

SYNTHESIS REPORT

FOR PUBLICATION

CONTRACT N° : **IIRE2.LT92.LI410**

PROJECT NO : CR.1065.1.91

TITLE : TECHNICAL INNOVATION OF RAW SILK DEGUMMING PROCESS WITH RECOVERY OF ORGANIC PRODUCTS (SERICIN)

PROJECT
COORDINATOR : FILTEX-COMO (I)

PARTNERS : Industrial partners:

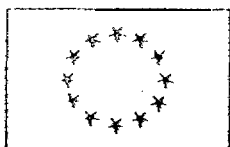
PROVERBIO SA (F)
H.R. S. ENGINEERING SRL (I)
APER ASSAINISSEMENT SA (F)
SILAB SA (F)

Research Institutes:

ENEA (I)
I.T.F. (F)
TESSILE DI COMO (I)

STARTING DATE : 01/02/1993

DURATION : 24 MONTHS



PROJECT FUNDED BY THE EUROPEAN
COMMISSION UNDER THE BRIT/EURAM
PROGRAMME

DATE : 20/04 {1995

1. ABSTRACT

Aim of the project was the optimization of the technologies employed for the degumming of silk, together with the study of various separation processes, in order to obtain from the waste waters "pure" sericin, which may be used in other industrial fields.

For this research it was decided to employ and compare, according to the previous results, ultrafiltration membranes, either alone, or coupled with ion exchange fabrics, examined by I.T.F.

2. INTRODUCTION

The "degumming" is a particular process carried out by specialized silk finishing/dyeing factories, aimed to remove the cover of the raw silk yarn of fabric, called "sericin" and leaving the silk core, made of fibroin.

The degumming is mainly carried out in a traditional way, that is, the silk yarn or fabric is placed into "star" machines, together with water at a temperature of 90°C and with the addition of some chemicals, such as surfactants and soda. With **this** treatment the raw silk leaves into the water its sericin cover, which is discharged together with the degumming bath.

Another degumming process which is presently used is the technology at high temperature; in this case, the silk product is placed into autoclaves together with water at a temperature of 120°C and in almost complete absence of chemicals.

In both cases, the discharged degumming baths are highly polluting, due to their sericin (organic) content.

The two mentioned degumming processes are performed by two textile partners inside our research programme. It must be anyway taken into consideration the direct degumming of cocoons or other wastes (specific for the "schappe" silk) performed for example by the associated partner CASCAMI SETA.

Some laboratory tests over sericin separation had been **already** carried out in the past, 'employing **various methods, but none of them represented** a system **suitable for the use on industrial scale.**

3. TECHNICAL DESCRIPTION

The research subject of this CRAFT project was developed into three main steps:

- First of all, several analyses were made in order to determine the composition, physical-chemical aspect and

behaviour of sericin AFTER the degumming process; this, in order to know as much as possible this particular substance; during this stage, the task was to spot, by means of a liquid chromatographic process, the distribution of the molecular weights of sericin downstream the degumming process, this in' order to determine its re-employment range.

- Secondly, all the possible separation technologies were investigated, in order to optimize the degumming process with the best separation, by means of ultrafiltration membranes and of ion exchange fabrics. Previous lab analyses were followed by tests carried out at FILTEX-COMO and PROVERBIO facilities, on little pilot plants.

The running data of the pilot plant at FILTEX are the following:

$v = 10 \text{ m}$

$C^{\circ} = 15 \text{ (g/l) (sericine)}$

$COD = 20,000 \text{ (mg/l)}$

while the operating conditions are:

$P = 3.5 \text{ bar}$

$T = 30-40^{\circ}\text{C}$

$VCR = 5$

$J = 15 \text{ (l/m}^2\cdot\text{h) (average value)}$

$R\% \text{ COD} = 97\%$

$R\% \text{ Ser} = 95\%$

$= 80\% \text{ (water recovery)}$

These tests were of preminent importance, since the treated baths came from two different degumming processes, as already explained. In particular, the FILTEX baths derived from high temperature degumming (with autoclave), while the PROVERBIO ones derived from traditional degumming (with star. machines).

During this stage, several types of membranes and ion exchange fabrics were employed, both in laboratory and directly on the pilot plants in the two factories, this, in order to find the best possible technical solution as per efficiency, cost and simplest maintenance.

- In the same time, market researches were made, in order to find all the possible markets for the recovered sericin.

