

## **Non-destructive Determination of the Moisture Content of Individual Wheat Grains by Nuclear Magnetic Resonance**

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### **ABSTRACT**

*The non-destructive determination of the moisture content of wheat samples as small as an individual grain would have a range of uses whether for repeated measurements, as in physiological studies of development, or to allow subsequent analysis for other factors such as pesticide residues. However, no such method has yet been described. A suitable method has now been developed using an ordinary nuclear magnetic resonance (NMR) spectrometer. With a calibration set of 100 grains, the relationship between NMR response and oven moisture content (range 3.3 to 19.6 %) was described by a full quadratic model with which there was no remaining lack of fit (1.465 ns), and the repeatability of the model was acceptable (standard estimate of error 0.9995). The quality of fit of the NMR predicted moisture content to the oven moisture content for three test sets each of 100 grains was also satisfactory (standard deviation of difference 0.973 to 1.352). Using two batches of 25 fumigated grains, the method has been used to show that the different amounts of residues of 1,1,1-trichloroethane were not related to moisture content, as had been previously suggested.*

**Key words:** Moisture content, wheat, individual grains, non-destructive determination, nuclear magnetic resonance, fumigation.

### **INTRODUCTION**

Cereal moisture content (mc) is an important parameter because it can influence the rate of growth and development of infesting insects, mites and microorganisms and

the rate of physical and chemical changes. However, the measured moisture content of a sample of grain is the average value of its component parts (subsamples) whose individual values may vary quite widely. It may be necessary to know the range of the individual values of the component parts, sometimes even down to the single grain level. This knowledge could, for example, assist plant breeders to develop varieties which mature more evenly, improve assessment of suitability for storage (since grains with higher moisture contents suffer the greatest risk of deterioration), and establish whether there is any connection between uneven distributions of moisture and pesticide residues.

There are various methods for the measurement of cereal moisture content (Hunt and Pixton 1974), but only a few of these methods can be used to measure the moisture content of individual grains. Those reported so far include oven or hot air drying (Beullier and Multon 1976; Kato and Yamazaki 1978), flotation (Miller *et al* 1977), near infra-red (NIR) transmittance (Finney and Norris 1978), and hygrometry (Kovadlo 1983). If the grain is needed for further analysis, the method may have to be non-destructive. Only the latter two of the techniques mentioned satisfy this additional constraint but both suffer drawbacks: the NIR results may include errors since only a portion of the central region of the kernel is examined, and the hygrometry method requires apparatus which is not widely available. In studies on the development of insects within wheat kernels (Chambers *et al* 1984), the moisture content of the insects was measured accurately by nuclear magnetic resonance (NMR). It was decided to see whether the same continuous-wave spectrometer, used routinely in chemical laboratories and capable of scanning the entire kernel, could be used to measure the moisture content of individual wheat grains non-destructively.

The use of NMR for moisture measurement of cereal samples weighing several grams is well established (Miller and Kaslow 1963; Pohle and Gregory 1968; Miller *et al* 1980; Morley *et al* 1984), and several NMR moisture analysers have been described (Rubin 1958). At the individual grain level, pulse NMR methods have been used to ascribe the signals of resonating protons to oil, water or solids (Persyn and Rollwitz 1971) and to study the binding of water (Kuzmina *et al* 1980; Askochenskaya and Golovina 1981). However, there has been no report on the possibility of measuring moisture content of individual wheat kernels using a standard laboratory continuous-wave high-resolution NMR spectrometer. The aim of the work reported here was to develop such a method and to illustrate its use in a simple study of some fumigated grains.

In studies with kilogram quantities of wheat it has been reported (Scudamore and Goodship 1982) that the amount of 1,1,1-trichloroethane adsorbed during fumigation under conditions of controlled temperature and relative humidity (RH) increases with moisture content and that the fumigant is lost more rapidly from grain of higher moisture content during subsequent airing. Studies of individual fumigated grain kernels have shown that a wide range in the amount of fumigant adsorbed occurs (Scudamore and Heuser 1973; also Scudamore K A unpublished) although no reason has been suggested for this. However, moisture contents of individual kernels have been shown to vary considerably even when conditioned together (Oxley 1948). It was therefore decided to attempt to use the newly

developed method for moisture content determination to see whether the amount of fumigant adsorbed increased with moisture content at the single grain level.

