Jaocs news feature

Chlorophyl content monitoring of Swedish rapeseed and its significance in oil quality

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The importance of the degree of maturity of rapeseed to the quality of rapeseed oil was not subjected to serious discussion and examination in Sweden until the mid-60's. In 1966, as a result of this discussion, seed delivered to Swedish Oil Extraction Ltd. was subjected to a continuous control and grading process. Experience gained with this process led the Swedish Oilseed Association to introduce a control and price regulation system based on the chlorophyl content of the seed. Starting with the harvest of 1970, this was applied to all deliveries of seed to country elevators. These control measures, together with the grading system, have proved beneficial to oil quality and have also led growers to show an increased interest in detecting and counteracting quality defects at an early stage.

Swedish Oil Extraction Ltd. (EXAB) and its relation to the Swedish margarine industry and the growers' associations have previously been described in great detail by Tingnell (1). For an understanding of EXAB's participation in solving the problems of quality to be discussed here, the following brief introduction should suffice.

Swedish Oil Extraction Ltd. owns and operates Sweden's only extraction plant for large scale production of vegetable oil. The capacity of the plant is 600 tons rapeseed per 24 hr period. In recent years 135,000 tons of rapeseed have been processed annually. The oil is exported or sold to the Swedish margarine factories that are joint owners of the company. The meal is used exclusively within the country, primarily as an ingredient in mixed cattle feed.

All of the rapeseed treated by EXAB is delivered by the growers' purchasing and retailing association, the Swedish Oilseed Association, which is obliged to purchase all the rapeseed grown on contract in Sweden. This constellation of one buyer and one seller has made it possible to achieve relatively rapid results in negotiations on seed control and price regulations based on various quality characteristics.

Rape harvest quality

The desire for high quality Swedish rapeseed is, of course, as old as Swedish rapeseed oil production. However the question of quality was confronted in a more organized way in the beginning of the 60's, when the margarine industry began to provide economic support for work on oilseed cultivation aimed at changing the fatty acid composition. It then seemed rather natural to also systematically study other factors that influence the quality of the seed. In 1962 an important step toward a better understanding of the problem of seed quality was taken, when quality screening of the autumn rape harvest was performed for the first time by Appelqvist and Lööf (2).

In addition to the determination of oil and moisture contents, the free fatty acid content, percentage of viable seeds, field-germinated seed content and purity were determined on a random selection of autumn rape samples representing the entire area of cultivation. This first rather comprehensive quality screening provided a new, substantial basis for discussion of quality, and initiated a series of similar quality screenings (3-7).

The quality factor of concern here is chlorophyl content as a measure of maturity, which was first included in quality screening for the 1964 harvest (4). In the summary of that investigation it is stated that "the content of chlorophyl proved to be the index of quality, which had the greatest variation within as well as between different types of seed. Especially high contents of chlorophyl were found in summer rape, but there were also high contents in the seed of winter rape."

The actual impetus for the increasing interest in maturity levels was, of course, complaints from the margarine industry in its capacity as big buyer of Swedish rapeseed oil. Not too often, but nevertheless regularly each year, we happened to produce a rapeseed oil that was very dark in color, and consequently difficult to refine. A bluish-green color was especially prominent in these oils. It was already well known that seed with a high chlorophyl content yielded discolored oil on extraction. At the same time it was uncertain whether this effect could be avoided by modification of the processing conditions or by storage of the seed with a suitable moisture content for an extended period. Such suggestions were made because the discolored oil most often appeared in October or November, when the new harvest was being worked up, but

TABLE I

Quality Demands and Normal Values for Crude and Freshly Refined and Deodorized Rapeseed Oil in Some Swedish Margarine Plants

