analytical chemistry

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NMR Sensor for Onboard Ship Detection of Catalytic Fines in Marine Fuel Oils

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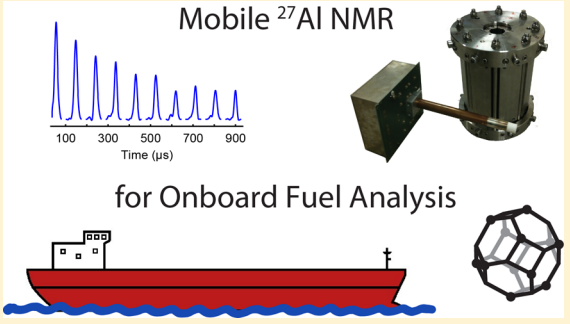
Supporting Information

ABSTRACT: A mobile, low-field nuclear magnetic resonance (NMR) sensor for onboard, inline detection of catalytic fines in fuel oil in the shipping industry is presented as an alternative to onshore laboratory measurements. Catalytic fines (called cat fines) are aluminosilicate zeolite catalysts utilized in the oil cracking process at refineries. When present in fuel oil, cat fines cause abrasive wear of engine parts and may ultimately lead to engine breakdown with large economical consequences, thereby motivating methods for inline measurements. Here, we report on a robust, mobile, and low-cost ^{27}Al NMR sensor for continuous online measurement of the level of catalytic fines in fuel oil onboard ships. The sensor enables accurate measurements of aluminum (catalytic fines) in ppm concentrations in good agreement with commercial laboratory reference measurements.



Marine heavy fuel oil (HFO) is derived from the lowest quality residual from petroleum refinery distillation and is used extensively as fuel in the shipping industry. The HFO is highly viscous and often contains sizable amounts of pollutants such as sulfur as well as catalytic fines (called cat fines) from oil cracking.[1,2] Cat fines are zeolite-type aluminosilicates that, when present in the fuel oil, cause abrasive wear of engine system parts, ultimately leading to costly engine breakdown. The degree of wear obviously depends on the cat fine concentration, which due to different base levels from the refineries as well as the potential for up-concentration due to sedimentation in storage tanks may be very difficult to control. For preventive action, the shipping industry performs onshore analysis of oil samples on a statistical level and they purify the fuel oil onboard prior to the engine inlet using large centrifuge systems. Both processes are subject to uncertainty as the cat fine content may vary substantially on the input level (bunkering source) and may be distributed nonhomogeneously in the fuel tanks with sediments mixing with good fuel in bad weather.

Considering the economic consequences of engine wearing and breakdown, it is of immense interest to establish online, continuous measurement systems that can prevent bunkering and engine loading of oil with undesirable cat fine concentrations. Such measurements could, for example, be taken upon bunkering and onboard before and after the onboard purification system to ensure safe operation. Addressing these needs, we here present a cat fine sensor based on mobile, low-cost nuclear magnetic resonance (NMR) instrumentation (see Figure 1) suitable for continuous real-time monitoring onboard ships. The sensor is tuned for detection of the ^{27}Al nucleus, one of the major species in cat fines. The other two constituents are silicon and oxygen. However, their NMR active isotopes ^{29}Si and ^{17}O NMR have lower natural abundance, and NMR wise possess lower sensitivity due to their intrinsic nuclear spin properties compared to ^{27}Al. Cat fine concentration traditionally refers to the combined aluminum plus silicon content. Typically 25−60 ppm of cat fines is considered the tolerable limit in various bunker oils,[3] but obviously, the lower the content the better. Major engine manufacturers recommend a maximum of 15 ppm cat fines for the engine inlet. Statistically, the silicon-to-aluminum ratio in cat fines is rather constant, and we determined a ratio of 1.1 by examination of laboratory data provided by DNV Petroleum Services, Singapore, from 185 308 bunkerings worldwide in the years 2009−2011. This agrees well with our own measurements taking 12 HFO samples and subjecting them to laboratory analysis (see Supporting Information). Overall, this implies that for large amounts of fuel oil accurate determination of cat fines can be based on the ^{27}Al NMR signal intensity.