## MATERIALS AND METHODS

### **Wheat**

The NMR calibration curve was established with one batch and tested with three batches each of 100 wheat grains from the previous year's UK harvest. The first three batches were of Maris Huntsman variety: batches A (the calibration set) and B came from a farm in Cambridgeshire, batch C came from a farm in Sussex. The variety of batch D was Flanders. All of the grain had previously been stored at 25°C and 60% RH and had an mc of approximately 14% (w/w fresh weight (FW)). In each batch grains of other moisture contents within the range 4–20% (w/w FW) were obtained either by drying in an oven at 50°C or by equilibration with the calculated amount of water in a sealed tube for 4 days. After conditioning, each grain was analysed by NMR. This was followed immediately by measurement of the mc by oven drying.

### **NMR analysis**

NMR spectra were recorded on a standard laboratory Varian EM360 60 MHz proton spectrometer and the resolution was optimised each day before use. The grains examined were not spun, as would be normal for high resolution work with liquid samples, since spinning made no difference to the wide-line spectra obtained. Neither was it necessary to adjust the horizontal orientation of the grain. However, the vertical position of the grain within the spectrometer was found to be surprisingly critical and was adjusted for each grain until the maximum signal was obtained. The spectrometer control settings were: sweep width 20 ppm, offset  $-6\delta$ , RF power 0.4 mG, scan time 1 min, filter 0.2 s, and spectrum amplitude  $10 \times 12$ . A series of iterative tests had shown that these would give the largest undistorted spectra which could be accommodated on the usual chart paper. The area of each spectrum was taken to be the mean of two readings with a planimeter (Allbrit 21105) between  $-6\delta$  and  $+14\delta$ . The baseline was constructed as a horizontal line between the spectrum at the lower of these two points and a vertical dropped from the other. With these broad peaks of unusual shape, the planimeter had been found to give much better precision than the spectrometer integrator.

### **Oven method**

Immediately after its NMR spectrum had been recorded, each grain was weighed on a Mettler H33 balance on a heavy weighing table. The balance zero was checked before and after every weighing. The grains were then dried in numbered dishes in a ventilated oven at 130°C for 20 h, reweighed, and the mc was calculated on a % wet basis. The conditions were based on those recommended by the American Society of Agricultural Engineers (ASAE 1978) for determining moisture contents of whole wheat grains.

### Fumigated grains

Fifty grains identical with those in batch C were fumigated at 25°C with methyl bromide:1,1,1-trichloroethane (1:19 by weight) for 70 h to give a total concentration-time product of 10 000 mg h litre<sup>-1</sup>. Twenty-five grains were analysed by NMR immediately and the remainder were analysed after storing individually in glass tubes for 14 days at 25°C and 60% rh. Before and after each batch of fumigated grains was analysed by NMR, control batches of ten grains, identical except that they had not been fumigated, were analysed first by NMR and then by the oven method.

Immediately after analysis by NMR, the fumigated grains were steeped individually in 10 ml acetone:water (5:1 by volume) for at least 48 h. After shaking with NaCl then CaCl<sub>2</sub>, the extracts were analysed by gas chromatography on a column of Apiezon L at 80°C followed by electron capture detection (Goodship *et al* 1982).

## RESULTS AND DISCUSSION

### Development of NMR method

Typical NMR spectra for wheat grains of various moisture contents are shown in Fig 1. Before attempting to establish a calibration to relate the NMR signal to the oven moisture content, it was necessary to perform a short series of preliminary checks. These were conducted to ensure that the spectra would be reproducible and to suggest the best way of retrieving information from them.

