ESD5

ENVIRONMENTAL SCIENCE DIVISION

OBTAINING ^{228}RA (MsTh 1) FROM THORIUM NITRATE

by

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SUMMARY

135 kilograms of thorium nitrate purified and recrystallised in 1958 have been treated to extract ^{228}Ra in radioactive equilibrium. Most of the thorium was eliminated by solvent extraction (T.B.P.) and final purification was by chromatography (Dowex 50 W x 8 and 1 x 8 resins). The total yield attained was 38% ± 4%.

1. INTRODUCTION

With a view to studying by β spectrometry, the weak energy transitions accompanying the disintegration MsTh 1 (^{228}Ra) $\xrightarrow{\beta}$ MsTh 2 (^{228}Ac), an activity of some mCi of MsTh 1 ($T^1/_2$ = 6.7 yr) is necessary.

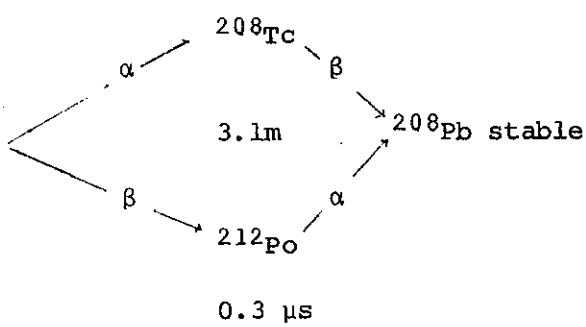
^{228}Ra is produced in the natural chain

$$^{232}\text{Th} \xrightarrow{\alpha} {}^{228}\text{Ra}\ (\text{MsTh 1}) \xrightarrow{\beta} {}^{228}\text{Ac}\ (\text{MsTh 2}) \xrightarrow{\beta} {}^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha}$$

$1.4\text{x}10^{10}$y 6.7y 6.13 hr 1.9y 3.64d

$$^{220}\text{Rn} \xrightarrow{\alpha} {}^{216}\text{Po} \xrightarrow{\alpha} {}^{212}\text{Pb} \xrightarrow{\beta} {}^{212}\text{Bi} \begin{cases} \xrightarrow{\alpha} \\ \xrightarrow{\beta} \end{cases}$$

54.5s 1.58s 10.6h 1.01h



It can easily be calculated that it is necessary to use 9 kg of thorium in radioactive equilibrium to obtain 1 mCi of ^{228}Ra. An important point to note: thorium minerals always contain some uranium which, by the disintegration

$$^{238}\text{U} \xrightarrow{\alpha} {}^{234}\text{Th} \xrightarrow{\beta} {}^{234}\text{Pa} \xrightarrow{\beta} {}^{234}\text{U} \xrightarrow{\alpha} {}^{230}\text{Th} \xrightarrow{\alpha} {}^{226}\text{Ra} \dots\rightarrow {}^{206}\text{Pb}$$

$4.5\text{x}10^9$y 24.1d 1.14m $2.7\text{x}10^5$y $8\text{x}10^4$y 1620y stable

leads in particular to the formation of ^{230}Th then ^{226}Ra; the ^{230}Th accompanies the thorium in the initial processing of the mineral. To obtain ^{228}Ra as pure as possible, it is therefore necessary to start with a thorium salt containing the smallest possible quantity of uranium so that the purification will not concentrate it too greatly. However, the purification cannot have been too recent, given the half life of ^{228}Ra is 6.7

years. Starting with a mineral containing 64.4% thorium 15.4% uranium, recrystallised in 1958 at Usine du Bouchet, - this operation gave salt having a content of 40.61% thorium and 9 ppm uranium - it can be calculated that 1 mCi of ^{228}Ra is formed from 15 kg of constituent thorium and that the ratio $\frac{^{226}Ra \text{ activity}}{^{228}Ra \text{ activity}}$ is not greater than 5%. We have decided to use 135 kg of thorium nitrate, being a total of 3.3 mCi of ^{228}Ra.

