

the **minispec**



Polymer Dossier

minispec Applications in the Polymer Industry



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Optics

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A Introduction

As the world-wide production of polymers steadily increases to keep up with rising demands and as global competition causes prices to fall, manufacturers now more than ever are looking to new analytical methods to help increase productivity, improve quality, and reduce costs. Improvement of quality control is an important step to reduced wastage, increased productivity, and improved product consistency. Suitable QC/QA analytical instrumentation can pay for itself in just a few months if the new analytical method can yield accurate results in a timely fashion. Of course, the instrumentation should be easy to use, robust enough to perform in the plant environment, and be capable of at-line, or in some cases, on-line measurements. If instruments can be linked into a central LIMS network then additional convenience, time savings, and user error reduction can be realized. Labour cost can be reduced if the analysis does not require skilled personnel and complicated sample preparation. In addition, direct costs of QA/QC can be reduced and safety can be improved if a method can be found that does not require the use of solvents and other chemicals.

BRUKER's *Low Resolution-Nuclear Magnetic Resonance (LR-NMR)* analyzer is able to fulfil all these requirements at an affordable price. The NMS-series minispec are highly automated, easy to use, 10 or 20 MHz NMR instruments which are dedicated to routine QC/QA applications. despite the relative simplicity of the minispec, BRUKER users have benefited from our know-how accumulated over 30 years of experience in building research NMR systems up to 800 MHz proton frequency. Once calibrated for a particular application, the NMS minispec yields accurate and reproducible results in seconds, in many cases without the need for any additional sample preparation.

This dossier presents a number of applications that have been tried and tested in various fields of the polymer industry. For reasons of confidentiality, we cannot publish all methods that have been developed for and by our users. However, the following serve as useful examples of the possibilities. New applications are constantly being developed, both by users already equipped with a BRUKER minispec and by the team of scientists in BRUKER's application labs on three continents.

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1 Elastomer in Polyamide

Type of Application: Absolute Application, using weight normalised amplitude of free induction decay (FID) correlated to given percentage of elastomer.

Application Parameters

minispec Soft - EDM	fid_n_v
Receiver Gain	60 dB
Recycle Delay Time	0.5 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Absolute
minispec System	mq20 with PA203

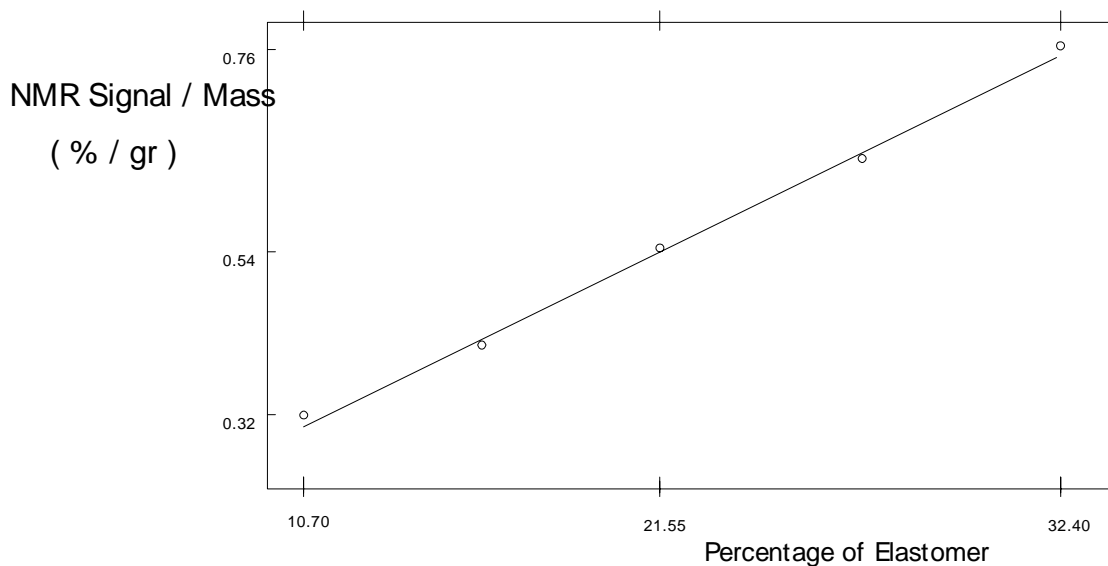
<u>Results:</u>	Calibrate Mode:	Linear Correlation:	0.999
		Slope:	0.103
		Intercept:	0.01997
	Measure Mode:	% Elastomer (given)	% Elastomer (NMR)
		10.7	10.3
		16.7	15.8
		21.8	21.1
		26.6	26.0
		32.4	32.5

Standard Deviation of 5 measurements: $\approx 0.1\%$

Remarks:

- Measuring time per sample approximately 15 seconds
- Sample preparation: weighing and (for improved accuracy) thermostating

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2 Polyethylene in Polyamide

Type of Application: Absolute Application, using weight normalised amplitude of free induction decay (FID) for correlation to given percentage of polyethylene.

Application Parameters

minispec Soft - EDM	fid_n_v
Receiver Gain	70 dB
Recycle Delay Time	0.5 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Absolute
minispec System	mq20 with PA203

