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EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

TRANSPLUTONIDE RESEARCH

Final Report

by

A. VAN DALEN, W. KRAAK and J. VAN OOYEN
(RCN)
and
P. POLAK and J. C. POST
(Instituut voor Kernphysisch Onderzoek, Amsterdam)

1966

Transplutonium Elements Program

Report prepared by the RCN
Reactor Centrum Nederland, Petten — Netherlands
Euratom Contract No. 005-61-11 TPUN

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Results are reported with alphahydroxy isobutyric acid and ethylene diamine tetraacetic acid as complexing agents.

Anion exchange separations of americium and curium were accomplished in column elution experiments with aluminium nitrate and magnesium nitrate solutions as eluants. Separation factors of 1.8 were obtained.

The problems of low efficiency counting were investigated with respect to the calibration of alpha-emitters. A counting device for soft gamma and Röntgen radiation was constructed and tested.

An alpha spectrometer based on the principle of a semiconductor is described as developed and built at IKO, Amsterdam, for the purpose of determining isotopic compositions of alpha emitting nuclides.

Various techniques for preparing thin and thick layers of uranium, neptunium, plutonium, americium, curium were investigated. These layers are to be used as targets for irradiations in a cyclotron. However under certain circumstances they may also be useful for reactor irradiations.

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INTRODUCTION.

This report covers the work performed in the period of November 1, 1961 - December 31, 1964, within the framework of Contract 005 - 61 - 11 TPUN between Euratom and Reactor Centrum Nederland.

Under the terms of this contract part of the work was to be done at Instituut voor Kernphysisch Onderzoek, Amsterdam. The work performed at both institutes is reported under one cover.

The research work at IKO included various investigations on radiometric methods for the determination of transuranium elements. At RCN methods for the separation and determination of the transplutonium elements americium and curium were studied. Prof.Dr. A.H.W. Aten Jr. (IKO) acted as à technical adviser for the contract work.

Manuscript received on November 8, 1965.

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ACKNOWLEDGEMENT

FIGURE LEGEND

ACTINIDE-LANTHANIDE SEPARATION BY TERTIARY AMINE EXTRACTION.

INTRODUCTION.

Liquid-liquid extraction with tertiary amines offers a good possibility for the separation of the trivalent transplutonium elements from the lanthanides. In general a separation of these two groups of elements is very difficult, in view of the similarity in properties such as ionic radius, the valency state in solution, the complex formation constants, etc. The extraction with a tertiary amine from a concentrated lithiumchloride solution gives a good separation factor of about 100 for these two groups of elements. A separation system based on that separation factor has been developed at ORNL, (1), (2), (3), (4).

There is some information about the extraction mechanism of the trivalent actinides and lanthanides from concentrated chloride solutions, (5,6). By variation of the extractant concentration in the organic phase, a slope of 2 is found in the logarithmic plot of the concentration of the extractant versus the extraction coefficient (1), (5). This indicates a ratio of 2:1 of amine to metal ion in the extracted complex. The simplest equations for the complex formation reactions are:

$$2\ R_3N \cdot HCl_{org} + MCl_{4aq}^{-} \rightleftharpoons (R_3NH)_2MCl_{5org} + Cl_{aq}^{-}$$

or:

$$2\ R_3N \cdot HCl_{org} + MCl_{3aq} \rightleftharpoons (R_3NH)_2MCl_{5org}$$

(watermolecules of hydration are omitted for simplicity).
From equilibrium measurements it cannot be decided to what extent these separate mechanisms play a rôle.

The nature of the metalchloride complex in aqueous lithiumchloride solutions is not clear. In the early literature on this subject negatively charged metalchloride complex ions were supposed to explain an anionexchange mechanism. Later also addition reactions were taken into account. Spectrophotometric measurements of the chloride complex formation of the trivalent elements U, Np, Pu and Am in LiCl solutions indicate the existence of complex ions MCl^{2+} and MCl_2^{+} (7), (8).
One objection against the formula of the amine complex in the organic phase is: a coordination number of five, as in this case, is not a common one. This combined with the ability of the amine salts in organic solution to associate (9) gives the idea that the formula is too simple.

In spite of several investigations the problem of the associations of the metal amine salt complexes in organic diluents is still not solved.

EXPERIMENTAL.

The tertiary amine used in our solvent extraction programme was tri-iso-actyl-amine (TiOA) obtained from Saramine, The Hague. Before use the amine was purified by vacuum distillation. The purity was controlled by titrations. To a sample an excess of 0.1 N hydrochloric acid was added. The excess hydrochloric acid and the hydrochloric acid amine salt were titrated with 0.1 N sodium hydroxide in a water-acetone mixture. The titration curve measured with a Beckman glass electrode is given in Figure 1. Curve 1 is from a sample of the unpurified amine; curve 2 is from a sample of the highest boiling fraction. The first endpoint in curve 1 gives the excess hydrochloric acid, the second the tertiary amine according to the reaction:

$$R_3NH^+ + OH^- \rightleftharpoons R_3N + H_2O$$

The third endpoint gives the secondary amine present in the untreated amine.

$$R_2NH_2^+ + \rightleftharpoons R_2NH + H_2O$$

After distillation no secondary amine was present as can be seen in curve 2. Calculation indicated a purity of the TiOA of 99,8%.

Before carrying out extraction experiments the amine was dissolved in xylene (20% = 0.5 N) and shaken with an equal volume of 2 N hydrochloric acid to convert the amine to the mono hydrochloric acid salt $R_3NHCl.H_2O$ (5). If the concentration of the hydrochloric acid in the pretreatment was too low a great amount of the activity of americium and europium in the extraction experiment was found on the glasswall of the extraction apparatus. The unneutralised amine extracts the small amount of hydrochloric acid from the slightly acid chloride solutions and caused hydrolysis of the trivalent lanthanides and actinides.
R.E. Leuze et al. (10) noted precipitation of the metalhydroxides when the solutions became acid deficient. Higher concentrations of hydrochloric acid in the pretreatment decrease the extraction of the metal ions by uptake of a second molecule of hydrochloric acid (5), (11) and forming $R_3NHCl.HCl$, which may be written as $R_3NH^+.HCl_2^-$ according to infrared analysis (12), (13).

The organic diluents were obtained from Merck and B.D.H., all reagent grade and used without further purification. The inorganic chemicals were obtained from Merck analytical grade. One time we used $MgCl_2$ (anhydrous) from Riedel de Haen. This batch of magnesiumchloride caused some difficulties in extraction experiments. Figure 2 gives the extraction coefficient E_a^o of tracer amounts of Am and Eu from 5.5 M $MgCl_2$ into 0.5 M TiOA.HCl in xylene. The deviation from the normally obtained curve was caused by an impurity of basic character in the magnesiumchloride. This was found by measuring the potential of a glass-electrode in the magnesiumchloride solution at different hydrochloric acid concentrations. Figure 3 gives the results: curve a from solutions of $MgCl_2$ anhydrous (Riedel de Haen); curve b from solutions of $MgCl_2.6H_2O$ (Merck). For such solutions a straight line is expected (14).

The metal ion extractions were carried out with trace amounts of ^{241}Am, ^{144}Ce, ^{147}Pm, $^{152-154}$Eu, ^{153}Gd and ^{160}Tb from RCC Amersham.

The mixer-settler experiment was made with a Bevatron mini mixer-settler of 8 stages. Batch extraction experiments were carried out with 2 ml of each phase in glass tubes with a glass stopper. After shaking for 5 min. and centrifuging, equal volume samples were taken from the upper and lower phase and counted for gamma radiation on a well-type NaI (Tl-activated) crystal (Harshaw). The countings were corrected for background and, in the case of ^{241}Am gammas, for varying selfabsorption of the two phases.

RESULTS AND DISCUSSION.

Influence on the metal extraction by variation of the extractant concentration.

Figure 4 gives the extraction coefficients of Am and Eu from 5.5 M $MgCl_2$ - 0.01 N HCl in an organic phase of varying concentrations of TiOA.HCl in xylene. The slope of the lines in the logaritmic plot is 1.7. The reason for the deviation from the expected slope is unknown; such deviations are also found by R.D. Baybartz and B.S. Weaver (1).

Influence on the metal extraction by the salting-out medium.

In general a solution of lithiumchloride is used as the concentrated chloride solution. In this programme also other chlorides were tried. Figure 5 shows the extraction coefficient as a function of the acidity at equilibrium of the chloride solutions The salts and their concentrations used in the extraction experiments are:

LiCl	12	M
$MgCl_2$	5.5	M
$CaCl_2$	5 0	M
$AlCl_3$	5.0	M

As is seen in the figure the extraction of Am is highest from LiCl solutions. The extraction coefficients from $MgCl_2$ solutions are reasonable, these from $CaCl_2$ and $AlCl_3$ are too low for an effective extraction of americium. It was decided to carry out the further experiments with solutions of magnesiumchloride. The extraction coefficients determined with a 0.5 M TiOA.HCl solution in xylene from 5.5 M $MgCl_2$ - 0.01 N HCl are for:

Am	0.39
Ce	0.003
Pm	0.003
Eu	0.004
Gd	0.004
Tb	0.004

The separation factors are also about 100 as in the lithiumchloride solutions. A mixer-settler experiment with a mixture of tracer amounts of Am and Eu was done. The flow ratio organic-aqueous was chosen as 2:1. No Eu could be detected in the organic phase. The recovery of Am was not complete. This was in agreement with the fact that the mixer-settler used had only 8 stages. In order to increase the extraction coefficient of americium, mixtures of 5 M $MgCl_2$ and 4 M $Mg(NO_3)_2$ were tried. Indeed the extraction became higher, but the separation factor from the lanthanides decreased to a value of about 2. This behaviour on addition of nitrates is also noted for lithium chloride solutions (2), (3). Extracting with $TiOA.HNO_3$ from the magnesiumchloride solutions gave the same effect. Only very small amounts of nitrates could be admitted to keep the separation sufficiently high; furthermore the increase in extraction of americium in the presence of small concentrations of nitrate ions is very low. So no positive results are obtained by adding nitrates to the chloride system.

Relation between the metal extraction and the water extraction by the diluent.

The complex metal ions in the aqueous phase and the hydrochloric acid amine salt in the organic phase are hydrated (5). So there must be a relation between the metal extraction and the concentration of water in the organic phase which is in equilibrium with the activity of water in the aqueous phase. The extraction dependence on the water activity of the salt solutions is difficult to measure because of the necessary condition of constancy of the other variables, for example the chloride ion activity. The problem in dilute solutions is often solved by the method of a constant ionic strength by addition a non complexing electrolyte usually a perchlorate. This method offered little promise for this problem. The lithium perchlorate is poorly soluble in concentrated lithiumchloride solutions and also perchloric acid is preferentially taken up by the tertiary amine, thus converting the amine hydrochloric acid salt to the perchloric acid salt. This results in decreased extraction of the trivalent actinides and lanthanides (2), (3).

This was confirmed by one experiment with a mixture of LiCl and $LiClO_4$ giving no extraction of americium. Therefore a study was made of the extraction on the free water concentration in the organic phase. The concentration of free water was supposed to be proportional to:

1. The amount of water soluble in the pure diluent (determined by Karl Fischer titration).
2. The water activity of the concentrated salt solution at extraction equilibrium (the water activities were taken from R.A. Robinson and R H. Stokes (15)).
3. The volume fraction of the diluent in the organic phase.

Variation of the concentration of water in the organic phase was effected by varying the diluent. A number of hydrocarbons (benzene, toluene, xylene, ethylbenzene, cumene, cyclohexane and dekaline) were taken, supposing that these would influence the metal extraction by their difference in water extracting capabilities.

Figure 6 gives the result in a logarithmic plot:

curve 1	20%	TiOA - 12 M LiCl	from data of F. Moore (16)
curve 2	0.5 M	TiOA - 12 M LiCl	this work
curve 3	0.5 M	TiOA - 8 N LiCl + 2 N $AlCl_3$	from data of K.B. Brown (17)
curve 4	0.5 M	TiOA - 10 M LiCl	this work

The shape of the curves can be interpreted as follows:
The number of water molecules of hydration of the amine-hydrochloric acid salt in the organic phase at extraction equilibrium conditions is a function of the water activity of the aqueous phase (5). Assuming that neutral species are transferred (18), it may be that these also contain a variable number of hydration molecules. The equilibrium equation then may be:

$$2\ R_3N.HCl.aH_2O + MCl_3.b.H_2O \rightleftharpoons (R_3NH)_2MCl_5 + (2a+b)H_2O.$$

With decreasing waterconcentrations the slope of the curves in Figure 6 decrease (low values for a and b). At the highest waterconcentrations obtained, the slope tends to -8. For the value a = 1, b becomes 6. The number of 6 watermolecules in the neutral complex is in accordance with the statement of C.K. Jørgensen (19) that the maximum coordination number of the lanthanides in aqueous solutions is probably 9.

In order to confirm the provisional conclusion on the relation between the extraction and the hydration phenomena the following experiments are planned:

1. Equilibrating slightly acid solutions of LiCl, $CaCl_2$ and $MgCl_2$ by the isopiestic method. At equilibrium the activities of water and hydrochloric acid are equal for all solutions, so the influence of the chloride ion activity on the extraction of Am can be studied.
2. Determination of the amount of water in $R_3NHCl.aH_2O$ in organic solutions of different diluents in equilibrium with an aqueous phase.
3. Study of the behaviour of mixtures of chloride salts in the aqueous phase on the extraction of the trivalent lanthanides and actinides.

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INVESTIGATIONS ON ELECTROPHORETIC SEPARATION OF AMERICIUM, CURIUM AND VARIOUS LANTHANIDE ELEMENTS.

Electrophoresis (electromigration) on paper has been used as a method for separation of various radio-elements (1). Literature on the application of paper electrophoresis to actinide elements, or mixtures of lanthanide and actinide elements, was found to be scarce (2,3). Therefore we have studied the potentialities of the method for separations in this field. The study of the actinide elements was restricted to americium and curium since among the transplutonium elements these two are the most difficult to separate.

THEORETICAL CONSIDERATIONS.

Paper electrophoresis is an empirical technique. It has been attempted to relate the observed zone mobilities to the mobilities of the ion in free solution. The most successful approach (1) assume that the ions travel through the paper support along winding channels. The zone mobility U_z is than given by

$$U_z = r \cdot U_F, \tag{1}$$

U_F being the free solution mobility and r the "obstruction factor". The value of this factor, however, is in general not known and varies with the electrolyte solution, type of support and various other experimental factors (4). It may be concluded that the zone mobility has a mainly relative value.

When a complexing agent is present in the system the experimental zone mobility found for a certain metal ion will depend on the mobilities and stability of all the species in equilibrium. Let us assume the equilibrium:

$$\left[M\ A_n\right]^{(x-ny)+} \rightleftharpoons M^{x+} + n\ A^{y-}$$

The overall migration of the metal through one square centimeter per second at a potential gradient of one volt per cm. u_c, is governed by the expression:

$$u_c . C = u_{cat} . c_{cat} + u_{compl} . c_{compl} \tag{2}$$

or:

$$u_c = u_{cat} . \frac{c_{cat}}{C} + u_{compl} . \frac{c_{compl}}{C} \tag{3}$$

in which u_{cat} and u_{compl} are the migration rates of uncomplexed metal cations and complex ions respectively, at unit potential gradient. $C = c_{cat} + c_{compl}$ is the total concentration of the metal in solution.

Introducing now the equilibrium constant:

$$K_c = \frac{c_{cat} \cdot c_{an}^{\ n}}{c_{compl}} \qquad (4)$$

in which c_{an} is the concentration of A^{y-}, we obtain from (3):

$$u_c = \frac{u_{cat}\ K_c + u_{compl}\ c_{an}^{\ n}}{c_{an}^{\ n} + K_c}$$

Activities can be substituted for concentrations in deriving formula (5). If we now consider as an example the case of a trivalent metal ion complexed with ethylene diamine tetraacetic acid (H_4EDTA) and assume the equilibrium:

$$M^{3+} + EDTA^{4-} \rightleftharpoons M\ EDTA^{-}$$

equation (5) becomes:

$$u_c = \frac{u_{M^{3+}} \cdot K_c + u_{(MEDTA^-)} \cdot c_{(EDTA^{4-})}}{c_{(EDTA^{4-})} + K_c} \qquad (6)$$

It is seen that u_c depends on K_c and $c_{(EDTA^{4-})}$. If the total concentration of EDTA is chosen constant, the overall zone mobility changes with the dissociation equilibrium of H_4EDTA and hence with the p_H of the solution. An example of the variation of the experimental zone mobility u_c as a function of solution acidity is shown in Figure 7 for a system of trivalent americium and H_4EDTA.

Consider the case of a specific complex forming medium containing ions of two different metals which are in the same valency state and very similar in ionic radius and chemical properties. Americium and curium in EDTA is such a system. The mobilities of the free metal ion and the complex ions will be almost identical and the curves of the mobility vs. p_H will almost overlap. However, if the complex formation constants of the two elements differ slightly, the curves will be displaced along the p_H scale, one relating to the other.

Electrophoretic separation is in principle possible at p_H values where the curves are sufficiently apart, that is near the inflection point in the curve.

EXPERIMENTAL.

The electrophoresis apparatus was obtained from the Locarte company (5). In this apparatus strips of Whatman 3 MM paper of 2 cm width are sandwiched between two polished aluminium plates of 75 cm length. To provide electrical insulation, polythene sheets are placed between the paper strips and the metal plates. The metal plates are pressed together with a pressure of 6 pounds per square inch and are cooled by the circulation of water through the plates. In our set-up the circulating water is cooled by a separate refrigerator. The ends of the paper strips are hanging in paper wicks in the electrode cells. A voltage, up to a maximum of 10.000 Volts, can be applied over the paper strips. The procedure for wetting the paper strip, application of the sample and performing the experiment is described in reference (5).

The elements studied in our experiments were used in tracer-concentration They were americium-241, curium-244, cerium-144, europium-152+154, gadolinium-153, terbium-160, thulium-170 and yttrium-91.

The lanthanides were measured with a Geiger-Müller tube or with a NaI (Tl)-crystal. The actinides were counted with a proportional counter or a scintillation counter. In many cases a 400-channel gamma-ray spectrometer was used to check the separation.

After completion of the electrophoresis, the paper strips were dried and cut into sections of 0.5 cm, which were counted for relative activities with the appropriate counter. This method gives a reliable and more quantitative indication of the degree of separation of adjacent peaks than other detection methods, like autoradiography or colour reactions on the paper. Different complexing agents in various concentrations were used in the experiments. In addition, the solution usually contained a buffer substance for stabilizing the acidity of the solution.

RESULTS AND DISCUSSION.

1. Alphahydroxy isobutyric acid as a complexing agent.

Alphahydroxy isobutyric acid being often used as complexing agent in the separation between lanthanides or between transplutonium elements on cation-exchange columns (6), was also used in our first electrophoresis experiments. For these experiments we chose americium and europium, since these two elements occupy corresponding places in the actinide and lanthanide series, respectively. The best separation was obtained at $p_H = 3.2$ using a concentration of 0.05 M of the complexing agent (0.046 M of the acid and 0.004 M of its ammonium salt, no other buffer was added to the solution). The voltage over the paper strip was 9 kV applied during 1, 2, 3 and 4 hours, respectively, causing a current of 6 mA.

The results are given in table 1, listing the relative concentrations of the radioactive tracers in each paper section in counts per minute. Both elements move to the cathode, europium somewhat faster than americium. This resulted in a complete separation between these two elements. With the same complexing agent, experiments were carried out on a mixture of americium and curium. No p_H value was found, however, where a separation was obtained.

Under the same experimental conditions as described above, a complete separation between americium or curium and the lanthanides studied has been obtained. Figure 8 shows the results of a 3 hours electrophoresis, the applied voltage again being 9 kV, the current amounting to 6 - 8 mA. The lanthanides move faster to the cathode than do americium and curium. Under various conditions as to p_H and complexant concentration, yttrium and the rare earth elements cerium, europium, terbium and thulium were completely separated from each other. Gadolinium was found to overlap thulium and terbium (Figures 8, 9a and 9b).

