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COMMUNICATION

Detection of environmental polyorganosiloxanes (silicones) by silicon-29 NMR spectroscopy

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The utility of ^{29}Si NMR spectroscopy has been demonstrated on sediment-like materials in the quantitative and qualitative determination of polyorganosiloxanes (silicones) in selected environmental samples. This technique is highly selective for polydimethylsiloxanes (PDMS) and is non-destructive to the sample. Also, specific identification of polyorganosiloxanes in sediment is possible, in contrast to previous methods which provided only quantitative information while consuming the sample. The detection limit for a 9 h experiment is approximately 45 ppm.

Keywords: polyorganosiloxanes, ^{29}Si NMR, polydimethylsiloxanes, sediments

INTRODUCTION

The presence of polyorganosiloxanes (silicones) in the sediments of a number of aquatic systems has been demonstrated over the past ten years.[1-5] Unfortunately, the method of analysis in each of these studies involved an instrumental technique that either destroyed the sample[1-3] or required the polyorganosiloxane to be re-extracted from potassium bromide (KBr) in order to be studied further.[4] In addition, previous methods, while providing highly precise data on the total concentration of silicon (which can be used to estimate the polyorganosiloxane concentration in the sample), were unable to define the specific species (e.g. dimethyl-, diphenyl-, or methylphenylsilicone) present.

Present work involving polydimethylsiloxane analysis by silicon-29 nuclear magnetic resonance (^{29}Si NMR) spectroscopy has demonstrated the utility of the INEPT (Insenstive to Nuclei Enhanced Polarization Transfer) NMR pulse sequence for the analysis of low-concentration polyorganosiloxane solutions. The ^{29}Si Fourier Transform (FT) NMR–INEPT method is both non-destructive and finely tuned to detect silicon–hydrogen two-bond couplings in various polyorganosiloxane polymers. The resulting NMR spectra are highly specific for silicon-containing compounds in general and specifically for the polysiloxanes under study.[6a, b]

EXPERIMENTAL

Sampling

The material used in this study was waste filter-cake obtained from the Blue Plains Wastewater Treatment Plant, Washington, DC, USA. This material was chosen both for its similarity in texture and chemical nature to sediments and also because of the documented presence of polyorganosiloxane in the samples.[1]

Sample processing

Approximately 1 dm^3 total of filter cake was placed in two clean (chloroform-rinsed) glass jars and freeze-dried. Two samples of the freeze-dried material (approximately 9 g each) were placed in Whatman cellulose thimbles and extracted for 3 h with 100 cm^3 $(C_2H_5)_2O$ in all-glass Soxhlet apparatus. The liquid was then rotary-evaporated to

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dryness and the solid residue taken up to approximately 5 cm^3 with siloxane-free chloroform. The liquid samples were then filtered using a 0.22 Millipore Type HA filter apparatus to remove small particulate matter. The resulting liquid was yellow in color and had a noxious odor but was visibly free of turbidity or particulate matter. Solution homogeneity is important in NMR analysis since small-particulate matter can cause spurious results.

Instrumental

Approximately 2 cm^3 of the above solutions were combined with 10 drops of $CDCl_3$ (necessary for internal lock on the NMR). The $CDCl_3$ contained 1% v/v TMS which was used as a chemical shift reference. It should be noted that even the minute amount of TMS present in the $CDCl_3$ was sufficient to give a reference peak that was immense compared with the siloxane peak. No additional TMS should be added, as excess TMS hampers the sensitivity of the spectrometer.

Samples were then scanned for approximately 9 h (nearly 30 000 transients) on an IBM 200 mHz (^{1}H frequency) FT-NMR spectrometer which was equipped with a Bruker ^{29}Si probe (10 mm) and dedicated ^{29}Si preamp (39.76 MHz).