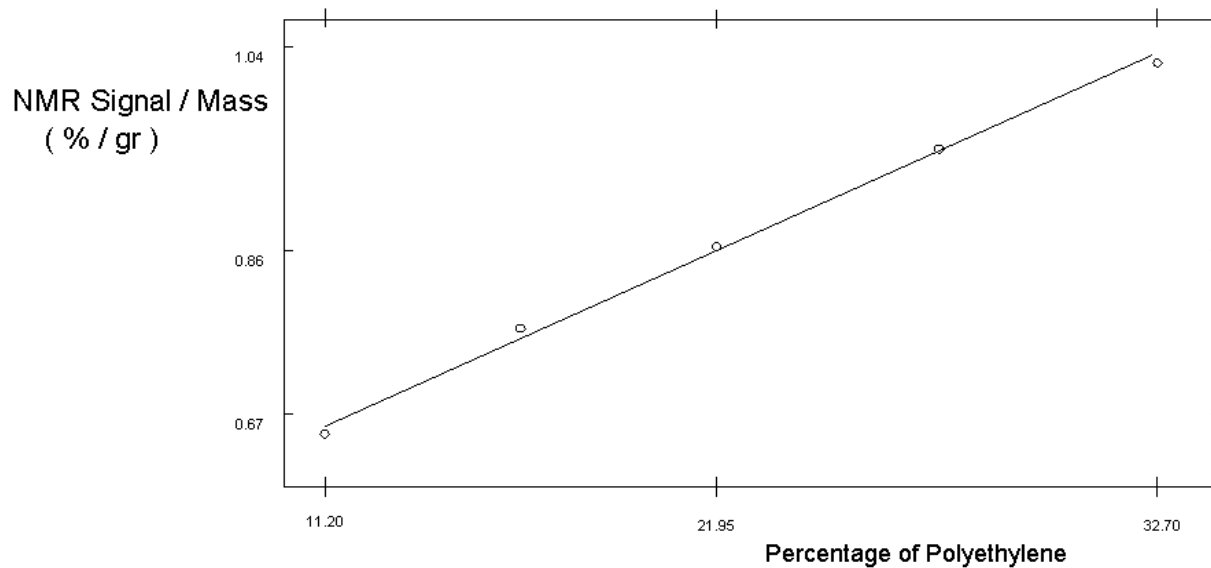
<u>Results:</u>	Calibrate Mode:	Linear Correlation:	0.995
		Slope:	0.483
		Intercept:	0.01745
	Measure Mode:	% Polyethylene (given)	% Polyethylene (NMR)
		11.2	10.9
		16.0	16.5
		21.3	22.4
		26.9	27.6
		32.7	32.5

Standard Deviation of 5 measurements: $\approx 0.2\%$

Remarks:

- Measuring time per sample approximately 15 seconds
- Sample preparation: weighing and (for improved accuracy) thermostating

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3 Polyethylene in Polypropylene

Type of Application: Absolute Application, using weight normalised amplitude of Hahn-echo (90° - 180° pulse sequence) for correlation to percentage of polyethylene.

Application Parameters

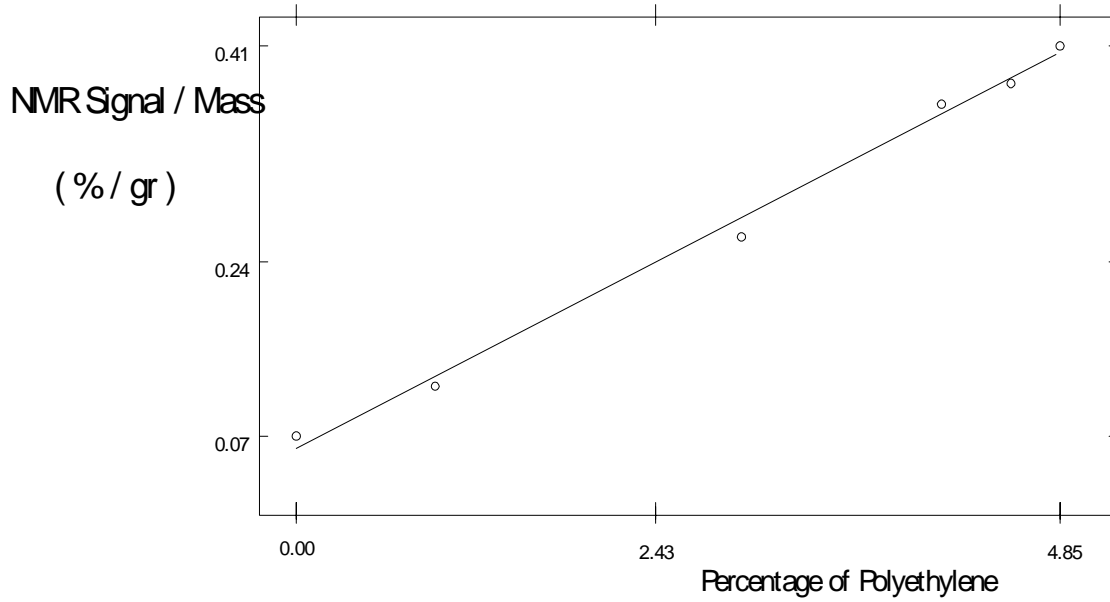
minispec Soft - EDM	spec_n_v
Receiver Gain	90 dB
Recycle Delay Time	0.2 sec
Bandwidth	narrow
Detection Mode	magnitude
Number of Scans	100
Probehead Type	Absolute
minispec System	mq20 with PA203

<u>Results:</u>	Calibrate Mode:	Linear Correlation:	0.982
		Slope:	0.07037
		Intercept:	0.05117
	Measure Mode:	% Polyethylene (given)	% Polyethylene (NMR)
		0	0.3
		1.1	1.1
		3.1	3.3
		4.0	4.6
		4.5	4.7
		4.9	5.2

Remarks:

- Measuring time per sample approximately 20 seconds
- Sample preparation: weighing and (for improved accuracy) thermostating

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4 Polybutadiene in Polystyrene

Type of Application: Absolute Application, using weight normalised amplitude of Hahn-echo (90° - τ - 180° - τ - *measure* pulse sequence) for correlation to given percentage of polybutadiene.

Application Parameters

minispec Soft - EDM	fid_n_v
Receiver Gain	80 dB
Recycle Delay Time	1 sec
Bandwidth	narrow
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Absolute
minispec System	mq20 with PA203

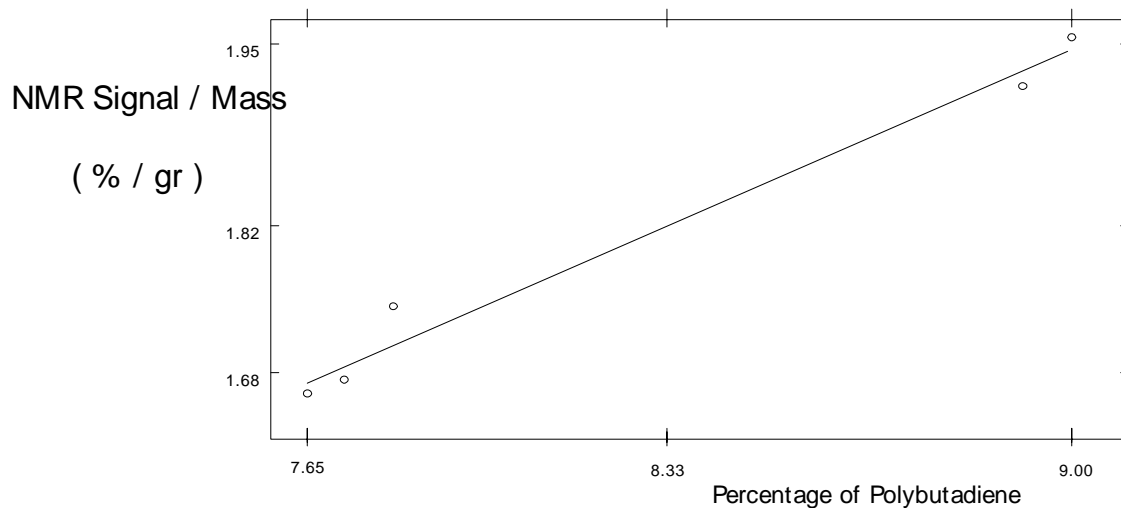
<u>Results:</u>	Calibrate Mode:	Linear Correlation:	0.936
		Slope:	0.181
		Intercept:	0.317
	Measure Mode:	% Polybutadiene (given)	% Polybutadiene (NMR)
		7.65	7.68
		7.70	7.67
		7.80	8.17
		8.86	8.82
		9.00	9.14

