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STUDY OF THE COPRECIPITATION OF CADMIUM WITH AMMONIUM DIURANATE*

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SUMMARY

The coprecipitation behaviour of the cadmium chelate compound with ethilenediaminetetraacetic acid and ammonium diuranate is studied. The influence of the concentration of EDTA, the presence of zinc used as hold-back carrier and the type of isotherm that rules the phenomenon are discussed.

INTRODUCTION

One of the final steps of uranium purification is the precipitation of uranium, with ammonia gas, as ammonium-diuranate (ADU). In this operation there is entrainment of several cations with the solid material and elements whose hydroxides are slightly soluble in basic medium will be entrained by the ADU precipitate. To avoid that entrainment a complexing agent such as ethylenediaminetetraacetic-acid (EDTA), has been used to keep cationic impurities in solution[1][2]. The high value for stability constants of a good number of complexes, at pH = 7.5, is a guarantee for a good decontamination of the metals.

However, decontamination by merely chelating the impurity is not completely absolute since some metals in the complex form may also be adsorbed on the ADU precipitate. This behaviour is specially important for the contamination of the high neutron absorption cross-section elements, such as cadmium. The study of the behaviour of the Cd-EDTA complex, on coprecipitation with ADU, is presented in this paper.

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EQUIPMENT AND REAGENTS

A - Equipment

1. Single channel gamma-ray spectrometer, Nuclear-Chicago Corp., Model 182-A, coupled to a NaI (Tl) scintillation detector Model DS5, well type, also from Nuclear-Chicago Corp.

B - Reagents

1. Cadmium carbonate, "Riedel-de-Haen A.G., Seelze B. Hannover".
2. Zinc granulated, P.A., "E. Merck Ag. Darmstadt".
3. Nitric Acid, "E. Merck Ag. Darmstadt", 65%, d=1.4.
4. EDTA chemically pure.
5. Uranium oxide (U_3O_8), nuclearly pure, produced in the Pilot Plant of the I.E.A. of São Paulo.
6. Ammonia gas, P.A.

PROCEDURE

Uranyl Nitrate Solution

Ammonium diuranate was calcined at 900°C. The U_3O_8 obtained was dissolved with nitric acid (1 ml of HNO_3 1:1 per gram of oxide) and filtered.

EDTA Solutions

EDTA was purified by precipitation with hydrochloric acid and dissolved in ammonia and brought up to volume at the desired concentration.

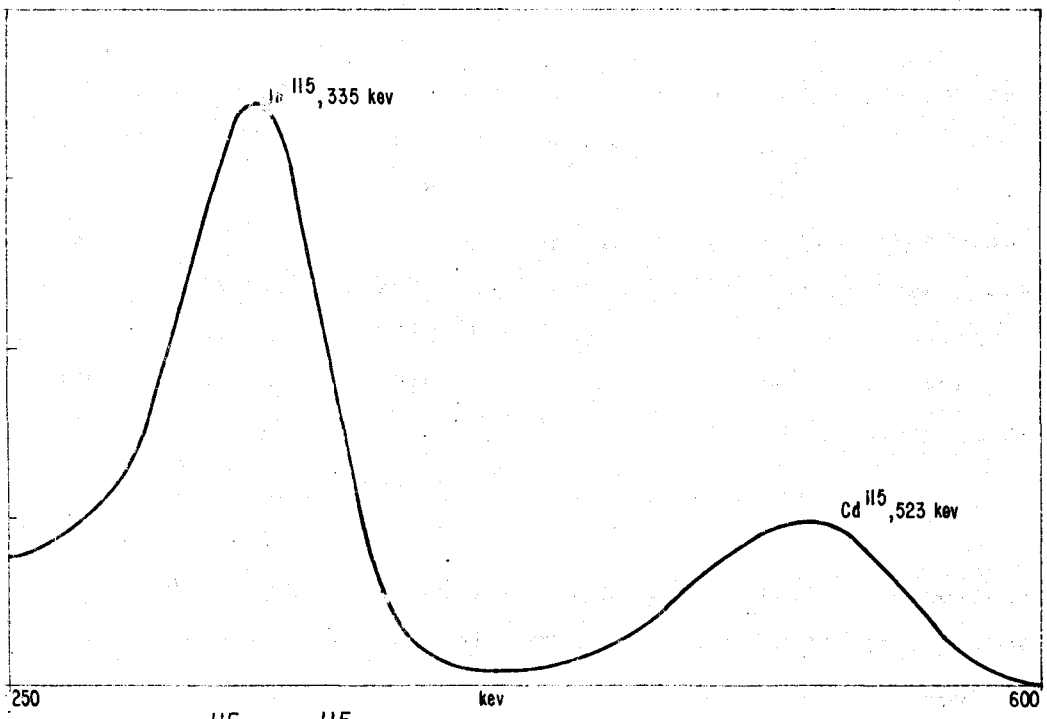
Precipitation and Filtering

Ammonium diuranate was precipitated with ammonia gas at constant flow and at the temperature of 75-78°C. The ammonia gas

was added until the pH of the ADU suspension reached 7.5. The solid salt was filtered and washed with ammonium nitrate 2%, pH = 7.5 . Each experiment was carried out by using 100 ml of a uranyl nitrate solution at the concentration of 30 g/l in U_3O_8.