Analysis	Refined and deodorized rapeseed oil		Crude rapeseed oil
	Max allowed	Normal values	Normal values
Free fatty acids, %	0.1	0.02-0.10	---
Phosphorus content, ppm	5	2-5	---
Peroxide value, AOCS Cd-8-53	0.0	0.0	---
Benzidine value, IUPAC II D15	3.0	0.5-1.5	---
Absorbance, A460 nm	0.20	0.02-0.05	10-18
Absorbance, A550 nm	0.03	0.002-0.010	0,2-0,4
Absorbance, A670 nm	0.03	0.000-0.008	1-2
Lovibond color, yellow	10	6	75-125
Lovibond color, red	1	0.6	1-3
Lovibond color, blue	0	0	0-2

TABLE II

Analysis Values for Freshly Harvested Spring Rapeseed at Various Levels of Maturity and for Extracted Oil

	Seed sample			
	A	B	C	D
	Harvest time			
Analysis	Sept. 14	Sept. 21	Sept. 26	Sept. 26
Moisture content, %	6.8	6.5	6.4	7.2
Oil content, %	44.2	45.2	47.2	47.9
Germination capacity, %	81	93	96	0
Free fatty acids, %	0.74	0.34	0.54	0.61
Peroxide value, AOCS Cd-8-53	0.5	0.4	0.7	0.5
Benzidine value, IUPAC II D15	1.5	1.7	0.3	1.7
A670 nm	10.4	2.25	1.02	0.88
Chlorophyl, AOCS Cc 13d-55	192	42	19	17

seldom later in the season.

In the course of continued maturity level screening of the Swedish rapeseed harvest, it became more and more clear that the amount of immature seed could be very large in certain years. Spring rape, which had the lowest average maturity level in the very first investigation, subsequently maintained its position as the most immature seed type on the average. Furthermore extreme levels of immaturity were found to occur almost exclusively in spring rape.

In view of the necessity of taking into account the customers' demands for quality in the crude rapeseed oil, EXAB had to attempt to reduce the effect of the occurrence of immature seeds in the seed bulk. Two ways seemed possible. One, which might lead to immediate improvements, involved sorting out immature seed lots at some stage of seed handling. The other, which should have a favorable effect in the long run, involved the introduction of price regulation based on chlorophyl content.

In order to be able to set up such a price scale, it was necessary to obtain more extensive knowledge about the correlation between the level of maturity of the seed bulk and the quality of the resulting refined and deodorized cooking fat.

TABLE III

Absorbance at 670 nm for Refined, Bleached and Deodorized Oils

Seed sample	Storage time of seed prior to extraction, weeks			
	0	5	10	56
A	0.018	0.022	0.013	0.010
B	0.014	0.008	0.008	0.002
C	0.006	0.004	0.006	0.003
D	0.009	0.003	0.007	0.002

Quality demands of margarine industry on rapeseed oil

The following are comments on quality requirements, made in 1966 by Ulla Holm at Margarinbolaget AB, Development Center, Södertälje (unpublished): "Demands on quality vary considerably depending upon the use for which the oil is intended. In refining oils for food products, it is especially important to remove substances that have, or rapidly give rise to, disagreeable tastes and odors. Further, it is important to eliminate unappetizing colors. If color additives are present in the finished product, the color of the oil itself must be reduced to such an extent that it does not change the final color impression. If these goals cannot be reached, the oil is unsuitable as food."

Around 1966, when the experiments with oils from immature seed were about to be started, these unspecifically formulated quality demands had the empirically observed counterparts in actual analytical values shown in Table I. The maximum allowed values given in the table were under no circumstances to be exceeded in a freshly refined oil, and indeed it was only in exceptional cases that they were approached. For the color value of interest in the present context, A670 nm, a value ca. 0.1 of the maximum (i.e., 0.003) was said to be "normal." However the stated objective was that A670 nm would not be measurable in the bleached oil. The normal values in the second column are still valid in 1972. In order to reach these low values through neutralization and bleaching according to the standard methods used in the Swedish margarine factories, the crude rapeseed oil had to meet certain quality requirements with respect to lecithin content, color intensity and degree of oxidation. For color intensity of crude oil the values in the last column of Table I were considered normal. The sporadically occurring dark-colored oils had considerably higher color values, particularly toward the blue end of the spectrum.

