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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

ANL-ET/99-17

**DEVELOPMENT OF A MAGNETIC RESONANCE SENSOR FOR ON-LINE
MONITORING OF ⁹⁹Tc AND ²³Na IN TANK WASTE CLEANUP PROCESSES:
FINAL REPORT AND IMPLEMENTATION PLAN**

by

S. L. Dieckman, J. A. Jendrzeczyk, and A. C. Raptis

Energy Technology Division
Sensors, Instrumentation & Nondestructive Evaluation Section

October 1999

Work Sponsored by
U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

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ABSTRACT

In response to U.S. Department of Energy (DOE) requirements for advanced cross-cutting technologies, Argonne National Laboratory is developing an on-line sensor system for the real-time monitoring of ⁹⁹Tc and ²³Na in various locations throughout radioactive-waste processing facilities. Based on nuclear magnetic resonance spectroscopy, the highly automated sensor system can provide near-real-time response with minimal sampling. The technology, in the form of a flow-through nuclear-magnetic-resonance-based on-line process sensing and control system, can rapidly monitor ⁹⁹Tc speciation and concentration (from 0.1 molar to 10 micro molar) in the feedstocks and eluents of radioactive-waste treatment processes. The system is nonintrusive, capable of withstanding harsh plant environments, and reasonably immune to contaminants. Furthermore, the system is capable of operating over large variations in pH, conductivity, and salinity. This document describes design parameters, results from sensitivity studies, and initial results obtained from oxidation-reduction studies that were conducted on technetium standards and waste specimens obtained from DOE's Hanford site. A cursory investigation of the system's capabilities to monitor ²³Na at high concentrations are also reported, as are descriptions of site requirements, implementation recommendations, and testing techniques.

1 INTRODUCTION

A lasting legacy of the cold war is a waste remediation task of unprecedented proportions. Radioactive and mixed waste with high concentrations of radioactive isotopes (e.g., Sr, Pu, ¹³⁷Cs, and ⁹⁹Tc) has been stockpiled at sites such as Hanford and Savannah River. For example, it is currently estimated that at Hanford alone, there are 21,000–23,000 Ci of ⁹⁹Tc. This material is distributed among ~150 storage tanks in several bewildering inhomogeneous chemical mixes.

Furthermore, the materials in these tanks are in various physical and chemical forms. The physical forms include salt cakes, sludge, and saturated solutions, whereas chemical species may exist in various oxidation states, as inorganic and organic molecular compounds, and as various ligand chelated species. Furthermore, radioactively induced chemical reactions are responsible for continual chemical modifications to the contents of the tanks. Under such conditions, it has been demonstrated that the ^{99}Tc in the pertechnetate species can undergo reduction to form species in a lower state of oxidation that are relatively stable when bound to organic ligands.

Despite the magnitude and complexity of the task, cleanup activities are in various stages at different facilities. This study can help cleanup efforts by developing on-line nuclear magnetic resonance (NMR) spectroscopy sensing technologies for monitoring ^{99}Tc and ^{23}Na in the waste streams of treatment processes. This document reports results from sensitivity studies and initial results from oxidation-reduction studies that were conducted on technetium standards and waste specimens from the U.S. Department of Energy (DOE) Hanford site. A cursory investigation of the capability to monitor ^{23}Na at high concentrations is also reported, as are implementation suggestions for an on-line sensor system.

2 BACKGROUND

Treatment of the waste at Hanford will include separation and vitrification of the radioactive constituents, e.g., Sr, Pu, ^{137}Cs , and ^{99}Tc . The separation and vitrification processes are contracted by DOE to a private partner, British Nuclear Fuels Limited (BNFL). Under this contract, DOE will provide waste to BNFL on a 5-M-sodium basis. Processing of the waste by BNFL will include preconcentration to a 7-M sodium equivalent, removal of insoluble materials via ultrafiltration, dilution of the waste filtration effluents to 5-M sodium equivalent, removal of ^{137}Cs through ion exchange, and, ultimately, separation and concentration of ^{99}Tc by ion exchange. The ion exchange columns are to be operated in two sets of lead and lag pairs. Removal of the ^{99}Tc from the ion exchange column will be performed with a nitric acid eluent.

To ensure the accurate removal of ^{99}Tc from the feedstocks, continuous on-line monitoring of the eluents from the ^{99}Tc column will be required. Such monitoring could detect column breakthrough due to saturation, premature saturation, column aging, or channeling. In this detection scenario, the output of the monitoring system may signal operators to regenerate the columns or correct otherwise unknown column difficulties. Similarly, it will be desirable to monitor the columns

during regeneration to determine optimal operational parameters (i.e., minimize volumes of nitric acid eluents while maximizing ^{99}Tc removal). Furthermore, it may be desirable to monitor the feedstocks for the ^{99}Tc process to determine mass balances that are required for ultimate optimization of the plant.

The monitoring requirements and operating conditions of the ^{99}Tc sensor system will place significant demand on the sensor technology and techniques and on the physical integrity of the instrumentation. The system must be capable of monitoring total ^{99}Tc concentrations with a minimal detection limit of 10- μM . The ^{99}Tc in the tanks is significantly aged, thus, it is only a long half-life beta emitter (half-life of 2.14×10^5 yr).¹ On this basis, the 10- μM limit is equivalent to 16.78- μCi per liter. A linear sensor response is desirable over 5 orders of magnitude. The reproducibility, resolution, and accuracy must be $\approx 5\%$ relative (i.e., a 100- μM measurement would be accurate to 5- μM). The fact that ^{99}Tc may be incorporated in various molecules and may exist in several oxidation states complicates the requirement for a low detection threshold. Although ^{99}Tc can be counted under conventional circumstances, a nonradiometric sensing methodology is required during tank waste cleanup because background activity levels are high, effluents may be contaminated by other isotopes, and applications must be flexible. The sensors must also function when effluent pH levels are extreme (from pH 12 with caustic to pH of perhaps 1 during acid wash cycles). The sensors will also encounter many counter ions, such as nitrites and nitrates of high pH. Furthermore, the waste effluents in many of the tanks are not well characterized, and judging from the wide distribution of molecular types, contain a bewildering array of inorganic and organic constituents. The temporal response of the sensor must be ≈ 15 min. In addition, the sensor must be sufficiently robust and intelligent to operate independently for prolonged periods (6 months to years). Finally, the system must be reasonably economical and sufficiently developed so it can be implemented in a plant environment.

In addition to the ^{99}Tc on-line waste-monitoring requirements in the BNFL waste processing facilities, opportunities exist at BNFL, Hanford, and with the DOE for on-line ^{23}Na monitoring technologies. For example, within BNFL's processing scheme, monitoring of input waste feedstocks that contain 5-M ^{23}Na , concentrated liquors that contain 7-M ^{23}Na , diluted liquors with 5-M ^{23}Na , and column eluents will be required for accurate process control and process accounting. In other areas, feedstocks are to be provided to BNFL on a 5-M sodium basis with the financial basis of payment tied directly to the 5-M sodium basis. Blending or diluting may be required by Hanford, and accurate monitoring of ^{23}Na concentrations and flow will be required for an accurate sodium balance.

The NMR spectral properties of the ^{23}Na nucleus are also quite favorable. The natural abundance of ^{23}Na is 100%, its spin is $+3/2$, and its relative sensitivity is $\approx 10\%$ of protons. Temporal response of such a ^{23}Na sensor may be ≈ 1 -5 min. It is desirable that the sensitivity cover a range of 0.01-10 M, with the resolution, accuracy, and reproducibility on the order of 1% relative (e.g., 1% of 5 M is ± 0.05 M). Furthermore, as with the ^{99}Tc sensor, the ^{23}Na sensor technology must also be capable of handling high and low pH extremes, high dissolved-salt concentrations, a myriad of inorganic and organic contaminants, and oxidizing/reducing environments. The physical sensor environment will be similar to that of the ^{99}Tc sensor, with high radiation backgrounds, elevated temperatures, and a harsh and dirty environment.

