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# EASY: A simple tool for simultaneously removing background, deadtime and acoustic ringing in quantitative NMR spectroscopy—Part I: Basic principle and applications

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<sup>25</sup>Mg

## ABSTRACT

Elimination of Artifacts in NMR Spectroscopy (EASY) is a simple but very effective tool to remove simultaneously any real NMR probe background signal, any spectral distortions due to deadtime ringdown effects and -specifically- severe acoustic ringing artifacts in NMR spectra of low-gamma nuclei. EASY enables and maintains quantitative NMR (qNMR) as only a single pulse (preferably 90°) is used for data acquisition. After the acquisition of the first scan (it contains the wanted NMR signal and the background/deadtime/ringing artifacts) the same experiment is repeated immediately afterwards before the T<sub>1</sub> waiting delay. This second scan contains only the background/deadtime/ringing parts. Hence, the simple difference of both yields clean NMR line shapes free of artefacts.

In this Part I various examples for complete <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F probe background removal due to construction parts of the NMR probes are presented. Furthermore, <sup>25</sup>Mg EASY of Mg(OH)<sub>2</sub> is presented and this example shows how extremely strong acoustic ringing can be suppressed (more than a factor of 200) such that phase and baseline correction for spectra acquired with a single pulse is no longer a problem. EASY is also a step towards deadtime-free data acquisition as these effects are also canceled completely. EASY can be combined with any other NMR experiment, including 2D NMR, if baseline distortions are a big problem.

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## 1. Introduction

Solid-state NMR is a widely used method for the investigation of the structure or composition of solids. Compared with other spectroscopic techniques, the area of a NMR resonance is directly proportional to the number of nuclei in a specific molecular group. This basic feature enables quantitative NMR investigations (qNMR) of the purity of substances provided that a single pulse (mostly 90°) is used to excite the spectrum and that the repetition delay is long enough to ensure full spin-lattice (T<sub>1</sub>) relaxation. The basics of qNMR have been formulated by Jahncke and Malz [1–3] for liquids. Meanwhile qNMR has also been extended to solids (e.g. [4–7]) including amorphous materials. In addition with the availability of higher and higher magnetic fields, NMR investigations of nuclei with low gyromagnetic ratios are possible, such as <sup>17</sup>O, <sup>25</sup>Mg, <sup>45</sup>Ca etc.

In practice, however, sometimes severe problems have to be overcome for precise measurements. These may be grouped into

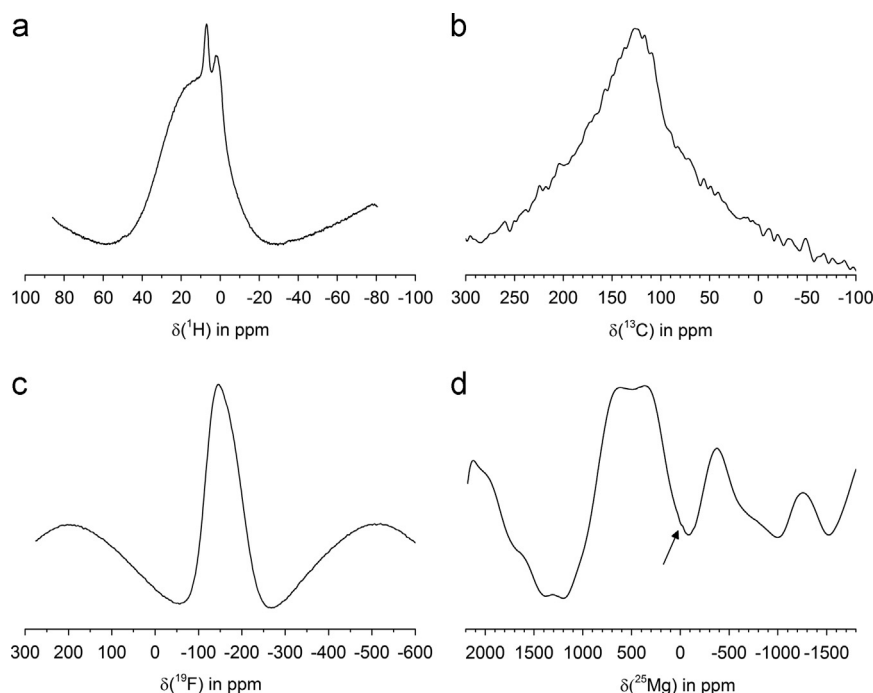
three different classes: (i) standard NMR probes exhibit strong background signals (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F etc. due to construction materials), (ii) acoustic ringing is a severe problem, particularly at low resonance frequencies (<sup>15</sup>N, <sup>17</sup>O, <sup>25</sup>Mg), and (iii) there are circumstances, where the NMR signal can be so weak (either low natural abundance and/or low NMR signal intensities) such that ringdown (deadtime) effects even at higher resonance frequencies (e.g. <sup>23</sup>Na) determine the baseline in a way that phase correction (and subsequently baseline correction) cannot be performed unambiguously.

Fig. 1 displays such typical background and artefact signals for a 2.5 mm MAS probe (Fig. 1a and c for <sup>1</sup>H and <sup>19</sup>F, respectively) and a <sup>13</sup>C background signature of a 4 mm MAS probe (Fig. 1b). The case of a strong <sup>11</sup>B background signal due to boron nitride used as stator material is shown in Fig. 7 further below. Fig. 1d shows a particularly intriguing case: low resonance frequency and low natural abundance: <sup>25</sup>Mg MAS NMR of Mg(OH)<sub>2</sub> using a single excitation pulse. The very small NMR resonance (indicated by the arrow) is much smaller than the acoustic ringing pattern caused by the low resonance frequency.