The proposed onboard sensor is based on a home-built digital NMR instrument suitable for large-scale production. The magnet is constructed as a dipolar Halbach cylinder array[4,5] with a static magnetic field of 1.5 T corresponding to a Larmor

Received: April 21, 2014
Accepted: July 2, 2014
Published: July 2, 2014

 © 2014 American Chemical Society dx.doi.org/10.1021/ac5014496 | *Anal. Chem.* 2014, 86, 7205−7208

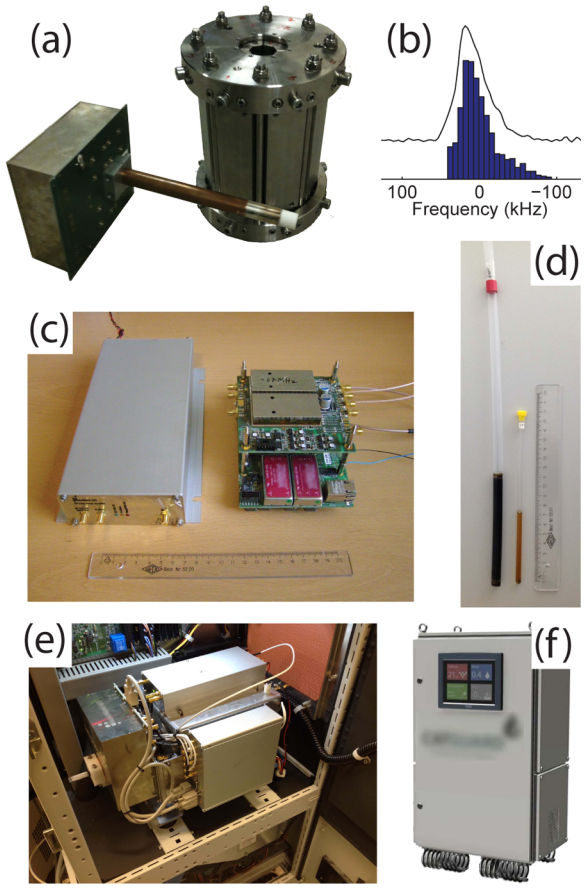


Figure 1. NMR cat fine sensor. (a) 1.5 T Halbach magnet (right) and ^{27}Al rf probe (left). (b) Binned distribution (380 ppm (0.6 mT) bin width) of magnetic field strengths measured by a Hall probe over a sample volume of 5 mL and an experimental ^{27}Al spectrum (line) of 1 M $Al(NO_3)_3$ in H_2O. (c) FPGA digital rf console (right) and 400 W rf power amplifier (left). A 20-cm ruler illustrates the scale. (d) Sample tube (9/8 mm outer/inner diameter) used for testing (left) shown in comparison to a regular 5-mm NMR tube (center) adjacent to the 20-cm ruler. In the marine vessel setup, the finite-length tube is replaced by an in-line setup allowing continuous fuel flow at the measuring point. (e) The ensemble instrumentation with the magnet in the middle (not visible), the power amplifier on the top, the console enclosed in the aluminum box on the front, and the base of the rf probe seen on the left. (f) Temperature regulated (25 ± 0.1 °C or 32 ± 0.1 °C) spectrometer cabinet hosting the overall spectrometer shown in (e) and including a PC with a Matlab-based user interface operated remotely or by the touchscreen on the front.

frequency of approximately 16.6 MHz for the ^{27}Al nucleus. For this setup to function for cat fine detection, a number of challenges were addressed. First, it is clear that detecting oil constituents at the ppm level is a challenge by itself as NMR intrinsically is a relatively insensitive method. This applies in particular at low magnetic fields, which is one of the motivations for the development of increasingly strong magnets for conventional applications of NMR spectroscopy. Disregarding the quadrupolar line-broadening encountered for ^{27}Al spins (see next point), the sensitivity (i.e., the signal-to-noise ratio, SNR) roughly scales with the magnetic field to power 3/2. This obviously provides a challenge for a spectrometer with a field being approximately 1/15 that of a state-of-the-art NMR spectrometer (corresponding to 1/60 in sensitivity or an increase by a factor of 3600 in measurement time for compensation in similar applications). Second, ^{27}Al in zeolites can adapt relatively large quadrupolar coupling interactions with coupling constants (C_Q) up to 10−16 MHz.[6,7] This causes severe line-broadening due to first- and second-order quadrupolar coupling interactions further lowering the SNR. Pursuing detection of ^{27}Al through the central transition, we need in particular to consider the second-order broadening, which unfavorably scales inversely proportional to the external magnetic field. Even at high field, this bears a challenge for quadrupolar coupling interactions of the size mentioned above, leading to the notation "invisible aluminum" in relation to zeolite studies.[6,8] For ^{27}Al with C_Q = 10 MHz, the second-order quadrupolar-coupling broadened line width will be 187 kHz at 1.5 T (relative to 11.8 kHz at 23.85 T) through scaling inversely with the static magnetic field and with C_Q to power 2.