TABLE IV

Taste Scores after 1, 3 and 7 Weeks' Storage of Deodorized Oils Extracted from Freshly Harvested or Stored Rapeseed at Various Levels of Maturity

Seed sample	Storage time of deodorized oil	Storage time of seed prior to extraction, weeks				
		0	5	10	28	56
A	1 Week[a]	3.7	3.7	3.1	3.0	3.0
B	(Normal value: 3.9)[b]	3.9	3.4	3.1	3.0	3.0
C		3.9	3.8	3.8	3.7	4.0
D		4.0	4.0	3.9	3.3	3.2
A	3 Weeks	3.3	2.7	2.5	—	2.7
B	(Normal value: 3.5)	3.3	3.3	3.0	—	2.7
C		3.7	3.6	3.7	—	3.3
D		3.7	3.7	3.9	—	3.0
A	7 Weeks	2.7	1.7	2.0	—	1.7
B	(Normal value: 2.6)	2.7	2.7	2.3	—	2.0
C		3.5	3.0	3.3	—	3.0
D		3.3	3.2	3.7	—	2.5

[a]Standard deviation: 0.13. Confidence interval: 95%.

[b]Normal value: average from several years of routine tests of commercial Swedish rapeseed oil.

Refining experiments on a laboratory scale

In order to be able to study the refining and deodorizing processes on a smaller scale, bench scale models had long been used at the research laboratory of Margarinbolaget. Sufficient data had been accumulated to allow a transfer of experience from bench scale to factory scale. It was now decided to take advantage of this experience in a more detailed study of the correlation between the chlorophyl content of the seed bulk and the desired quality characteristics of crude and refined rapeseed oil. A number of investigations of this kind were undertaken, and an account of one will be given here. The results of this investigation are representative.

The seed material used for this specific study was spring rape from an experimental field at the Swedish Seed Association in Svalöv. The seed was harvested at full maturity, as well as 1 and 2 weeks before full maturity. The seed samples, denoted A, B and C, were dried under mild conditions to a moisture content of 6-8% immediately after harvesting. Part of sample C, which had been harvested latest, was exposed to high temperature for a short time in order to decrease the vitality of the seed, and the sample thus obtained was denoted D.

Part of each sample was extracted at the Swedish Seed Association in Svalöv immediately after harvesting, in a laboratory extractor build to imitate a continuous countercurrent extractor. Seed from each series (A, B, C, D) was then stored and later extracted four more times (after 5, 10, 28 and 56 weeks' storage). The analytical results obtained for oils extracted from the freshly harvested samples are presented in Table II, which shows that even the initial values differ from each other to some extent. The very immature seed sample A has a high chlorophyl content and intense absorption at 670 nm, as well as a low oil content. The differences in germination capacity and free fatty acid (FFA) content are not significant. The germination capacity of sample D is zero, because the seed has been killed by heat. The chlorophyl content in the oil from the fully mature sample C is ca. 20 ppm.

Continued storage of the seed samples for up to 56 weeks under controlled conditions led to no change in the chlorophyl content. On the other hand, the FFA contents increased in all cases, but most rapidly in the immature sample A. The oxidation values did not change noticeably in the oils from samples A, B and C. In the oils from the artificially killed seed, D, the oxidation values were increased in certain cases.

All 20 samples of crude oil were refined in turn at the research laboratory of Margarinbolaget as they were extracted. The refining consisting of desliming, phosphoric acid treatment, neutralization, washing, bleaching with 1.5% active bleaching earth and deodorization for 2 hr at 220 C, with the addition of citric acid. Color values for the freshly deodorized oils are given in Table III. In this case it was concluded that all of the oils in series A had excessively high color values, considering the amount of bleaching earth that had been used. In series B, one value was too high, while two were on the limit and only one was clearly satisfactory. The oils in series C and D were judged to have very satisfactory color values except for sample D, 0 weeks. These results indicate that a chlorophyl content of ca. 20 ppm in the crude oil could be tolerated, but not 40 ppm or higher.