Standard Deviation of 5 measurements: $\approx 0.02\%$

Remarks:

- Measuring time per sample approximately 30 seconds
- Sample preparation: weighing and (for improved accuracy) thermostating
- Quoted accuracy of given polybutadiene contents was $\pm 0.2\%$

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5 Polypropylene in a complex industrial polymer mixture

Type of Application: Ratio Application, using the corrected ratios of two amplitudes on the free induction decay (percent solid) for correlation to given percentage of polypropylene.

Application Parameters

minispec Soft - EDM	sc_lc_co
Receiver Gain	70 dB
Recycle Delay Time	2 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Ratio (RTS or VTS)
minispec System	mq20 with PA207

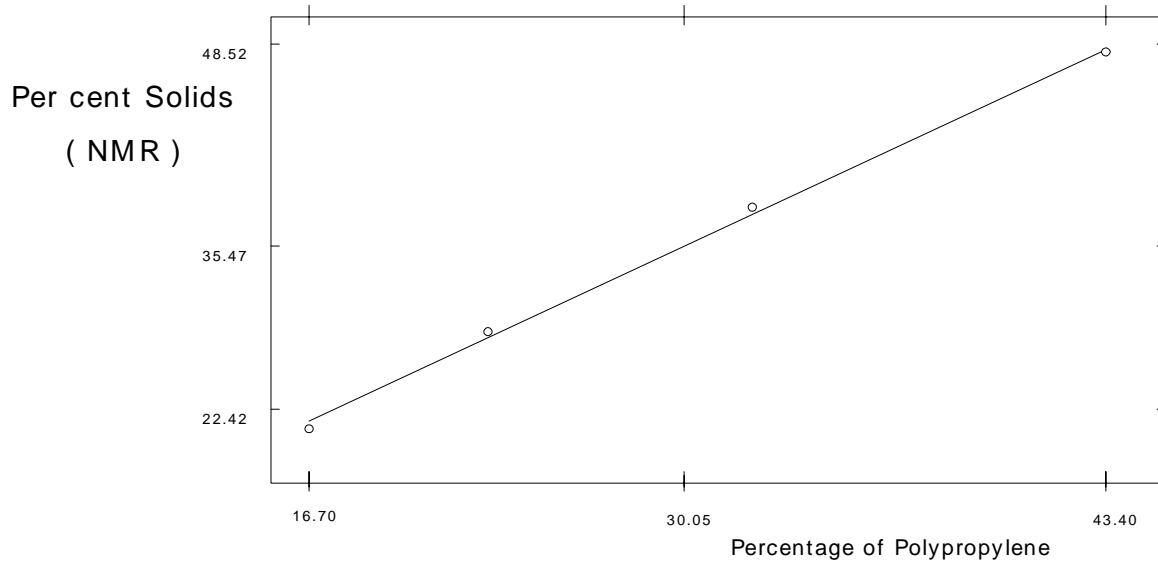
Results: Calibrate Mode: Linear Correlation: 0.999
 Slope: 0.975
 Intercept: 6.471

Percentage of solids (NMR) plotted against percentage of polypropylene (given).

Measure Mode: Standard Deviation of 5 measurements: $\approx 0.2\%$

Remarks: - Measuring time per sample less than one minute
 - Sample preparation: none

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6 Solids in Latex suspensions

Type of Application: Ratio Application, using the corrected ratios of two amplitudes on the free induction decay (percent solid) for correlation to given percentage of solids.