At the beginning of the project the cosmetological sector was considered, for recycling the recovered sericin, due to the experience of some enterprises in the past and also because this appeared as the sector with the best quantity/price ratio.

Nevertheless, during the development of the project, other sectors were explored, since in this case sericin

could be recycled with greater quantities and with market evaluations which are proportional to its purity grade.

4. RESULTS

The several tests carried out by ENEA and I.T.F.-LYON in lab and in the factories demonstrated that the separation of sericin from the degumming baths is technically possible.

The distribution of the molecular weights of sericin obtained by examining the samples of the degumming baths provided by FILTEX-COMO is represented into the diagram (A).

The optimization of this process has been completed, by focusing among the several employed ultrafiltration membranes and ion exchange fabrics, those ones with the best performances, also according to the type of degumming process which is carried out.

The different methods for concentrating and separating sericin influenced as per molecular weights and so it came out the possibility to obtain from the same ordinary product different fractions, to be conveyed to possible different markets.

In particular, the cosmetologic market could treat the product with higher molecular weight, while the pharmaceutical sector could better re-use the product with lower molecular weight.

Here are a couple of examples of separation obtained with ion exchange fabrics and with U.F. membranes:

Example A: filtration through ion exchange fabrics (see diagrams ref. A - ref. A1 - ref. EA)

Example B: filtration through Carbosep mineral membranes (see diagrams "bain initial" - "permeat 4.4").

The market researches were aimed to focus the best re-employment field for the recovered sericin.

Since the industrial sector where sericin can be evaluated at the utmost, even if the required quantities are particularly low, is cosmetology, some tests were done in order to prove the non-allergenicity of sericin (with positive results), but these tests still have to be completed by further analyses.

The allergenicity tests were performed at the Institute

BIOMATECH (France) over pure sericin, obtained with the degumming of sterilized cocoons at the Institute I.T.F.

Other possible re-employments were investigated and another field where huge quantities of sericin can be used, though with a lower evaluation in comparison with the cosmetological industry, is just the textile sector.

In fact, as per our studies, sericin could become an optimal sizing agent for synthetic **yarns**, in order to speed up their weaving process. The use of sericin in this case would **replace all** the chemical resins which are presently employed at a much higher cost.

This proposal already encountered positive reactions in the sizing agents producers, which are well disposed to a possible industrialization of the previous weaving tests made by I.T.F. with a little sample of polyester yarn.

There are other industrial sectors which could be of interest for a re-use of sericin, but the evaluation of the product would be lower than in the cosmetological field.

They are:

- 1) The animal fodder industry, where sericin could represent a precious additive to the normal feeding of animals, such as cattle;
- 2) The direct feeding of the silk worm; in this case, the replacement of the traditional mulberry leaves could lead to a piloted breeding of the silk worm. This means the possible elimination of the silk seasonal production, with consequent practical advantages.
- 3) The use of sericin as additive in specific cleansing agents for wool. It was found that sericin can give that particular "soft hand", typical in some softeners.

5. CONCLUSIONS

Since our **market researches** about the possible re-uses of sericin gave us various possibilities and since **the** encountered possible final users of sericin showed great interest for **our** proposals, we do believe that further researches have to be done, in order to spot where and how sericin can be re-employed in the best possible way.

The first industrial prototype plants will be set up at FILTEX-COMO and PROVERBIO facilities and the recovered

quantities of sericin will be the first test stand for the industrial application of this product.

In competition of the research, an economic analysis of a possible industrial application based on parameters supplied by FILTEX-COMO was developed.

The process cost analysis has been based on the ultrafiltration treatment.

The costs for the degumming solution treatment and overall the costs of the process would be discussed on the basis of an economic scheme used at Daimler Benz facilities, for testing a coupled microfiltration and ultrafiltration process to treat oily waters.

The unit would run 10 h/d for treating 10 m³ batch produced per day.

At present the cost of the ultrafiltration membranes can be assessed at about 150 Ecu/m², so the cost of the plant (50 m² of membrane area) would be of about 30,000 Ecu.

The energy consumption per cubic meter of treated solution produces very cheap power costs: 1,000 Ecu/year.

Water costs for membrane washing are also unimportant, even if a very high water consumption has been considered (about 2-3 m³/d): 500 Ecu maximum per year.

