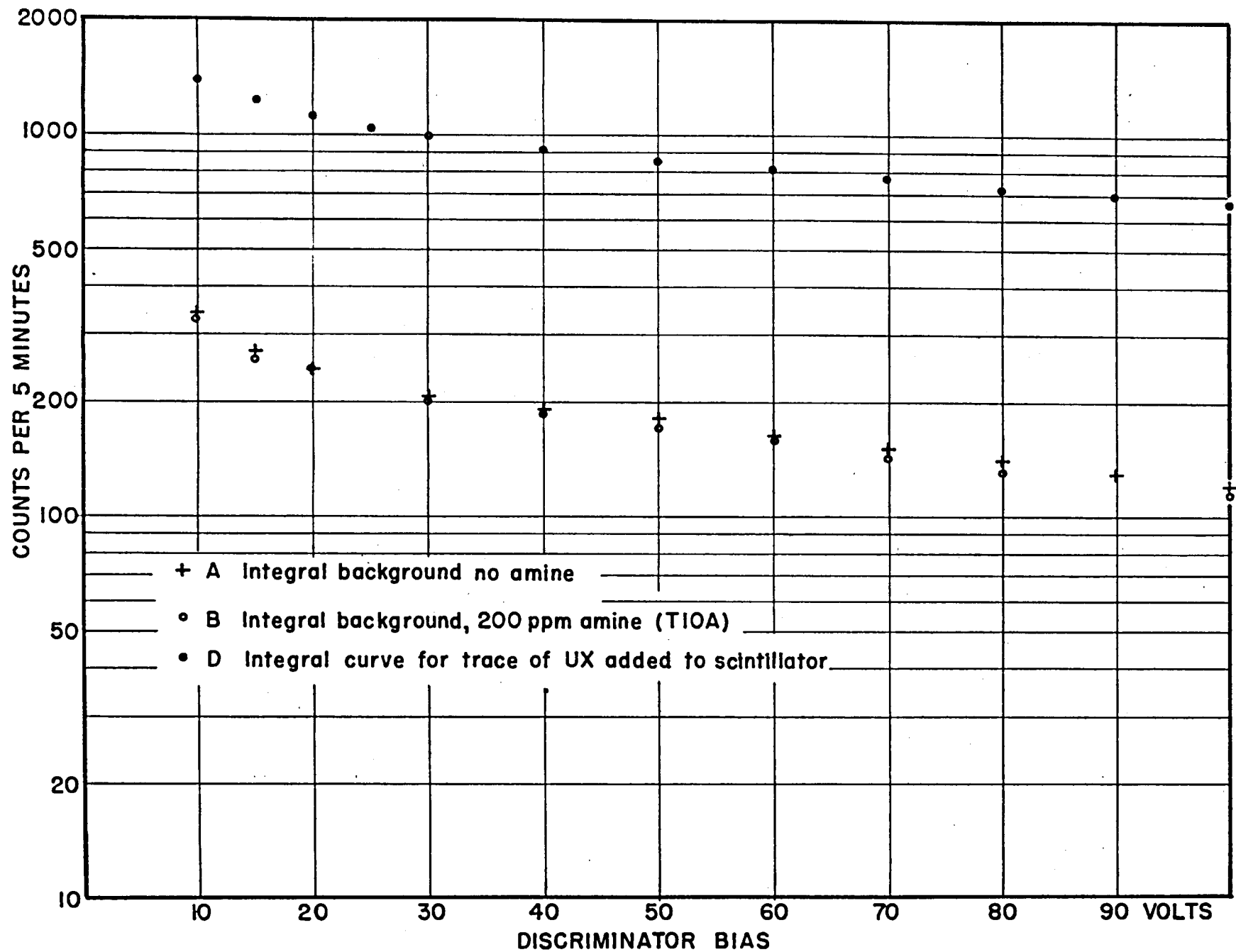


FIG.3 - PULSE QUENCHING BY AMINES AND ACTIVITY OF UX.

