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Solid-state ^{13}C NMR spectroscopic studies of soil organic matter at two magnetic field strengths

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Abstract

The characterization of soil organic matter by solid-state ^{13}C NMR spectroscopy is increasingly being carried out on NMR spectrometers with higher magnetic fields, despite reservations about the quantitative reliability of spectra acquired at these high magnetic fields. In this study, the performance of 200 and 400 MHz spectrometers is compared for the quantitative analysis of two soil organic matter samples of contrasting composition. The higher spinning rate (10 kHz) required on the 400 MHz spectrometer to keep spinning side-band interference at a manageable level results in a 35–40% decrease in signal intensity for cross-polarization (CP) spectra. However, this signal loss is largely non-selective, with only a slight decrease in carbonyl and aromatic signal apparent at the higher field. There is no improvement in spectral resolution at the higher field. Sensitivity is similar for the two spectrometers, with increases in the amount of signal acquired per scan on the higher field instrument negated by the need for a longer delay between scans to allow for slower rates of relaxation. Introduction of a ramped-amplitude CP pulse improves sensitivity relative to the standard CP experiment, especially at high spinning rates, but does not affect relative quantitation. Sensitivity to the Hartman-Hahn match is much greater at the higher MAS rate required on the 400 MHz spectrometer. The robustness of the Bloch decay technique is confirmed, with near identical spectra produced at the two different magnetic fields, and no dependence of signal intensity on the rate of magic angle spinning. The RESTORE technique is used to investigate the causes of the dependence of CP signal intensity on the spinning rate.

Keywords: NMR spectroscopy; Soil organic matter; Cross-polarization; Spin counting; Bloch decay

1. Introduction

Solid-state ^{13}C NMR spectroscopy is one of the most powerful tools for the analysis of soil organic matter (Preston, 1996; Kögel-Knabner, 2000; Preston, 2001). Whilst it is easy to obtain a solid-state ^{13}C NMR

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spectrum of soil organic matter, it is not trivial to obtain one with optimal sensitivity and quantitation. There are a number of acquisition parameters that, if incorrectly set, can adversely affect sensitivity and quantitation. Many of these parameters are inter-related, making the task of optimization quite complex.

The traditional measures of NMR performance are resolution—the ability to identify separate resonances that have similar chemical shifts—and sensitivity—the ability to detect a signal above background noise. For the analysis of a heterogeneous material such as soil organic matter, a third measure—quantitation—is usually of even greater importance (Fründ and Lüdemann, 1989; Kinchesh et al., 1995; Preston, 1996; Mao et al., 2000; Smernik and Oades, 2000a, b; Keeler and Maciel, 2003). Quantitation refers to the uniformity of sensitivity across different samples or across different chemical environments in the same sample. The main purpose of NMR analysis of soil organic matter is usually to determine the relative proportions of broad functional group classes, for example, alkyl, O-alkyl, aromatic, carboxyl. The success of this approach relies on each ^{13}C nucleus producing the same amount of NMR signal. Under ideal conditions, and barring certain interferences, each nucleus will produce the same amount of signal, regardless of its chemical environment. However, in the case of solid-state ^{13}C NMR spectra of soil organic matter, it is not always possible to guarantee the ideal conditions required to obtain quantitative spectra (Fründ and Lüdemann, 1989; Kinchesh et al., 1995; Preston, 1996; Mao et al., 2000; Smernik and Oades, 2000a,b; Dria et al., 2002; Mao et al., 2002; Keeler and Maciel, 2003; Peuravuori et al., 2003).

The defining characteristic of an NMR spectrometer is the strength of the magnetic field. Whereas in solution-state NMR spectroscopy the dictum "bigger is better" is almost universally true, this is not the case for solid-state NMR spectroscopy. A stronger magnetic field does provide more signal per nucleus, but this advantage can be offset if higher rates of magic angle spinning (MAS) are required to overcome difficulties presented by spinning side bands (SSBs). There are hardware limitations for magic angle spinning—faster spinning rates may only be possible with smaller volume rotors (Keeler and Maciel, 2003), resulting in lower sensitivity, or may require the use of materials that give rise to interfering background signal. The efficiency of cross-polarization (CP) is also affected by the rate of magic angle spinning—at higher spinning speeds less CP signal is generated and this effect may not be consistent across the spectrum, i.e. some resonances can be more affected than others. Thus both sensitivity and quantitation can be compromised at higher magnetic fields. Relaxation rates also are affected by both magnetic field strength (Fründ and Lüdemann, 1989) and the rate of magic angle spinning. These relaxation rates have the potential to influence both sensitivity and quantitation in ^{13}C CP NMR spectra of soil organic matter.

Sensitivity and quantitation are often competing goals, with optimization of one coming at the expense of the other. In early applications of ^{13}C NMR to soil organic matter analysis, optimization of sensitivity had to take precedence in order to obtain a spectrum at all. However, large improvements in NMR hardware enabled the consideration of optimization of quantitation (Fründ and Lüdemann, 1989). The trade-off between sensitivity and quantitation has been discussed at length in relation to solid-state ^{13}C NMR analysis of coals (Snape et al., 1989 and references therein), the outcome being "general agreement" (Jurkiewicz and Maciel, 1995) that the less sensitive but more quantitative Bloch decay (BD) technique, otherwise known as direct polarization (DP), should be preferred over the more sensitive but less quantitative cross-polarization (CP) technique for the analysis of coals. The BD technique has also been shown to be more quantitatively reliable than CP for the analysis of soil organic matter (Smernik and Oades, 2000b; Keeler and Maciel, 2003), but CP remains the most widely used technique on account of its greater sensitivity. Recently, techniques have been described both to improve the sensitivity of BD (Mao et al., 2000; Mao et al., 2002; Keeler and Maciel, 2003) and to improve the quantitation of CP (Cook et al., 1996; Cook and Langford, 1999; Smernik and Oades, 2003).

The purpose of this paper is to compare the performance of two spectrometers of different field strengths (4.7 and 9.4 T) for the analysis of two contrasting soil organic matter samples, in terms of sensitivity, resolution and quantitation. The effect of different MAS rates is gauged for the higher field instrument. Furthermore, the performance of four different NMR techniques—CP, Bloch decay, CP-ramp and RESTORE—is compared for each combi-