CANADA

CONTINUOUS MONITORING OF URANIUM LEACH SOLUTIONS

by

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SYNOPSIS

A method for the determination of uranium content in leach solution by scintillation alpha-ray detection has been developed for possible application to the continuous monitoring and control of breakthrough in ion exchange columns. The radioactive solution flows through a circular cell containing several thin disks of a plastic scintillation phosphor which respond to bombardment by alpha particles from uranium atoms in the solution. The fluorescence produced in the phosphor is observed and amplified by means of standard scintillation counter techniques. Breakthrough curves have been obtained by this method, and correlation with various alpha emitters has been attempted by the use of an alpha-ray spectrometer. Positive detection of activity to levels down to 0.2 g/l equivalent uranium content in solution seems possible on a continuous basis.

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Rapport de recherches de la Direction des mines R 59

CONTRÔLE CONTINU DE SOLUTIONS DE LESSIVAGE D' URANIUM

par

G.G. Eichholz[A]

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RÉSUMÉ

On est parvenu à déterminer la teneur en uranium d'une solution de lessivage à l'aide d'un scintillomètre des rayons alpha. Il se peut qu'on puisse appliquer ce procédé au contrôle continuel des interférences dans les colonnes d'échange des ions. La solution radioactive traverse un bac circulaire à plusieurs disques minces d'une substance plastique luminescente qui réagit au bombardement des particules alpha provenant des atomes d'uranium de la solution. La tache fluorescente que produit l'impact des particules sur la substance luminescente est détectée et amplifiée a l'aide d'un scintillomètre classique. On a ainsi enregistré des courbes d'interférence et, à l'aide d'un spectromètre à rayons alpha, on a essayé de les mettre en corrélation avec différentes substances radioactives émettant des particules alpha. Il semble possible de déceler l'activité de façon positive dans le cas de solutions qui contiennent aussi peu que 0.2 g/l d'équivalent d'uranium.

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CONTENTS

INTRODUCTION

In leach processes for the extraction of uranium from its ores and in subsequent chemical purification steps it would be advantageous if the actual uranium content of the various solutions could be monitored and recorded instantaneously and continuously. Such monitors might then be adapted to control the particular extraction process or to warn of excessive contamination in waste solutions. For this purpose it is tempting to turn to the peculiar property of uranium among natural substances, namely, that it is radioactive and emits high energy radiations. The practical difficulty that one encounters, however, is that purified uranium with all its daughter elements removed, emits only alpha particles. Though quite energetic, with an energy of 4.18 MeV, these particles have a short range in air and are easily absorbed in all solids and liquids, so that their range in water is only of the order of 25 microns.

For this reason attempts to monitor the uranium content of solutions continuously have not been very successful so far. The continuous monitoring of streams for fission products and other gamma emitters can be done fairly easily. (Wilson (1). Wingfield (2) and others), but for alpha emitters it has become customary to monitor by sampling the solution or stream automatically at fixed intervals. From these samples the uranium is extracted as an insoluble compound which is deposited on disks or filters and then

counted with a zinc sulphide scintillation counter. Such methods have been described by Smales et al. (3), LeFranc et al. (4), and Wingfield (5). The only equipment which has been described in the literature for direct continuous monitoring of alpha emitters in solution is that of Taylor and Abson (6). Their apparatus consisted essentially of a rotating drum which dipped into the liquid and pulled up a thin liquid film by surface tension. This film passed under a zinc sulphide scintillation counter, in close proximity but without contact, and the alpha emission from the solution was thus determined. This ingenious method, however, did not work out too well in practice, as it was difficult to maintain uniform films on the drum under operating conditions and the sensitivity proved to be insufficient.

The work at the Mines Branch, Ottawa, arose principally from a desire to monitor the breakthrough of uranium in ion exchange columns used for the extraction of uranium in acid leach circuits, but the system developed may well have wider applications. Its main principle consists of detecting the alpha particles continuously by placing the detector in contact with the liquid. To compensate for the low sensitivity attainable, and because it is only the surface layer of the detector which responds to the alpha particles, it is important to increase the surface area used to detect the alpha particles. A further difficulty arises from the acidity of the leach solutions which attack unprotected inorganic scintillators and this

requires careful design of the detector cell.

A first approach to this problem was attempted in 1951 by applying a thin coating to zinc sulphide films, the usual scintillating detector for alpha particles, to protect the zinc sulphide against corrosion from the solution (7). This protective coating had to be uniform and free of pinholes, yet thin enough to permit easy passage of the alpha particles, while being fully resistant to strong sulphuric acid solutions. These requirements seemed to be mutually exclusive and this approach was abandoned in favour of one using thin plastic scintillation phosphors which at that time had just been developed (8, 9).

The advantage of the plastic scintillators lies in the fact that they are made of polystyrene and are acid resistant and easy to manufacture in any desired shape or thickness. As plastic scintillators are also sensitive to gamma-rays, it is important to make them as thin as practicable to minimize counts from radium daughters and cosmic-ray background. The scintillation flashes produced by alpha particles in plastic scintillators are much smaller than in zinc sulphide and good optical coupling is important. The remainder of the detection equipment consists of standard photomultiplier tubes, a ratemeter and a recorder.

DESCRIPTION OF APPARATUS

For test purposes, work with different detectors was carried out inside a large light-tight box which permitted maximum flexibility in changing detector types and configurations. Figure 1 presents an overall view of the equipment used during measurements on barren solutions from a small ion exchange column. The ion exchange column can be seen on the shelf to the left. In the middle is the light-tight box, in the open position, in which the photomultiplier is supported vertically within its shield, and a detector cell rests on the light-sensitive photocathode of the photomultiplier. To the right of the box can be seen a rack with a linear amplifier and a scaler, and further to the right a ratemeter and a strip-chart recorder. Depending on the nature of the tests either the scaler or the ratemeter was used as the count indicator.

Figure 2 is a close-up picture of the interior of the box, showing, on the left, a 5-inch photomultiplier tube which was used in some tests and, on the right, a 2-inch tube covered by a stainless steel detector cell. Another, all-plastic detector cell can be seen above it. Most of the test work was done with the cheaper 2-inch photomultiplier tube, type 6292, since, contrary to expectations, no appreciable increase in sensitivity and performance was obtained with either of two 5-inch photomultipliers, type 6364, which were tried.