Reproducibility proved to be no problem. There were slight differences between repeated spectra of the same grains, but there was no regular trend as would have occurred for example with a grain of above ambient moisture content gradually becoming drier. The differences were therefore probably due not to actual changes in moisture content but to variations in the performance of the spectrometer. Such

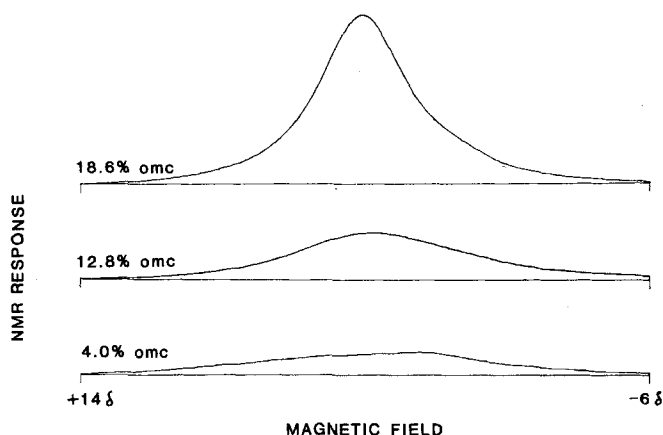


Fig 1. Typical NMR spectra for wheat grains of various oven moisture contents (omc).

variations were always small and there was close agreement between results from spectra recorded several days apart. Although all the work reported here was conducted on just one NMR spectrometer, it had not been modified in any way and there is no reason to suppose that any other proton spectrometer would not provide equally good results.

The NMR spectrometer used here may detect protons in a sample whatever the chemical that contains them. The feature which makes the present study possible is that the signal from liquids occurs over a narrower range of magnetic field than that from solids. Thus the NMR spectrum of a grain would be expected to consist of a narrower portion due to the more mobile molecules such as moisture, superimposed on a broader portion due to the solids such as starch. In other applications of NMR the best method of quantifying the signal is to measure its area. This proved to be the best method in the present study too. It had been hoped to keep the area measurement to as narrow a range of field as possible to optimise the proportion of liquid signal in the measured area. However, it is clear from Fig 1 that such an approach would exclude at least some of the liquid signal, because it was relatively broad compared with that from a true liquid. This is presumably due to interaction of the moisture with the other chemicals causing at least part of it to be present as water of hydration rather than as free water. In the current study, therefore, the signal areas were measured over the widest possible field range, between  $-6$  and  $+14 \delta$ . Attempts to quantify the signals by using narrower field ranges, and by using more easily measured peak heights (at  $+4 \delta$ ), were less successful. However, the wider the field range used for area measurement, the greater is the risk that part of the signal is due to sources other than moisture. One possible source would be the protons in the cereal lipids, since the lipid signal would be expected to be quite narrow and is indeed readily observable as a sharp signal between  $-1.2$  and  $1.6 \delta$  in spectra of developing insects (Chambers *et al* 1984). In the present study of cereal grains there is some evidence for a slight contribution by cereal lipid. The observed spectra in Fig 1 are asymmetric and the peak maximum shifts to higher field with decreasing water content. To assess this contribution a series of grains were dried in the oven and their NMR signals were measured over the range  $-6$  to  $+14 \delta$ . However, the areas of the dried grains were too small to be measured accurately, confirming that the proportion of the signal due to sources other than moisture could be ignored.

Since all the grains studied were smaller than the scanned volume of the sample tube, the NMR signals recorded were due to the entire grains. However, this meant that it was necessary to allow for the variation in size of the grains. This was achieved by dividing the NMR signal area by the wet weight of the grain. Other parameters, such as the mean diameter orthogonal to the crease, were tried but gave less consistent results.

In a study of moisture content of larger samples of cereal grains measured by pulsed NMR, Miller *et al* (1980) reported that the NMR response from samples of higher moisture contents depended on the history of the grain. Thus samples which had been wetted by soaking and drying gave different results from those which had been wetted by equilibration, and both these results differed from those obtained with samples of naturally high moisture content. In the present study, the

spectrometer operated with continuous-wave (CW) radiation and there was no obvious difference between the measured areas from grains whether they had been wetted by soaking and drying or by equilibration. Purely for convenience, however, all of the higher moisture content grains used for the main study were wetted by the equilibration method.