The item taken into consideration for a process cost evaluation corresponds to a simple UF treatment followed by a biological treatment of the permeate and membrane washings and recovery of sericin from concentrate. This last step, performed via spray-drying (yield 50%) on a sericin waste concentrated at a VCR = 4, can produce about 40-80 kg of protein per day (12-24 tons/year) in case of sericin concentration in the starting waste solution of 10-20 g/l (see next chapters) .

If the UF concentrate (sericin solution) is considered a **"product"**, its end use should be oriented in order to improve the economic balance **of** the process.

The use of the concentrated sericin solution can represent, according to different hypothesis, a direct revenue or require additional expenditures to up-grade the "quality-prize" of the by-product.

From the point of view of the waste waters treatment, various hypothesis can be done about the efficacy of the ultrafiltration on the contribution of the degumming solutions to the overall waste stream. Such hypothesis

will consider a factory producing a global amount of waste waters of 700 m³/d with a COD level of 1300 mg/l, for which the biological treatment costs about 0.60 Ecu/m³.

Waste waters contain also metals, dyes and other pollutants. Besides, the FILTEX-COMO degumming process contributes with 10 m³/d at a COD level of 10-30,000 mg/l. The real composition of the waste waters stream, excluding the degumming contribution, is unknown, but its COD level can be evaluated at about 600 mg/l.

Three different schemes about the process evaluation are:

- a) **biological treatment of the overall waste waters with a corresponding cost of about 136,000 Ecu/year**
- b) **ultrafiltration of the degumming contribution of sericin recovery (UF concentrate solution] and biological treatment of the stream obtained by mixing the ultrafiltration permeate with the main waste waters stream.**

According to this hypothesis, 690 m³ of waste main stream are mixed with 8 m³ of ultrafiltered permeate with COD = 2000 mg/l, which practically does not change the COD level of the receiving stream. The cost for the biological treatment are then reduced to 63,000 Ecu. The ultrafiltration treatment cost must **be** added.

The revenues are represented by 2 m³ of sericin solution at 40-80 g/l, whose value can be assessed in 0.50 Ecu/kg of dry protein. The revenues are then between 12,000 and 24,000 Ecu/year.

- c) **ultrafiltration of the degumming contribution for sericin recovery (UF concentrate solution) and reverse osmosis treatment of the stream obtained by mixing the ultrafiltration permeate with the main waste water stream.**

This hypothesis corresponds to the aim of recovering a valuable high quality process water, in order to optimize the management of the water process supply and waste water final treatment.

According to the results obtained during the RO tests on the UF permeate, at a VCR = 10, a quantity of 628 m³ of water with COD = 75 mg/l could be obtained from 698 m³ of initial RO feed (690 from the main waste water stream and 8 from the UF permeate). A RO unit equipped with 70 m² of membrane would be needed. Considering a cost of about 250 Ecu/m² and the same cost evaluation done for UF, the RO process costs can be calculated. The energy consumption corresponds to a RO performed at 35 bar with a recycling flow rate of 5 m³/h.

The costs seem quite relevant but in the present hypothesis two revenues have to be considered:

- the quality of the recovered water (600 m³/day) for process application with a value of 0.35 Ecu/m³ (if compared to the normal water supply) or 1 Ecu/m³ if considered as demineralized water; only 100 m³ are daily supplied to the water supply.
- the saving of the final biological treatment for at least 600 m³/day of recycled water.

From the forecasting elaborated by ENEA, it came out that the use of the simple UF scheme represents an economical saving on the overall waste waters treatments costs .

Moreover, the improvement of the quality of the sericin by-product can represent the way for increasing the useful economic balance of the total treatment and recovery process.

The recovered water from the cost point of view is inconsiderable. However, in case the total waste waters are treated with RO, a little further saving can be obtained. It is important to point out that if the degumming solution, without any processing, could be stored separately from the main waste water stream (biologically treated) and treated once a year, the global treatment cost would be:

- 3,000 Ecu/year for the collected degumming solutions;
- 62,000 Ecu/year for the daily treated waste waters.

The annual total cost would be of 92,000 Ecu with a saving of 118,000 Ecu/year.

The recovered sericin (UF permeate solution) can be furtherly processed for different proposed end-uses.