2. EDTA as a complexing agent.

Since no separation between americium and curium could be obtained with alphahydroxy isobutyric acid, we decided to look into the possibilities offered by EDTA (ethylenediamine tetraacetic acid), which was found by Fuger (7,8) to give in ionexchange experiments separations superior to those so far obtained with alphahydroxy isobutyric acid or other organic hydroxy acids.

It appeared notto be possible to perform the separation with EDTA, without adding a buffer to the solution. The reason for this was, that during electrophoresis a change in the acidity of the solution in the electrode cells occurred which caused an acidity-gradient over the paper strips. The behaviour of both americium and curium changes from cationic to anionic in a very small p_H-range and therefore the acidity of the solution has to be fixed very accurately. As was also found by Fuger in his ionexchange experiments, aminoacetic acid very well stabilizes the acidity. It was not found possible to fix the p_H so accurately that either americium or curium was at its iso-electric point and did not migrate at all in the electrical field.

A 0.001 M solution of EDTA was prepared, containing 0.1 M amino-acetic acid. The p_H was adjusted to 1.6 by the addition of perchloric acid. A tension of 3000 V was applied over the paper strip during 4 hours, causing a current through the paper of 30 mA. Both americium and curium moved to the cathode, americium somewhat faster than curium (see Figure 10). A separation of the peak position of americium and curium was obtained. Figure 10 shows that there is still an overlap in the middle. In fact, 87% of the curium was completely free of americium, and 85% of the americium was completely free of curium. The remainder of these elements was present as a mixture in the intermediate fraction. It might appear possible to obtain a better separation of the peaks on cellulose acetate membrane instead of paper (3). This will be investigated further. At p_H values higher than 2.0 both americium and curium moved to the anode and no separation between the elements was obtained. At $p_H = 1.6$ not only a separation between americium and curium was obtained, but also between these elements and the lower lanthanides as shown in Figure 11 (the curium peak is not plotted in this figure, but as is seen in Figure 10, the position of curium is to the left of the americium peak). The duration of the electrophoresis was 2.5 hours and in this case an americium fraction was obtained, completely separated from the lower lanthanides.

The same result was also obtained at higher p_H values. As an example Figure 12 gives the result obtained at p_H = 9 (after the addition of sodium hydroxide to the solution), where all metal ions present move to the anode. Also in this last case 3000 V was applied over the paper, giving a current through the strip of 4mA. The duration of electrophoresis was 2.5 hours. Here, as in the acid solution americium could be separated from the lower lanthanides present.

3. Other complex forming agents.

Two other complexants were investigated for the separation of americium and curium. These were diethylenetriamine pentaacetic acid (DTPA) and hydroxyethyl ethylenediamine triacetic acid (HEDTA). In acidic aqueous systems these two complexants are known to have a somewhat higher solubility than EDTA. Electrophoresis experiments were carried out with 0.01 - 0.0065 M solutions of either of the two complexing agents as supporting electrolyte. The p_H was adjusted in the range of 1.0 - 2.0, with and without the addition of 0.1 M aminoacetic acid as a buffer.

At a p_H of 1.5 - 1.6 there was practically no migration of americium and curium. Above that p_H, the elements moved both to the anode, below that p_H both moved to the cathode Separation of americium from curium due to differences in ionic mobility was not observed in any of the experiments. However, rather anomalous behaviour was found.
At all p_H values tested americium or curium travelled not as one single band, but in a rather unpredictable way as a number of bands. Moreover the migration distance was not found to be proportional to increasing electrophoresis time and voltage. Both complexants DTPA and HEDTA showed analogous effects.

It was found that this anomalous behaviour could be corrected somewhat by applying tracer solutions on the paper strips which had previously been equilibrated with the complexant. In previous work the samples had been applied to the paper strips as a tracer solution in 0.01 M nitric acid. Now the tracer solution was evaporated first and dissolved in a slightly acid solution containing the complexant in equal concentration as the supporting electrolyte used on the paper strip. With EDTA as a complexant, the electrophoresis results were identical with those obtained using the former procedure for treatment. With DTPA and HEDTA the diagrams were simpler and more reproducible with the new sample preparation procedures. A typical electrophoresis diagram obtained in a test with DTPA is shown in Figure 13, in which americium and curium are present in both peaks. A separation of americium and curium was not obtained under any condition tried. It was assumed that the complex formation of americium and curium with DTPA and HEDTA was a slow reaction, under the prevailing test conditions not leading to dynamic chemical equilibrium. As outlined in the section Theoretical Considerations equilibrium conditions are essential for obtaining good separations between complexed elements which are much alike in properties.

CONCLUSIONS.

a. Electrophoresis in a complexing system of alphahydroxy isobutyric acid is a useful tool for separation of americium and curium from various rare earth metals, and for separation of rare earth metals from each other.

b. Separation of americium from curium was not accomplished with alphahydroxy isobutyric acid.

c. In EDTA medium americium and curium can be separated from various lower rare earths in a wide p_H-range.

d. Americium can be separated from curium in EDTA medium in a very narrow acidity range ($p_H = 1.6$).

e. DTPA and HEDTA, although strong complexants, gave in weakly acid systems irregular results, probably due to slow equilibrium reaction rates. Separations between amercium and curium were not obtained in these complexants.

TABLE I

Migration distance of americium and europium in 0.046 M alphahydroxy isobutyric acid and 0 004 M of its ammonium salt (p_H = 3.2) in 1, 2, 3 and 4 hours, respectively.

Voltage 9 kV; current 6 mA. The concentrations are given in counts per minute of the radioactive tracers.

migration distance	1 hour		2 hours		3 hours		4 hours	
in 0.5 cm	Am	Eu	Am	Eu	Am	Eu	Am	Eu
1	-	-	-	-	-	-	-	-
2	30	-	-	-	-	-	-	-
3	82	-	-	-	-	-	-	-
4	349	78	-	-	-	-	-	-
5	649	92	59	-	-	-	-	-
6	72	257	113	-	-	-	-	-
7	-	356	116	-	-	-	-	-
8	-	1121	275	-	-	-	-	-
9	-	2096	447	47	-	-	-	-
10	-	188	126	73	150	-	-	-
11	-	-	-	208	181	-	-	-
12	-	-	-	667	372	-	-	-
13	-	-	-	1164	644	-	-	-
14	-	-	-	422	616	-	30	-
15	-	-	-	-	493	-	124	-
16	-	-	-	-	63	-	190	-
17	-	-	-	-	-	-	233	-
18	-	-	-	-	-	-	269	-
19	-	-	-	-	-	-	59	-
20	-	-	-	-	-	126	-	-
21	-	-	-	-	-	82	-	51
22	-	-	-	-	-	111	-	92
23	-	-	-	-	-	169	-	131
24	-	-	-	-	-	340	-	200
25	-	-	-	-	-	572	-	265
26	-	-	-	-	-	695	-	590
27	-	-	-	-	-	948	-	652
28	-	-	-	-	-	1058	-	336
29	-	-	-	-	-	804	-	53

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ANION EXCHANGE SEPARATIONS OF AMERICIUM, CURIUM AND VARIOUS LANTHANIDE ELEMENTS.

Separations between transplutonium elements are usually carried out on a cation-exchange resin and using complexing agents like glycolate (1), Lactate (2) or alpha-hydroxy isobutyrate (3). Very good separations are obtained between the elements heavier than americium, but the separation between americium and curium is always rather poor. The best separation factor for the separation between these two elements is obtained with alphahydroxy isobutyric acid as complexing agent and at elevated temperature. At 87° the separation factor between americium and curium was found to be 1.45 (3).

EDTA as complex forming agent was used by Fuger. He obtained about the same value for this separation factor. These separation factors were obtained by the column elution method at 80°C (5). In some cases higher separation factors were calculated from batch equilibrium experiments. Fuger predicted 2.04 for the separation factor between americium and curium from batch equilibrium measurements at 25°C (4).

Marcus and collaborators (6) studied anion-exchange separations between different metal ions in concentrated electrolyte solutions. Good results were obtained in concentrated lithium nitrate solutions for the separation of several of the lanthanide elements. Similar methods have been under study at our laboratory for separations within the group of the transplutonide elements and especially for the separation between americium and curium. Since the start or our work, two articles were published by other research groups on the separation between transplutonide elements on anion-exchange resins in lithium nitrate solution. Adar et al. (7) reported on separations in 4.2 M $LiNO_3$. A fairly nice separation between americium and curium was obtained, but still a small overlapping of the two peaks appears in the elution curve. Marcus et al. (8) also performed their anion-exchange experiments in lithium nitrate solutions (2 and 4 M $LiNO_3$) but did not obtain a complete resolution of the peaks of americium and curium.

EXPERIMENTAL.

The nuclides americium-241, curium-244, cerium-144, promethium-147, europium-152-154, gadolinium-153, terbium-160 and thulium-170 were used in tracer concentrations. The anion and cation exchange resins were Dowex 1 x 8, 200-400 mesh and Dowex 50W x 8, 200-400 mesh, analytical grade.

The resins were pretreated by successive washings with a 1 N NaOH solution, distilled water until neutral, acetone, water, concentrated HCl and water until neutral. Finally the anion resin was brought into the nitrate form with concentrated nitric acid and washed again with distilled water until neutral eluent.

For the determination of distribution coefficients in batch experiments, the resin was dried in air, kept overnight in an oven at 100°C and finally stored in a desiccator over sulphuric acid until needed. To avoid hydrolysis the (metal) nitrate solutions were kept slightly acidic by addition of 0.01 N nitric acid.

Batch experiments for the determination of distribution coefficients were carried out at 20°C, if not otherwise stated. 10 ml of tracer solution of known activity were stirred (by a magnetic stirrer) for two hours in a tube with 250 mg of ion exchange resin. After stirring the mixture was filtered through filterpaper and the radioactivity of the solution counted. The distribution coefficients were calculated from the activities according to:

$$K_d = \frac{C_i - C_e}{C_e} \cdot \frac{V_{sol}}{W_{resin}}$$

C_i is the initial activity per ml of solution.
C_e is the final activity per ml of solution.
V_{sol} is the volume of the solution in ml.
W_{resin} is the weight of the resin in grams.

The separation factor is defined as the ratio of the column elution peak positions of the two elements considered. Column separations were carried out at various temperatures by running water through the heating mantle of the column.

The water was heated in a thermostated bath with a temperature control to within $\pm$ 1°C. In all experiments column dimensions were 25 cm x 2.5 mm diameter. The elution rate was in general $\leqslant 1$ ml/cm^2.min.

Application of a slight overpressure on the eluting solution was necessary to obtain the desired elution rate.

In batch experiments the radioactivity of the rare earth elements and americium was determined with a NaI (Tl)-crystal. Curium was counted in solution with a ZnS scintillation counter arranged as shown in Figure 14. This counting system gave well reproducible results, however, with low efficiency. Alpha countings on samples obtained by a lengthy extraction procedure showed poor reproducibility, caused by co-extracted inactive salts. Our counting method was checked by comparing our results with those obtained by Adar et al (7): exactly the same figures were obtained.

In the case of column experiments a 400 channel gamma-ray spectrometer was used for counting the 59.6 keV gamma-ray of americium and the 18.3 keV X-ray of curium. The concentration of the different nitrates in solution was determined with the aid of a cation-exchange column in the H^+ form. The electrolyte solution was passed over this column and the liberated H^+-ions titrated[*]. The electrolytes used were the purest products commercially available.

RESULTS AND DISCUSSION.

Distribution coefficients of americium and curium were determined in a number of nearly saturated metal nitrate solutions, containing 0.01 N HNO_3. The results are given in table I.

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[*] The assistence of the analytical group under the direction of Dr. Tolk is kindly acknowledged.

T A B L E I

Distribution coefficients of americium and curium between nearly saturated metal nitrate solutions and Dowex-1 (20°C).

Solution	Normality NO_3^-	K_D of Am	K_D of Cm	Ratio $\frac{K_D^{Am}}{K_D^{Cm}}$
Aluminium nitrate	7.3	188	81	2.3
Ammonium nitrate	10.4	23	13	1.8
Calcium nitrate	9.7	16.5	10.3	1.6
Chromic nitrate	7.4	45	28	1.6
Cupric nitrate	11.2	8	-	-
Lithium nitrate	7.9	275	123	2.2
Magnesium nitrate	7.5	297	144	2.1
Manganous nitrate	9.7	34	20	1.7
Nickel nitrate	8.6	244	108	2.3
Sodium nitrate	7.6	35	17	2.1
Zinc nitrate	9.5	44	27	1.6

Since one of the highest ratios of the distribution coefficients was obtained in a concentrated aluminium nitrate solution, further experiments were in the first place carried out in this medium.

1. Aluminium nitrate as an eluant.

First the distribution coefficients of americium and curium were measured as a function of the aluminium concentration. In these, as well as in all other experiments, the nitrate concentration is for ease of comparison expressed in nitrate normality. The dependence of the distribution coefficient of both americium and curium on the aluminium nitrate concentration (at 20°C) is shown in Figure 15. The solutions contained 0.01 N nitric acid to prevent hydrolysis.

At 7 N $Al(NO_3)_3$ (in 0.01 N HNO_3) the influence of temperature on the distribution coefficients was measured (see Figure 16). Subsequently a column separation experiment was carried out between the two elements in a 7 normal aluminium nitrate solution, to which no nitric acid was added (p_H of the solution $\simeq$ 1).
In order to avoid very slow exchange reactions, the elution temperature was set at 60°C, in spite of the fact that from Figure 16 a better

separation might be expected at room temperature. The elution rate was 1 ml in 2 hours. The elution curve (Firgure 17) showed that complete separation of the two peaks was obtained; the free column volume in this curve is equal to half a fraction.

Similar column experiments were also carried out in 4 N, 5 N and 6 N aluminium nitrate solutions. Increase of the aluminium concentration gives a better separation. At 4 N and 5 N $Al(NO_3)_3$ no complete separation between americium and curium is obtained, while at 6 N $Al(NO_3)_3$ the peaks are just coming apart. At 7 N $Al(NO_3)_3$ and under our experimental conditions ten free column volumes separate the two peaks.

The influence of acid concentration in the eluent was also investigated. In batch equilibrium tests an increase in separation ratio (K_D^{Am}/K_D^{Cm}) from 1.9 to 2.5 was found for eluants with acid concentrations from 0.01 N to 1.0 N. (Table II)

TABLE II

Distribution coefficients of americium and curium in 7 N aluminium nitrate solution at various acid concentrations (Dowex 1 x 8).

Solution composition	K_D^{Am}	K_D^{Cm}	Ratio $\frac{K_D^{Am}}{K_D^{Cm}}$
7 N $Al(NO_3)_3$, 0.01 N HNO_3	142	67	1.9
7 N $Al(NO_3)_3$, 0.1 N HNO_3	129	62	2.1
7 N $Al(NO_3)_3$, 0.5 N HNO_3	79	34	2.3
7 N $Al(NO_3)_3$, 1.0 N HNO_3	51	20	2.5
7 N $Al(NO_3)_3$, 1.5 N HNO_3	35	16	2.2
7 N $Al(NO_3)_3$, 2.0 N HNO_3	26	13	2.0

In column elution tests, however, separation factors close to 1.8 were found for acid concentrations nil, 0.01, 0.1 and 0.5 N HNO_3 in 7 N aluminium nitrate. (Table III)

TABLE III

Summary of column elution test data on americium-curium separation.

Eluant composition	Peak elution volume (in Free Column Volumes) Am	Cm	Separation Factor Am/Cm	Elution Rate ml/hr	Notes
7N $Al(NO_3)_3$; $p_H = 1$	130	73	1.78	0.5	
7N $Al(NO_3)_3$; 0.01N HNO_3	120	66	1.82	1	
7N $Al(NO_3)_3$; 0.1 N HNO_3	86	47.3	1.82	1	
7N $Al(NO_3)_3$; 0.5 N HNO_3	76.8	42.8	1.79	0.3	
7N $Mg(NO_3)_2$; 1.0 N HNO_3	56	31.8	1.76	0.6	
7.12N $Ni(NO_3)_2$; 0.01N HNO_3	95	55	1.73	1	1)
10.1N $Ni(NO_3)_2$; 0.01N HNO_3	86	56	1.53	1.5	1)

Note 1) No complete separation of americium and curium obtained.

At increasing acid concentrations, it appeared more difficult to prevent gas bubble formation on the columns. It was supposed that the efficiency loss of the column at higher acid concentrations due to gas formation impaired the americium-curium separation.

It seemed of interest to investigate if separation of americium and curium could also be accomplished on cation exchange resin by nitrate complexing. For that purpose a number of batch equilibrium experiments were carried out in aluminium nitrate solutions of various concentrations. The distribution coefficient for americium on Dowex 50W x 8 was determined in the range of 0.1 N nitrate. As may be expected, the distribution coefficient increased rapidly with decreasing nitrate concentration (see table IV). At 0.4 N aluminium nitrate the distribution coefficient for curium was also determined. The obtained ratio of the distribution coefficients of americium and curium was only 1.3.

TABLE IV

Distribution coefficients of americium and curium between various aluminium nitrate solutions and Dowex-50.

Normality of the aluminium nitrate solution	K_D of Am	K_D of Cm	Ratio $\frac{K_D^{Am}}{K_D^{Cm}}$
4 N	1.3		
2 N	5.0		
1 N	16.4		
0.5 N	49.4		
0.4 N	81.5	62.8	1.3
0.1 N	1762		

Finally the influence of adding alcohol (methanol or ethanol) to a 7 N aluminium nitrate solution on the separation between americium and curium on an anion column was studied. As can be seen in Table V, both the addition of methanol and ethanol to the solution (25 v/v %), increased slightly the separation between americium and curium, while the distribution coefficient of both elements in question was considerably increased. The addition of the alcohol might be important, in separating macroquantities of these two elements, where the high radiation level may give rise to the production of radiolytic gas, which could disturb the equilibrium conditions on the column. This effect could probably be prevented by the addition of an alcohol (9).

TABLE V

Distribution coefficients of americium and curium in concentrated aluminium nitrate solutions containing an alcohol (resin: Dowex 1).

Solution	K_D of Am	K_D of Cm	Ratio $\frac{K_D^{Am}}{K_D^{Cm}}$
A	140	71	2.0
B	219	102	2.15
C	206	97	2.12

A is a solution of 7 N aluminium nitrate in 0.01 N HNO_3

B is a solution of 7 N aluminium nitrate in a mixture of 75% 0.01 N nitric acid and 25% methanol

C is a solution of 7 N aluminium nitrate in a mixture of 75% 0.01 N nitric acid and 25% ethanol.

2. Magnesium nitrate as eluant.

The influence of nitric acid concentration on the ratio K_D^{Am}/K_D^{Cm} in 7 N magnesium nitrate solution in equilibrium with Dowex 1 x 8 resin was tested. The results shown in Table VI were very similar to the data found for aluminium nitrate solution.

TABLE VI

Distribution coefficients of americium and curium in 7 N magnesium nitrate solution at various acid concentrations (Dowex 1 x 8).

Solution composition	K_D^{Am}	K_D^{Cm}	Ratio $\frac{K_D^{Am}}{K_D^{Cm}}$
7 N $Mg(NO_3)_2$; 0.01 N HNO_3	229	130	1.8
7 N $Mg(NO_3)_2$; 0.1 N HNO_3	196	79	2.47
7 N $Mg(NO_3)_2$; 0.5 N HNO_3	106	46.4	2.28
7 N $Mg(NO_3)_2$; 1.0 N HNO_3	71	20.0	2.50
7 N $Mg(NO_3)_2$; 1.5 NN HNO_3	43.5		2.18

As shown in Table III, magnesium nitrate was also tested as an eluant for americium and curium in a column separation experiment (Figure 18). Complete separation was obtained as in elution with aluminium nitrate of equal normality. Some tailing observed at the end of the americium peak might be due to the decreased column efficiency resulting from gas formation, as a rather high acidity was chosen for this experiment.

In batch experiments, distribution coefficients between Dowex 1 x 8 and americium, curium and several rare earth elements were determined. The results are tabulated below.