Both after bleaching and deodorizing, all of the oils had the peroxide value zero. All of the benzidine values were at an acceptable level. However the benzidine values were somewhat higher for oils extracted after 28 and 56 weeks' storage of the seed sample, than for oils extracted after a shorter period of storage.

The samples were evaluated organo-

TABLE V

Peroxide Values after Storage of Deodorized Oils Extracted from Freshly Harvested or Stored Rapeseed at Various Levels of Maturity

Seed sample	Storage time of deodorized oil	Storage time of seed prior to extraction, weeks				
		0	5	10	28	56
A	1 Week	0.1	0.2	0.0	0.2	0.1
B		0.0	0.1	0.1	0.0	0.1
C		0.0	0.0	0.0	0.0	0.0
D		0.0	0.0	0.0	0.0	0.1
A	3 Weeks	0.3	0.5	0.2	—	0.6
B		0.2	0.2	0.2	—	0.2
C		0.1	0.1	0.2	—	0.1
D		0.2	0.1	0.2	—	0.4
A	7 Weeks	0.5	0.6	0.6	—	1.8
B		0.5	0.4	0.5	—	0.3
C		0.1	0.5	0.3	—	0.2
D		0.3	0.5	0.3	—	0.7

TABLE VI

Grade Requirements for Rapeseed Applied in Connection with Grading according to Quality on Arrival at Extraction Plant

Analysis	Seed grade		
	1	2	Unacceptable
Chlorophyl content, ppm	≤30	31-70	>70
Free fatty acids, %	≤ 1.0	1.1-3.0	> 3
Moisture content, %	≤ 8	≤8	> 8
Purity, %	90-100	90-100	<90

leptically by an expert panel of eight persons after 1, 3 and 7 weeks' storage. The samples were stored at 18 C in the dark in half-filled 300 g brown bottles. The grading was from zero for extremely poor to six for excellent. The data in Table IV show that after 1 week's storage oils extracted from immature seed, series A and B, had lower taste scores than those extracted from mature seed. The same pattern is evident after 3 weeks' storage. After 7 weeks' storage the oils in series A and B were of poor quality, whereas the C series oils were still fair to good. The D series oils showed a tendency toward more rapid deterioration after a long period of storage of the seed sample. Changes in the corresponding peroxide values developed similarly (Table V).

On the basis of these results and a number of corresponding results from similar parallel experiments, it was possible to conclude that the refining methods normally used on a plant scale gave unsatisfactory results if the crude rapeseed oil had a chlorophyl content greater than 20-30 ppm. Consequently oils with higher chlorophyl contents required extra treatment on refining to achieve acceptable results concerning color values as well as time-dependent quality characteristics such as FFA content, oxidation values, and flavor stability. It was also established that crude oil with a chlorophyl content greater than 50-70 ppm was unsuitable as raw material for edible products.

Seed control and grading

During 1966, concurrent with the work just described, Swedish Oil Extraction Ltd., in cooperation with AB Karlshamns Oljefabriker, established a seed control laboratory. The purpose of the laboratory was to control all deliveries of rapeseed to the extraction plant with respect to chlorophyl content, FFA content, moisture content, appearance and odor. Appelqvist and Johansson (8) had previously carried out methodological studies to develop a means of rapid chlorophyl content determination. This method was now further developed, and also combined with a titration of free fatty acids.

On the basis of the analytical results, the seed deliveries were to be graded according to the scheme shown in Table VI. Seed grade 1 included the chlorophyl content interval 0-30 ppm and seed grade 2 the interval 31-70 ppm, while chlorophyl contents greater than 70 ppm made the seed unacceptable. The grade requirements were thus set at the maximum values recommended on the basis of laboratory experiments.