The handling of such a quantity of product initially requires a semi-industrial type separation method to eliminate most of the thorium, followed by a finer separation designed to form pure radium.

II CHOICE OF PROCEDURE FOR THE ELIMINATION OF MOST OF THE THORIUM

Several procedures are known for the separation Th-Ra:

- Precipitation of radium as sulphate with barium or strontium as carriers. This method is rejected because of the introduction of a carrier which diminishes the specific activity of the final product.
- Precipitation of thorium with ammonia; this procedure is not of interest for the present problem, some of the radium being absorbed by the precipitate.
- Separation by chromatography on resin, useful for small quantities of product, the capacity of ion exchange resins being some milliequivalents/gram.
- Solvent extraction of thorium, a well known procedure [1,2,3,4,5] appears the most adaptable separation mode in our case. The most commonly used solvents are methylisobutyl ketone, pentaether, mesityle oxide, thenoyltriflouroacetone, primary amines and tributylphosphate (commonly called TBP). We use TBP, available at a moderate price. It makes possible a high

extraction, but having a high viscosity, it must be diluted in an inert solvent. Common dilutants are carbon tetrachloride, xylene, white spirit, hexane, dodecane and benzene. Tests carried out with xylene and essence F have shown that the latter dissolves preferably in a nitric environment. In the course of the tests, various ratios of TBP/xylene were used; we have decided upon the value of 40% TBP, 60% xylene. This proportion is maintained during alterations of essence F. The density of the final mixture reached 0.845, a value favourable to a relatively rapid decantation from the aqueous phase.

It should be noted that, whilst not making use of a battery of mixer-decanters or of pulsating columns permitting a counter-current method of operation, we had to work on an irregular basis and so chose the conditions best suited to this situation.

III PRELIMINARY TESTS

(a) Choice of the thorium molarity and free acidity of the aqueous phase.

We looked for the conditions which permit the least possible number of operations. We varied the acidity of the aqueous solution as well as the concentration of the thorium, the organic mixture being always maintained at 40% TBP.

- Figure 1 gives the results obtained on maintaining the thorium molarity constant and varying the acidity.

  When M_{Th} = 0.86, the percentage extracted increased with acidity.

  When M_{Th} = 0.5, in the range of acidity studied, the extracted percentage remained practically the same.

- Figure 2 indicates the yield when the molarity was varied, the free acid being fixed. It was verified that yield diminishes when the initial concentration of thorium in the aqueous phase was increased.

These results show that it is advantageous to increase the acidity and decrease the molarity. It should be noted that with a free acidity > 3N the extraction of strontium and consequently radium by TBP is very slight [1].

What is particularly interesting is knowing the concentration of thorium in the TBP. With the percentages found previously we are able to calculate it.

Figure 3 indicates the measured values and shows there is an advantage in raising the initial concentration of thorium to saturate the TBP.

If you want to use the aforementioned conditions, without having to regenerate the TBP, on 50 kg of thorium, that is to say, to prepare a solution of 1.6 M thorium 3.1 N HNO_3, you have to dissolve the salt in 135 L of nitric solution.

After 4 extractions, supposing that you have added no more acid, the working volume is 540 L for each phase and the aqueous phase still contains about 8 kg of thorium. In fact, some acid goes into the TBP which necessitates adding more.

Alternatively, a known quantity of the aqueous phase (50 L) can be separated and the molarity fixed at 1.6 M and the acidity at 3.1 N, and it can be extracted with an equal volume of the organic phase, then regenerate the TBP saturated with thorium, and readjust the molarity and the acidity to initial values and proceed to a new extraction with the same solvent. We use this procedure which gives the advantage of using smaller volumes.

(b) Regeneration of TBP

The choice of procedure is a function of the number of steps and the volume required.

We have tested water rinses, dilute nitric acid, 0.02N, and sodium carbonate. The nitric acid or water washes demand 5 successive steps, the volume of the aqueous phase being 0.4 times the volume of the organic phase, to obtain 94% to 100% extraction.

