# APPLICATIONS OF $^{99}$Tc-NMR IN CHEMISTRY AND NUCLEAR MEDICINE

G.A. Kirakosyan[1,2], K.E. German[2], A.V. Afanasiev[2,3], S.N. Ryagin[3], A.V. Safonov[2], E.A. Kataev[4], F. Poineau[5], K.R. Czerwinski[5], E.V. Johnstone[5,6], A.P. Sattelberger[7]

[1]Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia
[2]Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, Russia
[3]Medical University Reaviz, Moscow branch, Russia
[4]Institute of Chemistry, Technische Universitat Chemnitz, Chemnitz, 09107, Germany.
[5]University of Nevada – Las Vegas, Chemistry and Biochemistry Department, Las Vegas, NV, USA
[6]Global Medical Isotope Systems (GMIS), Las Vegas, NV, USA
[7]Argonne National Laboratory, Chemistry Division, Lemont, IL, USA

DOI: 10.13140/RG.2.2.16251.36642

Long-lived $^{99}$Tc has the spin of the nucleus 9/2, so it is an NMR active isotope. Thus, $^{99}$Tc-NMR can be applied to investigations in chemistry and nuclear medicine. Some recent advances are summarized in an excellent review by Farnan and Berthon [1]. Here we present new results on Tc speciation and analyses.

Tc speciation was investigated the in $H_2SO_4$ from 2 M to 18 M, and the resulting complexes were characterized by NMR exchange spectra and EXAFS spectroscopy [2]. According to NMR, the $TcO_4^-$ species transformation is complete at 12 M.

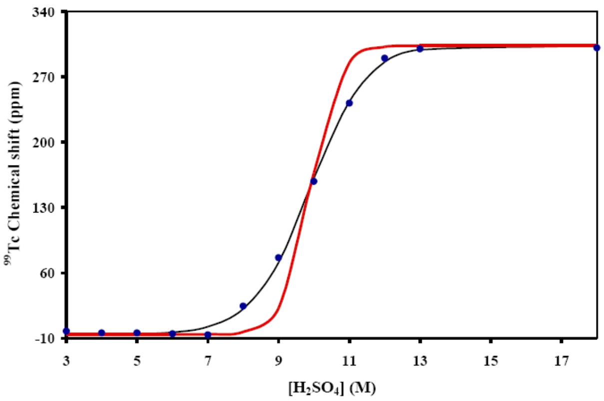


Fig.1. $^{99}$Tc NMR shift vs. $TcO_4^-$ of $KTcO_4$ dissolved in 3M and 18M $H_2SO_4$.

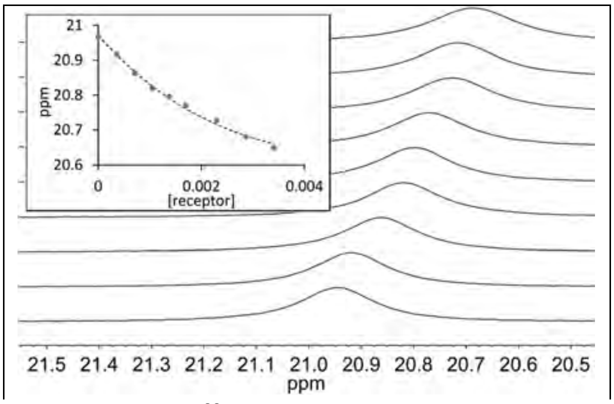


Fig. 2. Reverse $^{99}$Tc NMR titration with ligand-receptor in $CDCl_3$ - 5% DMSO. Insert: experiment (blue circles) and the fitting (dashed line).

When $KTcO_4$ is dissolved in 12 M $H_2SO_4$, EXAFS measurements on the resulting yellow solution indicated the presence of the $[TcO_3(H_2O)_3]^+$ cation.

NMR was applied to recognition receptor design and characterization. The reverse NMR-titration method, in which concentration of pertechnetate was kept constant, showed [3] good reproducibility (Fig.2). Binding constants of 4 for $TcO_4^-$ were found to be logK = 3.00.

Another application is based on the interaction of $^{99}$Tc nucleus spins with the spins of surrounding nucleus. $^{99}$Tc NMR has been suggested as an original method of evaluating the content of oxygen isotopes in oxygen $O^{18}$-enriched water, a precursor for the production of radioisotope fluorine-18 used in positron emission tomography. To this end, solutions of $NH_4TcO_4$ or $NaTcO_4$ (up to 0.28 mol/L) with natural abundance of oxygen isotopes in virgin or recycled $^{18}$O-enriched water have been studied by $^{99}$Tc NMR.

The method is based on $^{16}O/^{17}O/^{18}O$ intrinsic isotope effects in the $^{99}Tc$ NMR chemical shifts, and the statistical distribution of oxygen isotopes in the coordination sphere of $TcO_4^-$ and makes it possible to quantify the composition of enriched water by measuring the relative intensities of the $^{99}Tc$ NMR signals of the $Tc^{16}O_{4-n}{}^{18}O_n$ − isotopologues. $TcO_4^-$ ion was selected as a probe due to its high stability in aqueous solutions and the significant $^{99}Tc$ NMR shift induced by a single $^{16}O \rightarrow {}^{18}O$ substitution (−0.43 ± 0.01 ppm) in $TcO_4^-$ and spin coupling constant $1J(^{99}Tc–^{17}O)$ (131.46 Hz), favorable for the observation of individual signals of $Tc^{16}O_{4-n}{}^{18}O_{n-}$ isotopologues.

**References**


1. Ian Farnan and Claude Berthon. Applications of NMR in nuclear chemistry. RSC - Nucl. Magn. Reson., 2016, 45, 96–141. Series: Specialist Periodical Reports, ISSN: 0305-9804, DOI: 10.1039/9781782624103-00096.
2. F. Poineau, K. German, P. Weck et all. Speciation and Reactivity of Technetium in Sulfuric Acid. 2011.
3. A. Ravi, A.S. Oshchepkov, K.E. German, G. A. Kirakosyan, A.V. Safonov, V.N. Khrustalev, E. A. Kataev / Chem. Commun. DOI: 10.1039/c8cc02048e.
4. Tarasov V.P., Kirakosyan G.A., German K.E. 99Tc NMR determination of the oxygen isotope content in 18O-enriched water // Magn Reson Chem. 2018;56:183–189.
5. Nucl. Medicine and Biology.



The work was carried out with partial funding by the Ministry of Science and Higher Education of the Russian Federation (subject No. AAAA-A16-116110910010-3)