### Calibration

Throughout the main study, statistical analysis was conducted using the Generalised Linear Interactive Modelling (GLIM) computer package of the Royal Statistical Society of London, copyright 1977. The relationship between the NMR response (signal area  $\div$  wet weight) and the oven moisture content, the calibration curve, was established using the 100 grains of Maris Huntsman wheat which formed batch A. They ranged in oven moisture content between 3.3 and 19.6%. Attempts were made to fit various functions of the NMR response to the oven-measured moisture content. These functions consisted of combinations of a quadratic term, a linear term and an intercept. The analysis of variance for some of these models (Table 1) shows that the model was significantly worsened if any one of these terms was omitted. Although no simplification of the full quadratic model was possible, Table 1 also shows that with this model there was no remaining lack of fit ( $F_{23,97}$  1.465 ns) and therefore it would be suitable for testing with the other batches of wheat. The parameter estimates for the model are shown in Table 2 and the curve itself is shown in Fig 2. Table 3 shows the repeatability in the calibration model as used on the other batches of wheat, together with similar parameters for some related work. The repeatability in the present study appears to be slightly poorer than in the NMR studies using larger samples, some of up to 80 g, as might be expected. It was, however, of the same order as, if not slightly better than, the

**TABLE 1**  
Analysis of variance for some models of the calibration data

Source	DF	SS	Mean square	F
Quadratic term, given linear term and intercept	1	52.79	52.79	71.6***
Linear term, given quadratic term and intercept	1	264.09	264.09	358.1***
Intercept, given quadratic term and linear term	1	22.59	22.59	30.6***
Full quadratic model	97	96.91 <sup>a</sup>	0.999	0.738 ns
Lack of fit	74	79.95	1.080	1.465 ns
Pure error	23	16.96 <sup>b</sup>	0.7374	
Total	99	2379	—	

\*\*\*  $P < 0.005$  ( $F_{1,23} = 9.64$ ).

ns Not significant ( $F_{23,97} \sim 1.7$ ;  $F_{23,74} \sim 1.7$ ).

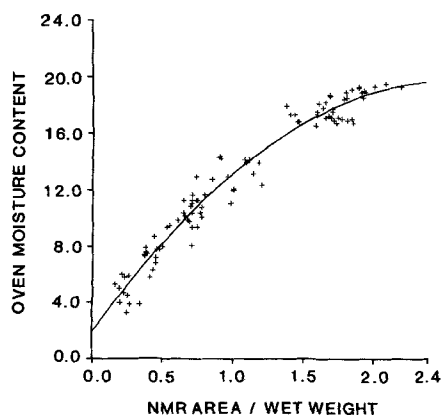
<sup>a</sup> NB: Residual sum of squares after the model has been fitted, *not* sum of squares attributable to this source.

<sup>b</sup> Estimated from replicated data.

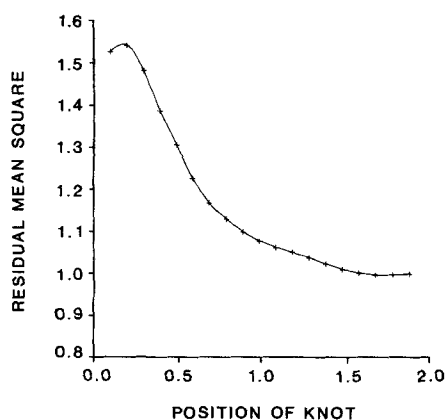
**TABLE 2**  
Estimates for the calibration model

Parameter	Estimate	Standard error
<i>a</i>	-2.788	0.339
<i>b</i>	14.13	0.75
<i>c</i>	1.879	0.330

Calibration model: predicted moisture content =  $ax^2 + bx + c$  where  $x = \text{NMR area} \div \text{wet weight}$ .



