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TG and NMR analysis of commercial plant oil seeds

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Abstract

Experiments were performed to obtain rapid quantitative information on the water and oil content, and on the ash residue of some plant oil seeds, all of considerable commercial interest.

TG, DTG and low-resolution NMR were used as the analytical techniques.

INTRODUCTION

We have recently carried out a series of studies with the aim of determining which modern analytical techniques can be suitably employed to characterise analytically certain foodstuffs. Thus, we have shown that TG analysis can be used to determine the water content and ash residues of flours, cereals, vegetables, powdered milk, dried alimentary pastes, etc. [1–4]. In general, the data obtained were compared with literature values, or with values determined by Karl–Fischer method or by NMR technique. Here we report the results of research concerning the rapid analysis by instrumental methods of samples of plant oil seeds of considerable commercial importance, depending on the amount of oil that can be obtained from them. The techniques used were TG, DTG and low-resolution NMR. The seeds examined were those mostly used as a source for oils for industrial or alimentary purposes.

EXPERIMENTAL

The plant seeds examined (soy, sesame, colza, poppy, sunflower, pumpkin and linseed) were all commercial products, stored in tin-sealed paper at room temperature; standard oils were supplied by the Department of Chemistry and Biological Active Substances Technology Studies of the First Rome University.

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The TG and DTG curves of these plant seeds were obtained with a Mettler TG 50 thermobalance, coupled with a Mettler TC10A-TA processor system and a Swiss dot-matrix printer. The heating rate used was 10 °C min^{-1}; the atmosphere was an air or nitrogen stream, with a flow rate of 100 cm^3 min^{-1}.

NMR measurements were taken at 40 °C, on a pulsed low-resolution spectrometer (Minispec Pc120), produced by Bruker, Karlsruhe, Germany, operating at 20 MHz for protons.

The decay of the transverse magnetisation of protons was monitored every 2.0 ms from $t = 2.0$ ms to $t = 200$ ms, using the Carr–Purcell–Meiboom–Gill [5] pulse sequence, $90^\circ_x - t - 180^\circ_y - [2t - 180^\circ_y]_n$, where $t = 1.5$ μs. The duration of the 90° and 180° pulses was adjusted empirically to give a maximum signal and a zero signal in the receiver coil, about 3.5 μs and 7.0 μs, respectively. Although the instrument conditions were stable, pulse durations were reoptimised between runs. The following set of instrumental parameters was used: number of sampled echoes, 100; delay between successive sequences "repetition rate", 1 s; attenuation, 30 dB; filter, low; number of accumulations, 36; detection mode, diode. Each measurement took about 40 s. The curve was obtained by plotting the echo amplitude against time, 2 t. The slope of this curve gave the transverse relaxation time T_2. Each reported value was the average of at least four separate measurements.

The fitting of the experimental graph was performed by least-squares non-linear analysis, using the subroutine EO4FCF, supplied by the NAG–FORTRAN Library; this subroutine employs the Gill and Murray algorithm [6].

The best fit was obtained by a bi-exponential analysis, according to the equation

$$A_{eco} = A_0 \exp(-t/T_{2a}) + B_0 \exp(-t/T_{2b}) \quad (1)$$

where $T_{2a} = 90$–200 ms and $T_{2b} = 2$ ms; A_0 and B_0 can be considered proportional to the oil content and to the bound water, respectively. By comparing A_0 values for a sample of weighed seed with the corresponding value found for the standard oil from the same seeds, the oil percentage of the sample can be easily obtained from the formula

$$\%_{oil} = (A_{0\,sample}/g_{sample})(g_{oil\,ref}/A_{0\,oil\,ref}) \quad (2)$$

The measurements of the percentage moisture content using the Karl–Fischer method, were performed on an automatic titration apparatus (Mettler DL 18) with a glass cell thermostatted by forced water circulation (thermostat Julabo 50, Schelbach). These measurements were carried out as described in a previous paper [3] at 50.0 ± 0.5 °C with magnetic stirring. The adopted "stir time" (during which the sample, is stirred into the solvent before performing the titration) was 500 s. The Karl–Fischer titrant was