If the volume of the organic phase is 50 L, you need 125 L of aqueous solution for the regeneration.

The use of a 20% $Na_2 CO_3$ solution allows for a smaller volume. However, if the molarity in the TBP exceeds 0.5M, it forms an abundant precipitate. The procedure is therefore used only after 2 water washes. By this method the rest of the thorium is extracted.

The volumes used are therefore approximately the following:

50 L organic phase

2 water washes of 20 L = 40 L

1 carbonate rinse 50 L

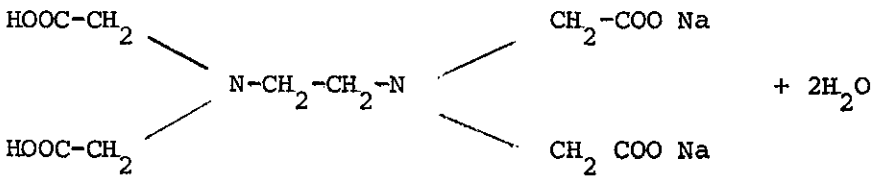
a volume of 90 L instead of 125 L in the previous method.

IV CONTROL OF OPERATION

In the course of the first assay, the molarity and the acidity were determined by an analysis with sodium hydroxide but the presence of $Th(OH)_4$ precipitate was annoying and the determination of the degree of neutralisation was difficult. We have abandoned this method and use titriplex III to measure the molarity, and potassium iodide to measure the acidity.

(a) Determination of thorium molarity [6]

Titriplex III is the disodium salt of EDTA.



It is a white granular powder, easily soluble in water and gives an acid reaction.

The thorium solution must not contain more than 100 mg of thorium per 100 mL. One takes, therefore, 1 mL of solution and dilutes it in 100 mL of water, keeping the pH between 1 and 2 by adding nitric acid or ammonia. After having added about 50 mg of xylenol orange you titrate with the 0.1 M titriplex III solution until you see a red or yellow that is very pure.

1 mL of 0.1 M titriplex III solution corresponds to 23, 204 mg of thorium, the molarity is able to be estimated to nearly 2% by this method.

(b) Determination of free acid [7].

The procedure described is used to determine the free acid of chloride, nitrate and uranyl sulphate solutions. It is also applicable to analysis of thorium solutions.

You precipitate the thorium with potassium iodate and determine the acidity with sodium hydroxide.

Place 5 mL of KIO_3 (0.3 M, pH slightly greater than 5) in a centrifuge tube and mix in 0.2 mL of solution to be analysed. Agitate for 30 seconds. Leave to settle for 5 min or less and then centrifuge for 5 min. Retain 4 mL of the supernatant and titrate with sodium hydroxide ($\sim$ 0.1 N) in the presence of a mixed indicator (2 volumes of 0.04% bromocresol in alcohol for 1 volume of 0.02% methyl red in alcoholic solution). End titration when you see a clear green tint. (If the methyl red is replaced with methyl orange, stop titrating on appearance of a yellow colour).

The found acidic normality is therefore N = 6.5 V.t

V = volume of sodium hydroxide

t = molarity

The relative error varies between 3 and 1.5% when the normality varies between 1N and 2N.

(c) Radioactive control

Also verify that, during the operation, radium is not extracted by the TBP. Some aliquots of organic phase and wash water are placed before a G.M. counter and over a NaI (TL) crystal. If ^{228}Ra is being extracted, growth of ^{228}Ac will be seen. In 24 hrs the activity of $MsTh_2$ is about 94% of equilibrium radioactivity.