To gain sufficient sensitivity to overcome the challenges listed above and thereby render in-line ppm-level ^{27}Al cat fine detection feasible, we have carefully optimized all elements in the design of the spectrometer and in the experimental setup with a focus on creating the highest possible SNR for ^{27}Al cat fine detection. Figure 1 summarizes various parts of the onboard NMR cat fine sensor. The home-built probe and the Halbach magnet array are shown in Figure 1a. The magnet array (220 mm length, 25 mm inner diameter, 150 mm outer diameter, and 25 kg total weight) is composed of 8 neodymium blocks arranged to form a magnetic field orthogonal to the magnet bore. The magnet is assembled to provide a high static field with reasonable homogeneity for the given application. Specifically, the magnet provides a field of about 1.5 T with a homogeneity of ±0.007 T over a volume of 8 × 8 × 80 mm^3. The homogeneity of the magnet was optimized during assembly using systematic Hall probe measurements in the test volume. Figure 1b illustrates a representative field distribution which on a frequency scale is compared with a ^{27}Al NMR spectrum of 1 M $Al(NO_3)_3$ in H_2O. The radio frequency (rf) probe contains low-noise preamplifiers and a solenoid rf coil (100 mm length, 10 mm inner diameter) in a shielded probe body. The sample container is a Teflon tube (9.2 mm inner diameter) with the oil flowing (at about 50 °C) through the magnet either in a continuous flow with a velocity of up to 0.42 mm/s or in a stopped-flow configuration. The effective cylinder shaped sample volume is 6.6 mL (9.2 mm diameter, 100 mm length). For demonstration purposes in our laboratory, the sample volume was reduced to 5.0 mL with a Teflon tube (8 mm inner diameter) as shown in Figure 1d. Figure 1c shows the home-built digital rf console containing a field-programmable gate array (FPGA) unit (10 × 16 cm^2), with build-in filters etc. along with a home-built 400-W amplifier. The console operates with a sampling frequency of 50 MHz. Figure 1e shows the ensemble instrumentation in a compact setup with the power amplifier and FPGA console positioned around the magnet. Finally, Figure 1f illustrates the overall temperature regulated (either 25 ± 0.1 °C or 32 ± 0.1 °C) spectrometer cabinet installed onboard ships for cat fine detection. Temperature regulation is important as the field of the neodymium Halbach magnet array varies by about −1200 ppm per °C.

Equipped with a sensitive spectrometer, numerous methods have been applied to allow for ^{27}Al NMR sensoring of cat fines at the ppm level. The first, related to the magnet and the rf probe, is to use a large sample volume. In the proposed setup for demonstration, we apply a sample volume of 5 mL (*vide supra*) which represents a good compromise with respect to