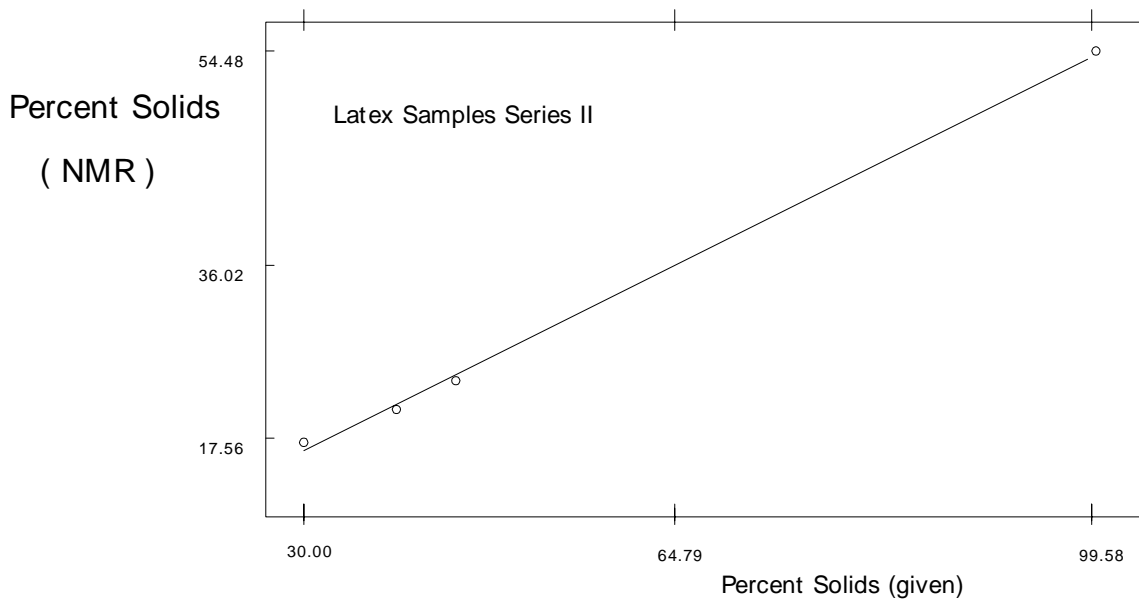
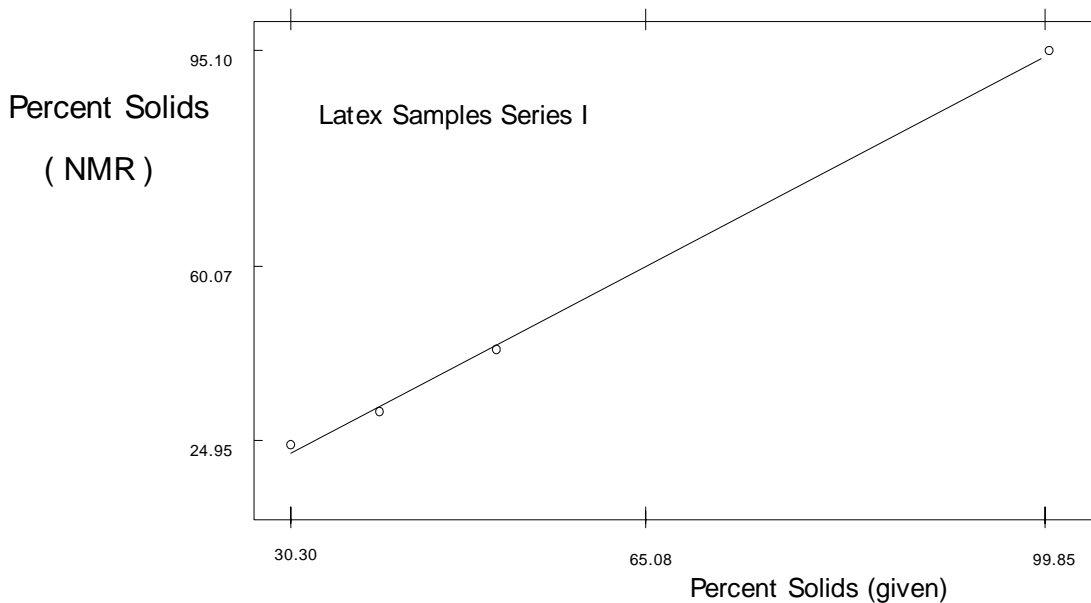
Application Parameters

minispec Soft - EDM	sc_lc_co
Receiver Gain	70 dB
Recycle Delay Time	2 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Ratio (RTS or VTS)
minispec System	mq20 with PA207

<u>Results:</u>	Calibrate Mode:	Series 1:	Linear Correlation:	0.998
			Slope:	1.022
			Intercept:	-7.394
		Series 2:	Linear Correlation:	0.998
			Slope:	0.542
			Intercept:	0.337
			Percentage of solids (NMR) plotted against percentage of solids (given) for two series of Latex suspensions.	
	Measure Mode:		Standard Deviation of 5 measurements: $\approx 0.2\%$	

Remarks: - Measuring time per sample approximately 10 seconds
 - Sample preparation: none

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7 Elastomer in Polyamide (Ratio Method)

Type of Application: Ratio Application, using the corrected ratios of two amplitudes on the free induction decay (per cent liquid) for correlation to percentage of elastomer (reference value).

Application Parameters

minispec Soft - EDM	sc_lc_co
Receiver Gain	70 dB
Recycle Delay Time	1 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Ratio (RTS or VTS)
minispec System	mq20 with PA207

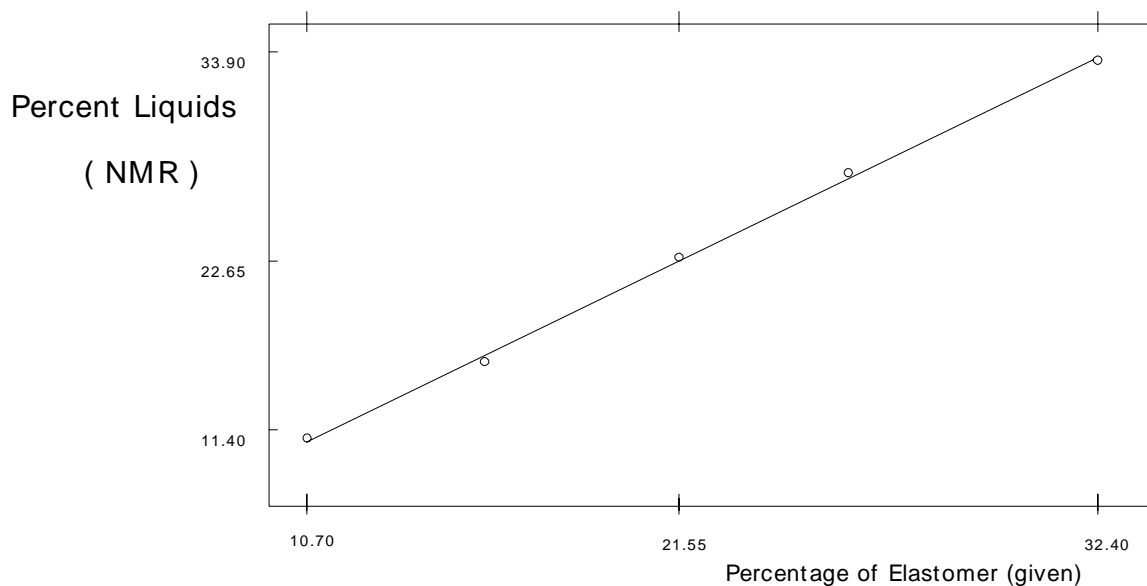
<u>Results:</u> Calibrate Mode:	Linear Correlation:	0.997
	Slope:	1.062
	Intercept:	-0.339

Percentage of liquids (NMR) plotted against percentage of elastomer (given).

Remarks:

- Measuring time per sample approximately 25 seconds
- Sample preparation: thermostating
- Advantage of this method (compared to the absolute method on page 4) is that no sample weighing is necessary.

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8 Hexene in Polyethylene/Polyhexene

Type of Application: Absolute Application, using weight normalised amplitude of Hahn-echo (90° - τ - 180° - τ - measure pulse sequence) for correlation to given percentage of hexene. Sample tempering at $T = 120^\circ\text{C}$ is important.

