

Uranium Analysis and Chemistry Literature
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1] Methods for Uranium Measurement in Urine, Seawater and Other Fluids

Flow injection method for determination of uranium in urine and serum by inductively coupled plasma mass spectrometry. A Lorber, Z. Karpas and L Halicz, *Analytica Chimica Acta* **334**, 295-301, 1996. This study in Israel found U concentrations in urine of unexposed individuals to be between 1 and 40 ng/L with a median around 10 ng/L. This method requires virtually no sample preparation and uses a flow injection technique, although the authors indicate this is analytically challenging for routine analysis because it is difficult to prevent contamination at such low levels. The lower limit of detection is 1.5 ng/L.

Inductively coupled plasma mass spectrometry as a simple, rapid, and inexpensive method for determination of uranium in urine and fresh water: comparison with LIF. Z. Karpas, L. Halicz, J. Roiz, R. Marko, E. Katorza, A. Lorber and Z. Goldbart, *Health Physics* **71(6)**, 879-885, 1996. Sample preparation involves a fifty fold dilution of urine in 2% nitric acid and no other treatment or separation. The analysis is completed in 3 min and can be fully automated to allow more than 100 samples to be analyzed per day by one technician. The limit of detection is 3 ng/L in the original urine sample. Unexposed subjects were found to have 6 to 30 ng U per L in urine samples. By comparison, laser induced fluorescence (LIF in the title) had a limit of detection of about 1.5 microg/L. Fresh water and drinking water could be analyzed by ICP-MS without any prior dilution of sample and had a limit of detection of about 0.15 ng/L.

Determination of uranium in urine by inductively coupled plasma mass spectrometry with pneumatic nebulization. M. Caddia and B.S. Iversen, *Journal of Analytical Atomic Spectrometry* **13**, 309-313, 1998. Urine samples were diluted (1:20) in 1% nitric acid before analysis by ICP-MS. The limit of detection is 0.32 ng/L, which is sufficiently low to measure uranium in non-exposed individuals. The precision at a concentration of 8.9 ng/L was 3.9% (RSD). The recovery for 20 ng/L added to ten different samples was 101.5%. The mean concentrations measured for non-exposed subjects was 16.1 ng/L (presumably in Italy where this work was performed).

Determination of uranium in environmental samples using inductively coupled plasma mass spectrometry. D.W. Boomer and M.J. Powell, *Analytical Chemistry* **59**, 2810-2813, 1987. Reports the lower limit for quantitation of uranium in environmental samples is 0.1 ng/mL, with a linear range up

to 1000 ng/mL. Comparison with a conventional fluorometric method is given.

Investigation of the direct determination of uranium in plasma and urine by inductively coupled plasma mass spectrometry. P Allain, S Berre, A Premel-Cabic, Y Mauras, T Delaporte, A Cournot, *Analytica Chimica Acta* **251**, 183-185, 1991. The limit of quantification by this group using this very sensitive technique was 35 ng/L, which would not be suitable for measuring U in unexposed individuals.

Spectrophotometric method for the determination of uranium in urine. IK Kressin, *Analytical Chemistry* **56**, 2269-2271, 1984. This method uses arsenazo III [3,6-bis[(2-arsenophenyl)azo] 4,5-dihydroxy-2,7-naphthalenedisulfonic acid] as a colorimetric agent to measure uranyl ion with a limit of detection of about 1 microg in a large aliquot of urine, or about 5 microg/L.

Analysis of uranium in urine by delayed neutrons. H.M. Ide, W.D. Moss, M.M. Minor and E.E. Campbell, *Health Physics* **37**, 405-409, 1979. This method can measure levels of U-235 by delayed neutron counting, meaning there is a fission reaction of the U-235 that generates neutrons. This would not be a suitable method for determining depleted uranium because it doesn't give levels for U-238.

Development of a rapid, economical and sensitive method for the routine determination of uranium in urine. TJ Miller, *Analytical Letters* **24(4)**, 657-664, 1991. Urine is treated with concentrated HCl and the uranyl tetrachloride anion bound to an ion exchange column, washed with 6 M HCl and then eluted with 0.1 M HCl followed by evaporation, dissolved in conc. nitric acid, evaporated, dissolved in ammonium sulfate, followed by electrodeposition of uranium, addition of 50% ammonia, drying and finally alpha liquid scintillation counting. It doesn't seem like such a rapid method, but was used to measure uranium in urine of uranium industry workers.

On-line time-resolved laser-induced fluorescence of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ in supercritical fluid CO_2 . R. S. Addleman and C.M. Wai, *Analytical Chemistry* **72**, 2109-2116, 2000. The title method is shown to be effective for on-line measurement of uranyl chelates in supercritical fluid CO_2 extraction procedures. The method was applied to the kinetic analysis of uranium extraction from acidic solutions with tributyl phosphate modified supercritical CO_2 .

Direct determination of dissolved uranyl(VI) in sea-water by cathodic stripping voltammetry. R. Djogic and M. Branica, *The Analyst (London)* **120**, 1989-1993, 1995. The authors used square-wave cathodic stripping voltammetry to measure uranyl ion in untreated estuarine sea-water on a static mercury drop electrode. By the standard addition method, uranyl concentrations in water samples ranged between 4.3 and 15 nmol per L. The detection limits were between 2.4 and 10 nmol per liter, depending on conditions.

