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A nuclear magnetic resonance spectrometer concept for hermetically sealed magic angle spinning investigations on highly toxic, radiotoxic, or air sensitive materials

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A concept to integrate a commercial high-resolution, magic angle spinning nuclear magnetic resonance (MAS-NMR) probe capable of very rapid rotation rates (70 kHz) in a hermetically sealed enclosure for the study of highly radiotoxic materials has been developed and successfully demonstrated. The concept centres on a conventional wide bore (89 mm) solid-state NMR magnet operating with industry standard 54 mm diameter probes designed for narrow bore magnets. Rotor insertion and probe tuning take place within a hermetically enclosed glovebox, which extends into the bore of the magnet, in the space between the probe and the magnet shim system. Oxygen-17 MAS-NMR measurements demonstrate the possibility of obtaining high quality spectra from small sample masses ($\sim$10 mg) of highly radiotoxic material and the need for high spinning speeds to improve the spectral resolution when working with actinides. The large paramagnetic susceptibility arising from actinide paramagnetism in $(Th_{1-x}U_x)O_2$ solid solutions gives rise to extensive spinning sidebands and poor resolution at 15 kHz, which is dramatically improved at 55 kHz. The first ^{17}O MAS-NMR measurements on NpO_{2+x} samples spinning at 55 kHz are also reported. The glovebox approach developed here for radiotoxic materials can be easily adapted to work with other hazardous or even air sensitive materials. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4805017]

I. INTRODUCTION

Recent developments in solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) make this spectroscopy a very powerful analytic method, for the study of local structure in organic[1,2] and inorganic[3–5] materials. Moreover, recent advances in computing the magnetic response of a material's electronic structure determined from first principle quantum mechanical methods mean that NMR interaction parameters measured in experiments can be unambiguously related to the structure.[6–8] Since the inception of the MAS technique,[9,10] numerous technological improvements have increased the sensitivity and the resolution of the spectra. Very high magnetic fields are now available and facilitate the study of quadrupolar nuclei (nuclear spin quantum number, $I > \frac{1}{2}$) in inorganic materials,[3,11] or more recently, the first 23.5 T commercial instrument in Lyon, France.[12] Further, the suppression of significant homogeneous and inhomogeneous broadening interactions has been achieved by spinning samples up to 70 kHz (in 1.3 mm commercial sample carriers (rotors)) compared to a maximum of 35 kHz only 15 years ago.[5,13]

Despite all these technological improvements and the wide variety of compounds which can be analysed by NMR, to our knowledge, only one solid-state structural analysis experiment has been performed previously on materials containing transuranic elements (highly radioactive Pu-containing

