

Comparison of the Solid State CPMAS and Solution Carbon-13-NMR Spectra of Humic Acids Extracted from Composted Municipal Refuse

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The solution and CPMAS spectra of humic acids extracted from the composted municipal refuse of three Spanish cities (Sevilla, Granada and Puerto Real) have been obtained at 75.4 MHz.

The spectra are discussed qualitatively and the signals assigned to the various chemical structures forming the humic acids.

It is attempted to learn the limits for the quantitative determination of signal areas for the different chemical structures.

It is concluded, that aliphatic- and carbohydrate structures contribute most to these compounds.

Introduction

In a previous paper [1] the title compounds were characterized by a variety of chemical and physical methods. The latter including solution C-13-NMR spectra at 25.2 MHz. Although these spectra revealed considerable details of the chemical structure and composition, the poor signal to noise ratios obtainable with the old spectrometer did not permit the attempt to evaluate the spectra quantitatively. The results given in the following were obtained at 75.4 MHz. Their signal to noise ratio is much higher than found in the old data thus permitting a more detailed discussion of the spectral features. In addition it was possible to vary for the humic acids the experimental conditions for the solution spectra and also to obtain several solid state C-13 CPMAS-spectra. These data will be taken in the following for the better description of the humic acids of the previous publications and in addition they should contribute to the still controversial question, whether C-13-NMR-spectra can be evaluated quantitatively [2].

Experimental

The preparation of the samples has been given previously [1]. The solution spectra were obtained from 150 mg of the freeze dried humic acids from municipal refuse from Sevilla (HA-S), Puerto Real

(HA-PR) and Granada (HA-G) dissolved in 3 ml 0.5 normal sodiumhydroxide. They were taken on a Bruker MSL-300 Spectrometer at 75.4 MHz under continuous broad band decoupling conditions with 90° RF pulses and pulse delays of 0.5 s. The decoupler power was 100 W with an attenuation of 25 dB. In the case of HA-S in a second experiment a pulse delay of 5 s was used in order to study the influence of the different longitudinal relaxation times upon the relative intensities. 30,000 free induction decays were accumulated for each sample. The sweep width was 25 kHz, the filter width was set to 30 kHz. 8192 points were sampled for each FID, yielding an acquisition time of 0.164 s. The solution spectra are calibrated against an external capillary filled with TMS. No attempts were made to correct for magnetic susceptibility effects. The chemical shifts given are judged reliable to ± 1 ppm. The solid state spectra were obtained at the same frequency on a Bruker CXP-300 under Cross-polarisation-magic-angle-spinning-conditions (CPMAS). The pulse delay was 5 s, the contact time 1 ms. For each spectrum 1000 cycles were accumulated. The sweep width was 31.25 kHz, the filter width was set to 37.5 kHz. The data table had a size of 1 K. The acquisition time was 0.016 s. The MAS rotation frequency was varied between 4.3 and 5.08 kHz.

Results and Discussion

The solution spectra are compiled in Fig. 1. Although the spectra appear fairly different at first

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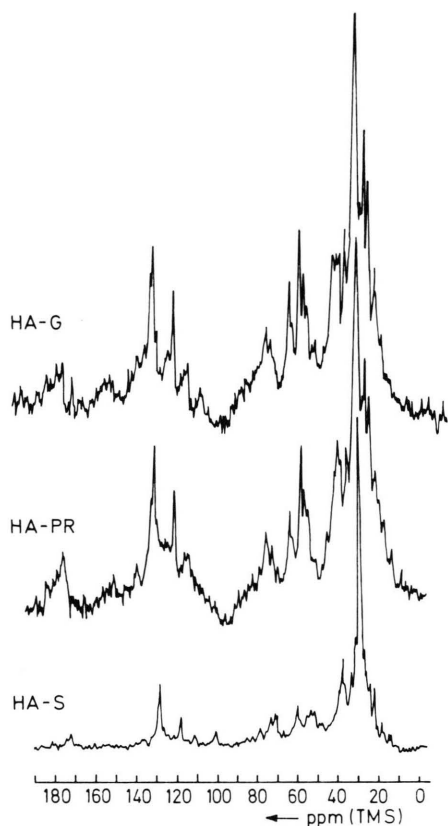


Fig. 1. 75.4 MHz C-13 NMR solution spectra in D₂O of the humic acids extracted from the municipal composts of the cities Sevilla, Granada, Puerto Real. Pulse delay 0.5 s.

sight, a closer inspection shows, that they are qualitatively and quantitatively very similar the most pronounced difference being the much higher resolution and signal to noise ratio of the HA-S-sample. The experimental progress is most impressive, when these spectra are compared to the 25.2 MHz spectra of the previous publication [1]. The exceptionally high signal to noise ratio of the HA-S sample can be explained either by a higher amount of low molecular weight products in this probe or by a higher fraction of more mobile groups.