Dissolved uranyl complexed species in artificial seawater. R. Djogic and M. Branica, *Marine Chemistry* **36**, 121-135, 1991. Calculated the distribution of uranyl species based on stability constants and compared with experiments in artificial seawater. In the presence of sufficient hydrogen peroxide the uranyl-dicarbonato-hydrogenperoxo complex probably predominates. This work was based on recent discovery of hydrogen peroxide in surface waters (photic zone) of the seas. Electrochemical determination of dissolved uranium in Krka River estuary. R. Djogic, I. Pizeta and

M. Branica, *Water Research* **35(8)**, 1915-1920, 2001. Cathodic stripping voltammetry was used to measure uranium in the Krka River (Croatia) during various seasons and along different depth profiles. It was necessary to acidify samples, purge with nitrogen gas to remove CO₂ and then neutralize the sample prior to electrochemical measurements to remove the carbonate complexes of uranyl ion. The measured concentrations of uranium varied from 4 to 33 nmol per L. Comparison of measurements with an x-ray fluorescence method confirmed the applicability of the method, but pointing out the limitations caused by the matrix of the solution, i.e., suspended organic matter.

Square-wave cathodic stripping voltammetry of hydrolyzed uranyl species. R. Djogic and M. Branica, *Analytica Chimica Acta* **305**, 159-164, 1995. This technique, which is usually used for detection of nonmetals or metalloids, relies on adsorption of the neutral uranyl hydroxide complex (UO₂(OH)₂ apparently). Following adsorptive accumulation of the uranyl species on the mercury electrode surface, followed by square-wave reduction in a cathodic scan. The method is able to detect uranyl ion as low as 20 nmol/L.

Applicability of synergistic adsorption in electroanalysis of dissolved uranium in seawater. M. Mlakar and M. Branica, *Marine Chemistry* **46**, 61-66, 1994. Found that ligand pairs, such as salicylic acid-tributylphosphine oxide (TBP), 2-thenoyltrifluoroacetone-TBP, and acetylacetone-TBP improve the sensitivity for uranyl measurement by cathodic stripping voltammetry, with a limit of detection of about 0.10 nM with the TTA-TBP pair or 1 nM with the SA-TBP pair. Dissolved uranium in natural water samples were measured at 7 to 40 nM.

Characterization of uranium(VI) in seawater. R. Djogic, L. Sipos and M. Branica, *Limnology and Oceanography* **31(5)**, 1122-1131, 1986. Studied the various dissolved uranium(VI) species in sea water with varying pH and carbonate concentration. Below pH 4, "free" hydrated uranyl ion is present, with stepwise formation of carbonate complexes at increasing pH in the presence of CO₂ or carbonate, with the tricarbonato complex predominating above pH 8 in carbonate solution.

Adsorption voltammetric techniques for the determination of uranium(VI) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone as complex forming agent. S. Sander and G. Henze, *Fresenius Journal of Analytical Chemistry* **349**, 654-658, 1994. This method eliminates necessity to pretreat polluted water samples with uv-radiation or microwave digestion. The limit of detection using this method was about 24 ng/L or about 0.1 nM uranyl ion.

The electrode synergistic adsorption of mixed ligand complexes. Part I. Uranium(VI) salicylic acid/TBP system. M. Mlakar and M. Branica, *Journal of Electroanalytical Chemistry* **256**, 269-279, 1988. This method uses accumulation of the mixed uranyl complex with salicylic acid and tri-n-butyl phosphate in aqueous solution on a mercury drop electrode prior to cyclic voltammetry. The sensitivity was on the order of 1 to 100 nM in uranyl ion.

Determination of uranium in sea water by x-ray fluorescence spectroscopy. M. Nagj, J. Makjanic, I. Orlic, S. Tomic, V. Valkovic, *Journal of Radioanalytical and Nuclear Chemistry* **97/2**, 373-380, 1986. Used the x-ray spectrometric method to determine uranium in sea water following either: (1) precipitation with the chelating agent ammonium-1-pyrrolidine dithiocarbamate (APDC) in the presence of Fe(II) as a carrier, or (2) complexation with APDC followed by adsorption on activated carbon. The former procedure was easier and faster, but the latter gave better recovery of uranium. It

is claimed that both procedures would be suitable for measuring uranium at the ppb level.

The determination of uranium in natural waters at ppb levels by thin-film x-ray fluorescence spectrometry after coprecipitation with an iron dibenzylthiocarbamate carrier complex. GS Caravajal, KI Mahan, DE Leyden, *Analytica Chimica Acta* **135**, 205-214, 1982. U in natural waters was preconcentrated with the title iron carrier complex and the precipitate was analyzed by x-ray fluorescence spectrometry. UV radiation was used to decrease humic substances and allow filtration of larger volumes of sample for determination of lower concentrations of U. The detection limit was 0.4 microg/L for 500 mL samples.

Determination of uranium(VI) in sea water by cathodic stripping voltammetry of complexes with catechol. C.M.G. Van Den Berg and Z.Q. Huang, *Analytica Chimica Acta* **164**, 209-222, 1984. Found optimal conditions for measuring uranium in sea water by cathodic stripping voltammetry include pH 6.8, with 2 mM catechol, at a collection potential of -0.1 to -0.4 V (vs Ag/AgCl). The limit of detection was 0.3 nM after a 2.5 min collection time and there was a linear relationship with uranyl concentration up to 50 nM. Organic surfactants at unnaturally high concentrations reduced the peak height for uranium. Addition of EDTA removed interference by Cu(II).

