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MASS OIL CONTENT AND HUMIDITY DETERMINATIONS IN SUNFLOWER SEEDS USING NUCLEAR MAGNETIC RESONANCE METHOD

To develop new varieties of oil crops breeders are obliged to evaluate productivity of a large portion of initial material. One of the major criteria is oil content of the seeds. At the All-Union Research Institute for Oil Crops some 100,000 analyses a year had been carried out until 1968 to determine the oil percentage in different oil crops. However, these numerous analyses were not as numerous as needed by breeders. The analyses were carried out in the Biochemical Department by extraction method. Extraction methods do not allow to conduct fast analyses of the sample since technologically the process lasts several days. In some cases the analysis is entirely useless for the sample is destructed in the process. Mass analyses by extraction methods ensure analytical accuracy of not more than $\pm 0,5\%$ of absolute value. To get more accurate results analyses had to be done in several replications to get the mean value.

Intensification of breeding process was restrained by the possibilities of extraction methods of seed analyses. There emerged an urgent need to develop a method and an instrument of a rapid analysis giving high accuracy and productivity without sample destruction.

Oil content and humidity had to be determined simultaneously. Humidity is to be determined in order to define oil content; moreover, humidity itself is an important qualitative property of the seed. Standard methods of humidity determination do not possess necessary rapidity and productivity.

The most prospective way of developing new highly productive methods of analysis meeting modern requirements are the physical methods of research.

The VNIIMK has since 1968 carried out research to develop methods and instruments utilizing nuclear magnetic resonance (NMR) for oil and humidity determinations in seeds of oil crops. Though similar research is carried out in many countries no industrial instrument has so far been developed in many countries for mass analyses and oil and humidity determination.

This may be explained by the fact that present-day quantity analyzers use stationary NMR methods, such as the method of differential passage and the method of adiabatic rapid passage which in principle do not allow sufficiently accurate separation of NMR signals from water and oil in the seeds. Besides, all industrially produced wide range NMR analyzers, such as RAT-20 Varian, MK-P Newport, and Minispec R-20 Brooker are universal instruments with numerous tuning arrangements requiring qualified personnel for operation. Specificity of mass analyses makes special requirements on analyzers. We have studied factors influencing accuracy, rapidity and productivity in mass analyses, and found that the operator represents the main source of mistakes when tuning the instrument and carrying out measurements. Rapidity of analyses depends on sample preparation, that is on weighing, drying and calculating oil content and humidity. In mass analyses periodical tuning and calibration of measuring instrument should be added to above-mentioned processes.

Further studies have shown that impulse methods of NMR are most suitable for rapid and mass determinations of oil and moisture content of the seed. They allow easy and accurate separation of NMR signals from water and oil. Moreover, impulse NMR methods

are considerably more informative than stationary NMR methods and do not require high-quality magnetic systems.

Since 1969 we have developed an analytical calculating set (ACS) for mass analyses based on impulse NMR method.

The main parameters of ACS are as follows: 1. Range of sample weights from 1 g to 20 g; 2. Maximum sample volume 30 cub. cm; 3. Duration of one analysis 30 sec.; 4. Mean productivity for 8 hours about 800 analyses; 5. Accuracy $\pm$0,5%; 6. Analysis is carried out automatically, the result is given in oil percentage and printed out; 7. Analysis is not destructive, seed samples can be utilized for sowing; 8. One operator is needed for set operation; 9. Price of one analysis is 1.5 copeck.

The ACS is constructed as a fully automatic instrument. It works according to a specially designed algorythm assuring the accumulation of NMR signals, their mathematical treatment and the automatic correction of results. Between 1971 and 1976 nearly one million analyses were carried out by the ACS complex.

In 1973 we began developing a new set, a rapid analyzer for simultaneous determination of oil and moisture percentage in oil crop seeds and in products of their processing. We studied reguliarities of parametrical changes in the NMR signals from water and oil in the seeds, the range of these changes in different seed samples with different oil and moisture percentages. We found that in the seeds the period of spin-spin relaxation of T_2 protons of molecules of water and oil differs in an order and more at seed moistures up to 20%. The T_2 of oil is practically independent of seed oil content and is about 80+90 ms at 20°C. The T_2 of water is strongly dependent on moisture content, but in the range 3+20% it changes only from 0.5 ms to 6 ms. Further increase of moisture content sharply increases the T_2 pe-

riod of water up to values equal or over T_2 of water.

Basing ourselves on these data, on experience of operating the MMR analyzers, and on requirements for accuracy, rapidity and productivity of analyzers we have developed the method of separation and measurement of NMR signals from water and oil assuring high accuracy and rapidity. This method allows to eliminate all operations of sample preparation, that is the sample should not be dried, weighed, etc. We have constructed a NMR analyzer implementing this method. Analyses are carried out automatically, results are printed out instantly in percentages of oil and moisture content. Analytical accuracy does not depend on the operator's skill as operator only introduces the sample for analysis and withdraws it out of the instrument. Operator can be replaced by an automatic device. The NMR instrument has no tuning organs. Tuning and calibration of the instrument are carried out during its production while no tuning of any kind is needed during its operation. The main technical parameters are as follows. 1. Period of one analysis not more than one minute; 2. Mean productivity for 8 hours is 400 analyses; 3. Automatic sample weighing; 4. Accuracy $\pm$0.5%; 5. Maximum sample volume 30 cub. cm; 6. Measuring range: (a) seed oil content 15 + 65%, (b) seed moisture content 3 + 20%; 7. Analysis is carried out automatically, accuracy does not depend on operator's skill. The result of the analysis is displayed numerically and printed out. The number of an analysis, oil percentage and moisture content are printed in one line.

Documentation of our NMR analyzer has been submitted to an enterprise of the Ministry of Instrument-making for serial production. It should be noted that the NMR analyzer developed at the VNIIMK will be the first instrument of its kind produced in the USSR on an in-

dustrial scale. Technical parameters of the analyzer are considerably higher than those of similar foreign instruments. Industrial production of these analyzers will allow their wide employment in agriculture, food industry and elsewhere with considerable economic effect.