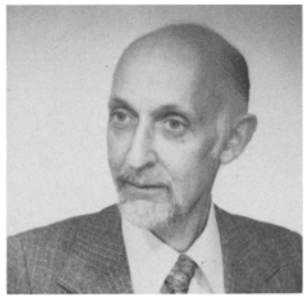
Residual Hexane in Meals



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ABSTRACT

It is now possible to determine in a reliable way the residual hexane in meals. In the case of rapeseed, tests performed in the experimental pilot plant of GERDOC have revealed three parameters, which to our knowledge have not previously been studied, and which have a favorable influence on the desorption of hexane: drying the seeds with hot air before they are crushed, dehulling the seeds, and decreasing the length of the extraction time.

The residual hexane content of meals, and, more particularly, of rapeseed meals is an extremely important problem in virtue of its close connection with safety and pollution of the atmosphere. The Institut des Corps Gras has set out to study the following procedures: (a) the determination, as quickly and as rapidly as possible, of the residual hexane content of meals; and (b) the evaluation, in an experimental workshop, of different parameters that can affect this content.

DETERMINATION OF THE RESIDUAL HEXANE

It may seem surprising that this determination still requires work in the laboratory. But the work done by AFNOR in France, the Commission on Fats and Oils of IUPAC, and ISO TC 34/SC 2 on the international level have shown the following: that the determination is a very delicate matter; that national standards are few and varied; and that, if the results obtained by proposed methods are in general repeatable, they are not reproducible. A comparative study of the most used methods has been done by Prevot and Coustille (1).

The analytical technique that gives the most satisfying results is the method of "head space" performed on the meal with an addition of 50% of its weight in water. This method, described in Table I, stems from the method of Dupuy (2). It was the subject of a cooperative analysis organized by AFNOR in which six French laboratories and five European and American laboratories participated. The results of this circular analysis are given in Table II.

TABLE I

Determination of Residual Hexane by the Technique of Head Space with Water Added

Test portion
5 g in a bottle of ca. 60 mL with septums in perbunan
Water added
2.5 mL
Desorption of hexane
90 min at 110 C for soybean and rapeseed 60 min at 110 C for sunflower
Analysis by chromatography in the gaseous phase
Injector and detector: 120 C Oven: 40 C Carrier gas pressure: 0.3 bar Capillary column of glass of 30 m, diameter 0.3 mm, coated with SE 30 or Full column of 1.7 m, packed with SE 30 on Chromosorb WAW (150-180 μm) Calibration: with liquid hexane (e.g., 2-5 and 10 μL)

A succinct statistical analysis taking into account the results of the 11 laboratories shows that the coefficient of variation is 9% for repeatability and lies between 21% (soy) and 30% (rapeseed) with respect to reproducibility.

Without prejudging any decisions that may be made by IUPAC and ISO, we have therefore considered that the repeatability and significance of the method described in Table I were sufficient to allow us to study, in an experimental workshop, some of the parameters affecting the retention of hexane in a meal.

PARAMETERS AFFECTING THE RESIDUAL HEXANE CONTENT OF MEALS

In addition to laboratory studies relating to the desorption of hexane, we have performed, in an experimental workshop, tests relating to the influence of various technological parameters on this retention.

The experimental pilot plant of GERDOC put together jointly by CETIOM (Centre d'études techniques interprofessionnel des oléagineux métropolitains, i.e., Interprofessional center for technical studies of oilseeds of metropolitan France) and the Institut des Corps Gras includes the following: (a) A grain-crushing pilot plant equipped with smooth and grooved crushing rolls that make it possible to crush grain and prepare flakes, and also equipped with a continuous press with an hourly capacity of about 300 kg and preceded by its own toaster. (b) A pilot plant for extraction by hexane (or by solvents with density greater than 1) of which the extractor—analogous to a French basket extractor—makes it possible to process by percolation from 100 to 700 kg of prepared fatty meals or of grains with a low oil content. The desolventizer-toaster (DT) has two levels and can operate with or without the steam injection.

The entire facility operates in batches in order to be able to guarantee the purity of each processed lot, even if we have only 200-300 kg of raw material. All tests mentioned hereafter concern lots of French rapeseed without erucic acid (Primor or Jet 9).

The residual hexane content depends, as is well known, on the length of time the material remains in the DT. We studied the kinetics of desolventizing for 3 hr. But it is quite evident that such a long treatment entails a significant degradation in the quality of the proteins. These kinetics must be used to define the qualitative influence of various parameters and not to optimize the industrial conditions of manufacture.