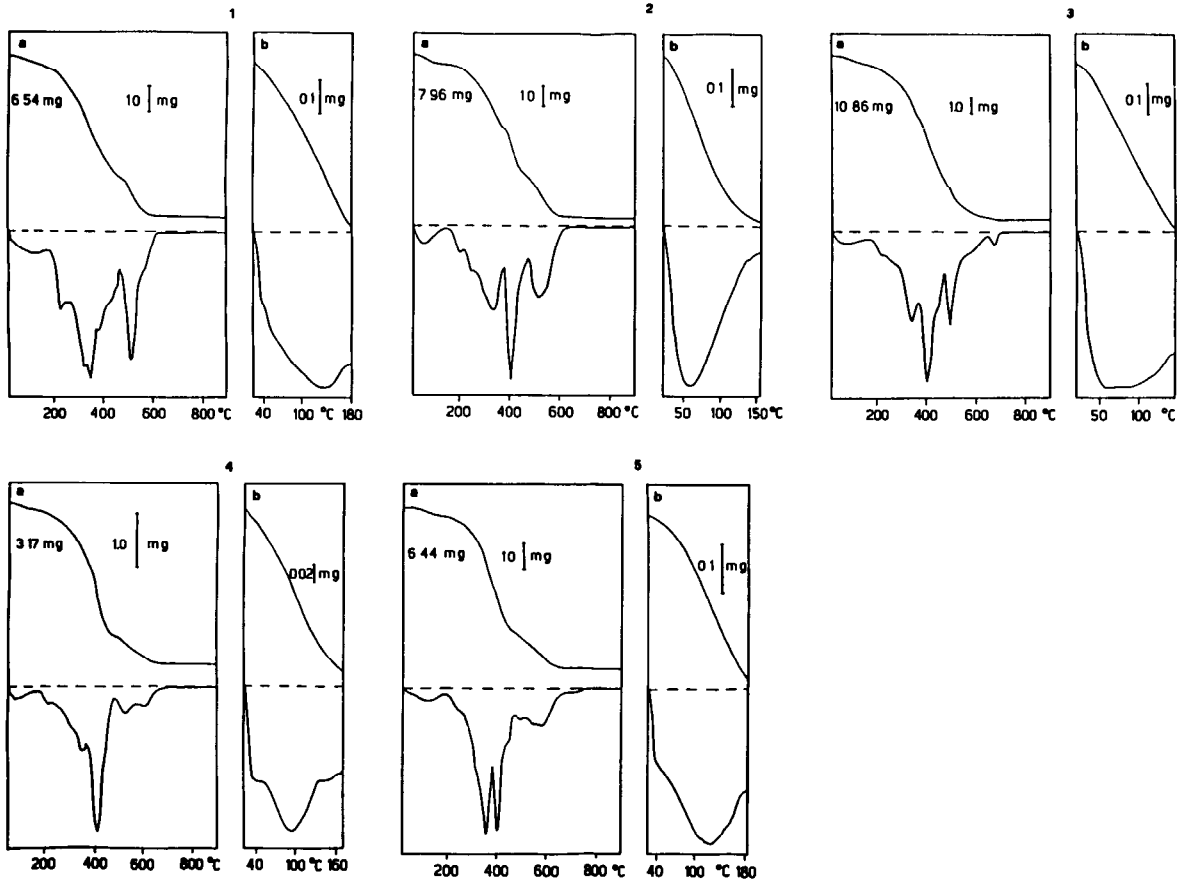

Fig. 1 TG and DTG curves for analysis of soy seeds (curves 1), colza seeds (curves 2), poppy seeds (curves 3), sunflower seeds (curves 4), pumpkin seeds (curves 5). (a) Full TG and DTG curves in the range 20–900 °C; (b) TG and DTG curves (in an expanded scale) showing only the water-loss process. Flowing air, 100 cm^3 min^{-1}; heating rate, 10 °C min^{-1}.

