Age-dating methodology for ^{137}Cs ceramic sources

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Abstract

Age dating radioactive sources containing ^{137}Cs as chloride salt or glass could be adapted for sources where the ^{137}Cs is incorporated into a ceramic matrix. We evaluated the potential effects a cesium- and barium-doped aluminosilicate might have for applying the age-dating method, including dissolution, separation, and measurement of the ^{137}Cs and ^{137}Ba isotopes. Recovery of barium in a fraction eluted with 1% acetic acid was consistently low, with an average recovery of 98.3% ± 2.3%. We did a short study of alternative eluents for the barium fraction and found that adding a complexant such as EDTA in place of acetic acid improved the recovery (99.4 ± 0.8%). This improvement constitutes a major reduction in the overall uncertainty of the age dating method since variability in the barium recovery is the largest single contributor to the combined uncertainty in the measured age.

Keywords

Extraction chromatography, EDTA, age dating, nuclear forensics Cs-137, ceramic, RDD

Introduction

The date on which a radioactive source material was last separated from its decay daughters is a useful parameter in deducing the material's origins and history for nuclear forensics investigations. In general, the date of interest is obtained by measuring the relative amounts of the parent radionuclide and its daughter isotopes in a sample of the source material on a known reference date established when the sample is analyzed and using the daughter/parent ratio to calculate the time that would have elapsed since the daughter was absent according to the appropriate decay formula. The elapsed time is commonly called the "age" of the material and the process of determining its value is known as "age-dating."

The process by which the age of a source material is typically determined involves three steps. First, a sample of the material is brought into solution to provide a representative, uniform, and easily dividable sample configuration amenable to subsequent chemical manipulations and measurements. Next, if necessary, measured portions of the source solution are treated to isolate individual constituents of the solution to facilitate measurement of the parent and daughter nuclides. Finally, the parent and daughter nuclides are measured in a way that allows accurate determination of their amount ratios for input to the model decay formula and calculation of the time since purification, as the age of the material is also called.

Cesium-137 sealed sources are some of the most popular and widely used radioactive sources for medicine and industry because of the favorable energy of their gamma emission and advantages associated with the nuclide's 30-year half-life. Because these sources are so broadly available, concerns have long existed that a ^{137}Cs source might be incorporated into a radioactive dispersal device (RDD) for malevolent purposes. In recognition of this situation, the nuclear forensics community has investigated methods for age dating ^{137}Cs materials for a number of years. Early methods were developed for sources containing encapsulated ^{137}CsCl salt because this configuration was especially common in older radiation devices [1]. Expanded understanding of the consequences of

a ^{137}CsCl RDD prompted restrictions on the use of that material and a global shift among manufacturers of ^{137}Cs sources to produce and sell other chemical forms of ^{137}Cs when possible. Thus, sources in which the ^{137}Cs is incorporated into glass or ceramic matrices are the current preferred manufacturing process [2]. To produce their radioactive sources, sealed-source manufacturers have been purported to incorporate ^{137}Cs into various types of ceramic matrices. Performance of the ceramic forms are typically judged using criteria such as the extent to which the ^{137}Cs can be leached from the matrix, resistance of the material to corrosion, and the amount of ^{137}Cs that can be interstitially stored relative to the total volume of the ceramic source.

Nonetheless, one major difficulty we encountered in pursuing investigation of an age-dating method for the ^{137}Cs ceramic matrix was determining a representative composition for designation as the "ceramic." There exist a number of materials that fit this classification, some with similar chemical composition and some that are chemically very different. Despite the common conjectures made in the literature regarding materials that might be used by sealed-source manufacturers for ^{137}Cs source materials, we found actual evidence in the open-literature only for aluminosilicate-types of cesium ceramic having been used [3-5]. Thus, we concluded that an aluminosilicate ceramic is the most likely material to be encountered in the event that a ^{137}Cs ceramic source should be interdicted. Consequently, it was decided that a cesium-containing aluminosilicate would be an attractive material on which to base the targeted age-dating method.

In past work, Argonne has developed an age dating method for separating ^{137}Cs glass sources by using a lanthanide enriched waste glass with known amounts of Cs and Ba. This age dating separation method was developed using a manually operated gas pressurized extraction chromatography (GPEC) apparatus that has been described elsewhere [6]. However, our experience with using the manual GPEC has not realized previous expectation and GPEC systems have not become widely available as once anticipated. Consequently for this ^{137}Cs ceramic age dating method, we investigated an alternative apparatus based on the readily available and inexpensive Omnifit® column kit, a configuration to which we were introduced when we participated in a round-robin

exercise for age dating ^{60}Co [7] . Evidence is presented that shows the dissolution procedure to be effective both in decomposing the sample matrix and allowing for quantitative recovery of the cesium and barium constituents. An alternative separation approach than previously reported using a more conventional column configuration but with pumped eluents is proposed and evaluated [1,6]. We determined that this approach allowed much more convenient operation, better utilization of sample, and a potential for more control over separation conditions than the GPEC. More important, during our studies of the cesium/barium separation with the Omnifit® system, we learned that recovery of barium in a fraction eluted with 1% acetic acid was consistently low by about 2% and varied substantially from one run to another (average recovery was 98.3% with a standard uncertainty of 2.3%); this condition was reported in other studies that used the GPEC apparatus, but was not followed up on in the past [1,6-9]. We did a short study of alternative eluents for the barium fraction and found that adding a complexant such as EDTA in place of acetic acid improved the recovery (99.4 ± 0.8%). This improvement constitutes a major reduction in the overall uncertainty of the age dating method since variability in the barium recovery is the largest single contributor to the combined uncertainty in the measured age, as illustrated in our detailed uncertainty analysis. Refinement of the separation conditions for the conventional column approaches using the alternate eluent, 0.05 N EDTA, for barium recovery is recommended.