Determination of uranium by adsorptive stripping voltammetry. N.K. Lam, R. Kalvoda and M. Kopanica, *Analytica Chimica Acta* **154**, 79-86, 1983. Describes the cathodic stripping voltammetry of adsorbed U(VI)-catechol complex on a mercury electrode. The method is used to measure uranium in natural waters in the range from 0.4 microg/L (~1.6 nM) to 0.2 mg/L. The method is less sensitive than the previous one (Van Den Berg and Huang) due to treatment of water samples prior to analysis.

Selective determination of trace uranium by stripping voltammetry following adsorptive accumulation of the uranium-cupferron complex. J. Wang and R. Setiadji, *Analytica Chimica Acta* **264**, 205-211, 1992. Used a uranyl-cupferron complex for adsorptive deposition on a mercury electrode prior to stripping voltammetry or potentiometry with detection limits of less than 1 nM over a relatively broad pH range (3.5 to 7) and without oxygen interference.

Square-wave voltammetry of uranyl-humate complex. M. Mlakar, *Analytica Chimica Acta* **276**, 367-372, 1993. The uranyl-humate complex was formed in the reaction cell and the limit of detection was about 5 nM in 0.55 M NaCl solution and similar in artificial or natural sea water. This technique would be useful for water samples laden with soil runoff.

Square-wave voltammetric peak current enhancements by adsorption and reversibility of the redox reaction. M. Lovric and M. Branica, *Journal of Electroanalytical Chemistry* **226**, 239-251, 1987. Studied the square wave voltammetric peak currents for 10 different metal ions (including uranyl) in different electrolyte solutions.

Study of uranyl(VI) ion reduction at various ionic strengths of sodium perchlorate. R. Djogic and M. Branica, *Analytica Chimica Acta* **281**, 291-297, 1993. The reduction of uranyl to U(V) was studied by square-wave voltammetry in non-complexing NaClO₄ electrolyte media at different ionic strengths to determine the number of coordinated water molecules involved in the redox reaction. It was found 2 water molecules are lost upon reduction.

Absorptiometric determination of microgram amounts of uranium with rhodamine B. H.H.P. Moeken and W.A.H. Van Neste, *Analytica Chimica Acta* **37**, 480-483, 1967. Uranium(VI) or uranyl was extracted as a complex with rhodamine B into a benzene-ether-hexone solvent from benzoate buffered solution. The uranium complex in this solvent had maximum absorbance at 555 nm with a molar absorptivity of 102.7 M⁻¹ cm⁻¹. The limit of detection for uranyl was about 0.02 microg per mL or 0.02 mg/L (or 0.1 microM). The interference by several ions was studied.

Separation of uranium from seawater by adsorbing colloid flotation. Y.S. Kim and H. Zeitlin, *Analytical Chemistry* **43(11)**, 1390-1393, 1971. This procedure uses a positively charged ferric hydroxide collector to adsorb the stable uranyl tricarbonate species from seawater. Upon adding the anionic surfactant, sodium dodecyl sulfate and bubbling air through the solution, the colloidal particles enriched in uranium float to the top and are skimmed off for analysis. Uranium was analyzed spectrophotometrically using the Rhodamine B complex absorption at 555 nm.. The average recovery of uranium from seawater by this method was 82%.

An improved separation and determination of uranium in seawater. G. Leung, Y.S. Kim and H. Zeitlin, *Analytica Chimica Acta* **60**, 229-232, 1972. This is an improvement on the previous report, using thorium hydroxide in place of ferric hydroxide in the collector and using fluorescence of the rhodamine B complex for greater sensitivity.

Tetravalent uranium in calcite. N.C. Sturchio, M.R. Antonio, L. Soderholm, S.R. Sutton, J.C. Brannon, *Science* **281**, 971-973, 1998. X-ray absorption and fluorescence techniques show that 35 million year old calcite from a Mississippi Valley-type zinc ore deposit indicates substitution of tetravalent U for divalent calcium. This suggests that calcite provides a sink for uranium in groundwater aquifers, although this reviewer would ask whether the uranium was deposited during the calcium carbonate formation by marine organisms.

2] Studies of Uranium in the Environment

Note: The United Nations Environment Programme (UNEP) has published reports of post-conflict environmental assessments in the Balkans (Kosovo, Bosnia-Herzegovina, Serbia and Montenegro) and Iraq. These reports are available at the UNEP website - <http://www.unep.org>

High energy x-ray microscopy for characterisation of fuel particles. B. Salbu et al. (12 authors), *Nuclear instruments and Methods in Physics Research A* **467-468**, 1249-1252, 2001. The title x-ray technique was used to show particle characteristics, including weathering rates and mobilization of associated radionuclides. Fuel particles released during explosion are characterized by UO₂ cores with surrounding layer of reduced U with low weathering rates. In contrast, fuel particles released during a subsequent fire show UO₂ cores with surrounding oxidized layers of U₂O₅ and U₃O₈, which have high weathering rates.