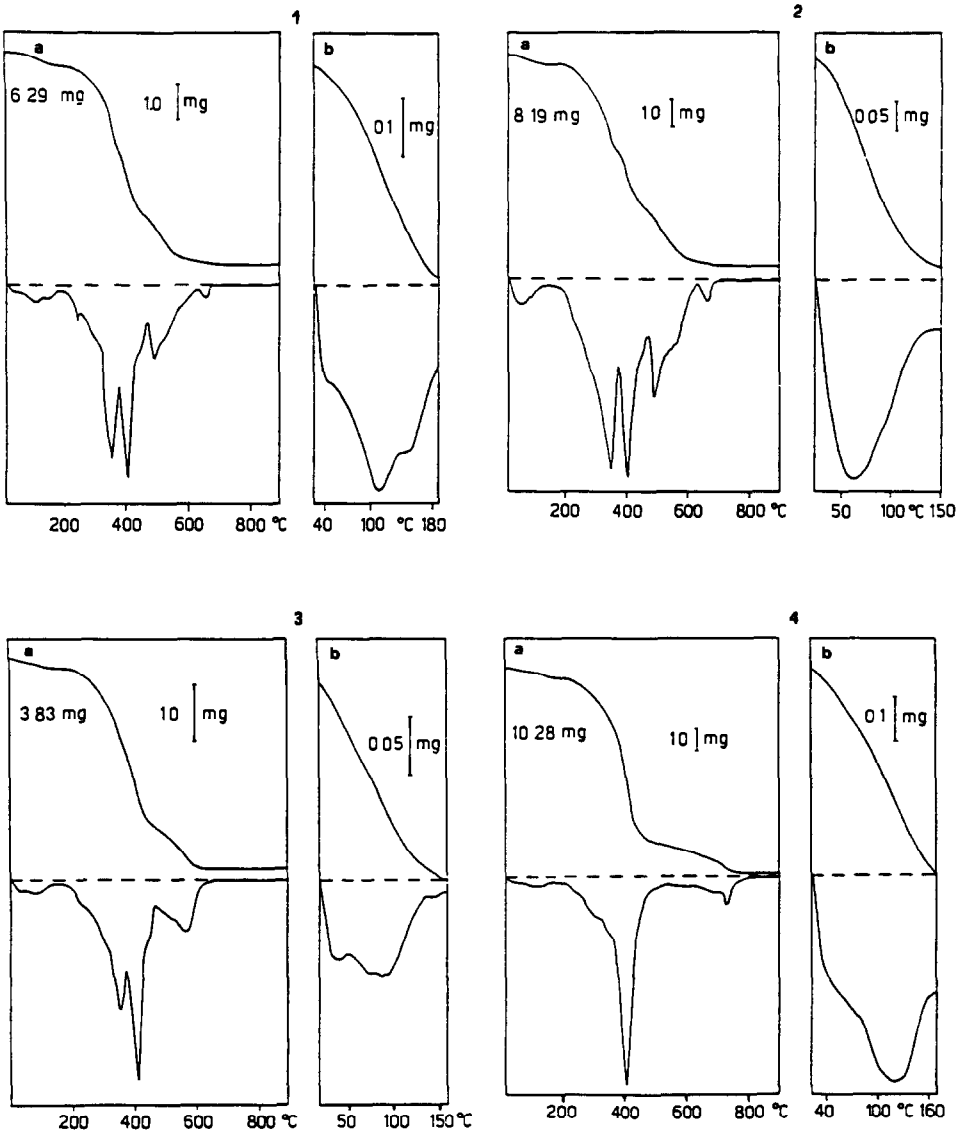

Fig 2 TG and DTG curves for analysis of linseeds. intact (curves 1); cut in coarse pieces (curves 2); peeled and in pieces (curves 3), in an air stream (100 cm^3 min^{-1}); cut in coarse pieces and in a nitrogen stream (100 cm^3 min^{-1}) (curves 4). (a) Full TG and DTG curves in the range 20–900 °C, (b) TG and DTG curves (in an expanded scale) showing only the water-loss process Heating rate, 10 °C min^{-1}.