zircons)[14] and it shows the interest and the potential of MAS-NMR to reveal local structure in such materials. A simple explanation for the lack of experimental development in this area is the radiotoxicity of these materials, for example, plutonium is an α-emitter and can only be handled in dedicated gloveboxes. For the MAS-NMR investigation of highly radioactive $^{238/239}$Pu-containing samples mentioned above, rigorous precautions had to be taken. Farnan *et al.*[15] proposed the use of an efficient triple-containment MAS sample carrier to perform the NMR measurements. The sample was a ceramic pellet to avoid potential dispersion of powders, contained in a hard ceramic aluminium nitride primary container which in turn was fitted inside a polytetrafluoroethylene (PFTE) secondary container inserted in a 7.5 mm rotor, which itself acts as a third level of containment. Moreover, as Pu isotopes can be highly radiotoxic, the sample must be handled with great care to prevent contamination of operating personnel. The handling of all these materials, even in smallest quantities, must be performed in hermetically isolated enclosures, i.e., ventilated gloveboxes, located in laboratories equipped with controlled ventilation and monitoring of potential airborne particles. In the triple containment experiment, the sample carrier was rotated at 3.5 kHz, in addition, constant operator surveillance was needed throughout the experiment. Moreover, compared with a rotor used in routine measurements, the amount of sample, and concomitantly the coil filling factor and thus the sensitivity[16] of the measurement, was reduced, simply due to the space required for the triple containment of the sample. To overcome the
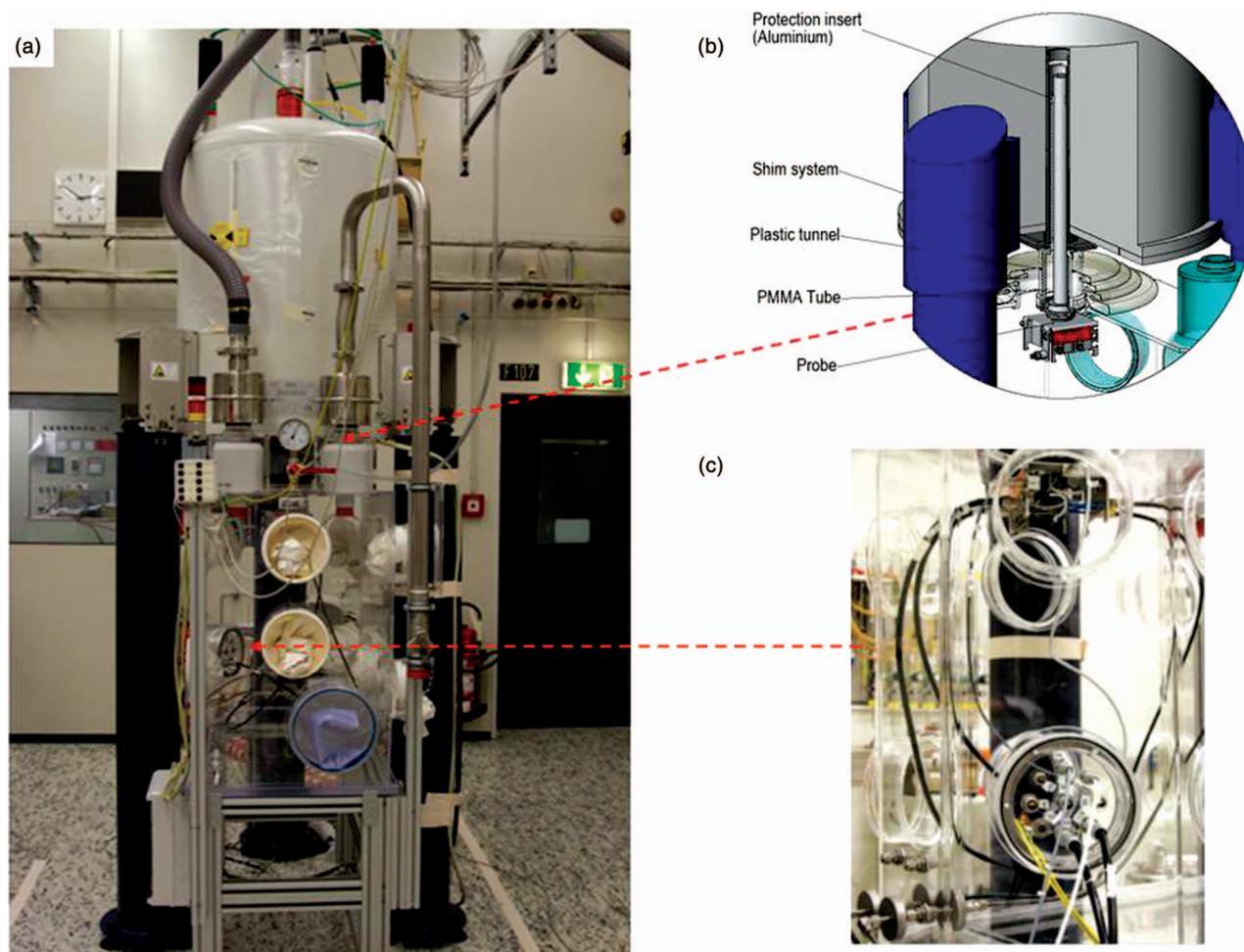
FIG. 1. (a) Photo of the 9.4 T NMR spectrometer with the glovebox, (b) cut-away drawing displaying the probe, glove box, and magnet, and (c) extended connection cables.

sensitivity drawback, it has been proposed to use a magic angle coil spinning (MACS) technique[17] where an extra tuned coil is inserted inside the 7.5 mm rotor. This rotor encapsulation scheme has provided very conclusive results and opened new routes for the analysis of these compounds. However, rapid rotation speeds are needed to narrow the paramagnetically broadened lines that will be very common in NMR spectra of actinide containing materials. The fundamental limit on rotation frequency is the diameter of the MAS rotor. Thus, when spinning fast, the rotor will be too small to accommodate secondary or tertiary containment designs. In addition, the manual dexterity requirements for the preparation and the handling of MACS rotor systems in an alpha glovebox mean that they cannot be used easily for routine MAS-NMR experiments.