**Fig 2.** Calibration curve obtained with the 100 grains of Maris Huntsman wheat in Batch A.



**Fig 3.** Residual mean square for attempts to fit to the calibration set a series of continuously differentiable functions consisting of a quadratic curve below a knot and a straight line above it. The knot position is expressed in units of NMR signal area divided by wet weight.

**TABLE 3**  
Repeatability in the calibration model

	Per cent variation explained by the model, $r^2$	SEE <sup>a</sup>
Present study of individual wheat grains by CW NMR	95.9	0.9995 <sup>b</sup>
Bulk wheat by CW NMR (Morley <i>et al</i> 1984)	99.9	—
Bulk wheat by pulse NMR (Miller <i>et al</i> 1980)	98.8	—
Individual maize kernels by NIR (Finney and Norris 1978)	92.2-94.1	2.69-4.95

<sup>a</sup>SEE = Standard estimate of error =  $\sqrt{\text{Error mean square}}$ .

<sup>b</sup> $\sqrt{\text{Residual mean square after fitting quadratic}}$ .

repeatability in the study of individual maize kernels by NIR (Finney and Norris 1978).

In most other applications of NMR, the observable response is directly proportional to sample size. Thus the calibration curves obtained in other studies using larger samples are linear over most of the range of moisture contents studied. However, deviation from linearity has been observed at the lower end of the range, below about 7% moisture content (Miller and Kaslow 1963; Miller *et al* 1980) and has been ascribed to the moisture being bound. A test was therefore undertaken to establish whether the relationship in the present study was in fact a curve joined to a straight line. This was achieved by attempting to fit a series of spline functions consisting of a linear line above a knot and a quadratic line below. Figure 3 shows the residual mean square for the series of functions as the position of the knot was varied. Had the relationship been of this type, there would have been a minimum in the graph at the knot value where the two functions met. There is however no minimum, so in this study the relationship is truly curved throughout the range studied. This difference from other work could have arisen in a number of ways. The most obvious would be a machine problem due to either non-linear response from the amplifier system or radio-frequency saturation effects. The former is improbable since calibration curves obtained in other work with liquids were linear. The latter is also unlikely since care was taken in setting up the method to ensure that the curves were not distorted; however, it cannot be ruled out. Other reasons might be differences in spectrometer design, or in the manner of retrieving information from the spectra, or the need in this study to allow for the size of the sample being less than the scanned volume of the NMR sample tube. Nevertheless the quality of fit of the data obtained from the wheat in batch A to the full quadratic model was sufficiently impressive to warrant testing the calibration with the data from the three other batches of wheat.

### Test samples

The calibration equation established with the wheat in batch A was used to convert the NMR response into predicted moisture content for each of the grains in the independent batches B (Maris Huntsman, Cambridge, like the calibration batch A), C (Maris Huntsman, Sussex) and D (Flanders). Table 4 shows the quality of fit of these three test sets to the calibration model, together with related data for previous studies. Whether judged by correlation coefficient or, more soundly, by the standard deviation of difference between the observed and predicted values, it seems that the quality of fit in the present study is less good than in the NMR study with larger samples (Morley *et al* 1984), but similar to that achieved in the NIR study of individual grains of maize (Finney and Norris 1978). Comparisons of the oven moisture contents with the values predicted using the NMR responses from the individual grains in batches B, C and D are presented in Figs 4, 5 and 6 respectively and further show the agreement between the two methods.