V. APPARATUS USED

It comprises 2 identical stainless steel vats of about 150 L each. In the lower vat we carry out the dissolution of thorium in nitric acid (∿ 60 L), the thorium concentration is maintained between 1 and 1.4 M until the salt is exhausted, conditions in which the dissolution is rapid and complete. The normality of the acid stays between 3.3 and 4.4 N. The organic phase (50 L) is always left in the upper vat. The aqueous phase is pumped into the upper vat. Mixing is carried out for 10-15 min, the separation about 30 min. The aqueous phase is drawn off into the lower vat. You then adjust acidity and molarity. The organic phase is washed twice with 20 L of water, once with 50 L of 20% sodium carbonate, finally, in certain cases, once with 20 L of water. In these conditions, the quantity of thorium retained in the organic phase is not more than 6% of the amount extracted. At each repetition we add 4-5 L of organic mixture. We continue the cycle of operations 6 times until exhaustion of the thorium salt. The volume of the aqueous phase, which is increased by the addition of thorium nitrate and nitric acid, is by this

time very important. We must take only a fraction of this phase and mix with the equivalent volume of organic phase.

The outline of a series of steps is represented in Table I. Because of fractionation of the aqueous phase we finally obtain two aqueous solutions in which the thorium molarities are 0.04 M and 0.09 M. We evaporate the less concentrated in a rotary evaporator under vacuum, type "Rotavapor R" (Buchi). The loss by evaporation is of the order of 500 mL hr^{-1} when conditions of equilibrium are achieved. The volume is reduced to about 20 L and returned into the vat with the 0.09 M thorium. The mixture of the two phases occupies a volume of 80 L. Then carry out an extraction of thorium with 50 L of freshly prepared organic mixture. After decantation the aqueous phase finally contains about 0.02 M/L or 370 g Th/80 L.

A final extraction with 25 L of fresh organic mixture on this aqueous phase, given the acidity is readjusted to 3.1 N, leaves about 0.05 M/L in the aqueous phase, or about 95 g Th/80 L.

VI COMPLETE ELIMINATION OF THORIUM

We have at our disposal then a solution of radium still containing 95 g Th/80 L.

This aqueous phase is evaporated in the rotavapour (to reduce to 4 L), the evaporator operates for 1 month.

The thorium is extracted from fractions of 800 mL with 800 mL of organic mixture (40% TBP - 60% essence F). The residue is then about 30 g Th/4 L of 6.6 N HNO_3 solution.

With such a quantity of thorium one can envisage separation by chromatographic resin. Two solutions are possible:

- on anionic Dowex 1 x 8 resin one can fix Th under conditions of 8 N HNO_3, conditions in which the radium is not retained.
- on cationic Dowex JOW x 8 resin, where under conditions of 1 N HCℓ Ra, Ac, Th are fixed, the elution of radium and actinium can then be effected with 6 N HNO_3.

Thus, we use both types of resins, the anionic for elimination of thorium, the cationic for the removal of sodium which is accumulated in the course of the different washes of the organic phase (the sodium is possibly not fixed on the 50 W x 8 resin in 1 N HCℓ). The quantity of the $Na_2\ CO_3$ being in the order of 4 kg, it is necessary to repeat the operations of fixation, washing, extraction, regeneration of the resin a number of times and the complete elimination of sodium requires about a month (we have used 3 columns of 800 mL of Dowex 50W x 8, 200-400 mesh).

A final purification is effected on 500 mL of 50W x 8 resin, 200-400 mesh. After an abundant wash with 0.1 N HNO_3, the radium is eluted with 3 N HNO_3.

VII DETERMINATION OF TOTAL YIELD

To estimate the yield of the operation, we use two processes:

1) A method of comparative activities.

We record the γ spectrum, in a NaI crystal well, of low energy using a standard solution of thorium nitrate and the same aliquot of the elutant collected after the final purification. The ratio of the areas of the peaks at 336 keV corresponds to the transitions of ^{228}Ac ($M_s Th_2$) and thereby supplies an evaluation of yield. In this way we obtained R = (40 ± 6)%. The indicated error takes into account the principle uncertainties on the evaluation of the bases of the γ peaks.

2) A method of measuring absolute activity.

With the aid of a NaI crystal ($1^3/_4$" x 2") standardised in the laboratory [9] we measure the absolute activity of an aliquot of the final elutant. For this, we work on γ energies of 209 and 336 keV for ^{228}Ac using the branching estimated by previous work [10]; we obtain a total activity of about 1.27 mCi, the yield is therefore R = 38 ± 4%, a value comparable with the preceding value.