The seed control laboratory is now entering its seventh crop season. Its maximum capacity is 100 analyses per day. The time required for a complete analysis is ca. 6 min, and a total of 3500 samples is analyzed per season. The routine measures taken in connection with receipt of seeds are as follows: (a) sampling from delivery truck according to a standard procedure; (b) analysis of moisture, chlorophyl and FFA contents; (c) purity and odor control; (d) grading of seed bulk as first grade, second grade or unacceptable; (e) weighing of the delivery truck; (f) unloading to a suitable silo depending upon the result of the grading; and (g) weighing of the empty delivery truck.

During the past seasons with seed delivery control, it has been fully confirmed that spring rape in particular is often entirely too immature at harvest. More surprisingly, however, we have also seen that in certain years the autumn rape can be less mature than the spring rape. This occurred in 1968, according to the data in Table VII. It is also apparent from the table that spring turnip rape may be very poor, but that autumn turnip rape generally has a low chlorophyl content. It should be noted that the values given for 1966-68 are based on the previously described delivery control at the extraction plant, involving ca. 3500 analyses per year on a seed quantity corresponding to 65-75 wt % of the entire harvest. The analysis results for 1969-71 are based on a considerably larger number of samples, since in that case *all* growers' deliveries to drier-stocker companies were analyzed. The number is ca. 50,000 and encompasses the entire Swedish harvest.

The same is true for Table VIII, which shows how much of the seed delivered to EXAB (1966-68) and how much of the entire harvest (1969-71) was completely unacceptable as raw material for edible products.

Calculation of the mean chlorophyl contents of the different seed types for the years 1969-71 showed that spring rape had the highest content, 30-60 ppm, while autumn turnip rape had the lowest, 10-15 ppm. The corresponding figures were, for autumn rape, 20-25 ppm and, for spring turnip rape, 15-25 ppm.

Effect of seed grading

The immediate practical result of seed grading before storage at the extraction plant was that, beginning in 1966, the poor quality seed could be

TABLE VII

Percentage of Seed with Chlorophyl Content Higher than 30 ppm for 1966-71

Seed type	1966	1967	1968	1969	1970	1971
Autumn rape	14.2	0.9	21.5	14.4	10.8	19.5
Autumn turnip rape	5.4	0.2	1.2	1.4	3.2	5.2
Spring rape	57.5	9.0	7.0	39.5	66.5	56.1
Spring turnip rape	11.2	0.7	4.2	6.9	10.5	23.0

worked up at a predetermined time by appointment with the margarine plants. In spite of the somewhat reduced price of the poor quality oil, the margarine plants preferred to completely avoid it after only a few years' experimentation. The quality of the refined oil left something to be desired, in spite of increased supervision as well as the use of larger amounts of chemicals in the refining procedure. Consequently the dark-colored oil from unripe seed now goes exclusively to hydrogenation.

A few analytical results for freshly produced first and second grade crude oils are given in Table IX. We see that the color values are quite high for the second grade oil. Further, FFA and lecithin contents as well as oxidation values are higher for second grade oil than for first grade oil. However this could be due partly to a bigger influence from variations in the processing conditions when processing a few thousand tons of second grade seed, compared to the continuous processing of first grade seed over a considerably longer period of time.

TABLE VIII

Percentage of Seed with Chlorophyll Content Higher than 70 ppm for 1966-71

Seed type	1966	1967	1968	1969	1970	1971
Autumn rape	0.03	0	0.04	0.4	1.3	1.2
Autumn turnip rape	0	0	0	0.3	0.2	0.2
Spring rape	4.7	0	0.4	6.1	26.6	8.1
Spring turnip rape	0	0	0	1.6	1.7	2.3

TABLE IX

Analysis of Freshly Produced Rapeseed Oil

	Total Lovibond color[a] 1 in. cell		Free fatty acid, %		Benzidine value		Peroxide value		Lecithin content, %	
Year of harvest	Grade 1	Grade 2	Grade 1	Grade 2	Grade 1	Grade 2	Grade 1	Grade 2	Grade 1	Grade 2
1964	—	—	1.1	—	1.2	—	0.7	—	0.6	—
1965	—	—	1.3	—	0.9	—	0.6	—	0.6	—
1966	155	234	1.0	1.1	1.1	—	0.5	—	0.5	—
1967	127	215	0.8	1.2	0.8	2.1	0.5	0.9	0.4	0.6
1968	145	171	0.9	1.2	0.8	2.7	0.6	0.4	0.4	0.6
1969	151	191	0.7	0.9	0.6	0.9	0.7	1.2	0.4	0.4
1970	149	231	0.8	1.4	0.6	1.2	0.6	0.6	0.4	0.5

[a]Total Lovibond color = yellow + 10 red + 10 blue.