The details of the INEPT polarization transfer pulse sequence are given in the literature.[7,8] In general, the INEPT technique allows the experiment to be linked to the relaxation of the hydrogen nucleus rather than the silicon nucleus. As the relaxation time of the silicon nucleus in polyorganosiloxane is on the order of 60 times greater than that of the hydrogen nucleus,[9] considerable time is saved by using this method. It would take approximately three days to obtain the requisite number of scans that can be obtained in 9 h using an INEPT sequence to improve the signal-to-noise ratio and to simplify the spectrum. The advantages of this NMR technique are significant due to the non-destructive nature of the experiment and the extreme specificity of the chemical shift information obtained for siloxane-type compounds.

Previous reports on silicon NMR[10] have shown the advantages of paramagnetic relaxation agents such as chromium(III) acetylacetonate $[Cr(acac)_3]$ in reducing the long relaxation times of the silicon nuclei, for example in silicones. This addition of relaxation agents such as $Cr(acac)_3$ was deemed unacceptable for this study due to the line broadening that occurs in low-concentration solutions.

A further advantage of the INEPT pulse sequence is that it is very specifically linked to the coupling of the silicon atoms with methyl hydrogens (e.g. the organosilicon species). The INEPT sequence will not be affected by direct Si–H or Si–C coupling, which of course is a situation beneficial to the experimental analysis of environmental polydimethylsiloxanes. These other resonances could clutter the spectrum and possibly mask peaks of environmental interest.

RESULTS AND DISCUSSION

^{29}Si-INEPT (decoupled) spectra of a typical sample of extracted filter-cake were recorded after 10 400 and 28 942 scans, respectively, with the former demonstrating a typical spectrum at a point representing an early appearance of the siloxane peak. The resonance located at -21.9 ppm corresponds to 500 cs polydimethylsilicone (PDMS) fluid.[11] This resonance can be assigned to the specific PDMS compound for several reasons:

(a) the INEPT sequence used is highly specific for PDMS compounds,
(b) the resonances of several various PDMS compounds are well defined in the -21 to -22 ppm range (relative to TMS), and
(c) short-chain polymers would give separate peaks for each of the silicon atoms in the chain, while the signals collapse to a single peak in longer-chain polymers.

Since previous work[1] has shown the concentration of silicones in the filter-cake examined to be approximately 45 ppm, the limit of detection for an approximately 10 000-scan (3 h) experiment is approximately 45 ppm. The lower limit of detection could be decreased further simply by increasing the number of scans, although a practical limit to sensitivity will eventually be reached since the signal-to-noise ratio increases proportionally to the square root of the number of scans.

Several distinct advantages of the NMR technique reported in this study should be noted. Perhaps most important (given the general difficulty in obtaining large numbers of suitable samples) is the fact that, upon completion of the experiment, the sample may be used again for another analysis under different conditions (e.g.

to detect silicon in compounds other than polyorganosiloxanes) or for analysis by a totally different technique (e.g. atomic absorption for quantitative determination of the total amount of silicon present in the sample). Also of considerable importance is the high degree of compound specificity provided by the technique. Since chemical shift values for the polyorganosiloxanes are already present in the literature,[6b] a spectrum obtained from environmental material can be correlated quickly and with good accuracy with known compounds.

In the past, most NMR techniques have been generally unacceptable for use in a quantitative sense because of problems with line broadening and reproducibility of the integrals used in the measurements. Preliminary work with quantitative solutions of octamethylcyclotetrasiloxane (OMCTS or D_4) has demonstrated that by using precisely the same conditions in the NMR–INEPT experiments, a linear calibration plot of very good correlation can be generated in the part-per-thousand concentration range. Further work in this area will attempt to determine more quantitatively the amounts of PDMS compounds in filter-cake and sediment cores.

CONCLUSIONS

This study demonstrates the application and utility of a new analytical method, ^{29}Si FT-NMR with an INEPT pulsing sequence, for the determination of silicones in environmental samples. The techniques is both non-destructive to the sample and highly specific to the desired compounds. Additional work will show the application of this technique to sediment samples, as well as the quantitative determination of silicones in these samples.

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