TABLE VII

Distribution coefficients of Am, Cm and several rare earth elements on Dowex 1 x 8 in 7 N magnesium nitrate solution.

Am : K_D = 287
Cm : K_D = 129
Ce : K_D = 550
Pm : K_D = 133
Eu : K_D = 51.2
Gd : K_D = 34.0
Tb : K_D = 31.9
Tm : K_D = 25.7

The data in Table VII suggest that separation between lanthanide elements may be feasible with higher separation factors than those reported by Marcus and Nelson (6). More work on this subject has been planned.

CONCLUSION.

Aluminium and magnesium nitrate solutions can be used successfully as eluants for separation of americium and curium on Dowex 1 x 8 anion exchange resin. The separation factor calculated from column elution experiments was about 1.8 and complete separation of the two elements was obtained.

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CALIBRATION OF ALPHA EMITTERS IN LOW-GEOMETRY COUNTERS.

INTRODUCTION.

Using a low-geometry system we wanted to see if it is possible to calibrate α-sources as accurately as was done by Robinson 1). A few differences exist between the system used by this author and our counters. Instead of using a ZnS screen covered with a silver layer (in order to increase the pulse height) we looked for the optimum thickness of the ZnS screen itself. If the screen is made thin, some (or all) of the α's will pass through without generating a sufficiently large amount of light. Besides, the possibility of local thin spots or holes makes the efficiency smaller than the calculated geometric efficiency. On the other hand, making the screen too thick, we lose light by absorption in the ZnS. Calculation of the geometry (Gp) goes as follows: 2).

$G_{p'} = 1/2(1 - \frac{z}{D})$ (geometric efficiency for a point source on the axis) See Figure 19. (1)

$$G_p = G_{p'} - \frac{3}{8}r^2 \frac{a^2 z}{D^5} + \frac{15}{32}r^4 \frac{a^2 z}{D^9}(z^2 - \frac{3}{4}a^2) - \frac{35}{64}r^6 \frac{a^2 z}{D^{13}}(z^4 - \frac{5}{2}a^2 z^2 + \frac{3}{8}a^4) + \dots \qquad (2)$$

(geometric efficiency for points off the axis, provided $r < D$)
This may be written alternatively:

$$\frac{Gp}{Gp'} = 1 - \frac{3}{4}r^2 \frac{z(z+D)}{D^4} + \frac{15}{64}r^4 \frac{z(z+D)}{D^8}(7z^2 - 3D^2) + \qquad (3)$$

$$- \frac{35}{256}r^6 \frac{z(z+D)}{D^{12}}(33z^4 - 30z^2D^2 + 5D^4) + \dots$$

For a homogeneous and circular sample placed perpendicular to the axis the average efficiency G_s is given by:

$$\frac{G_s}{Gp'} = 1 - \overbrace{\frac{3}{8}b^2 \frac{z(z+D)}{D^4}}^{A} + \overbrace{\frac{5}{64}b^4 \frac{z(z+D)}{D^8}(7z^2 - 3D^2)}^{B} + \qquad (4)$$

$$\overbrace{-\frac{35}{1024}b^6 \frac{z(z+D)}{D^{12}}(33z^4 - 30z^2D^2 + 5D^4)}^{C} + \dots$$

For the three counting geometries that were normally used, the correction terms A, B and C are presented in Table I.

In the cases where the correction for finite source dimensions becomes appreciable, the values for the measured activities may be too low if the source is not uniform. However, even if all the activity would be deposited along the edge of the source (the very worst case) the error introduced by this effect is in first approximation equal to the term A.

EXPERIMENTAL.

The counters (Figure 20,21) were equipped with a detachable ZnS-screen so that different screens could be mounted in the same geometry. We measured the self-absorption of α's in an electropolated ^{241}Am-sample on a tantalum backing by taking an α-spectrum. It turned out to have FWHM of 35 keV, while the position of the maximum (at 5476 keV) was shifted by less than 2 keV. Using this sample we determined the plateaus for a number of ZnS-screens. We also used a ^{239}Pu-source, made by evaporation on a platinum-disc. In this case the peak-width was of the same order as the resolution of the α-spectrometer itself (~22 keV). In the same counter a 2 mm thick CsI crystal was mounted instead of a ZnS screen using a smaller solid angle in this case, as the crystal was not big enough to cover the whole photomultiplier. A smaller collimator was mounted close to the CsI-crystal (see Fig. 22) and plateaus were determined at different high voltages.

RESULTS AND DISCUSSION.

Although the energies of ^{239}Pu and ^{241}Am α's are almost identical (5.15 and 5.47 MeV for the major decay modes) the plateaus measured with both nuclides are different in that the Pu plateaus are not as flat as those of Am. (See Fig. 23-28). This cannot be explained by the selfabsorption as shown by α-spectrometric measurement. The maximum energy loss of the α's in the source is equal to or smaller than 100.keV.
Screen thicknesses smaller than 8 mg/cm^2 gave appreciable slopes although the lines were approximately straight so that extrapolation to discr. setting = 0 is always possible. However, a commercial screen made by deposition of 4.5 mg ZnS/cm^2 on a plastic foil had so many pinholes that even after extrapolation a loss in the countrate of about 5% remained. The optimum thickness is 10-16 mg/cm^2.

The curve obtained at the thickness 23 mg/cm^2 shows that the absorption of light in the detector begins to play an important role: the pulses are smaller, although they are still fairly well defined in size. The comparison of a ZnS-screen of optimum thickness (12 mg/cm^2) with a CsI-crystal shows that within the accuracy of the counting (~0.4% due to deficient electronics) the count rates for both detectors are the same. It must be remarked that the plateau for CsI is definitely better (slope = 0) than that for ZnS, as expected from the pulse-spectrum.

A comparison was made between counters I and III using ZnS screens of 18 and 14 mg/cm^2 respectively.

The total activities are calculated:

Counter I	Counter III
eff. = 0.06104% (distance = 303.7 mm)	0.5661% (distance z = 62.5 mm) *)
1.045×10^6dpm ± 0.2%	1.046×10^6dpm ± 0.2%

*) These distances were larger than the ones mentioned in table I, due to the fact that thin Pt-backing was used instead of 1 mm glass-discs.

A number of sources were prepared from a stock solution belonging to the International Comparison of Americium-241 in 1963 (3). These sources were counted in counter III. The results obtained are shown in Table II. It should be mentioned that the average activity in the international comparison amounted to 11.29 dps ± 0.2% per mg of the solution for all methods combined and 11.24 ± 0.5% dps per mg for the low geometry measurements only.

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TABLE I

Counting system I. z = (302.8 ± 0.2)mm **) a = (15.020 ± 0.001)mm

Radius of the source b	Correction term *)				Average geometry G_s (%)
	$A \times 10^5$	$B \times 10^5$	$C \times 10^5$	(-A+B-C)x100%	
0	-	-	-	-	0.06140
1	1	-	-	-0.001	0.06140
2	3	-	-	-0.003	0.06140
4	13	-	-	-0.013	0.06139
8	52	-	-	-0.052	0.06137
16	208	5	-	-0.203	0.06129
Counting system II. z = (302.8 ± 0.2)mm **) a = (5.012 ± 0.001)mm					
0	-	-	-	-	0.006849
1	0.5	-	-	-	0.006849
2	1.5	-	-	-0.001	0.006849
4	6.5	-	-	-0.006	0.006849
8	26	-	-	-0.026	0.006847
16	105	-	-	-0.105	0.006842
Counting system III. z = (61.6 ± 0.1)mm **) a = (9.486 ± 0.001)mm					
0	-	-	-	-	0.5825
2	76	-	-	-0.076	0.5821
4	304	1	-	-0.303	0.5807
6	683	5	-	-0.678	0.5785
8	1210	16	-	-1.20	0.5755
10	1900	39	-	-1.86	0.5717
12	2730	81	1	-2.65	0.5671
14	3720	150	6	-3.58	0.5616
16	4850	255	14	-4.61	0.5556
18	6140	410	28	-5.76	0.5489
20	7580	625	53	-7.01	0.5417

*) See formula (4).

**) The values for z differ slightly from those found in the drawings of the counters due to thickness corrections for source supports.

T A B L E II

International Calibration of ^{241}Am solution.

Ampoule nr.	Sample nr.	Support	Diameter	dps/mg	dps/mg **)
37	1 *)	1mm glass disc	11 mm	10.87	10.94
	2	"	9	11.08	11.12
	3	"	12	11.01	11.08
	4	"	13	10.99	11.07
	7	0.1mm Ta-disc	8	11.03	11.06
	8	"	8 à 10	11.12	11.16
	9	"	11	11.12	11.19
	10	"	13	11.03	11.11
20	15	1mm glass disc	8	11.20	11.23
	16	"	9	11.09	11.13
	17	"	6	11.22	11.23
	18	"	8	11.12	11.15

Above activities were measured with ZnS screen of 15 mg/cm^2 and calculated as average of readings at discr. 1 and 4.

21	23 ***)	1mm glass disc	12	11.11	11.18
	24	"	12	11.08	11.15
	25	"	12	10.90	10.97
	26	"	10	11.12	11.17
	27	0.1mm Ta-disc	11	11.12	11.18
	28	"	10	11.02	11.07
	29	"	10	11.16	11.21
	30	"	10	11.04	1..09

These activities were measured with a 17.5 mg/cm^2 ZnS-screen and calculated as average of readings at discr. 1 and 8.

*) Aliquots of 38-56 mg of the stock solution.

**) Activities corrected for source dimensions (see Table I).

***) Aliquots of about 100 mg of the stock solution.

Samples 1, 2, 7, 8, 15, 16 were prepared by evaporation to dryness at room temperature.

Samples 3,4,9,10, 17, 18, 23, 24, 25, 26, 27, 28, 29, 30 were prepared by treatment with colloidal silicate soltuion (Ludox-SM) and evaporation to dryness at room temperature.

SOFT GAMMA AND RöNTGEN SCINTILLATION COUNTING.

GENERAL PURPOSE.

Most alpha-emitting actinides have soft gamma radiation in low intensities and due to high conversion coefficients they nearly always emit L x-rays of rather high intensity. For determination of L x / α ratios of actinides a simple counting apparatus for x-radiation was desired. High counting efficiency and low background were essential in order to obtain good statistics A thin crystal scintillation counter was constructed for this purpose.

DISCUSSION.

1. Construction of the thin crystal counter.

A thin NaI crystal with a diameter of 3 inches and a thickness of 1 mm is mounted by means of a quartz light conductor on a specially selected 3 inch Dumont photomultiplier *). The photomultiplier must be selected for low noise characteristics. The crystal is covered with a 25 μ window of aluminium.

Beryllium is more transparent for radiation of very low energies, but it has two major disadvantages. In the first place, it is rather difficult to make the window construction air- and watertight. Secondly, the beryllium gives a rise in background around 28 keV which is not understood.

The photomultiplier is directly connected to a low-noise preamplifier. High voltage stabilization and noise-free power supply are essential requirements.

The shielding consists, starting from the outside, of subsequent layers of 7 cm of lead, 3 cm of antique lead (200 years old), and 2 cm of copper which is essentially activity-free. The whole arrangement is schematically shown in Figure 29. The antique lead has a low activity because most of the radium D has decayed, but it is still contaminated by uranium and radium. The sample holder is made of activity-free copper.

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*) This "integral line" unit was supplied by Harshaw-Van Den Hoorn, Utrecht.

In preliminary experiments it has been found that antique lead covered with one mm of cadmium and 0.2 mm of copper gives a slightly higher background around 70 keV than antique lead covered with a thick layer of copper.

2. Background.

The background has been found as follows:

10 - 20 keV	4.99 cpm
20 - 30 "	2.43 "
30 - 40 "	1.67 "
40 - 50 "	2.01 "
50 - 60 "	3.03 "
60 - 70 "	2.85 "
70 - 80 "	2.52 "
80 - 90 "	2.46 "
90 - 100 "	2.27 "
10 - 100 "	24.22 ± 1.56 cpm.

3. Determination of efficiency curve.

For determining the efficiency curve of the thin crystal we used the following sources:
^{109}Cd, ^{137}Cs, ^{210}Pb, ^{241}Am, ^{203}Hg, ^{198}Au.

^{109}Cd. This source cannot be calibrated, but it has a well determined ratio between the intensities of the K x-ray peak of 22 keV and the gamma peak of 89 keV (ratio = 23.80 (1)). This gives the efficiency for 22 keV if the efficiency for 89 keV is derived from the well-known efficiencies at 72 and 74 keV.

^{137}Cs. This source can be calibrated easily and accurately by standard procedures ($4\pi\beta$ liquid scintillation counting). The ratio K x/β = 0.0698. This gives a well defined efficiency for 33 keV (K x-ray of Ba).

^{210}Pb. Initially we thought that a source of ^{210}Pb in equilibrium with ^{210}Bi could be calibrated by beta counting of the ^{210}Bi. However, this proved to be very intricate because of the activities of

^{210}Pb itself and of the ingrowing daughter activity of ^{210}Pb. We have not yet succeeded in properly calibrating ^{210}Po. If calibration of these sources would still appear possible this would be very helpful for the determination of the efficiency-curve.

$\underline{^{241}\text{Am}}$. The most used and best known standard source for energies around 60 keV is ^{241}Am. The ratio of the intensity of this energy to the alpha-activity is 0.359 (2). The ratio of the intensities of the L x-rays and alpha's is 0.376 (2). This gives a reliable and absolute calibration for 17 and 60 keV. Gamma radiation of 26 keV with an intensity of 0.025 gamma per alpha gives a minor correction as does the escape-peak of the 60 keV gamma around 31 keV. ^{241}Am can be easily standardized by low-efficiency alpha-counting.

$\underline{^{203}\text{Hg}}$. Calibration of ^{203}Hg is very easy with $4\pi\beta$ liquid scintillation counting. Nevertheless mercuric nitrate sources never gave satisfying results. Evaporating on a disc caused losses of up to 30% of the activity and each day more activity was found to have disappeared by sublimation. A good source proved to be mercuric sulphide made by slow evaporation of an aqueous mercuric solution in a hydrogen sulphide atmosphere. The efficiency for 74 keV agrees well with that of 72 keV, determined with ^{198}Au. The ratio K x/β is 0.127 (1).

$\underline{^{198}\text{Au}}$. If gold is irradiated with a low neutron flux (less than 10^9 n/cm^{2}sec.) during a short time (20 min.), ^{198}Au is formed essentially free of ^{199}Au. Calibration of ^{198}Au can be done easily by $4\pi\beta$ liquid scintillation counting. The ratio K x/β is 0.0255. This gives a good measuring point for the efficiency-curve for 72 keV.

The efficiency-curve derived from measurements of the sources discussed above is shown in Figure 30. Other possible standard sources are ^{210}Pb for 46.5 keV (as discussed above) and ^{88}Y for 14 keV. Both possibilities are being further investigated. The curve has been made using a perspex absorber of 921.5 mg/cm^2. This absorber is necessary to remove possible beta-rays.

The form of the efficiency-curve has been found to be independent of the position of the source. The ratio of the efficiency on a given shelf to the efficiency on shelf 2 is independent of the energy. This was neither expected nor understood.

4. Resolution.

The resolution of the various energies in the crystal is not very good, because there are always small defects in the crystal and in the cathode of the photomultiplier. The resolution can be defined as full width at half maximum divided by the peak-position expressed as a percentage. The square of this percentage plotted versus the inverse of the energy is shown in Figure 31. This gives a straight line as expected, but in general the resolution is rather poor. The L x-rays are not included here because they will always show very broad peaks due to the complex nature of the L x-rays.

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ALPHA-SPECTROMETRY.

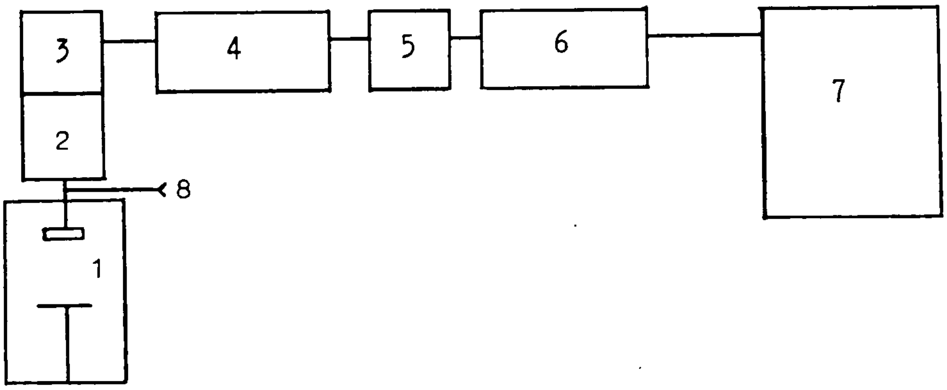
GENERAL.

For determination of the isotopic abundances of alpha-emitting nuclides in a mixture, we needed an alpha-spectrometer. The instrument we used was developed and built at IKO. This instrument, using a semiconductor detector, is essential for routine determination of the activities of nuclides with different alpha-energies. We bought and were given different types of detectors. For routine work the silicon surface barrier detectors are the most useful.

EXPERIMENTAL.

1. Instrumentation.

In principle the instrument is arranged as shown in the following diagram.



1. vacuum chamber with sample and detector
2. charge load amplifier
3. preamplifier
4. linear amplifier
5. pulse shaper
6. window amplifier
7. pulse height analyzer
8. connection for mercury pulse generator.

The detector is situated in a vacuum chamber. For good resolution a vacuum better than 0.1 Torr is needed. The very small pulses from the detector require very short connections with capacities as small as possible.

For this reason a charge load amplifier and a preamplifier, working with six nuvistors is located immediately on top of the vacuum chamber. Between detector and charge load amplifier there is a connection for a cable leading to a precision mercury pulse generator. The combined amplifiers give a total amplification of about twenty times and pulses after amplification are no longer sensitive to small changes of the capacities. The preamplifier is connected to a very good and stable, adjustable linear amplifier, followed by a pulse-shaper, to convert pulses to a shape, detectable by a pulse-height analyzer. After this pulse-shaper and linear amplifier a window amplifier can be used. With this instrument the channel range of a normal 100 channel pulse-height analyzer can be shifted to correspond to the channel range of 900 to 1000. If necessary, the channel range can be shifted continuously to other ranges between 100 and 1000 channels, for instance from channel 400 to channel 500. All efforts have been made to stabilize all parts of the instrument by air-cooling, by air-conditioning the room, stabilizing the main-voltage and by many other electronic methods. In this way the stability of the instrument is better than 10^{-3} over a period of 24 hours. An adjustable precision mercury pulse generator can satisfactorily simulate an alpha-pulse originating from a surface barrier detector. Once the pulse generator is calibrated, it is very easy to determine the energy of unknown peaks in a spectrum and to set the instrument working on a desired energy range. In fact this pulse generator is indispensable.

2. Detectors.

Farout the best alpha detectors are the gold-plated silicon surface barrier detectors. A resolution of 20 keV full width at half maximum is only possible with this type of detectors. Best commercial detectors are those of ORTEC, but in Saclay detectors are made just as good and detectors made by the research department of the Philips Company are very similar. Detectors with a sensitive area of 20 mm^2 have the best resolution, but with less resolution it is possible to make spectra using detectors with surfaces of up to 300 mm^2.

3. Sources.

Sources for calibrating and counting must be as thin as possible to have the best results. Samples with a thickness less than 10 μg/cm^2 are always good, above 100 μg/cm^2 resolution becomes very bad. Most of our sources used in alpha-spectrometry are made by electroplating.

DISCUSSION OF RESULTS.

1. Efficiency.

In most cases the minimum distance between source and detector is 15 mm. With a 20 mm^2 detector this gives an efficiency of about 0.7%. With weak sources and low relative abundances for alpha's to be investigated, this demands long counting times requiring maximum overall stability.

2. Linearity.

In nearly all cases a linearity of better than 10^{-3} is found and any deviation can be explained by the thickness of the sample and differences in data from literature. Using the table of alpha emitting nuclides, listed according to increasing energy of the alpha radiation (1) all deviations of linearity are less than 10^{-3}.

