THE APPLICATION OF N.M.R. (NUCLEAR MAGNETIC RESONANCE) IN THE PROCESSING OF SUNFLOWER SEEDS.

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Nuclear Magnetic Resonance is a physical phenomena first used in the mid 1940's since which time it has become a standard analytical tool in the field of chemistry. Since 1968 Newport Instruments have been manufacturing a broad line low resolution instrument called the Newport Analyser. This instrument is now used in 40 countries world wide as a quality control tool in the food industry.

The Newport Analyser provides a rapid non-destructive means of measuring the oil content of oil seeds and meals.

SLIDE 1

This slide shows the Newport Analyser MK111A complete with the sample temperature controller WR111.

The unit consists of two pièces of equipment.

1) The electronics console

2) The temperature controller including the sample assemply and permanent magnet. The temperature is adjustable in steps of 0.1°C between - 19.9°C and + 99.9°C

SLIDE 2

This slide shows three of the four possible sample sizes

1) 2ml maximum, this can be used for single seed measurements

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but is usually used when measuring the solid liquid ratio in fats where the n.m.s. measurements can replace dilatometry.

2) 6.5ml maximum, this can be used to measure all of the rape seeds from a single plant.

3) 40ml maximum this is the tube for general use and can hold up to 16g of sunflower seeds.

4) 150ml maximum this sample size is not ilustrated but will hold up to 62g of sunflower seed. Regardless of the method of analysis the sample to be anlysed must be representative of the whole sample and therefore as sunflower seeds are very bulky the larger the sample volume the more representative it will be of the whole sample.

SLIDE 3

Nuclear Magnetic resonance measures the signal from all the mobile hydrogen atoms (or protons) in a sample. These mobile protons are usually present in liquid and in sunflower seeds this is found in the form of water or oil and it is therefore necessary to dry the seeds before measuring them in the Newport analyser. This slide shows the time taken by various seeds for the n.m.r. signal to reduce to a constant. From the slide it can be seen that for the seeds illustrated here one hour at 130°C is sufficient to achieve constant signal. This does not mean however that the seeds are dry but only that any moisture left has a resonance width that is broader than the width of the electronic gate in the measuring circuit.

Drying at 130°C is used only for commercial purposes, for plant breeding it is necessary to dry the seeds at a lower temperature for a longer time to maintain the viability.

SLIDE 4

This slide shows the variation in the n.m.r. signal with % oil in the sample it can be seen that there is a linear relationship between these two variables for rape seed oil and other work has shown that this is true for other oil bearing seeds including sunflower.

SLIDE 5

This slide compares some extraction figures with n.m.r. figures. The samples were various seeds and meals. It should be remembered

that the scatter on the graph is not only due to instrumental errors but also to the extraction process itself and the inherent inaccuracies in it.

The % oil in a sample is calculated by comparing the signal from a reference of known oil content either a seed sample or an oil sample to the signal of a known weight of the unknown sample. The results may be quoted on either a wet weight or dry weight basis. As the n.m.r. response is temperature dependant the sample and reference must be measured at the same temperature. The variation with termperature dependes on the material and for sunflower has been found to be only 0.2% oil per 1°C change in temperature.

Another factor which affects the n.m.r. oil content is the fatty acid profile of the seeds. As the fatty acids change so does the hydrogen content and therefor the n.m.r. response. Robertson and Morrison have found that for each 1% decrease in linoleic acid the n.m.r. oil content of sunflower seeds increases by O.1%. This effects has also been found with rape seeds, where the erucic acid content can vary between 0 and 50%. If the erucic acid content of the seeds is not known and a single oil standard used for all rape seeds errors of up to 1.5% oil can occur. Because of this effect the choice of reference sample is critical for greatest accuracy. The reference should h ave a similar fatty acid content to the sample.

SLIDE 6

This slide compares two different extraction methods with n.m.r. in terms of time taken to achieve a result and the number of samples which can be analysed in one day. In method three itshows two hours drying which although necessary for some seeds is not necessary for sunflower and so the time from sampling to obtaining a result is reduced by one hour to $1\frac{1}{3}$ hours however the number of determinations a day does not increase as it is only drying time which is reduced and not the time the operator is actually weighing out the sample or measuring in the analyser.

Method four is a recently developed method using the MK111A analyser and its variable gate facility. It is possible to determine the oil and moisture content on seeds by taking two measurements at different gate widths and correlating the difference to moisture content and oil content. This method is explained in the paper given by a colleague called "N.M.R. as a tool for the Plant Breeder".

