DETERMINATION OF OIL CONTENT IN RAPESEEDS USING TWO METHODS – SOXHLET EXTRACTION AND PULSED NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

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Introduction

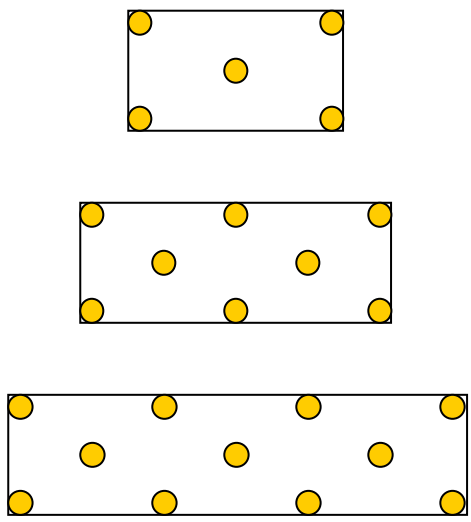
After cereals, oil crops are the second most important source of edible calories for human societies. They are also sources of many industrial products, and have the potential to provide raw materials for many more. The four major global traded oil crops are soybean, oil palm, rapeseed and sunflower, respectively. Together, these four crops account for 72% of worldwide vegetable-oil production [1]. Therefore an accurate and fast determination of oil content is important to breeders, growers and buyers.

The traditional method of oil determination in oilseeds is based on solvent extraction (Soxhlet). This method is laborious, time consuming and uses large volumes of organic solvents, moreover results depends on operator attention. Currently, the alternative techniques to solvent extraction are supercritical fluid extraction [2], NIR spectroscopy [3] and pulsed nuclear magnetic resonance spectrometry [4].

In this article the Soxhlet method was compared with the pulsed nuclear magnetic resonance spectrometry (pulsed NMR).

Materials and methods

Samples of rapeseeds were taken in accordance with current international methods of sampling described in ISO standards: PN-EN ISO 542:1997 [5] and PN-EN ISO 664:1997 [6]. In the first instance increment samples ware taken from tracks. The number of sampling points, where the increment samples are taken, was defined according to lot size. The sampling points should have been uniformly distributed throughout the lot volume, according to the principles described in PN-EN ISO 542:1997 (Fig. 1) [5].



Lot size: > 15 tonnes

Number of incremental samples:
5 sampling points

Lot size: 15 – 30 tonnes

Number of incremental samples:
8 sampling points

Lot size: 30 – 50 tonnes

Number of incremental samples:
11 sampling points

Fig. 1. The number of sampling points [5].

The increment samples were combined and mixed thoroughly to form bulk samples, which were used to create laboratory samples. Part of laboratory samples were collected and combined together. The final analytical samples were selected from this mixture [6].

In this paper the analytical samples were marked 1, 2, 3, 4, 5, 6. The total oil content in rapeseeds was determined in the test samples (5 g), which were obtained from representative and homogenous analytical samples. Four test samples were taken from each analytical samples.

The rapeseeds used in the study were acquired from different growers in Poland.

Soxhlet extraction. The solvent extraction was conducted according to official methods PN-EN ISO 659:1999 [7] and PN-73/R-66164 [8] with petroleum ether (boiling point 40-60ºC) as the extraction solvent. The oil was extracted from 5 g samples in Soxhlet apparatus. These samples were prepared by drying rapeseed at 103 ±2ºC. The water contents in all seeds should have been less than 10 % (*m/m*). For each test sample it was necessary to carry out three extraction cycles (4 + 2 + 2 hours) to achieve complete oil recovery from seeds. The oil extraction was repeated for each test sample three times to ensure full oil recovery. After each extraction cycle seeds were grounded carefully in the mortar.

The oil percentage of the collected oil in the seeds was determined gravimetrically and expressed as a weight percent relative to initial weight of the raw oilseeds.

Pulsed nuclear magnetic resonance spectrometry. The total oil content was analyzed directly on Bruker minispec Pulsed NMR analyzer (operating at 10 MHz) in accordance with international standard PN-EN ISO 10565:1999 [9]. Five grams of rapeseed were used for each test. Oilseeds shouldn't have been cleaned and prepared in any way. The water contents of all seeds should have been less than 10 % (*m/m*).