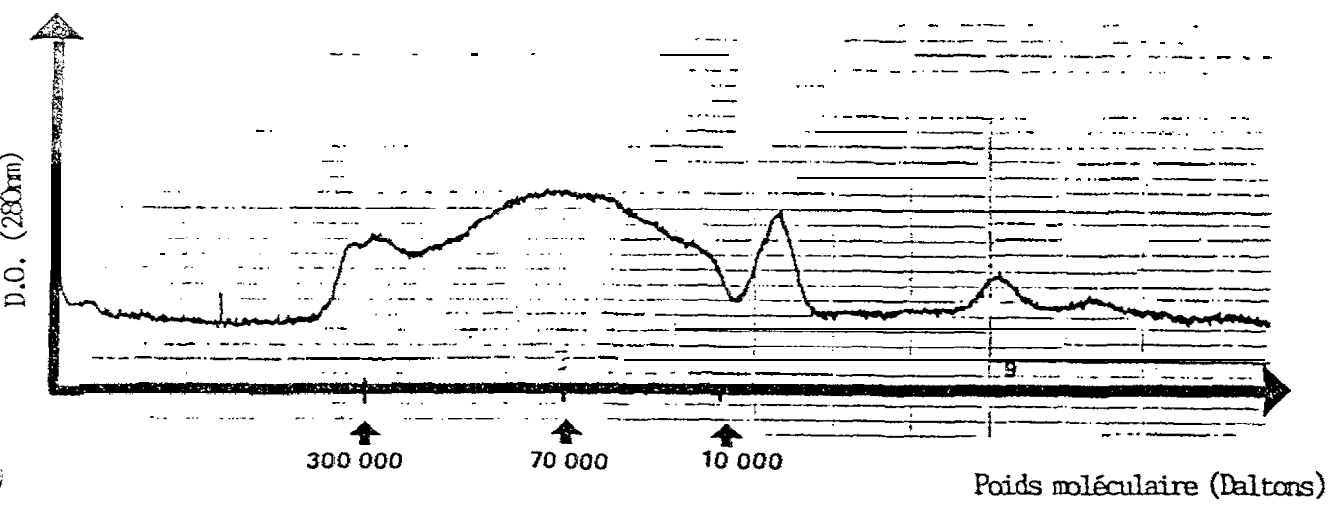
6. ACKNOWLEDGEMENTS

The development of the above described CRAFT project (n° CR.1065.1.91) was possible thanks to the support of the EUROPEAN COMMISSION - DG XII, that financed 50% of the research expenses and with which the partnership signed the relative Contract (n° BRE2.CT92.0410). Another important contribution was granted by ENEA, that partially supported the research with its own financing.

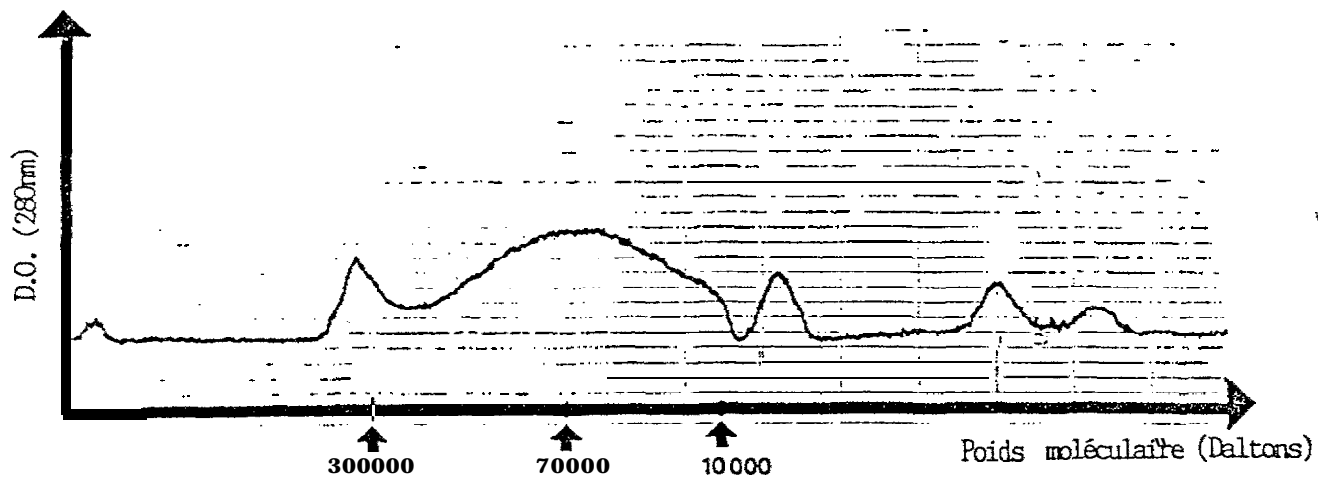
7. REFERENCES

- * FILTEX-COMO patent application no 20164A of 11.04.1988 having as subject the new "high temperature" degumming process
- * The specific activity of I.T.F.-LYON, which is created and since then has been dealing into the textile sector as research institute
- * The basic knowledge of the processes in which silk is involved was supplied by TESSILE DI COMO
- * The fundamentals for the research about the proteins and aminoacid was supplied by ENEA