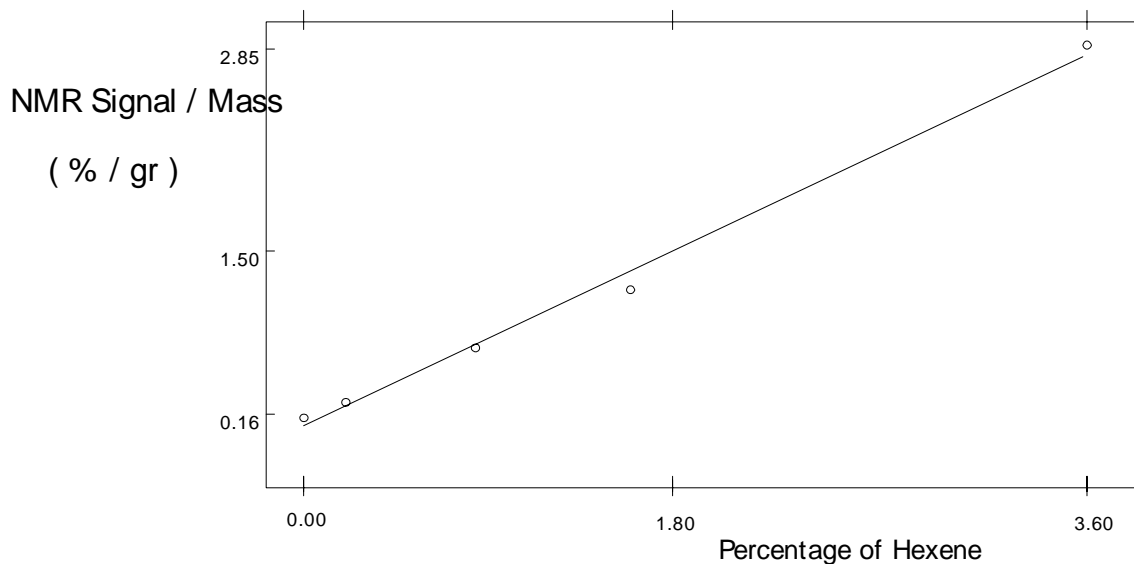
Application Parameters

minispec Soft - EDM	spec_n_v
Receiver Gain	70 dB
Recycle Delay Time	1.5 sec
Bandwidth	narrow
Detection Mode	magnitude
Number of Scans	5
Probehead Type	Absolute
minispec System	mq20 with PA203

Results:	Calibrate Mode:	Linear Correlation:	0.992
		Slope:	0.749
		Intercept:	0.082
	Measure Mode:	% Hexene (given)	% Hexene (NMR)
		0	0.1
		0.2	0.2
		0.9	0.7
		1.6	1.4
		3.6	3.7

Remarks: - Measuring time per sample approximately 10 seconds
 - Sample preparation: weighing and thermostating at $T = 120^\circ\text{C}$

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9 Glass in Nylon

Type of Application: Absolute Application, using weight normalised amplitude of Solid-echo (90° - 90° pulse sequence) for correlation with percentage of glass.

Application Parameters

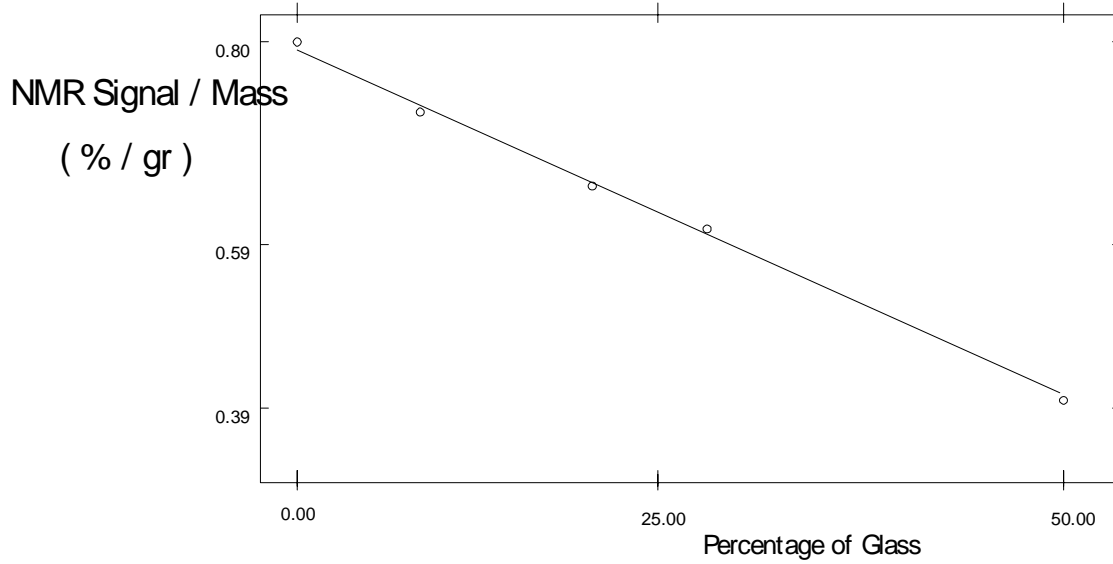
minispec Soft - EDM	soec_n_v
Receiver Gain	70 dB
Recycle Delay Time	0.5 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Absolute
minispec System	mq20 with PA203

Results:	Calibrate Mode:	Linear Correlation:	0.995
		Slope:	-0.00814
		Intercept:	0.797
		Signal due to nylon measured using a Solid-echo pulse sequence.	
	Measure Mode:	% Glass (given)	% Glass (NMR)
		0	-0.7
		10	11.8
		20	20.4
		30	30.3
		50	50.6

Remarks:

- Measuring time per sample approximately 15 seconds
- Sample preparation: weighing and thermostating
- Quoted accuracy of given per cent glass values $\pm 2\%$

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10 Polyvinylacetate in Polyethylene

Type of Application: Relaxation Time Application, correlating the spin-lattice relaxation time (T_1) - received with the help of a Saturation Recovery Pulse Sequence - with the percentage of vinylacetate.