Price regulation

While the grading and refining experiments were in progress, negotiations about price regulation based on the chlorophyll content were under way with the growers' association, the Swedish Oilseed Association. The purpose of the proposed price regulation was to direct the growers' attention to the problem of maturity, and to convince them to take recommended steps to gradually raise the average quality of Swedish oilseed for the benefit of all interested parties.

After several years' negotiation and deliberation, price regulation was finally introduced in 1970. From the purely practical viewpoint, this implied that all growers' deliveries, ca. 50,000, had to be analyzed with regard to chlorophyll content. Results from these analyses, which were introduced on a trial basis as early as 1969, have already been presented in Tables VII and VIII.

In setting up the first price scale, the margarine industry's assessment of the costs involved in refining oils with various chlorophyl contents was taken into account. Furthermore the fact that a chlorophyl content greater than 50-70 ppm in the refined oil made it unfit for human food greatly influenced the elaboration of the price scale. The maximum price reduction came to be 56% of the base seed price, and this price reduction was valid at chlorophyl contents of 110 ppm and up.

An unfortunate combination of circumstances (unfavorable weather, legislative measures leading to decreased possibilities for combating insects and other destructive animal pests, etc.) made the 1970 price regulation an unexpectedly hard blow for the growers. Not less than 66.5 wt % of the spring rape was subjected to the price regulation, and the average chlorophyl content was 60 ppm, which implied a price reduction of ca. 6%. Various growers' associations reacted strongly to this state of affairs, and the question of price reduction on the basis of chlorophyl content had to be reconsidered. The result was, on the one hand, compensation for those growers who had suffered the greatest losses and, on the other hand, a completely new price scale for the 1971 harvest. The new scale is regressive in order to discourage mixing of very immature seed with mature seed. It has also become considerably milder than the original scale, in the assessment of seed lots with chlorophyl contents greater than 50 ppm. Table X shows that the maximum price reduction 20% of the base price is reached at a chlorophyl content of 200 ppm.

TABLE X

Seed Price Regulation according to Chlorophyl Content

Chlorophyl content, ppm	Price deduction in % of seed price after regulation of moisture and oil contents
Present regulation	
30-70	0.15% for each ppm above 30
70-110	6% + 0.125% for each ppm above 70
110-200	11% + 0.1% for each ppm above 110
More than 200	20%
Former regulation	
30-40	0.1% for each ppm above 30
40-50	1% + 0.2% for each ppm above 40
50-60	3% + 0.3% for each ppm above 50
60-70	6% + 0.4% for each ppm above 60
70-100	10% + 0.5% for each ppm above 70
100-110	25% up to 56%
More than 110	56% (meal price at the time being)

Conclusions

It is still too early to draw any far reaching conclusions about the long term effect of the price scale on the quality of rapeseed in Sweden. Nonetheless we are of the opinion that the growers have become much more careful about the maturity level of the seed at the time of harvest. A vigorous debate has been going on in the professional journals—and by this time most farmers are acquainted with the problems of high chlorophyl content—which we hope will be of benefit for seed quality in the future. Several of the larger drier-stocker companies have acquired equipment for rapid chlorophyl content monitoring. By means of this service, the growers are helped to judge maturity levels before harvest.

The development that began with a survey of the Swedish rapeseed harvest with respect to maturity level has quite logically led to grading and price regulation based on chlorophyl content. Neither Swedish Oil Extraction Ltd. nor the margarine industry is considering a return to the previous system, in spite of the expense associ-

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