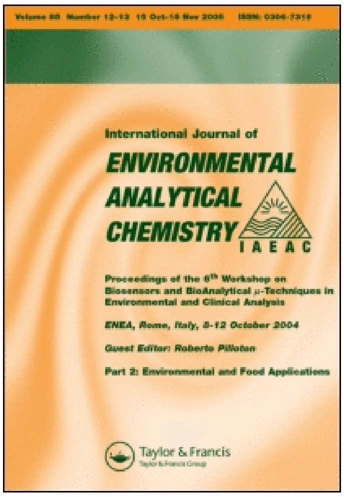

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^{119}Sn-NMR Study on Bis(Tri-Butyltin)oxide Derivatives of Phenolic Compounds

E. Kolehmainen[a]; J. Paasivirta[a]; R. Kauppinen[a]; T. Otollinen[a]; S. Kasa[a]; R. Herzschuh[b]
[a] Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland [b] Karl-Marx-Universität, Sektion Physik und Chemie, Zentrallabor für Kohlenanalytik, VEB Chemieanlagenbaukombinat Leipzig-Grimma, Leipzig, DDR

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^{119}Sn-NMR STUDY ON BIS(TRI-BUTYLTIN)OXIDE DERIVATIVES OF PHENOLIC COMPOUNDS

E. KOLEHMAINEN, J. PAASIVIRTA, R. KAUPPINEN, T. OTOLLINEN and S. KASA

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä, Finland

R. HERZSCHUH

Karl-Marx-Universität, Sektion Physik und Chemie, Zentrallabor für Kohlenanalytik, VEB Chemieanlagenbaukombinat Leipzig-Grimma, Linnestr. 5/Talstr. 35, 7010 Leipzig, DDR

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^{119}Sn-NMR spectroscopy has been utilized in the characterization of various phenolics as their bis(tri-butyltin)oxide, TBTO, derivatives. The present method has been applied both for determination of simple model compounds and for characterization of complex biopolymeric material originating from spent bleach liquor fractionated by an ultrafiltration technique. Based on the large range of ^{119}Sn-NMR chemical shifts of TBTO derivatives of the phenolic compounds and the similar relaxation properties of ^{119}Sn nuclei located in those derivatives, both qualitative and quantitative analytical conclusions can be drawn.

KEY WORDS: ^{119}Sn-NMR spectroscopy, determination of phenolics, spent bleach liquor.

INTRODUCTION

^{119}Sn-NMR spectroscopy has been shown to be useful in the characterization of phenolics as their bis(tri-butyltin)oxide, TBTO, derivatives in coal liquefaction products.[1,2] Both qualitative and quantitative analytical conclusions can be drawn when comparing these results with the ^{119}Sn-NMR data of the TBTO derivatives of the model compounds and their mixtures.[1–3] Further, ^{119}Sn-NMR spectroscopy has been applied to evaluate the extent of σ-π conjugation in related benzyltin compounds.[4]

The ^{119}Sn isotope with a nuclear spin of 1/2, a natural abundance of 8.6% and a relative receptivity of 25.2 (the corresponding value of the ^{13}C isotope is set to 1.0),[5] has been proved to be a practical NMR nucleus. In addition, ^{119}Sn-NMR signals can be efficiently enhanced by polarization transfer via the proton magnetization using the INEPT pulse sequence.[6]

Various phenolics found in pulp mill effluents form a remarkable source of environmentally harmful chemicals.[7,8] Therefore, the present study is aimed at developing useful analytics for the determination of various phenolics as structural fragments of chlorolignins and related chlorine-containing biopolymers formed in the chlorobleaching of pulp in kraft pulp mills. The determination of these complex structures has proved to be a difficult task if performed solely by conventional, analytical methods.

EXPERIMENTAL

All model phenolics studied as well as TBTO were commercially available p.a. products and were used without further purification.

The bis(tri-butyltin)oxide TBTO derivatives of phenol, *o*- *m*- and *p*-cresol, thiophenol, *o*-chlorophenol, salicyl alcohol, 1,2-dihydroxybenzene (catechol), 1,2,3-trihydroxybenzene, 1,2,4-trihydroxybenzene, 2,4,6-trihydroxybenzaldehyde and induline were prepared by refluxing them with TBTO in toluene.[9]

Six samples of waste water taken from the acid chlorination stage (spent bleach liquor, SBL) of a kraft pulp mill were separated into three fractions with an ultrafiltration method.[10] The concentrated fractions as well as part of the original SBL sample were reacted with TBTO similarly as the model compounds mentioned above.