Application Parameters

minispec Soft - EDM	t1_sr_mb
Receiver Gain	70 dB
Recycle Delay Time	0.1 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	4
Probehead Type	Any Probe
minispec System	mq20 with PA207

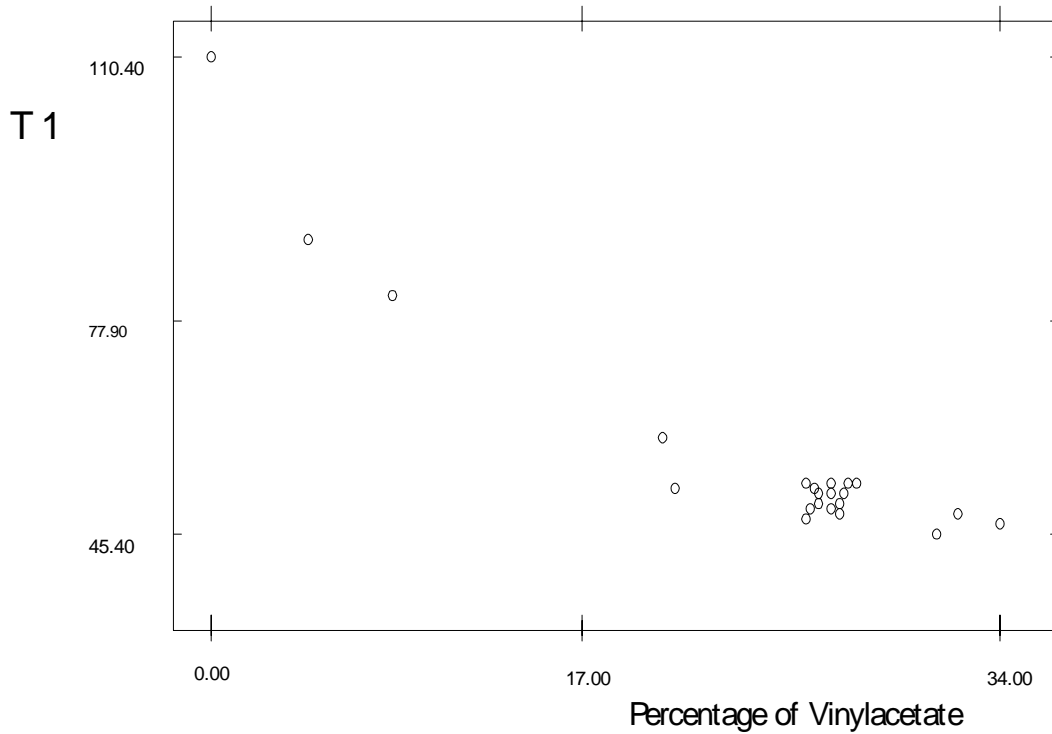
Results: T_1 (msec) measured as a function of the percentage of vinylacetate (see plot).

T_1 is observed to decrease as the vinylacetate content of the samples increases.

Remarks:

- Measuring time per sample approximately 1 minute
- Sample preparation: none
- Results independent of 'melt index' (*i.e.* molecular weight) of sample

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11 Degree of Polymerization of a Polymethacrylate

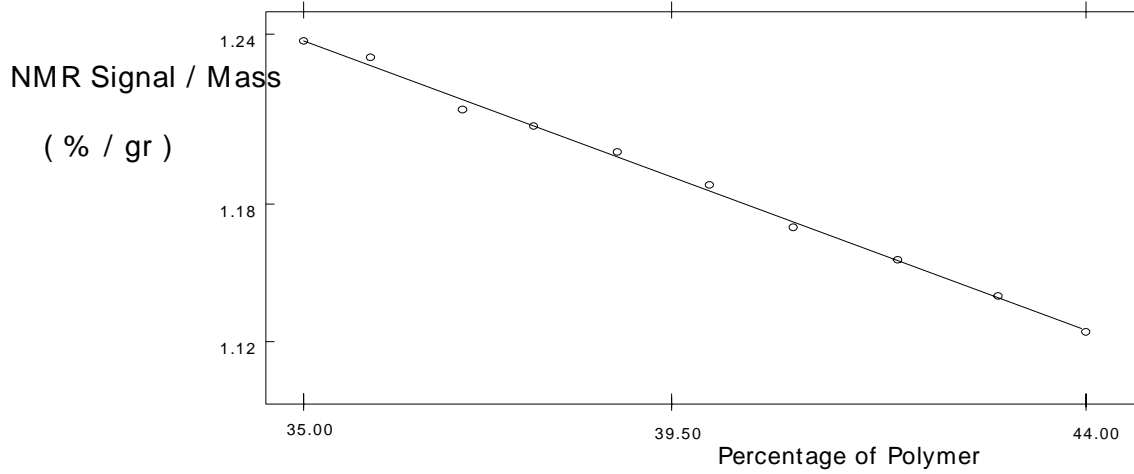
Type of Application: Absolute Application, using weight normalised amplitude of Hahn-echo (90° - τ - 180° - τ - *measure* pulse sequence) for correlation with percentage of polymerization of polymethacrylate.

<u>Application Parameters</u>	
minispec Soft - EDM	spec_n_v
Receiver Gain	60 dB
Recycle Delay Time	2 sec
Bandwidth	narrow
Detection Mode	magnitude
Number of Scans	5
Pulse Separation	$\tau = 1$ msec
Probehead Type	Absolute
minispec System	mq20 with PA203

<u>Results:</u> Calibrate Mode:	Linear Correlation:	0.996
	Slope:	-0.0131
	Intercept:	1.700
Measure Mode:	% Polymer (given)	% Polymer (NMR)
	44.0	44.0
	43.0	43.0
	42.0	42.0
	41.0	41.2
	40.0	39.8
	39.0	38.8
	38.0	38.0
	37.0	37.5
	36.0	35.7
	35.0	35.0

Remarks: - Measuring time per sample approximately 10 seconds
 - Sample preparation: weighing and thermostating

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12 Plasticizer in PVC Foils

Type of Application: Absolute Application, using weight normalised amplitude of free induction decay (FID) for correlation with percentage of plasticizer.

