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ANALYSIS OF DILUTE NATURAL URANIUM SOLUTIONS
BY GAMMA-RAY EXCITED X-RAY FLUORESCENCE

by

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ABSTRACT

Application of a gamma-ray excited X-ray fluorimeter to batch analysis of uranium solutions containing less than $10 \text{ g } \ell^{-1}$, and particularly of dilute impure solutions, is described. An outline is given of design details of the gamma-ray excited X-ray source and of the comparison of backscattered incident X-rays and fluorescent X-rays as a means of compensating for variations in the matrix solution. For pure solutions the lower limit of detection was $0.03 \text{ g } \ell^{-1}$, compared with $0.05 \text{ g } \ell^{-1}$ for typical impure solutions. In the range 0.1 to $10 \text{ g } \ell^{-1}$, an accuracy of ± 5 per cent was obtained, while in the range 0.05 to $0.1 \text{ g } \ell^{-1}$, the accuracy was ± 30 per cent.

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ACCURACY; CALIBRATION; COUNTING RATES; ELECTRONIC EQUIPMENT;
QUANTITATIVE CHEMICAL ANALYSIS; URANIUM; URANIUM COMPOUNDS;
X-RAY DETECTION; X-RAY FLUORESCENCE ANALYSIS; X-RAY SOURCES;
X-RAY SPECTROMETERS

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1. INTRODUCTION

Radioisotope instruments are finding increasing application to measurement and control in processing plants (IAEA 1966, 1970). As part of the AAEC program of research into processes for the production of nuclear grade uranium dioxide from Australian ores (Alfredson 1970, 1972), simple, accurate and reliable instruments were required for the rapid analysis of uranium solutions in the range 0.01 to 400 g ℓ^{-1} . Most analyses were required for solvent extraction processes in which we are concerned with either relatively pure concentrated solutions or impure dilute solutions. In both cases, analysis on a batch basis, by withdrawing a sample from the process stream and measuring the uranium concentration, was satisfactory although on-line analysis is also advantageous. A gamma absorptiometer (Yates & May 1970) was developed for uranium determinations in the range 10 to 400 g ℓ^{-1} with an accuracy of 1 per cent and 1 to 10 g ℓ^{-1} with an accuracy of 5 per cent. This report describes a gamma-ray excited X-ray fluorimeter for the batch analysis of uranium solutions (particularly impure solutions) containing less than 10 g ℓ^{-1} .

X-ray generators have been widely used for analysis by X-ray fluorescence, but recently radioisotope X-ray sources have been demonstrated and used for the analysis of several elements, including uranium (Rhodes 1966, Watt 1967, Snyman 1971). Radioisotope X-ray sources are simple, compact and of low cost compared to conventional X-ray generators. Mackay & Thorne (1960) suggested the use of a radioisotope X-ray source (employing americium-241) for on-line determination of uranium and plutonium by X-ray fluorescence and Mackay (1961) discussed various aspects of the type of source, counter and required geometry. Several workers have indicated that a sensitivity of 0.04 g ℓ^{-1} can be achieved (Mackay 1961, Forberg & de Ruvo 1965, Rhodes 1968). The design of our instrument was based on that of Mackay (1961), but particular attention was given to its accuracy for the analysis of impure solutions and methods of compensating for variations in these impurities. This report records this experimental work for comparison with the performance of modern commercial instrumentation including solid state detectors.

2. PRINCIPLES OF X-RAY FLUORESCENCE ANALYSIS

2.1 Theory

Analysis by X-ray fluorescence is based on the excitation and detection of the fluorescent X-rays characteristic in energy of the desired element. While photons interact with matter by pair production, the photoelectric effect and Compton scattering, only the photoelectric effect produces a characteristic X-ray. Since this effect is found to decrease with increasing

incident photon energy, the highest sensitivity is obtained when the element is excited by mono-energetic X-rays of energy just above its critical absorption edge.

Gunn (1963) has shown that for thin films of low concentration of absorber

$$C \propto I_d \quad \dots(1)$$

The notation is defined in Section 8.

For thick samples Ellis *et al.* (1968) showed

$$C = k_1 N_f (\mu_i + \mu_k) \quad \dots(2)$$

The X-rays incident on the detector (intensity N_1) not only include the wanted fluorescent X-rays but also those from the matrix elements together with scattered X-rays produced by both Compton and coherent scattering of the exciting X-rays. If the intensity (N_s) of the scattered X-rays is measured, the intensity of the wanted fluorescent X-rays is given by

$$N_f = k_2 + N_1 + k_3 N_s \quad \dots(3)$$

Matrix effects can be compensated for by using a mean mass absorption coefficient to replace $(\mu_i + \mu_k)$. This mean mass absorption coefficient (μ) is determined from a measurement of the scattered X-ray intensity (N_s)

$$\mu = k_4 / N_s \quad \dots(4)$$

If there is no element with an absorption edge between the energies corresponding to μ and μ_i or μ_k then

$$(\mu_i + \mu_k) = k_5 \mu \quad \dots(5)$$

The presence of an element with an absorption edge in this energy region can be allowed for by a further correction factor if the concentration C_B of that element is known;

$$(\mu_i + \mu_k) = k_5 \mu + k_6 C_B \quad \dots(6)$$

An estimate of the value of $k_6 C_B$ can be obtained from

$$k_6 C_B = k_7 N_1 + k_8 \quad \dots(7)$$

Thus Equation 2 becomes

$$C = k_1 (k_2 + N_1 + k_3 N_s) (k_8 + \frac{1}{N_s} + k_7 N_1) \quad \dots(8)$$

The use of a pulse height analyser to restrict the energy range of the measured X-rays allows the correction term $(k_3 N_s + k_2)$ for the interfering

X-rays to be ignored. Further, the absence of any elements whose absorption edge lies between the energies corresponding to μ and μ_i or μ_k (as in this work) allows the correcting term $(k_7 N_1 + k_8)$ to be neglected. Thus Equation 8 becomes

$$C = k_9 \frac{N_1}{N_S} \quad \dots (9)$$

2.2 Matrix Effects

Changes in the solution matrix (*i.e.* presence of impurities) cause considerable variations in the intensity of the fluorescent X-rays owing to variations in the mass absorption coefficients of Equation 2, enhancement of the fluorescent X-rays by other elements and the effects of heterogeneity. Since this application was concerned only with the analysis of solutions, heterogeneity was not a problem. Enhancement of the fluorescent X-rays has been reported by Rhodes (1966) to be small except when elements (*e.g.* strontium, molybdenum) are present producing fluorescent X-rays of similar energy to those of uranium.

Many attempts have been made to compensate for matrix effects and the most useful methods are listed in Table 1. Most of these methods are not suitable for the present application because they significantly increase the time required for analysis and/or the complexity and cost of the instrument. However, comparison of the backscattered incident X-rays and the fluorescent X-rays is a relatively simple method of compensating for the matrix and was adopted in this case.

3. DESCRIPTION OF THE INSTRUMENT

The instrument comprised the gamma X-ray source, sample cell, detector and associated electronic equipment. Figure 1 outlines the components of the system, Figure 2 shows the arrangement of the head assembly and Figure 3 is a general view of the equipment.

3.1 Gamma Ray Excited X-ray Source

X-ray fluorescence may be based on the excitation of either the K or L X-rays. In this work, we chose to excite the L X-rays of uranium rather than the K X-rays because photoelectric absorption is much higher at the L level and Compton scattering is less significant. Thus an X-ray source was required with energy greater than 21.75 keV (the L_1 absorption edge), but less than 70 keV at which fluorescence efficiency is poor and shielding a problem (Mackay 1961). However, because a xenon-methane filled proportional counter was used as the detector (see Section 3.3), the upper energy level was limited to 34.6 keV (the K absorption edge for xenon) to avoid xenon fluorescence.