Fig. 2 contains the expanded aliphatic region of the HA-S spectrum. At least 15 lines are discernible and can be used for the attempt of an assignment.

Considering the probable composition of the starting material for the composting, a fairly detailed assignment of most of the lines can be given. The organic, slowly decomposing fraction consists partly of wood and cellulose decomposition products. Signals corresponding to these compounds are seen in the chemical shift region 130 and 50 ppm. Where at the low field side well resolved lines for aromatic lignin units are seen, and also the methoxyl peak at 53 ppm is a strong indication for the presence of this product. Overall however the aromatic region of these spectra is less prominent than in humic acids extracted from soils [3]. In the chemical shift range between 100 and 60 ppm the resolved peaks can all be assigned to carbohydrates consisting of glucose containing oligo-

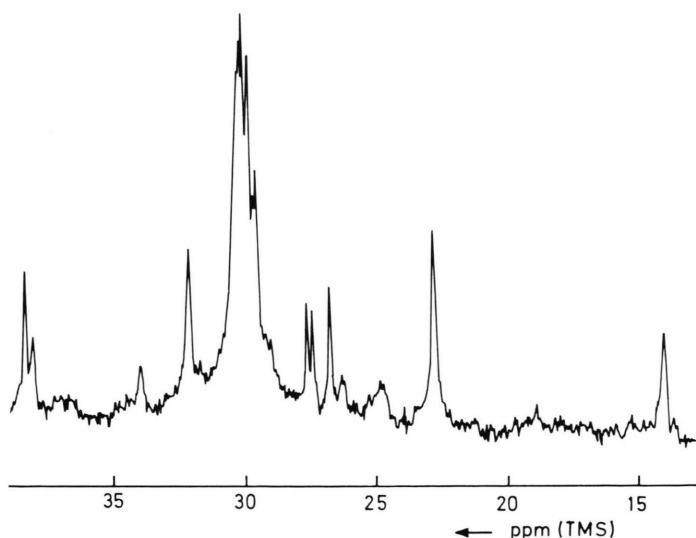


Fig. 2. Expanded spectrum of the aliphatic region of HA-S.

Table I. Possible assignments of the C-13 signals in the low field region of the humic acid spectra.

[ppm]	Possible assignments
~ 170	COOH groups
129.5	arom. C-atoms C-1 in Phenylcumaran
119	arom. C-atoms C-6 in Guajacyl
101.6	C-1' in cellobiose or anomeric C-atom in amylose
79.6	C-4 in cellobiose or C-4 in amylose
74.3	C-3, C-5 in amylose or cellobiose
72.5	β -2, C-2' in cellobiose
71.5	α -3, α -5, α -2 in cellobiose
60.8	C-6 in cellobiose
~ 53	OCH ₃ in carbohydrates or lignine derivatives

and polysaccharides. This region is less pronounced than in the soil humic acids [3]. Possible assignments for this range are compiled in Table I. The most intense lines in these spectra are seen in the range, where the pure hydrocarbon signals appear. Especially in the HA-S sample many well resolved lines are apparent, that permit interesting conclusions. Table II compiles possible assignments. An inspection of these data makes it obvious, that this region of the spectrum cannot be described by long chain *n*-alkyl groups alone, but that in addition branched alkyl groups have to be considered. The origin of the latter groups remains unknown.

In Fig. 3 the C-13 CPMAS-spectrum of HA-S is given. The most striking difference is, that the spectral region between 150 and 200 ppm which repre-

Table II. Possible assignments of the C-13 signals in the high field region of the humic acid spectra.

[ppm]	Possible assignments in linear alkyl groups
13.99	methyl groups in long alkane chains, <i>e.g.</i> C-1 in <i>n</i> -decane 14.0, in <i>n</i> -nonane 13.9
22.73	C-2 in longer alkanes, <i>e.g.</i> <i>n</i> -pentane 22.6, <i>n</i> -nonane 22.9
29.48	C-4 in <i>n</i> -heptane and <i>n</i> -octane 29.3 resp. 29.5
29.80	C-4 in <i>n</i> -nonane and <i>n</i> -decane 29.7 resp. 29.8
30.00	C-5 in <i>n</i> -nonane and <i>n</i> -decane 30.0 resp. 30.1
32.07	C-3 in <i>n</i> -hexane and longer chains 31.9–32.3
[ppm]	Possible assignments in branched alkyl groups
26.69	C-4 in C-2 methylated long chain alkanes, <i>e.g.</i> 2-methylheptane 27.2
27.38	methylated C-2 in longer alkanes, <i>e.g.</i> 2-methylheptane 27.2
37.97	C-3 in C-2 methylated long chain alkanes
38.25	