3 NMR BACKGROUND

With the above requirements for monitoring instrumentation, NMR spectroscopy was identified as an appropriate candidate technology that will be capable of monitoring the ^{99}Tc and ^{23}Na in the DOE feedstocks and effluents. NMR, a noncontact, nondestructive, quantitative analytical technique, is reasonably sensitive and exhibits a linear response over a concentration range of parts per million (ppm) to 100%.¹⁻⁸ Pulsed radio frequency (RF) waves in the 100-MHz region are used to examine the nuclear spin of the isotopes of interest. Unlike optical or electrochemical analytical techniques, NMR instrumentation does not experience interference due to optical port or electrode coating and is generally immune to variations in sample matrix, interference from other chemicals or isotopes, high radioactive backgrounds, and harsh operating conditions.

It has also been shown that ^{99}Tc is an ideal isotope for analysis and process monitoring via magnetic resonance.²⁻³ This species, with an isotopic abundance of 100%, is the fifth most sensitive isotope to the magnetic resonance phenomenon, and exhibits a fast nuclear relaxation time that allows near-real-time analysis measurements (i.e., analysis in the millisecond range). Moreover, the high isotopic spin number of $9/2$ provides spectroscopic peaks with narrow line widths that are easily detected. Given that the isotope relaxation times are very fast, and that the sensitivity of the isotope is 40% of the sensitivity of hydrogen, it is no surprise that early magnetic resonance studies have shown that signals from pertechnetate species are easily detected and that narrow lines are observed.²⁻³

During conventional concentration studies with pertechnetate standards, it was observed that the concentration of pertechnetate in the waste tanks was significantly less than the total technetium.^{9,10} Hence,

oxidation of ^{99}Tc to pertechnetate became a concern. Additional studies have been conducted on ^{99}Tc for fuel reprocessing.¹¹ In this study, the concentration of pertechnetate was monitored as hydrazine was oxidized by nitrate. Under these conditions, it was possible to observe the complex behavior of pertechnetate with NMR spectroscopy. Recent NMR spectroscopic studies on ^{99}Tc isotopes have also shown the breadth of this technique for sensing a large variety of chemical species.¹² These recent studies included inorganic and organic molecules and determined that the ^{99}Tc resonances may span a shift in chemical concentration in the range of ≈ 8000 ppm.

However, although current conventional commercially available systems work well in a laboratory environment, they are not designed for on-site or in-process monitoring. For example, conventional superconducting laboratory-based spectrometers are large, heavy (i.e., they generally weigh up to 2000 lb), and expensive (often costing $> \$500,000$). In addition, the commercially available spectrometers require continuous operation by highly trained personnel, and their magnets generally require weekly nitrogen fills and monthly liquid helium fills.

In contrast to conventional spectrometers, the NMR technologies that are under development at Argonne National Laboratory (ANL) are designed for on-line intelligent process control. For example, the ANL technologies provide autonomous operation, effortless installation, and require few resources. One such NMR system that is under development is designed to weigh ≈ 150 lb (dominated by magnet weight), cost $\$20,000$ to $\$30,000/\text{unit}$, and fit into a short 19-in. NEMA 4 industrial instrumentation rack. The system has been programmed with advanced heuristics and is capable of complete automation without human interaction for periods of 6 months to years. ANL has leveraged this technology in combination with hardened electronics and magnet technology to provide an intelligent, efficacious, and economical solution to Hanford's on-line ^{99}Tc and ^{23}Na monitoring needs.

3.1 The Magnetic Resonance Phenomenon

Nuclei with either an odd atomic number or an odd mass number contain a nuclear magnetic or a simple magnetic moment.⁴⁻⁷ When a sample that contains such nuclei is placed in a homogeneous static magnetic field (\mathbf{B}_0), the nuclei align (according to Maxwell-Boltzmann statistics) along the direction of the magnetic field (along the z axis by definition) and precess (spin); see Fig. 1A. The precession rate (ω) is given by $\omega = \gamma \mathbf{B}_0$, where γ is the nuclear gyromagnetic ratio (a constant for given nuclei). Once aligned along the z axis, the net nuclear magnetic

component can be perturbed (tipped away from z) by application of additional magnetic fields (Fig. 1B).

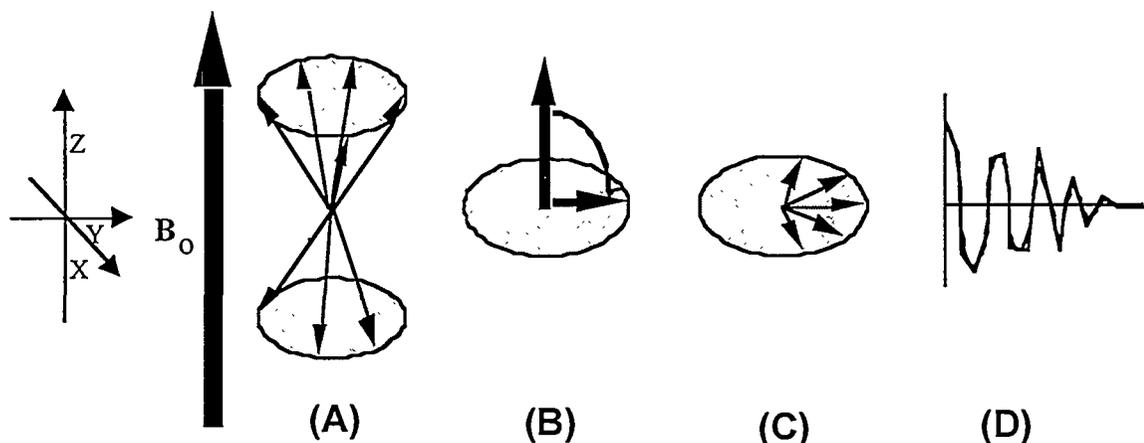


Fig. 1. (A) Alignment of nuclei with applied static magnetic field, (B) perturbation of net nuclear moment, (C) dephasing of net nuclear spins, and (D) resultant free induction decay (FID).

The alignment and perturbation are typically performed in modern NMR experiments by application of short RF pulses through an inductive transceiver coil at or near the precession rate in a direction normal to B_0 . After the perturbation, the net xy component of the magnetization can be measured as a function of time by the same transceiver coil. This function has the form

$$F(t) = \alpha M_0 \exp(-t/T_2) \exp\{i[(\Delta\omega - \omega_c)t + \phi]\}, \quad (1)$$

where α is a proportionality constant due to the receiver level, sample volume, and probe response; M_0 is the total spin magnetization; t is the time between the RF pulse and the acquisition of a discrete data point; T_2 is the effective time constant that is related to the dephasing (Fig. 1C) of the aligned spins (discussed in greater detail below); $\Delta\omega - \omega_c$ is the difference between the resonance frequency of the nuclei and the carrier frequency of the superheterodyne NMR receiver; and ϕ is a reference phase constant of the signal. The signal obtained from the experiment is generally an exponentially damped sinusoid (with damping constant T_2), known as a free induction decay (FID); see Fig. 1D. Because of its low level (mV), the signal is averaged to maximize the signal-to-noise ratio as the experiment is repeated.

The noise level, given by the root mean square noise threshold N_{rms} can be expressed by the Nyquist equation as⁸

$$N_{ms} = (4kTR\Delta\nu)^{1/2}. \quad (2)$$

The amount of signal received from a sample of volume ΔV is given by

$$\xi = \omega_0 \hat{B}_{1,xy} M_0 \Delta V. \quad (3)$$

Adding the advantage of signal averaging ($n^{1/2}$, where n is the number of averages), the signal-to-noise ratio can be expressed as

$$\Psi_n = \xi_n / N_{ms} = n^{1/2} \omega_0 \hat{B}_{1,xy} M_0 \Delta V / (4kTR\Delta\nu)^{1/2}, \quad (4)$$

where k is Boltzman's constant, $B_{1,xy}$ is the field generated by the coil, T is the absolute temperature, R is the apparent resistance of the RF coil, and $\Delta\nu$ is the band width in Hertz. The voltage V of the sinusoidal signal received at the RF coil is

$$V = -\omega L I_0 \sin \omega t, \quad (5)$$

where I_0 is the current in the wire, t is time, and L is the inductance of the coil. Note that in Eq. 4, R is related to the quality factor of the coil as $Q = \omega L / R$. R depends on real resistive losses in the coil structure itself, radiative losses to the outside world, and ionic losses to the sample. These ionic losses are dissipated in heat, but both radiative losses and ionic losses play a minimal role below a coil radius of 2 cm and magnetic field strength of 2 T.⁸ Thus, for a given magnetic field, temperature, and sample volume, it is desirable to maximize $B_{1,xy}$ and minimize coil losses. Furthermore, for a given magnet field quality (i.e., homogeneity over a given volume), it is desirable to maximize the sample and coil volumes. This often depends on both the homogeneity of the magnet and on the intrinsic line width of the detected NMR peaks.