A gamma-ray excited X-ray source (γ X source) comprising 10 mCi of americium-241 was used in conjunction with a tin or silver target. The americium/tin source has a K_{α_1} X-ray of energy 25.3 keV while K_{α_1} for the americium/silver source is 22.2 keV (Fine & Hendee 1955). The americium/tin source was preferred because of the greater separation between its back-scattered K X-rays and the L X-rays of uranium. Mackay (1961) showed that reflection geometry is less sensitive to sample thickness and position. An annular configuration has been found to give the most efficient collection of fluorescent X-rays (Watt 1967). The geometry of the γ X source and the sample cell is shown in Figure 2.

3.2 Sample Cell

The most desirable sample is either a thin film or an infinitely thick slab (Leibhafsky 1960); however, the poor sensitivity attainable with a thin film dictates the use of an infinitely thick sample. Mackay & Thorne (1960) showed that a sample thickness of 16.2 mm or greater acts as an infinitely thick sample. Since nearly all materials absorb low energy X-rays, the present cell is open at the top with the detector window and the source mounted vertically above the sample. If a closed cell must be used, e.g. with very volatile solvents or in circumstances where the cell window cannot be horizontal, a 6 μ m Mylar film may be used as a cell window. To obtain reproducible results, the sample must be located accurately with respect to the detector and the source.

A convenient cell was a 62 mm i.d. polypropylene beaker cut down to have a total volume of 75 cm³. A sample volume of 50 cm³ gave a sample depth of 16.4 mm. Accurate location of the cell was achieved by using the supports of the X-ray source to locate the cell.

3.3 Detector

A xenon-methane filled proportional counter detector tube (20th Century Electronics Ltd., type PX130b/Xe) was chosen because of its good energy resolution and reasonable detection efficiency (Mackay & Thorne 1960). The counter had a beryllium window 0.3 mm thick x 34 mm diameter.

3.4 Electronic Equipment

The output of the proportional counter was connected via amplifier units to the two pulse height analysers and scalers, one to record the fluorescent X-rays, the other to record the backscattered X-rays as shown in Figure 1.

4. EXPERIMENTAL

4.1 Calibration

Initially the equipment was standardised by established procedures.

Calibration of the fluorimeter was a two-stage operation. First, the bias voltages of the pulse height analysers for the fluorescent and backscattered X-ray energies were found. Figure 4 shows typical bias voltages for the fluorescent uranium X-rays and the backscattered X-rays. Bias voltages were selected to count uranium L X-rays in the range 13.6 to 17.2 keV and backscattered X-rays in the range 23 to 25 keV. Calibration was then completed by determining the normalised count rate for a series of standard uranium solutions in the concentration range 0.01 to 10 g ℓ^{-1} . The count rate was determined from the average of the number of counts obtained in three 100-second counting periods.

In the presence of the matrix only, the incident X-rays suffered only Compton and coherent scattering. However, in the presence of a uranium-containing sample, some of the incident X-rays were absorbed by the uranium and emitted as fluorescent X-rays characteristic of the uranium and the remainder suffered Compton and coherent scattering as before (Figure 4). From Equation 9, the concentration of the uranium can be correlated with the normalised count rate;

$$I \text{ normalised} = \frac{\text{count rate for sample}}{\text{count rate for matrix only}} \quad \dots(10)$$

The normalised fluorescent count rate (I_F) was defined as

$$I_F = \frac{\text{total count rate (13.6 to 17.2 keV) for the sample}}{\text{total count rate (13.6 to 17.2 keV) for the solvent}} \quad \dots(11)$$

and the normalised backscatter count rate (I_B) was defined as

$$I_B = \frac{\text{total count rate (23 to 25 keV) for the sample}}{\text{total count rate (23 to 25 keV) for the solvent}} \quad \dots(12)$$

A normalised corrected fluorescent count rate (I_C) was then defined as

$$I_C = I_F / I_B \quad \dots(13)$$

Calibration curves for uranium in various solvents in terms of both I_F and I_C are shown in Figures 5 to 8 for the following solvents:

- (i) Amine solvent (5 vol.% alamine-336, 3 vol.% nonanol in odourless kerosene) used in uranium ore processing.
- (ii) 20 vol.% tributyl phosphate in odourless kerosene used in uranium refining.
- (iii) Typical uranyl sulphate and nitrate leach and raffinate liquors arising from uranium ore processing and refining.

- (iv) 1.5 M ammonium sulphate solution used for stripping loaded amine solvent in uranium ore processing.

A single calibration curve (in terms of I_C) was obtained for the sulphate and nitrate leach and raffinate liquors and for water as solvent (pure solutions).

4.2 Accuracy and Limits of Measurement

A wide range of uranium solutions having diverse matrix compositions has been analysed by γ X-ray fluorescence and by conventional chemical methods having an accuracy of 1 per cent. Tables 2 to 7 compare the γ X-ray fluorescence results both with and without compensation for variations in matrix composition in terms of backscattering, and results of analyses by chemical methods.

The lower limit of detection for this instrument was found to be 0.03 g ℓ^{-1} for pure uranium solutions and 0.05 g ℓ^{-1} for impure solutions. For pure uranium solutions containing 0.03 to 0.1 g ℓ^{-1} the accuracy of the X-ray fluorescence results increased from 30 per cent at 0.03 g ℓ^{-1} to 5 per cent at 0.1 g ℓ^{-1} . For concentrations between 0.1 to 1 g ℓ^{-1} an accuracy of 5 per cent was achieved, and for concentrations greater than 1 g ℓ^{-1} an accuracy of 3 per cent was attained.

For impure samples, the accuracy of uranium analysis by X-ray fluorescence depended upon compensation of the results for variation of the matrix composition. Figure 9 compares the accuracy of the γ X-ray fluorescence results, with and without compensation, for variations in the matrix as a function of uranium concentration. For uranium concentrations in the range 0.1 to 10 g ℓ^{-1} , an accuracy of 5 per cent was obtained with compensation, but at lower concentrations the accuracy decreased rapidly to about 30 per cent at 0.05 g ℓ^{-1} .

With ammonium sulphate solutions, a simple correction factor to account for variations in the concentration of ammonium sulphate could also be applied to the uncompensated results to obtain an answer comparable in accuracy to the compensated result. Ellis *et al.* (1968) showed that, when a single matrix component causes most of the matrix absorption effect, a measurement of the concentration (C_B) of that element can be used to determine a mean mass absorption coefficient (μ);

$$\mu = k_{10} C_B + k_{11} \quad \dots(14)$$

Substitution in Equation 2 gives

$$C = k_1 (N_1 + k_{10} C_B + k_{11}) \quad \dots(15)$$

Thus a corrected result could be obtained from the following expression

$$U_C = U_F + 1.6(\pm 0.4)M - 2.3(\pm 0.6) \quad \dots(16)$$

Equation 16 was derived by least squares regression of the results in Table 5 and the standard deviations of the parameters are shown in brackets.

5. PROSPECTS FOR FUTURE DEVELOPMENT

The γ X-ray equipment described above was developed for batch analysis only but is amenable to on-line applications. The sample solution may be continuously circulated past the detector assembly, the appropriate count rates determined, processed by suitable electronic circuitry (digital or analogue) and recorded. The detector assembly could use either a flow-through sample cell or an immersion cell, but there may be difficulties associated with the thin fragile windows which must be used because of the low energy of the L X-rays (see Section 3.2). Problems may arise in providing adequate mechanical strength for the sample cell and in obtaining satisfactory service life owing to erosion of the film.

The recent development of semi-conductor detectors of reasonable size and cost should enable improvements in on-line X-ray fluorescence. Thus lithium-drifted germanium detectors have excellent resolution and pulse rate capabilities to ensure a good signal to background ratio in the energy range of uranium K X-rays (Snyman 1971). Because the energy of K X-rays is high, a larger effective sampling volume is obtained and matrix absorption effects are minimised, reducing the lower concentration limit for analysis and/or the errors in X-ray fluorescence analysis (Kuusi *et al.* 1972). Snyman (1971) has described such an instrument, using cobalt-57 as a source of X-rays, which had a lower limit of detection of $8 \text{ mg } \ell^{-1}$.