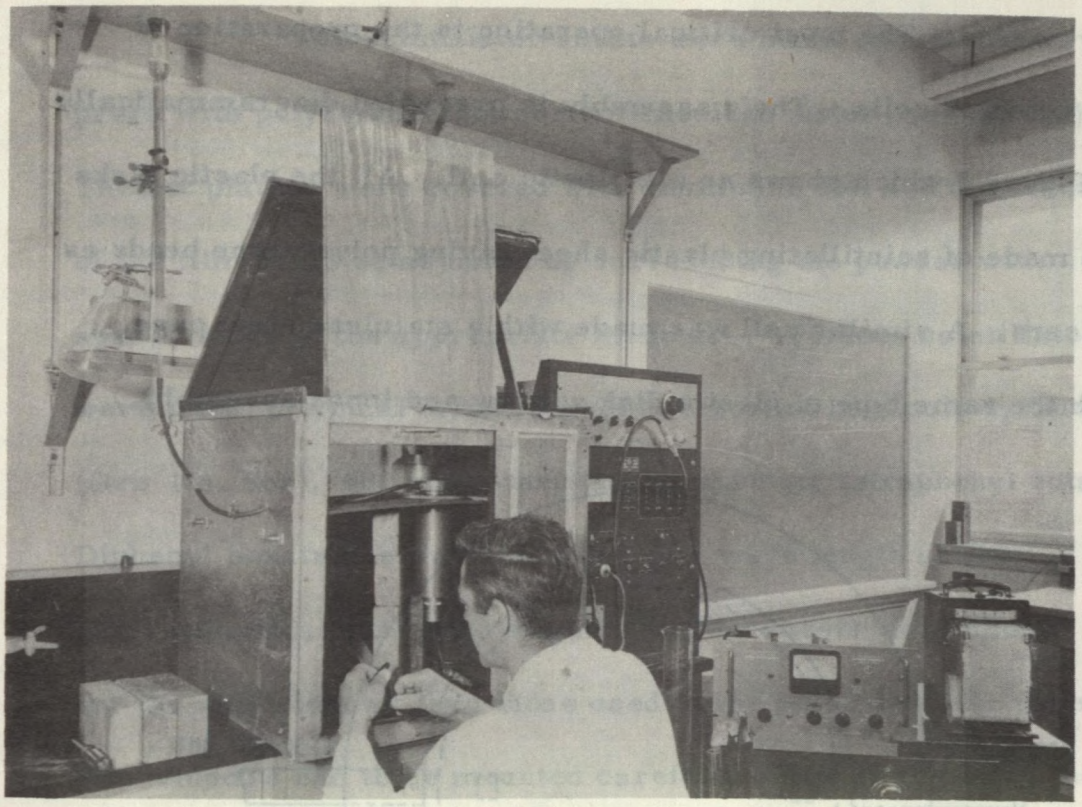

Fig. 1.- View of Experimental Equipment

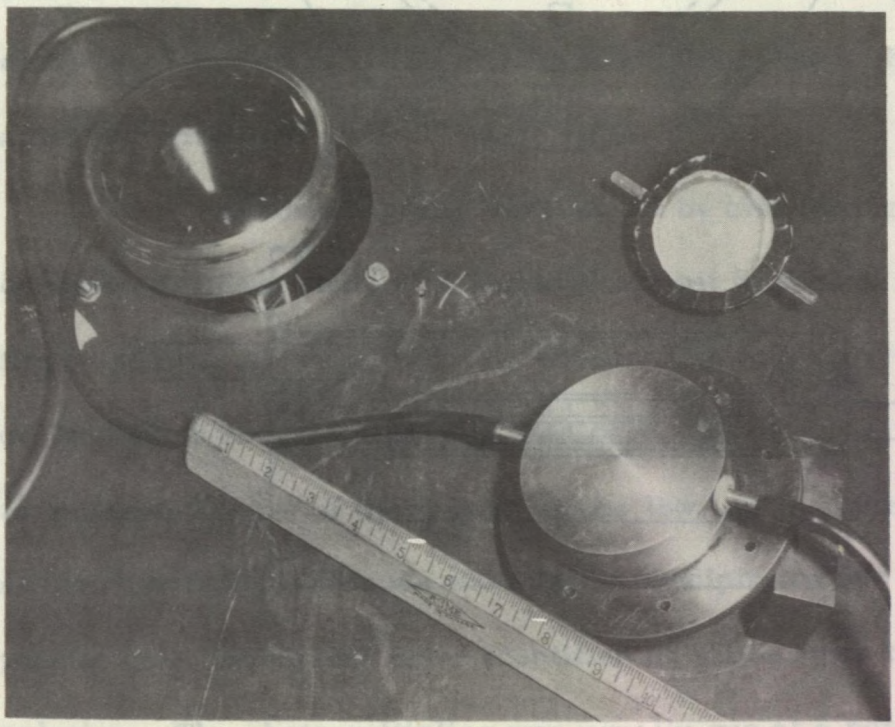

Fig. 2. - View of Detector Cells

The most critical operation is the preparation of the detector cells. Their assembly is presented diagrammatically in Figure 3 which shows an all-plastic cell. All the plastic disks are made of scintillating plastic sheet having polystyrene beads as spacers. A similar cell was made with a stainless steel case, with the same type of plastic disk window and inner assembly.