3.2 The Chemical Shift

As discussed above, the resonance frequency is established by the main magnetic field and the gyromagnetic ratio of the nuclei (i.e., $\omega = \gamma B_0$). However, the electronic environment that surrounds the nuclei can cause small perturbations in the resonance frequency and lead to the phenomenon known as the chemical shift. These perturbations are generated by the shielding of the nuclei from the magnetic field by the surrounding electrons. The amount of shielding is given by σ (the isotropic shielding parameter). Thus, B_{eff} , the effective magnetic field encountered by nuclei, is $B_{\text{eff}} = (1-\sigma)B_0$, and the resultant resonance frequency of the nuclei is $\omega = \gamma B_{\text{eff}}$. In general, the shielding parameters

are quite small (i.e., generally 1-10 ppm), and they vary with molecular structure (i.e., the functional molecular groups such as methylene, methyl, aromatic, etc., have differing shielding parameters). This phenomenon is routinely applied to the spectroscopic structural characterization of molecules.

In addition to the genuine chemical shift caused by various molecular environments, it is possible to observe additional resonances (i.e., pseudo-chemical shift resonances) that are due to placement of the sample in a slightly different magnetic field (i.e., in accordance with $\omega = \gamma \mathbf{B}_0$). This is of particular interest in generating internal standard reference resonances for a quantitative reference baseline and is quite helpful as a reference for equipment operation. This phenomenon will be applied in the process monitor to allow quantification with internal standards of ^{99}Tc that are placed near the probe.

4 EXPERIMENTAL SYSTEM

A photo of ANL's prototypical on-line NMR system is included in Fig. 2. This system includes a user-friendly, hardened spectrometer enclosed in a NEMA 4 cabinet. The system, specifically designed to be highly flexible, allows various magnet configurations, experimental sequences, and optional equipment. Within the NEMA cabinet is an industrial PC, an RF module, and an input/output (I/O) module. In addition, the cabinet contains sufficient space to accommodate the small 0.5-T magnet shown on the right in Fig. 3. This system is designed to weigh ≈ 150 lb (dominated by magnet weight), and cost \$20,000 to \$30,000 per unit, depending on specific optional equipment and intended experiments.

The monitoring system is designed as a general-purpose process controller and includes features such as intelligent alarms, automated data processing, data logging, and process feedback. Recent reductions in hardware components have been implemented specifically to minimize component failure and electronic imbalances that may occur in a processing-plant environment. For example, the NMR's transceiver has been designed to require fewer components and provide more accurate data processing than conventional laboratory NMR spectrometers (see Fig. 2). The on-line monitor, which also contains a user-friendly graphical-user interface (GUI) that provides complete sensor control, flexibility of operation, and an intuitive operational environment, can easily be preprogrammed for intelligent process monitoring and feedback control (see Fig. 4).

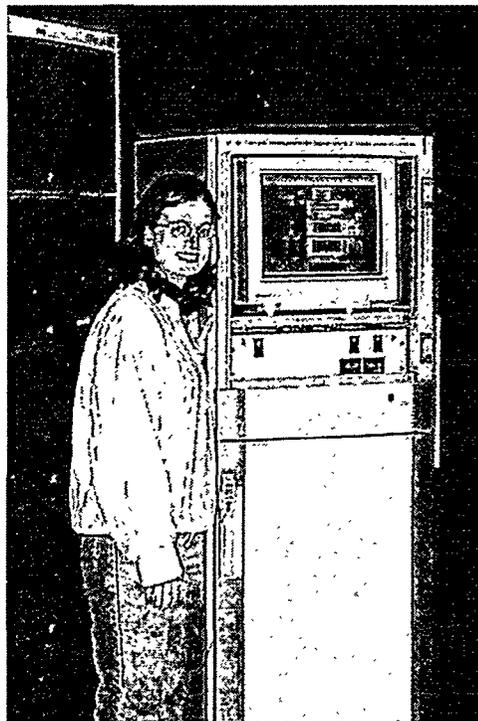


Fig. 2. Prototype ^{99}Tc and ^{23}Na NMR system shown with graduate student Karen Balss.



Fig. 3. Magnet systems available at ANL, including (from left to right) a superconducting 7.05-T magnet, a permanent 2.05-T magnet, and a 0.5-T permanent magnet.

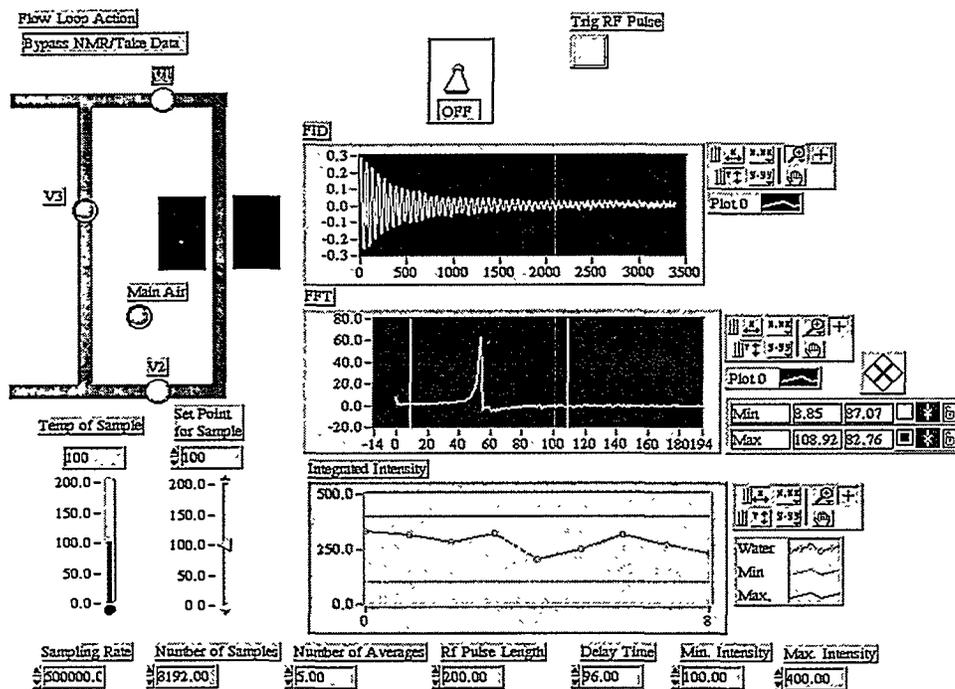


Fig. 4. View of user interface of on-line NMR spectrometer developed at ANL.

In addition to the on-line monitoring system that is enclosed in the NEMA 4 cabinet, on-line application must include an NMR magnet. Three such magnet systems are shown in Fig. 3. Each magnet system has advantages for specific applications. For example, the larger of the two permanent magnets provides a field that is sufficiently homogeneous to allow moderate resolution for chemical-shift spectroscopy. The smaller of the permanent magnet systems provides adequate homogeneity and field strength to monitor high concentrations of ^{23}Na . The superconducting system will provide the highest field strength and maximal homogeneity but at a higher cost and support burden. For example, the particular superconducting magnet shown in Fig. 3 requires a nitrogen fill every week and a helium fill every 6 weeks. Other cryogenic magnets are available with increased cryogen hold times of up to nearly 1 year for liquid helium.

To control the spectrometer and optional equipment, the ANL system was developed around an intuitive, highly flexible GUI. An example of this interface is included in Fig. 4. The popular software package Labview (National Instruments) was chosen for the system. We have found that this system can be nearly intuitive at first sight, and that technicians with minimal experience can derive useful codes within a few days. The system tracks various parameters, displays flow loop operation, controls sample and magnet temperatures, and reports alarm conditions

and operation parameters in a visually pleasing and intuitive manner. Additional information, such as trend analysis, various statistics, and self-diagnostics reports, can be portrayed. Also, the system can be configured to communicate with remote users or external control hardware by various means (e.g., RS232, IEEE 488, 20 mA current loop, or Ethernet).