3. Noise.

The electronical noise of the instrument without detector has a full width at half maximum of about 11 keV measured with a 63 Hertz mercury pulse generator.

4. Background.

A detector, which is not contaminated (for instance by recoil atoms) has a background of less than 0.01 cpm/channel.

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PREPARATIONS OF SOURCES AND TARGETS OF ACTINIDES.

GENERAL INTRODUCTION.

Many investigators have published methods for making thin and thick sources of actinides. Thin and very homogeneous sources are required for α- and β-spectrometry work and for absolute counting. Much thicker sources are required as irradiation targets. The methods used for making thin and thick sources and targets are in general the same. These methods can be classified as follows:

a. electroplating and electrophoresis (references (1) and (2))
b. electrospraying (reference (3))
c. sublimation in vacuo.

ad.a. Electroplating and electrophoresis is most commonly used but with very divergent results. It seems that every expert has his own procedure which works more or less well only for himself. Duplicating of published results is in most cases impossible. Most probably small differences in the procedures have a big influence on the results and the authors are not aware of all these seemingly unimportant conditions. In general it can be said that electrolysis of very small quantities of activities gives low plating efficiencies.

ad.b. Some authors have published a method of making very homogeneous layers of actinides by electrospraying. This technique gives good results only when all the circumstances and details of the apparatus are very well under control. In the Bureau Central de Mesures Nucleaires of Euratom at Geel, Belgium, for instance, a good team is working in this field. Of all sources of actinides, those made at Geel are the best, especially the thin ones for counting standards. However, this method is too difficult and too expensive for making cyclotron targets.

ad.c. Sublimation in vacuo of chlorides of the actinides gives nice counting sources. But sublimation on to too big surfaces like 7 cm^2 is very difficult and worst of all, at least 30% of the starting material is lost somewhere in the vacuum chamber. Because the actinide chloride spreads as a dry powder, very strict safety measures have to be taken to avoid contamination. Such a procedure is too elaborate for us to try on a large scale as is required for making cyclotron targets.

In our Institute we restrict ourselves to electroplating and electrophoresis because:

instrumentation is simple
no dry powders are used
hardly any of the starting material is wasted
all manipulations can be done in normal glove boxes
one or two platings a day can be done by one technician
the methods are rather reliable and cheap.

THE ELECTROLYSIS CELL.

The construction of the cell is shown in Figure 32. For each type of activity we use a different perspex (lucite) cylinder because these cylinders become heavily contaminated and it is difficult to clean them. Cooling is done by placing the whole cell in a small water bath.

DISCUSSION OF RESULTS.

1. Electroplating of thin layers.

Thorium.

We have never been able to plate thorium from aqueous solutions.

Uranium.

As is commonly done, we plate uranium from a solution of 5 M ammonium oxalate. A uranyl nitrate solution in nitric acid is evaporated to dryness and dissolved again in nitric acid. This is repeated several times. After the uranyl nitrate is dissolved in 5 M ammonium oxalate, electroplating can be carried out on a variety of metals such as copper, nickel, platinum, stainless steel, but the best of all is nickel. Cathode metals must be made absolutely free of any dirt, grease and oxides. Cleaning with ethylene trichloride followed by immersion in hot nitric acid is normally satisfactory. Temperature is maintained at 80°C. The anode is made of platinum.
The distance between anode and cathode is about 15 mm. and the current density is kept between 30 and 50 mA/cm^2 (of the cathode).

The starting solution has to be weakly acid (p_H 2 to 4). In the course of the plating, the solution becomes neutral or basic and then a brown precipitate of uranyl hydroxide occurs. This can be dissolved by adding some oxalic acid up to p_H 2 to 4 and the plating can be continued. The plating is almost complete within one hour but in most cases it will be continued for 3 or 4 hours. Efficiency is between 90 and 100%. The resulting black layer adheres very well to the metal and is fairly homogeneous. In the centre the thickness is at least 90% of that at the edge. Sources of 30 mm diameter or less can be made in this way.

Neptunium.

Neptunium can be plated in the same way as uranium. We use an electrolyte solution of ammonium oxalate at 80°C. High yields are possible on nickel, platinum, stainless steel and tantalum. Stirring or vibration of the platinum anode is necessary. Thorough cleaning and etching of the cathode material is essential. The neptunium nitrate has to be extremely pure to get adherent layers with high yields. Repeated plating gives layers with a thickness of up to 1 mg/cm^2 on 7 cm^2 discs.

Plutonium.

Of all actinides plutonium is the most difficult element to electroplate, especially on large surfaces. Initially we tried to plate just like uranium in oxalate solution. This requires hexavalent plutonium, made by oxidizing with sodium bromate. This is not easily done for a high percentage of the plutonium and plating is nearly impossible with sodium, bromate and bromide ions in the solution. Only very few platings succeeded on small surfaces. Therefore we abandoned this method. Electroplating in a 0.075 M solution of ammonium formate in 0.05 M sulphuric acid gives much better results. Here tetravalent plutonium is needed. A plutonium solution is evaporated to dryness with nitric acid and dissolved again in nitric acid. This is repeated several times. Finally the plutonium IV nitrate is dissolved in the formate solution. The plating is possible on platinum, gold, copper, stainless steel and tantalum. Clean cathode surfaces are extremely necessary. Temperature is maintained between 30° and 50°C. The anode is made of platinum. The anode-cathode distance is 15 mm and the current density through the cell is between 30 and 50 mA/cm^2 on the cathode. Good adherent layers are obtained with a yield of 40 - 60%, seldom much better. The yield is very much dependent on the composition of the solution. Foreign ions diminish the plating yield heavily. Therefore the plutonium solution has to be freed rigorously from all ions except ammonium and formate. The p_H has to be kept at about 2. The plating is completed in about 4 hours.

Americium and Curium.

The transplutonium elements can be plated easily from aqueous formate solutions, just like plutonium. Cathode materials can be platinum, gold, stainless steel and tantalum. The yield is in most cases 60 - 100%. No special difficulties are met and plating time is less than one hour.

2. Electroplating of thick layers.

Uranium.

With no more trouble than with thin layers it is possible to electroplate uranium on nickel discs with an active diameter of 30 mm. Plating time is about 4 hours and from time to time oxalic acid has to be added to the plating solution to keep the solution weakly acid. With repeated electrolysis the layer thickness can be made as high as 1.7 mg/cm^2.

Neptunium.

This element gives more trouble than expected at first and we have little experience with it up till now.

Plutonium.

Really thick layers of plutonium are very difficult to make. With plating solutions of ammonium oxalate we never succeeded and with the formate procedure we found only one more or less workable way at last. First of all, one has to be sure to have very pure tetravalent plutonium nitrate without any other contamination than ammonium ions. The procedure is just the same as with thin layers but only gold cathodes will give results and only pure (24 carat) gold will do (22 carat gold didnot work). The gold cathode is cleaned and pretreated in the following way. During one hour the plating solution without activity is put into the cell and a very high current is applied. This electrolysis of the solution cleans the cathode throroughly. The solution is removed and a new portion of the same solution is put into the cell. After some minutes of normal electrolysis with a 50 mA/cm^2 current density, the current is reversed during 5 or 10 minutes. On the cathode an oxide layer is formed, with a red colour. Then very carefully the current is put in the normal direction. Within one minute the red colour changes over to bluish green and to greenish black. Then the active electrolysis solution is poured into the cell. For best results the platinum anode can be vibrated to remove all gas bubbles. (Normal platinum is not strong enough to resist the vibration, but a platinum 10% iridium alloy will do). On such a pretreated gold plate it is possible to make thick plutonium layers but with increasing diameter the layer thickness diminishes. For 3 mm diameter it is possible to have 2 mg/cm^2 but for 30 mm diameter only 0.3 mg/cm^2. This can be done only by repeated electrolysis. The layer is adherent and looks nice but we are not satisfied with these results for use as cyclotron targets.

Americium and Curium.

We have no experience with thick layers of transplutonium elements.

3. Electrophoresis.

General.

According to several authors (2) it is rather easy to use electrophoresis to put a layer of an oxide on a metallic base. If a non-aqueous solution of thorium or rare earths is put into a cell with an aluminium cathode and a platinum anode and if a very small current is maintained between these electrodes a thin layer of the oxide is formed on the cathode. Naturally this aluminium base has to be very clean and as smooth as possible. The same cell is used as for electrolysis. We have had experience only with plutonium.

Plutonium.

Very clean and thoroughly separated plutonium has to be used in order to obtain good results. A solution of plutonium is made by absorbing tetravalent plutonium in 7 molar nitric acid on a Dowex 1 x 8 column and eluting it with 0.5 molar hydrochloric acid. The solution is evaporated to dryness and the residue is dissolved in ethyl alcohol.

This solution has to be fresh and the alcohol must be kept in a glass bottle and not in a polyethylene bottle. We had bad experiences with plastic bottles. The solution for the electrophoresis has to contain some, but not too much water; a few drops of water in 20 ml pure ethanol is enough. This solution is poured into the cell.

Electrophoresis on aluminium discs with an active surface of 30 mm diameter can be carried out with only 25 volt and 15 mA. In one run between 8 and 14 mg can be precipitated on the aluminium disc within 2 to 4 hours. We got some discs with very nice and adherent layers, but also some with loose parts in the middle. The discs with good adherence are very useful as cyclotron targets. Although it is possible to make a thick layer in one run, it is always better to precipitate only 5 mg at a time and to repeat the procedure. We know nothing of the homogeneity of the layers up till now. The total activity is determined by counting the 30-415 keV gamma radiation of the sample on a NaI crystal in comparison with the same gamma activity of a source of 0.5 mg on the same surface of 7 cm^2. This standard source can be counted for alpha activity in a low efficiency absolute counter.

Electrophoretic deposition on supports other than aluminium is not feasible.

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FIGURE LEGEND

1. Titration of TiOA.HCl with NaOH in water-acetone
   curve 1 a sample of the untreated amine
   curve 2 a sample of the highest boiling fraction

2. Extraction of Am and Eu as a function of the hydrochloric acid concentration in the aqueous phase
   organic phase 0.5 M TiOA.HCl
   aqueous phase 5.5 M $MgCl_2$ (Riedel de Haen)

3. Acidity of a $MgCl_2$ solution as a function of the hydrochloric acid concentration. Acidity is expressed as the potential in mV of a glass electrode versus a calomel electrode
   curve a 5.5 M $MgCl_2$ from Riedel de Haen
   curve b 5.5 M $MgCl_2$ from Merck

4. Extraction of Am and Eu as a function of the TiOA.HCl concentration in xylene
   Aqueous phase: 5.5 M $MgCl_2$ - 0.01 N HCl

5. Extraction of Am as a function of hydrochloric acid concentration
   Organic phase 0.5 M TiOA.HCl in xylene
   Aqueous phase the chloride salts: LiCl 12 M; $MgCl_2$ 5.5 M; $CaCl_2$ 5.0 M; $AlCl_3$ 5.0 M

6. Extraction of Am as a function of the free water concentration in the organic phase. The free water concentration is expressed as moles litre^{-1}
   Diluents used: benzene, toluene, xylene, ethylbenzene, cumene, cyclohexane and dekaline
   curve 1 20% TiOA - 12 M LiCl
   curve 2 0.5M TiOa - 12 M LiCl
   curve 3 0.5M TiOA - 8 N LiCl + 2 N $AlCl_3$
   curve 4 0.5M TiOA - 10 M LiCl

7. Zone mobility of americium EDTA complex as a function of p_H of the solution. Voltage 3 kV, duration 2 hours, temp. 10-11°C composition of the supporting electrolyte 0.001 M EDTA, 0.0001 M Ce^{3+}, 0.01 M aminoacetic acid
   p_H adjusted with $HClO_4$ or NH_4OH

8. Electrophoresis of americium and various lanthanides in a 0.05 M alphahydroxy isobutyric acid solution, $p_H = 3.2$

9. Separation of yttrium and some of the rare earth elements by electrophoresis; $p_H = 3.5$, alphahydroxy isobutyric acid (a) 0.03 M; (b) 0.003 M

10. Electrophoretic separation between americium and curium in a solution containing 0.001 M EDTA as complexing agent and 0.1 M aminoacetic acid as a buffer
Voltage 3 kV; current 30 mA; duration 4 hours; $p_H = 1.6$ obtained after the addition of perchloric acid

11. Electrophoretic separation between americium and different lanthanides
Duration 2.5 hours; other circumstances the same as in Figure 10.

12. Electrophoretic separation between americium and different lanthanides
The solution contained 0.001 M EDTA as complexing agent and 0.1 M aminoacetic acid as buffer
Voltage 3 kV; current 4 mA; duration 2.5 hours
$p_H = 9$, obtained by addition of sodium hydroxide to the solution

13. Electrophoresis of americium/curium mixture with DTPA. Supporting electrolyte: 0.0065 M DTPA, adjusted to $p_H = 1.6$ with $HClO_4$.
Sample: americium/curium tracer in 0.0065 M DTPA, 0.001 M HNO_3
Voltage 3 kV; current 33 mA; duration 3 hours. Whatman paper 3 MM.
Americium and curium are present in both peaks.

14. Schematic drawing of ZnS-scintillation counter for direct counting of solutions

15. Distribution coefficients of americium and curium on Dowex 1 x 8 in $Al(NO_3)_3$ solution (0.01 M HNO_3) as a function of the nitrate concentration

16. Influence of temperature on the distribution coefficients of americium and curium in 7 N aluminium nitrate (0.01 N HNO_3)

17. Ion-exchange separation between americium and curium
Resin: Dowex 1 x 8, 200 - 400 mesh
one fraction is 1.5 ml
column dimensions: 25 cm x 2.5 mm
temperature: 60°C
elution velocity: 1 ml in 2 hours

concentration: tracer amounts
the solution contained 7 N $Al(NO_3)_3$, no nitric acid was added:
$p_H \cong 1$.

18. Ion-exchange separation between americium and curium (tracer concentrations).
Resin: Dowex 1 x 8, 200 - 400 mesh
column dimension: 25 cm x 2.5 mm
temperature: 60°C
elution velocity: 1 ml in 2 hours
one fraction is 1.5 ml
eluant: 7 N $Mg(NO_3)_2$, 1.0 HNO_3.

19. Calculation of the geometry of low-geometry counters: relative position of sample and collimator

20. Cross-sectional drawing of counting system I. Baffles and collimator machined to 45° angles. Material: nickel plated brass. Maximum sample radius b_{max} = 20 mm

21. Cross-sectional drawing of counting system III b_{max} = 17 mm

22. Mounting of the different types of detectors

23. Plateau.(count-rate vs. discriminator setting) of ^{241}Am sample, measured with ZnS screen of thickness 8.1 mg/cm^2

24. As Figure 21, screenthickness 15.0 mg/cm^2

25. As Figure 21, screen thickness 23.2 mg/cm^2

26. Plateau of ^{239}Pu sample, measured with ZnS screen of thickness 8.1 mg/cm^2

27. As Figure 24, screen thickness 15.0 mg/cm^2

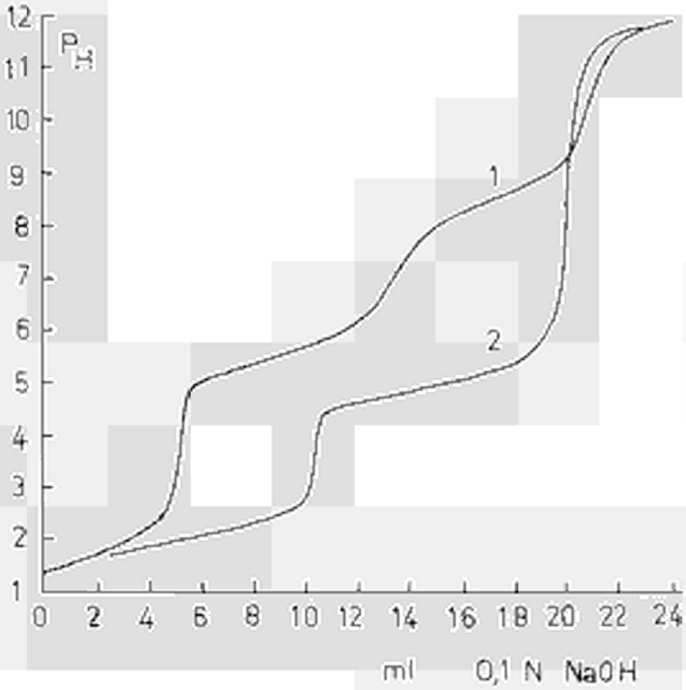
28. As Figure 24, screen thickness 30.2 mg/cm^2

29. Simplified design of the shielding of the thin crystal counter

30. Efficiency curve of the thin crystal counter. Perspex absorber, 921.5 mg/cm^2. Source in fixed, arbitrary position

31. Resolution of the thin crystal counter plotted versus the inverse of the radiation energy (keV^{-1})

32. Cell for electroplating and electrophoresis. Before use the parts are screwed together.



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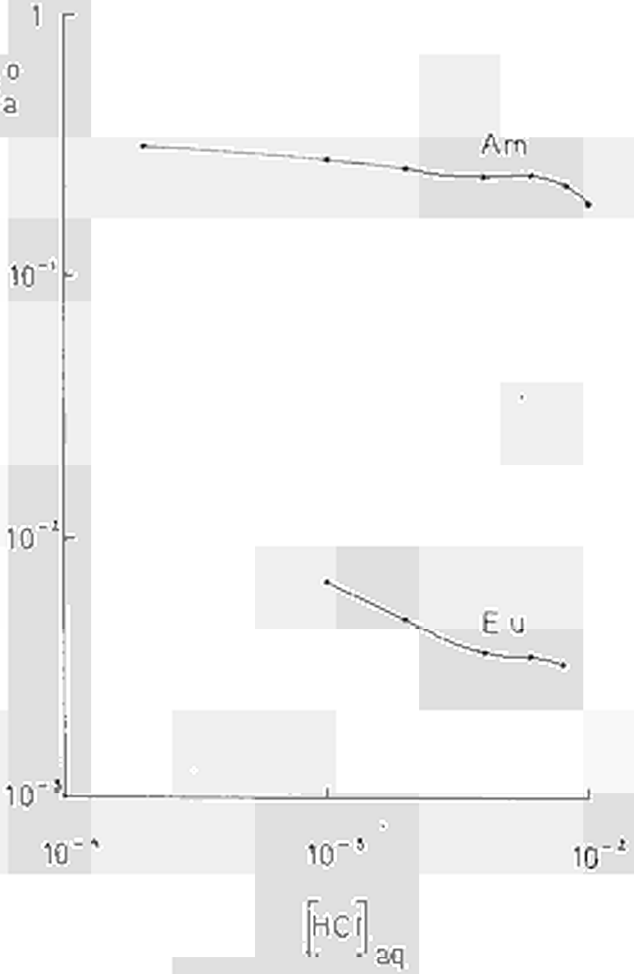