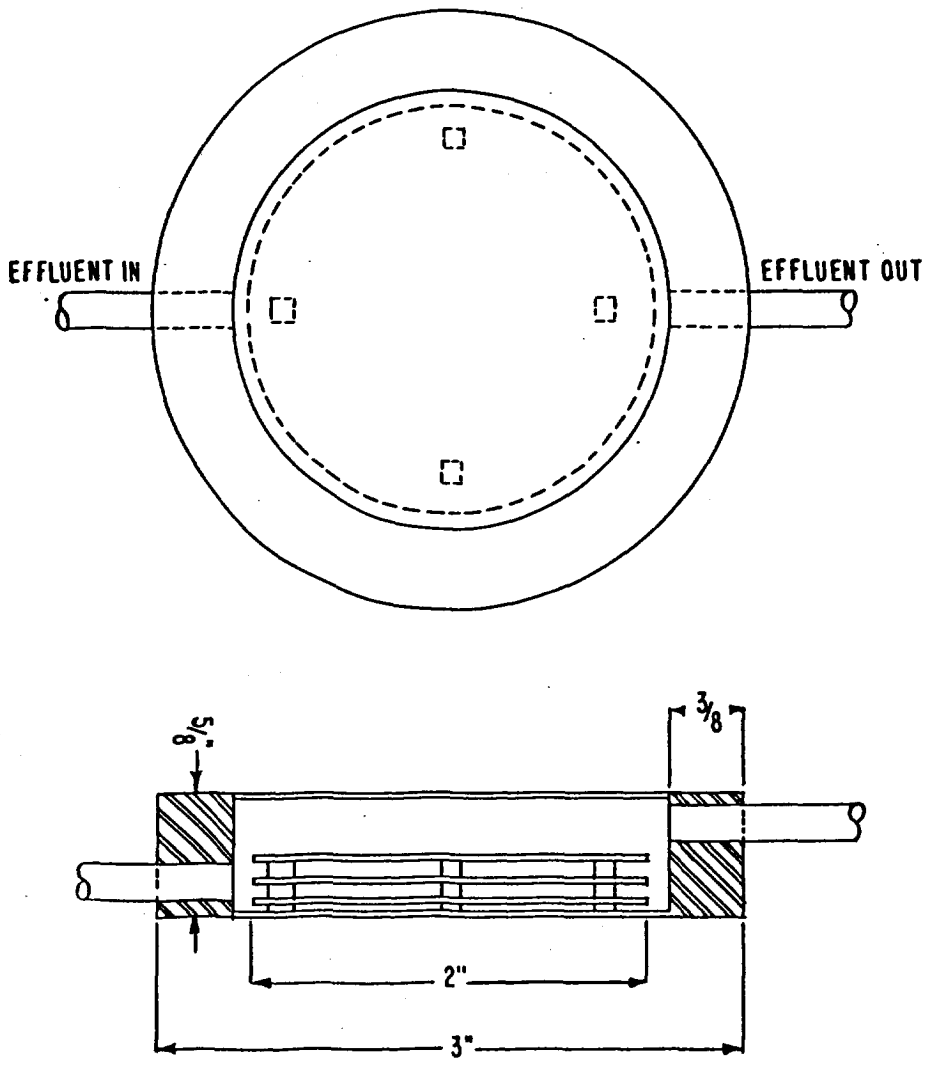

FIG.3-SCINTILLATING PHOSPHOR DETECTOR CELL FOR ALPHA COUNTER.

The scintillator sheets were made on a laboratory press with polystyrene powder hot-moulded under pressure (8). The hot platens were covered with aluminium foil and the thickness of the film could be adjusted by surrounding the powder with spacer rings of the appropriate thickness. Various scintillators were tried; a typical mixture would consist of 10 g polystyrene (Dow No. 666), 400 mg p-terphenyl and 10 mg tetraphenyl butadiene. Diphenyl hexatriene was also used as a wave length shifter. For mechanical strength, slightly thicker sheets were chosen for the cell windows than those used in the inner detector assembly. The windows had to be mounted carefully since in operation they are subjected to considerable liquid pressure, and leaks could be disastrous. Absolute cleanliness is essential to avoid grease films on the detector disks. The disks were cut out with a sharp point around a heavy cylindrical guide.

Calibration was carried out by circulating solutions of known uranium content in a closed circuit by means of a Sigma finger pump. All runs with test solutions from the ion exchange column were done with gravity feed only. It was found important to maintain the pH of the test solutions low, as in some early tests at near neutral pH a dense solid layer precipitated out on the plastic cell, which was later identified as silica from the leach solution. The photomultiplier was usually run at a potential of around 1100 volts.

TEST RESULTS

Owing to the intermittent nature of this project over the years 1954-1959, conditions varied from test to test and only typical results will be quoted here.

1. Detector Tests

Experiments were carried out with various detector configurations and have been described more fully in a previous report (10). Only the main conclusions will be summarized here. Figure 4 shows the effect of scintillator thickness on count rate. It is seen that for thicker films there is considerable self-absorption of the fluorescent light. In practice, detector sheets were kept well below 15 mils.

Figure 5 shows the response curve obtained with high grade solutions in a four-disk detector cell. The response is seen to be linear over most of the range. At the upper end it appears to level off, but this effect is ascribed to loss of light in passing through the solution, which was noticeably yellow at the higher concentrations. This light loss sets an upper limit to the number of disks that can usefully be employed. Table 1 presents results obtained in a typical case with different numbers of detectors.

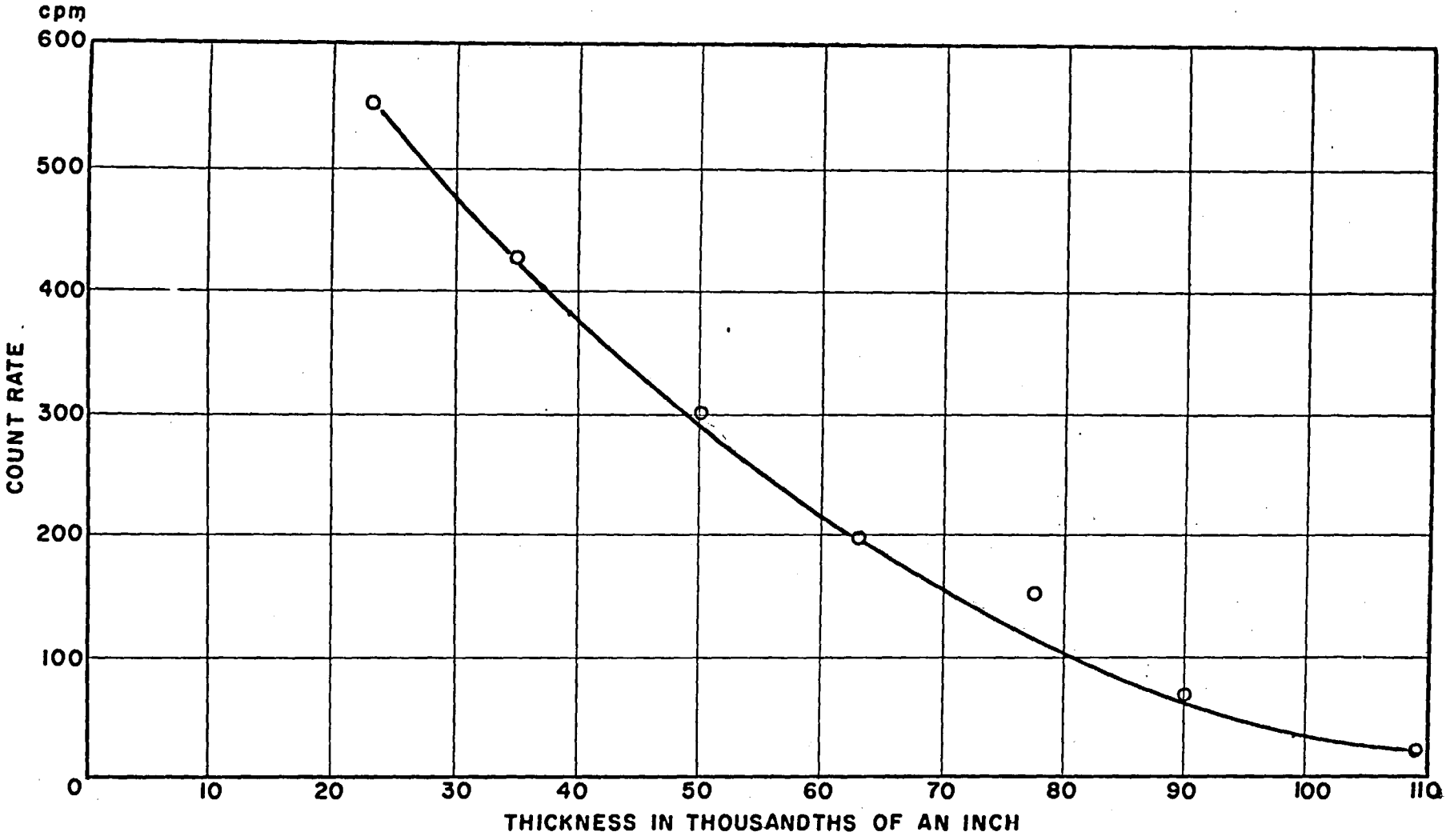

FIG. 4 - EFFECT OF PHOSPHOR THICKNESS ON ALPHA-RAY DETECTION.

