Solubility Testing of Actinides on Breathing Zone Air Samples

Dr. Robert Metzger

PERALS® Workshop VIII

November 1998

Internal Dose

- Dose Assessment from airborne nuclides requires knowledge of:

- The isotope and activity inhaled.
- Deposition pattern of the dusts in the lung
- The lung clearance times.

Lung Clearance - ICRP 30

- Couples mechanical clearance and dissolution into 3 classes:
- Class D are compounds that have clearance half-times within 10 days.
- Class W compounds that have clearance half-times between 10 and 100 days.
- Class Y compounds that have clearance half-times greater than 100 days.

Lung Clearance - ICRP 66

- Expands lung model to 5 compartments.
- Correctly treats dissolution and mechanical clearance as competing processes.
- Dissolution is based on solubility while mechanical clearance is treated with a mathematical model.
- NRC is considering use of this method.
- Is incorporated in DCAS & British (?) code.

Solubility Test

- Commonly performed on a scoop of the final product only.
- Sample is sandwiched between two membrane filters and is soaked in Gamble's solution. The filter sandwich is moved to new beakers of soak solution in a pattern over a period of 30 days.
- The soak solutions are then analyzed for the concentration of the isotopes of interest.

Impact of Solubility Testing

- Poor estimates of lung clearance profiles can result in order of magnitude errors in intake assessment and dosimetry.
- If incorrect lung clearance profiles are used both for intake assessment for bioassay data and then again for the dose estimate, the error propagates.

Solubility Tests - Limitations

- The “scoop of product” may not be representative of the airborne particles.
- No data on intermediate product.
- Lacks sensitivity to use air samples for analysis.
- Very **expensive**.
- Very few compounds have been tested.

Improved Solubility Test

- Uses advanced separation chemistry methods to analyze the uranium in Gamble's solution by solvent extraction and PERALS® spectroscopy.
- Simpler and more reliable than conventional methods and has improved sensitivity. Only 40 pCi of uranium needed to perform a test.
- Allows solubility tests to the performed on Breathing Zone air samples collected in the workplace.

Improved Solubility Test

- New test allows solubility profiles to be generated in each section of a plant where airborne suspensions of isotopes are present.
- It is much less expensive. Cost is approximately $6,000 for a ten sample characterization.

Simplified Method

- Synthesize Gamble's solution (takes about 1 to 2 days). Measure pH carefully and store under CO_2.
- Take Breathing Zone air samples in work areas using Gelman GN4 membrane filters. It is desirable to have 40 - 200 pCi of activity on sample.
- Form a filter sandwich using a clean GN4 filter and submerge in Gamble's solution.

Simplified Method

- Change the filter sandwich to a new beaker every day for one week and then every week until the end of the month.
- Wet ash the Gamble's solution with HNO_3 and H_2O_2. Bring to "near" dryness.
- Solubilize residue with DI H_2O to about 20 - 30 mL and adjust pH to 2.5 to 3 for U.
- Extract with ALPHAEX®

Simplified Method

- If other natural chain isotopes are present, use DTPA to chelate the other isotopes before extraction.
- Recovery normally exceeds 95%.
- U-234 may be used to trace recovery.
- See *Radioac. Radiochem* or *NUREG* articles for other isotopes.

PERALS®

- Photon-Electron Rejecting Alpha Liquid Scintillation.
- Uses pulse-shape discrimination to reject pulses from beta/gamma emissions.
- Alpha pulses processed using pulse height analysis to yield energy spectrum.

PERALS®

- Light pulses produced by alpha particle interactions in a high resolution scintillator are longer than those produced by beta/gamma interactions (30 to 40 nsec longer)>
- Pulse shape (time) analysis can be used to separate the alpha from the beta/gamma pulses.

PERALS®

- Alpha Energy Resolution: 240 keV FWHM.
- Counting Efficiency: 99+%.
- Typical background: 0.03 counts/hour under a typical alpha peak.
- Uses extractive scintillators for rapid extraction of the nuclides of interest.

Extractive Scintillators

- ALPHAEX® uses bis(2-ethyl-hexyl) hydrogen phosphate (HDEHP).
- Extracts uranium and other actinide nuclides from a nitrate system.
- Distribution coefficient is low for Americium and Curium.

Fitting the Data

- The data is fitted to the triple exponential shown below.
- The equation is non-linear and must be fit by iterative means.
- The fit is not unique. Several starting points should be used and the lowest SSE chosen.
- % undissolved = $A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} + A_3 e^{-\lambda_3 t}$

Data Analysis

- Fitted data from the solubility test represents only the dissolution fraction of lung clearance.
- Use of D, W, and Y estimates from the solubility tests as total lung clearance in CINDY or INDOSE can lead to significant errors for compounds with significant Class W and Y components.
- This is the origin of the “Super Class Y” error.