Labelled Cadmium

The labelled cadmium (^{115}Cd) was obtained by irradiation of cadmium carbonate for 12 hours, in a thermal neutron flux of 10^{12} n/sec.cm^2. Before used, a cooling period of 17 hours was observed in order to attain the $^{115}Cd \rightarrow {}^{115}In$ equilibrium. The irradiated material was dissolved in hydrochloric acid 6N and brought up to volume to 25 ml. The purity of the labelled cadmium was verified by gamma-ray spectrometry, Fig. 1, half-life determination and aluminium absorption curve.



SCANNING OF Cd 115 - In 115 USED AS LABELED MATERIAL

FIGURE 1

Preparation of sample for counting

The volume of the filtrate was reduced by evaporation and adjusted to 25 ml and aliquots of 2 ml were taken for counting. In order to avoid loss of Cd-EDTA by adsorption on the walls of the flasks, carrier solutions of Cd-EDTA were added to the flask where the filtrate was collected.

RESULTS

Coprecipitation of Cadmium

The use of EDTA, as a way to improve the separation of cadmium from ADU, is based on the formation of $CdY^{=}$ complex, at pH = 7-8, in accordance with:

$$Cd^{+2} + HY^{-3} \rightleftharpoons CdY^{=} + H^{+} \quad (\log K = 16)$$

Taking into account the high stability constant of the chelate compound, the precipitation must occur in total absence of Cd^{+2}. Thus, the contamination, internal or on the solid surface, will be as Cd-EDTA complex. However, the hypothesis of internal contamination was foresaken, since in preliminary experiments (when the contaminant had been added after the diuranate formation) it was verified that the coprecipitated fraction was the same as when the Cd-EDTA compound was present when the ADU precipitation took place.

To verify the adsorption of Cd-EDTA complex on the ammonium diuranate surface, uranyl nitrate solutions, to which increasing amounts of metal contamination was added, were precipitated, as described, by using ammonia gas. Results are presented in Table I.

TABLE I

FRACTION OF CADMIUM COPRECIPITATED AS FUNCTION OF INITIAL AMOUNT OF CADMIUM

m_i	f	m_s	m_l	D
5	0.588	2.94	2.06	1.70
10	0.577	5.77	4.23	1.73
20	0.543	10.96	9.14	1.84
50	0.525	26.35	23.8	1.90
100	0.424	42.41	57.6	2.36
150	0.354	53.11	97.0	2.82
400	0.202	80.8	319	4.95
500	0.164	82.0	418	6.10
600	0.125	75.0	525	8.00
700	0.086	60.2	640	11.61

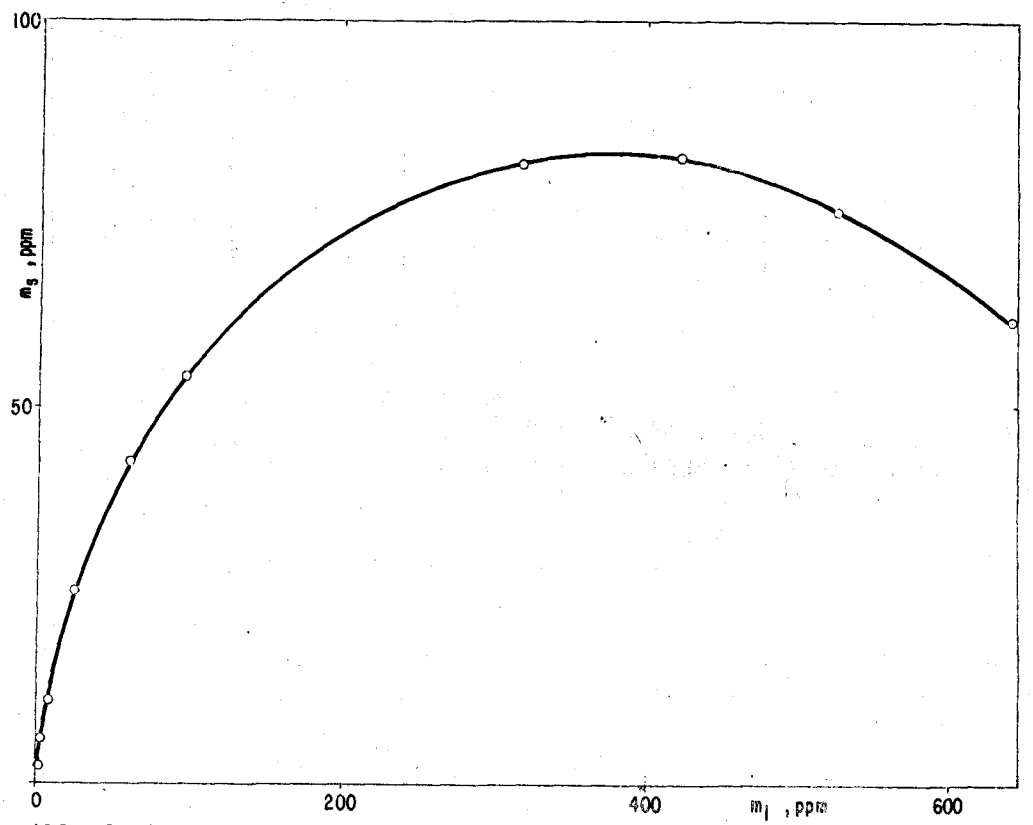
Data: U_3O_8 = 30 g/l
EDTA = 10 times the stoichiometric required to complex cadmium
t = 75 - 78º C
m_i - Initial amount of cadmium (ppm)
m_s - Cadmium in the solid phase (ppm), at equilibrium
m_l - Cadmium in the liquid phase (ppm) at equilibrium
f - Coprecipitated fraction
D - Decontamination factor