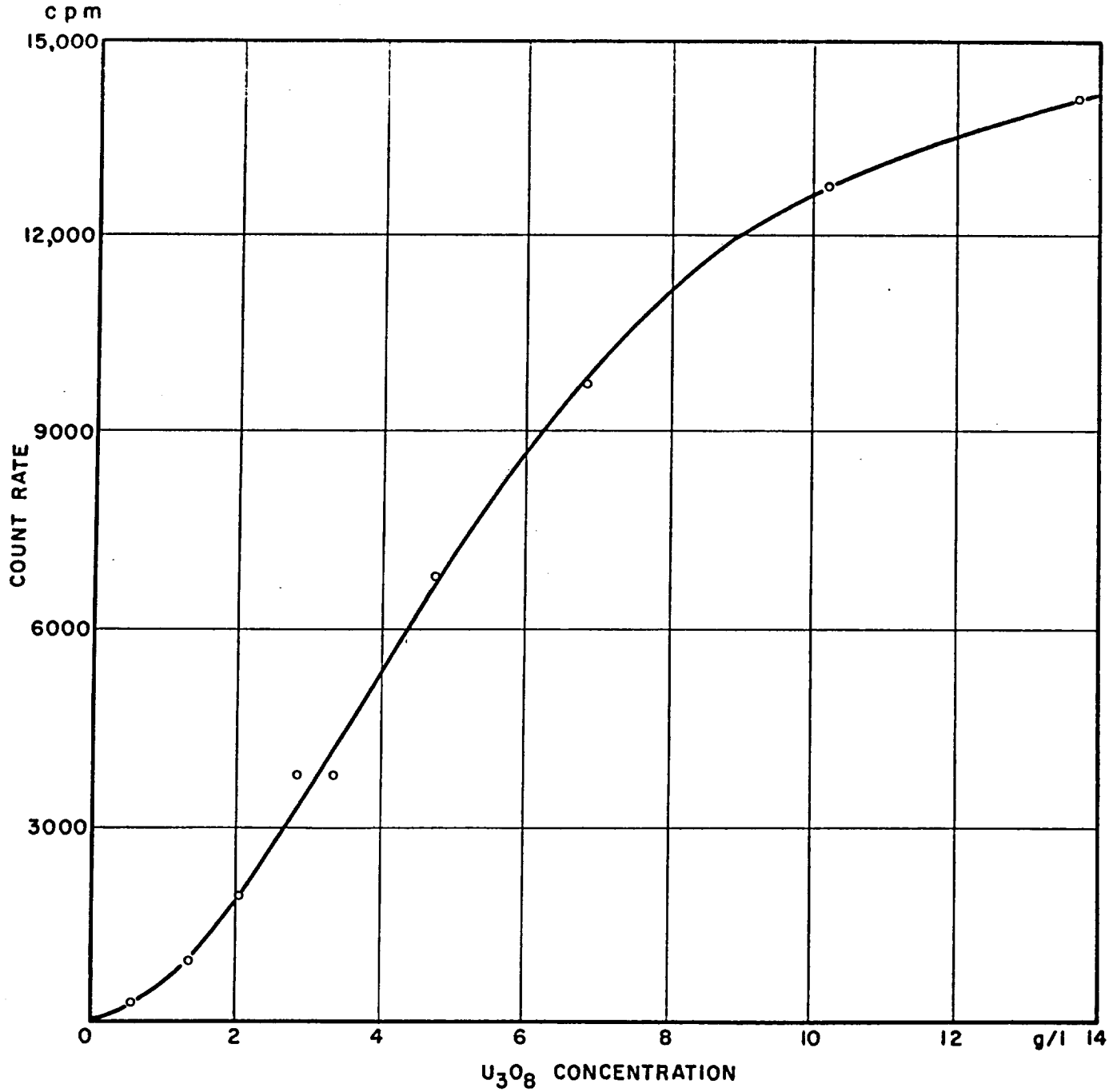

FIG. 5 - EFFECT OF CONCENTRATION ON COUNT RATE.

TABLE 1

Effect of Varying the Number of Detector Disks

Number of detectors	Count rate
1	3437 cpm
2	7345
3	11958
4	14743

It is seen that the count rate goes up steadily for all disk assemblies shown. In practice, four or five disks have been used for convenience. Larger assemblies pose problems in parallel mounting.

2. Calibration

The system was calibrated by circulating synthetic uranium solutions through it. The solutions contained between 0.1 and 2 g/l U_3O_8. Figure 6 shows the appearance of the recorder chart for such a calibration, and Figure 7 is the corresponding calibration curve. It is seen that with the ratemeter time constant used, 0.1 g/l U_3O_8 is almost indistinguishable from background and represents the practical limit for the particular detector cell used. The recorder trace can be smoothed out by using a longer time constant in the ratemeter, and this is satisfactory when no abrupt changes in uranium content of the effluent are anticipated.

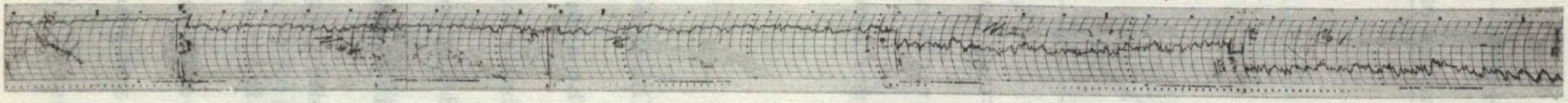

Fig. 6. - Recorder Trace of Calibration Runs
(Each step corresponds to different standard solution)