Several proposals have been published for removing background effects in NMR in the past. The comprehensive review of

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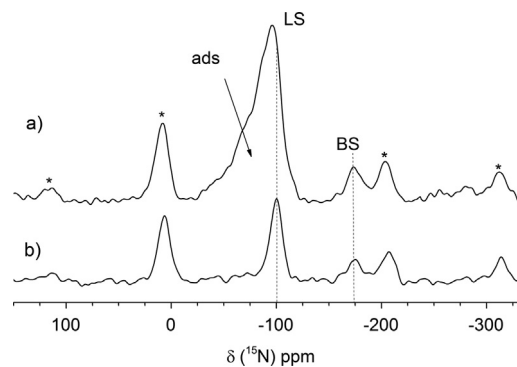
**Fig. 1.** Typical NMR MAS probe background and artefact signals: (a)  $^1\text{H}$ : empty 2.5 mm rotor, 600 MHz; (b)  $^{13}\text{C}$  background signal of a 4 mm MAS probe, empty rotor, 100.6 MHz; (c)  $^{19}\text{F}$  background, empty 2.5 mm rotor, 564.5 MHz; and (d) strong acoustic ringing,  $^{25}\text{Mg}$  NMR of  $\text{Mg}(\text{OH})_2$ , 4 mm MAS probe, single excitation pulse, 24.5 MHz, the arrow indicates the NMR signal position.

Gerothanassius [8] in 1987 summarizes the state-of-the-art at that time considering various methods for removing background and ringing artifacts in NMR including probe construction, application of multiple pulse sequences and of mathematical manipulations both in the time and frequency domains. Further proposals have been published since e.g. [9–16]. Out of the various approaches the DEPTH sequence [14] is well known. The application of (rotor-synchronized) echo detection is another commonly used method for ringing and background suppression. The echo works in two different ways: (i) ringing is sufficiently suppressed because the data acquisition starts only after a full rotor period after the  $180^\circ$  echo pulse and (ii) echo formation of any background signal is suppressed because the effective pulse angle is very small for the construction parts “far” outside the coil. Hence, echo detection is often used to suppress  $^1\text{H}$ ,  $^{11}\text{B}$ , or  $^{19}\text{F}$  background signals.

Although it has been shown that echo intensity losses can be recalculated in specific cases [17], it must be noted that echoes cannot be used for qNMR purposes in general. There are obvious reasons: (i) the Hamiltonian is changed in an echo pulse sequence, (ii) echo formation depends on molecular motions (well known in  $^2\text{H}$  NMR e.g. [18]) and (iii) for quadrupolar nuclei the pulse lengths depend on the strength of the quadrupolar interaction itself. In that case, NMR signals of sites with different quadrupolar interactions cannot be refocused with the same intensity.

Fig. 2 shows an example how molecular motion can change a NMR spectrum.  $^{15}\text{N}$ -labeled pyridine molecules were used to study Brønsted and Lewis sites at the surface of nanoscopic magnesium hydroxide fluorides [19]. Due to molecular exchange processes the rotor-synchronized echo spectrum (Fig. 2b) refocuses only the signals of pyridine at Lewis (LS) and Brønsted (BS) sites. In contrast, the single pulse spectrum (Fig. 2a) displays also the broad resonance of weakly adsorbed pyridine molecules (ads) at about  $-88$  ppm. It is obvious that echoes cannot be used at all for suppressing ringing and background artifacts if quantitative results are in the focus of the investigations.

Consequently a few years ago, Chen et al. [20] published a simple scheme for probehead background suppression using one-pulse



**Fig. 2.** Comparison between single pulse  $^{15}\text{N}$  MAS NMR spectrum (a) and rotor-synchronized echo detected  $^{15}\text{N}$  MAS NMR spectrum (b) of a pyridine loaded nanoscopic magnesium hydroxide fluoride sample [19]. The echo formation suppresses the broad signals of weakly adsorbed (ads) pyridine due to molecular motion. LS and BS: pyridine at Lewis and Brønsted sites; \*denote MAS sidebands of the LS signal.

$^1\text{H}$  NMR. The idea for removing the  $^1\text{H}$  background is that the effective pulse flip angle outside the coil is small such that the background signal is in the linear excitation regime. They proposed to acquire two spectra (separated by the  $T_1$  waiting delay) with different pulse lengths (e.g.  $90^\circ$  and  $180^\circ$  pulses). In that case, the second spectrum contains only the background signal, however twice as strong as in the first spectrum. If its intensity is divided by a factor of two and after subtraction from the first spectrum the  $^1\text{H}$  background signal can be eliminated.

In this paper an effective approach for removing background and ringing artifacts is described called Elimination of Artifacts in NMR Spectroscopy (EASY). It is (i) a simple and robust routine method which uses (ii) only a single pulse length, (iii) it is faster than comparable approaches, (iv) it eliminates background and artifact signals (acoustic ringing, deadtime) simultaneously, (v) the measurements can be started even in the deadtime while maintaining (vi) the principles qNMR at the same time.

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