Oxidation states of uranium in DU particles from Kosovo. B Salbu, K Janssens, OC Lind, K Proost, PR Danesi, *Journal of Environmental Radioactivity* **64**, 167-173, 2003. DU particles collected from Ceja Mtn. nearly 2 years after the conflict were analyzed at IAEA labs in Seibersdorf, Austria. Particles were uranium oxides ranging in size from submicron to 30 micron, with average <2 micron. with about 50% UO₂ and the remaining U₃O₈ or mixed oxides. It should be noted that UO₃ particles

would not be expected due to weathering and dissolution over this time period. This was part of the UNEP assessment in the Balkans.

Depleted uranium particles in selected Kosovo samples. PR Danesi et al (11 authors), *Journal of Environmental Radioactivity* **64**, 143-154, 2003. Samples collected nearly 2 years after conflict were analyzed at IAEA labs. The particle size distribution is reported, with >50% of the particles having <1.5 micron diameter. The same samples described in the paper by Salbu et al.

Evidence for a higher natural uranium content in world rivers. A Mangini, C Sonntag, G Bertsch, E Mueller, *Nature* **278**, 337-339, 1979. This study showed that uranium content of world rivers and groundwater correlates reasonably well with bicarbonate content - carbonate and bicarbonate increase uranyl solubility, and does not seem to correlate with contamination levels from mining and other activities.

3] Bioremediation of Uranium in the Environment

Reduction of U(VI) in goethite (alpha-FeOOH) suspensions by a dissimilatory metal-reducing bacterium. J.K. Fredrickson, J.M. Zachara, D.W. Kennedy, M.C. Duff, Y.A. Gorby, S.W. Li and K.M. Drupka, *Geochimica et Cosmochimica Acta* **64 (18)**, 3085-3098, 2000. The dissimilatory metal-reducing bacterium, *Shewanella putrefaciens*, a subsurface bacterium, was able to reduce UO₃ (uranium trioxide dihydrate) and uranyl ion as the carbonate complex either in the absence or presence of the mineral goethite (alpha-FeOOH) using lactate as an energy source. The U(VI) was reduced to insoluble UO₂ (uranium dioxide). These bacteria are capable of reducing other metals, including Mn(IV), Cr(VI) and Fe(III).

Influence of Mn oxides on the reduction of uranium(VI) by the metal-reducing bacterium *Shewanella putrefaciens*. J.K. Fredrickson, J.M. Zachara, D.W. Kennedy, C. Liu, M.C. Duff, D.B. Hunter and A. Dohnalkova, *Geochimica et Cosmochimica Acta* **66(18)**, 3247-3262, 2002. It was found that pyrolusite (beta-MnO₂) and bixbyite (Mn₂O₃) will abiotically oxidize uraninite (UO₂) to soluble U(VI) species. Consequently, these manganese oxides will lower the overall rate of U(VI) reduction by these bacteria relative to the rate in the presence of gibbsite (Al(OH)₃). Mn(II) concentrations increased with increasing initial U(VI) concentration in the presence of the bacteria, indicating a uranium mediated reduction of the Mn oxides. It was found that reduced U resided in the periplasmic space of the bacteria, however, in the absence of Mn oxides, the UO₂ accumulated as copious fine-grained particles external to the cells.

Modeling the inhibition of the bacterial reduction of U(VI) by beta-MnO₂(s). C. Liu, J.M. Zachara, J.K. Fredrickson, D.W. Kennedy and A. Dohnalkova, *Environmental Science and Technology* **36**, 1452-1459, 2002. Pyrolusite (beta-MnO₂) could be reduced at a faster rate than U(VI) by *S. putrefaciens* CN32 cells. Furthermore, when U(VI) was reduced microbially in the presence of MnO₂, there was an abiotic reoxidation of the UO₂ by MnO₂. This study shows that reduction of soluble uranyl ion to the insoluble UO₂ by dissimilatory bacteria can be complicated by the presence of oxidizing minerals in the environment.

Inhibition of bacterial U(VI) reduction by calcium. S.C. Brooks, J.K. Fredrickson, S.L. Carroll, D.W. Kennedy, J.M. Zachara, A.E. Plymale, S.D. Kelly, K.M. Kemner and S. Fendorf, *Environmental*

Science and Technology **37**, 1850-1858, 2003. This study found that the presence of calcium (at mM concentrations) reduced the rate of U(VI) reduction by *S. putrefaciens* CN32, as well as by the obligate anaerobes, *Desulfovibrio desulfuricans* and *Geobacter sulfurreducens*. XAFS measurements showed that calcium forms a complex with the U(VI)-carbonate species in solution, which accounts for the decreased rate of reduction.

Reduction of uranium(VI) by mixed iron(II)/iron(III) hydroxide (green rust): formation of UO₂ nanoparticles. E.J. O'Loughlin, S.D. Kelly, R.E. Cook, R. Csencsits and K.M. Kemner, *Environmental Science and Technology* **37**, 721-727, 2003. Green rusts, or mixed Fe(II)/Fe(III) hydroxides, are found in many low oxygen environments (e.g., subsurface soils). EXAFS was used to show that uranyl ion was reduced to UO₂ (U(IV)) by green rust. This reviewer would like to point out that the UO₂ nanoparticles are susceptible to relatively rapid oxidation in the presence of oxygen. Larger particle sizes are not readily oxidized.

Uranium(VI) sorption to hematite in the presence of humic acid. J.J. Lenhart and B.D. Honeyman, *Geochimica et Cosmochimica Acta* **63(19-20)**, 2891-2901, 1999. This study used computer simulation models for the effects of humic acid (common organic matter in soils), hematite (common iron ore, Fe₂O₃), and carbonate on U(VI) binding or distribution in this system. The aim of the study was to determine the effects of humic acid on U(VI) sorption by hematite in soils.