Hydranal n. 34801, the solvent, Hydranal n. 34800 and the standard was sodium tartrate dihydrate, Hydranal n. 34803, all supplied by Riedel-De Haën AG, Seelze-Hannover.

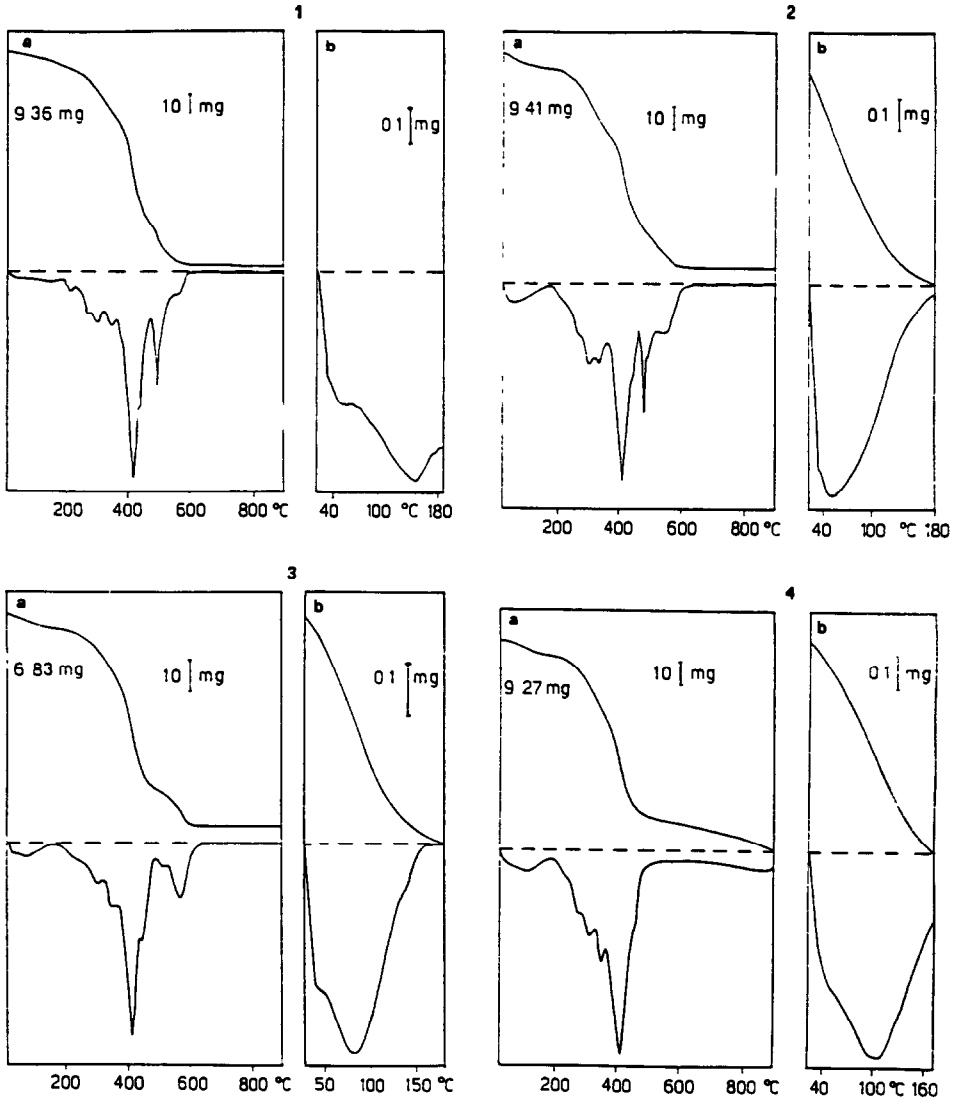

Fig. 3. TG and DTG curves for analysis of sesame seeds: intact (curves 1); cut in coarse pieces (curves 2), peeled and in pieces (curves 3), in an air stream (100 cm^3 min^{-1}), cut in coarse pieces and in a nitrogen stream (100 cm^3 min^{-1}) (curves 4). (a) Full TG and DTG curves in the range 20–900 °C; (b) TG and DTG curves (in an expanded scale) showing only the water-loss process. Heating rate, 10 °C min^{-1}

RESULTS

The water contents and ash residues were determined by TG. The aim of the research was to optimise the method for this particular type of sample matrix from the point of view of the working atmosphere (air or nitrogen stream) and the sampling (seeds intact, cut in coarse pieces or peeled, etc.).

TABLE 1

Thermal data for the water-loss process of the examined plant oil seeds in an air or nitrogen stream (100 cm^3 min^{-1}) and for the residue ash at 700 °C (heating rate 10 °C min^{-1})

Number	Sample	Water loss in an air stream (%)	T (°C) [a]	Water loss in a nitrogen stream (%)	T (°C) [a]	Ash residue at 700 °C (air stream) RSD% ≤ 1)
1	Soy seeds [b]	7.5	24–180	7.5	24–180	6 5
2	Linseeds [b]	6.4	24–170	6.2	24–170	4 0
3	Sesame seeds [b]	4.2	24–150	4 5	24–160	5 5
4	Colza seeds [b]	5.2	24–155	5.2	24–155	5 5
5	Poppy [c] seeds	4.7	24–140	4 5	24–140	6 4
6	Sunflower seeds [d]	5 0	24–170	5.1	24–180	5.5
7	Pumpkin seeds [d]	5 1	24–180	5.2	24–180	5 9

[a] Temperatures range from start to end of process.
[b] Analysed after cutting directly into coarse pieces