6. CONCLUSIONS

A γ X-ray fluorimeter has been developed for rapid, simple and reliable analysis of uranium in pure and impure solutions in the range 0.05 to $10 \text{ g } \ell^{-1}$. An accuracy of 5 per cent was obtained in the range 0.1 to $10 \text{ g } \ell^{-1}$, while at lower concentrations it decreased rapidly to approximately 30 per cent. The lower limit of detection was $0.03 \text{ g } \ell^{-1}$ with pure uranium solutions and $0.05 \text{ g } \ell^{-1}$ with impure solutions. A major advantage is the time saving involved; a uranium determination can be obtained in less than five minutes compared with at least thirty minutes for chemical methods.

The recent development of semi-conductor detectors should enable improved accuracy and a reduction of the lower limit of detection to at least $0.01 \text{ g } \ell^{-1}$.

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8. NOTATION

C	= concentration of the wanted element
C_B	= concentration of matrix element
I_d	= intensity of detected fluorescent X-rays
$k_1, k_2 \dots k_{11}$	= constants
M	= concentration of ammonium sulphate (<u>M</u>)
N_1	= intensity of all X-rays incident on detector
N_f	= intensity of the detected fluorescent X-rays of the element whose concentration is to be measured
N_s	= intensity of the scattered X-rays
U_C	= corrected uranium concentration $g \ell^{-1}$
U_F	= uncompensated uranium concentration based on the I_F curve ($g \ell^{-1}$)
μ	= mean mass absorption coefficient
μ_i	= mean mass absorption coefficient of the sample at the incident X-ray energy
μ_k	= mean mass absorption coefficient of the sample at the fluorescent X-ray energy.

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TABLE 1
SOME METHODS TO COMPENSATE FOR DIFFERING MATRICES

	Methods	References
1	Addition of a low absorption diluent.	Greensides 1965; Rhodes 1966; Rhodes <i>et al.</i> 1964; Rhodes <i>et al.</i> 1965.
2	Use of internal standards.	Larson & Van Cleave 1963.
3	Application of thin films.	
4	Correction for known interfering elements.	Clayton & Cameron 1966; Dzuinikowski 1970; Ellis <i>et al.</i> 1968, 1969; Meyer 1961; Mitchell 1963; Rhodes <i>et al.</i> 1967.
5	Careful choice of incident and detected energies to compensate automatically for a known element.	Boyce & Ahier 1967.
6	Separation of uranium and matrix.	Van Niekerk <i>et al.</i> 1961.
7	Use of balanced filters.	Carr-Brion & Rhodes 1965; Ellis <i>et al.</i> 1968, 1969; Watt 1967.
8	Employment of balanced targets.	Rhodes 1966; Rhodes <i>et al.</i> 1967; Watt 1967.
9	Measurement of photon transmission through the sample.	Carr-Brion & Rhodes 1965; Ellis <i>et al.</i> 1968, 1969; Goldman & Anderson 1968; Rhodes 1966; Rhodes <i>et al.</i> 1964; Watt 1967.
10	Ratio of the characteristic rays of the required element to the backscatter incident rays.	Andermann & Kemp 1958; Boyce & Ahier 1967; Ellis <i>et al.</i> 1968, 1969; Enomoto 1968; Martinelli & Blanquet 1965; Rhodes 1966, 1968; Rhodes <i>et al.</i> 1967.
11	Combination of techniques.	Ellis <i>et al.</i> 1968; Watt 1967.

TABLE 2
URANIUM ANALYSES FOR PURE SOLUTIONS

Uranium Concentration					Medium
Chemical Methods	X-ray Fluorescence with Matrix Compensation		X-ray Fluorescence without Matrix Compensation		
$g\ l^{-1}$	$g\ l^{-1}$	Accuracy %	$g\ l^{-1}$	Accuracy %	
0.01	< 0.03	-	< 0.03	-	Sulphate
0.025	< 0.03	-	< 0.03	-	Sulphate
0.03	0.05	+ 66.7	0.04	+ 33.3	Nitrate
0.05	0.04	- 20.0	0.04	- 20.0	Nitrate
0.10	0.105	+ 5.0	0.105	+ 5.0	Nitrate
0.105	0.105	< 1.0	0.110	+ 4.8	Sulphate
0.27	0.26	- 3.7	0.26	- 3.7	Nitrate
0.50	0.52	+ 4.0	0.50	< 1.0	Nitrate
0.53	0.55	+ 3.8	0.50	- 5.7	Sulphate
0.76	0.73	- 3.9	0.78	+ 2.6	Sulphate
1.0	1.05	+ 5.0	1.05	+ 5.0	Nitrate
1.05	1.03	- 1.9	1.03	- 1.9	Sulphate
2.7	2.65	- 1.8	2.7	< 1.0	Nitrate
5.0	5.0	< 1.0	5.1	+ 2.0	Nitrate
5.3	5.2	- 1.9	5.4	+ 1.9	Sulphate
10.0	9.9	- 1.0	9.8	- 2.0	Nitrate
10.5	10.2	- 2.9	10.3	- 1.9	Sulphate

TABLE 3

URANIUM ANALYSES FOR SULPHATE LEACH AND RAFFINATE SOLUTIONS

Sulphate Concentration \underline{M}	Uranium Concentration				
	Chemical Methods	X-ray Fluorescence with Matrix Compensation		X-ray Fluorescence without Matrix Compensation	
		$g\ l^{-1}$	$g\ l^{-1}$	Accuracy %	$g\ l^{-1}$
0.36	0.049	0.055	+12.2	0.045	- 8.2
n.a.	0.050	0.05	< 1.0	n.a.	n.a.
n.a.	0.0525	0.07	+33.3	n.a.	n.a.
n.a.	0.0527	0.05	- 1.4	n.a.	n.a.
n.a.	0.055	0.055	< 1.0	n.a.	n.a.
n.a.	0.0564	0.07	+24.1	n.a.	n.a.
n.a.	0.0575	0.08	+39.1	n.a.	n.a.
n.a.	0.0592	0.054	- 9.3	n.a.	n.a.
n.a.	0.060	0.05	-16.7	n.a.	n.a.
n.a.	0.0625	0.063	+ 0.8	n.a.	n.a.
0.32	0.064	0.070	+ 9.4	0.050	-21.9
n.a.	0.065	0.057	-12.3	n.a.	n.a.
n.a.	0.0657	0.05	-23.9	n.a.	n.a.
n.a.	0.0657	0.054	-17.8	n.a.	n.a.
n.a.	0.0675	0.064	- 5.2	n.a.	n.a.
n.a.	0.0694	0.08	+15.2	n.a.	n.a.
n.a.	0.0694	0.08	+15.2	n.a.	n.a.
n.a.	0.07	0.06	-14.3	n.a.	n.a.
0.32	0.091	0.089	- 2.2	0.10	+ 9.9
0.36	0.100	0.10	< 5.0	0.13	+30.0
0.49	0.21	0.20	- 5.0	0.21	< 2.5
0.45	0.26	0.26	< 2.0	0.26	< 2.0
0.36	0.29	0.275	- 5.2	0.29	< 1.7
0.36	0.295	0.31	+ 5.1	0.35	+18.6
0.41	0.32	0.30	- 6.2	0.35	+ 9.4
0.37	0.39	0.38	- 2.6	0.37	- 5.1
0.36	0.55	0.52	- 5.5	0.51	- 7.3
0.36	0.64	0.61	- 4.7	0.59	- 7.8
0.36	0.77	0.75	- 2.6	0.77	< 1.0
0.36	0.78	0.80	+ 2.6	0.75	- 3.8
0.36	0.81	0.82	+ 1.2	0.75	- 7.4
0.36	0.81	0.83	+ 2.5	1.0	+23.5
0.36	0.87	0.86	- 1.1	0.69	-20.7
0.36	0.91	0.90	- 1.1	1.4	+54.0

n.a. not available.