### Fumigated grains

The above study shows that the NMR method can be used to predict the moisture content of individual wheat grains non-destructively. The value of such a method



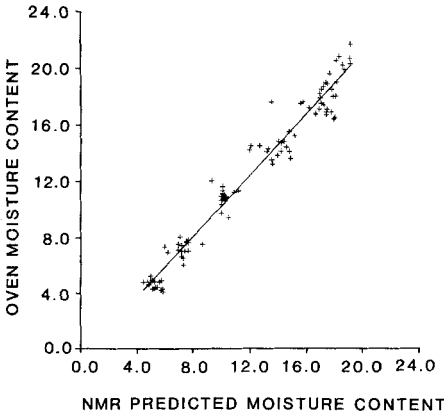
**TABLE 4**  
Quality of fit of test sets to calibration model

Test set	Correlation between observed and predicted, <i>r</i>	SDD <sup>a</sup>
Present study of individual wheat grains by CW NMR:		
Batch B	0.968	1.148
Batch C	0.951	1.352
Batch D	0.979	0.973
Bulk wheat by CW NMR (Morley <i>et al</i> 1984)	0.996	'Very low'
Individual maize kernels by NIR (Finney and Norris 1978)	0.965	0.75-3.92

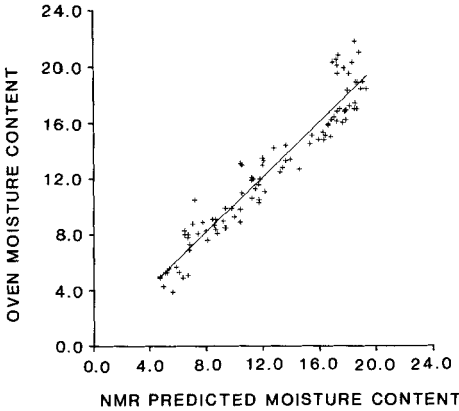
<sup>a</sup>Standard deviation of difference  
= Root mean square deviation

$$= \sqrt{\frac{1}{N-1} \sum_{k=1}^N (y_{\text{obs},k} - y_{\text{pred},k})^2}$$

where *N* = number of points, and *y*<sub>obs</sub> and *y*<sub>pred</sub> are the observed and predicted values respectively.



**Fig 4.** Comparison of the oven moisture contents of the 100 grains of Maris Huntsman wheat in Batch B with the values predicted using the NMR responses.



**Fig 5.** Comparison of the oven moisture contents of the 100 grains of Maris Huntsman wheat in Batch C with the values predicted using the NMR responses.

was illustrated in a short study of some fumigated wheat grains. This was designed to investigate whether the amount of 1,1,1-trichloroethane adsorbed during fumigation, and subsequently lost during airing, might increase with moisture content at the single grain level, as has been reported to be the case with kilogram quantities of wheat (Scudamore and Goodship 1982).

Two batches of 25 fumigated grains were analysed by NMR immediately before

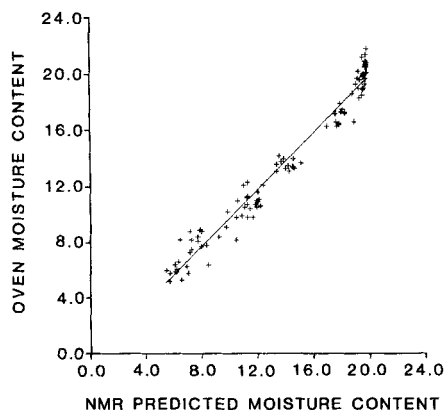


Fig 6. Comparison of the oven moisture contents of the 100 grains of Flanders wheat in Batch D with the values predicted using the NMR responses.

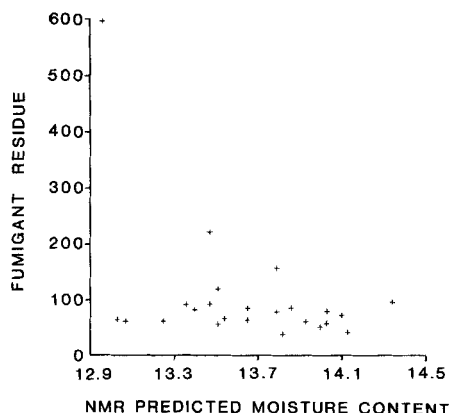


Fig 7. Plot of residues of the fumigant 1,1,1-trichloroethane against the NMR predicted moisture content for the 25 grains of Maris Huntsman wheat analysed immediately after fumigation.