[c] Analysed without any pretreatment (seeds very small).
[d] Cotyledons analysed, cut in pieces, after removal of their tegument.

Figure 1(a) shows the complete TG and DTG curves in the temperature range 20–900 °C in an air stream, for five different kinds of seeds. The first small step in these curves is the loss of water (the most important step in

TABLE 2

Thermal data for the water-loss process of samples of two different plant oil seeds (linseeds and sesame seeds), analysed intact, cut in coarse pieces, or peeled; in an air stream (100 cm^3 min^{-1}) (heating rate 10 °C min^{-1})

Sample	Water loss of intact seeds (%)	T (°C) [a]	Water loss of seed cut in coarse pieces (%)	T (°C) [a]	Water loss of seeds peeled and cut in pieces (%)	T (°C) [a]
Linseeds	6.6	24–190	6.4	24–170	6.2	24–145
Sesame seeds	5 5	24–190	4.2	24–150	4.5	24–145

[a] Temperature range from start to end of process.

TABLE 3

Comparison of percent water content, referred to the weight of dried sample, found in the examined plant oil seeds by TG analysis in an air or nitrogen stream, and by Karl–Fischer chemical method; values are the mean of at least four determinations

Number	Sample	Water found by Karl–Fischer method (%) [d] (RSD% ≤ 4) (*a*)	Water found by TG in an air stream (%) (RSD% ≤ 1.5) (*b*)	Water found by TG in a nitrogen stream (%) (RSD% ≤ 1.5) (*c*)	$\frac{b-a}{a}$ (%)	$\frac{c-a}{a}$ (%)	$\frac{c-b}{b}$ (%)
1	Soy seeds [a]	8.0	8.1	8.1	+1.3	+1.3	0
2	Linseeds [a]	6.6	6.8	6 6	+3.0	0	−2.9
3	Sesame seeds [a]	4.5	4.4	4.7	−2.2	+4.4	+6.8
4	Colza [a] seeds	5.7	5.5	5.5	−3.5	−3.5	0
5	Poppy [b] seeds	4.7	4.9	4.7	+4.3	0	−4.1
6	Sunflower [c] seeds	5.4	5.3	5.4	−1.9	0	+1.9
7	Pumpkin [c] seeds	5.3	5.4	5.5	+1.9	+3.8	+1.9