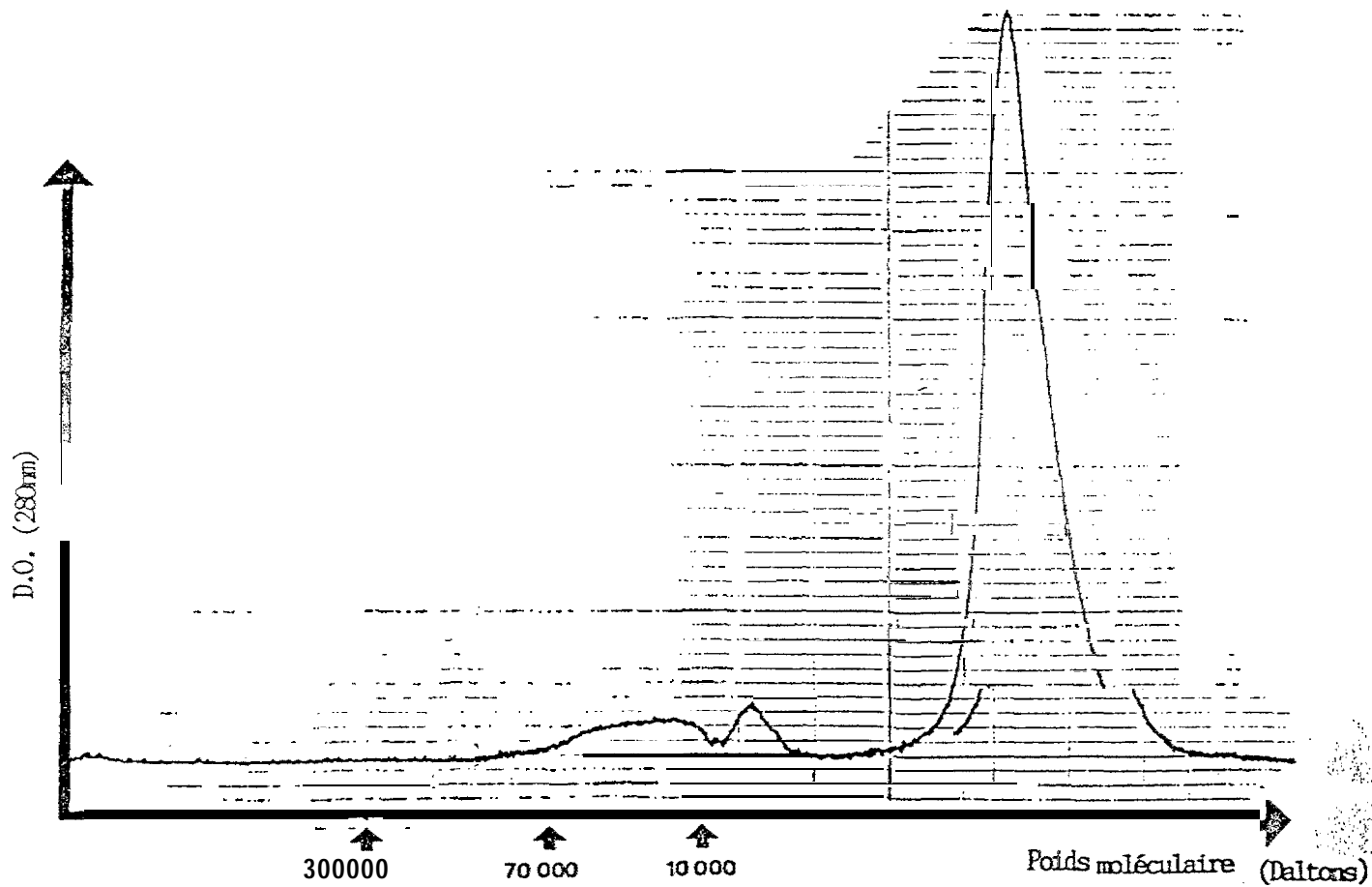
- réf A SERICINE DE BASE.