TABLE 4
URANIUM ANALYSES FOR AMINE SOLUTIONS

Uranium Concentration					Remarks
Chemical Methods	X-ray Fluorescence with Matrix Compensation		X-ray Fluorescence without Matrix Compensation		
$g\ l^{-1}$	$g\ l^{-1}$	Accuracy %	$g\ l^{-1}$	Accuracy %	
0.063	0.050	- 20.6	0.055	- 12.7	Stripped Solvent
0.092	0.089	- 3.3	0.088	- 4.3	
0.14	0.14	< 3.3	0.14	< 3.3	
0.69	0.73	+ 5.8	0.75	+ 8.7	
3.0	3.1	+ 3.3	3.1	+ 3.3	
3.1	3.2	+ 3.1	3.0	- 3.1	
3.6	3.5	- 2.8	3.7	+ 2.8	Loaded Solvent
3.6	3.7	+ 2.8	3.6	< 1.4	
4.0	4.0	< 1.3	4.3	+ 7.5	
5.2	5.3	+ 1.9	5.1	- 1.9	
5.5	5.5	< 1.0	5.4	- 1.8	
5.9	5.9	< 1.0	5.9	< 1.0	
7.2	7.1	- 1.4	7.1	- 1.4	

TABLE 5

URANIUM ANALYSES FOR AMMONIUM SULPHATE SOLUTIONS

Ammonium Sulphate Concentration <u>M</u>	Uranium Concentration				
	Chemical Methods $g\ l^{-1}$	X-ray Fluorescence with Matrix Compensation		X-ray Fluorescence without Matrix Compensation	
		$g\ l^{-1}$	Accuracy %	$g\ l^{-1}$	Accuracy %
1.5	0.62	0.62	< 1.0	0.57	- 8.1
1.5	0.89	0.84	- 5.6	0.82	- 7.9
1.5	2.8	2.7	- 3.6	2.7	- 3.6
1.3	3.0	3.1	+ 3.3	3.2	+ 6.7
1.5	3.3	3.3	< 1.5	3.2	- 3.0
1.7	5.3	5.2	- 1.9	4.8	- 9.4
1.5	5.4	5.4	< 1.0	5.3	- 1.9
1.6	6.3	6.3	< 1.0	6.2	- 1.6
1.6	6.9	6.8	- 1.5	6.3	- 8.7
1.6	8.1	8.0	- 1.2	7.5	- 7.4
1.8	9.2	9.3	+ 1.1	8.7	- 5.4
1.5	9.6	9.4	- 2.1	9.3	- 3.1
1.4	10.7	10.8	+ 1.0	10.7	< 1.0

TABLE 6
URANIUM ANALYSES FOR NITRATE RAFFINATES

Chemical Methods	X-ray Fluorescence with Matrix Compensation		X-ray Fluorescence without Matrix Compensation	
	g l ⁻¹	Accuracy %	g l ⁻¹	Accuracy %
0.050	0.050	< 1.0	n.a.	n.a.
0.0525	0.053	< 1.0	n.a.	n.a.
0.055	0.059	+ 7.3	n.a.	n.a.
0.055	0.05	- 9.1	0.05	- 9.1
0.0575	0.06	+ 4.2	n.a.	n.a.
0.060	0.05	- 16.7	n.a.	n.a.
0.0625	0.055	- 12.0	n.a.	n.a.
0.065	0.065	< 1.0	n.a.	n.a.
0.0675	0.065	- 3.7	n.a.	n.a.
0.070	0.06	- 14.3	n.a.	n.a.
0.076	0.080	+ 5.3	0.060	- 21.1
0.100	0.10	< 5.0	0.13	+ 30.0
0.110	0.11	< 4.61	0.11	< 4.6
0.125	0.13	+ 4.0	0.125	< 1.0
0.130	0.125	- 3.8	0.10	- 23.1
0.140	0.135	- 3.6	0.18	+ 28.6
0.190	0.2	+ 5.3	0.19	< 2.6
0.200	0.21	+ 5.0	0.26	+ 30.0
0.260	0.26	< 1.9	0.27	+ 3.8
0.290	0.30	+ 3.4	0.32	+ 10.3
0.370	0.39	+ 5.4	0.38	+ 2.7
2.7	2.65	- 1.9	2.6	- 3.7

n.a. not available.

TABLE 7

URANIUM ANALYSES FOR TRIBUTYL PHOSPHATE IN KEROSENE SOLUTIONS

Chemical Methods	X-ray Fluorescence with Matrix Compensation		X-ray Fluorescence without Matrix Compensation	
	g l^{-1}	Accuracy %	g l^{-1}	Accuracy %
0.25	0.25	< 2.0	0.25	< 2.0
0.25	0.26	+ 4.0	0.26	+ 4.0
0.32	0.30	- 6.2	0.32	< 1.6
0.32	0.31	- 3.1	0.29	- 9.4
0.36	0.38	+ 5.6	0.42	+ 16.7
0.40	0.40	< 1.3	0.41	+ 2.5
0.45	0.45	< 1.1	0.47	+ 4.4
0.69	0.68	- 1.4	0.65	- 5.8
0.79	0.78	- 1.3	0.80	+ 1.3
1.2	1.25	+ 4.2	1.15	- 4.2
1.3	1.3	< 3.8	1.4	+ 7.7
1.8	1.9	+ 5.5	2.4	+ 33.3
2.0	2.1	+ 5.0	1.8	- 10.0
2.1	2.2	+ 4.8	2.2	+ 4.8
7.2	7.0	- 2.8	7.1	- 1.4