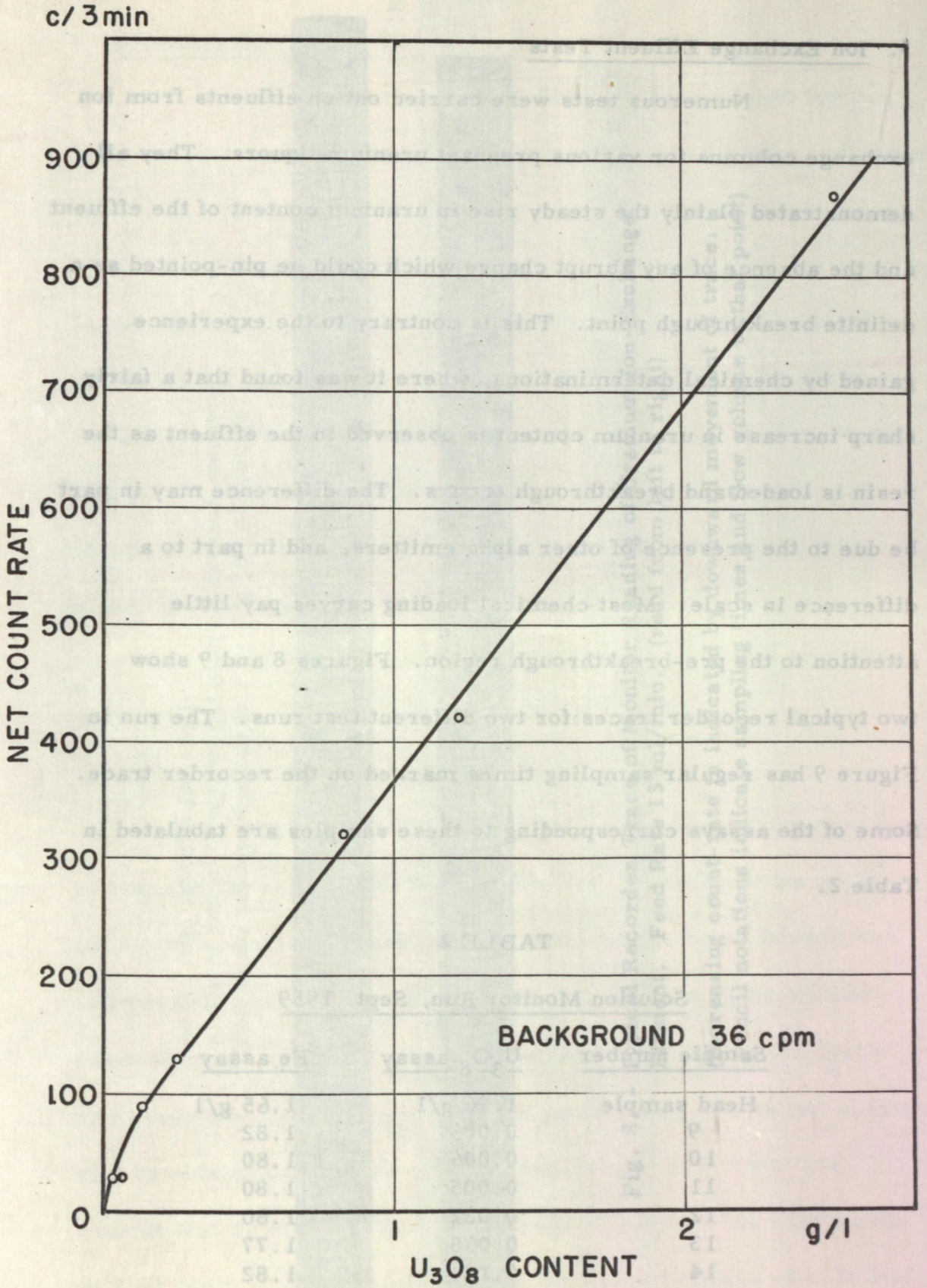

FIG. 7 - CALIBRATION FOR URANIUM SOLUTIONS.

3. Ion Exchange Effluent Tests

Numerous tests were carried out on effluents from ion exchange columns for various pregnant uranium liquors. They all demonstrated plainly the steady rise in uranium content of the effluent and the absence of any abrupt change which could be pin-pointed as a definite breakthrough point. This is contrary to the experience gained by chemical determinations, where it was found that a fairly sharp increase in uranium content is observed in the effluent as the resin is loaded and breakthrough occurs. The difference may in part be due to the presence of other alpha emitters, and in part to a difference in scale. Most chemical loading curves pay little attention to the pre-breakthrough region. Figures 8 and 9 show two typical recorder traces for two different test runs. The run in Figure 9 has regular sampling times marked on the recorder trace. Some of the assays corresponding to these samples are tabulated in Table 2.

TABLE 2

Solution Monitor Run, Sept. 1959

Sample number	U_3O_8 assay	Fe assay
Head sample	1.96 g/l	1.65 g/l
9	0.006	1.82
10	0.006	1.80
11	0.005	1.80
12	0.022	1.80
13	0.068	1.77
14	0.14	1.82
15	0.21	1.62

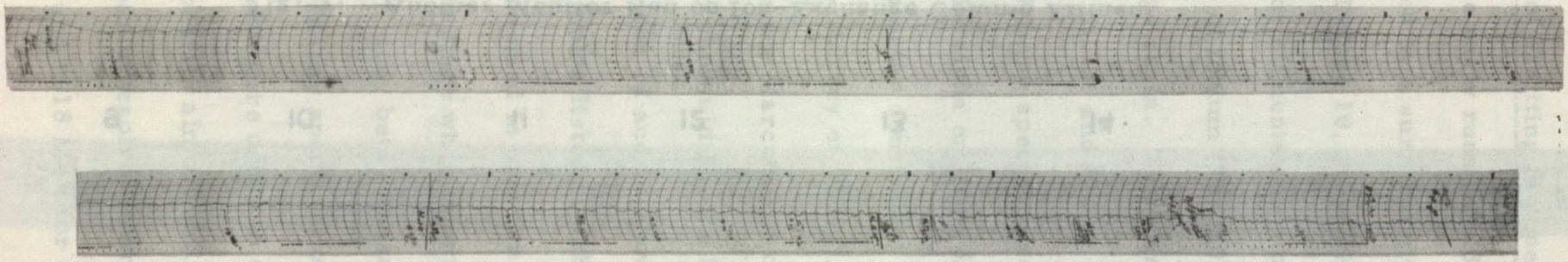

Fig. 8. - Typical Recorder Trace of Monitor Reading of Uranium Ion-Exchange Effluent. Feed Rate 13 ml/min. (read from left to right)

(Increasing count-rate is indicated by downward movement of trace. Pencil notations indicate sampling times and flow volume to that point)