Literature values taken from: Breitmaier, 1978; Bremser, 1981; Hesse, 1984.

sents the carboxyl groups is much more pronounced in the solid state spectra, than in the solution spectra. These signals, which stem from quarternary carbon atoms are obviously partially saturated in the solution spectra when a pulse delay of 0.5 s is applied. In additional experiments, the pulse delay for the HA-S

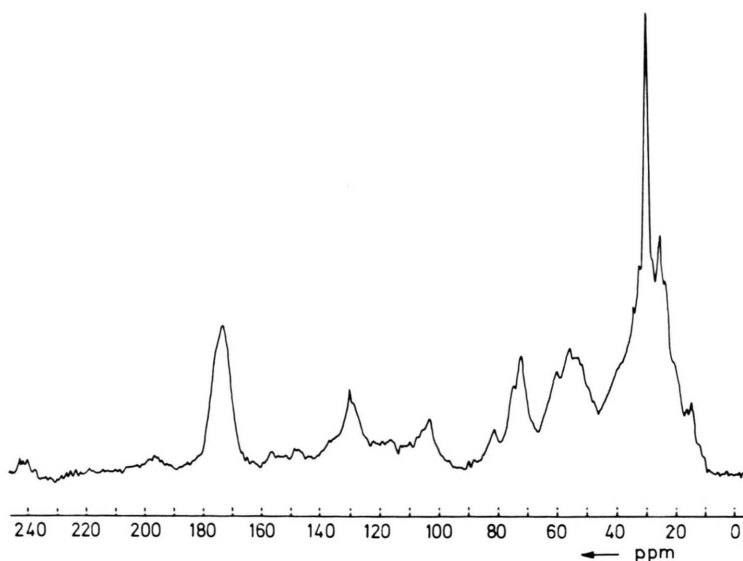


Fig. 3. 75.4 MHz CPMAS spectrum of HA-S. Rotation frequency 5.08 KHz.

Table III. Quantitative evaluation of the HA-S spectra.

	Chem. shift groups [ppm]	10–46 aliphatic	46–110 alcoholic	110–150 aromatic	150–200 carboxylic
CPMAS	Rotation frequency 5.08 KHz	42%	30%	13%	15%
	Rotation frequency 4.64 KHz	42%	30%	13%	15%
	Rotation frequency 4.30 KHz TOSS ^a	39%	24%	18%	19%
Solution	Pulse delay 0.5 s	57%	29%	13%	1%
	Pulse delay 5.0 s	53%	24%	13%	10%
Total area equal 100%					

^a TOSS = total spinning side band suppression.

solution was raised to 5 s. This led to a significant increase of the carboxyl peak. However, a comparison of the resp. numbers in Table III shows, that it is still less intense than in all solid state spectra. No further relative intensity changes were seen, when the pulse delays were raised to 15 s. Saturation of the lines in the solution spectra can thus only in part explain the quantitative difference between CPMAS and solution spectra. Comparison of the spectra in Fig. 1 and 3 reveals, that the solid state spectra show a much lower resolution than the solution spectra. With spectra of the quality of Fig. 3 no detailed assignments of the aliphatic structures is possible.

Finally it was attempted to determine the relative concentrations of the four classes of carbon atoms from the area under the signals. The results are compiled in Table III. Obviously the data of the solution spectra and the CPMAS-spectra show at best qualitative agreement. Even in the totally relaxed solution spectrum (HA-S pulse delay 5 s) the carboxyl groups show a greatly reduced contribution compared to the solid state spectra. The aliphatic region on the other

hand is much more pronounced in the liquid state spectra. Deviations in the intensity of the alcoholic and aromatic groups appear tolerable. Attempts to eliminate spinning side bands by the TOSS-pulse-program (Total Suppressing of spinning side bands) does lead to significant intensity distortions, showing the hazards of the application of this program to moderately resolved spectra. It is quite obvious, that the complicated magnetisation transfer occurring in the process of cross polarisation, will render the quantitative analysis of spectra *via* the determination of relative peak areas fairly hazardous [4]. The situation could probably be a little improved, when systematic variations of the experimental conditions during CPMAS-measurements, such as numbers of contacts per cycle and contact times are varied and their influence on relative intensities studied.

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