In addition to the computer system, the NEMA cabinet contains an RF module (Fig. 5), a power I/O control module, and other modules. As with the other components, these modules are designed for simplicity of operation, high flexibility, and minimal maintenance. For example, the computer-controlled RF module allows the selection of a narrow receiver band width (see Eq. 2) over a wide frequency range (2-500 MHz), thus providing the capability to perform low-noise NMR analysis on any relevant nuclei. This RF design also provides flexibility in the choice of magnet field, from high-field superconducting magnets, to small permanent magnet systems.

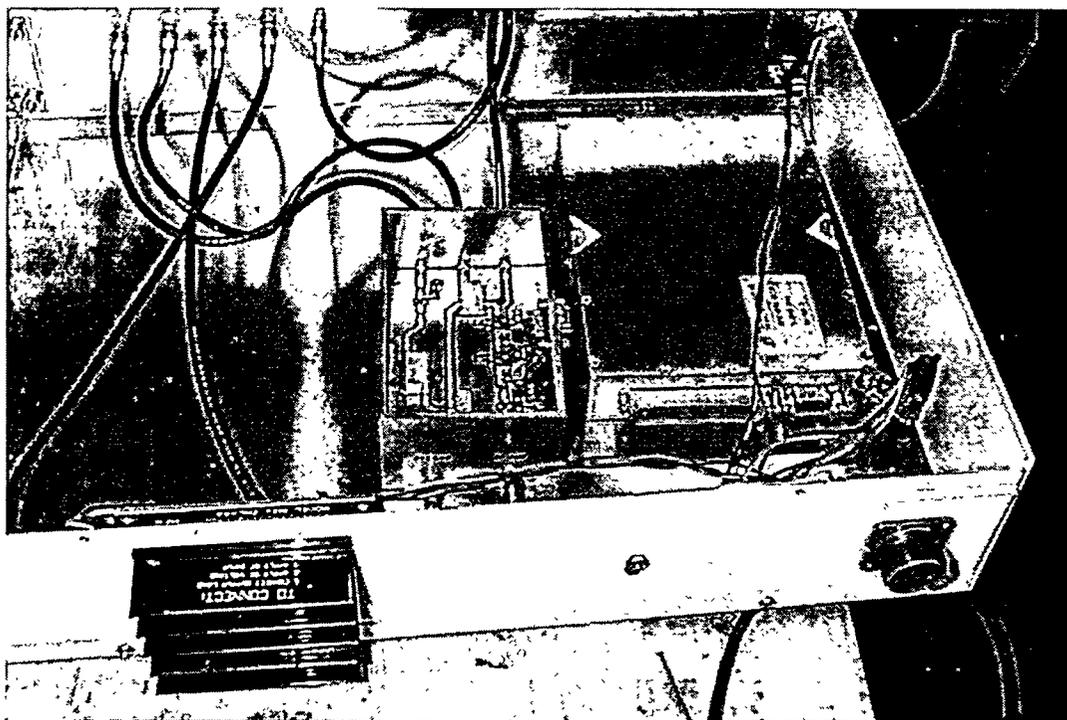


Fig. 5. Radio frequency module containing synthesizer, transceiver, and power amplifier.

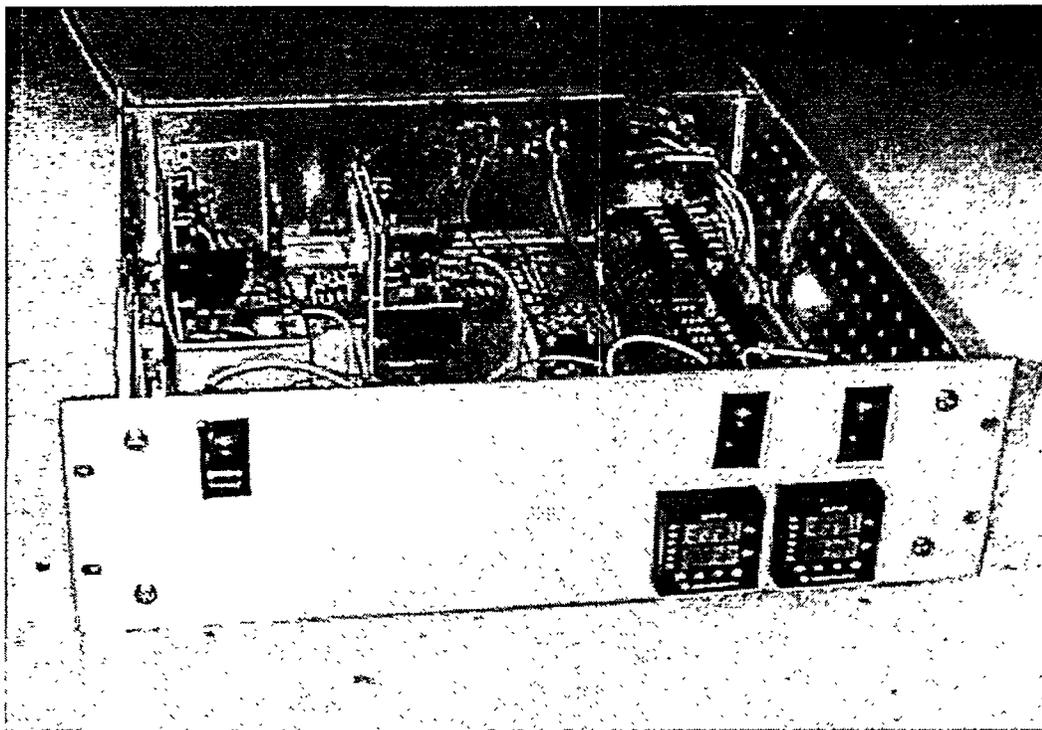


Fig. 6. Power supply, temperature, and valve control module.

The prototype also contains a power and I/O control module (Fig. 6). This module contains the power supplies that are required for operating various circuit components. The unit also contains commercial-grade computer-controlled I/O modules that are required for interfacing with common plant environments. The modules are ideal for pump control and have been successful at driving 110-V air-actuated liquid valves on a flow loop system. Finally, this unit contains two RS232-programmable temperature controllers that are used to trace the heating of the transfer tubing of the sample and/or the heating of a miniature reactor that may be required for sample conditioning. These devices are controlled by the industrial computer in the NEMA rack, and operated under the GUI.

5 RESULTS

5.1 Technetium Sensitivity Studies

Initial experimental studies focused on developing appropriate spectroscopic techniques and operational parameters (e.g., relaxation delay constants, acquisition times, and pulse widths) for the pertechnetate analysis. In this pursuit, standards were developed that covered five orders of magnitude from 10 μM to 0.1 M. Specifically,

appropriate aliquots of a 0.109-M ^{99}Tc (in 1-M aqueous nitric acid solution) standard reagent were placed in standard 5-mm NMR tubes and diluted as required with 1-M nitric acid solution. These samples were subsequently sealed with 5-min epoxy.

Initial ^{99}Tc spectra were acquired on a high-resolution 7.05-T wide-bore (89-mm) magnet. This system includes a 5-mm proton-carbon probe that was tuned for ^{99}Tc at 67.55 MHz by the application of a conventional tank circuit. The circuit responded with an unloaded quality factor of 225. Although spinning of the sample is typically performed in conventional NMR analysis to maximize spectral resolution, all of our ^{99}Tc spectra were acquired without spinning the sample to on-line conditions. The initial spectra confirmed the high sensitivity and narrow line width that are obtained for the pertechnetate resonance. This resonance generally produced a line width on the order of 0.1 ppm (≈ 6 Hz) that was dominated by the very fast intrinsic spin-lattice relaxation times of the pertechnetate species, and not by the homogeneity of the magnet, as is often the case with spectroscopic studies on nonquadrupolar nuclei. These relaxation rates were sufficiently short to allow data acquisition with the shortest relaxation delay possible on the instrument without adversely affecting the quality of the signal.