Data Analysis - Possible Solutions

- Authors of CINDY and INDOSE are not eager to incorporate ICRP 66 lung models into their codes.
- Improved estimates of lung clearance values can be produced by pre-processing the solubility test data through the ICRP 66 lung model to estimate “true” lung clearance from the solubility test data.

Irigary Uranium Plant

- *In situ* plant injects a carbonate leach solution into the ground along with an oxidant which leaches the U out of the rock. U laden solution is then pumped from the well field to the plant.
- U is concentrated by ion exchange and the loaded IX resin is stripped with a chloride solution at a pH of 10.

Irigary Uranium Plant

- Pregnant eluate is stripped with hydrogen peroxide to produce UO_4, which is then dried at 540 degrees C. There is no solubility data for this product.
- Traditional plants precipitate U out of solution using anhydrous ammonia to produce U_3O_8, which is commonly dried at 600 - 1220 degrees. U_3O_8 dried at high temperature is largely Class Y (Alexander).

Irigary Solubility Test

- Air samples were collected in each area of the plant during routine operations. BZ samples on worker's lapels were used where possible. Low airborne activity required medium volume air samples in filter press area and control room. Two samples were collected in each area.
- Solubility test was performed on the samples using the new method.

Human Data

- All published comparisons of in vitro solubility testing with in vivo results have been done with rodents or dogs.
- There are no published intercomparisons between solubility tests results and human uptake and retention of the same compound.
- Irigary bioassay and air sampling program provided such an intercomparison.

Bioassay Analysis

- Personnel submit a urine sample at the beginning of the shift every 2 weeks.
- The uranium in the urine is checked against a screening level. If the level is exceeded, the test is repeated.
- Intake assessment and internal dosimetry is not performed except after large intakes (very rare).

Intake Assessment Requires 2 of 3

- Requires the complete bioassay profile (>4 - 6 points after an acute uptake) or,
- Lung clearance profile and spot bioassay data, or,
- Air sampling results (intake) and spot bioassay or lung clearance data.

Intake Assessment

- Estimates the intake of a nuclide based on bioassay data (urine most often), and the ICRP 30/66 model.
- The lung clearance profile is needed to estimate the intake from the bioassay data and to perform internal dosimetry estimates.
- Errors in the lung clearance profile can produce order of magnitude errors in intake and dose estimates.

Irigary Tank Rupture Incident

- A yellowcake thickener ruptured on August 1, 1994, dumping a thick slurry of yellowcake on the plant floor. Cleanup required several days.
- Air samples were collected during the cleanup time.
- Spot bioassay data was recorded for the cleanup personnel.

Observations on Irigary Tests

- Using the incorrect assumption of 100% Class Y caused a 20-fold error in dosimetry estimates for inhaled uranium in this plant.
- The error compounds when the incorrect solubility profile is used for both bioassay analysis and dosimetry purposes.
- The incorrect solubility profile causes the plant to underestimate the kidney toxicity of the product.

Scientific Contributions

- 1. New Separations Methods for Uranium and other Actinides from Gamble's Solution.
- 2. New Solubility Test Method.
- 3. Human Data for Verification of the *In Vitro* Test Data.

Scientific Contributions New Solubility Testing Method

- Improved Sensitivity
- Allows Use of BZ Samples to Characterize the Solubility of Airborne Nuclides
- Allows Characterization of all Work Areas where Airborne Nuclides are Present
- May be Used with Bioassay Data for Intercomparison/Validation
- Easier and Cheaper

Scientific Contributions Operating Facilities

- No Longer Necessary to Base Solubility on Assumptions of Chemical Compounds and Their Estimated Solubility in the Lung.
- Improved Dosimetry Estimates.
- Test Assumptions of Solubility Made in the Past.
- Improves the Analysis of Bioassay Data.

Additional Work

- Uranium is the prevalent radionuclide in Arizona drinking waters.
- The standard method for analysis of U in water does not work well for water with high dissolved solids.
- The ALPHAEX ® extraction using the DTPA chelating agent was modified for use in the analysis of drinking water.

Additional Work

- The new method has been submitted to two rounds of interlaboratory trials and has passed both rounds of tests.
- In the first test, the method was submitted with other new U methods and was judged to be superior.
- The second round of tests was performed on samples with U and high activities of other actinides.

Additional Tests

- The new method received final approval from ASTM and should be published in Volume 11.02 by summer, 1999.
- The method, D6239, will be available on the ASTM web site, http://www.astm.org
- The method may also have application in the analysis of urine samples for routine bioassays.