Figure 1, relating to the kinetics of desolventizing the same meal at three different temperatures of the DT, is very representative of the influence of residence time on the residual hexane content. It also shows that the temperature of the DT at the time of the elimination of the hexane does not seem to be a preponderant factor in the final hexane content of the meal. It seems, though this result would have to be confirmed, that an increase in temperature does not have a favorable influence on the elimination of hexane.

Three factors, on the other hand, have a very positive effect on the speed with which hexane is removed and, therefore, on the residual hexane content at the outlet of the DT.

TABLE II

Determination of Residual Hexane in Meals (results in mg/kg [ppm])

Laboratory	Rapeseed		Soybean		Sunflower	
	Determination	Mean	Determination	Mean	Determination	Mean
1	1065 1035 1060	1053	390 360 390	380	485 315[a] 490	430
2	650 720 720	697	260 270 290	273	410 380 380	390
3	1140 1120 1130	1130	420 410 410	413	480 480 490	483
4	1163 1128 1075 1106	1118	453 438 473 471	459	570 570 614 551	576
5	990 900 875 900	916	400 380 420 415	404	470 530 495 435	482
6	960 966 —	963	428 438 —	433	524 523 —	523
7	951 945 992	963	431 408 400	413	411 399 420	410
8	577 635 625	612	320 324 301	315	267 260 248	258
9	1086 1598 1122	1269	536 311 445	431	579 545 426	517
10	814 840 842	832	409 438 366	404	411 470 466	482
11	1420 1350 1510	1427	500 520 550	523	580 560 560	567

[a]Stopper was not tight at time of entry into the drying oven at 110 C.

Prior Drying of the Grains

Figure 2 relates to desolventizing meals coming from the same lot of grains subjected to more or less prolonged drying by air at 70 C, then at room temperature, which has made the moisture of the grain being processed go from 7.5% (raw grain) to 6.3% and 4.5%. Data in this figure show that heat treatment prior to preparation of the flakes effects a considerable decrease in the residual hexane content. This result was reconfirmed by the Lesieur Company on an industrial scale.

It should be noted that the decrease in residual hexane content is much more rapid than the decrease in moisture content of the grains being processed. It may then not be the latter factor that plays a role in the decrease of residual hexane, but rather the surface conditions of the grains modified by the drying.

Dehulling the Grains

Elimination of hulls by a process developed by CETIOM and the Société Hydromecanique et Frottements also makes it possible to reduce residual hexane, as is shown in Figure 3. Grains from one lot of seed were processed under the same conditions of pressure, extraction, and desolventizing, either without or with prior dehulling. The hexane content of meals from dehulled kernels is 1/2 to 1/3 that of meals from undehulled whole grains.

The results are highly comparable to those obtained by drying at 6.3% moisture, but are less satisfying than those obtained by drying to 4.5% moisture. It should be stated precisely that the dehulled seeds came from a semi-industrial dehulling operation involving several tons and that the dehulling, although good, was not perfect.

Now, as complementary tests have shown, the residual hexane content, under rigorously identical conditions of pressure, extraction, and desolventizing, is increased if the hull content is increased. These results emphasize the important role that the rapeseed hull apparently plays in the retention of hexane in the meals.

Reducing the Time of Contact Between Hexane and Fatty Meal During Extraction

Laboratory observations having indicated to us that the residual hexane content of the meal seemed to increase considerably when the extraction time of the oil by the hexane increased. We tried to verify this conclusion in an experimental pilot plant. The design of our facility makes it possible to vary the length of the extraction operation easily, but the defatted meals thus obtained do not have the same residual oil content.

Figure 4 shows residual hexane on two identical lots of rapeseed meal that have been extracted with hexane for

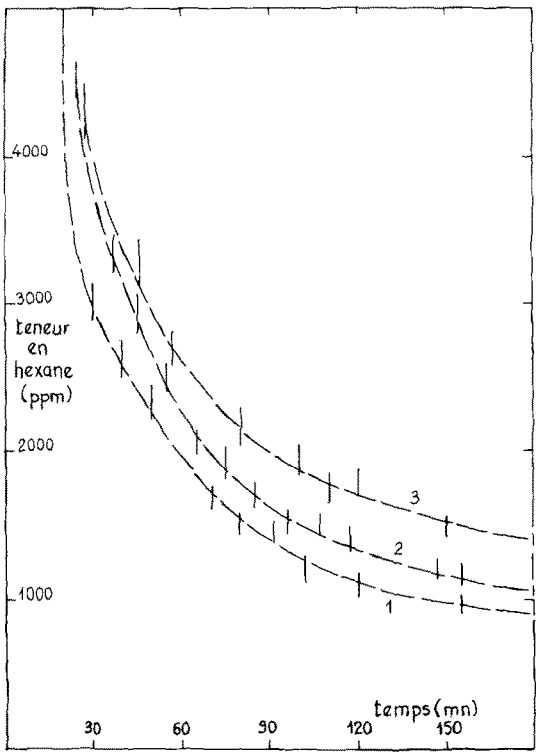

FIG. 1. Kinetics of desorption of hexane in the DT (case of the rapeseed meal): (1) DT at 100 C; (2) DT at 105 C; (3) DT at 110 C.