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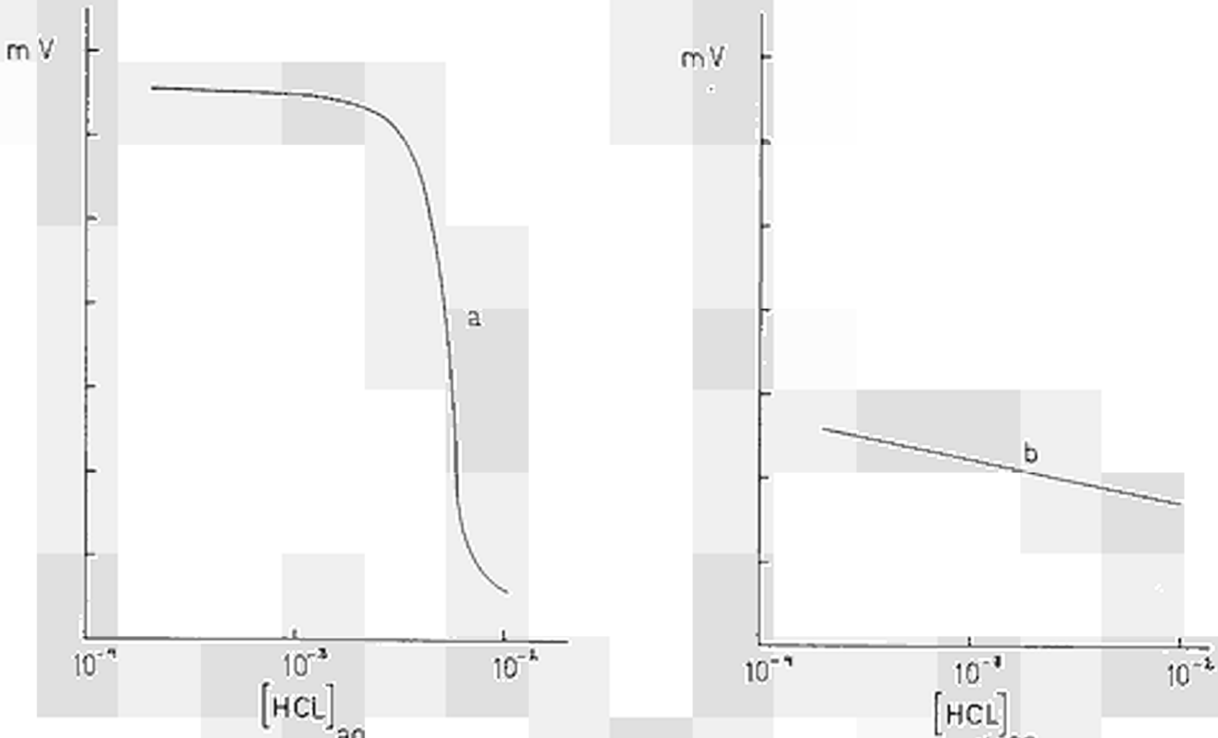

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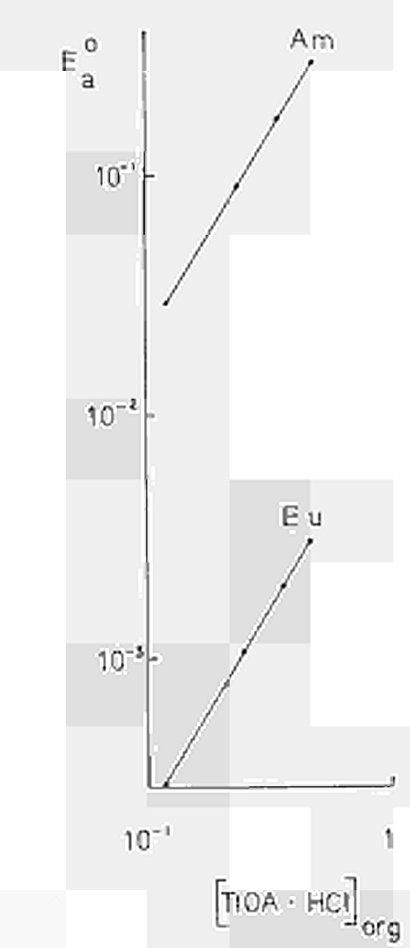

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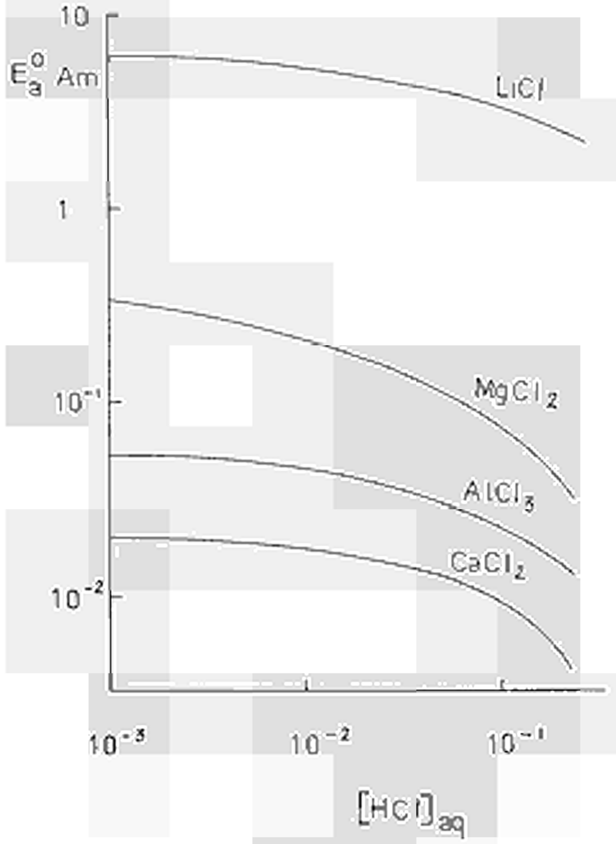

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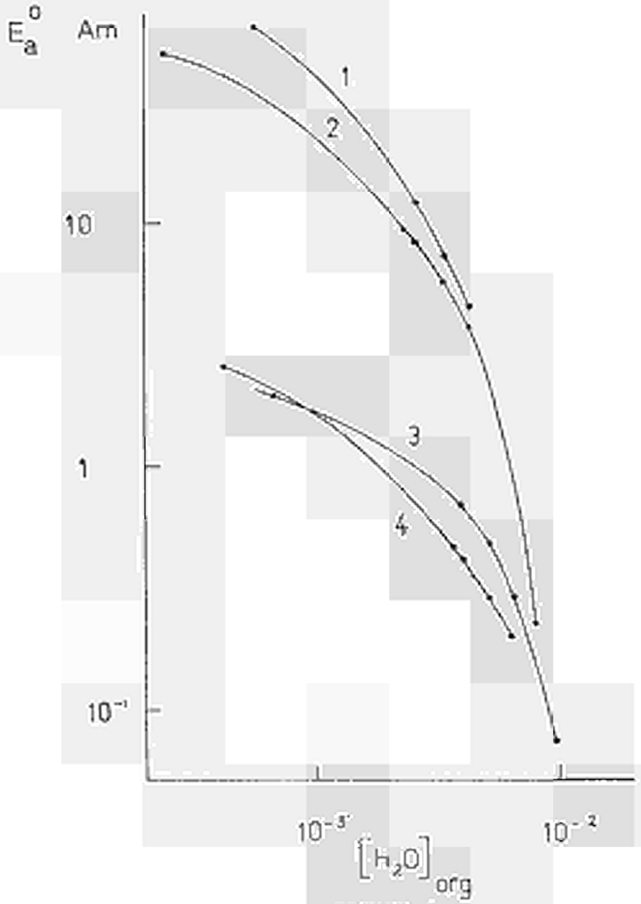

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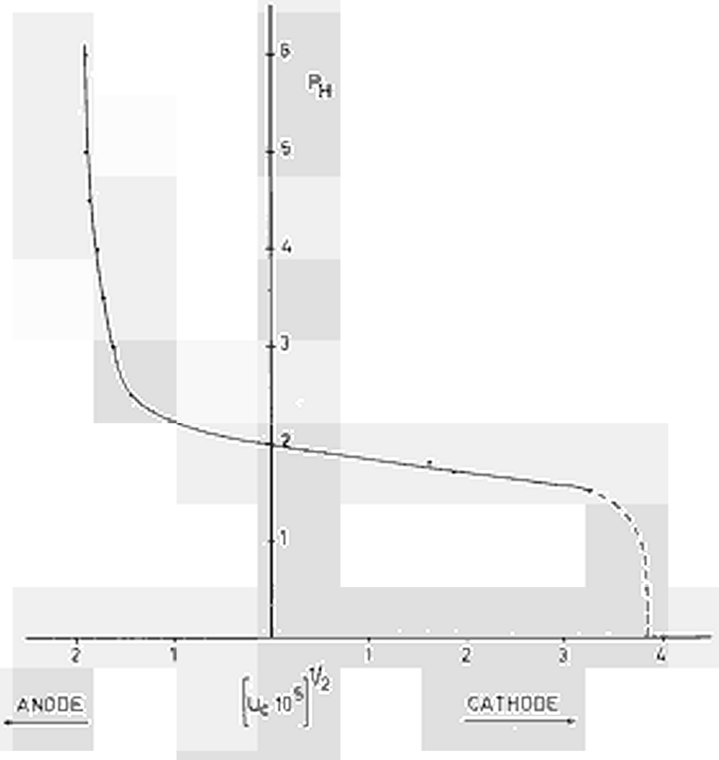

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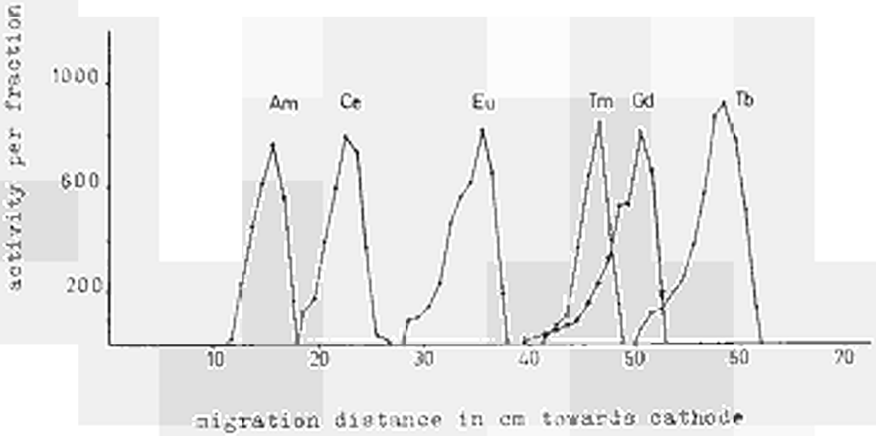

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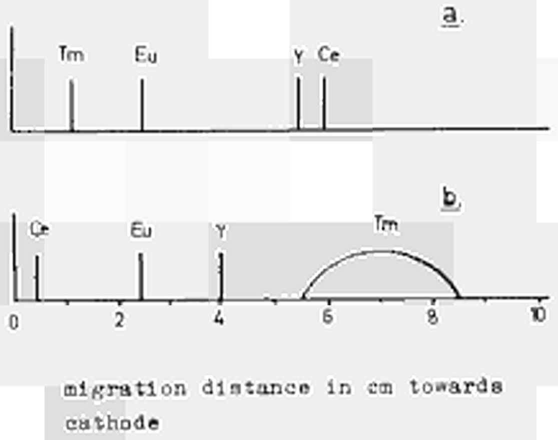

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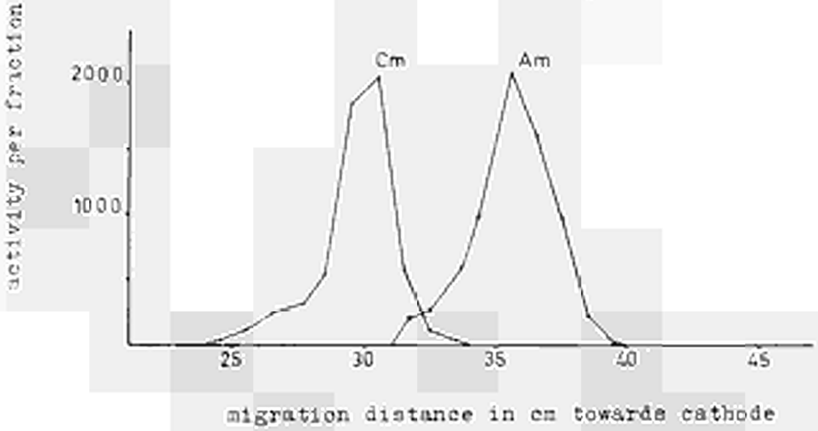

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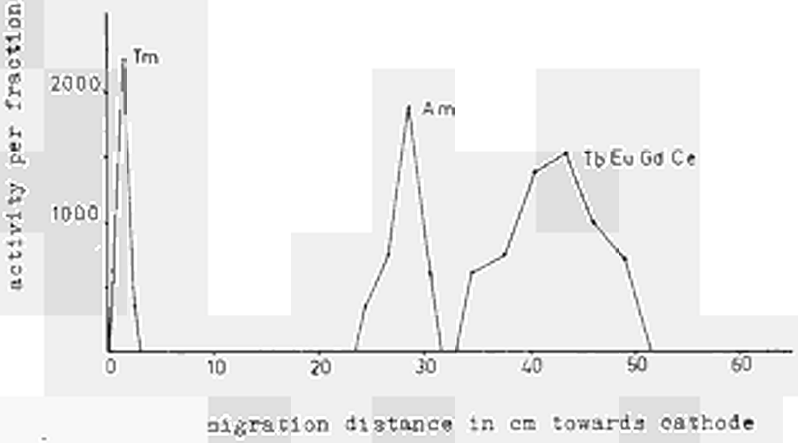

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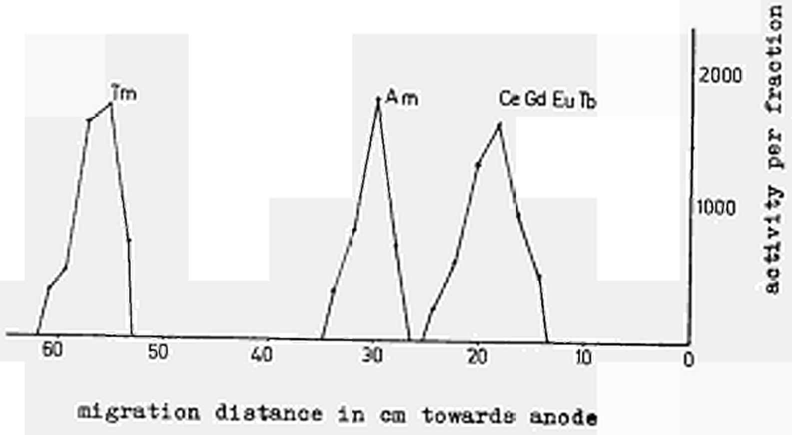

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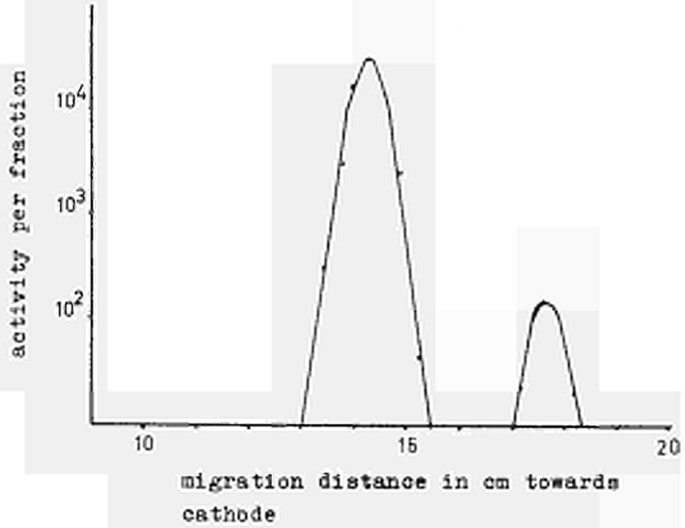

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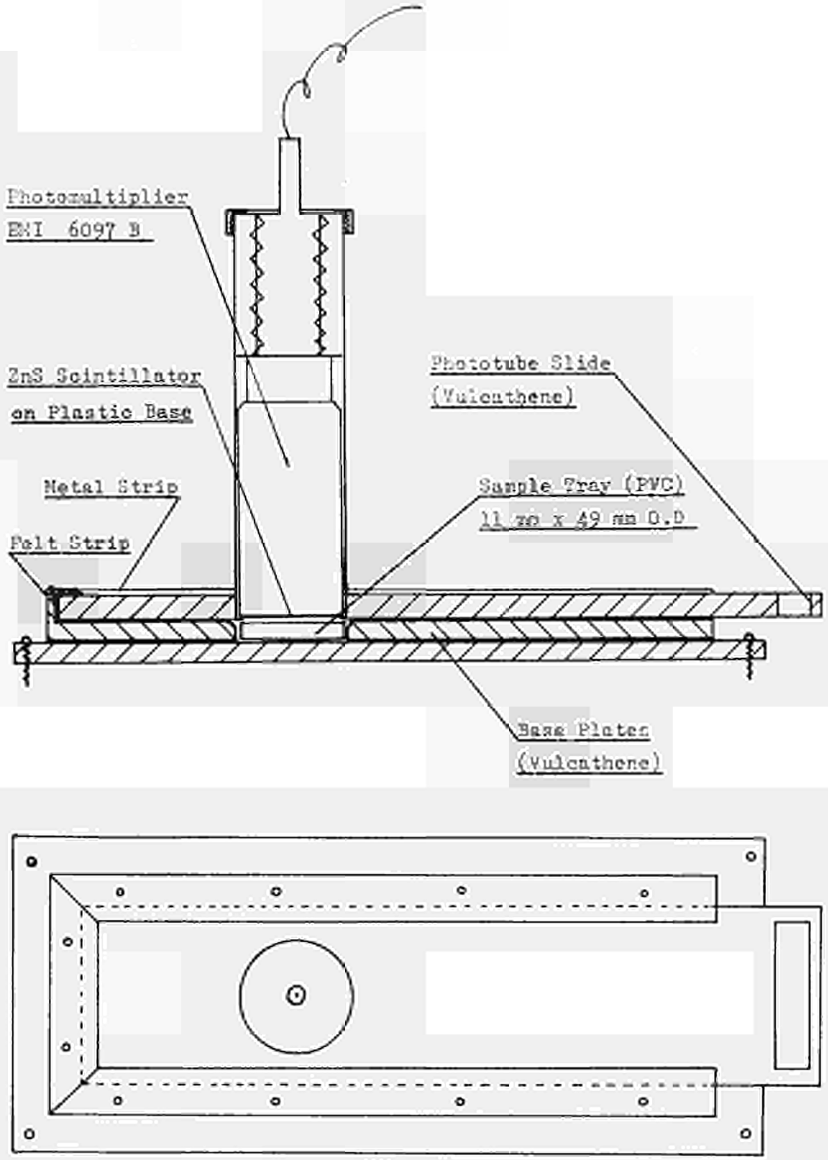