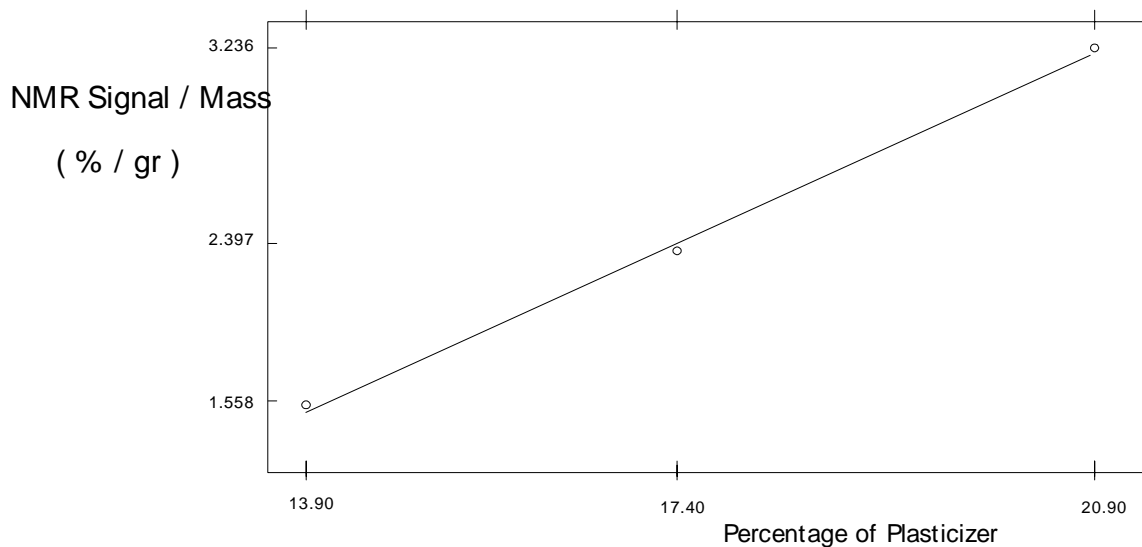
Application Parameters

minispec Soft - EDM	fid_n_v
Receiver Gain	80 dB
Recycle Delay Time	1 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Centre of Sampling Window	30 μ sec
Probehead Type	Absolute
minispec System	mq20 with PA203

<u>Results:</u> Calibrate Mode:	Linear Correlation:	0.995
	Slope:	0.240
	Intercept:	-1.807
Measure Mode:	% Plasticizer (given)	% Plasticizer (NMR)
	17.4	17.2
	18.3	18.1
	18.2	17.9
	16.6	16.2
	20.9	21.1
	13.9	14.1

Remarks: - Measuring time per sample approximately 25 seconds
 - Sample preparation: weighing and thermostating at T = 40 °C

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13 Vinylacetate in Polyvinylacetate/Polyvinylchloride

Type of Application: Absolute Application, using weight normalised amplitude of free induction decay (FID) for correlation with percentage of vinylacetate.

Application Parameters

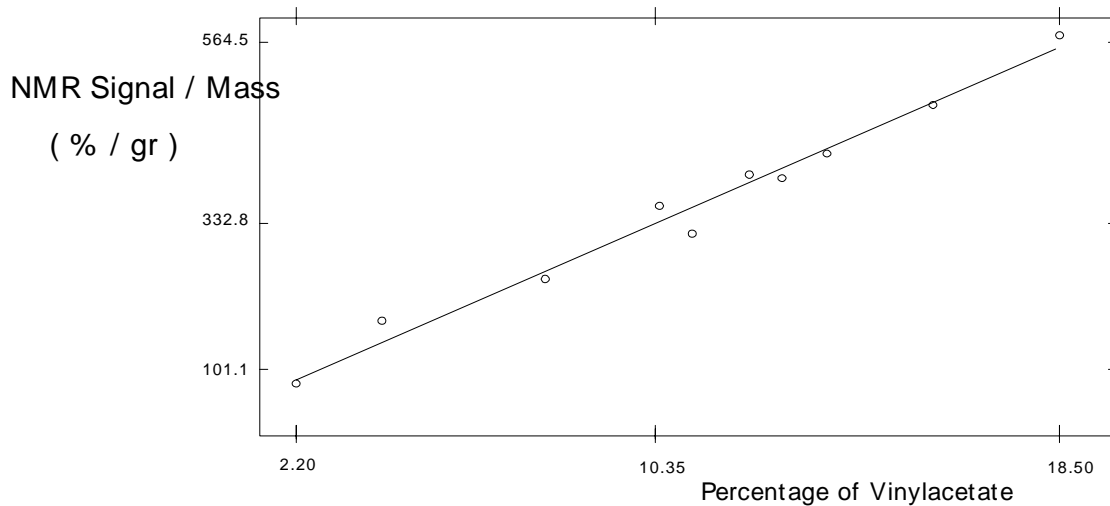
minispec Soft - EDM	fid_n_v
Receiver Gain	90 dB
Recycle Delay Time	2 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	10
Centre of Sampling Window	50 µsec
Probehead Type	Absolute
minispec System	mq20 with PA203

<u>Results:</u> Calibrate Mode:	Linear Correlation:	0.958
	Slope:	25.77
	Intercept:	50.61
Measure Mode:	% VA (given)	% VA (NMR)
	2.2	2.0
	4.2	5.4
	8.0	7.4
	10.7	12.0
	13.1	13.6
	14.1	13.3
	15.0	14.4
	16.6	16.5

Remarks:

- Measuring time per sample approximately 20 seconds
- Sample preparation: weighing and (for best accuracy) thermostating
- Quoted accuracy of standard values approximately $\pm 1 - 2 \%$

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14 Butadiene in Polystyrene/Polybutadiene

Type of Application: Absolute Application, using weight normalised amplitude of free induction decay (FID) for correlation with percentage of butadiene. Tempering at T = 100°C is important.