The proton-decoupled ^{119}Sn-NMR spectra of the TBTO derivatives of the phenolics were measured with a Jeol GSX 270 FT NMR spectrometer. The measuring conditions were as follows: spectrometer frequency 100.62 MHz, spectral width 5 KHz, digital resolution 1 Hz, number of scans 1000 in the case of model compounds and their mixtures and 10 000 in the case of SBL samples, pulse delay 10 s and flip angle 90°. An apodization with a 10 Hz exponential line broadening factor was used prior to FT to improve the S/N ratio. The chemical shifts were referenced to the resonance of an external $(CH_3)_4Sn$, TMSn, sample inserted coaxially in the NMR tube.

EPR spectra of TBTO derivatives of polyhydroxyaromatics in $CDCl_3$ under reduced pressure were measured by a Bruker ESP 380 ST EPR spectrometer under the following conditions: microwave frequency 9.4 GHz, microwave power 0.502 mW, field center 3339.55 G, sweep width 24.9 G and data resolution 4096 points.

RESULTS AND DISCUSSION

The general structure of TBTO derivatives of monohydroxyaromatics is: phenyl-O-$Sn(Bu)_3$.[1,2] The derivatization of di- and trihydroxyaromatics probably results in complicated structures and/or some paramagnetic species as will be discussed later.

The ^{119}Sn-NMR chemical shifts of the TBTO derivatives of the model compounds studied varied from 50 to 124 ppm (see Table 1). ^{119}Sn-NMR spectra of the TBTO derivatives of *o*-, *m*- and *p*-cresol, thiophenol and *o*-chlorophenol are shown in Figure 1. As can be seen they all give spectra characterized by sharp

Table 1 ^{119}Sn-NMR chemical shifts of TBTO derivatives of various compounds containing phenolic groups referenced to the signal of $(CH_3)_4Sn$

TBTO derivative of	*Solvent*	*Temp. (°C)*	*δ (ppm)*
Phenol	50%/Aceton-d_6	30	107.7
Phenol	50%/$CDCl_3$	60	103.3
o-Cresol	50%/$CDCl_3$	60	104.2
m-Cresol	50%/$CDCl_3$	60	105.4
p-Cresol	50%/$CDCl_3$	60	102.8
o-Chlorophenol	50%/$CDCl_3$	60	119.6
Thiophenol	50%/$CDCl_3$	60	73.6
Thiophenol	50%/$CDCl_3$	30	73.7
2,4,6-Trihydroxybenzaldehyde	50%/$CDCl_3$	60	123.9
2,4,6-Trihydroxybenzaldehyde	50%/$CDCl_3$	30	111.3
Salicyl alcohol	50%/$CDCl_3$	60	50–120[a]
Catechol	50%/$CDCl_3$	60	50 broad
1,2,4-Trihydroxybenzene	50%/$CDCl_3$	60	70 broad
Induline	neat + TBTO	90	94.0

[a] Complex multiplet.

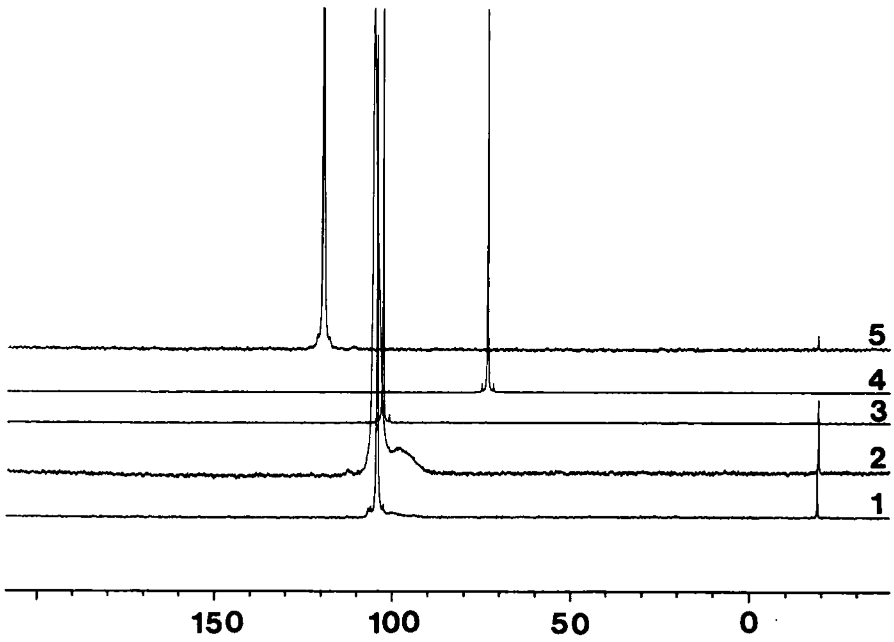

Figure 1 ^{119}Sn-NMR spectra of TBTO derivatives of *o*-cresol (1), *m*-cresol (2), *p*-cresol (3), thiophenol (4) and *o*-chlorophenol (5). The chemical shift scale is fixed to the chemical shift of an external $(CH_3)_4Sn$ sample.

resonances. A small signal at ca. −20 ppm originates from an impurity of TBTO. The chemical shifts are referenced to the signal of an external tetramethyltin, TMSn, sample measured earlier under similar conditions.