The yield obtained can be explained by various losses, difficulties of evaluation, and difficulties which occurred at the time of the final treatments and for that recovery of activity not able to take place. The wastes have also carried a certain amount of radium. These being tested for several days to detect the accumulated ^{228}Ac activity; the loss corresponding to a maximum of 0.2 mCi. The testing of the resins used for the final purification shows that the loss arising from these operations did not exceed 0.2 mCi. Then again, in spite of a careful purification, glassware is always contaminated, but it is impossible to calculate the activity lost in this manner.

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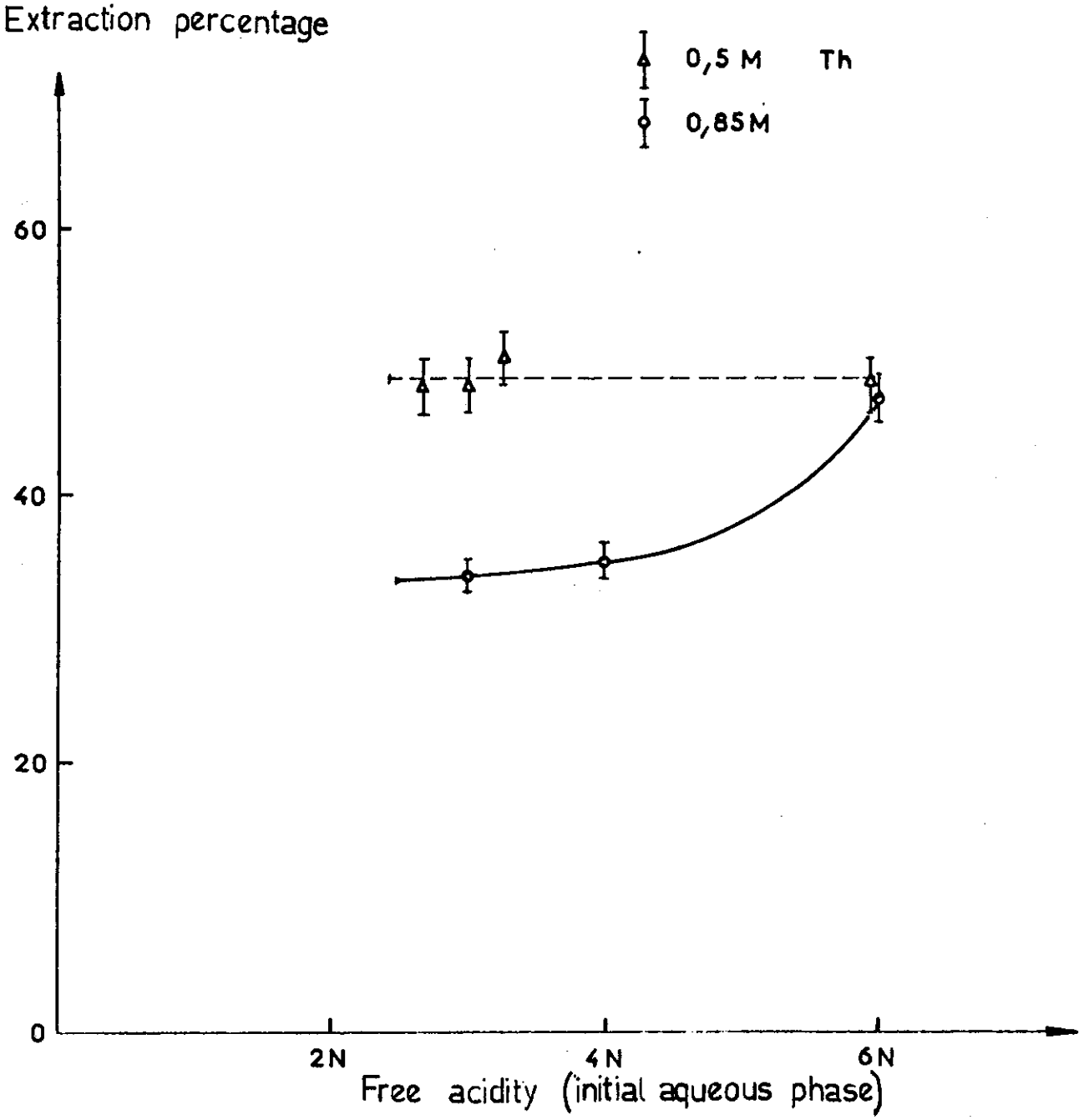
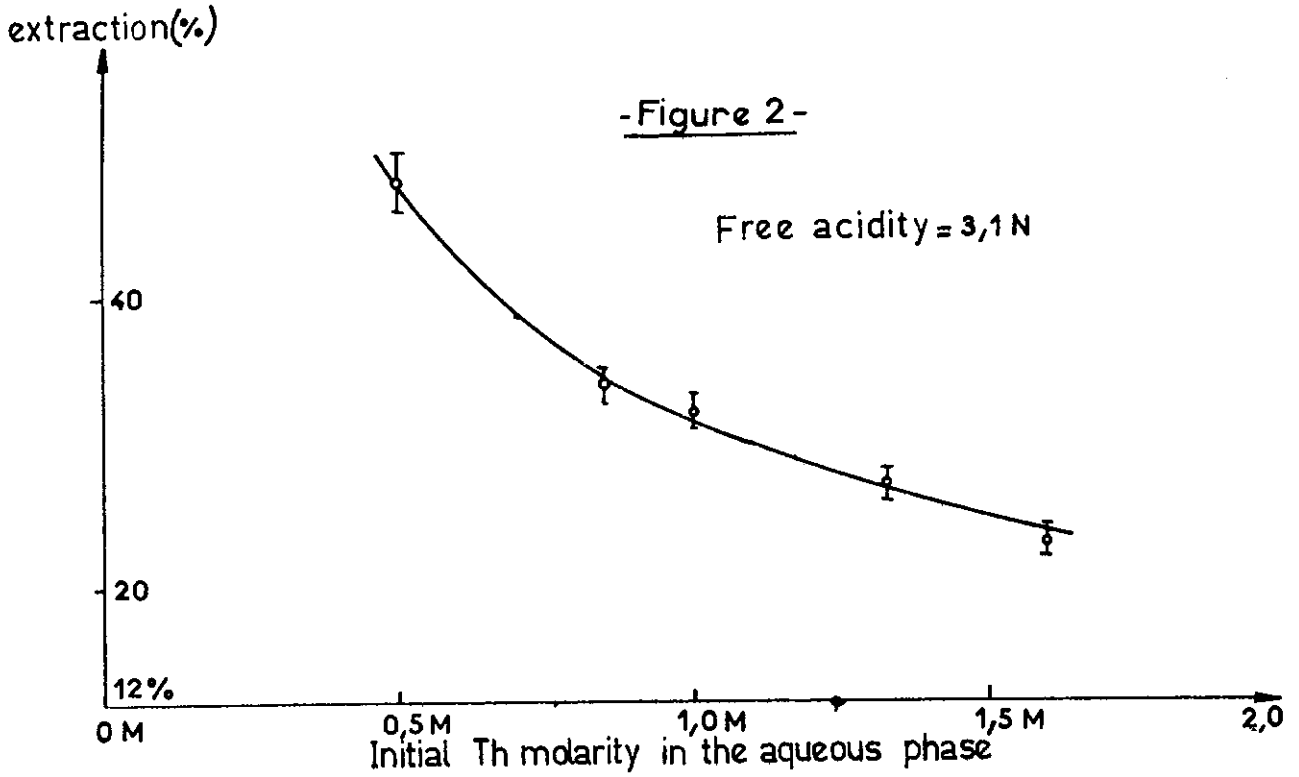
TABLE 1

