Determination of the Actinides in Fecal and Urine Samples with Total Sample Dissolution Using a Lithium Metaborate Fusion

Steven E. Bohrer and David S. Sill
Radiological and Environmental Sciences Laboratory
Department Of Energy, Idaho Operations Office

Since the early days of the atomic age, there has been a need to determine accurately the radiological exposure to man from internally deposited radionuclides. Publications dating back to 1964[1-4] document numerous internal exposures and elimination pathways for a variety of radionuclides including activation and fission products as well as actinides. Initially, the predominant path of elimination for the majority of the radionuclides encountered was through the gastrointestinal (GI) tract and into the feces. Only a few specific radionuclides including isotopes of hydrogen, iodine, mercury, cesium and molybdenum-technetium were found in the urine in easily detectable quantities. All the other radionuclides were eliminated so exclusively by way of the GI tract that the nuclide could not be detected in the urine in a 1000-minute count on a 24-hour sample by gamma spectrometry. An accidental exposure to plutonium involving 78 individuals yielded only 6 urine samples that contained detectable activity; while 68 fecal samples from 22 individuals showed easily detectable levels of plutonium. As pointed out previously,[1] the experimental data shows that the path for clearance of most radionuclides that are inhaled or ingested is more dependent on the physical characteristics of the particles than on the chemical characteristics of the radionuclides. Although urinalysis is routinely used and accepted as an indicator of internal exposure, radiochemical analysis of fecal samples, though unpleasant, continues to be the most sensitive method to obtain accurate analytical data that will be used in dose calculations, particularly in the initial period following a suspected exposure. This paper describes a reliable chemical method for the determination of the actinides as well as gamma-emitting radionuclides in fecal and, if needed, urine samples[5]. This method has also been applied successfully for the analysis of large (20L) environmental water samples, and may be used to prepare samples for analysis by mass spectrometry.

Complete dissolution of the sample is undoubtedly one of the most important parts of any chemical procedure. For a desired chemical reaction to occur, the element of interest must be in a specific oxidation state. Furthermore, if an analytical procedure is expected to produce an accurate result, the sample and the analyte of interest must be dissolved completely, and isotopic exchange of the analyte with tracer must be guaranteed. These elementary concepts should be well known and should be the foundation from which every analytical procedure is developed. Unfortunately, the initial dissolution of the sample is usually neglected; especially when dealing with compounds that are difficult to dissolve such as quadrivalent oxides, siliceous materials, and samples like feces that contain high concentrations of calcium and phosphate. The omission of the appropriate type of front-end dissolution chemistry, by itself, will lead to the failure of even the finest chemical procedure. Likewise, isotopic exchange of the tracer with the analyte of interest is usually assumed rather than guaranteed. Even when dissolution techniques properly address the matrix and analyte of interest, the rigor necessary to control the oxidation state and prevent hydrolysis is too often overlooked. The importance of the appropriate type of front-end dissolution technique and the

conditions needed to avoid hydrolysis of large ter- and quadrivalent elements cannot be over emphasized.[6]

Potassium fluoride and/or pyrosulfate fusions have been used routinely and reliably in this laboratory for over 30 years and are still the dissolution methods of choice for most sample matrices. However, when this method[7] was applied to the dissolution of the ash from an entire fecal sample, a clear pyrosulfate fusion could not be obtained in a reliable fashion. The incomplete dissolution was due to a combination of factors: the large sample size (entire fecal sample taken for analysis), the high concentrations of phosphate and calcium that were present, and the production of insoluble condensed phosphates from dehydrating conditions produced in pyrosulfate fusions. It became obvious that another dissolution technique had to be used to ensure that the chemical procedure could be used reliability on a variety of fecal samples with different sample sizes. Donivan[8] used lithium metaborate to completely dissolve mill tailings for the determination of ^{230}Th; which demonstrated the fundamental principles of sample dissolution described above and contributed heavily to the choice of lithium metaborate by the current authors. The lithium metaborate fusion dissolves the sample efficiently and completely without interference from the sample matrix under these conditions. This fusion method has also been used successfully for the analysis of large (20L) water samples which contain high concentrations of calcium that interferes with the pyrosulfate fusion. The lithium metaborate fusion is a much simpler technique for total sample dissolution in this case.