dx.doi.org/10.1021/ac5014496 | *Anal. Chem.* 2014, 86, 7205−7208

sample volume, static field homogeneity, rf field performance (strength and homogeneity), and detection filling factor. This effective sample volume is about 25−50 times larger than in regular liquid-state NMR probes for 5 mm standard tubes. An increase of the volume by a factor of 25−50 corresponds to a factor of 5.0−7.1 improvement of the SNR.[9] Relying on Halbach magnets (Figure 1a), it is here worth noting that this specific application does not require spectral resolution (which by all means is challenged by large second-order quadrupolar broadenings and temperature-related field variations even upon stabilization to ±0.1 °C) implying that the quantitative data can be acquired using spin−echo sequences. Accordingly, to obtain a cost-efficient setup, it suffices to use an unshimmed Halbach magnet, which during construction has been optimized to provide a field with the inhomogeneity causing a full-width at half-maximum not exceeding 2500 ppm across a sample volume of 5 mL (cf. the field distribution and ^{27}Al NMR spectrum of 1 M $Al(NO_3)_3$ in Figure 1b). The second source to high sensitivity is fast experiment recycling. Here, we exploit the very short T_1 relaxation time of cat fine ^{27}Al spins being on the order of a few milliseconds. With repetition delays (τ_r) as low as 5−30 ms, we obtain SNR improvements of up to an order of magnitude compared to commonly used delays in the order of 1 s. Fast experiments of this kind require fast operation of the rf transmission and sampling stage which the FPGA digital rf console has been customized to. Furthermore, it is important that the probe quality factor (Q) and probe ringing is handled appropriately through the design of the rf probe and the electronics. Probe ringing is particularly severe at low NMR frequencies and for the measurement of very weak NMR signals. In order to minimize acoustic and spurious ringing, we found, after examining several materials and using recommendations of Buess and Petersen[10] and Fukushima and Roeder,[11] optimal performance using an rf coil wound from a flat silver wire (1.7 mm width, 0.1 mm thickness) shielded by copper plated polyimide (PI) film (0.018 mm copper, 0.025 mm PI thickness). A third handle to sensitivity enhancement is to apply efficient excitation and detection schemes. For this purpose, we applied a WURST[12−14]-QCPMG[15,16] pulse sequence, while optimal control design procedures[17,18] provided similar performance for the excitation. Using the QCPMG (Quadrupolar Carr−Purcell−Meiboom−Gill) pulse sequence, several spin echoes are sampled in one experiment. To acquire the spin−echo signals as efficiently as possible, very short echo delays are applied to avoid excessive loss due to fast relaxation. Such experiments are governed by the very fast decline of the free-induction-decay (FID) due to the large quadrupolar interaction and the inhomogeneous static field. This implies that an echo can be recorded every 70−200 μs until the decay of echo intensities causes unfavorable time consumption in relation to the recycle delay. Figure 2 shows examples of ^{27}Al WURST-QCPMG echo trains (Figure 2a,c,e) and corresponding spectra (Figure 2b,d,f) acquired of HFO samples with approximately 103, 27, and 1 ppm aluminum, respectively. In combination with short recycle delays (10−30 ms) and short WURST (Wideband, Uniform Rate, Smooth Truncation)[12] polarization enhancements pulses (400 μs, 1.2 MHz sweep width, 45 kHz rf amplitude), this allows for recording of around 400 full echoes per second, or 24.000 echoes per minute, which is quite impressive relative to standard NMR experiments.

The performance of the proposed onboard sensor was evaluated in a correlation study with 13 samples, including 12 representative marine HFOs and one high-concentration sample (with sedimented and thus up-concentrated cat fines). The samples were blended to ensure good homogeneity and hereafter divided into subsamples. The subsamples were examined at five replicates of the NMR sensor (with ^{27}Al resonance frequencies of 16.47, 16.50, 16.51, 16.59, and 16.73 MHz) and sent for analysis at seven different commercial laboratories for comparison with the current standard procedure to monitor cat fines (including measurement of silicon and aluminum content, see Supporting Information). The laboratory analyses were performed twice on 80 mL subsamples using a standardized quantification protocol relying on inductively coupled plasma spectroscopy requiring complete ashing of the samples.[19] The results of one laboratory were excluded as outliers. For the six remaining laboratories, the mean standard deviation is 3.5 ppm for the Al + Si measurements and 2.1 ppm for the aluminum measurements alone (see Figure 3). The ^{27}Al NMR measurements were conducted using the described WURST-QCPMG pulse scheme with a recycle delay of 20−30 ms and 10 echoes from which the intensities were obtained as the sum of all data points of each echo weighted with their expected relative intensities.

Figure 3 shows the correlation between the laboratory reference data and the calibrated amount of cat fines aluminum obtained from NMR measurements of 6 h duration each. The results demonstrate good agreement with a standard deviation of 1.3 ppm between the mean values from NMR and laboratory measurements. The estimated mean standard deviation on 6 h