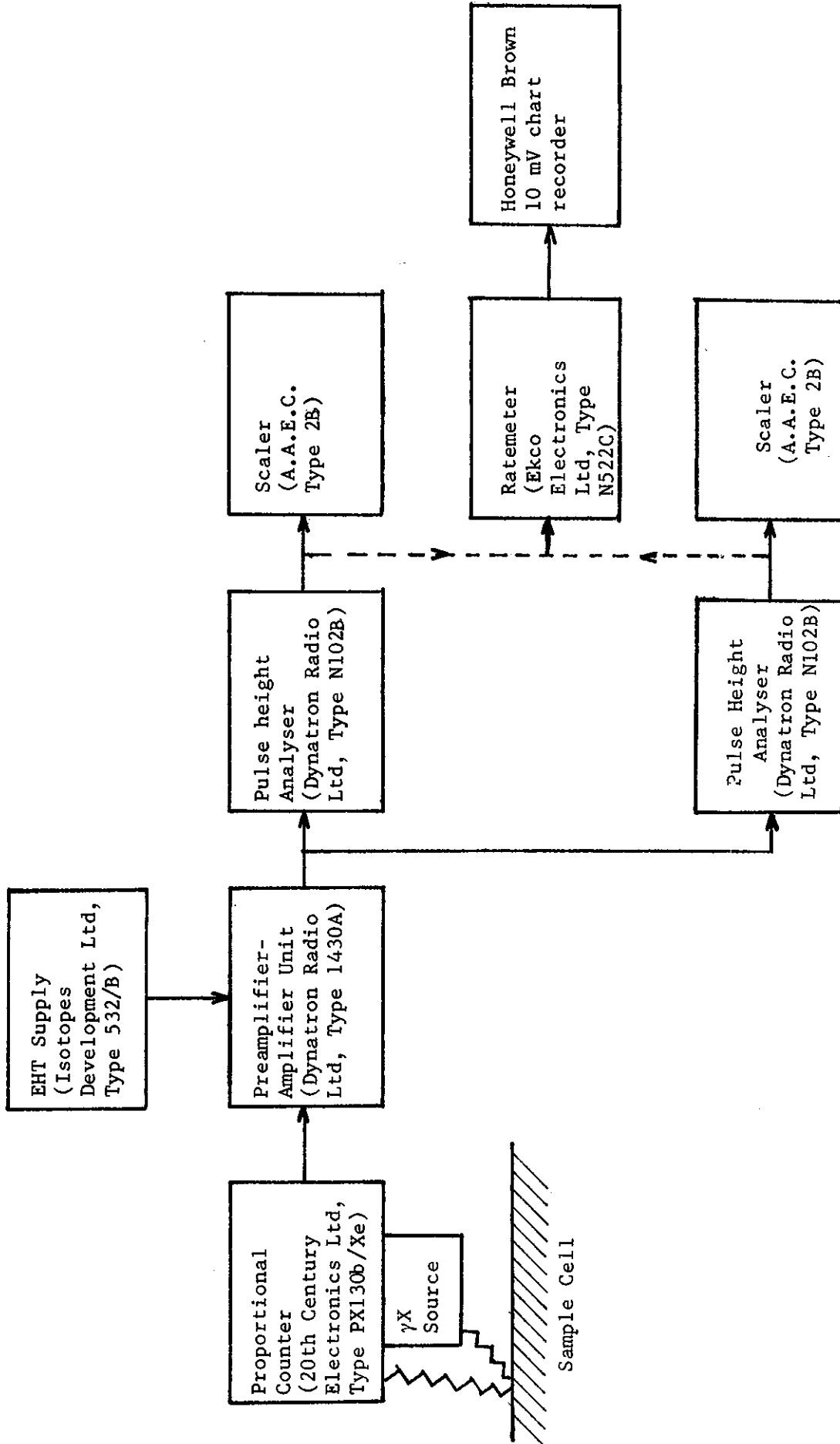


FIGURE 1. γ X-RAY FLUORESCENCE EQUIPMENT

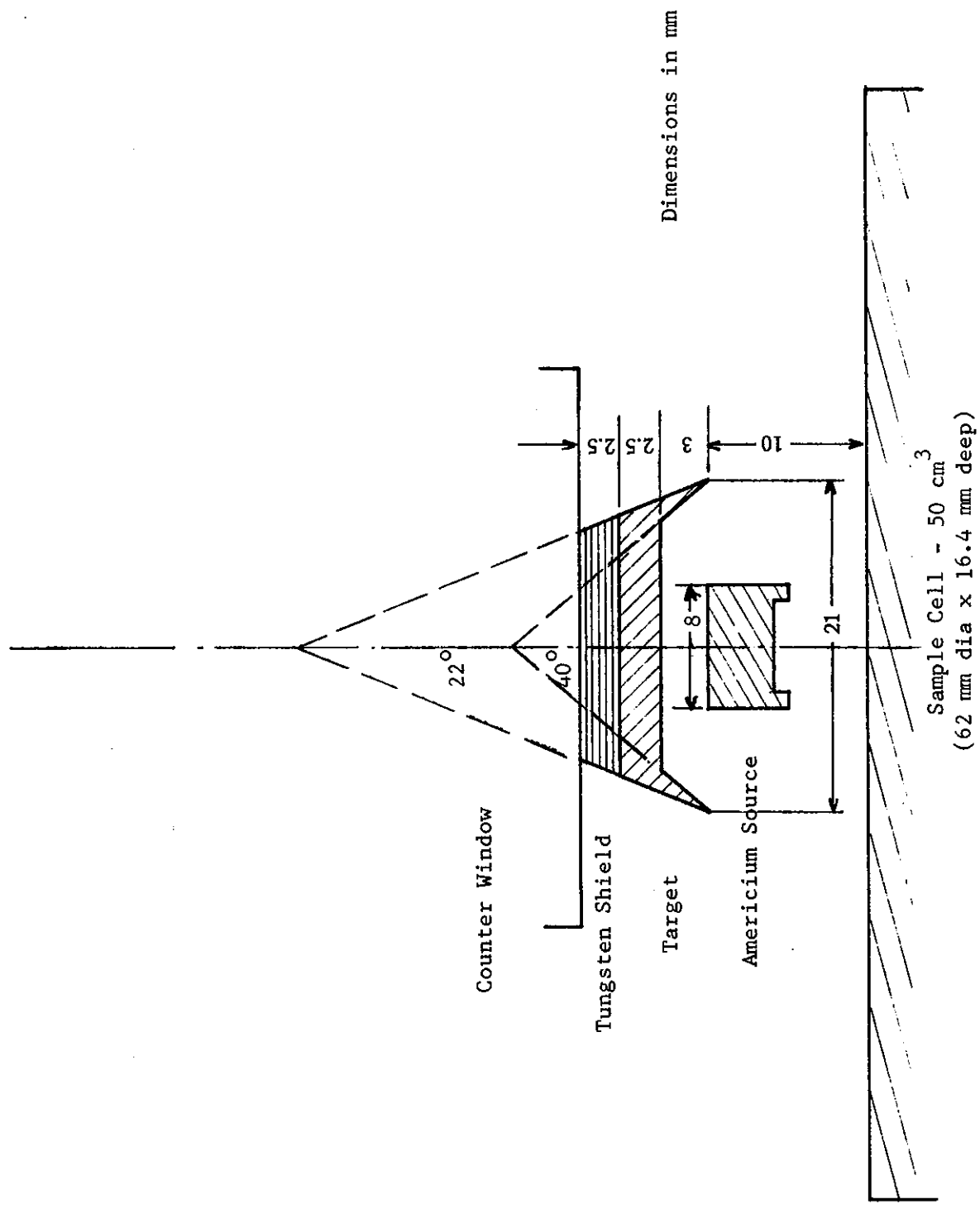


FIGURE 2. γ -RAY FLUORESCENCE - SOURCE AND SAMPLE

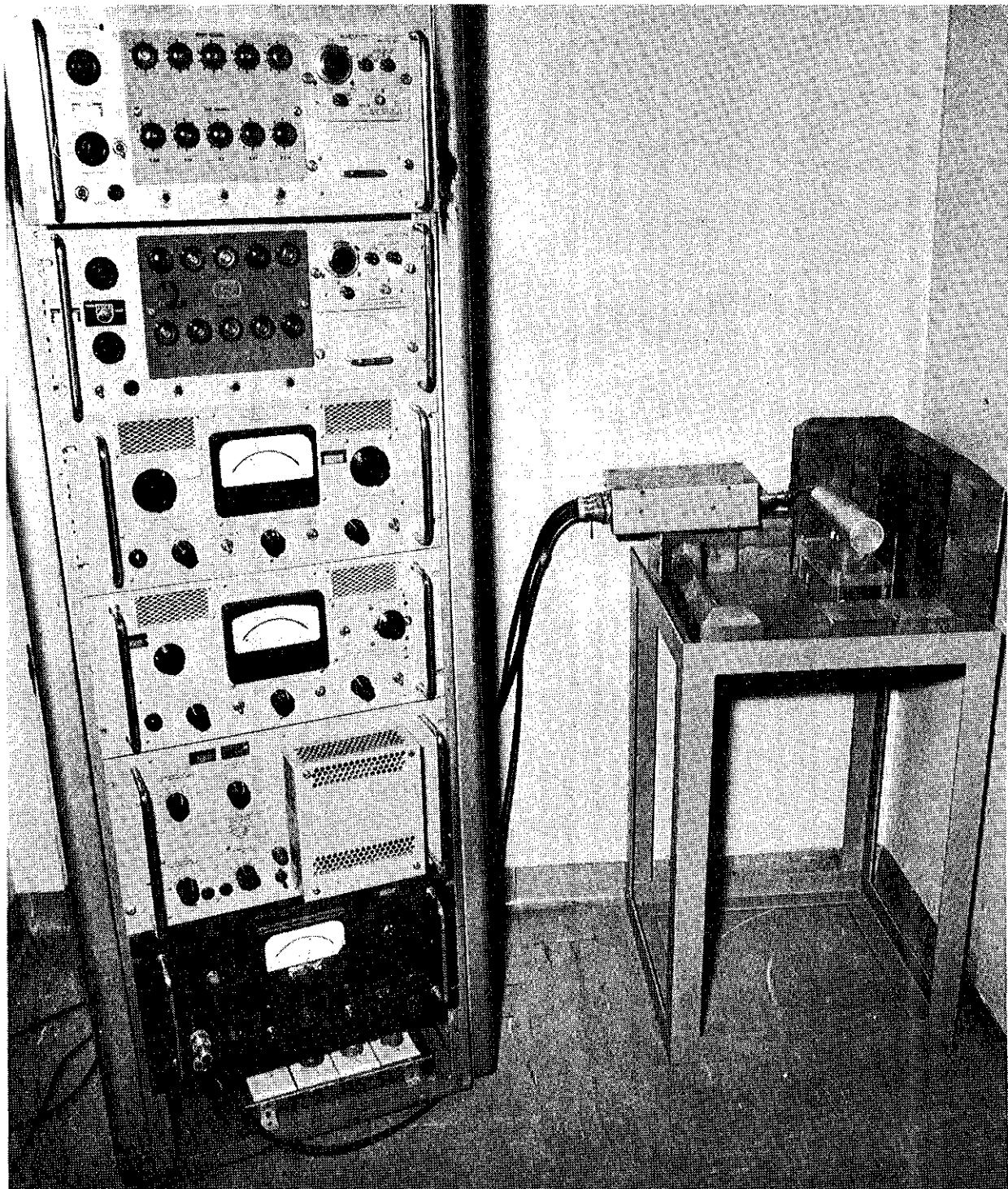


FIGURE 3. GENERAL VIEW OF EQUIPMENT