^{99}Tc spectra were acquired on the concentration standards described above with the 7.05-T magnet. Signal-to-noise measurements from this series are plotted in Fig. 7. This data exhibited good linearity, with a signal-to-noise ratio of 1.4 at a concentration of 9 μM ^{99}Tc . The optimal data acquisition conditions for the pertechnetate resonance analysis include 512 complex data points, 45-ppm band width (900 Hz), a 0.005-s interexperiment relaxation delay, and a time of 0.287 s per sample. A time of 10 min was required per analysis.

Spectra from the 2-T magnet system were acquired with a 5-mm NMR probe that was tuned for ^{99}Tc resonance at 20.265 MHz with a conventional tank circuit. This probe responded with a reasonable quality factor of ≈ 200 . As with the case above, the spectra were acquired on static samples, and exhibited line widths that were quite narrow. As in the case of the higher field, the spectral line widths were limited by the intrinsic relaxation parameters and not by the homogeneity of the NMR magnet. Data acquisition parameters that were designed to optimize the signal-to-noise ratio of the pertechnetate resonance were also applied. The resultant signal-to-noise measurements are indicated as triangles in the plot in Fig. 7. These data also show the expected degree of linearity. The reduction in the signal-to-noise ratio from the 7.05-T magnet is also as expected, based on the lower magnetic field, as indicated in Eq. 4. A low threshold sensitivity of ≈ 20 μM has been

determined for this magnet under these conditions. Several approaches can be taken to increasing the sensitivity and thus the signal-to-noise ratio of this magnet. These approaches are discussed in following sections.

An additional data set was acquired on the 7-T magnet system for both a 5.66- and 0.55-mM pertechnetate standard, as indicated in Fig. 8. As with other averaging techniques, the signal-to-noise ratios in the spectra follow the square root of the number of averages, as indicated in Eq. 4. Such relationships make it possible to construct an appropriate data acquisition scenario that is based on expected sample concentration, applied magnetic field strength, temporal sampling requirements, and required sensitivity of the ultimate measurement.

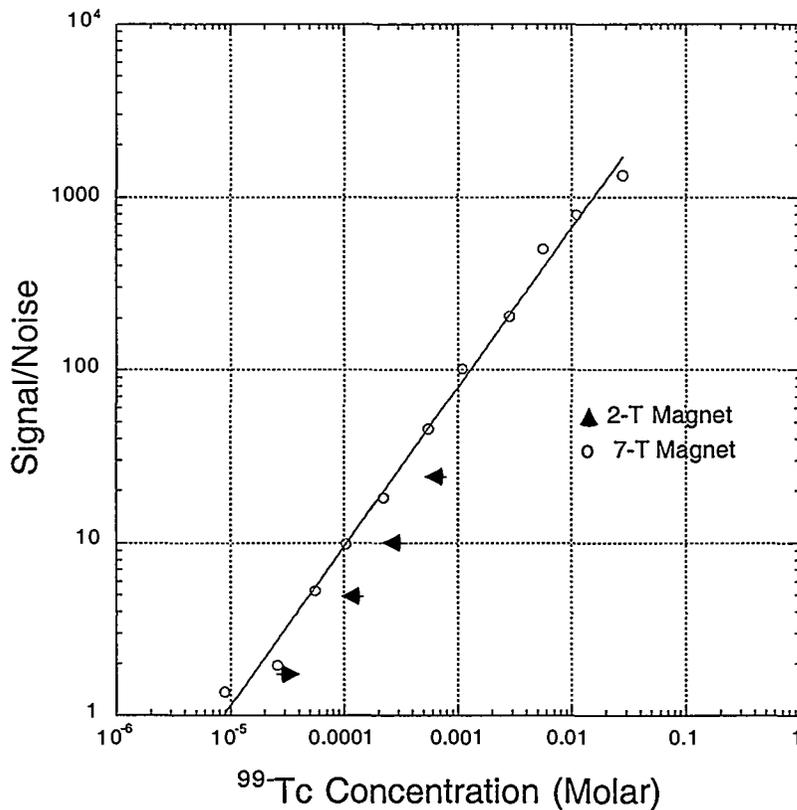


Fig. 7. Plot of Relative signal-to-noise ratio vs. pertechnetate concentration. Data were acquired with 2048 averages, 512 complex data points, and a bandwidth of 900 Hz. Each analysis required 10 min.

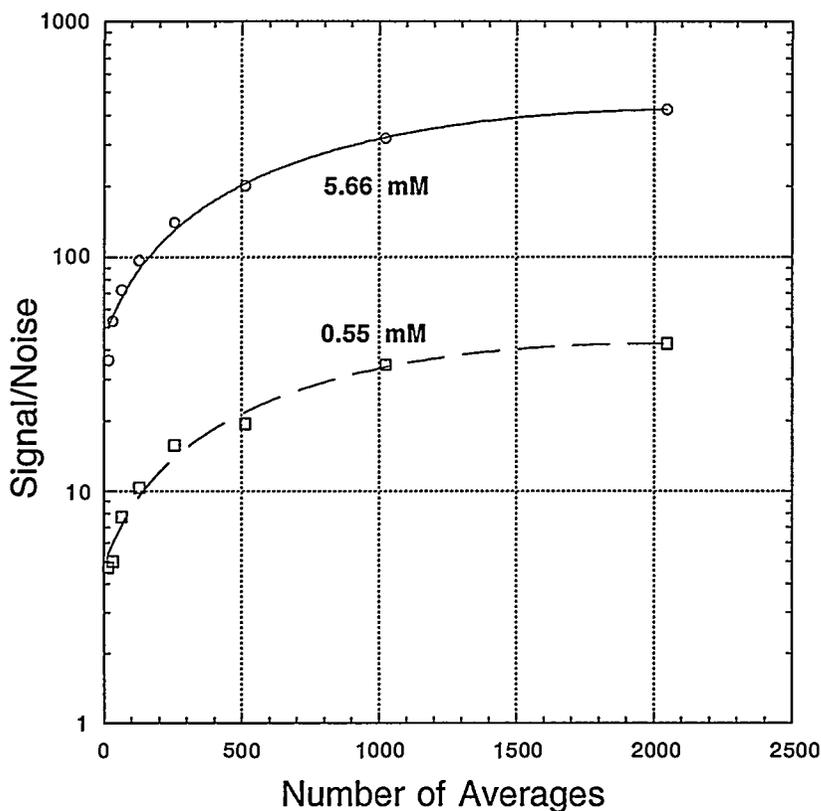


Fig. 8. Signal-to-noise ratio of pertechnetate resonance acquired on two ^{99}Tc standards as a function of number of free induction decay averages.

5.2 Technetium Redox Studies

Redox experiments were performed to verify that on-line oxidation or reduction of pertechnetate could be performed and monitored with the 2-T magnet system. These experiments were performed on a 0.005-M pertechnetate standard (derived from Tc metal in 1-M aqueous nitric acid solution). The pertechnetate was reduced with aqueous stannous chloride. When the reduction reactions were performed under ambient conditions (i.e., 23°C), they appeared to be instantaneous. With subsequent additions of reducing agent, the color progressed from a clear yellow to a reddish-brown. Between subsequent additions, spectra were acquired with minimal signal averaging (requiring ≈ 2 min per spectrum) on the 2-T magnet system (Fig. 9). The integrated peak intensities from the pertechnetate resonance are plotted in Fig. 10.

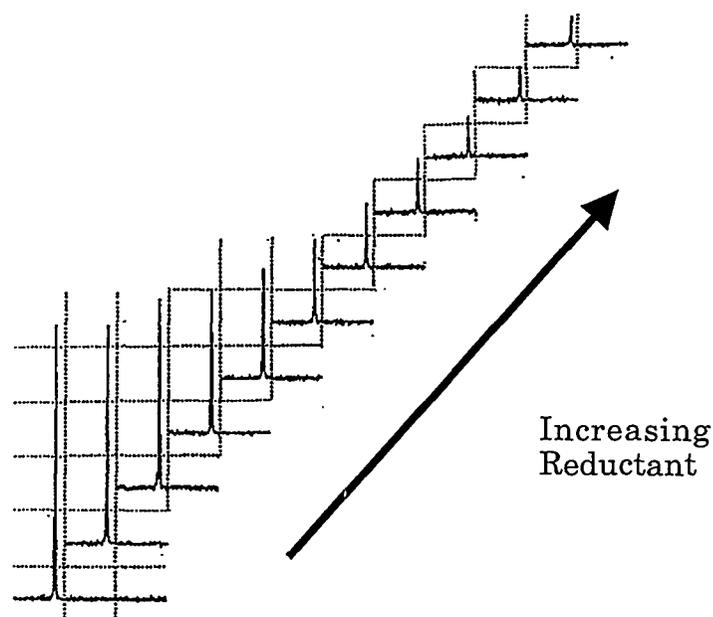


Fig. 9. Two-dimensional stack plot of pertechnetate resonance acquired with 2-Tesla NMR magnet system. Spectra are presented as a function of increasing reducing agent (lower pertechnetate concentrations) from left to right.