COUNT RATE - ARBITRARY UNITS

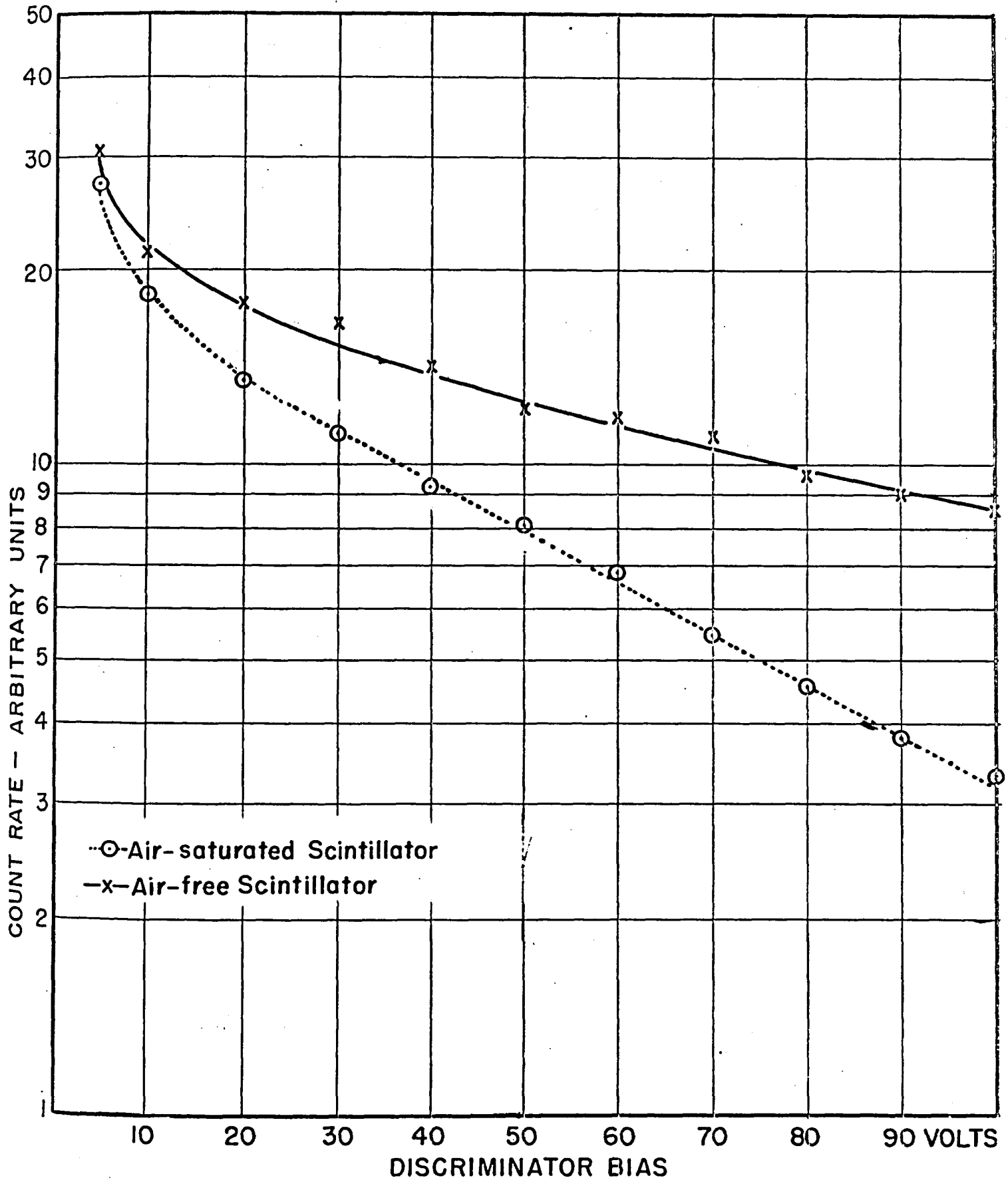


FIG.4 - PULSE QUENCHING BY AIR, INTEGRAL BIAS CURVE.

found to be true. Several tests run by adding to the phosphor contaminants likely to be found in the liquor, or by varying the thickness of shielding, proved that the regression coefficients remained the same within experimental error (see Figure 3). Actually, the background increases exponentially with decreasing energies, as expected, until it goes up sharply at the discriminator bias that allows noise from the multiplier to be counted. Plotting the results on semi-log paper allows for easy correction of fluctuations and easy calculations of tracer content.

Measurements

In order to obtain a representative value of the amount of kerosene lost in the barren raffinate, a total of twenty 1-litre samples were extracted, followed by two 2-litre samples for further checking.

The extractions and measurements were performed on the day following sampling, to minimize the effect on background of the growth of UX from any uranium that might have been extracted along with the kerosene and the amine.

After flushing with argon for about 20 minutes, no further improvement on the pulse height was noticed, and 10-minute readings were then taken at 5-volt intervals of the discriminator bias. Usually, three complete spectra (up to 300 kev) gave a reasonable statistical accuracy.

The external Cs¹³⁷ standard was used to calculate the correction for quenching. As the effect of quenching is shifting of the activities towards lower energies, the corrections have to be done

accordingly; so, instead of multiplying the number of counts by (1 + quenching factor), the readings are moved towards higher energies on the graph by a fraction equal to the quenching factor (Figure 3). The quenching factor was of the order of 5%. After the measurements on the sample were completed, 0.05 ml of the recycle solvent was added to the scintillator, argon was bubbled through, and another set of three spectra was counted as in the case of the tracer alone. Here again, the Cs^{137} external standard was used for quenching corrections. It was found that the amine contained in the recycle solvent had a small but measurable quenching effect.

Three pairs of results were normally used for the calculations, those pairs giving the activity of the tracer with and without the internal standard, for three 15 kev-wide-energy bands centred roughly at 30, 45 and 60 kev (Figure 5). The ratio of the net activities, of extracted tracer to internal standard, gave the kerosene content of the barren raffinate in terms of 50 ppm, as follows:

$$\text{ppm kerosene} = \frac{0.05 \text{ ml} \times a}{b \times 1000 \text{ ml}} = \frac{a}{b} \cdot 50 \times 10^{-6}$$

where a = activity of tagged kerosene extracted from
1000 ml barren raffinate, and

b = activity of 0.05 ml tagged kerosene.