The large range of ^{119}Sn-NMR chemical shifts observed for the TBTO

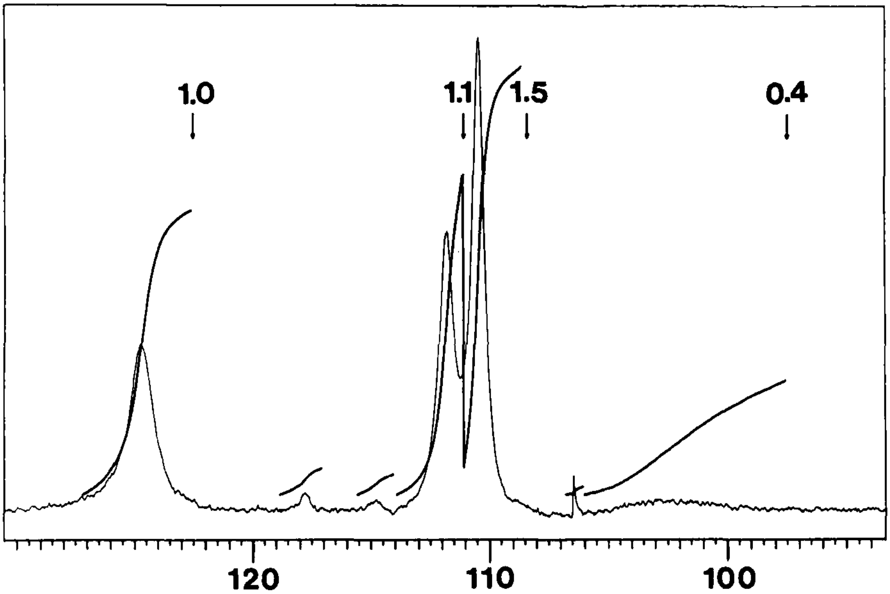

Figure 2 ^{119}Sn-NMR spectrum of the mixture of TBTO derivatives of *o*-chlorophenol, phenol, *p*-cresol and *β*-naphthol in $CDCl_3$. The molar ratios of the mixture are 1.0/0.9/1.3/0.3 and the corresponding ^{119}Sn-NMR intensities 1.0/1.1/1.5/0.4, respectively.

derivatives of the phenolics studied allows an easy assignment of signals from mixtures of various phenolic compounds (see Figure 2). The quantitative determination of the different phenolics by this method is also quite reliable. As an example, the molar ratios in a weighed mixture of *o*-chlorophenol, phenol, *p*-cresol and *β*-naphthol were 1.0/0.9/1.3/0.3 and the corresponding intensities of the ^{119}Sn-NMR signals 1.0/1.1/1.5/0.4.

In general, the ^{119}Sn-NMR signals of the TBTO derivatives studied are well resolved, but in the case of polyhydroxy compounds such as 1,2-dihydroxybenzene (catechol), 1,2,3-trihydroxybenzene and 1,2,4-trihydroxybenzene, there appeared only very broad NMR signals. Their widths at half height were greater than 20 ppm. This signal broadening may be due to some paramagnetic species present in the samples, since these samples also show strong well resolved signals in EPR spectroscopy. This phenomenon may open new analytical possibilities due to the high sensitivity of EPR spectroscopy. Work in this area is in progress now in our laboratory.

The ^{119}Sn-NMR spectra of the TBTO derivative of the total sample of SBL and TBTO derivatives of three fractions differing by their molecular size distribution separated by ultrafiltration are presented in Figure 3. Signals at 135, 105 and 95 ppm (overlaps partly with the signal of TBTO itself) were characteristic for the total, i.e. non-fractionated SBL sample (A). They were in the same shift range as the signals of the monohydroxyaromatics and induline used as model compounds (see Table 1). The 95 ppm peak was the only one observed in the largest-size fraction ($M_r > 100$ K; D). The 135 ppm signal appeared in the 10–100 K fraction