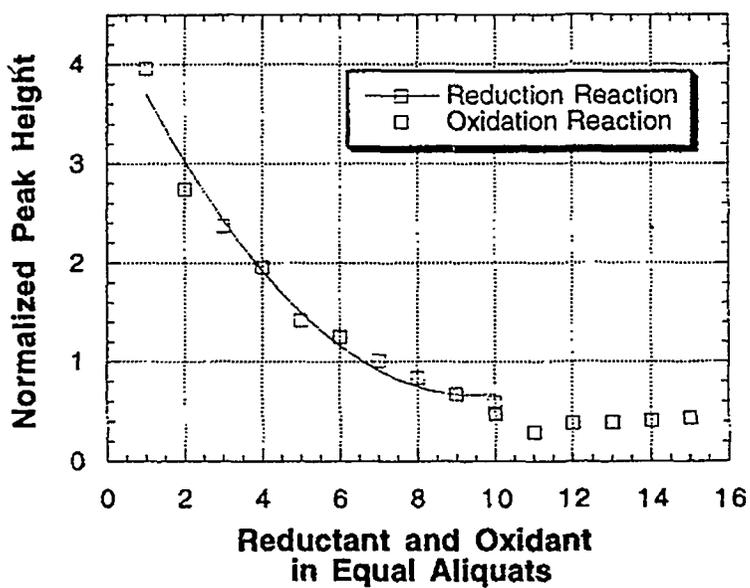


Fig. 10. Titration results with stannous chloride reducing agent and subsequent oxidation with peroxodisulfate.

Excess reagent was added in an attempt to force the reduction reaction to completion (i.e., eliminate the pertechnetate resonance completely). However, despite a several-fold excess of the reducing agent, a pertechnetate signal was observed. Given the complexity of oxidation states involved with Tc, additional reduction reactions may be occurring, placing the Tc into lower oxidation states and thus not significantly reducing the pertechnetate resonance. It is postulated that the electropotentials for other species (e.g., nitrate) are equally as likely to react with the stannous chloride and thus use up the reagent. Finally, competing oxidation reactions with the reduced Tc are likely to occur in the presence of the strong nitrate concentration in the solution.

Upon completion of the reduction reactions, oxidation experiments were conducted on the same partially reduced sample. In oxidation sequences, NMR has a particular advantage over conventional laboratory techniques, in that it requires no filtering or separation washing steps. Thus, the reaction was performed inside the NMR tube by simple injection of the oxidizing agent. Ammonium peroxodisulfate solution (2.0-M aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$) was used for the oxidation. Data were acquired on the 2-T NMR 15 min after addition of the oxidant. Oxidation occurred as indicated by the pertechnetate integrated signal intensity shown in Fig. 11. During this reaction, the initial aliquot of the oxidant reacted with the excess reducing agent in a competing reaction. After this reaction was complete, the oxidation began in earnest. The peak intensities in Fig. 11 were corrected for volume increases in the NMR tube, producing pertechnetate concentrations that were greater than the original sample. Although this is perhaps plausible, it is equally likely that an error occurred during calculation of the correction factor for the change in volume of the RF probe. This is not a trivial calculation because we must know the active volume of the RF field within the sample very accurately. Because sample volumes are limited, it is possible that part of the RF field remained uncovered during the initial phases of the study but was filled during the final phases of the titration. Whereas this leads to significant error in this particular analysis, it is of little consequence for the final on-line analysis, because sample volume under all conditions will be sufficient to completely fill the RF field volume. Under any envisioned probe design, the maximum required volume is ≈ 1.0 mL.

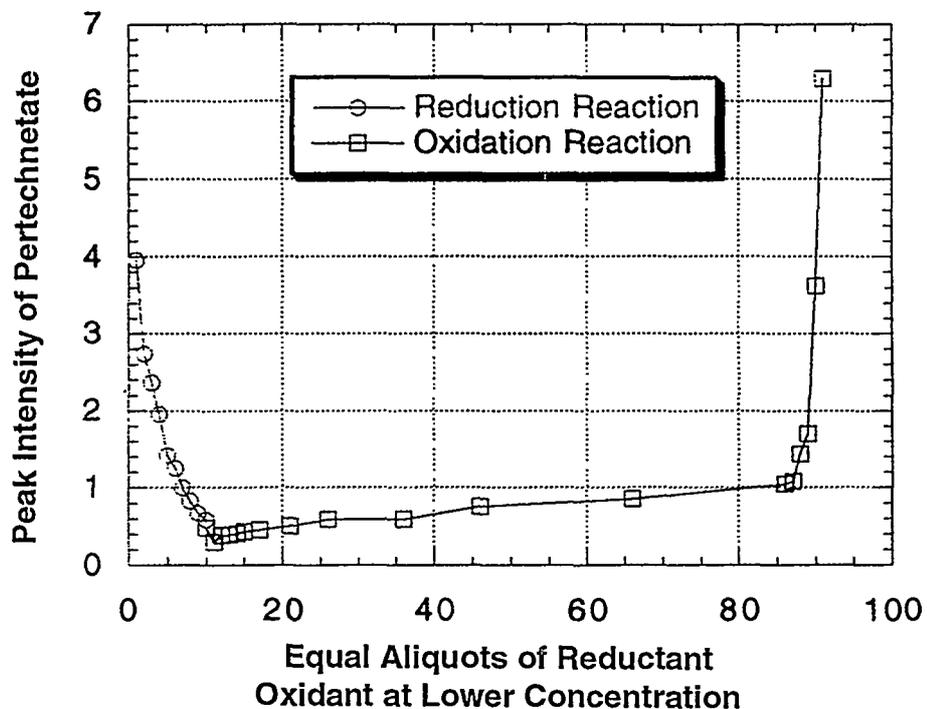


Fig. 11. Integrated peak intensity of ⁹⁹Tc pertechnetate resonance as a function of reducing and oxidizing agents.

Several additional experiments were performed to test effectiveness of other relatively effective oxidizing and reducing agents. For example, sodium bisulfite proved to be an adequate reducing agent, but could not be used at high pH because of precipitation. An economical version of this reagent is commonly available in most hardware stores as the household product Iron Out, which is a mixture of sodium sulfite and sodium bisulfite and works well as a reducing agent under low-pH conditions. The use of a reducing agent in a nitric acid rinse to elute Tc from the ion exchange columns has been suggested to minimize the number of column volumes that are required to regenerate the columns. Sodium bisulfite appears to be an efficacious reagent for this purpose under low pH conditions. The effectiveness of ceric sulfate as an oxidant was also investigated. Qualitatively, this reagent was somewhat less reactive than ammonium peroxodisulfate.

A significant attempt was made to obtain spectra from ⁹⁹Tc in states than the pertechnetate. This attempt was carried out to >8000 ppm, with other data acquisition parameters optimized. However, despite these efforts, it was determined that resonances for states other than the pertechnetate could not be observed. If indeed the ⁹⁹Tc is in a Tc(IV) oxidation state (and possibly an O₂Tc-TcO₂ complex), it is unlikely that it

will be observed by the NMR because of decreased spin lattice relaxation times.

Brief studies were performed to estimate the total usable volume of the magnetic field of the 2- and 7-T NMR magnets. A small sample was placed near the RF probe, and spectra of the specimens were acquired to estimate the homogeneity of the magnetic field. We determined that it is possible to significantly increase the sample volume of both magnet systems. Such an increase in sample volume will increase the signal-to-noise ratio of the spectra and thus the ultimate sensitivity. The increase is similar to but just less than the volume increase due to decreased probe Q observed with larger sample volumes. An estimate of the ultimate sensitivity of the magnet systems is included in Table 1. Corroborating experiments could be performed to verify the data in Table 1 if sufficient resources are available for probe development and sufficient sample volumes are available. Note again that the total sample volume required for the on-line analysis is ≈ 1 mL.