The shape of the curve $m_s = f(m_l)$, in which m_s is the amount of Cd-EDTA entrained per 10^6 grams of ADU and m_l the concentration of Cd-EDTA in the liquid phase, at equilibrium, suggests that a Langmuir's isotherm is followed. By graphic method, equation (1) was established:

$$m_s = \frac{m_l}{0.674 + 0.0131\, m_l} \qquad (1)$$

Equation (1) is not valid for m_l larger than 500 ppm since, at this value, a decreasing of m_s is observed, in accordance with Figure 2. The maximum of $m_s = F(m_l)$ shows the end of surface effect influence. Figure 3 shows that, for the

values of m_s larger than 500 ppm, the decontamination factor increases.



ISOTHERM OF ADSORPTION FOR **Cd** IN **ADU**.

FIGURE 2

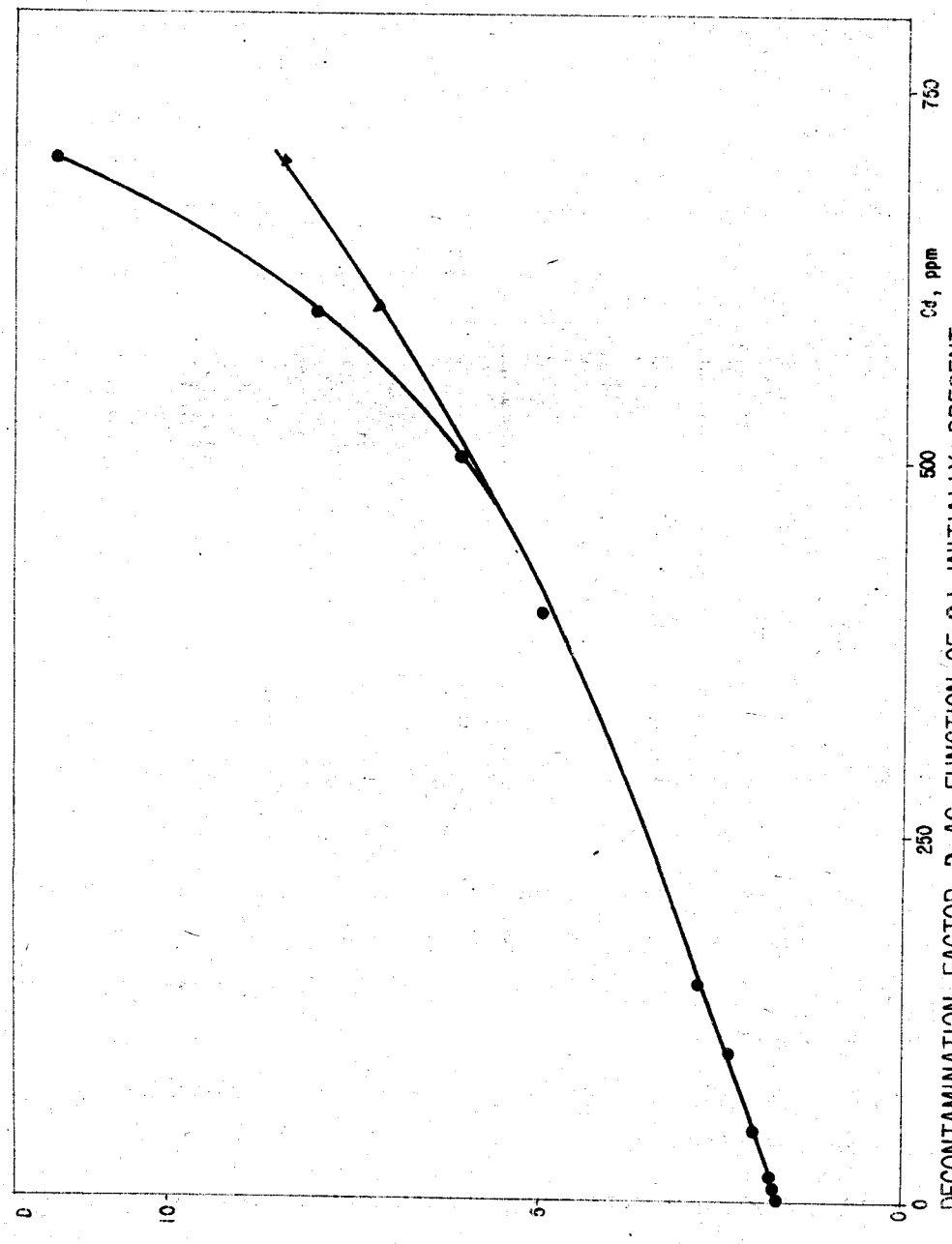
Coprecipitation of Cadmium in the Presence of Zinc

The effect of adding zinc, as Zn-EDTA, on the decontamination of cadmium, was also studied.