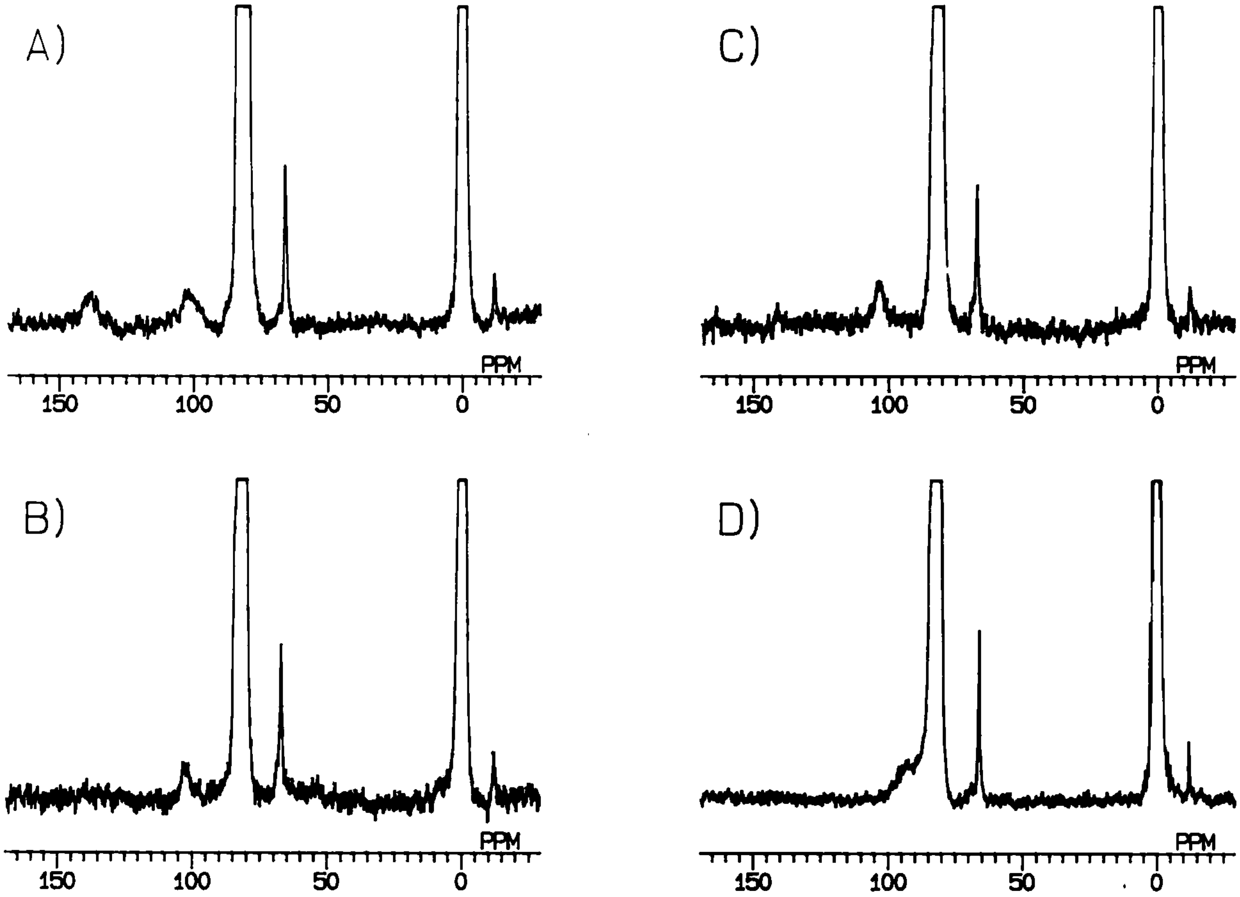

Figure 3 ^{119}Sn-NMR spectra of TBTO derivatives of a spent bleach liquor, SBL, sample taken from the process of a kraft pulp mill and its different molecular size fractions separated by ultrafiltration. A represents the total SBL sample and B, C and D fractions with a molecular weight range of 1–10 K, 10–100 K and > 100 K, respectively.

(C) only. The 105 ppm resonance was visible in the 1–10 K (B) as well as in the 10–100 K fractions (C). If signals exist in these spectra originating from polyhydroxyaromatics, they are too broad to be observed.

The strong signals in the spectra originate from the residual TBTO and TMSn used as the external reference. A special phenomenon is that a signal with a chemical shift of 61 ppm in the TBTO/TMSn reference sample, is shifted about 6 ppm in the low field direction after derivatization of the samples.

CONCLUSIONS

The present observations support the idea that TBTO derivatives of simple phenolics and their mixtures can be determined by ^{119}Sn-NMR spectroscopy.

The preliminary results dealing with the total SBL of a kraft pulp mill and its ultrafiltrated fractions suggest that SBL and its fractions contain different types of phenolic groups. For a more accurate analysis, a more efficient separation of the various species existing in the SBL samples is needed. The present results imply, however, that ^{119}Sn-NMR spectroscopy has some potential in the characterization of wood-originated biopolymers such as lignin and related structures, as their TBTO derivatives.

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