Molarity of the Aqueous Phase	Free Acidity	% Extract	Comments
1.44	4.3	37.0	At each manipulation
1.06	4.4	22.6	4 L of fresh organic
1.20	4.3	22.5	mixture is added
1.29	3.8	16.2	
			Variation of the organic mixture
1.36	3.5	28.0	Addition of 10 L of
1.10	4.3	50.0	organic mixture at each manipulation
			Additions of thorium terminated.
			Fractionation of the aqueous phase
0.85	3.8	68	
0.62	3.3	79	Addition of 10 L of
0.40	3.4	82	organic mixture at
0.25	3.45	84	each manipulation

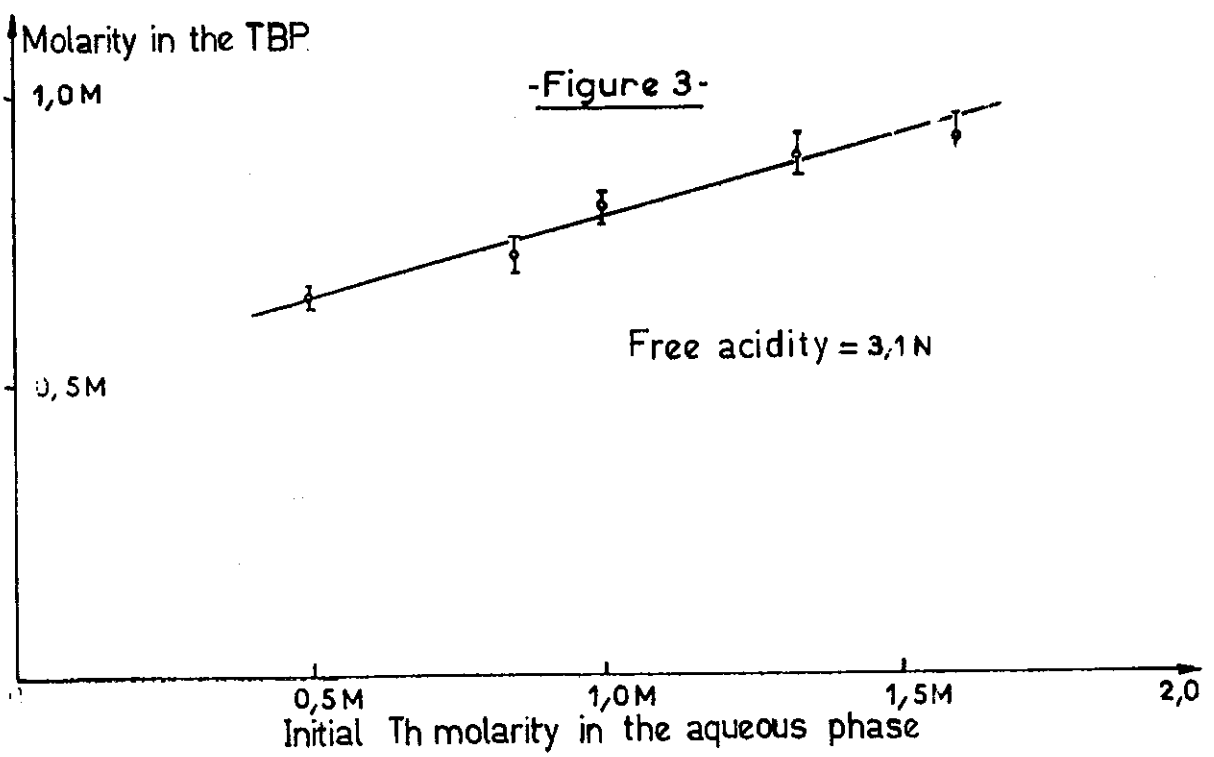
-Figure 1-


Extraction percentage
0,5 M Th
0,85 M
60
40
20
0
2N
4N
6N
Free acidity (initial aqueous phase)



