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Communication

Elemental analysis by NMR

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ABSTRACT

We explore the possibility for elemental analysis by NMR. To keep the efficiency of the signal acquisition common for all spin species, we propose to fix the frequency and vary the magnetic field to cover the isotopes involved in a sample. We introduce constant-frequency receptivity for quantitative elemental analysis in the frequency-fixed NMR experiment. Field-variable NMR experiments are demonstrated using a cryogen-free superconducting magnet. In addition to elemental analysis in liquid solution, solid-state NMR under magic-angle spinning is also described.

1. Introduction

To analyze the composition of atoms in unidentified materials of chemical interest, a number of elemental analysis techniques have been established [1]. They include combustion method, Atomic Absorption Spectrometry (AAS) [2], Electron Probe Micro-Analyser (EPMA) [3], Electron Spectroscopy for Chemical Analysis (ESCA) [4], Inductively Coupled Plasma (ICP), Secondary Ion Mass Spectrometry (SIMS) [5], and so on. In most techniques, the sample is destroyed by the measurement, except for EPMA, which, however, can only analyze the elements on solid surfaces. Currently, there is no convenient way of nondestructive elemental analysis of bulk samples that include living organisms. In this work, we explore the possibility of complementing these existing techniques by NMR spectroscopy.

The NMR elemental analysis that we propose here can be categorized into those observing isotopes. The isotopes can be identified by their mass number. For radioactive isotopes, radiation from the material and its decaying profile tell their existence. NMR enables us to access another important attribute of the isotope: the spin. There are many atomic elements possessing the spin. Each has a specific gyromagnetic ratio γ, giving the magnitude of the nuclear Zeeman interaction according to $\omega_0 = -\gamma B_0$, where B_0 and ω_0 is the magnetic field and the Larmor frequency. Hence, by observing the NMR signal at ω_0, one can tell the existence of an atom with γ.

Here, we aim at verifying the existence of the nuclear spin species in the sample of interest from a set of NMR measurements covering the resonance conditions. In the conventional NMR system using a high-field superconducting magnet, one encounters practical difficulties toward this goal. That is, in order to realize the resonance conditions of a number of different spin species, it would be necessary to vary the resonance frequency of the NMR probe circuit. However, retuning or replacement of the radiofrequency (rf) circuit would be quite tedious and elaborate. Even though one endures to do it, quantitative comparison of the signal intensities of different spin species becomes difficult. One solution may be to employ a non-resonant transmission line probe that enables broadband excitation and detection [6], in which one still have to calibrate the frequency responses of the other rf circuits, such as filters, and mixers.

In this work, we adopted an unconventional option of fixing the resonance frequency and varying the external magnetic field. As shown below, this allows quantitative NMR measurement of different spin species. For the variable external field, an electromagnet using iron cores may be convenient. However, the maximum attainable field is low. It is difficult to vary the field of the superconducting magnets used in the conventional NMR systems. In this work, we therefore employ a cryogen-free, field-variable superconducting magnet. In the following, we describe the principle of NMR elemental analysis and an experimental setup we have developed. Then, we show demonstrations in liquid solution and solid samples.

2. Principle

Using a probe tuned at a frequency $|\omega_0|$, we are to observe NMR signals from a set of nuclear spin species with gyromagnetic ratios γ_k $(k = 1, 2, 3, \ldots)$ by varying the external field B_{0k}. The resonance condition for the kth nuclear spin species is given by

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$$B_{0k} = -\frac{\omega_0}{\gamma_k}. \quad (1)$$

In thermal equilibrium at temperature T, the magnetization M_k of the kth nuclear spin species is represented by the Curie's law as

$$M_k = \frac{N'_k \gamma_k^2 \hbar^2 I_k(I_k+1) B_0}{3k_B T}. \quad (2)$$

Here, k_B is the Boltzmann's constant, and I_k and N'_k are the spin quantum number and the number of the spins in the sample, respectively. Using the number N_k of the atoms and the natural abundance x_k, N_k may be expressed as

$$N'_k = x_k N_k. \quad (3)$$

At the resonance condition (Eq. (1)), Eq. (2) is rewritten as

$$M_k = \frac{-x_k N_k \gamma_k \hbar^2 I_k(I_k+1)\omega_0}{3k_B T}. \quad (4)$$

The NMR signal induced across the terminals of the coil after pulse excitation is given by the time derivative of the magnetic flux penetrating through the loop of the coil. Thus, the signal intensity is proportional to both the magnetization M_k and the frequency ω_0. In the present work, ω_0 is fixed, so that the efficiency of signal transmission from the probe to the preamplifier of the spectrometer is common for all nuclear spin species. For excitation, since the nutation rate is proportional to the gyromagnetic ratio γ_k, the pulse width τ has to be adjusted to $\tau = \theta/(|\gamma_k|B_1)$ to ensure the common tip angle θ of the pulse with an intensity B_1 for all target spin species. The relative signal intensity S_k can thus be determined solely by the magnetization M_k with the present approach, which depends linearly on the gyromagnetic ratio γ_k and the number N'_k of the spins:

$$S_k \propto N'_k \gamma_k I_k(I_k+1) = x_k N_k \gamma_k I_k(I_k+1). \quad (5)$$

Since γ_k and I_k are constants, the relative number N_k of the nuclear spins in the sample can be calculated straightforwardly from S_k.