Table 1. Achieved and projected optimal ^{99}Tc NMR pertechnetate sensitivity of the ANL on-line NMR spectrometer.^a

Sensitivity	7-T Magnet	2-T Magnet
Achieved	10 μM (1.6 ppm) ^b	20 μM (3.26 ppm)
Projected ^c	5 μM (0.75 ppm)	10 μM (1.6 ppm)

^aValues in this table were obtained by assuming a 1-mL sample volume and a 12-min analysis.

^bppm concentrations are calculated by weight of pertechnetate in water.

^cProjected values are conservative estimates.

In addition to providing an accurate estimate of the total sample volume available for analysis in the magnets, these experiments also led to the development of an accurate real-time standardization method. This method is particularly useful in on-line analysis of low concentration signals, because it accurately assesses the health of the sensor system, even when the signal from the process stream is below the detection limit of the sensor (a likely case under conditions of high ion exchange column absorption). Moreover, this technique provides an external concentration standard that is acquired with each analysis; the magnetic field outside of the RF coil provides an external spectral reference spectrum. In the magnetic field outside the RF coil, the magnet field is reduced relative to that of the sample environment. Given that the nuclei

resonate at $\omega = \gamma B_0$ with a slightly reduced B_0 , the signal from the external resonance appears as a pseudo-chemical shift. This method is particularly useful for pertechnetate analysis, where pertechnetate could be placed in the system as a reference and appear in a second reference. Inasmuch as this sample is permanently designed into the RF probe mechanism, the standard will provide a long-term reference for months or years. This is particularly advantageous for on-line analytical techniques where system health degradation is always a concern.

5.3 Evaluation of Sodium Sensitivity

Cursory demonstration experiments with aqueous solutions in 5-mm NMR tubes were performed to establish the capability of the NMR technique to monitor sodium at process-relevant concentrations. The concentration range of 1-10 M ^{23}Na was chosen to correspond to the 5-7 M ranges in process feed streams. Probe tuning was far from optimal inasmuch as a poor quality factor and additional RF probe resonances were observed. Experimental conditions included a data acquisition time of 3 min per analysis, sample tuned at 79.35 MHz, a 3000-Hz spectral width, and 512 data points acquired per FID. As with the ^{99}Tc studies, internal concentration standards were not employed. A single resonance was observed for each standard, with a line width of ≈ 45 Hz. The area under this resonance was integrated and plotted in Figure 12. The results indicate a linear fit that is proportional to the concentration of the sample. An estimated error of ≈ 0.25 M per analysis was observed. Although this error is relatively high (≈ 2.5 -5% relative), it is well within the expected range, considering the lack of internal standards.

Several methods are available to reduce the relatively high error. One technique is to include additional data averaging. For example, if four times the number of averages are acquired (i.e., acquire data for 12 min), the error could be reduced by a factor of 2. Because a portion of the error is associated with probe design, another technique would be to design a nucleus-specific probe for ^{23}Na . In addition, for on-line analysis, the real-time pseudo-chemically shifted standard technique described in the previous section could be used. If these techniques are used, it may be possible to reduce the error to perhaps 1 relative percent and still provide automated on-line analysis every 3-12 min.

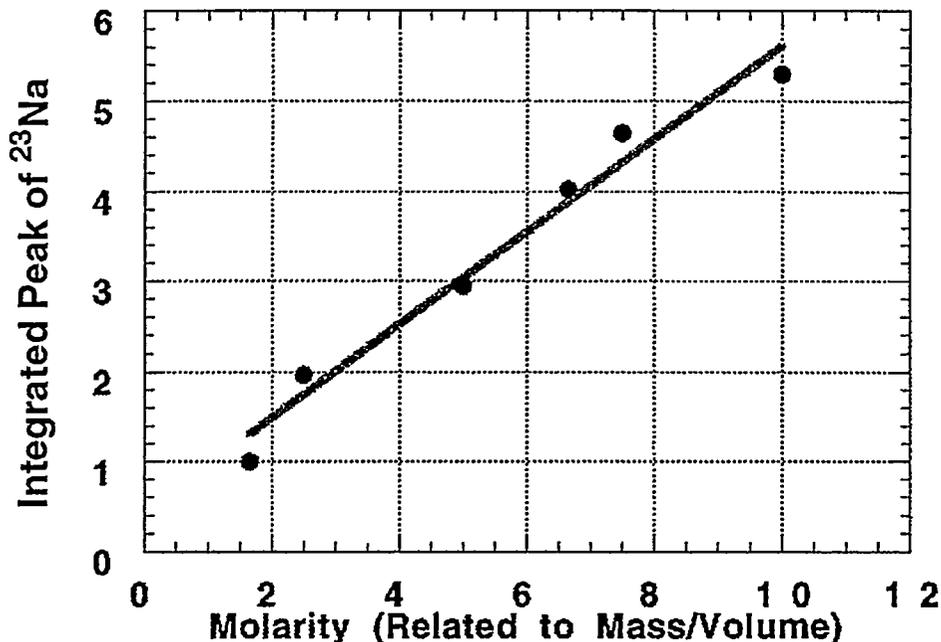


Fig. 12. Integrated intensity of ^{23}Na resonance as a function of NaCl concentration.

6 INSTALLATION PLAN

The on-line NMR instrumentation has been specifically developed as a multinuclear, broadband monitoring system. That system provides great flexibility in nucleus type, magnetic field, process interfacing, sampling techniques, data reporting, etc. As with any general on-line monitoring and control system, each installation will require careful planning to maximize the effectiveness of the system and minimize the cost and any potential deleterious impact on the process. The areas of concern are generally in the following four categories: measurement issues (i.e., material to be monitored), instrumentation specifications, auxiliary concerns, and startup requirements. Each of these categories will now be discussed in general terms. The discussions will include the specifics associated with monitoring ^{99}Tc and ^{23}Na .

6.1 Measurement Issues

For general on-line installation, the initial step is to define the required measurement parameters and the physical constraints in the local environment of the sensor system. This step requires a detailed understanding of the process and in-depth knowledge of the distribution and statistical parameters of the material to be monitored, other chemical and nonchemical interference, and in-plant physical

environment of the sensor. A noninclusive list of the chemical and physical parameters on the material to be analyzed includes the species to be monitored (e.g., nuclei or molecule), approximate concentration range of interest, dynamic range of the required measurement, and the accuracy and precision of the measurement. A knowledge of the fundamental statistical distribution of materials (e.g., temporal, and perhaps spatial, distribution) is necessary for accurate design of sampling requirements (i.e., stop-flow or flowing stream requirements). Several physical properties of the materials must also be known to determine piping and pumping needs. The requirement for one or more sample preparation steps must also be assessed. For example, the most appropriate analysis scheme for total ^{99}Tc will include a robust oxidation to pertechnetate. Finally, one must assess the presence of interfering chemical species (i.e., generally materials with similar functional groups in concentrations relevant to the material to be analyzed). The presence of interfering species may require the application of high spectral resolution or unique NMR pulse techniques.

Before developing instrumentation specifications, one must also address several plant-specific issues. For example, one must be aware of process-specific environmental interference such as mechanical vibration, electromagnetic fields caused by nearby pump motors, temperature extremes, or large concentrations of dust in the ambient conditions. The availability of plant services (i.e., power, clean, dry, compressed air, and perhaps vacuum) and the capabilities and availability of plant service and quality assurance personnel must also be assessed. Finally, certain installations may represent unique challenges. For example, in the case of ^{99}Tc , installations in a hot area may require that systems be designed for minimal or remote-control maintenance and quality assurance activities.