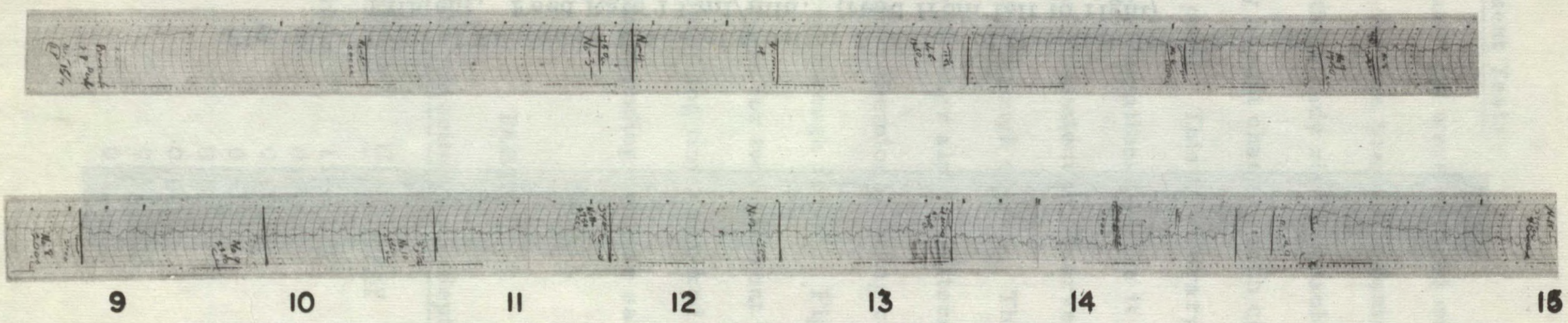

Fig. 9. - Another Monitor Run on Ion-Exchange Column Effluent

(Low count region between No. 14 and 15 represents break in run to check background by passing distilled water only through the cell)

4. Identification of Emitting Isotopes

Some early runs with different pregnant leach liquors were characterised by a surprisingly rapid rise in detector indication. This is shown in Figure 10, in which the monitor indications for typical leach liquor effluents are plotted. The early rise was ascribed to the appearance of ionium (Th-230), which is replaced by uranium on the ion exchange resin. This was reportedly one of the difficulties encountered with Taylor and Abson's equipment (6). To investigate this point, an alpha-ray spectrometer was set up as an aid in the identification of the alpha emitters in the various samples. The alpha-ray spectrometer consists of an ionization chamber of the type described by Harvey et al.(11), followed by a linear amplifier, AEP type 1444, and a Marconi six-channel pulse height analyser. This equipment is shown in Figure 11.

Figures 12 and 13 show the alpha-ray spectra corresponding to some of the samples listed in Table 2. According to the usual, arbitrary criterion used in uranium leach work, breakthrough was considered to take place when the uranium content in the effluent exceeded 0.01 g/l, i.e. between samples No. 11 and 12. Figure 12 compares the alpha-ray spectrum of sample No. 12 with two spectrum curves obtained with pure uranium standards. It is seen that sample No. 12 consists almost entirely of thorium-230 with a peak at 4.68 MeV, clearly resolved from the uranium peaks at 4.76 MeV for uranium-234 and 4.18 MeV for uranium-238.

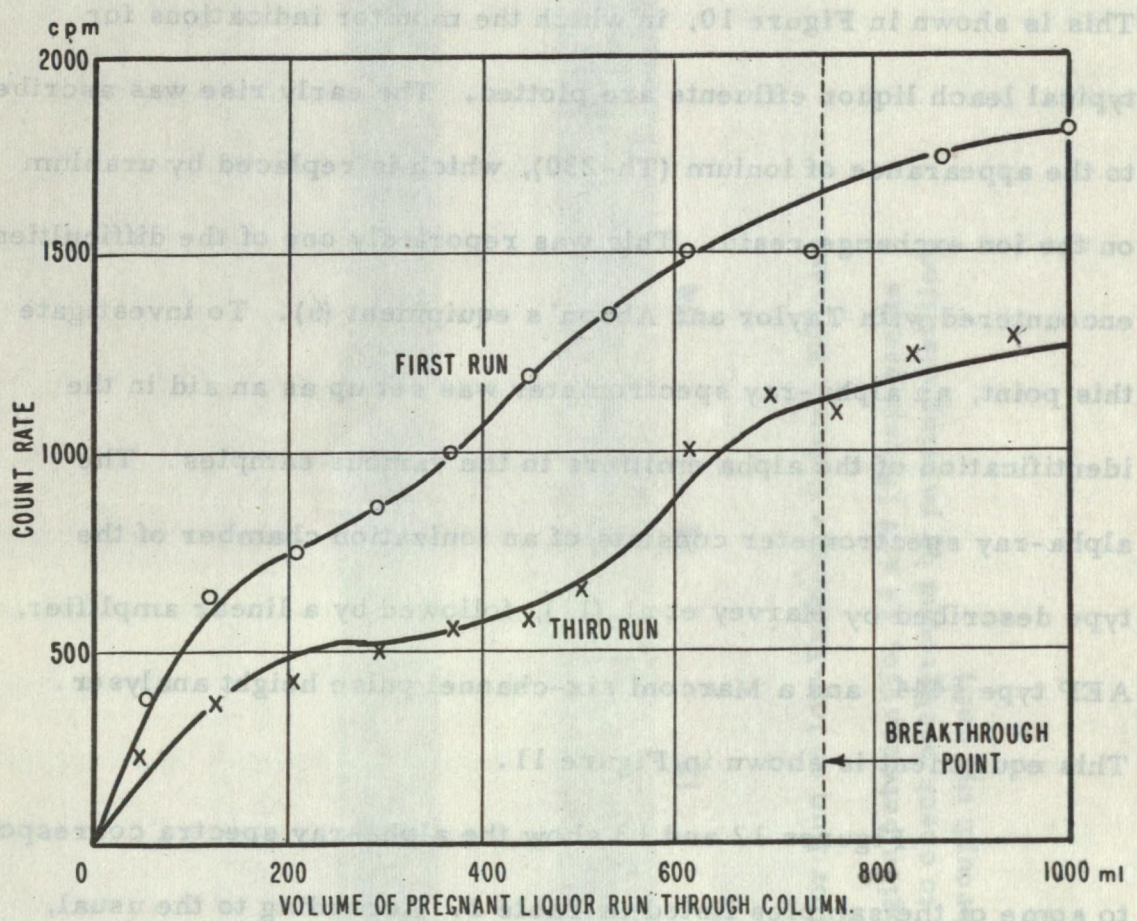

FIG. 10 - MONITOR INDICATION OF URANIUM CONTENT IN TYPICAL TEST RUNS.

(BREAKTHROUGH POINT DETERMINED COLORIMETRICALLY.)