the destructive analysis for 1,1,1-trichloroethane. One batch was analysed immediately after fumigation, the other after storing for 14 days. Since there was an interval of several months between this study and the NMR study of batches A to D, a further 40 grains were analysed by NMR and oven drying to verify the NMR method and to act as a calibration set for the fumigated grains. The 40 control grains were not themselves fumigated, but there is no reason to suppose that the presence of relatively minute amounts of fumigant in the fumigated grains would affect the relationship between NMR response and moisture content. The control grains were analysed in groups of ten before and after each batch of fumigated grains but since there had been no evidence for any change in NMR response over such a period, it was reasonable to treat them as one batch of 40 grains. The range of oven moisture contents was between 10.6 and 16.6%. Statistical analysis of their results was conducted in exactly the same way as used previously for calibration batch A. Again it emerged that no simplification of the full quadratic model was possible. In this case the estimates for the new calibration model, together with their standard errors, were as follows: quadratic term  $-0.004\,689 (\pm 0.002\,392)$ ; linear term  $0.5198 (\pm 0.0934)$ ; intercept  $5.916 (\pm 0.887)$ . These values differ numerically from those shown in Table 2 largely because of a different arbitrary scaling factor applied to the planimeter readings. Apart from this it is encouraging that the new calibration model, based on just 40 grains covering a relatively short range of oven moisture contents, should be so similar to the earlier model.

The estimates for the new calibration model were then used to convert the NMR response for each of the fumigated grains to the predicted moisture content. Plots of residue of 1,1,1-trichloroethane against predicted moisture content for the two batches of fumigated grains are shown in Fig 7 for the grains analysed immediately after fumigation, and in Fig 8 for those analysed 14 days later. Inspection of Figs 7 and 8 shows that, regardless of predicted moisture content, in neither case do the grains fall along the fumigant residue axis according to a symmetrical, normal

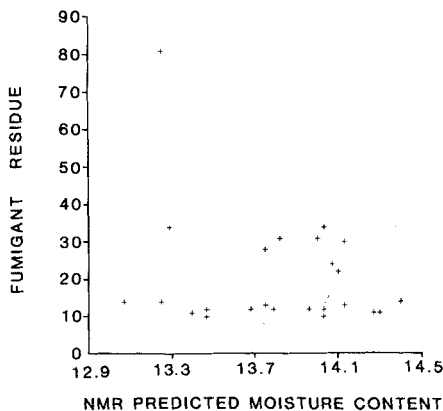


Fig 8. Plot of residues of the fumigant 1,1,1-trichloroethane against the NMR predicted moisture content for the 25 grains of Maris Huntsman wheat analysed 14 days after fumigation.

distribution. To assess statistically whether there was any relationship between the predicted moisture content and the fumigant residue it was therefore assumed that the arrangement of grains along the fumigant axis would be better described as following a gamma distribution.

Attempting to fit a function consisting of a linear term and an intercept to the data from all 25 grains in Fig 7 suggested that there was indeed a relationship between fumigant residue and moisture content,  $\chi^2(95\%)$  calculated = 27.27, tabulated = 3.84. However, when this exercise was repeated but excluding the grain with the fumigant residue of 597 mg kg<sup>-1</sup>, the highest value by far, it was clear that there was no relationship,  $\chi^2(95\%)$  calculated = 0.471. Such a dramatic difference between the two calculated values of  $\chi^2$  confirms that, despite the assumption of a gamma distribution, this one grain was exerting an undue influence upon the analysis and could justifiably be rejected as an outlier. Although this study was limited to a small number of grains, there is no evidence that the residue of 1,1,1-trichloroethane adsorbed by grains during fumigation is related to their individual moisture contents.