The fecal sample is ashed in a bread pan lined with vellum and cellulose. Urine samples are evaporated and absorbed on cellulose. The samples are dried on a hotplate and then ashed overnight at 550° C. The ashed sample is dissolved completely with a lithium metaborate fusion. The fused sample is then dissolved in 25% HCl. At this point, the sample is stable for up to two weeks, and may be counted by gamma spectrometry in a reproducible geometry; eliminating the need to count the inhomogeneous fecal ash directly. Next, the sample is reheated, all of the actinides including uranium are coprecipitated with barium sulfate, and the supernate containing the interfering calcium, phosphate, etc. is discarded. The barium sulfate is dissolved in EDTA and the actinides are coprecipitated with titanium(III) hydroxide. At this point the sample may be dissolved in nitric acid and analyzed by mass spectrometry. This sample dissolution technique has been used successfully to eliminate the effects of matrix interferences in the analysis of uranium in urine samples. To continue with alpha spectrometry, the titanium(III) hydroxide precipitate is dissolved in acid and the actinides are separated by successive oxidation/reduction and coprecipitation with neodymium fluoride as outlined in Figure 1. The time needed to analyze six fecal ash samples for the actinides listed above by high resolution alpha spectrometry is about three days. The chemical yields for all of the actinides determined are routinely better than about 85% (with some as high as 95%), and there are no known radiochemical interferences that adversely affect the accuracy of the results.

Table 1 lists the results obtained from analysis of artificial fecal samples prepared by NIST and analyzed by RESL on a single blind basis for the purpose of laboratory performance evaluation. In all cases, every experimental result agrees with its known value within the statistics of the measurement. All random and the best estimate of any systematic uncertainties encountered anywhere in the entire measurement process have been propagated to the final result. The final uncertainty is expressed as one standard deviation.

Table 1. Artificial Fecal Sample - Single Blind PE Standard Prepared by NIST

Nuclide	Experimental Activity	NIST Value	Ratio (Expt'l/Known)
Am-241	3.89 ± 0.12 Bq/g	3.89 ± 0.01 Bq/g	1.00 ± 0.03
Pu-238	3.91 ± 0.12 Bq/g	3.88 ± 0.01 Bq/g	1.01 ± 0.03
U-238	3.96 ± 0.12 Bq/g	3.91 ± 0.02 Bq/g	1.01 ± 0.03
U-234	3.81 ± 0.12 Bq/g	3.77 ± 0.02 Bq/g	1.01 ± 0.03

Uncertainties are one standard deviation

Radiochemical analysis incorporating a lithium metaborate fusion has proven to be an accurate and reliable technique for the quantification of actinides in fecal and urine samples. Total sample dissolution and complete isotopic exchange with tracers are ensured, and chemical interferences are eliminated. The resulting data from analyses of blind samples demonstrate the accuracy and reliability of this method.

REFERENCES

1) C. W. Sill, J.I. Anderson, and D. R. Percival, "Compariaon of Excretion Analysis with Whole-Body Counting for Assessment of Internal Radioactive Contaminants"; *Assessment of Radioactivity in Man,* Vol. 1, p. 217, IAEA. Vienna, 1964.

2) C. W. Sill, G. L. Voelz, D. G. Olson, and J. I. Anderson, "Two Studies of Acute Internal Exposure to Man Involving Cerium and Tantalum Radioisotopes," Health Phys. 16, 325 (1969).

3) W. Daggett Norwood MD, *Health Protection of Radiation Workers*, 1975 p 316

4) C.W. Sill, "Routine Surveillance For Internal Contamination By Alpha Emitters In Humans,"23th Annual Bioassay Conference September 15-16, 1977

