Large Volume NMR Spectroscopy with a Whole Body Imager

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A whole body NMR imager (1.5 T) has been operated with large samples and a home built coil to study NMR signals of heteronuclei at very low concentrations. Typical examples of $^{27}$Al, $^{51}$V, and $^{81}$Br are given, signals of 1 pmolal aqueous solutions of e.g. NaVO$_3$ can be detected. $^{129}$Xe was observed in xenon gas at atmospheric pressure with one scan. A $^{129}$Xe gaseous state NMR image is presented in a xenon containing sample. Also some typical measurements of longitudinal relaxation times of $^{27}$Al, $^{51}$V, and $^{129}$Xe are given.

**Key words:** Heteronuclear MR, Gaseous state NMR imaging, Large volume, Low concentration, $^{129}$Xe gas.

**Introduction**

Nuclear Magnetic Resonance (NMR) spectroscopy is an insensitive spectroscopic method since the nuclear magnetization at the usual experimental conditions as room temperature and $B_0$-fields around 10 T is rather small. $B_0$-fields as high as possible to increase the nuclear magnetization and the Larmor frequencies of the nuclei under consideration are advantageous. A further approach to increase the induced e.m.f. is to use large sample volumes, but the space is limited in the very high field magnets. Contrary to this, the magnets of whole body imagers working e.g. at 1.5 T have ample space to use large samples and the homogeneity is better than $3 \cdot 10^{-8}$ over volumes of litres [1]. So a gain of e.g. 1000 can be achieved going from 1 ml as usual in high field NMR spectrometers to 1000 ml in whole body imagers. Clearly this gain from increasing the sample will partly be compensated by the higher $B_0$-field used with small sample spectrometers.

In the following we present some typical NMR signals of heteronuclei (see Table 1) in very dilute aqueous solutions and of $^{129}$Xe at atmospheric pressure, some examples of $T_1$ measurements, and a $^{129}$Xe gaseous state NMR image.

**Experimental**

The investigations have been performed with a Siemens MAGNETOM 63 whole body imager working at 1.5 T (Proton Larmor frequency: 63.57 MHz). A head coil with a diameter of 25 cm which is a commercial product by Siemens, Erlangen, and which is prepared for sodium imaging has been used for a part of the large volume measurements. It can be tuned to lower frequencies to detect the NMR signals of $^{27}$Al and $^{51}$V and has been applied to obtain images also with these nuclei [2]. To get a better filling factor a solenoidal coil with 3 turns and an inner diameter of 12 cm was built. This coil, which is also tunable around the Larmor frequency of $^{23}$Na, gains a sevenfold higher signal-to-noise ratio in comparison with the head coil. For all measurements 500 ml spherical samples have been used with one exception given in the text.

With spherical samples no susceptibility correction for chemical shift measurements have to be performed. Further, the magnetic field across the whole sample is

**Table 1. NMR parameters for the nuclei observed; the NMR receptivity is given for 1 mmolal aqueous solutions taking the proton signal of water as 1 (without taking into account the relaxation times).**

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural abundance [%]</th>
<th>Larmor frequency at 1.5 T [MHz]</th>
<th>NMR receptivity</th>
<th>Spin</th>
<th>Quadrupole moment [10$^{-28}$ m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}$Na</td>
<td>100</td>
<td>16.82</td>
<td>$8.33 \cdot 10^{-7}$</td>
<td>$\frac{3}{2}$</td>
<td>+0.10</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>100</td>
<td>16.56</td>
<td>$1.86 \cdot 10^{-6}$</td>
<td>$\frac{5}{2}$</td>
<td>+0.15</td>
</tr>
<tr>
<td>$^{51}$V</td>
<td>99.76</td>
<td>16.71</td>
<td>$3.44 \cdot 10^{-6}$</td>
<td>$\frac{7}{2}$</td>
<td>-0.052</td>
</tr>
<tr>
<td>$^{81}$Br</td>
<td>49.46</td>
<td>17.17</td>
<td>$4.39 \cdot 10^{-7}$</td>
<td>$\frac{5}{2}$</td>
<td>+0.31</td>
</tr>
<tr>
<td>$^{129}$Xe</td>
<td>26.44</td>
<td>17.58</td>
<td>$2.07 \cdot 10^{-6}$</td>
<td>$\frac{3}{2}$</td>
<td>-</td>
</tr>
</tbody>
</table>