Here, we will present the new concept developed at the Joint Research Centre (JRC), Institute for Transuranium Elements (ITU) for the study of such highly radioactive materials. It is based on the isolation in a radioactive-glovebox of the MAS probe itself, and not the multiple containment of the sample within the rotor. The design implemented in this work eliminates the disadvantages of earlier concepts and enables the use of MAS-NMR in a straightforward way. This combination between a commercial wide bore (WB) 9.4 T spec-

trometer, a radioactive-glovebox, and a commercial 1.3 mm probe, which allows the NMR analysis at very high spinning speed is very efficient. The first successful and encouraging results are presented.

II. EXPERIMENTAL METHOD

A design has been developed so that instead of very effectively isolating the sample to prevent the possibility of dispersion of radioactive material if there is a rotor crash, the MAS probe itself has been entirely contained within a glovebox. The MAS-NMR probe is thus housed in a hermetically sealed glovebox as shown in Figure 1. The heart of the installation is a conventional 9.4 T WB magnet supplied by Bruker, Rheinstetten, Germany. It has an 89 mm internal bore diameter and a usable room temperature bore of 72 mm with shim coils installed. This magnet is mounted on extended legs to permit the insertion of a glovebox underneath, and so that it can be used at a comfortable working height. To ensure its stability against a high centre of gravity, the magnet is held by steel support cables fixed to the ceiling of the laboratory. A 3 m rail track is installed on the floor below the magnet, the glovebox is mounted on these rails so that it can be removed easily from its position below the magnet. This allows a relatively

rapid transition from actinide (highly radioactive) to normal (non-radioactive) NMR operation. A closed end plexiglass cylinder 70 mm outside diameter and 60 mm inner diameter, which allows insertion of "standard bore" MAS-NMR probes, extends into the bore of the magnet and is connected to the lower glovebox by means of a long hermetically sealed sack. The sack is long enough to allow the cylinder to be lowered from the magnet bore, clear of the magnet into the glovebox, and the glovebox to be removed along the rails. A probe mount is installed at the glovebox opening with the manufacturer's bayonet mechanism for easy positioning of the probes. Consequently, the probes were ordered with extended body length (standard lengths for a taller 600 MHz NMR magnet) so that the NMR coil is still positioned at magnet centre while being mounted 100 mm lower than in normal operation. Probe tuning is obtained, as in normal operation, by manual rotation of tuning and matching rods which are readily accessed through the gloves of the glove box.

Only helium leak tight connectors (Lemo) are certified to operate in a plutonium glovebox. This necessitated the manufacture of a connector interface with the glovebox (see Figure 1(c)) where the radiofrequency cables, spin-rate detector cable, and all electrical connections could enter the glovebox. The glovebox is currently operated under air at a small under pressure (0.95 atm) with respect to that of the laboratory to ensure that any leaks will always be inward and dispersal of radioactive material from the glovebox avoided. The gas flow requirements of the MAS-NMR system had to be carefully considered as gas flows of nearly $200 \, l \, min^{-1}$ are entering the glovebox and any over pressure in the glovebox will trigger an alarm. Thus, the exit of gas from the glovebox is achieved by high flow high-efficiency particulate air filters to extract the spinning gas into the separate off-gas ventilation systems available in the laboratory. The nitrogen gas, supplied for the sample rotation, enters the glovebox via pairs of absolute filters. In the future, this glovebox will be upgraded to operate entirely with nitrogen in conjunction with a closed cycle purification system enabling measurement on air sensitive samples as well.

With this innovation, minimum adaptation of the spectrometer has been made and the isolation of the entire probe in the glovebox permits the use of all commercial narrow bore probe designs. Powdered samples can be loaded directly into standard rotors in a separate glove box and transferred for measurement. Samples are loaded in separate gloveboxes and enter and leave the glovebox through the standard bag in/bag out procedure. An extra large port is installed for bagging in and out of NMR probes. The ability to move the glovebox away from the magnet on the rails allows for easy operation of a standard sack welding device. It has a power supply, which is a massive ferromagnetic object, and is not wanted close to the NMR magnet.