Based on close values of stability constants for Cd-EDTA and Zn-EDTA complexes, and chemical behaviour resemblance, the addition of zinc, as Zn-EDTA complex, might contribute to the uranium purification, since it would act as a hold-back carrier.

For nuclear purposes the cadmium-zinc substitution might be advantageous taking into account the contribution of each metal to the boron equivalent (BE) [1] of uranium since the zinc cross-

-section is much larger than for cadmium (σ_{Cd} = 33 barns; ..... σ_{Zn} = 1.1 barns).



DECONTAMINATION FACTOR D AS FUNCTION OF Cd INITIALLY PRESENT
FIGURE 3

In order to study this substitution, 100 ml of uranyl nitrate solutions, at the concentration of 30 g/l in U_3O_8, contaminated with 5 and 10 ppm of cadmium and different amounts of zinc, from 0 to 700 ppm, were precipitated as ADU, as described. Concentration of EDTA was 10 times the stoichiometric required to chelate Cd plus Zn ions present. Results are shown in Table II and Figure 4.

TABLE II

FRACTION OF CADMIUM COPRECIPITATED AS FUNCTION OF AMOUNT OF ZINC ADDED

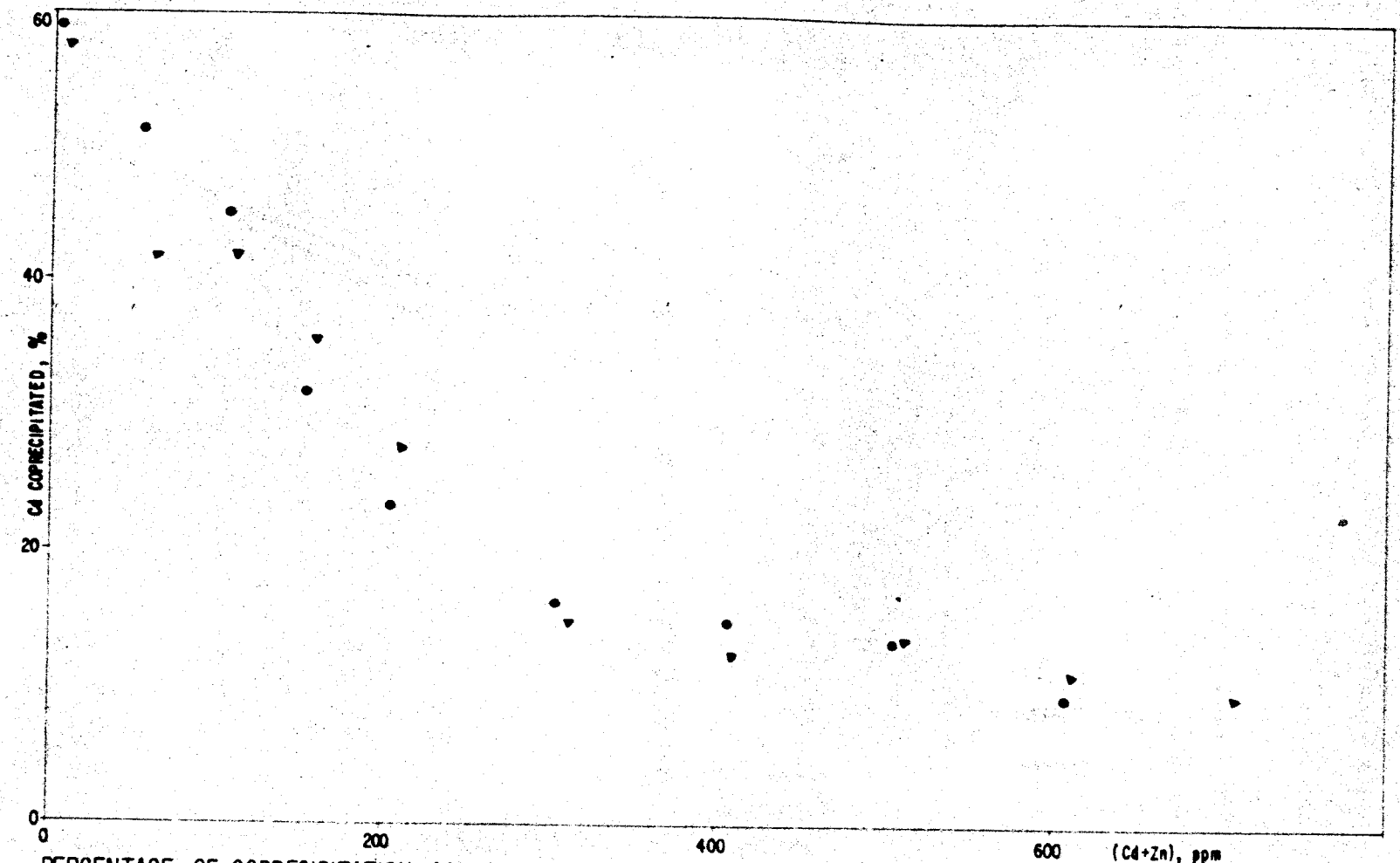
Zn. add.	m_2	f	D
0	10	0.577	1.74
50	60	0.418	2.38
150	160	0.360	2.77
200	210	0.282	3.55
300	310	0.153	6.60
500	510	0.137	7.30
600	610	0.111	9.00
700	710	0.095	10.51