* 11 gas at 20°C and a pressure of 1000 hPa, proton in 1 H$_2$O: 1.
more homogeneous than in cylindrical samples, a fact which has been verified using the MAGNEX field imaging method [3]. \(^1\text{H}\) line widths of 2 Hz in a 500 ml sphere containing a 1 μmolal aqueous solution of NaVO\(_3\) can be achieved. The whole system in the spectroscopic mode was shown to have a time stability of about 1 Hz/hour using protons [1], that means \(1 - 2 \times 10^{-8}\). The standard rectangular HF-pulses of the imager with a length of 500 μs were used; the free induction decay was observed after a delay of 400 through 2000 μs.

The spectral resolution resulting from the time stability and the homogeneity is sufficiently good for the study of many heteronuclei which often show a large chemical shift range and, due to the quadrupole moment, a favorable line width. The great advantage is the large sample volume which allows the study of very dilute solutions. So the experimental conditions allow the detection of NMR signals of the nuclei given in Table 1.

Results

**Signals of Quadrupolar Nuclei**

The NMR signals of \(^{51}\text{V}\) (and \(^{23}\text{Na}\)) have been observed in a 1 μmolal aqueous solution of NaVO\(_3\). The \(^{51}\text{V}\) signal which has been taken within 27 min is given in Figure 1. A narrow line of 15 Hz has been found, indicating that a symmetrical vanadate species is detected. This is probably H\(_2\)VO\(_4\), but to our knowledge measurements at such low concentrations have not yet been reported [4, 5]. To demonstrate that no vanadium contamination of the deionized water contributes to the signal, the spectrum obtained from the water used is also given.

Figure 2 gives an example of a \(^{27}\text{Al}\) NMR signal of a 2 μmolal aqueous solution of AlCl\(_3\) which was acidified to a pH 1.84 with HCl. Again a comparison with a water sample acidified with HCl is presented, precluding an aluminium contamination of the water and chloric acid used. A line width of 6 Hz was observed, which is something higher than found earlier for acidified AlCl\(_3\)-solutions [6] due to the Al(H\(_2\)O)\(_6\)^3+ species. Due to the longer \(T_1\) (see later), the pulse repetition time was 400 ms and the resulting measuring time nearly two hours, so a slight drift broadening might be possible. In an other measurement with a 100 μmolal acidified solution a 3 Hz line width was observed.

A whole body imager is usually not built up to detect broad NMR signals, that means to observe the free induction decays after a short HF-pulse and a short dead time. Figure 3 shows a 370 Hz broad signal of \(^{81}\text{Br}\) in a 10.3 mmolal aqueous solution of LiBr, indicating that also signals of quadrupolar nuclei with greater line widths can be detected with reasonable measuring times (in this case 1 min 43 sec).
Fig. 2. $^{27}$Al NMR spectra of a) half a litre of a 2 μmolal aqueous solution of AlCl$_3$, with a pH of 1.84 by adding HCl, and b) half a litre of the same water with pH 1.97 adjusted with the same chloric acid. a) and b) scans: 16 384, TR: 400 ms, spline function to correct the baseline.

In Fig. 4 the $^{27}$Al spectrum of a sample consisting of two coaxial cylinders is given: the inner cylinder ($\phi = 63$ mm) holds 250 ml of a 10 μmolal aqueous solution of AlCl$_3$ (pH 1.9, adjusted with HCl) and the outer one ($\phi = 95$ mm) 280 ml of a 20 μmolal aqueous solution (pH = 11.1, adjusted with NaOH). The signal at lower frequency is due to the Al(H$_2$O)$_5^{3+}$ species and the broader (18 Hz) 80 ppm to higher frequency stems from the Al(OH)$_4^{-}$ found in basic solutions [7].