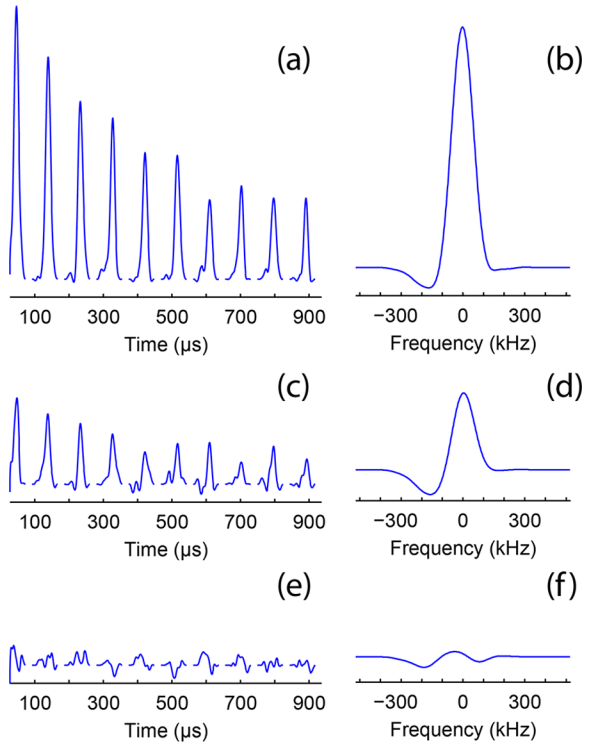


Figure 2. Examples of ^{27}Al spin echoes (a,c,e) and corresponding spectra (b,d,f) obtained for three examined HFOs with aluminum concentrations of about 103 ppm (a,b), 27 ppm (c,d), and 1 ppm (e,f), respectively. Each echo train shows 10 echoes acquired with an echo separation of 94 μs, at 16.51 MHz ^{27}Al resonance frequency, and accumulated over 20 h (see Supporting Information for further details). The spectra were obtained as the Fourier transform of the weighted sum of the sequential echoes. An artifact occurs in the spectra at −150 kHz.

dx.doi.org/10.1021/ac5014496 | Anal. Chem. 2014, 86, 7205−7208

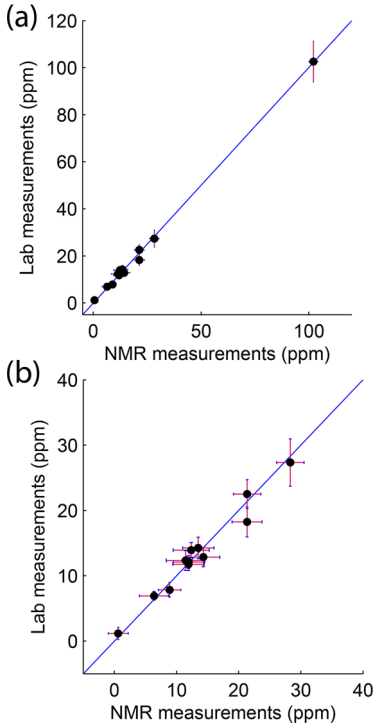


Figure 3. Calibrated ^{27}Al NMR intensities of cat fines in 13 HFO samples analyzed at five identical sensors (6 h per measurement, 15 measurements per sample in total) and correlated with the reference measurements from six commercial laboratories (analyzed twice at each laboratory, 12 measurements per sample in total). The correlation data is shown as mean values with error bars showing the standard deviations for each sample with (a) representing all 13 samples and (b) a close-up of the 12 natural samples. Each NMR measurement was acquired by the WURST-QCPMG pulse sequence with 10 echoes (94 μs separation) and 700 000 scans concatenated of acquisitions with recycle delays of 20−30 ms (see Supporting Information).

NMR measurements is 1.8 ppm for the full in-line volume (0.8 ppm for 20 h measurements, see Supporting Information). This enables reliable cat fine detection, and the standard deviation for NMR data correlated to laboratory Al + Si data is 3.0 ppm, which is on the order of the deviation of the laboratory measurements.

In conclusion, we have designed a highly sensitive mobile ^{27}Al NMR sensor for detection of cat fines in heavy fuel oil suitable for continuous online monitoring onboard ships. We have demonstrated a high precision for ppm-level detection of cat fine aluminum in good agreement with reference measurements from commercial laboratories. Additionally, the described highly sensitive NMR sensor is flexible and may provide a platform for numerous monitoring applications when tuned for ^{27}Al or other nuclei.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interest(s): Ole Jensen has a patent on aluminum NMR detection of cat fines in marine fuel oils.

■ ACKNOWLEDGMENTS

We thank DNV Petroleum Services, Singapore, and Lloyd's Register, London, UK, for access to historical worldwide data and help collecting HFO samples, and we acknowledge financial support from the Danish Advanced Technology Foundation and the Lauritzen Foundation.

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