Process NMR Associates, LLC
87A Sand Pit Rd, Danbury, CT 06810 USA
Tel: (203) 744-5905 Fax: (203) 743-9297 Web: http://www.process-nmr.com

Application Note: Maltodextrin Adulteration of Licorice Observed by NMR

Three samples were analyzed to determine if liquid or solid-state NMR techniques could be utilized to quantify adulteration of licorice powders by maltodextrin. Samples analyzed were:

Maltodextrin, Licorice #1, Licorice #2

Licorice #1 and Licorice #2 were analyzed by a combination of liquid-state ^{1}H and ^{13}C NMR on a Varian Unity-300 spectrometer, and solid-state ^{13}C NMR on a Varian UnityPlus 200 spectrometer. The resulting spectra are shown in the attached plots.

One of the Licorice samples is adulterated by maltodextrin to an unknown concentration, the other licorice sample is pure licorice. Which sample was which was not known during the analysis. Initially it was hoped that the addition of maltodextrin to the licorice would be readily observed as new peaks appearing in the spectrum of the licorice sample. However, it can be seen that in both the ^{1}H and ^{13}C NMR there is considerable overlap of the peaks in the spectra of pure licorice and maltodextrin.

When no observable maltodextrin peaks could be assigned it was decided to simply use the quantitative integral data from the regions of the spectrum where the maltodextrin overlaps with the licorice spectrum compared to the integrals obtained from regions solely assignable to licorice. In Tables 1-3 are the quantitative results for each of the experiments performed.

Table 1: ^{1}H NMR Integral Regions

Normalized on Reg 4				
Range (ppm)	5.6-5.2	4.3-3.2	8.8-6.4	3.2-0.0
1H	Reg 1	Reg2	Reg 3	Reg 4
Maltodextrin	8.6	58.1	0.0	0.0
Sample #1	3.5	48.3	3.8	22.2
Sample #2	2.7	38.4	4.0	22.2
Sample #1+	10.2	71.2	13.3	22.2
Sample #2+	6.9	64.6	9.0	22.2

Regions 1 and 2 contain maltodextrin/licorice peaks.
Regions 3 and 4 contain only licorice peaks …. Data was normalized to region 4. The normalization normalizes the licorice signal intensity. Thus the increased intensity of regions 1 and 2 in sample #1 is indicative that this sample contains maltodextrin. Samples #1+ and #2+ were made by adding more maltodextrin to the samples. Sample #1+ contains a further 10.9 wt % maltodextrin, while sample #2+ contains 11.4 wt% maltodextrin. The values were used to calculate the maltodextrin content in sample #1.

The ^{1}H analysis indicates that there is 3.3 wt% maltodextrin in sample #1

Table 2: ^{13}C NMR Integral Regions

Normalize on Region 7							
Range (ppm)	104-94	82-68	63-58	210-104	94-82	68-63	58-0
13C	Reg 1	Reg 2	Reg 3	Reg 4	Reg 5	Reg 6	Reg 7
Sample #1	8.68	33.36	8.49	33.15	5.76	3.19	23.28
Sample #2	7.16	28.45	8.14	26.09	3.57	4.96	23.28
Sample #1+	9.98	39.42	10.53	29.70	4.54	4.54	23.28
Sample #2+	8.66	35.46	10.16	22.89	3.16	5.32	23.28

Regions 1-3 were common to licorice and maltodextrin signals, while regions 4-7 were exclusive to licorice signals. Normalization on region 7 sets the licorice at a normalized intensity. Again the intensty of regions 1-3 increases from sample #2 to sample #1 indicating the presence of maltodextrin in sample #1.

Calculation indicates that there is 6.1 wt% maltodextrin in the sample.

Table 3: Solid-State ^{13}C Integral Regions

Solids 13C CPMAS	Normalized to Reg 3		
Range (ppm)	116-40	265-116	40 to -10
13C	Reg 1	Reg 2	Reg 3
Sample #1	77.46	18.74	17.46
Sample #2	64.35	16.11	17.46

Region 1 contains maltodextrin and licorice signals, while regions 2 and 3 contain only licorice signals. Again, the intensity of region 1 increases from sample #2 to 31 upon normalization of the licorice only region 3. This confirms the presence of maltodextrin in sample #1. Samples #2+ and #1+ were not analyzed by solid-state NMR. This ^{13}C analysis is much faster than the liquid-state NMR and would be a plausible short cut to quantify maltodextrin content.

Upon completion of the analysis it was revealed that the adulteration value was 5% maltodextrin.

Accompanying Documents – Licorice Adulteration NMR Spectra.pdf