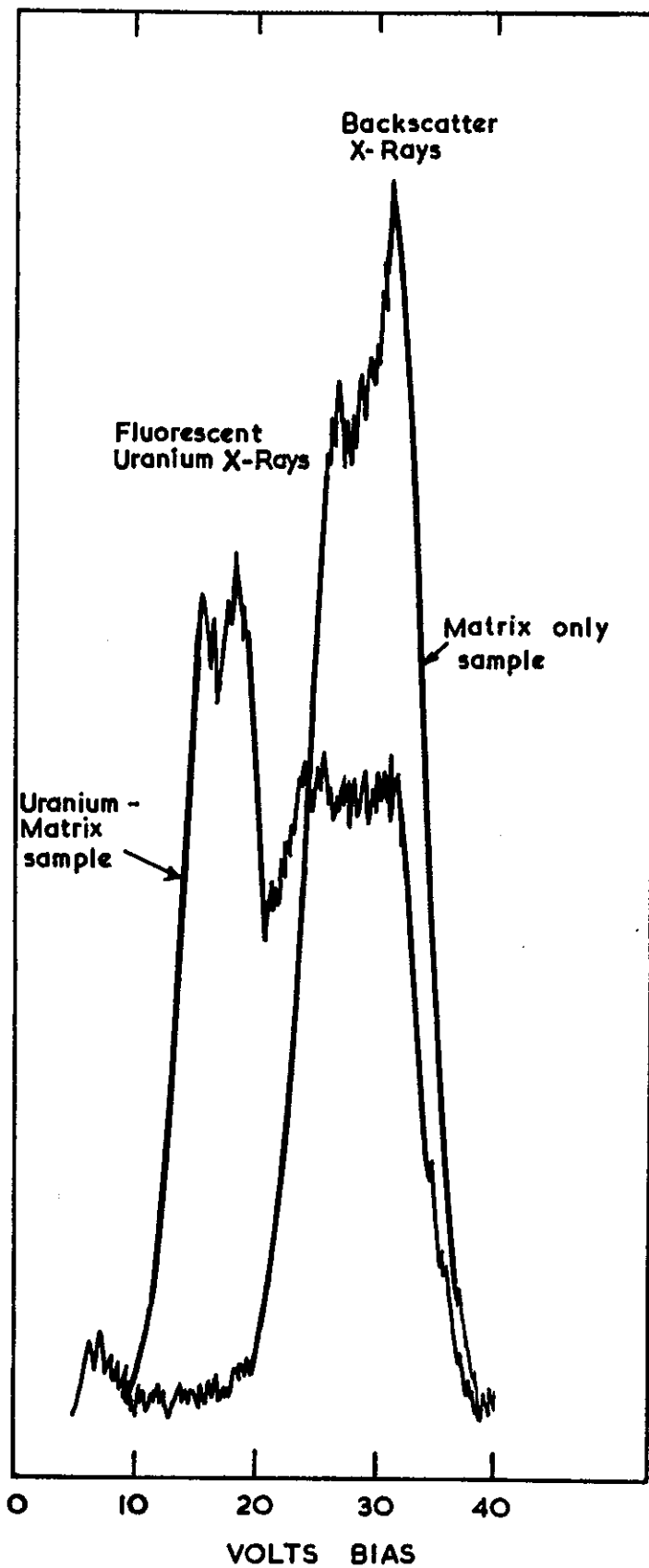


FIGURE 4. TYPICAL BIAS VOLTAGES FOR URANIUM FLUORESCENT AND BACKSCATTER X-RAYS

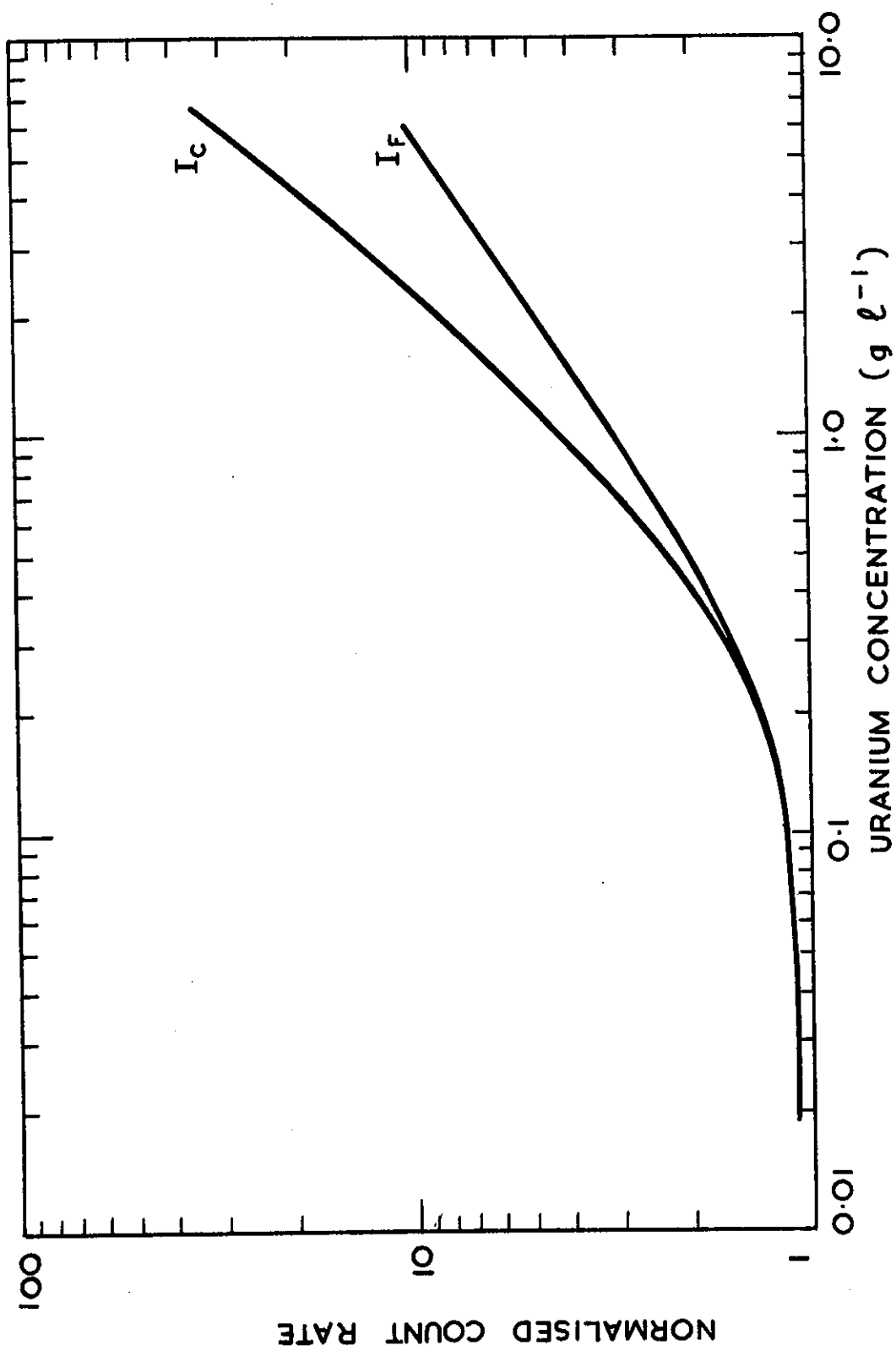


FIGURE 5. CALIBRATION CURVES FOR URANIUM IN 5% ALAMINE-336 -