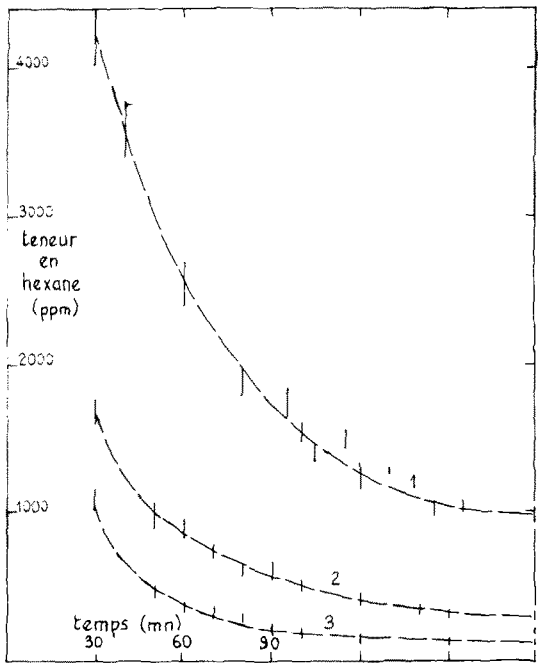

FIG. 2. Influence of drying the seed before crushing on the kinetics of desorption at 105 C of hexane in the DT: (1) undried seed meals (7.5% moisture); (2) dried seed meals (6.2% moisture); (3) dried seed meals (4.5% moisture).

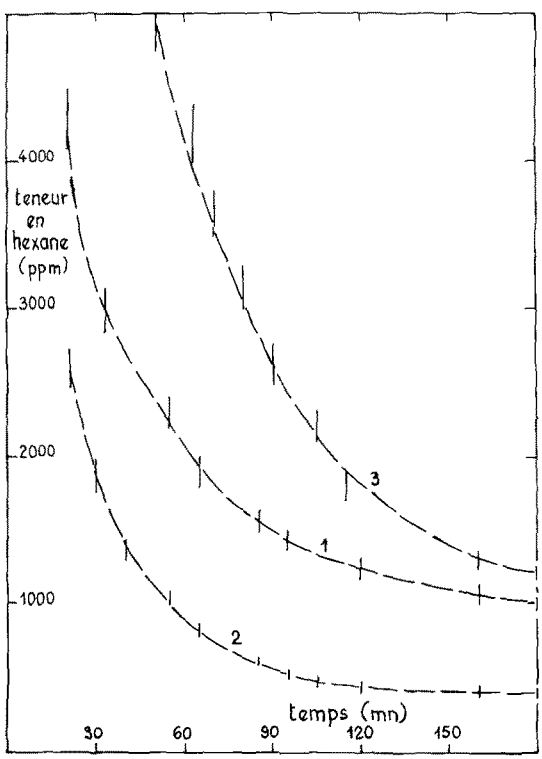

FIG. 3. Influence of dehulling rapeseed seeds on the kinetics of desorption at 105 C of hexane in the DT: (1) whole-seed meals; (2) kernel meals; (3) hull meals.

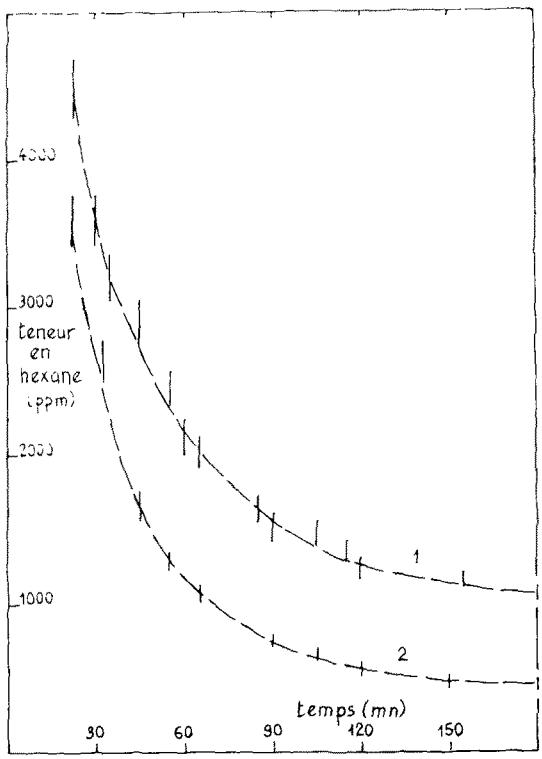

FIG. 4. Influence of length of extraction time on the kinetics of desorption at 105 C of hexane in the DT: (1) extraction time 6 hr; (2) extraction time 2 hr.