6.2 Instrument Specifications

Once the measurement and environmental issues are well understood, the primary specifications for the instrument can be developed. After the required sensitivity, concentration distribution of the material to be analyzed, and spectral and temporal resolutions are defined, the magnetic field, homogeneity, sample volume, and general instrument sensitivity specifications can be developed. These specifications often vary significantly. For example, high-sensitivity monitoring of ^{99}Tc requires a sensitive low-noise electronic package, a large sample volume (1-mL), moderately high field (2 T or greater field strength), and moderate spectral resolution (magnetic field homogeneity of 0.1 ppm over the 1 mL sample volume). Because the ^{99}Tc may be in its various oxidation states and molecular structures, the ANL NMR

technique will also require careful design of sampling systems, and the incorporation of a heated oxidation reactor. On the other hand, the analysis of ^{23}Na on a molar level will require a relatively insensitive NMR system that utilizes a magnet with minimal field and homogeneity (e.g., 0.5 and 1 ppm homogeneity over a 1-mL volume). Such a system could also incorporate flow-through techniques that minimize valve and control requirements.

Once the minimal configuration of the spectrometer and sampling system have been chosen, the environmental factors (e.g., vibration, electrical, and possibly acoustic noise) must be evaluated and possibly mitigated. Often it is possible to shield the spectrometers from many of these influences by incorporating vibration-isolating equipment, installing the spectrometers in instrument shacks, or adding electromagnetic shielding (Faraday cages) around the instruments.

6.3 Auxiliary Concerns

Connecting the system within the process will require some thought and testing and a considerable amount of coordination with plant engineers. The system control scenario, pump schedule, and valve requirements depend on the mode of operation (e.g., sample-and-hold mode or in a continuous manner). Because many processes and associated hazards are unique, the connections to the process and pump schedules are often at the discretion of plant personnel and not the instrument manufacturers. It is likely that plant engineers will have specific types of valves, fittings, and pumping systems available at a given location. Additional concerns include the need for and possible design of sample filtering systems, bypass loops, and lines to return the sample back to the process.

Finally, several computer-related and data management issues must be addressed. Such issues may include the level of flexibility in experimental design provided to the operators, level of statistical analysis and trending that is provided, and the specifics of generating alarms for the users. Other concerns may include integration of a computer platform, data feedback requirements, communication format (i.e., RS232, IEEE488, 4-20 mA, ethernet), data formats, etc. It is also desirable to define data distribution, access, and pathways, data archiving, and overall security concerns.

6.4 Startup Requirements

Once the monitoring system is installed and functioning with the rest of the process, accurate initial data must be acquired on well-

calibrated standards. Upon completing an accurate analysis with standard specimens, the instrument must be operated on-line in its conventional manner. Operational data must then be compared with accurately analyzed data that were acquired on equivalent grab samples. It is imperative that one attempt to define and understand the source of errors in the measurement (i.e., whether the errors are systematic or random). One must also attempt to quantify the frequency distributions of the error (i.e., normal distribution, bimodal, etc.), determine the confidence limits, and quantify the uncertainties of the measurement. Once these parameters have been determined, it is desirable to program the controller to autoreject outliers and initiate alarm features and data-base-building and data-archiving activities. The routine maintenance and quality-monitoring schedules of the instrument must be developed and integrated into the plant schedule. Finally, when the instrument capability and on-line performance are well characterized, there must be a conscious effort to integrate the response of the instrument into the day-to-day operation of the plant.

7 IMPLEMENTATION RECOMMENDATIONS FOR ⁹⁹Tc AND ²³Na

Implementation and evaluation of the on-line NMR technology in a pilot plant facility is currently recommended, because such an installation and the associated experimental series can easily determine the long-term efficacy of the techniques and ultimately their utility in Hanford's waste processing sequence. Furthermore, the pilot plant results will be available in a timely manner to significantly affect BNFL's process operation. Such a pilot treatment facility is soon to come on-line at the Savannah River Site (SRS). According to William Spencer (SRS), the facility will test pertechnetate ion exchange with 5-M NaOH and 7-ppm Tc feed. Stripping concentrations of the pertechnetate will approach 50 ppm. Currently, the detection limit of the 2-T magnet is 20 μ M pertechnetate (3.25 ppm, on a weight basis with TcO₄ in water). Furthermore, we believe that we can lower this limit to 1.5 ppm by using a new probe design.

In the pilot plant experimental sequence, we recommend that the 2-T magnet and associated spectrometer be placed at the SRS facility for an extended period. Depending on the experimental plan, the NMR system could perform sampling alternately on both the column feedstocks and the column effluents. This would provide an indication of the health of the column. In addition, the NMR should be employed to monitor column regeneration, because it may determine appropriate regeneration volumes.

The exact configuration of the NMR system somewhat depends on the feed materials that are to be monitored. For example, if the Tc is predominantly in the pertechnetate form, and if the ratio of pertechnetate to nonpertechnetate is invariant, it may be possible to perform NMR without subjecting the pertechnetate to initial preconditioning oxidation. This is a likely scenario, given the concentration range at the pilot facility and the sensitivity of the NMR technique (particularly with the development of the larger-volume RF probes). Under these conditions, it will only be necessary to develop a probe with a larger-volume body that incorporates the pseudo-chemical-shift concentration ^{99}Tc standard. Under this scenario, continuous flow-through analysis of the ^{99}Tc will be possible.

If the ratio of pertechnetate to nonpertechnetate Tc varies, or if the pertechnetate portion of the total ^{99}Tc is sufficiently low to be under the detection limits of the 2-T magnet, a robust oxidation step may be required. Under this scenario, an automated miniature 1-mL reactor will be designed into the NMR system (possibly into the probe body). It has been determined that robust oxidation with peroxodisulfate (at 80°C for 15 min) can be performed while the previous analysis is being performed. Temperature and pumping-valve controls are currently available in the NMR system for this option.

During the pilot plant tests, it will also be practical to evaluate the ability of the NMR to analyze ^{23}Na analysis. Such an experimental sequence will only require the development of a ^{23}Na RF probe that incorporates a pseudo-chemical-shift standard. We recommend that ^{23}Na analysis be performed under ambient conditions with flow-through techniques.

8 CONCLUSIONS

To support the requirements of Hanford's radioactive tank waste cleanup technology, this investigation has studied the design and development on an on-line NMR spectrometer for ^{99}Tc and ^{23}Na . An on-line NMR spectrometer for monitoring ^{99}Tc and ^{23}Na under process-relevant conditions was designed and tested in a laboratory setting. Sensitivities of 10- and 20- μM have been achieved for ^{99}Tc with 7.05- and 2.05-T magnets, respectively. These analyses require no sample preparation, can be performed automatically, and require a data acquisition time of 12 min per analysis. Furthermore, ^{23}Na concentrations have been demonstrated at 1-10 M ^{23}Na , with a 3-min analysis, and errors of ≈ 2.5 -5 relative percentage. Redox studies (reduction and oxidation) of technetium-containing species have also been demonstrated and monitored on-line with the NMR system. An

approach to performing on-line oxidation and analysis of total ^{99}Tc with a 12-min peroxodisulfate oxidation in a microreactor that is built into the NMR system has also been conceived.

We have concluded that the 2.05-T magnet system has achieved the sensitivity required for the BNFL process. Furthermore, this sensitivity can be enhanced by more than a factor of 2 by using a new, larger-volume RF probe. We have further concluded that on-line tests are now necessary to further evaluate the material handling and oxidation capabilities of the probe/reactor combination and therefore recommend that such tests be performed in the immediate future, preferably at a pilot waste-processing facility.

ACKNOWLEDGMENTS

We thank Dr. John Meiser (ANL/Ball State University), Cliff Conner (CMT-ANL), Ronald Lanham (ET-ANL), and Judy Carlson (ET-ANL), for technical support; Dr. Norman C. Schroeder (Los Alamos National Laboratory), and Dr. David Blanchard (Pacific Northwest National Laboratory), for technical input and samples; and Mike Johnson (British Nuclear Fuel Limited), Tom Thomas (Idaho National Engineering and Environmental Laboratory), Dr. Bruce Friedrich (University of Iowa), Tom Bastiaans (Ames Laboratory), J. Vince Panesko (Pacific Rim Enterprises), and William Spencer and Dr. Frank Kinard (Savannah River Site) for technical insight.

Financial support for this program is provided by the U.S. Department of Energy, Office of Environmental Management, within the Characterization and Monitoring Sensors Technology Crosscutting Program, under Contract W-31-109-Eng-38.

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