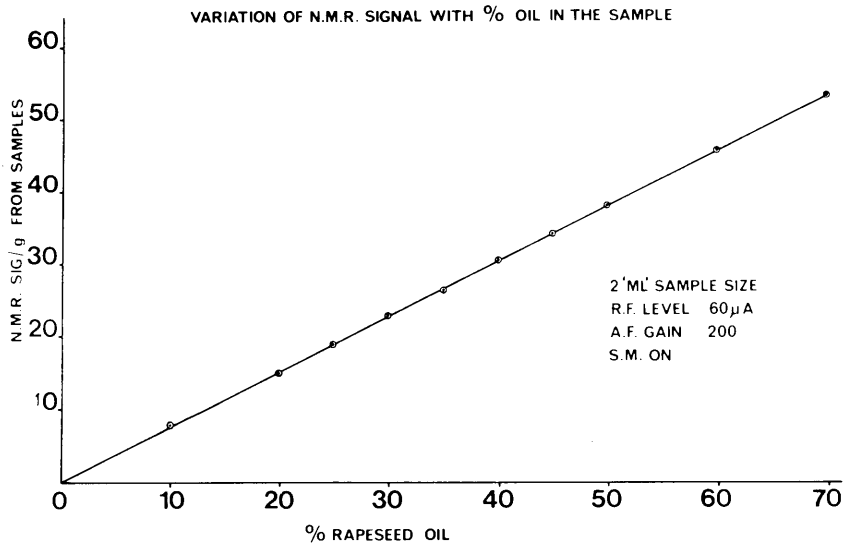
In the oil processing industry the oil content of the seeds can be

measured rapidly and accurately when the seeds are first received at the mill. The seeds can then be passed through the crushers and extractors. Samples of press cake can then be analysed for oil content and the residual oil content calculated from the n.m.r. measurements. Knowing the amount of oil obtained after processing, the amount of residual oil and also the amount of oil present in the seeds before crushing it is possible to monitor the efficiency of the extraction process.

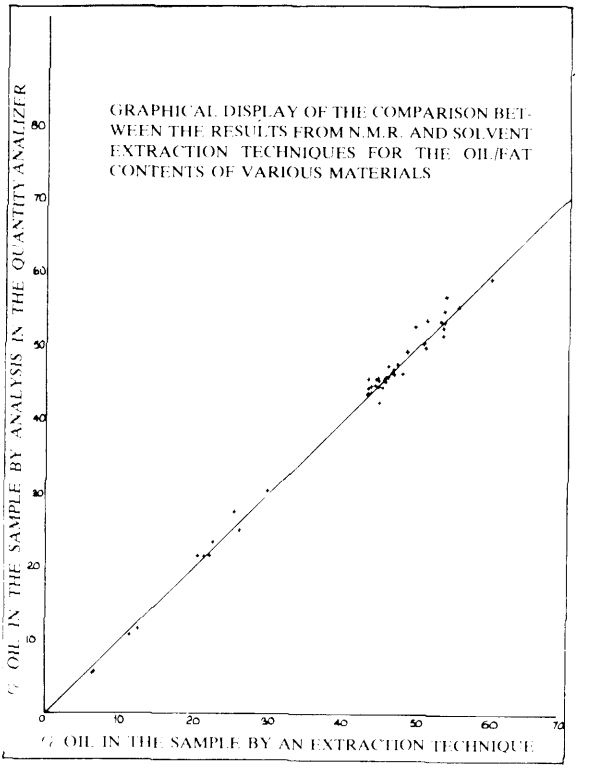
Il the extracted oil is then going to be used to produce margarine n.m.r. measurements can be used to replace dila tometry in the measurement of the Solid Fat Index.

CONCLUSION

The determination of the oil content of seeds has traditionally involved some type of extraction process. These processes have been comparatively slow, used large quantities of solvents and required skilled operators. N.M.R. measurements with the Newport Analyser has the advantage of speed, ease of standardisation and low operating costs.