III. PERFORMANCE

A. Effect of the glovebox

The effect of the glovebox on the system performance, especially the effect of the extended cables, has been evalu-
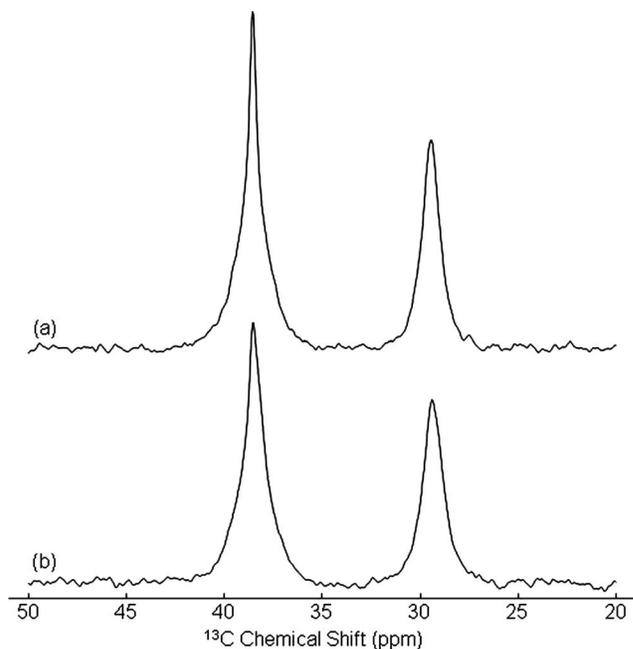
FIG. 2. ^{13}C MAS spectra of adamantane acquired (a) without and (b) with the glovebox. ($\nu_r = 55$ kHz). Pulse durations of 2.5 μs ($\pi/2$), 128 transients, and 5 s recycling delay.

ated with a set of measurements made using a 1.3 mm rotor filled with adamantane as a reference (Figure 2). The ^{13}C-MAS spectra of this sample were acquired at 55 kHz with and without glovebox (same shim file and no ^1H decoupling) to test the effect of the extra long cable connection between the spectrometer and the probe (approximately double) and the effect of the glovebox bore extension. Two peaks corresponding to CH and CH_2 units were observed and calibrated at 29.45 ppm and 38.48 ppm relative to tetramethylsylane (0 ppm), respectively.[18] By comparing the experiment conducted with and without the glovebox, only a slight decrease of about 1% in the signal intensity was observed and a minor increase in the full width at half maximum (FWHM) of these two peaks was also observed. The CH and CH_2 FWHM increase from 96 Hz and 104 Hz to 107 Hz and 120 Hz, respectively. For solid state studies, this is insignificant and since the spectrometer pulse-width calibration nor magnet shimming were adjusted between these measurements, these control measurements clearly indicate that the spectrometer performance is not affected by the protection used to isolate the NMR probe in the glovebox and the use of extended cables.

B. High spinning speed of radioactive samples

Actinides with unpaired 5*f*-electrons cause a paramagnetic susceptibility, which broadens static NMR resonances. Under MAS, this broad line will break up into a pattern of spinning sidebands.[19] To improve resolution, the use of high spinning speeds is very useful as it simplifies the spectra by removing overlapping sidebands and reduces their individual width. Sideband intensity is recovered in the central peaks and so sensitivity is also improved. To demonstrate the effect of the spinning speed, a 40% uranium-thorium oxide solid
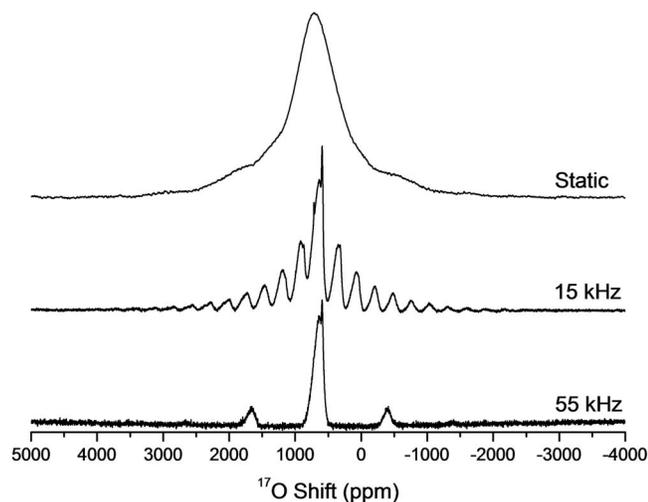
FIG. 3. Spectra of the $(U_{0.6}Th_{0.4})^{17}O_2$ sample acquired at three different spinning speeds ($B_0 = 9.4$ T). The samples were referenced to water enriched in 17-oxygen. The static and 55 kHz spectra have been acquired using a (synchronised for MAS) Hahn-echo experiment (pulse durations 3 μs (π/2) and 6 μs (π) with an echo delay of 7.2 μs at 55 kHz and 18.2 μs without spinning). Due to the numerous spinning sidebands, the spectrum at 15 kHz has been acquired using a synchronised solid echo (pulse durations of 4 μs (π/2) with a delay of 64 μs). A recycling delay of 2 s has been set for all the experiments and 2048 transients were used.