Surface catalysis of uranium(VI) reduction by iron(II). E. Liger, L. Charlet and P. Van Cappellen, *Geochimica et Cosmochimica Acta* **63(19-20)**, 2939-2955, 1999. This study found that Fe(II) in homogeneous anaerobic solution did not reduce U(VI) over several days, even though the reaction is thermodynamically feasible. However, in hematite suspensions, which bind U(VI) on the surface, there is reduction of the U(VI) by Fe(II) on the surface of the hematite particles. The reaction exhibited a first order dependence on the concentration of U(VI) extracted from the hematite particles. There was a pH dependence as well. A mechanism is discussed.

N-compound reduction and actinide immobilisation in surficial fluids by Fe(II): the surface Fe(III)OFe(II)OH species, as major reductant. L. Charlet, E. Silvester and E. Liger, *Chemical Geology* **151**, 85-93, 1998. The abiotic reduction of U(VI) by sorbed Fe(II) involves inner sphere electron transfer, with 3 kinetic steps: adsorption of uranyl ion (forming an inner sphere complex), and two reductive steps leading to formation of UO₂/Fe(OH)₃ mixed solid phase. It is suggested that these reduction reactions may have led to the formation of insoluble uranium ores and removal of uranium from surface waters.

Interaction between aqueous uranium(VI) and sulfide minerals: spectroscopic evidence for sorption and reduction. P. Wersin, M.F. Hochella, Jr., P. Persson, G. Redden, J.O. Leckie and D.W. Harris, *Geochimica et Cosmochimica Acta* **58(13)**, 2829-2843, 1994. A study of the sorption and reduction of uranyl ion from solution on galena (fool's gold) and pyrite mineral surfaces. The uranyl uptake is dependent on pH with maximum uptake (>98%) above pH 5.5 under certain conditions. X-ray photoelectron spectroscopy (XPS) gives some indication of the processes taking place, including reactions with iron and sulfide on the surface. Formation of a U₃O₈ type species indicates partial reduction of uranyl by sulfide on the surface.

Enzymatic uranium precipitation. Y.A. Gorby and D.R. Lovley, *Environmental Science and*

Technology **26**, 205-207, 1992. Cultures of the metal-reducing bacterium, GS-15 were grown under anaerobic conditions (N₂/CO₂, 80:20) with acetate as the sole electron donor and Fe(III) citrate as the terminal electron acceptor. The organisms reduced uranyl ion in the medium resulting in formation of a UO₂ (U(IV)) precipitate. The UO₂ precipitate was extracellular, but in early stages of reduction, the particles passed through a 0.2 micron filter, indicating <0.2 micron particle size. At later stages, the particle size became greater than 0.2 micron.

Bioremediation of uranium contamination with enzymatic uranium reduction. D.R. Lovley and E.J.P. Phillips, *Environmental Science and Technology* **26**, 2228-2234, 1992. *Desulfovibrio desulfuricans* readily removed uranium from solution in a batch system or when separated from uranium-containing water by a semipermeable membrane. High concentrations of copper inhibited the reduction of uranyl, but other anions and heavy metals that were tested did not.

XPS and XANES studies of uranium reduction by *Clostridium* sp. A.J. Francis, C.J. Dodge, F. Lu, G.P. Halada and C.R. Clayton, *Environmental Science and Technology* **28**, 636-639, 1994. This study showed that *Clostridium* species under anaerobic conditions would reduce uranyl ion to U(IV) and possibly U(III), as detected by the title x-ray techniques. The reduction took place only with viable organisms and not by extracellular components of the medium or by heat killed organisms. Addition of higher concentrations (>0.21 mM) uranyl to the medium retarded growth of the bacteria.

Nanometer-size products of uranium bioreduction. Y. Suzuki, S.D. Kelly, K.M. Kemner and J.F. Banfield, *Nature* **419**, 134, 2002. This study shows that UO₂ particles formed from uranyl reduction by bacteria in soils and sediments are typically less than 2 nanometers in diameter, which has important implications for transport and reactivity. EXAFS studies and transmission electron microscopy (TEM) suggest there are a large percentage of U atoms at the surface of these fine particles, resulting in contraction of U-U spacing and affecting bond order. This results in a billion fold increase in the solubility product compared with crystallized uraninite. Flocculation should reduce transport of these nanoparticles and perhaps facilitate aggregation to larger particle sizes, although that must still be shown.

Reductive precipitation of uranium(VI) by zero-valent iron. B. Gu, L. Liang, M.J. Dickey, X. Yin and S. Dai, *Environmental Science and Technology* **32**, 3366-3373, 1998. Iron (metal) filings were found to be more effective than adsorbents (such as peat materials, iron oxides and carbon based adsorbents) at removing uranyl ion from contaminated water. It was found that U(IV), the reduced uranium species adsorbed on the iron surface could be reoxidized and potentially remobilized when the reduced system becomes more oxidized (e.g., upon exposure to air).