These four examples demonstrate the potential of large sample NMR spectroscopy for very dilute solutions. This is important for studies of solutions with
Al(OH)$_4^-$
basic

80 ppm

Al(H$_2$O)$_5^{3+}$
acid

Fig. 4. $^{27}$Al NMR spectrum of a sample of 2 concentric cylinders: the inner cylinder ($\phi = 63$ mm) contains 250 ml of a 10 µmolal aqueous solution of AlCl$_3$ (pH 1.9), the outer ($\phi = 95$ mm) 280 ml of a 20 µmolal aqueous solution of AlCl$_3$ (pH 11.1), showing the Al(OH)$_4^-$ and the Al(H$_2$O)$_5^{3+}$ signals with a chemical shift of 80 ppm. - Scans: 4096, TR: 300 ms, spline function to correct the baseline.

low concentrations resulting e.g. from compounds which are not readily soluble or of solutions where the chemical shifts are expected to change at low concentrations [8].

**Longitudinal Relaxation Times $T_1$**

From the signal-to-noise ratios found in the given examples it can be derived that longitudinal relaxation times can be measured also at low concentrations e.g. with the inversion recovery method. In Fig. 5 a stacked plot of a $T_1$ measurement of $^{51}$V in a 500 µmolal aqueous solution of NaVO$_3$ is given. The whole measuring time was 13 min. A three parameter fit gives $T_1 = 29.5$ ms. As a further example, the result of a $T_1$ measurement of $^{27}$Al in a 100 µmolal aqueous solution of AlCl$_3$ (pH 2.0) is mentioned: $T_1 = 196$ ms. This is a rather long value and is consistent with earlier data at higher concentrations [9].

Measurements of $T_1$ as a function of concentration, also at very low concentrations, are of interest for a comparison with theoretical results for ionic nuclei in electrolyte solutions [10, 11].

Gaseous Xenon:

At standard conditions, about $3 \cdot 10^{19}$ gas atoms are available per ml. With large samples it seems to be possible to detect NMR signals of gases at atmospheric or lower pressure. In Fig. 6 the $^{129}$Xe NMR signal of a 500 ml sphere filled with 99.99% xenon gas at 980 hPa and 22 °C is given. Only one HF-pulse has been applied, and the free induction decay after 2 ms was detected for 1024 ms. The sample has been magnetized for 8.5 hours in the magnet because the longitudinal relaxation time under these conditions is very long, about 3–4 hours. The $T_1$ of the spin 1/2 nucleus $^{129}$Xe can be shortened drastically by adding (paramagnetic) O$_2$-gas [12]: an inversion recovery experiment has been performed with a sample which was a mixture of xenon gas and oxygen gas with a mixing ratio of about 5:1 at a total pressure of 920 hPa at room temperature. Figure 7 shows the three parameter fit of the data, resulting in $T_1 = 15.9$ s. The observed line width was 1.7 Hz. The chemical shift between the two samples is 1 Hz with the pure xenon gas at lower frequencies.

The $T_1$ of the oxygen containing sample allows the detection of a $^{129}$Xe NMR image in the gaseous state: Figure 8 shows a result together with the experimental imaging data.

From the signal-to-noise ratio observed it is obvious that $^{129}$Xe measurements at lower pressures are possible, and it is hoped to get more insight into the
In conclusion, NMR spectroscopy with a whole body imager using large samples can be performed at low pressure in gases and at low concentrations in solutions. So studies of weak interactions seem to be possible. Since a non-invasive method is used, also non-destructive investigations in food stuffs or beverages can be performed as well as human in vivo studies with heteronuclei. The studies are not limited to the nuclei given above but also other interesting nuclei can be used if the appropriate HF-channels are available. Further investigations on these subjects are running.

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