Data: U_3O_8 = 30 g/l
Cd = 10 ppm
t = 75 - 78ºC
EDTA = 10 times the stoichiometric amount required to complex Zn plus Cd

It is seen that the contamination fraction f does not reach the value 1 when (Cd + Zn) decreases to 0, but comes near to 0.6 which is the same value for f as when only cadmium was present as impurity.

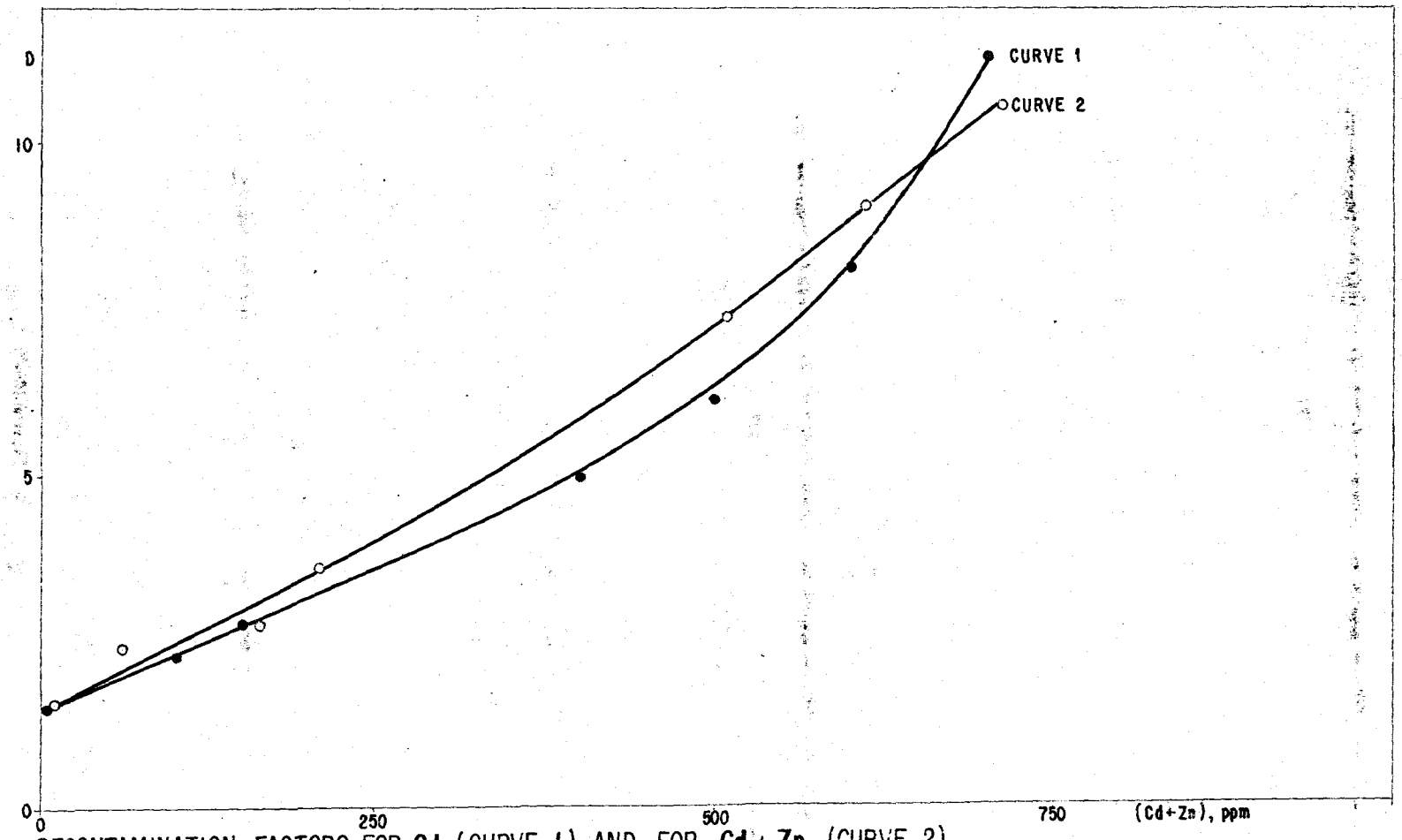
For an addition of 300 ppm of zinc, the f value becomes constant and equal to 10%.

The influence of zinc on the coprecipitation of cadmium can be observed in Figure 5. Decontamination factor is larger when zinc is present up to a total value of (Cd + Zn) of 650 ppm.