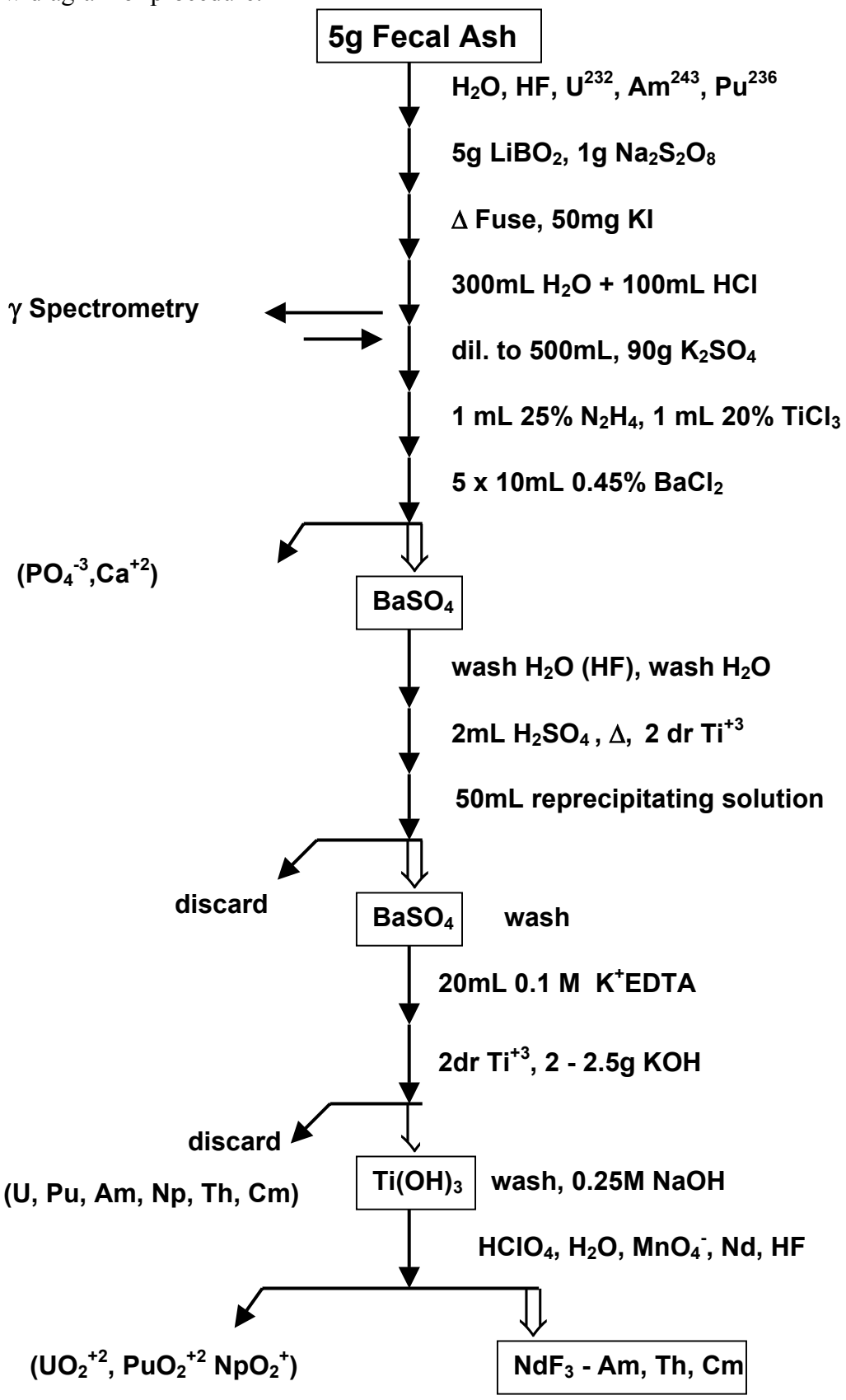
5) D.S. Sill, S.E. Bohrer, "Sequential Determination of U, Pu, Am, Th and Np in Fecal and Urine Samples with Total Sample Dissolution", *Radioatc. Radiochem.*, Vol 11, No. 3, 2000, p7-18