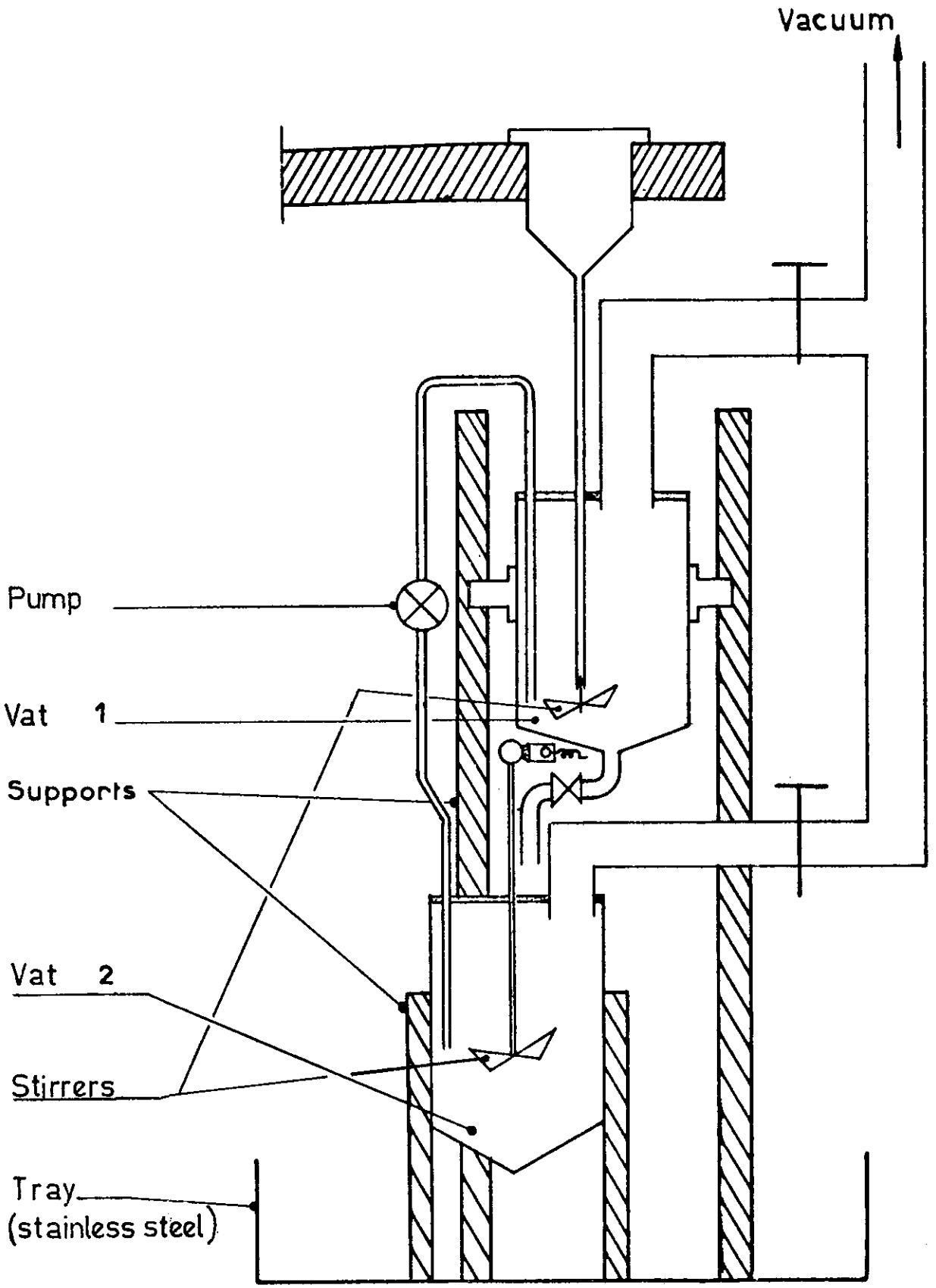
-Figure 2-

Free acidity = 3,1 N



-Figure 3-

Free acidity = 3,1 N


Vacuum
Pump
Vat 1
Supports
Vat 2
Stirrers
Tray
(stainless steel)

-Fig: 4-