Understanding the mechanism of uranium removal from groundwater by zero-valent iron using x-ray photoelectron spectroscopy. J.N. Fiedor, W.D. Bostick, R.J. Jarabek and J. Farrell, *Environmental Science and Technology* **32**, 1466-1473, 1998. Due to concern about groundwater contamination in the Bear Creek Valley near the Oak Ridge Y-12 Plant (for uranium processing), these investigators studied the sorption and reduction of uranyl ion by iron oxides and iron metal, respectively. Uranyl is rapidly and strongly adsorbed to the surface of hydrous ferric oxide particles (rust), whereas uranyl is slowly and incompletely reduced to U(IV) by iron metal under anaerobic conditions.

Uranium in open ocean: concentration and isotopic composition. T-L. Ku, K.G. Knauss and G.G.

Mathieu, *Deep-Sea Research* **24**, 1005-1017, 1977. Shows a good correlation between uranium and salinity for polar oceans, but not for Atlantic and Pacific. The average world river uranium concentration (0.3 to 0.6 microg/L) and U234/U238 activity ratio (1.2 to 1.3), as well as other parameters, are consistent with a steady state model for uranium in the ocean.

Migration of plutonium in ground water at the Nevada Test Site. A.B. Kersting, D.W. Efur, D.L. Finnegan, D.J. Rokop, D.K. Smith and J.L. Thompson, *Nature* **397**, 56-59, 1999. It is suggested that observed rates of plutonium migration in ground water is due adsorption to colloid particles of submicrometer size that are suspended naturally in ground water. Models for plutonium migration in ground water would underestimate the rate if colloid suspensions are ignored.

4] Chemical Properties of Uranium Ions and Complexes

Chelation of uranyl ions by adenine nucleotides. IV. nuclear magnetic resonance investigations, H-1, P-31, of the uranyl-adenosine 5'-diphosphate and uranyl-adenosine 5'-triphosphate systems. KE Rich, RT Agarwal and I Feldman, *Journal of the American Chemical Society* **92(23)**, 6818-6825, 1970. Shows formation of dimeric sandwich-type 2:2 complexes of U-ATP in pH 7.7 to 11 range, where U is bound to phosphate groups and ribose hydroxyls, but at lower pD (pH) the uranyl is bound only to the phosphates. The complexes with ADP were different, with non-sandwich type 1:1 complex.

Chelation of uranyl ions by adenine nucleotides. III. Further nuclear magnetic resonance investigation of the uranyl nitrate-adenosine 5'-monophosphate system at basic pH (7.5-11.4). I. Feldman and KE Rich, *Journal of the American Chemical Society* **92(15)**, 4559-4564, 1970. A 2:2 sandwich-type complex present above pH 10.9 disproportionates at lower pH to form a 2:1 U:AMP complex, which is present at pH 7.5.

Chelation of uranyl ions by adenine nucleotides. II. Proton magnetic resonance investigation of the uranyl nitrate-adenosine 5'-monophosphate chelate in D2O at basic pD. RP Agarwal and I. Feldman, *Journal of the American Chemical Society* **90(24)**, 6635-6639, 1968. Spectra are interpreted to support a sandwich-type 2:2 chelate with uranyl coordinated to phosphate and ribose 2' and 3' hydroxyl groups. Shifts in purine proton resonances are attributed to destacking caused by U complexation.

Studies of the carbonate-uranium system. C.A. Blake, C.F. Coleman, K.B. Brown, D.G. Hill, R.S. Lowrie and J.M. Schmitt, *Journal of the American Chemical Society* **78**, 5978-5983, 1956. A thorough study of the uranyl ion complexes with carbonate in sodium carbonate solutions. The uranyl ion will bind 1 to 3 carbonate or bicarbonate ions in aqueous solutions, which will dominate in solutions that are in equilibrium with carbon dioxide in the atmosphere. Solubility products and complex formation equilibria in the systems uranyl hydroxide and uranyl carbonate at 25 C and I=0.1 M. U. Kramer-Schnabel, H. Bischoff, R.H. Xi and G. Marx, *Radiochimica Acta* **56**, 183-188, 1992. A study of the solubility of uranyl hydroxide and uranyl carbonate and the formation constants of the complexes present in solution under the given conditions. The authors refer to work by Grenthe et al (J. Chem. Soc, Dalton Trans, 11, 2439, 1984) that claims uranyl complexes with hydrogen carbonate (HCO₃⁻) don't exist.

Studies on metal carbonate equilibria. Part 10. A solubility study of the complex formation in uranium(VI)-water-carbon dioxide (g) system at 25 C. I. Grenthe, D. Ferri, F. Salvatore, G. Riccio, *Journal of the Chemical Society, Dalton Transactions*, (11), 2439-2443, 1984. A study of the equilibrium constants for complex formation between uranyl ion and carbonate ion in the title system.

Hydrolysis of uranium (VI): ultracentrifugation and acidity measurements in chloride solutions. Rush, R.M., Johnson, J.S. and Kraus, K.A. *Inorganic Chemistry* **1**, 378-386, 1962. This is a report of the degree of polymerization of uranyl ion in aqueous media containing chloride and other ions. It indicates that uranyl ion polymerizes very little, with trimers being the upper limit.

The hydrolysis of metal ions. Part 2. Dioxouranium(VI). Sylva, R.N. and Davidson, M.R. *Journal of the Chemical Society, Dalton*, 465-471, 1979. Found evidence for several different species of uranyl ion with hydroxide ion in aqueous solution, including 1:1, 2:2, 3:4, 3:5, and 4:7, indicating varying degrees of polymerization of uranyl ion in aqueous solution in the slightly acidic pH range, and uranyl ion (+2) below pH 3.