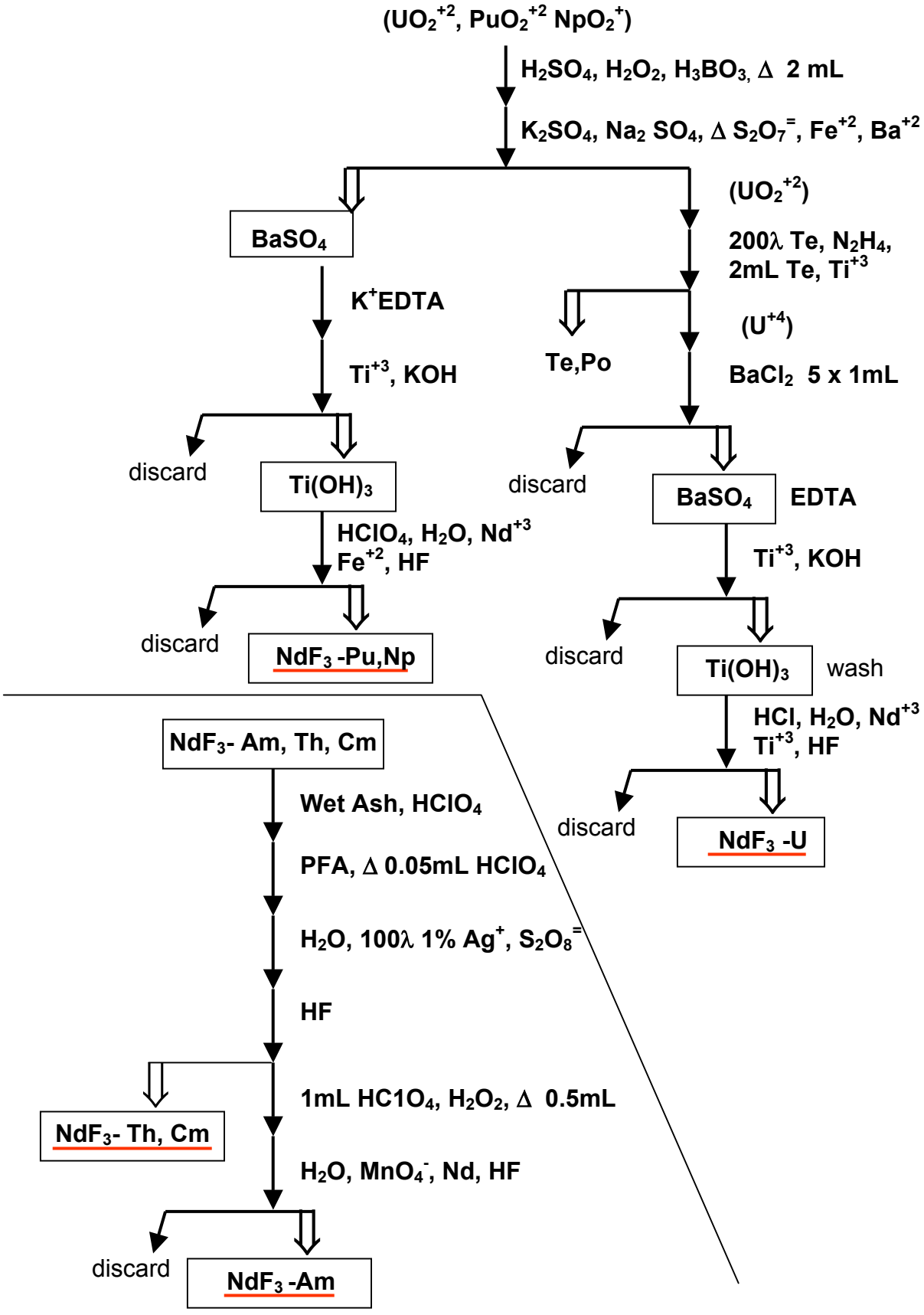
6) C.W. Sill, D.S. Sill, Sample Dissolution, *Radioatc. Radiochem.*, Vol 6, No.2, 1995, p8-14

7) D.S. Sill, C.W. Sill, Simultaneous Determination of the Actinides in Small Environmental Samples, *Radioactivity & Radiochemistry*, Vol 5, No.2, 1994, p8-19

8) S. Donivan, M. Hollenbach, and M. Costello, "Rapid Determination of Th230 in Mill Tailings by Alpha Spectrometry" Anal. Chem 59 2556 (1987).

Figure 1. Flow diagram of procedure.




$(UO_2^{+2}, PuO_2^{+2}\ NpO_2^{+})$
$H_2SO_4, H_2O_2, H_3BO_3, \Delta$ 2 mL
$K_2SO_4, Na_2\ SO_4, \Delta\ S_2O_7^{=}, Fe^{+2}, Ba^{+2}$
$BaSO_4$
(UO_2^{+2})
200λ Te, N_2H_4, 2mL Te, Ti^{+3}
$K^{+}EDTA$
(U^{+4})
Te,Po
Ti^{+3}, KOH
$BaCl_2$ 5 x 1mL
discard
$Ti(OH)_3$
discard
$BaSO_4$
EDTA
$HClO_4, H_2O, Nd^{+3}$ Fe^{+2}, HF
Ti^{+3}, KOH
discard
NdF_3 -Pu,Np
discard
$Ti(OH)_3$
wash
HCl, H_2O, Nd^{+3} Ti^{+3}, HF
discard
NdF_3 -U
NdF_3- Am, Th, Cm
Wet Ash, $HClO_4$
PFA, Δ 0.05mL $HClO_4$
H_2O, 100λ 1% Ag^{+}, $S_2O_8^{=}$
HF
1mL $HC1O_4$, H_2O_2, Δ 0.5mL
NdF_3- Th, Cm
H_2O, MnO_4^{-}, Nd, HF
discard
NdF_3 -Am