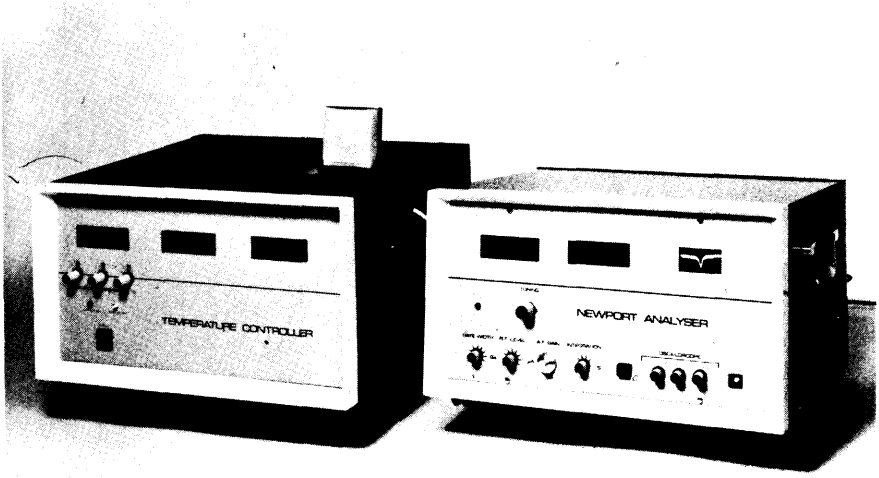


SLIDE FOUR

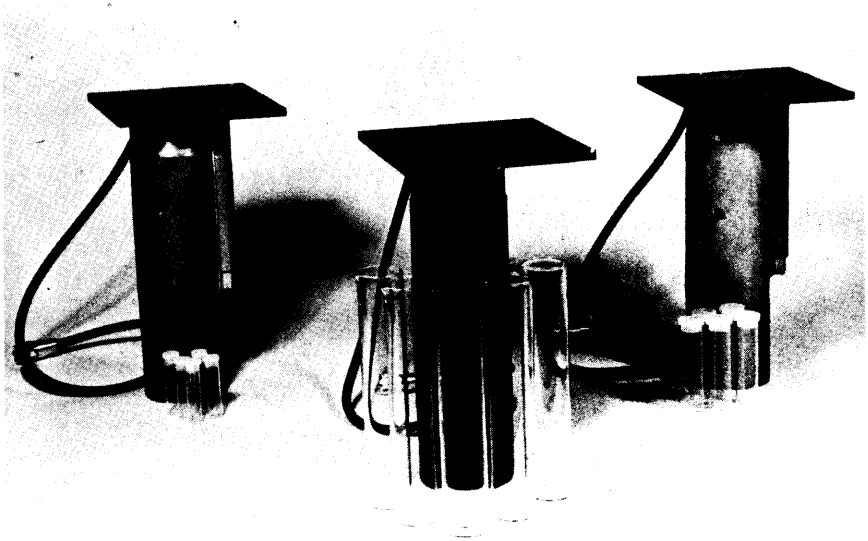


The saving in man-hours can be seen in the following table, which has been drawn up for seeds containing oil which is liquid at room temperature, e.g. rape, sunflower, groundnut, etc.

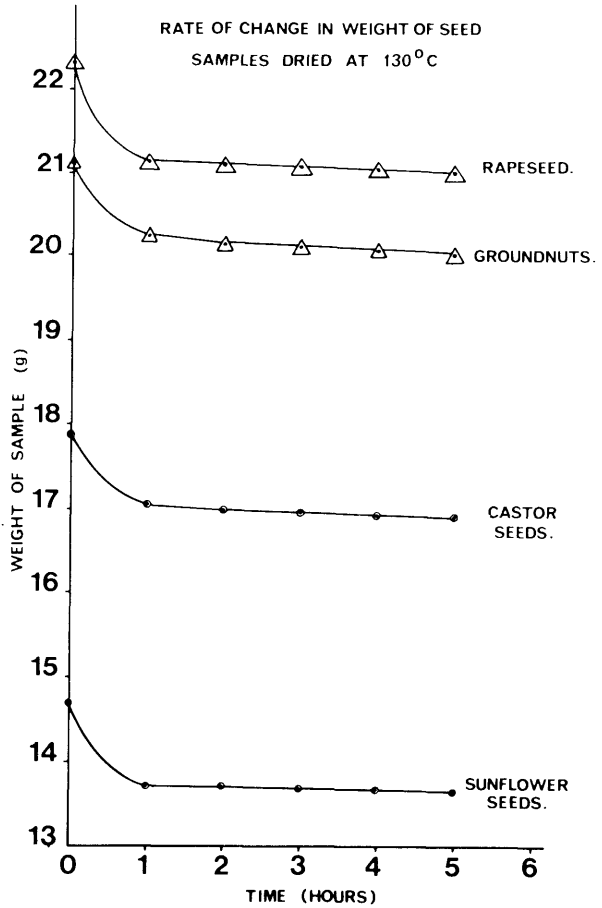
Method	Number of analysts	Number of determinations per day	Time from sampling to result	Repeatibility % oil (95% confidence limits)
1. SOXHLET 3 hrs. extraction, regrind then a further 3 hrs. extraction. A bank of 6 sets of apparatus.	1	6	for one sample 9 hrs.	0,7%
2. SVALOV cold extraction in steel bottles containing steel balls on a vibrator	2	96	3 1/4 h.	0,5%
3. ANALYSER 2 hrs. drying, 5 mins. oil determination	1	84	2 1/3 h.	0,3%
4. ANALYSER MkIIIA No drying, 3 mins. oil and moisture determination	1	100+	3 mins.	0,3%



SLIDE ONE



SLIDE TWO


RATE OF CHANGE IN WEIGHT OF SEED
SAMPLES DRIED AT 130°C
RAPESEED.
GROUNDNUTS.
CASTOR SEEDS.
SUNFLOWER SEEDS.
WEIGHT OF SAMPLE (g)
TIME (HOURS)
22
21
20
19
18
17
16
15
14
13
0
1
2
3
4
5
6

SLIDE THREE