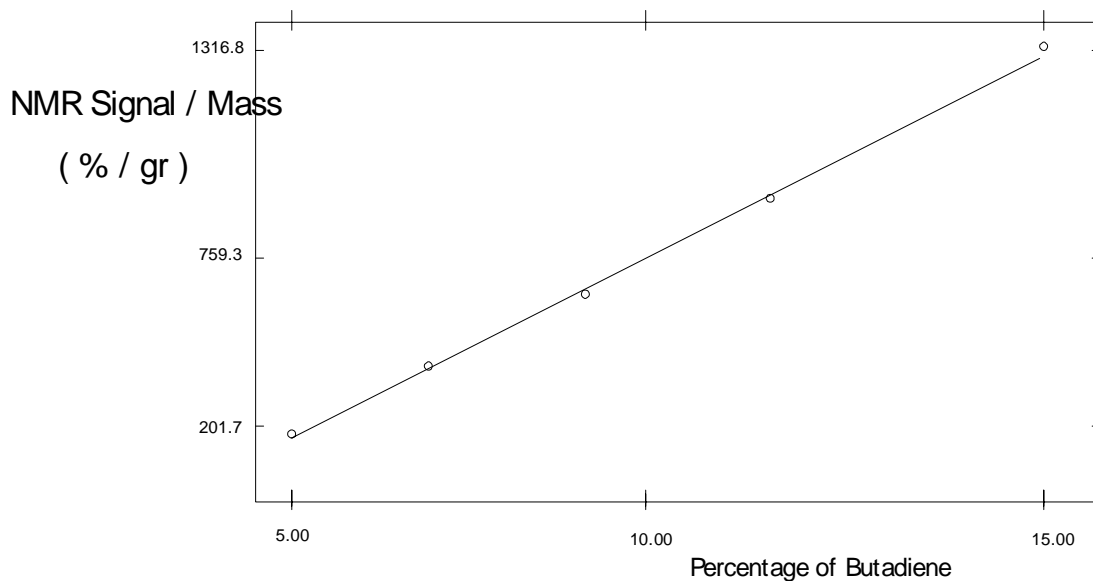
Application Parameters

minispec Soft - EDM	fid_n_v
Receiver Gain	70 dB
Recycle Delay Time	0.5 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	5
Centre of Sampling Window	70 µsec
Probehead Type	Absolute
minispec System	mq20 with PA203

<u>Results:</u>	Calibrate Mode:	Linear Correlation:	0.997
		Slope:	110.36
		Intercept:	-364.43
	Measure Mode:	% BD (given)	% BD (NMR)
		5	5.1
		7	7.0
		9	8.7
		12	12.1
		15	15.2

Remarks: - Measuring time per sample approximately 3 seconds
 - Sample preparation: weighing and thermostating at T = 100 °C

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15 Mobile Component in Polypropylene (R₂₁ - Value)

Type of Application: Ratio Application, using the corrected ratios of two amplitudes on the free induction decay (percent liquid) for correlation with percentage of mobile polypropylene (R₂₁ - value). Tempering at T = 50 °C is important.

Application Parameters

minispec Soft - EDM	sc_lc_co
Receiver Gain	70 dB
Recycle Delay Time	2 sec
Bandwidth	broad
Detection Mode	magnitude
Number of Scans	25
Probehead Type	Ratio (VTS)
minispec System	mq20 with PA207

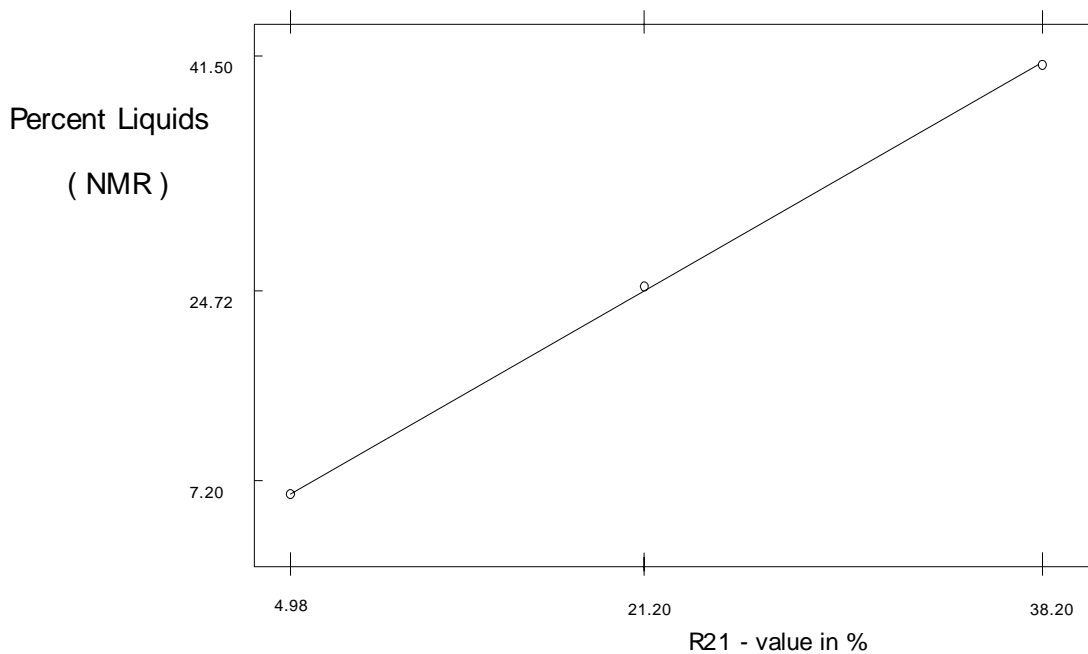
Results: Calibrate Mode: Linear Correlation: 0.997
 Slope: 1.210
 Intercept: 0.001

Percentage of liquids (NMR) plotted against R₂₁ - reference values (given).

Remarks:

- Measuring time per sample less than one minute
- Sample preparation: thermostating at T = 50 °C
- Advantage of this method is that no sample weighing is necessary.

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B Summary and Outlook

As pointed out in the introduction, this dossier provides a sample of polymer applications that we are able to share publicly. We are not able to cover the complete field of polymer applications for reasons of confidentiality. However the applications included herein demonstrate the great potential of low field pulsed NMR as an analytical method for the polymer industry. It is easy to predict that the use of this method will continue to expand in the future, especially in this industry. More and more facilities have realized that the addition of relatively simple, table-top, low resolution pulsed NMR capability is particularly important if costs are to be reduced and productivity needs to be increased.

A few aspects of further and future applications are:

- Numerous scientific papers report NMR measurements on polymers at high temperatures (above 120°C). These temperatures are especially suitable for investigating the characteristics of polymers. The next step is to extend this capability to routine investigations and for this reason Bruker has developed a special variable temperature probehead for the NMS-series minispec which can be used in the range of -100 °C to +210 °C.
- Encouraging results have been derived from NMR signal curve analysis, more specifically, the fitting of NMR signals with suitable mathematical functions in order to describe the components of the signal. It seems that very reproducible results can be obtained with these methods. Bruker minispecs are already being used for these kind of investigations. The stand-alone system software offers all the necessary mathematical features. This seems to be the right time for methods that rely on curve fitting to be transferred from research to production control. A further step in this development is available in Bruker's software package *WIN-NMS* for Windows 95, which is available for the NMS system as an option. *WIN-NMS* controls the Bruker NMS-series minispec from a personal computer through a network connection. Curve fitting algorithms are an integral part of this package.