PERCENTAGE OF COPRECIPITATION AS FUNCTION OF TOTAL AMOUNT OF (Cd+Zn),

FIGURE 4



DECONTAMINATION FACTORS FOR **Cd** (CURVE 1) AND FOR **Cd** + **Zn** (CURVE 2)

FIGURE 5

Decontamination as Function of EDTA Concentration

In order to study the effect of varying the concentration of EDTA, experiments were carried out in which the amount of cadmium was maintained constant and the concentration of EDTA were the ones corresponding to 50, 100, 200 and 400 ppm of zinc present. No zinc was added to this series of experiments. Results are presented in Table III and Figure 6.

TABLE III

FRACTION OF CADMIUM COPRECIPITATED AS FUNCTION OF EXCESS OF EDTA OVER STOICHIOMETRIC AMOUNT REQUIRED TO COMPLEX THE CATION

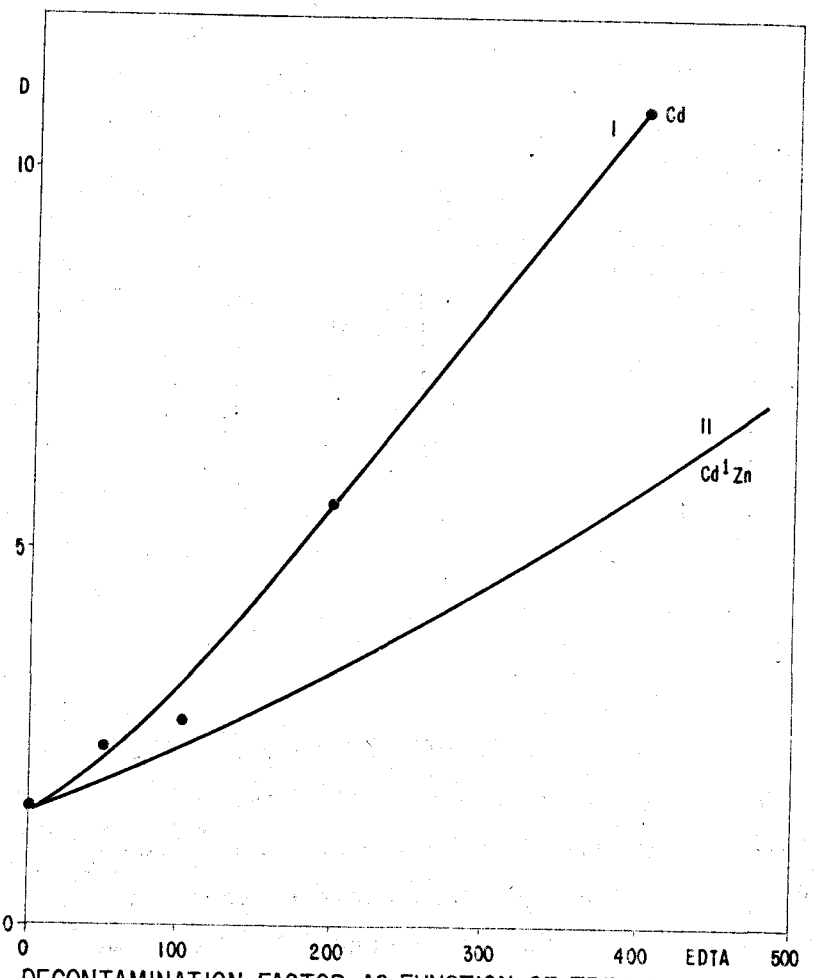
EDTA (ex)	f	D
0	0.589	1.70
50	0.425	2.45
100	0.363	2.75
200	0.178	5.61
400	0.090	10.80

Data: U_3O_8 = 30 g/l
Cd = 10 ppm
t = 75 - 78º C

The values of the decontamination factor on Curve I are larger than those on Curve II. It is seen that the complex agent addition by itself could promote the increase of purification in relation to the cadmium contamination. However, as it was observed before[1], a too large excess of EDTA gives, as result, a bulky precipitate of ADU which is very difficult to filtrate and to wash.

Experiments were also carried out in order to study the decontamination of cadmium when no excess of EDTA was used. In these experiments the stoichiometric amount required to complex cadmium plus zinc, or only cadmium when no zinc was present, was

used. Results are presented on Table IV and Figure 7.



DECONTAMINATION FACTOR AS FUNCTION OF **EDTA** CONCENTRATION

FIGURE 6

TABLE IV

FRACTION OF CADMIUM COPRECIPITATED AS FUNCTION OF AMOUNT OF ZINC ADDED: CONCENTRATION OF EDTA: STOICHIOMETRIC WITH (Zn + Cd)

Zn add	f	D
0	0.891	1.12
50	0.693	1.44
100	0.623	1.61
150	0.681	1.47
200	0.552	1.81
300	0.549	1.82
400	0.550	1.82
500	0.458	2.18
600	0.515	1.94

Data: U_3O_8 = 30 g/l (100 ml)
Cd = 10 ppm
EDTA = stoichiometric amount required to complex (Cd + Zn)

DISCUSSION

If one admits that the entrainement of cadmium is possible only for the element as cation Cd^{++}, decontamination would only be due to the presence of cadmium as the anionic species of the chelate compound. If such was the case the fraction of coprecipitation "f" could be calculated from the equilibrium equation.

$$K = \frac{[CdY^{--}]\ [H^{+}]}{[Cd^{++}]\ [HY^{---}]}$$

from this equation one gets

$$\frac{[CdY^{--}] + [Cd^{++}]}{[Cd^{++}]} = 1 + \frac{K\ [HY^{---}]}{[H^{+}]}$$

and since it is supposed that the fraction coprecipitated "f" would be equal to the fraction of ionic cadmium Cd^{++},

$$\frac{[CdY^{--}] + [Cd^{++}]}{[Cd^{++}]} = 1/f = 1-K' [HY^{---}] \qquad (2)$$

in which $K' = K [H^{+}]$

However, in actual experimental cases, values of 1/f were not linearly correlated with $[HY^{---}]$ as is shown by the lack of constancy for K', table V and Figure 8.