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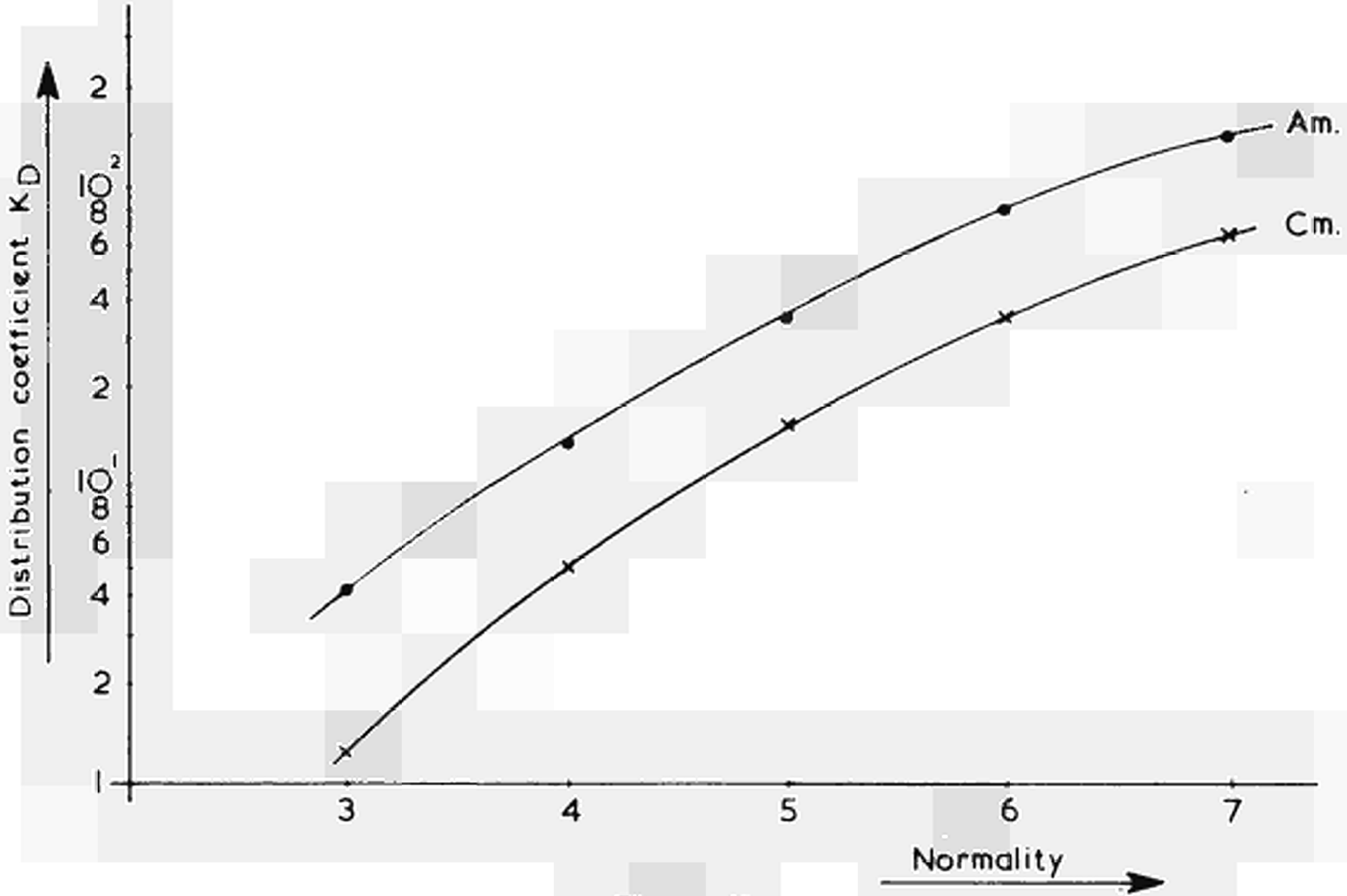

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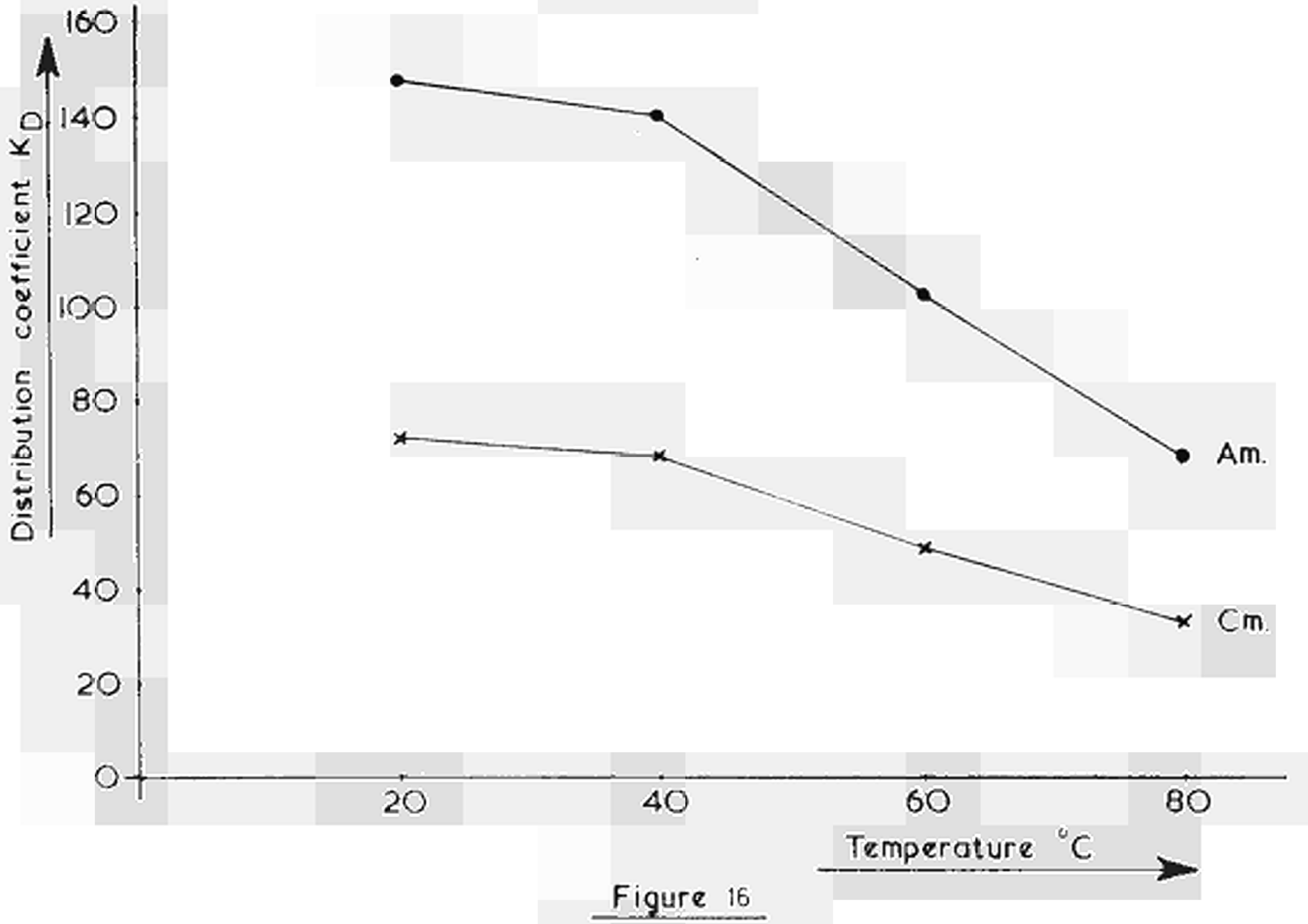

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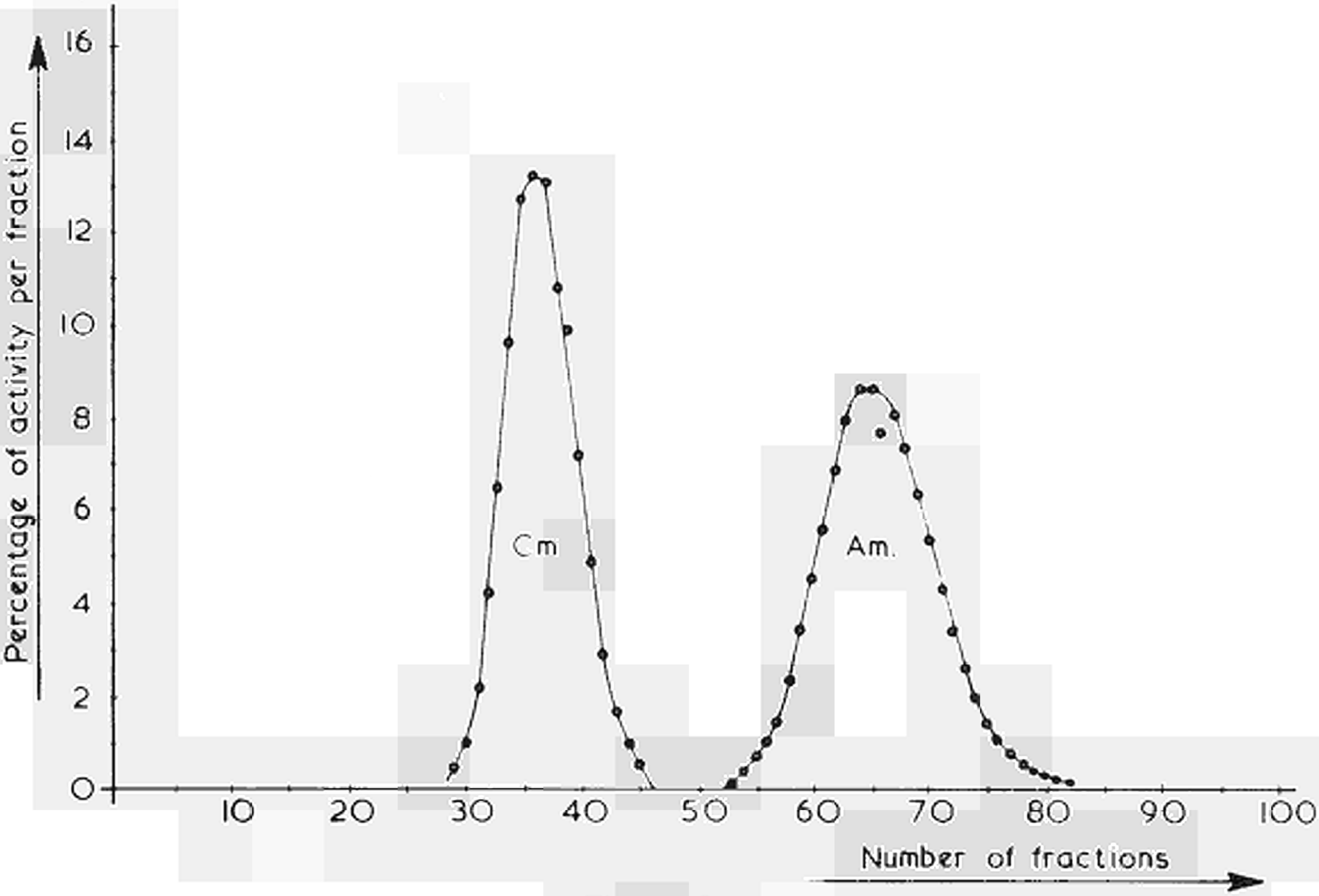

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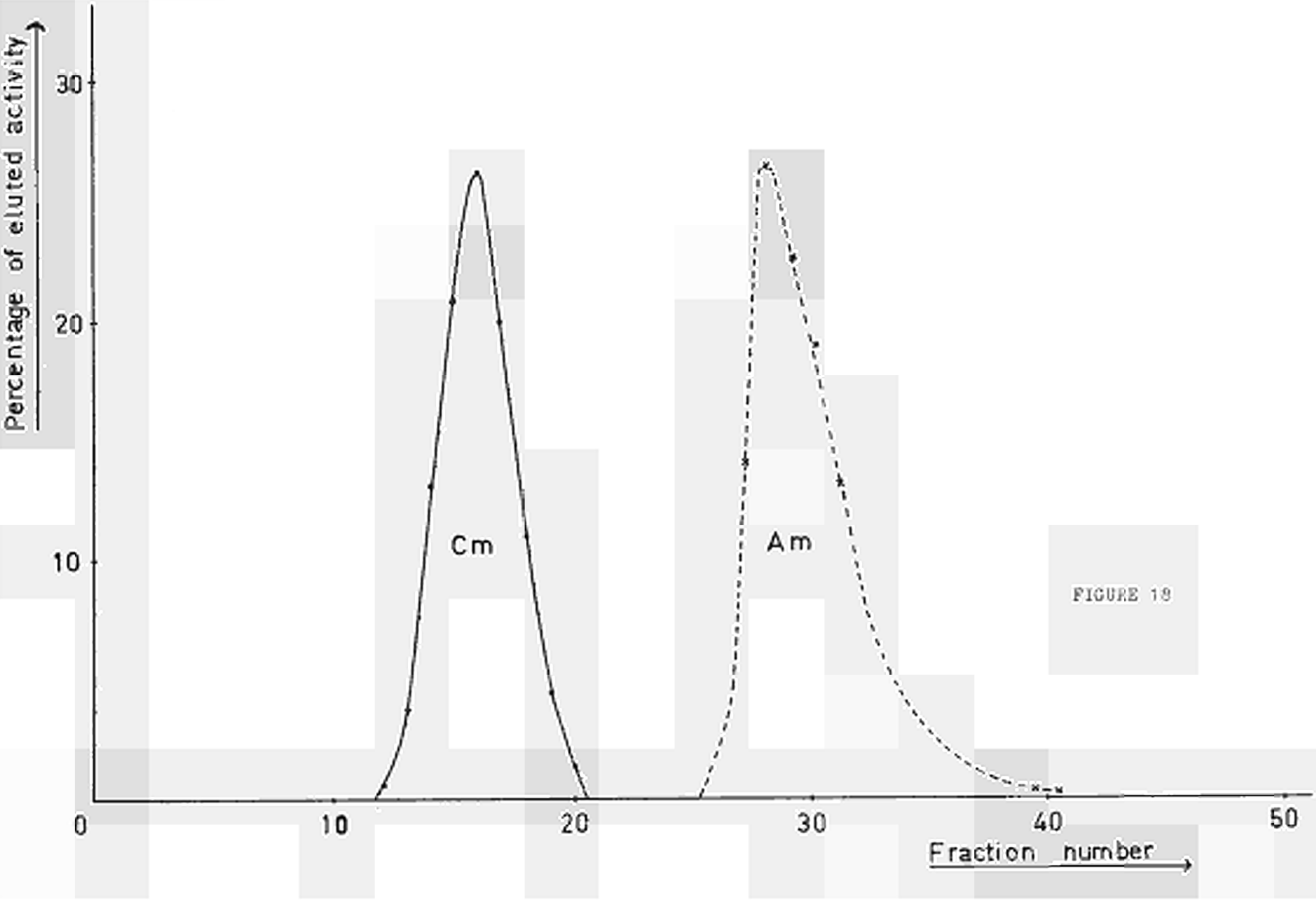

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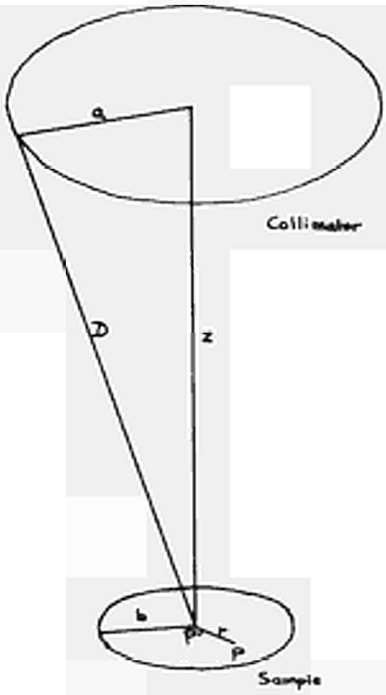

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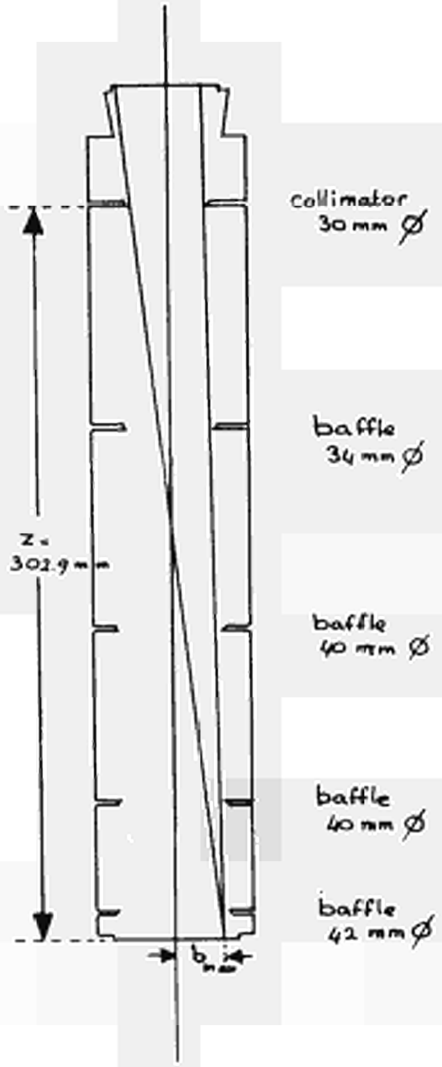

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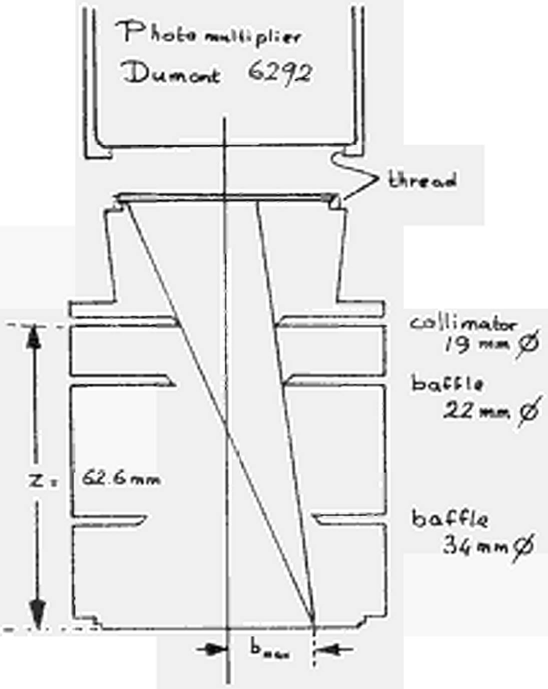

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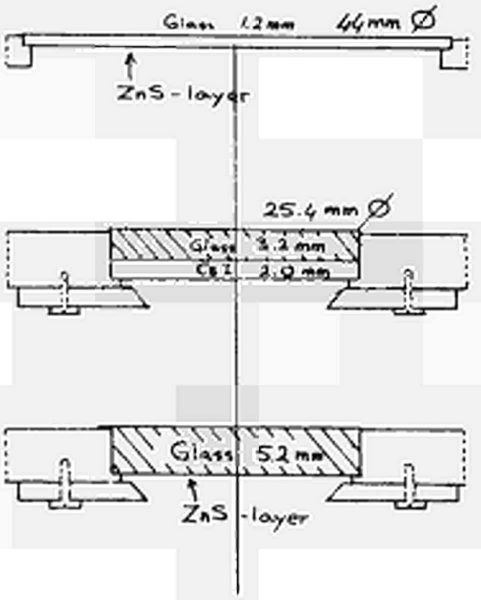

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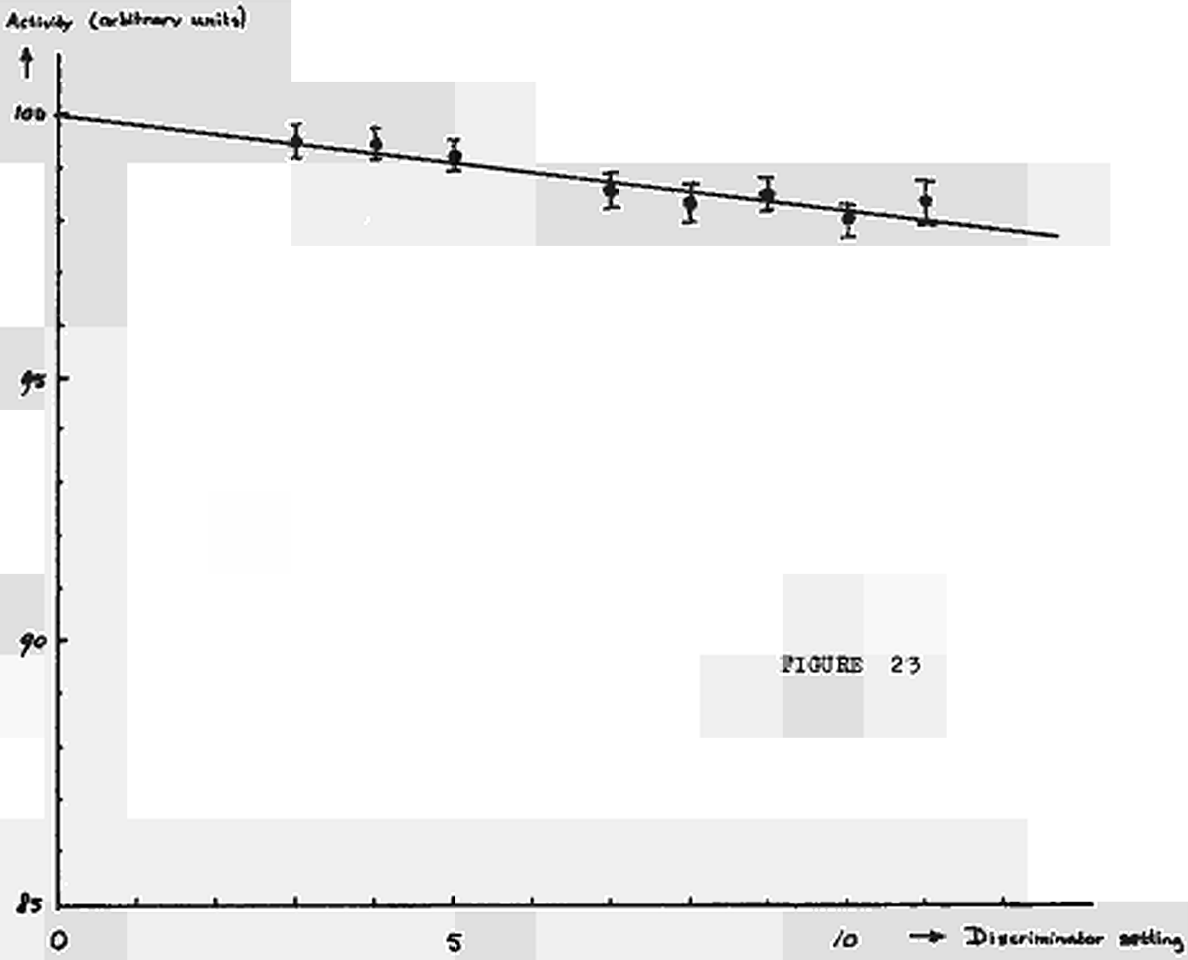