The calibration prior to each series of measurements was checked using three verification samples of known oil contents [9].

Four analysis were carried out on test samples taken from the same homogenous analytical sample.

Statistical analysis. In this study standard deviation (S_R) was estimated by range (R) and coefficient k_n according to the following formula [10]:

$$\mathbf{S_R = k_n \cdot R}$$

The range is the largest value minus the smallest value in a data set. This formula can be used when the number of determinations (n) is less than 7 [10].

All extraction and analyses were carried out four times. In this paper k_n = 0,4857 where n = 4 [10].

Results and Discussion

The oil content in rapeseed was determined using two methods Soxhlet extraction and pulsed NMR and results are listed in Table 1.

The NMR results are not comparable with Soxhlet solvent extraction data. The mean values of oil content determined by this method (~ 42,5 %) were lower then the the Soxhlet extraction (~ 45,7 %).

Table 1. Determination of oil content in rapeseed using two methods – Soxhlet extraction and pulsed nuclear magnetic resonance spectrometry.

Number of analytical samples	Soxhlet method				pulsed NMR method			
	C	C_M	SD_R	RDS	C	C_M	SD_R	RDS
1	45,69 46,21 46,18 46,09	**46,04**	0,25	0,54	35,90 39,40 41,00 50,00	**41,60**	6,90	16,60
2	45,66 46,07 46,06 46,03	**45,95**	0,19	0,41	48,80 43,00 35,90 38,00	**41,50**	5,20	12,50
3	44,59 44,59 44,60 44,59	**44,59**	0,01	0,02	31,10 52,60 40,20 50,20	**43,50**	10,40	23,90
4	45,80 45,78 45,79 45,80	**45,79**	0,01	0,02	39,40 40,00 37,00 35,40	**38,00**	2,30	6,00
5	46,69 45,88 45,90 46,08	**46,13**	0,39	0,85	48,00 44,90 49,30 45,40	**46,90**	2,10	4,40
6	45,20 46,00 45,01 45,70	**45,47**	0,48	0,01	42,30 50,10 44,30 37,60	**43,70**	6,10	13,90

C – the oil content in test samples, which were taken from the same homogenous analytical sample [% of dry mass],
C_M – mean value of the oil content in test samples [% of dry mass],
SD_R – Standard deviation [10],
RDS – Relative standard deviation [%].

The Soxhlet system is repeatable technique for determination of oil content in rapeseed. The values of standard deviation varied from 0,01 to 0,48. For comparison, SD and RSD values obtained for NMR analysis are higher and range between 2,10-10,40 and 4,40-23,90 %, respectively. The Soxhlet method has excellent precission with less than 1% relative standard deviation.

In the case of NMR, data distribution was very high and some statistical errors occured.

The calibrate procedure cannot be ignored when using this methods. Pulsary NMR is difficult to calibrate. The calibration curve shall be obtained by measuring the signal from the three calibration samples with known oil content (Procedure A) [7] or the one standard of known oil content (Procedure B) [7]. In this study the working calibration curve was obtained according to Procedure A. The series of standards was prepared in a concentration range near to the expected unknown concetration (test sample). All samples were measured in the working range of calibration curve. The correlation coefficient for this linear regression is high (0,98). It means that the calibration model works properly. There could be other couses that could affect final results (sample presentation, water content, different nature of calibration standards then samples, slope of the curve).

In conclusion, the proposed pulsary NMR method is relativelly simple, convenient, rapid and non-destructive, without sample preparation. This technique offers considerable savings of solvent disposal costs and analysis time (time of measurments is not more then 2 min.) also eliminates the exposure of laboratory staff to toxic and flammable solvents. The results in Table 1 suggest that the pulsed NMR tehnique can be used for estimation of oil assay in rapeseed. The best results, in respect of precision are obtained using the conventional Soxhlet extraction. Therefore this method can be useful for the determination of oil content in rapeseed.

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