When a similar statistical analysis was performed on the results from all 25 grains shown in Fig 8, ie those that had been stored for 14 days, it was clear that there was no relationship between their fumigant residue and predicted moisture content,  $\chi^2(95\%)$  calculated = 1.42, tabulated = 3.84. The NMR method could predict the moisture content only at the time of analysis whereas the fumigant residue might have been influenced by a change in moisture content at any time during the storage period. However, it is most unlikely that any such changes occurred because the conditions of storage were carefully controlled. Some supporting evidence comes from comparison of the predicted moisture contents of the two batches of fumigated grains (13.8% and 13.7%). These two batches originated from the same source and were fumigated together, but although there was a time difference of 14 days between their analyses there was no significant difference between their predicted moisture contents,  $F_{1,48}(95\%)$  calculated = 2.57, tabulated ~ 4.0. Thus it is reasonable to state that this study provides no evidence that the residue of 1,1,1-trichloroethane in grains 14 days after fumigation is related to their individual

moisture contents. Furthermore, since the first part of this study showed there to be no relationship between the amount of 1,1,1-trichloroethane initially adsorbed and moisture content, it follows that losses during airing are probably independent of moisture content.

These results with individual grains are clearly different from those found with bulks of grain where the uptake and desorption of fumigant have consistently been shown to depend on the moisture content (Scudamore and Goodship 1982), yet there is an explanation. The work with single grains elucidates the contribution each individual grain makes to an observed parameter for the bulk. As supported by the findings in the current work, it is not unusual for the range of fumigant residues of individual grains to follow a distribution which is not normal, and that in any batch there can be 'outlier' grains which have much higher residues than the rest. If these outlier grains contribute sufficiently to the bulk parameter, then fumigant residue might indeed appear to rise with moisture content (by chance). While the present work shows that fumigant residue is not related directly to moisture content, it does not preclude the possibility that fumigant residue is influenced by a third factor which is itself influenced by moisture content. If either of these influences were based on a function which is not continuous, the apparent contradiction between results with bulk grain and individual grains could disappear. This third factor could be due to structural differences between the grains such as the nature of the starch granules, the presence of internal cracking, the maturity of the grains or the degree of biodeterioration occurring during storage, but further work would be required to establish which.

### General comments

It has been shown that the NMR method can be used to predict the moisture content of individual wheat grains non-destructively with an accuracy which is understandably poorer than that achievable by NMR studies on much larger samples, but which is at least as good as that obtained in a study of individual maize grains by NIR. Both the NIR and NMR methods are relatively rapid and have low running costs but an advantage of the latter is that the entire grain is scanned. This aside, the choice between methods might well be governed by the availability of a suitable machine.

In the present study, a single calibration curve proved suitable for studying wheat of the same variety from two different sources and one other variety. Further work would be required to establish how widely applicable one calibration could be. This might be limited by variations in lipid content since the spectra drawn by the NMR spectrometer used in the present study would probably not allow distinction to be made between protons in moisture and those of any other liquid such as oil. The success of the NMR method in predicting moisture content must therefore rest on the amount of other liquids remaining relatively constant between samples, as is likely to be true for the grains used in the present study.

Reference has also been made earlier to the suggestion by other workers (Miller and Kaslow 1963; Miller *et al* 1980) that the NMR response at lower moisture contents is influenced by binding of water to other materials. While it is true that in the present study the width of the NMR signals ascribed to moisture was greater

than that expected for a true liquid, thereby implying some interaction with other materials, the continuous-wave (CW) NMR spectrometer used here should not be regarded as an appropriate machine to investigate binding. This would be much better studied using a pulse NMR spectrometer, preferably in conjunction with an assessment of the biological significance of each of the different states in which the water is found.

Despite this limitation, the CW NMR spectrometer can be used to provide valuable information: in the present study the different residues of 1,1,1-trichloroethane found in a batch of individual wheat grains have been shown to be independent of differences in moisture content. This finding does not preclude further contribution of the NMR technique to the elucidation of this problem. Moisture content is merely the result, observed at one moment in time, of a dynamic exchange of water between the grain and its surrounding atmosphere. It should be possible to use the same CW NMR spectrometer in a modification of the method described here to assess whether the different residues of fumigant are due to different rates of exchange of water.

### ACKNOWLEDGEMENTS

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