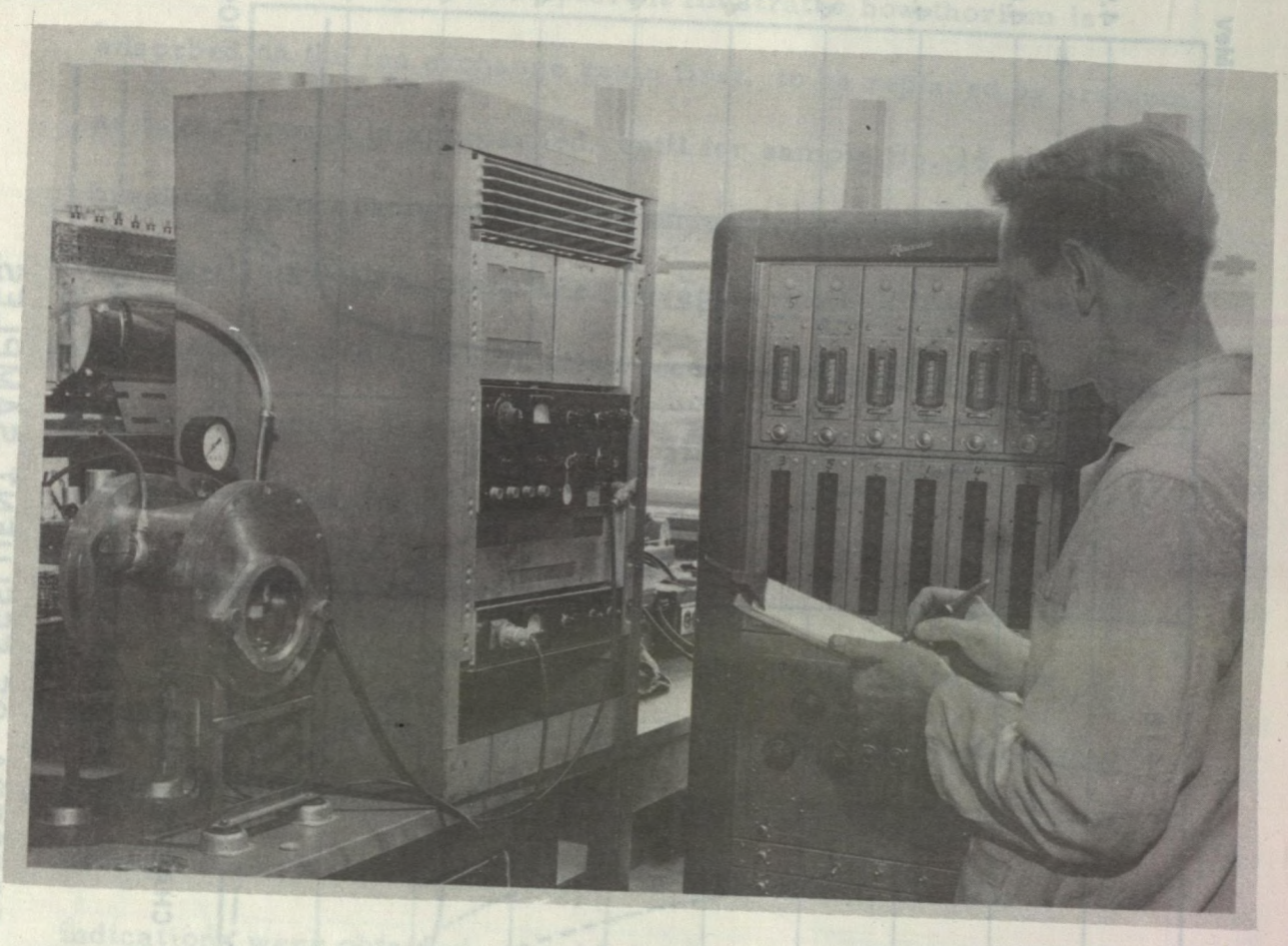

Fig. 11. - Alpha-ray Spectrometer

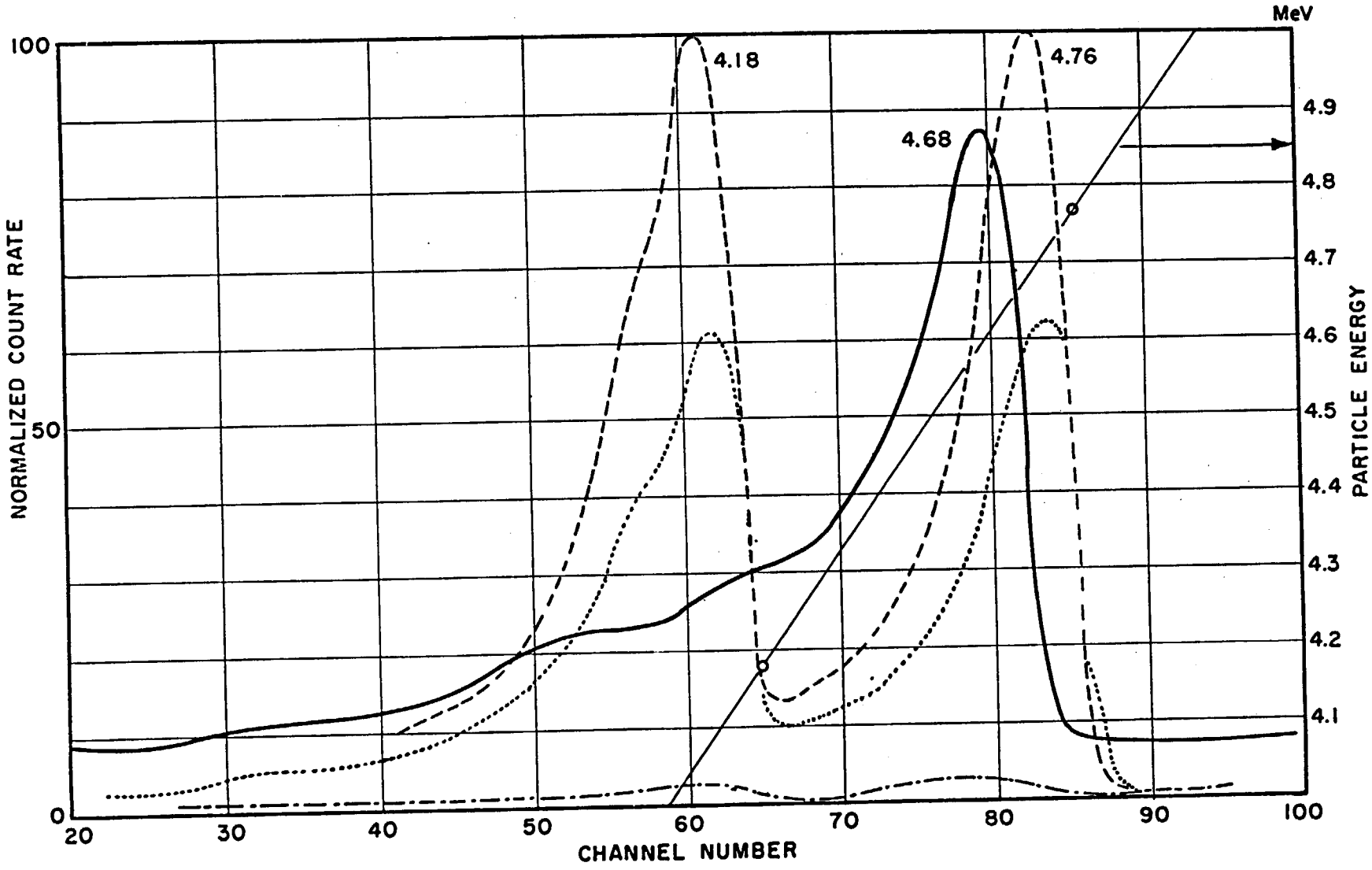

FIG. 12 - ALPHA-RAY SPECTRA OF EFFLUENT SAMPLES.