3% NONANOL - 92% KEROSENE

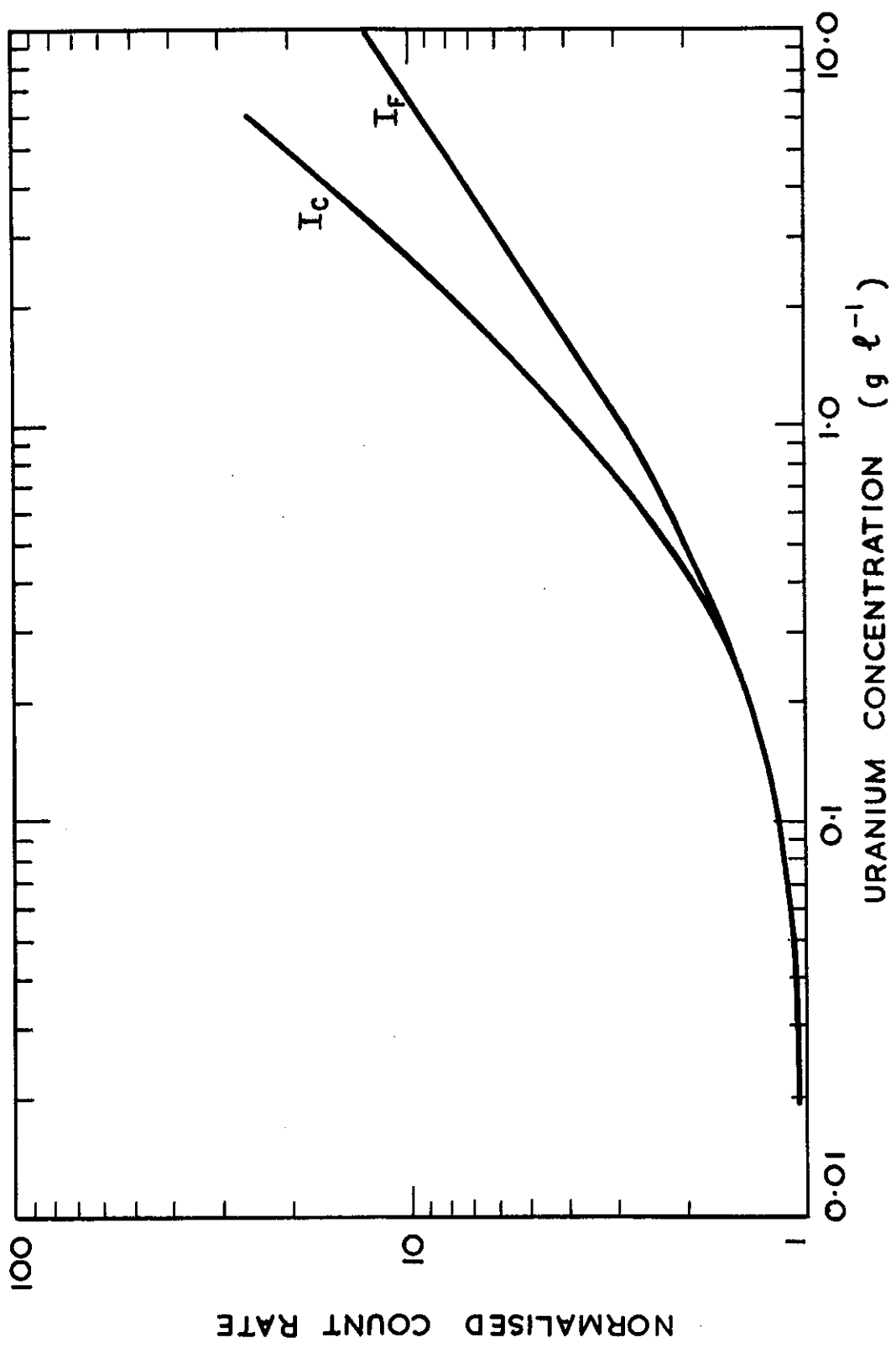


FIGURE 6. CALIBRATION CURVES FOR URANIUM IN 20% TRIBUTYL PHOSPHATE - 80% KEROSENE

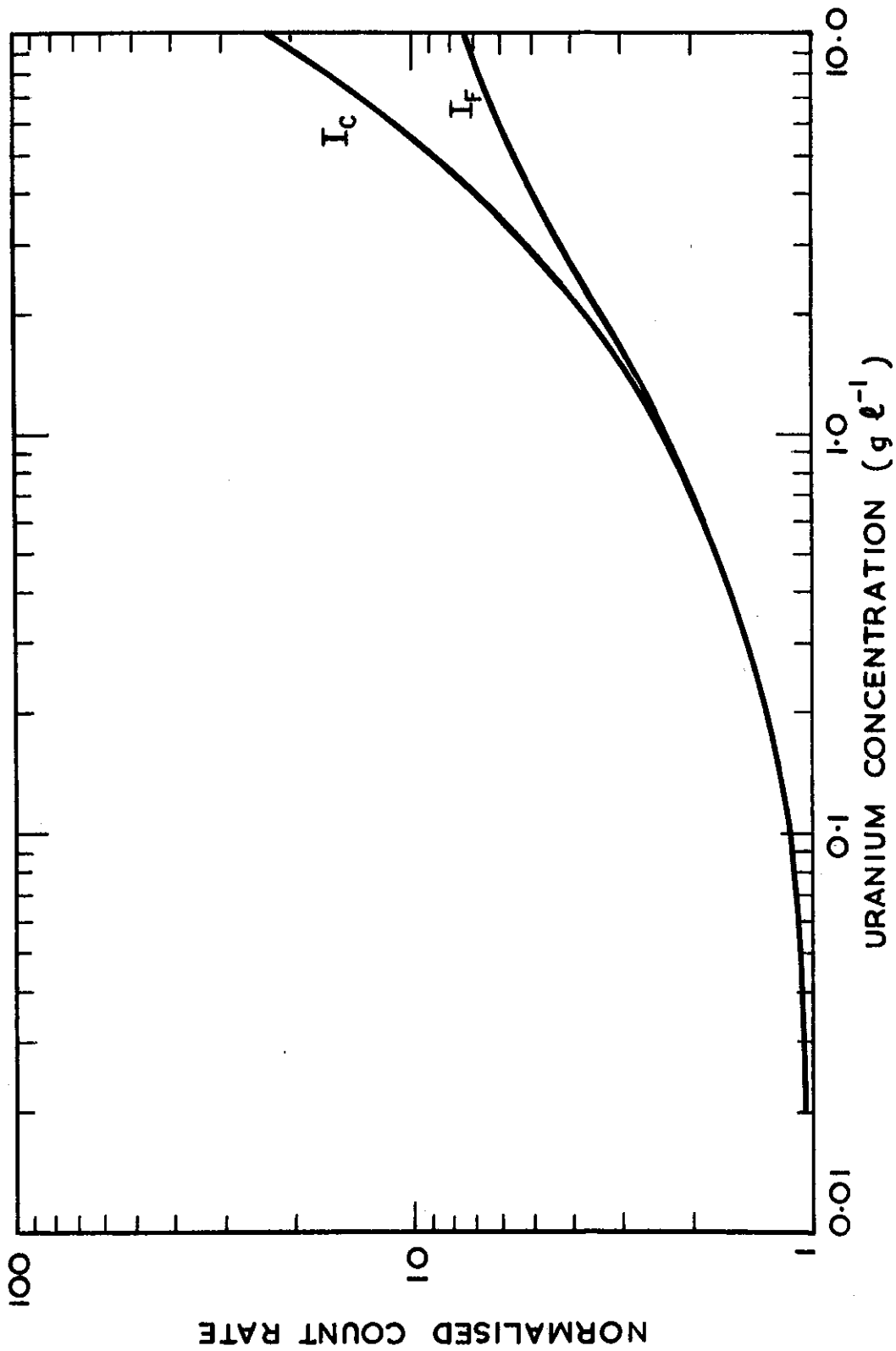


FIGURE 7. CALIBRATION CURVES FOR URANIUM IN AMMONIUM SULPHATE SOLUTIONS