solution $(U_{0.4}Th_{0.6})O_2$, has been analysed using ^{17}O MAS-NMR. For these investigations, the sample has been isotopically enriched in ^{17}O to 20% using a gas exchange process.[3] Measurements made on this sample under different conditions are shown in Figure 3. In the static spectrum, several broad features are observed related to the presence of defects in this cubic system, which introduce electric field gradients at some oxygen sites, which in turn leads to a splitting of the NMR line by quadrupolar effects.[20] However, the main broadening mechanism is paramagnetic susceptibility due to the $5f^2$ electrons of U^{4+}. By spinning the sample at 15 kHz (in a 4 mm probe), the spectrum is broken into a pattern of spinning sidebands. However, a quantitative fitting of site populations would be very difficult with such a spectrum. This clearly shows that at moderate spinning speeds assignment of individual features could be fraught with difficulties in actinide containing samples. Increasing the spinning speed to 55 kHz in a 1.3 mm probe, leads to an improvement of the spectral resolution and two site types can be identified (those with U first neighbours and those with no U first neighbours). A complete study over the entire stoichiometric range of $(U, Th)^{17}O_2$ solid solutions has been completed and will be published shortly.[21]

C. Highly radioactive materials at high spinning speed

A first transuranic compound, NpO_{2+x}, has been investigated using ^{17}O MAS-NMR. It has also been ^{17}O-enriched as previously described. Thanks to the radioactive-glovebox, the sample could be spun at a speed of 55 kHz. The high-resolution spectrum acquired is shown in Figure 4. Further fitting of this spectrum using the dmfit software[22] identifies
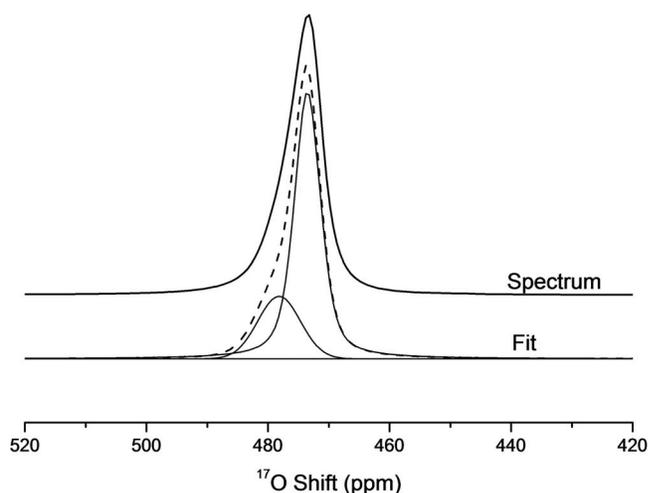
FIG. 4. ^{17}O Hahn-echo MAS-NMR spectrum and its corresponding fit acquired for the $Np^{17}O_{2+x}$ sample at 55 kHz. Pulse durations 3 μs (π/2) and 6 μs (π) with an echo delay of 18.2 μs (1 rotor period). Four hundred transients were used with a recycling delay of 2 s.

two separate oxygen resonances at 478 ppm and 473 ppm. This demonstrates the efficiency of NMR to identify the nature of interstitial substitution in hyperstoichiometric actinide oxides. The results obtained thus far clearly show the potential of the MAS-NMR method to unravel site specific information in materials with complex electronic structure as found in actinide (5f) bearing compounds.

IV. CONCLUSIONS

A concept to integrate a commercial MAS-NMR probe in a glovebox has been developed and successfully tested. The results show that the glovebox has minimal effect on the sensitivity of the instrument. High spinning speeds (up to 70 kHz) can be achieved as no modifications of the sample holder is required. Preliminary studies on uranium-thorium mixed oxides have shown the necessity of such high spinning speeds to increase the overall resolution of the spectrum. Moreover, the first high-resolution spectrum on a highly radioactive neptunium dioxide has shown the efficiency of this apparatus to acquire high resolution spectra ($\nu_r = 55$ kHz).

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