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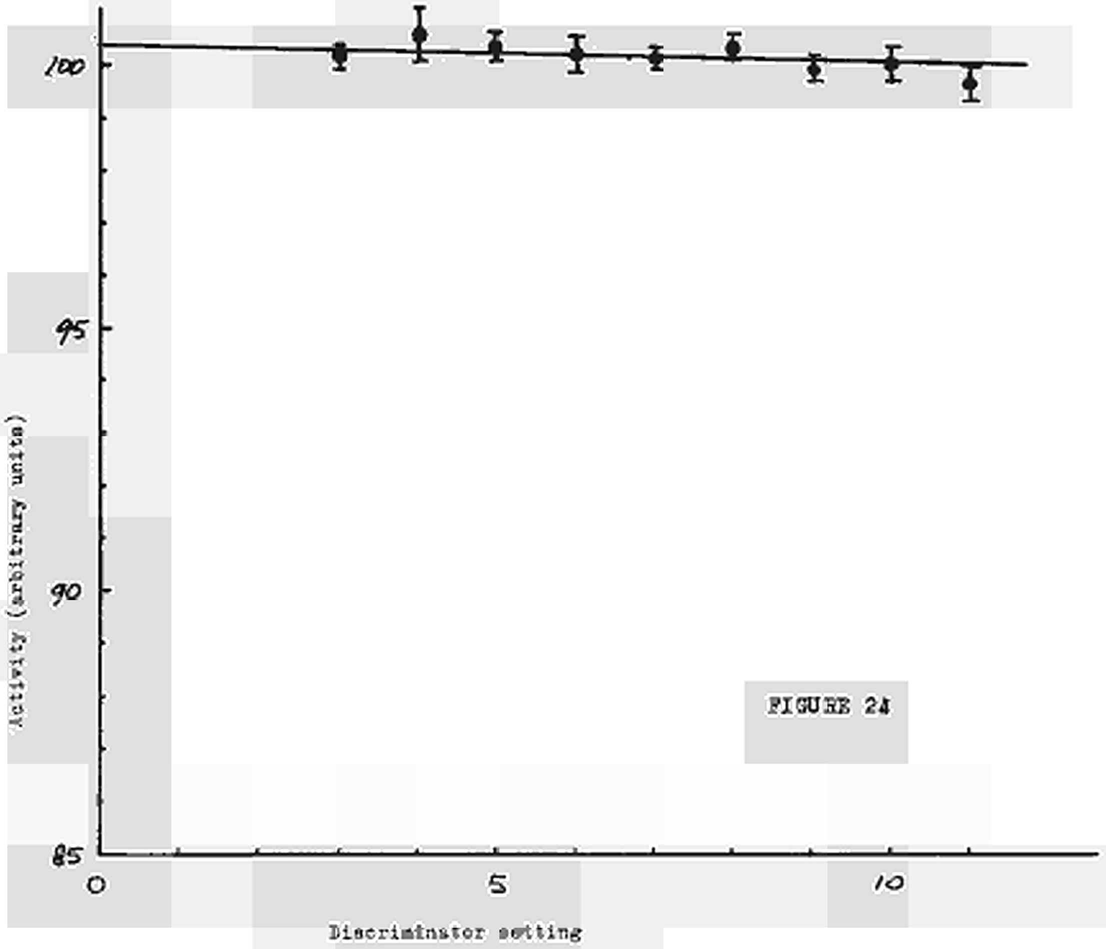

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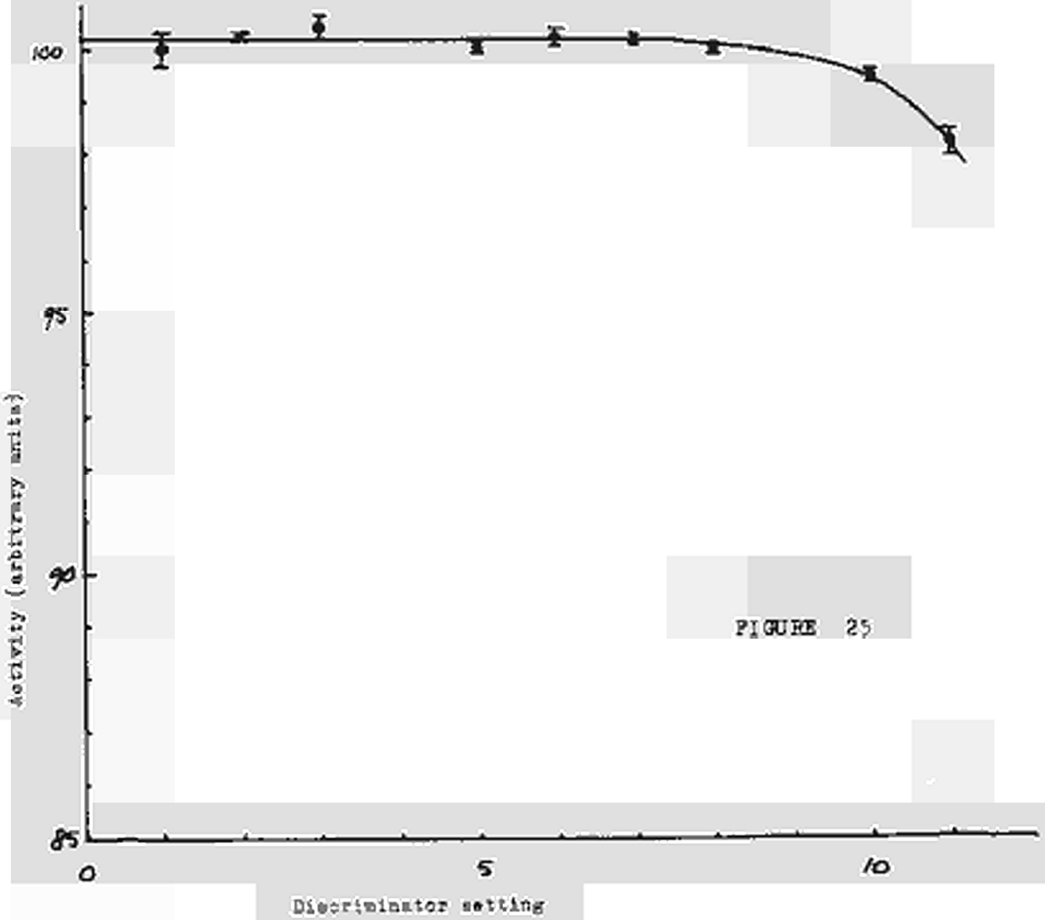

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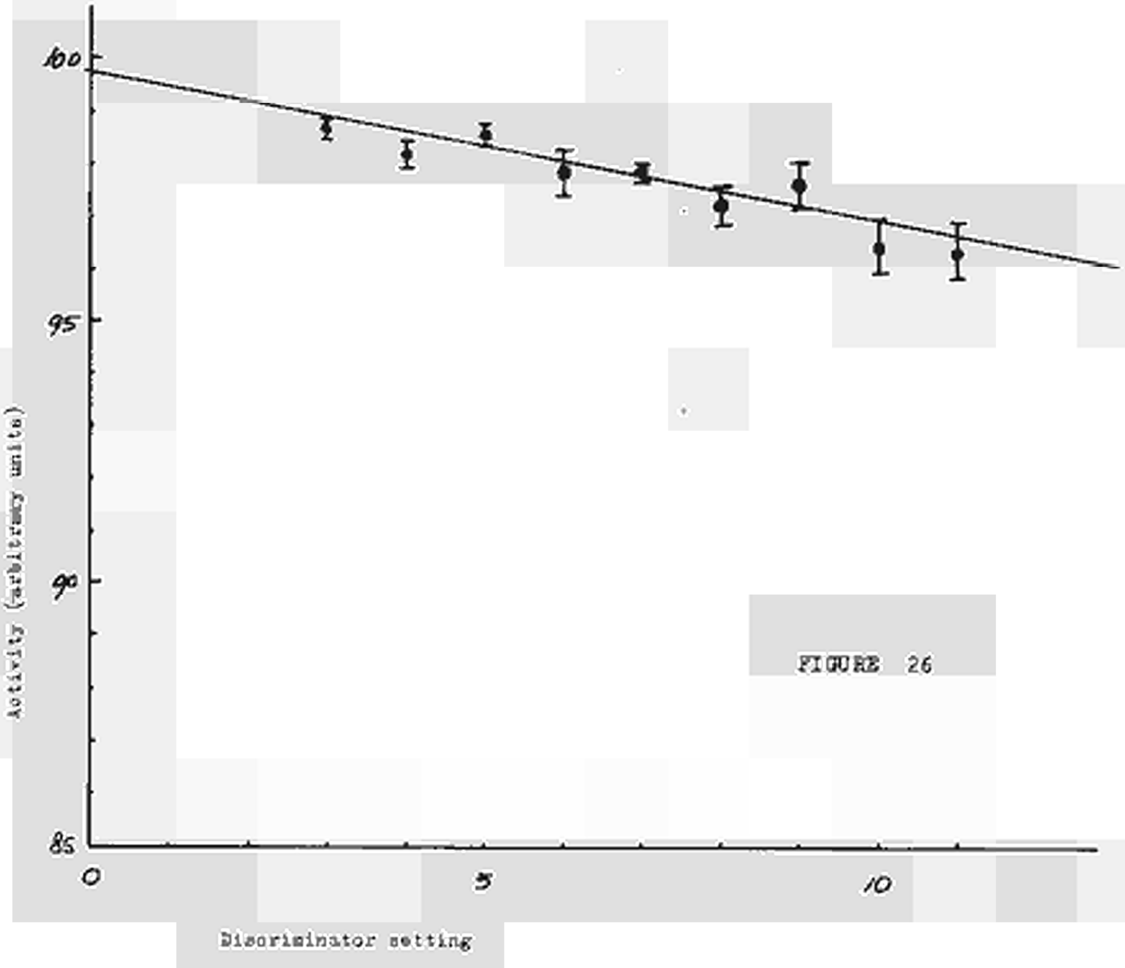

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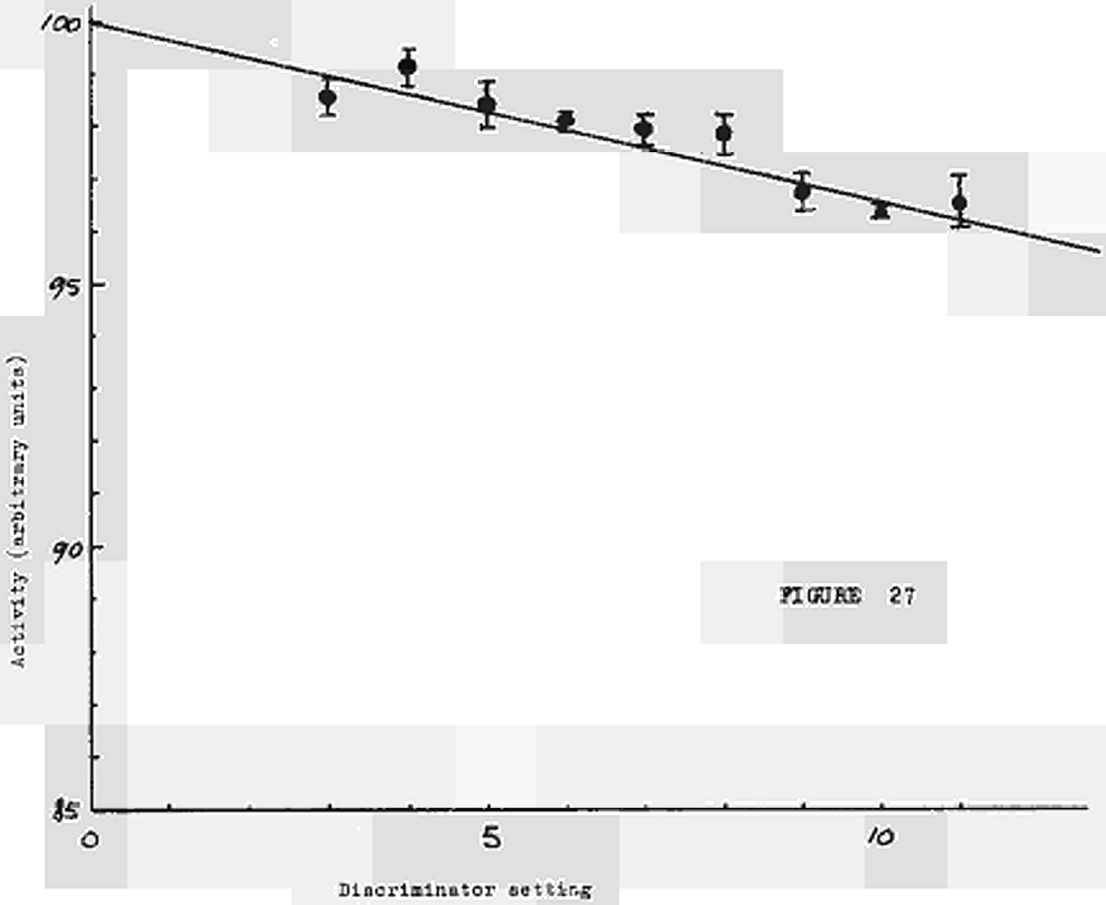

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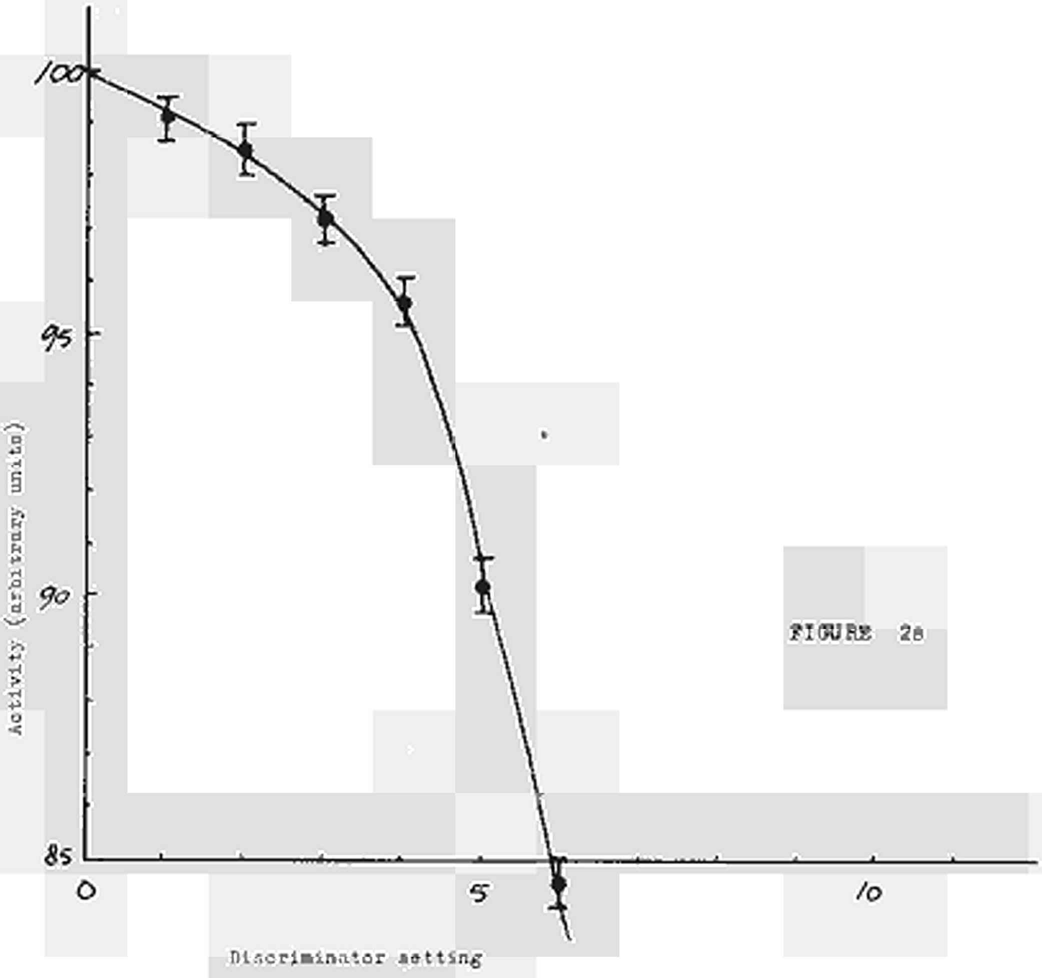

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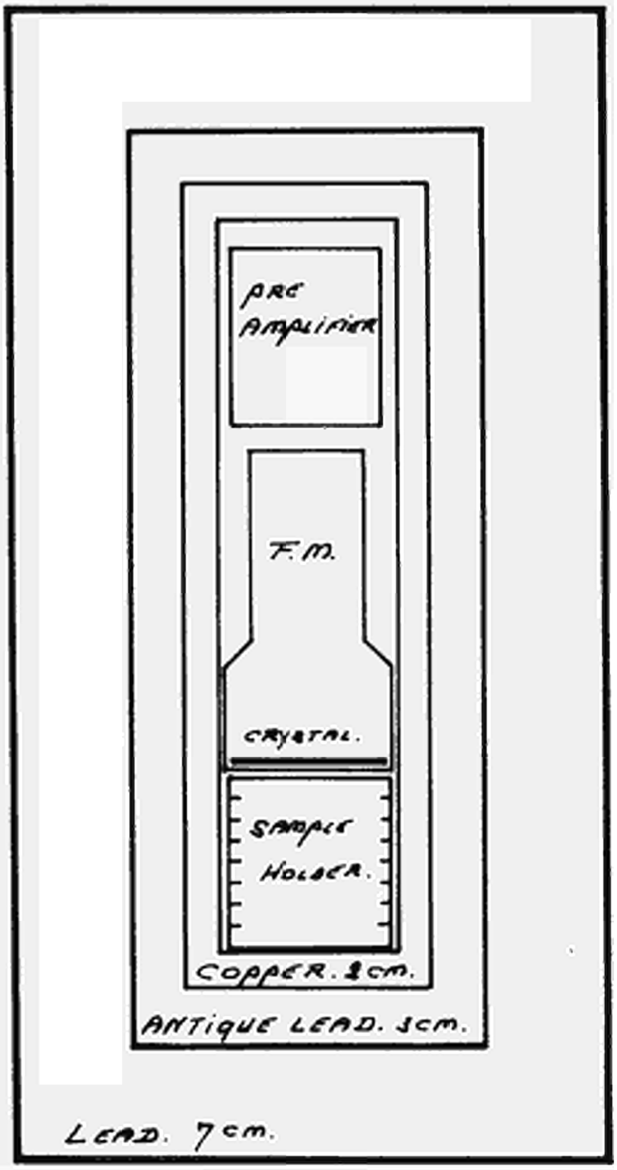