For comparison, let us briefly discuss the case of a constant static field, where the thermal magnetization M_k and the Larmor frequency are proportional to γ_k^2 and γ_k, respectively, resulting in the overall signal intensity given by the cube of the gyromagnetic ratio [7]. For this reason, the receptivity D is conventionally defined as [8]

$$D = x_k|\gamma_k|^3 I_k(I_k+1). \quad (6)$$

However, the γ^3-dependence of the signal intensity has to be modified if we take account of the efficiency of the circuit, which depends on the frequency and thereby the gyromagnetic ratio. In contrast, the proposed experiment at a constant frequency leads to unambiguous measurement of the nuclear magnetization, because of the common circuit efficiency. In order to look at how the signal intensity depends on the nucleus, we define constant-frequency receptivity (CFR) D_{CF}, which, in contrast to the conventional receptivity D given in Eq. (6), is represented as

$$D_{CF} = x_k|\gamma_k|I_k(I_k+1). \quad (7)$$

To compare the frequency-variable and the field-variable experiments, D and D_{CF} are plotted in Fig. 1a and b for several nuclear spin species. In both cases, the vertical scales are normalized to the value for the ^{1}H spins. As well known, the conventional receptivity is the highest for ^{1}H, due to its natural abundance close to 100%, the largest gyromagnetic ratio γ among the stable isotopes, and the γ^3-dependence of D. In terms of CFR, however, ^{1}H is no longer the most sensitive spin species. Since D_{CF} increases only linearly with γ, the gain with the higher gyromagnetic ratio is much smaller compared to the case of the conventional receptivity. Hence, in the case of D_{CF}, the effect of the $I^2 = I(I+1)$ term becomes important. Indeed, CFRs for many nuclei are higher than that of ^{1}H. For example, ^{23}Na ($I = 3/2$) has a gyromagnetic ratio of 11.270 MHz/T, which is lower than that of ^{1}H (42.577 MHz/T) [8]. However, with the $I(I+1)$ term of ^{23}Na five times higher than that of ^{1}H, the CFR of ^{23}Na is ca. 1.3 times larger than the CFR of ^{1}H.

3. Experimental

Fig. 2a shows a diagram of the experimental setup for NMR elemental analysis. In addition to a home-built NMR spectrometer [9–11], a cryogen-free, field-variable superconducting magnet (mCFM-7T-50-H3, Cryogenic Ltd.) is equipped. This desktop

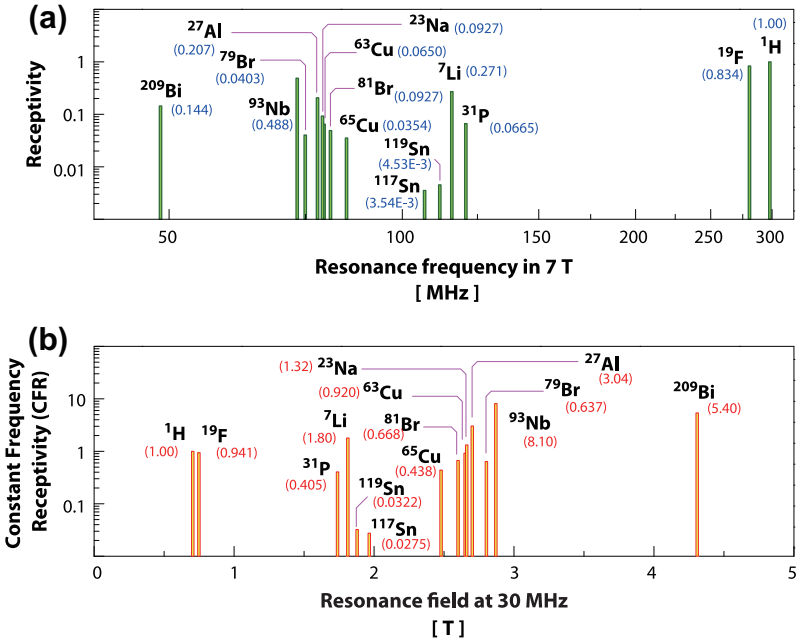

Fig. 1. (a) The receptivity versus the resonance frequency in a magnetic field of 7 T for several nuclear spin species. The receptivity was calculated according to $x_k|\gamma_k|^3 I_k(I_k+1)$ and normalized by the proton receptivity. (b) The constant-frequency receptivity (CFR) plotted as a function of the resonance field at a constant frequency of 30 MHz.