RESULTS AND DISCUSSION

The average of twenty-two determinations, corresponding to 66 pairs of readings, gave a kerosene content of 33 ppm in the barren raffinate, with extreme values of 22 and 45 ppm. This is

COUNTS/5 MINUTES

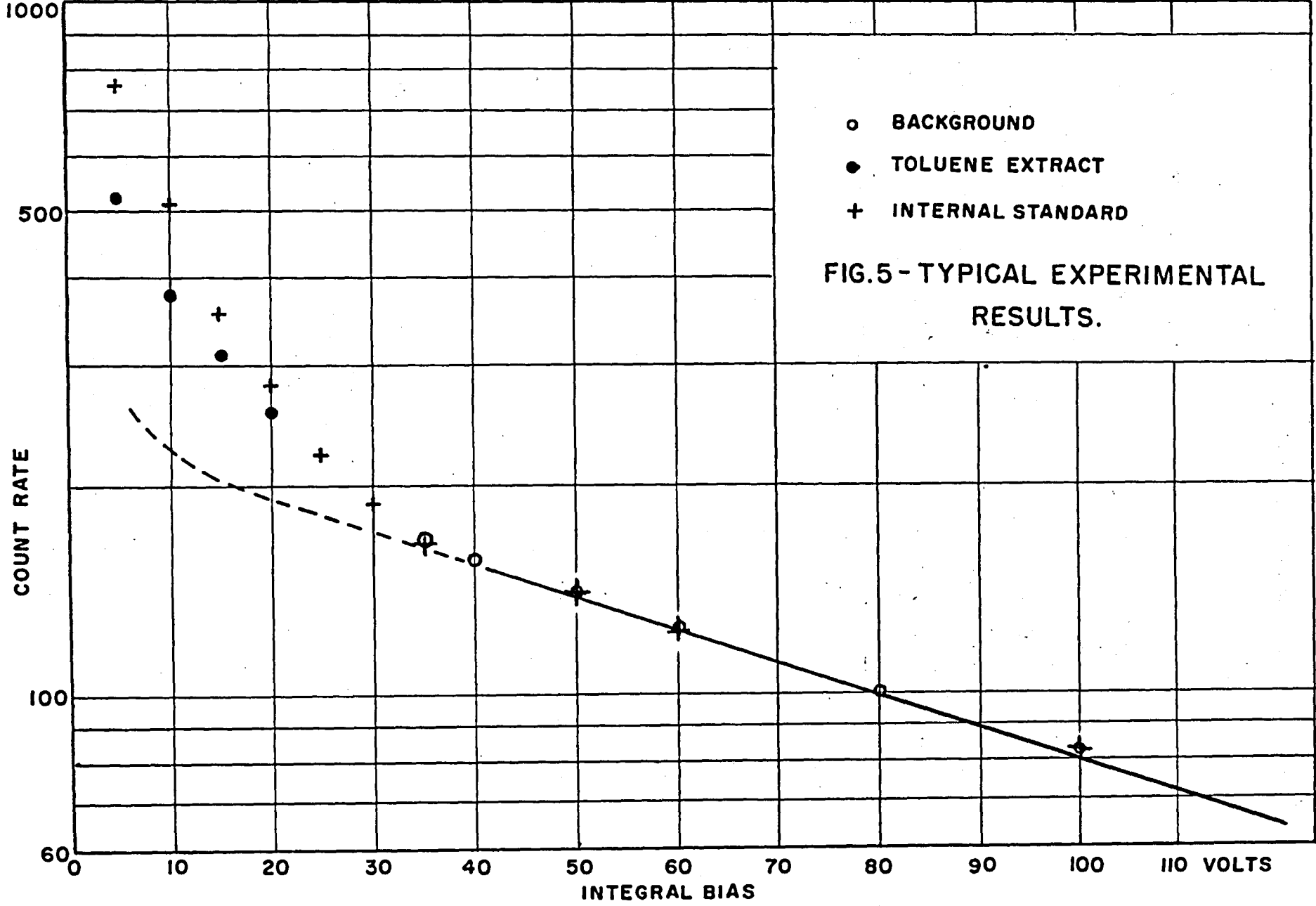


FIG.5 - TYPICAL EXPERIMENTAL RESULTS.

to be compared with a value of 11 ppm obtained in one infra-red spectrometer determination on a carbon tetrachloride extract⁽⁴⁾. It is intended to undertake a systematic study of the two methods in order to explain the apparent discrepancy.

Values for total kerosene losses, based on inventory differences, range anywhere from 50 to 500 ppm. Indeed, spillage and evaporation constitute the main factors in the total losses, and these items will be relatively more important in a small-scale apparatus than in a production plant. One plant (E. M. and R., Port Radium) operating with arctic fuel oil instead of kerosene, and under conditions where evaporation and spillage are kept to a minimum, reports total losses comparable with probable entrainment losses.

ACKNOWLEDGMENTS

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