TABLE V

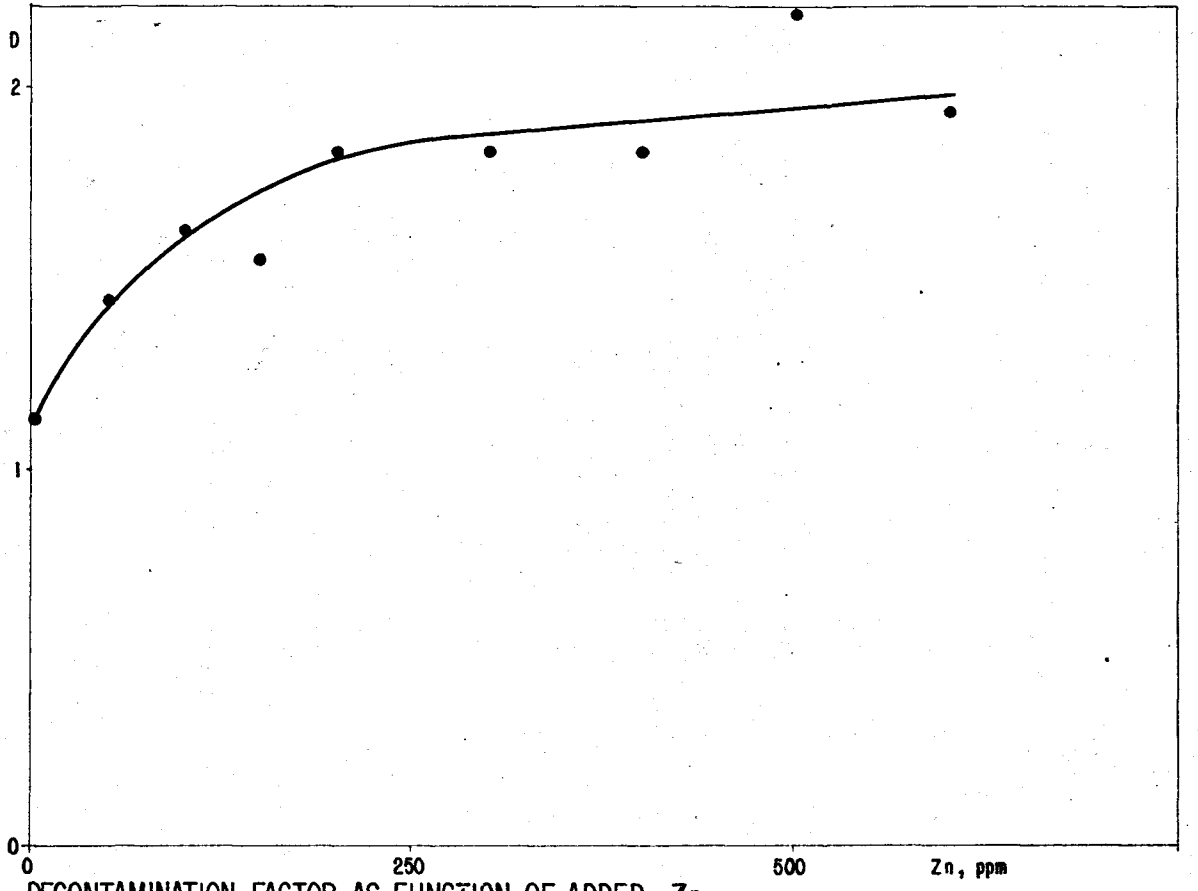
VARIATION OF SLOPE K', IN EQUATION (2), WITH $[HY^{---}]$ (*)