Figure 13 shows the progressive change in the alpha-spectra from sample to sample. It illustrates how thorium is adsorbed on the ion exchange resin first, to be replaced by uranium as breakthrough is approached, until for sample No. 16, long after breakthrough, uranium clearly predominates in the effluent. In this particular case, therefore, the appearance of ionium (Th-230) in the effluent and on the monitor records is linked so closely with the occurrence of breakthrough for uranium that it cannot be considered objectionable.

5. Other Uranium Solutions

To test the usefulness of the equipment in other applications, carbonate solutions from the leach plant of Eldorado Mining and Refining Limited at Beaverlodge, Sask., were run through the system. It was found that satisfactory monitor indications were obtained, provided that the liquors were filtered to remove all solid residues.

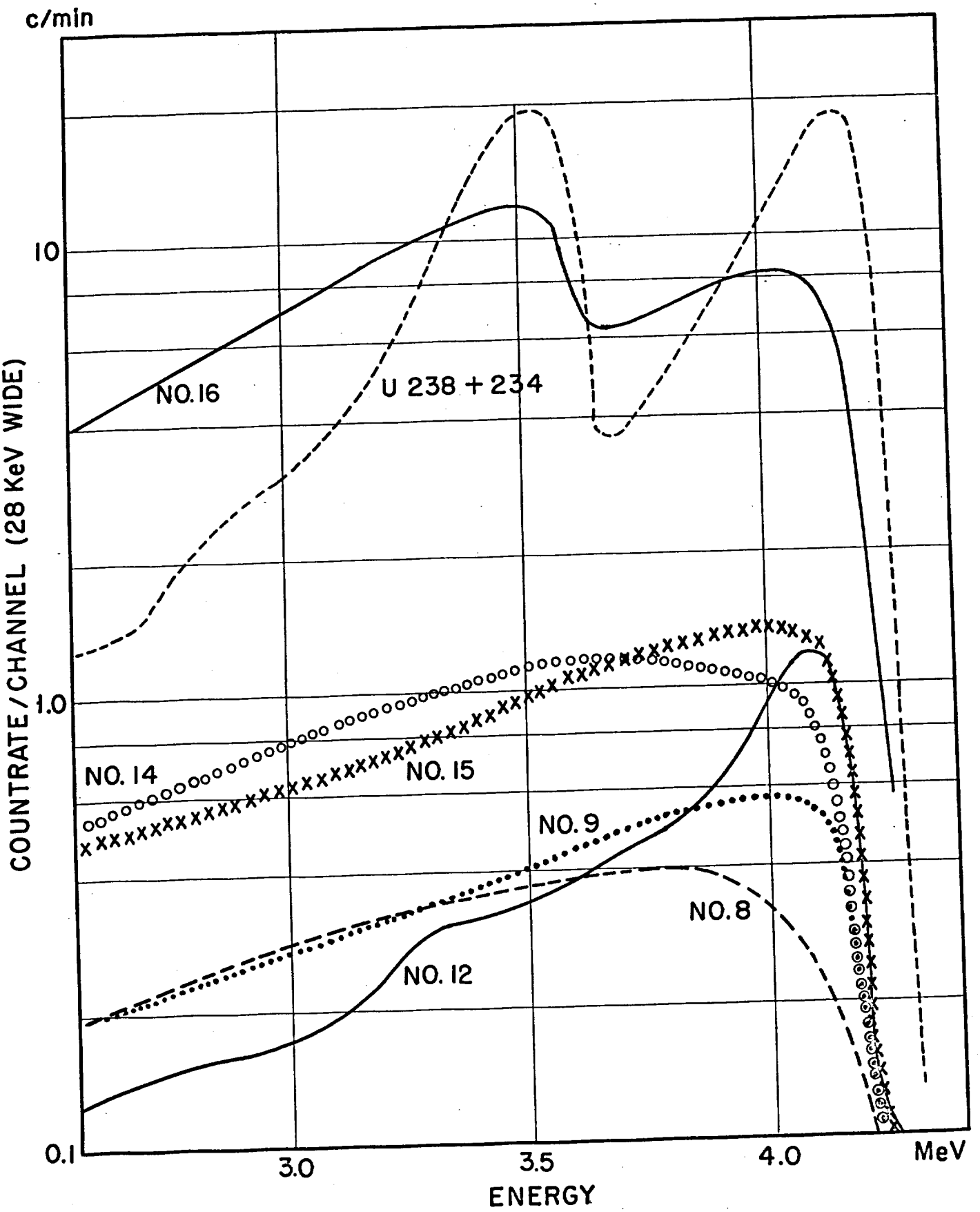

FIG. 13 - ALPHA-RAY SPECTRA OF EFFLUENT SAMPLES.

CONCLUSIONS

The tests indicate that it is possible to monitor uranium-bearing solutions continuously by the use of a plastic scintillator detector cell. While this method is less sensitive than methods using intermittent sampling and radiochemical purification, it is faster and more convenient. The limit in sensitivity for a given detector is set by the spontaneous fluctuations in count rate, which in turn depend on the time constant of the ratemeter. Where a slow response is adequate, a longer time constant may be used to give a smoother output indication. For a sensitive, rapid response the fluctuations are too great and the variation in count rate too slow to permit actual control of the ion exchange column by breakthrough indication. However, the monitor can serve as a useful indicator of improper operation of the column or of premature breakthrough. It may also be useful in plutonium plants and in uranium refining.

ACKNOWLEDGMENTS

It is a pleasure to record the patient and persevering assistance of J.M. Lefebvre who prepared all the detectors and carried out much of the test work, and the contributions of H.H. Schwartz and R.A. Wilkinson. Dr. J.D. Keys set up the alpha-ray spectrometer and C. McMahon and J.L. Horwood obtained the spectra. This project was suggested by the late Dr. E.A. Brown and the author owes much to discussions with him on various aspects of this work.

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