[a] TG analysis was performed on seeds cut into coarse pieces.
[b] Analysed without any pretreatment.
[c] Cotyledons analysed cut in pieces after removal of their tegument.
[d] The analysis by Karl–Fischer method was performed on the same samples, more finely ground.

terms of our research). Figure 1(b) shows this first TG step for the five samples of plant seeds in an expanded scale. In Figs. 2 and 3, the same kind of TG and DTG curves are presented for linseeds and sesame seeds respectively, both in an air and in a nitrogen stream. The same figures also show the TG and DTG curves of the same seeds obtained from differently prepared samples (seeds intact, cut in coarse pieces, or peeled and cut in pieces).

Table 1 summarises the thermogravimetric data of the dehydration process for all the examined seed samples, both in an air and in a nitrogen stream, the percent ash values found at 700 °C in an air stream are also reported.

Table 2 shows data from the dehydration process of linseeds and sesame seeds using a different sampling process.

In Table 3, the percentage water contents, deduced from TG, are shown for all the samples, both in an air and in a nitrogen stream, and are compared with those obtained by the Karl–Fischer method, employing the working conditions optimised in a previous paper [3].

The measurement of the oil content, by low-resolution NMR depends on the fact that the transverse relaxation time T_2 of the oil protons is higher than that of the other constituents of plant seeds, such as proteins, carbohydrates and water. The analysis of the decay curves of the transverse magnetisation of the samples, which is possible by the Carr–Purcell technique, leads to the determination of the oil content of seeds with low water

TABLE 4

Pulsed low-resolution NMR data of five samples of different plant oil seeds and of five standard oils from the same seeds, obtained by a Carr–Purcell–Meiboon–Gill pulse sequence at 40 °C [a]

Standard oil	Weight of sample (mg)	Relaxation time T_2 (ms) (SD = ± 5 ms)	Plant oil seeds	Weight of sample (mg)	Relaxation time T_2 (ms) (SD = ± 5 ms)
Soy oil	373	109	Soy seeds	3725	155
Linseed oil	353	142	Linseeds	1510	188
Sesame oil	322	103	Sesame seeds	728	96
Colza oil	368	90	Colza seeds	1200	110
Sunflower oil	369	200	Sunflower seeds	611	110

[a] Both oil and seed samples were analysed in a glass tube, 1 8 cm diameter, without any pretreatment, except for sunflower seeds, whose cotyledons were analysed after removal of their tegument

TABLE 5

Percent oil content of five samples of different plant oil seeds, obtained by low-resolution NMR method compared with data reported in the literature [7]; results are the mean of at least four determinations

Plant oil seeds	Oil content found by low-resolution NMR (%) (RSD% ≤ 1.5)	Oil content reported in literature (%)
Soy seeds	16.2	16
Linseeds	34 6	34
Sesame seeds	46.1	44
Colza seeds	34 5	35–37
Sunflower seeds	36.7	35–44

contents (< 10% w/w). In practice, the oil content of a seed sample was determined by comparing the NMR decay curves of the seed sample with that of a standard oil (extracted from the same seeds) by a Carr–Purcell–Meiboom–Gill pulse sequence [5].

The principal experimental NMR data corresponding to five different seed samples and to five different oil standards from the same seeds, are summarised in Table 4. In Table 5, some literature data concerning the percent oil content of the five different kinds of plant seeds examined in this report are compared with those obtained from the low-resolution NMR method.

Lastly, Fig. 4 shows, as an example, the decay curves for a sample of soy seeds and for a soy oil standard.