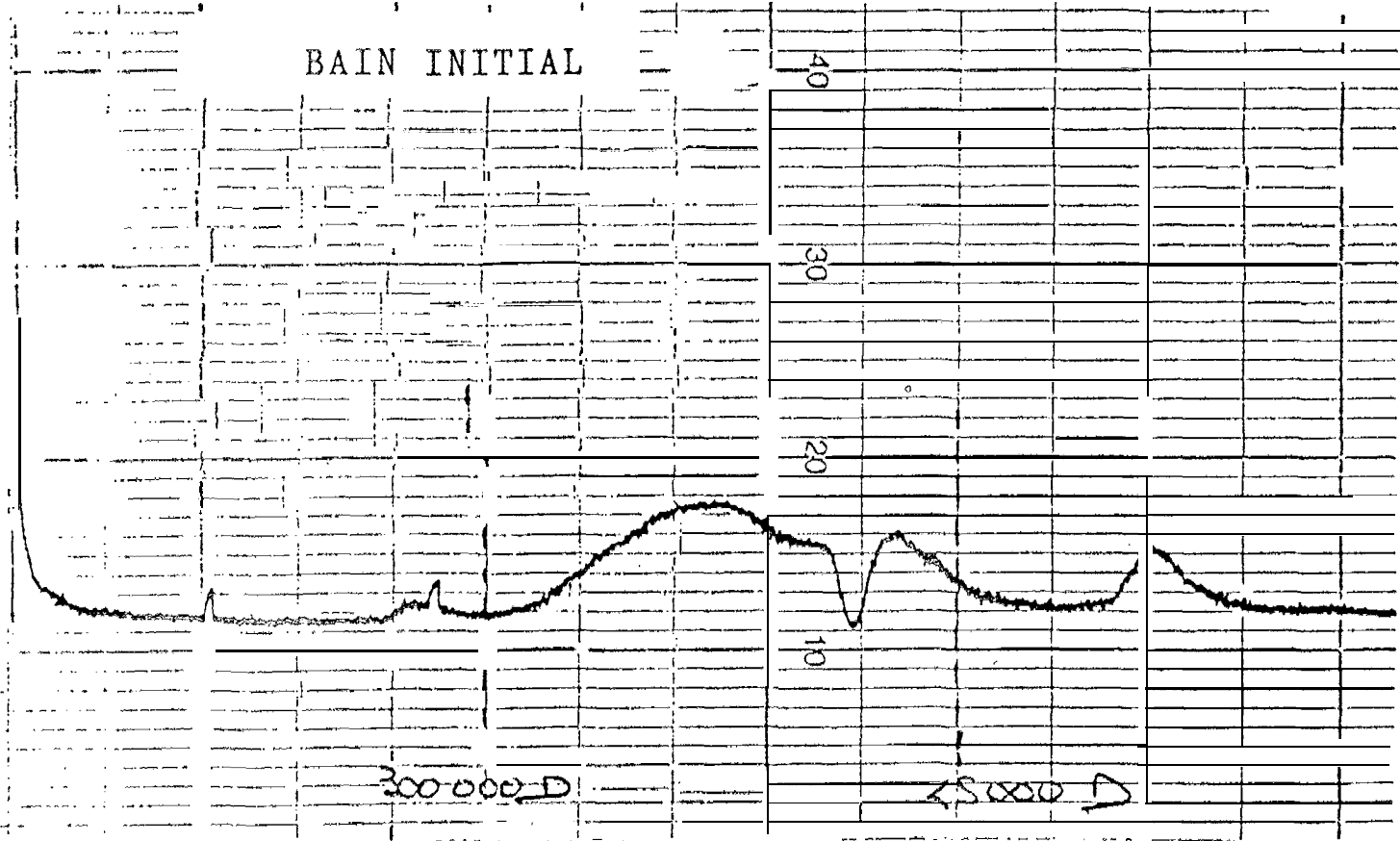
- réf A1 FILTRAT SUR TEI FORME $\text{COO}^- \text{Na}^+$



- réf EA ELUAT DU TEI $\text{COO}^- \text{Na}^+$ (avec HNO_3)



BAIN INITIAL



PERMEAT pH 4,4

W

0 80 90 100

35000 Daltons ←

20 20 1