Characterization of uranyl-monoperoxo species in 0.7 mol L⁻¹ LiClO₄. R. Djogic and M. Branica, *Electroanalysis* **4**, 151-159, 1992. Shows that the predominant species in the presence of equimolar concentrations of uranyl ion and hydrogen peroxide in the pH range of 5 to 7 is the uranyl peroxide neutral complex (UO₂O₂), with a stability constant of 2x10⁵ M. The reduction potential for hydrogen peroxide shifts from -0.95 V without uranyl to -0.70 when uranyl concentration is 0.5 x H₂O₂ concentration, indicating the diperoxo complex also forms although there is marked hydrolysis at pH>5.

A theoretical study of the structure of tricarbonatodioxouranate. L. Gagliardi, I. Grenthe and B.O. Roos, *Inorganic Chemistry* **40**, 2976-2978, 2001. Theoretical calculations indicate there would be only minor geometrical rearrangements resulting from the one electron reduction of U(VI) to U(V) in the uranyl tricarbonate complex, confirming the reversibility of this reduction (citing D. Ferri et al, *Inorg. Chem.* **22**, 3163, 1983, below).

Studies on metal carbonate equilibria. 7. Reduction of tris(carbonato)dioxouranate(VI) ion, UO₂(CO₃)₃⁴⁻, in carbonate solutions. D. Ferri, I. Grenthe and F. Salvatore, *Inorganic Chemistry* **22**, 3162-3165, 1983. Report the stability constant for the tris(carbonato)dioxouranate (V) complex (log B₃ = 13.3) in alkaline media. The reduction potential for the reactions: U(VI) tricarbonate to U(V) tricarbonate complex is: E⁰ = -0.5236 V.

Solvent effects on uranium(VI) fluoride and hydroxide complexes studied by EXAFS and quantum chemistry. V. Vallet, U. Wahlgren, B. Schimmelpfennig, H. Moll, Z. Szabo and I. Grenthe, *Inorganic Chemistry* **40**, 3516-3525, 2001. Found that fluoro(n)-aquo(5-n) complexes of uranyl ion all have pentagonal bipyramid geometry, while the tetrahydroxy complex has square pyramidal geometry.

Structure and bonding in solution of dioxouranium(VI) oxalate complexes: isomers and intramolecular ligand exchange. V. Vallet, H. Moll, U. Wahlgren, Z. Szabo and I. Grenthe, *Inorganic Chemistry* **42**, 1982-1993, 2003. Studied several uranyl oxalate complexes by EXAFS and determined bond distances. Some minor computing errors are reported (op cit, p. 8598.).

The mechanism for water exchange in $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ and $[\text{UO}_2(\text{oxalate})_2(\text{H}_2\text{O})]^{2-}$, as studied by quantum chemical methods. V. Vallet, U. Wahlgren, B. Schimmelpfennig, Z. Szabo and I. Grenthe, *Journal of the American Chemical Society* **123**, 11999-12008, 2001. The activation energies for dissociative, associative and interchange mechanisms for water exchange in the coordination sphere of uranyl ion were determined. The activation energy for dissociative exchange is about 3 times that for associative or interchange in the former title complex and activation energy for both dissociative and interchange mechanisms are about 4 times greater than for the associative mechanism of the latter title complex.

Rates and mechanism of water exchange of $\text{UO}_2^{2+}(\text{aq})$ and $\text{UO}_2(\text{oxalate})\text{F}(\text{H}_2\text{O})_2^-$: a variable temperature 17-O and 19-F NMR study. I. Farkas, I. Banyai, Z. Szabo, U. Wahlgren and I. Grenthe, *Inorganic Chemistry* **39**, 799-805, 2000. Studies on the mechanism of water ligand exchange for uranyl ion in aqueous solution are faster than for the oxalate complex in solution.

Investigation of the interaction between 1-hydroxyethane-1,1'-diphosphonic acid (HEDP) and uranium (VI). C. Jacopin, M. Sawicki, G. Plancque, D. Doizi, F. Taran, E. Ansoborlo, B. Amekraz and C. Moulin, *Inorganic Chemistry* **42(16)**, 5015-5022, 2003. The title complexation reaction was studied by several spectroscopic methods to show that only a 1:1 complex is formed at low concentration ($<10^{-4}$ M). A 1:2 (metal/ligand) complex was observed at higher concentrations ($>10^{-2}$ M).

Hydrolysis of uranium(VI): ultracentrifugation and acidity measurements in chloride solutions. R.M. Rush, J.S. Johnson and K.A. Kraus, *Inorganic Chemistry* **1(2)**, 378-386, 1962. Ultracentrifugation techniques were used to show formation of uranyl dimers, trimers and (rarely) tetramers in aqueous solutions at various pH as a result of hydroxide formation from coordinated water to allow bridging hydroxides.

The first hydrolysis constant of uranium(VI). M.S. Caceci and G.R. Choppin, *Radiochimica Acta* **33**, 207-212, 1983. Derives the equilibrium constant for formation of $\text{UO}_2(\text{OH})^+$ ion at 25C in solutions of varying ionic strength with NaClO_4 . A stability constant for the U(VI)-diglycolate complex is also derived in this study.

Continuities in the spectra and structure of the actinyl ions. J.T. Bell, *Journal of Inorganic and Nuclear Chemistry* **31**, 703-710, 1969. Uses molecular orbital theory to explain the uv-vis absorption spectra of actinides, especially uranyl ion.