2 hr and 6 hr. The shorter extraction time produced a meal with less residual hexane.

If the residual oil content is not one of the essential parameters in the retention of hexane by the meal, it is nevertheless impossible to neglect it entirely.

In order to try to eliminate the possible influence of the residual oil in the extracted meals, we made the following tests on a different lot of processed fatty meals: (1) extraction for 6 hr (residual oil content 2.4%); (2) extraction for 2 hr (residual oil content 3.5%); (3) extraction for 2 hr and continuation of the contact between the meal and the hexane without any circulation of hexane for 4 hr (residual oil content 3.2%); and (4) extraction for 1 hr (residual oil content 6.0%).

Figure 5 shows the kinetics of the desorption of hexane in these four tests. It confirms that the length of the extraction is an essential factor in the retention of hexane, since, for samples 2 and 3, which have comparable oil contents but hexane-meal contact times that vary by a factor of 1 (sample 2) to 3 (sample 3), the residual hexane contents, for a constant length of stay in the DT, vary almost from 1 to 3. With 6% of residual oil, but only 1 hr of extraction (sample 4), the desorption of the hexane is almost as fast as for the meal at 3.5% oil that has been extracted for 2 hr.

On dehulled kernels (Table III), the same conclusions are reached. The decrease in extraction time gave a decrease in the residual hexane content, comparable in relative value to that observed on the whole-seed meals shown in Figure 5.

ACKNOWLEDGMENTS

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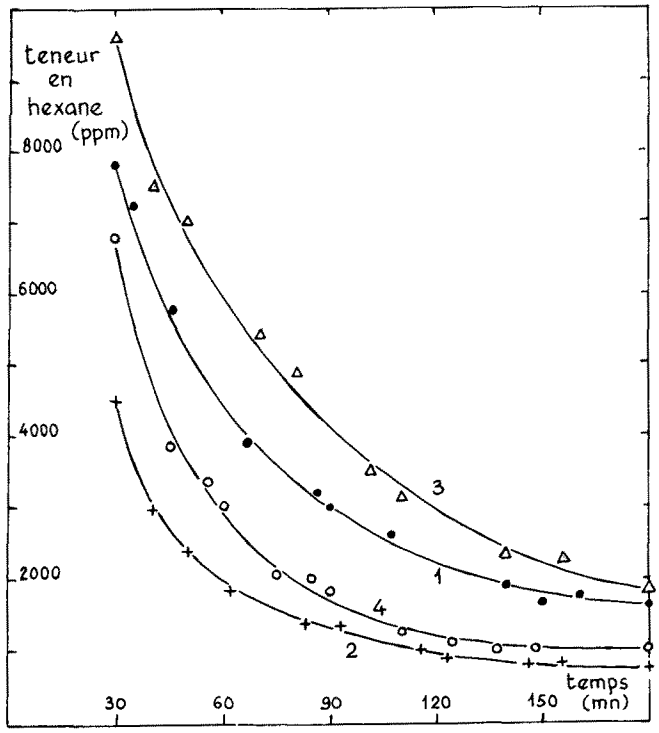

FIG. 5. Influence of length of extraction time on the kinetics of desorption at 105 C of hexane in the DT: (1) ●——● extraction time 6 hr (residual oil content 2.4%); (2) +——+ extraction time 2 hr (residual oil content 3.5%); (3) △——△ extraction time 2 hr + 4 hr of contact without circulation of hexane (residual oil content 3.2%); (4) ○——○ extraction time 1 hr (residual oil content 6.0%).

TABLE III

Influence of Length of Extraction Time on Hexane Retention in Extracted Rapeseed Meals with and without Dehulling

Length of stay at 105 C in the DT (min)	Residual hexane in ppm			
	6 hr of extraction time		2 hr of extraction time	
	Undehulled	Dehulled	Undehulled	Dehulled
60	2140	1000	1180	740
90	1540	600	740	380
120	1220	460	560	260