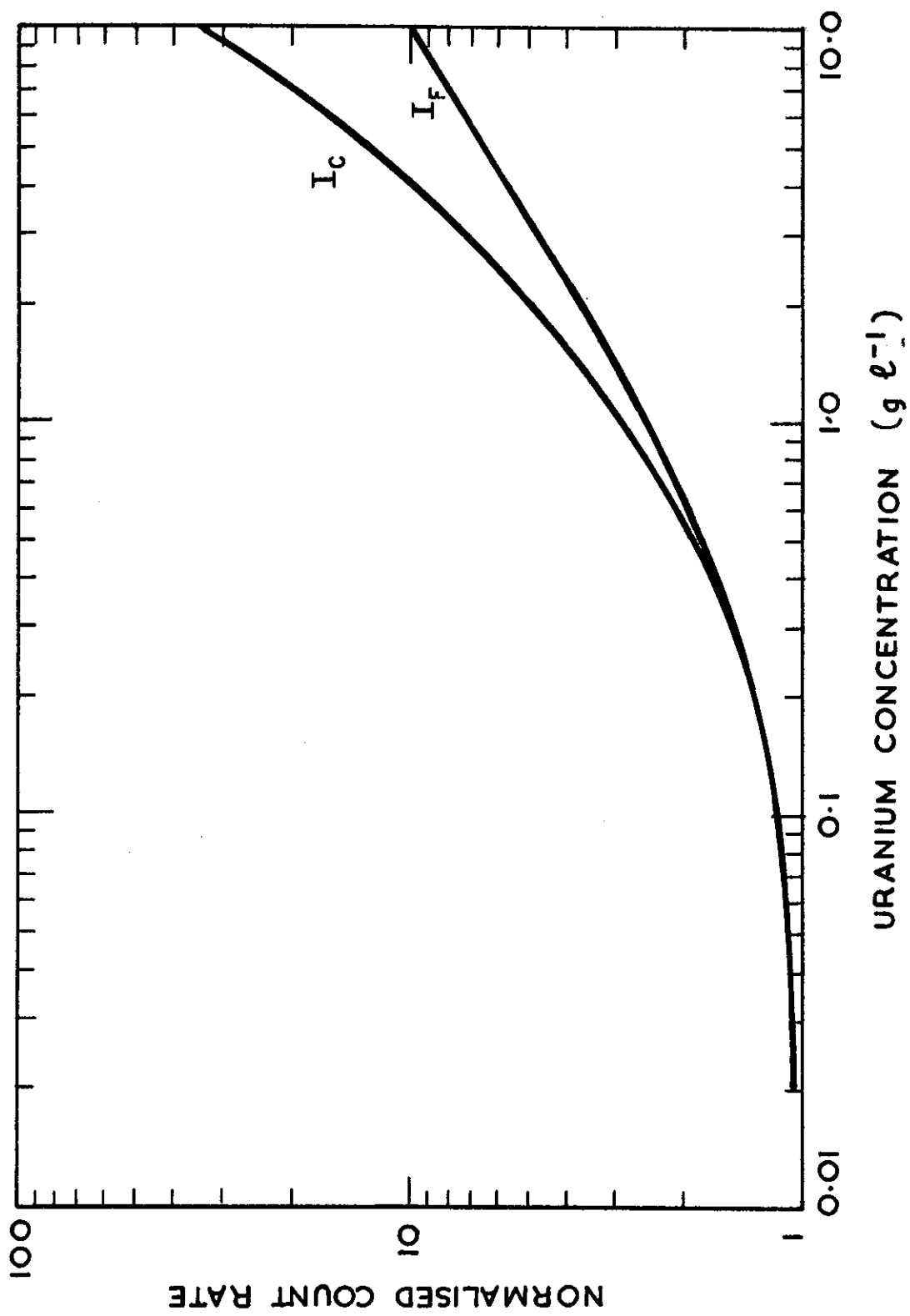


FIGURE 8. CALIBRATION CURVES FOR LEACH AND RAFFINATE SOLUTIONS

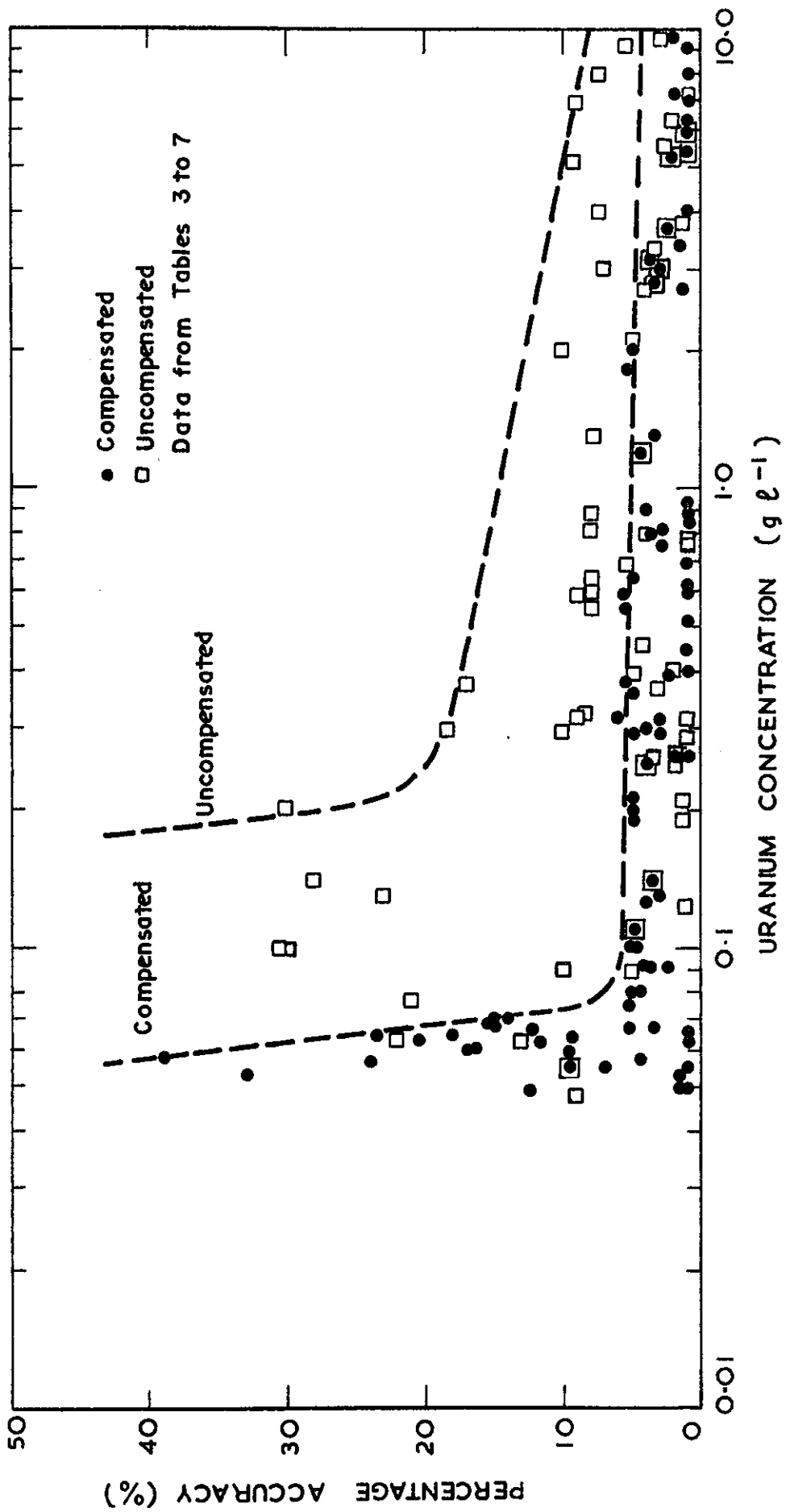


FIGURE 9. ACCURACY OF X-RAY FLUORESCENCE RESULTS AS A FUNCTION OF URANIUM CONCENTRATION