PMR and magnetic susceptibility of uranium(V) pentaethoxide. D.G. Karraker, T.H. Siddall III and W.E. Stewart, *Journal of Inorganic and Nuclear Chemistry* **31**, 711-714, 1969. Proton magnetic resonance shows alkoxide bridged dimers and 6-coordinate U(V) ions, i.e., mixtures of monomers and dimers at room temperature, but only dimers at low temperatures.

On the chemiluminescence in the oxidation of tetravalent uranium to the uranyl ion by dimethyldioxirane. D.V. Kazakov et al. (10 authors), *Luminescence* **17**, 293-298, 2002. Reaction of U(IV) salts in sulfuric and perchloric acid solutions with acetone was studied and the nature of the reaction with dimethyldioxirane is reported. Singlet oxygen was found to be an intermediate in the reaction. The reaction gives chemiluminescence at 510 to 540 nm.

IR spectroelectrochemical study on U(V)O₂⁺ complex: first evidence for weakening of U=O bond strength in uranyl moiety with reduction from U(VI) to U(V). K. Mizuoka and Y. Ikeda, *Inorganic Chemistry* **42**, 3396-3398, 2003. Reduction of uranyl complexes with N,N'-disalicylidene-o-phenylenediaminate (saloph) in dimethylsulfoxide (DMSO) solvent yields a stable U(V) complex that allowed the spectroscopic studies that revealed weakening of the U=O bond upon reduction.

Raman and infrared spectroscopic studies of the uranyl ion: the symmetric stretching frequency, force constants and bond lengths. J.I. Bullock, *Journal of the Chemical Society (A)*, 781-784, 1969. The title spectroscopic techniques support x-ray crystallographic data regarding the bond length for the bonds in several uranyl compounds, confirming the linearity of the O=U=O moiety in these compounds.

Neutron diffraction study of uranyl nitrate dihydrate. N.K. Dalley, M.H. Mueller and S.H. Simonsen, *Inorganic Chemistry* **10(2)**, 323-328, 1971. The crystal structure of uranyl nitrate dihydrate was determined by neutron diffraction and is in disagreement with previous work. In this study the uranyl group O=U=O is surrounded by a planar hexagon of O atoms donated from each of two equivalent bidentate nitrate groups and two O atoms from equivalent water molecules, similar to the structure reported for uranyl nitrate hexahydrate.

An ultrafast time-resolved fluorescence spectroscopy system for metal ion complexation studies with organic ligands. G. Geipel, M. Acker, D. Vulpius, G. Bernhard, H. Nitsche, Th. Fanghanel, *Spectrochimica Acta (part A)* **60**, 417-424, 2004. The title method was used to study a 1:1 uranyl-dihydroxybenzoate complex in the pH range 3.0 to 4.5 and ionic strength 0.1 M. Fluorescence of the uranyl ion is affected by dynamic quenching of the non-dissociated ligand and static quenching due to complex formation.

Uranyl complexes with diamide ligands: a quantum mechanics study of chelating properties in the gas phase. B. Coupez and G. Wipff, *Inorganic Chemistry* **42**, 3693-3703, 2003. This study assesses the chelate effect of bidentate ligands and the influence of ring size on the chelate effect, as well as the effect of neutralizing counterions.

Complexation of uranium(VI) and samarium(III) with oxydiacetic acid: temperature effect and coordination modes. L. Rao, A.Y. Garnov, J. Jiang, P. di Bernardo, P.L. Zanonato and A. Bismondo, *Inorganic Chemistry* **42**, 3685-3692, 2003. Binding constants and enthalpies of complexation for three uranyl ODA complexes were determined.

5] Uranium Catalyzed Oxidation or Hydrolysis of Biological Compounds or Materials

Kinetics of metal ion and metal chelate catalyzed oxidation of ascorbic acid. IV. Uranyl ion catalyzed oxidation. M.M. Taqui Khan and A.E. Martell, *Journal of the American Chemical Society* **91(17)**, 4668-4672, 1969. Uranyl ion catalyzed oxidation of ascorbic acid in air proceeds by a path first order in ascorbic acid, catalyst, molecular oxygen and hydrogen ion. Uranyl ion was found to be less active (by about 1/1000) as a catalyst for this reaction than vanadyl ion. Uranyl forms a complex with ascorbic acid in solution. The proposed mechanism also has O₂ bound to the uranyl catalyst, similar to mechanisms for ferric, cupric and vanadyl mechanisms. Hydrogen peroxide is proposed as the

product of this catalytic reaction, but like the other metal catalysts (ferric, cupric and vanadyl), subsequent reduction of hydrogen peroxide would give the powerful oxidant, hydroxyl radical (OH).

Kinetics of metal ion and metal chelate catalyzed oxidation of ascorbic acid. III. Vanadyl ion catalyzed oxidation. M.M. Taqui Khan and A.E. Martell, *Journal of the American Chemical Society* **90(22)**, 6011-6017, 1968. Another in the series of the studies of metal ion catalyzed oxidations of ascorbic acid.

Actinide (uranyl) hydrolysis of phosphodiester. RA Moss, K Bracken and J Zhang, *Chemical Communications* 563-564, 1997. Uranyl ions increased the rate of hydrolysis of p-nitrophenyl phosphodiester by >1000 in aqueous solutions at pH 4.9.