DISCUSSION

From the results in Table 1 it can be observed that for the plant seed samples studied by TG, the results for the water-loss process are practically independent of the nature of the flowing gas. Thus, under the experimental conditions used between the start and end temperature reported in Table 1, the mass loss must be due to evaporation; the oxidation processes do not yet have any marked importance. In contrast, it is obvious that the degradation processes as shown in the TG and DTG curves, proceed rather differently in an air or in a nitrogen atmosphere. Hence, the determination of the ash residue has to be performed under an air stream at about 700 °C, as established in a previous paper [3], which reports a detailed study on samples very similar to those of this research.

From Figs. 2 and 3 and Table 2, it can be concluded that the mode of sampling the plant seeds for the TG analysis plays an important role with respect to the results obtained for the water-loss process. Firstly it is clear

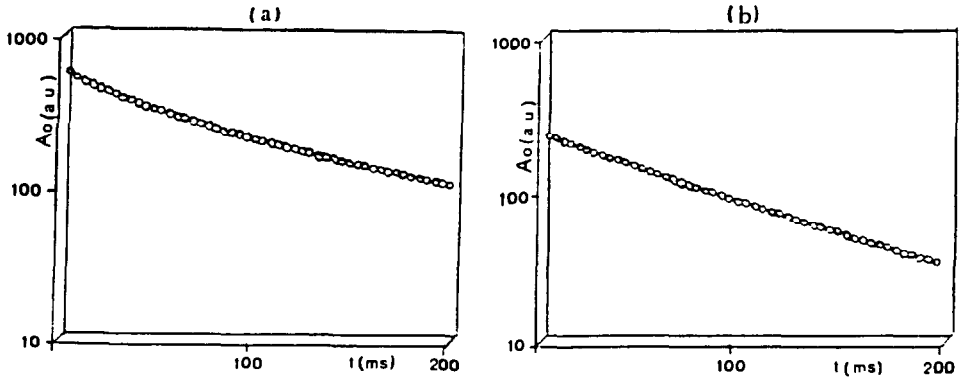

Fig. 4 Low-resolution NMR analysis Decay curves of transverse magnetisation (T_2), obtained by a Carr–Purcell–Meiboom–Gill pulse sequence at 40 °C. (a) Decay curve of soy seeds; (b) decay curve of standard soy oil

that with very small seeds, such as poppy seeds, it is sufficient to perform the analysis without any pretreatment, while in the case of large seeds which are easily peeled, such as pumpkin or sunflower seeds, it is best to perform the TG analysis of the cotyledon free of the tegument. Lastly, the best way to perform TG analysis on readily peeled seeds that are not too small, seems to be to cut them directly into coarse pieces; water is released from intact seeds at higher temperatures so that the water content values determined would be higher than the correct ones. In some cases intact seeds can explode, so that the chance of obtaining reliable results is decreased.

However, by selecting the correct sampling procedure for the plant seeds, depending on their nature, reliable results, as in Table 3, can obtained by TG analysis for water content and ash residue for this type of sample; as can be observed, the TG data of Table 3, referring to the water content, agree well with that determined by the Karl–Fischer method. The choice of this method to provide the reference data is based on a well-defined, specific, stoichiometric reaction involving water. The good correlation of the TG data shows that the mass loss of the first step was correctly assigned to the evaporation of the contained water; therefore, using the experimental conditions adopted, the eventual evaporation processes of any other substances do not affect the results, at least within the limits of the experimental errors of the method.

Lastly, a comparison of the data of Table 5 with that of the literature indicates that the application of low-resolution NMR to this kind of sample is particularly useful for the determination of the oil content, with sufficient precision and accuracy.

CONCLUSIONS

The application of the two techniques, TG and NMR, can provide the main analytical data which are also of commercial interest, for plant oil

seeds such as those examined here, combining good reproducibility and accuracy with a simple, rapid operation.

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