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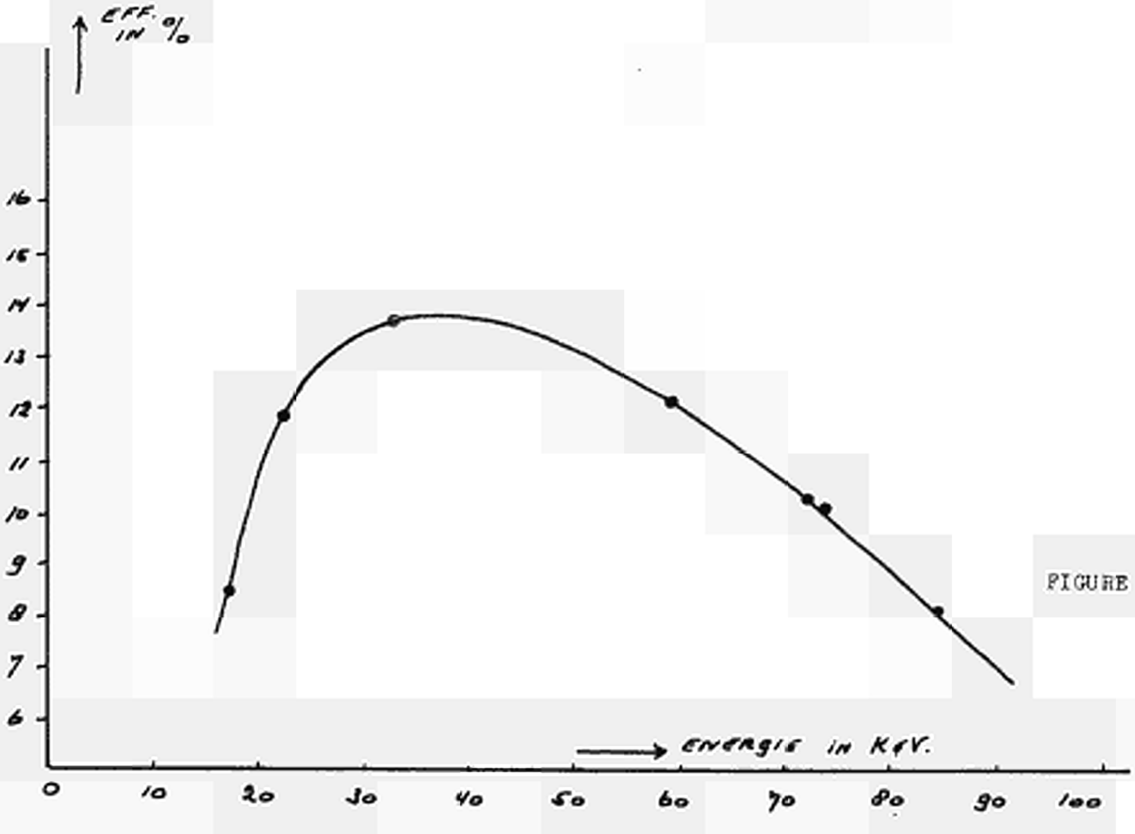

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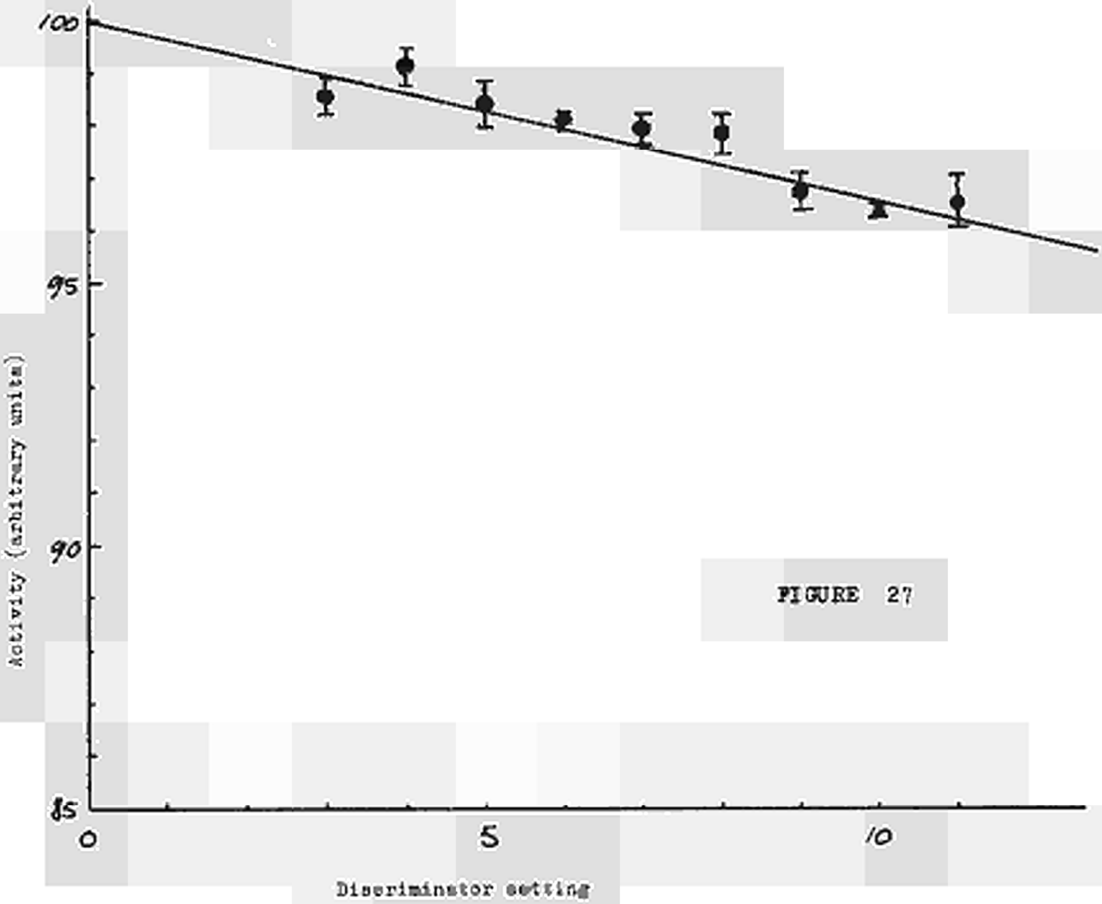

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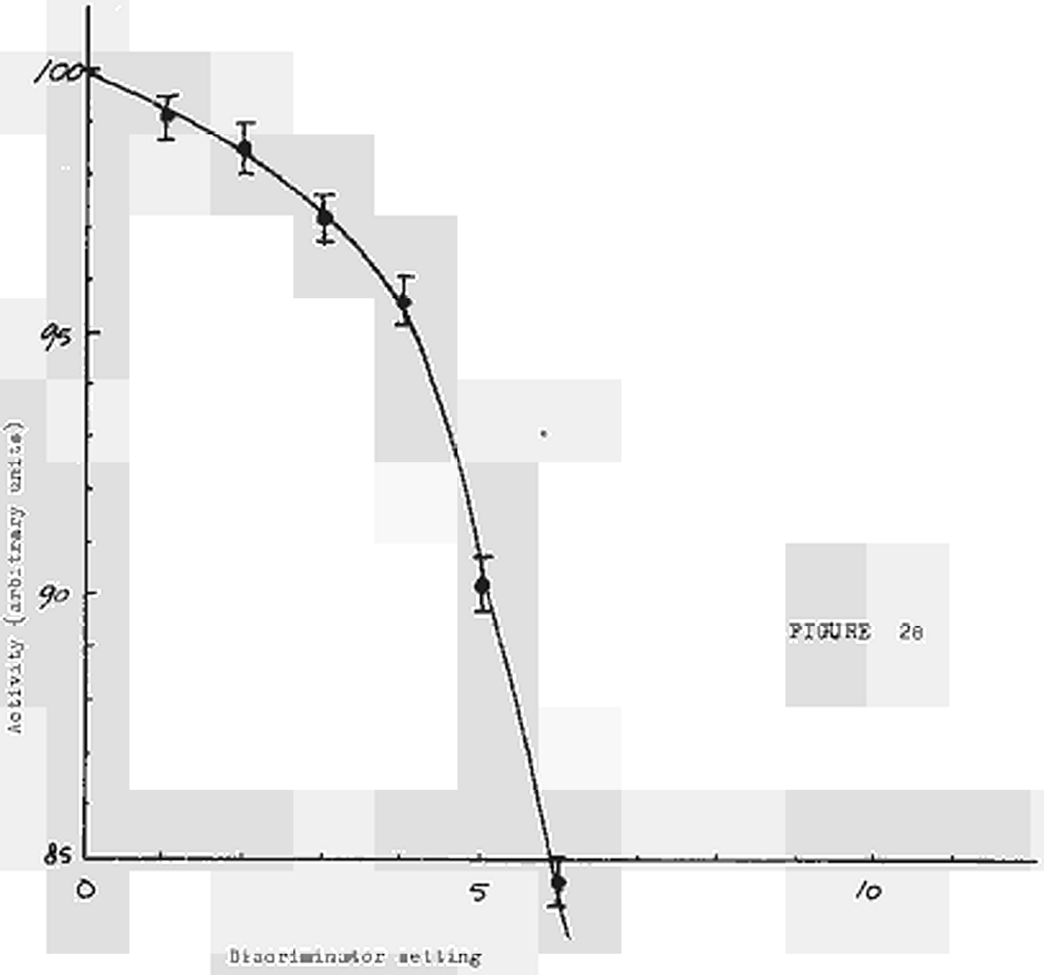

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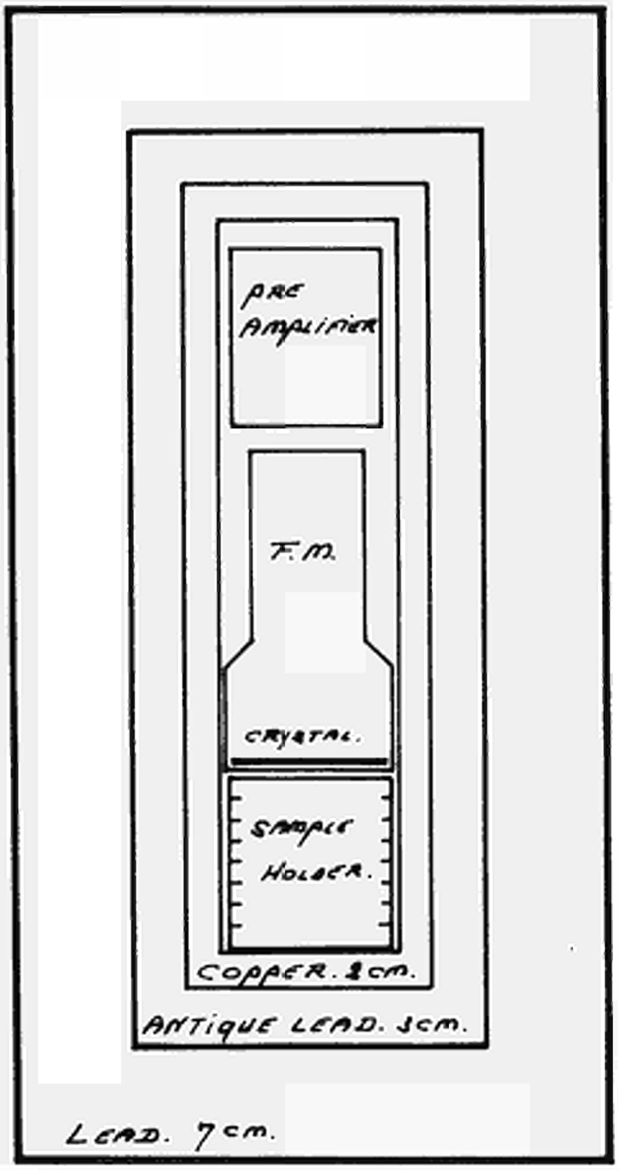

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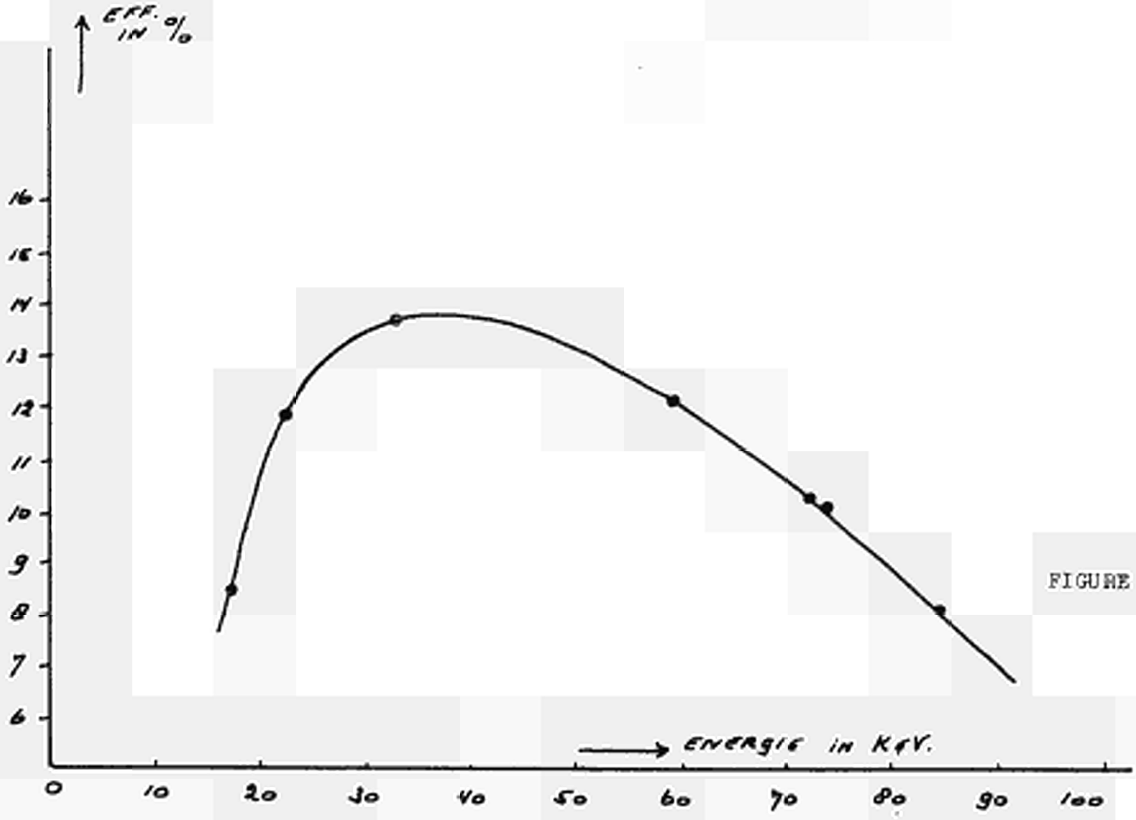

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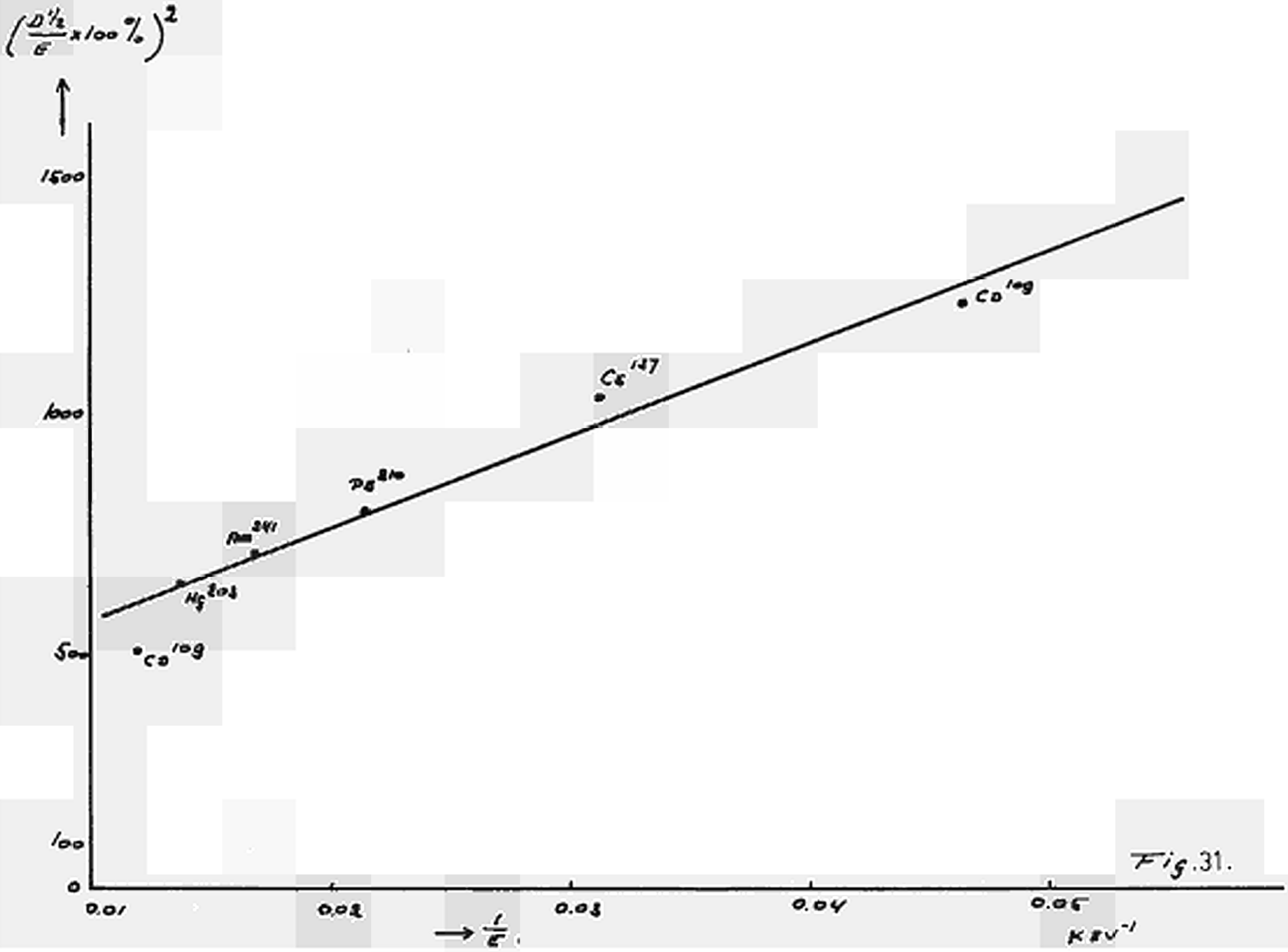

Fig.31.

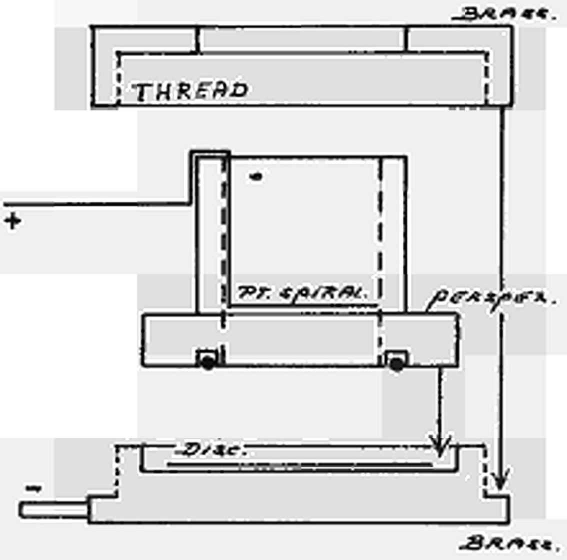

FIGURE 32

> To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.
>
> Alfred Nobel

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