$[HY^{---}]$	K'
200	1.0×10^{-2}
400	1.2×10^{-2}
600	1.6×10^{-2}

(*) Concentration of $[HY^{---}]$ in terms of ppm of impurity

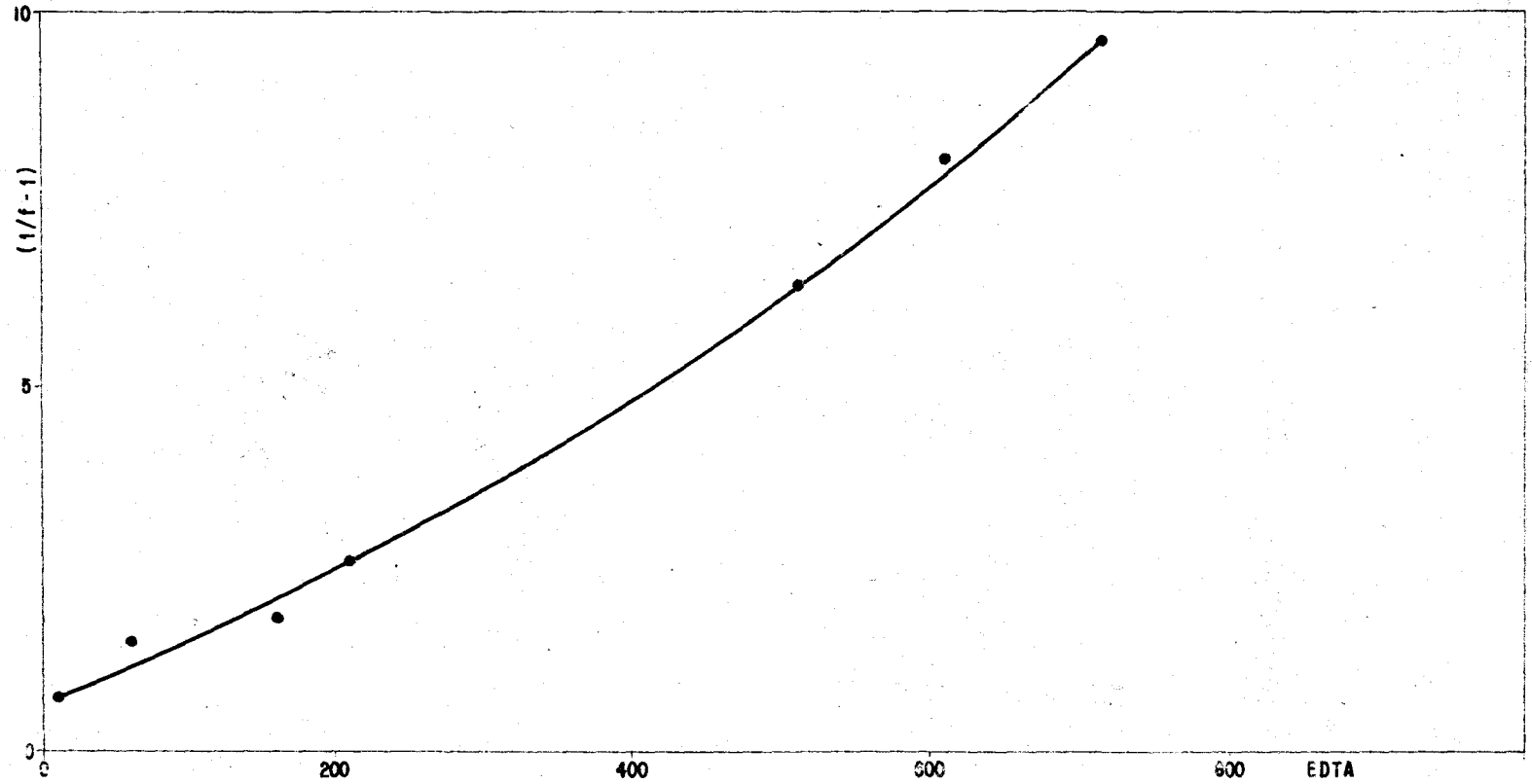
The coprecipitation mechanism of cadmium EDTA complex with ammonium diuranate is by adsorption, following a Langmuir isotherm up to a value of 500 ppm of initial cadmium contamination; above this value the surface effects end. From this value on variation of surface tension of the Cd-EDTA solution is such that the concentration at the interface is diminished and the simple Langmuir isotherm is not followed.

For the amounts of cadmium corresponding to 5 and 10 ppm the variation of the coprecipitated fraction as function of the amount of zinc added, follows the same curve within experimental



DECONTAMINATION FACTOR AS FUNCTION OF ADDED Zn.
AMOUNT OF EDTA : STOICHIOMETRIC FOR Cd + Zn.

FIGURE 7



VARIATION OF 1/f WITH **EDTA** CONCENTRATION. (CONCENTRATION OF **EDTA** IN TERMS OF **ppm** OF IMPURITY).

FIGURE 8

errors. This range of impurity concentration is the most important to be studied with the aim of getting additional decontamination on the step of ammonium diuranate precipitation, since any preceeding purification procedure will reduce cadmium to that value or less.

Dilution of the Cd-EDTA complex impurity with Zn-EDTA, made with the intention of using a hold-back carrier technique for cadmium, was not efficient as it was in the case of rare earths in which yttrium-EDTA complex was used as hold-back carrier for rare earths elements, also complexed as RE-EDTA[1].

RESUMÉ

On a fait un étude de la coprecipitation de la composé Cd-EDTA avec diuranate d'ammonium. L'influence de la présence de l'ion zinc, utilisé comme porteur de retention, de la concentration du EDTA sont discutée. Le type de isotherm d'adsorption de cette coprecipitation est aussi étudié.

RESUMO

Estuda-se o comportamento do composto quelado de cádmio com o ácido etilenodiamino tetracético no que diz respeito à sua coprecipitação com diuranato de amônio. Discute-se a influência da concentração de EDTA, da presença de ions zinco usados como carregadores de retenção bem como o tipo de isotérmica que descreve o fenômeno em discussão.

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