Experimental

Considerations in Approach to Synthesis of Surrogate Ceramic

Although selection of the aluminosilicate ceramic for the age-dating ceramic simulant was a clear choice, choosing the method by which the cesium aluminosilicate ceramic would be fabricated was not as straightforward. Procedures to create generic cesium-containing aluminosilicates do exist in the open literature with sufficient detail for replication. However, published procedures specific to the fabrication of commercial ^{137}Cs ceramic sealed sources are virtually nonexistent, most likely because such procedures are regarded as proprietary information or trade secrets and are rarely released publicly by the manufacturer. Given this lack of access to the manufacturer's process

information, authentically replicating a ceramic used in a commercial sealed source is next to impossible.

After considering alternative options, we chose to fabricate a ceramic surrogate *via* sodium aluminosilicate, loading the material by ion-exchange with known amounts of Cs and Ba from certified spectroscopic standards. Sodium aluminum silicate, a common starting material for synthesizing other aluminosilicates, was selected for the base material due to its low cost and abundant availability as an industrial food additive. We also elected to use the loaded powder form of the ion-exchanged base material as our ceramic surrogate. The reasoning behind this choice of fabrication approach was two-fold. First, our chemists, based on considerable experience with aluminosilicate materials, predicted that there should be little difference in the dissolution behavior between the ion-exchanged aluminosilicate precursor and any ceramic form produced from it by sintering, as long as hydrofluoric acid were used to decompose the silicate matrix. Traditional ceramics are generally high fired in a furnace at a temperature that transforms the material from powder to a ceramic monolith [10]. With some types of ceramics, the chemical properties of the starting material are quite different from the fired product. For example, γ-alumina powder dissolves in strong acids and bases while sintering the powder to a ceramic produces α-alumina, which is very much more resistant to chemical attack. With cesium aluminosilicates, a fired ceramic is expected to dissolve almost as readily as the precursor powder in an acid mixture containing HF, HNO_3, and HCl. Thus, firing the precursor powder to a ceramic would not be required for the purpose of developing a dissolution method.

The second factor we considered in selecting our approach to fabricating the surrogate ceramic was an ability to control the chemical composition of the product. When developing a dissolution and separation procedure for age-dating a cesium ceramic source, a particularly useful measure of the quality of the developed processes is quantitative recovery of the cesium and barium originally present in the material. To reliably evaluate the recovery, it is desirable to know the amounts of cesium and barium present in each sample with a high level of certainty. Numerous reports in the literature

for cesium ceramics studied as chemical waste forms indicate volatilization losses of cesium in the ceramic at certain firing temperatures, up to as much as 4% of the initial cesium loading. By firing our surrogate, we would introduce an unnecessary source of uncertainty in the amount of cesium present in the ceramic, and make evaluation of recovery more difficult. Along these lines, we did investigate the possibility of using a cesium-containing aluminosilicate that was previously manufactured in our facilities for evaluation as a potential waste form matrix [11]. We concluded that the levels of impurities and extraneous elements in the material, as well as uncertain amounts of cesium and barium, would produce unnecessary complications for the dissolution procedure (e.g., incomplete dissolution of elements in the waste form that likely would not even be present in an actual ^{137}Cs ceramic sealed source) and limit the accuracy of recovery estimates. The fabrication approach based on soaking a sodium aluminosilicate with cesium and barium and creating the ceramic simulant *via* ion exchange at room temperature mitigates the risk of volatilizing cesium due to firing the ceramic, produces a surrogate that is anticipated to have representative dissolution properties, and at the same time allows exacting control over the chemical composition of samples produced for study. A procedure describing the fabrication process can be found in the next section.

Inductively Coupled Plasma Mass Spectrometry

Instrument

ICP-MS isotope ratio and elemental concentration measurements were made with a Perkin-Elmer/SCIEX™ ELAN DRC-II® quadrupole ICP-MS (Perkin Elmer, Norwalk, CT) equipped with an SC-2-DX auto-sampling system (ESI, Inc., Omaha, NE) and a discrete dynode detector. An all Teflon® sample-introduction system, consisting of a Peltier-cooled PFA- Teflon® cyclonic spray chamber (Model PC3, ESI, Inc.) and low-flow self-aspirating PFA-Teflon® nebulizer (ESI, Inc.) were used to introduce samples into the plasma. We found that the Peltier-cooled spray chamber substantially improved the precision of replicate measurements during analysis of a given sample and strongly recommend its use for isotope ratio measurements. All samples were run in pulse-counting mode with a dead-time-correction setting in the Perkin Elmer software equal to

62 ns. All data sets were run in quantitative-analysis mode. The instrument analysis method was set up with defined parameters of 100 ms/sweep, 15 sweeps per replicate, and 7 replicates per sample for all analysis runs.

All reagents used for ICP-MS dilutions were prepared in FEP-Teflon® bottles due to their superior leach-resistance properties. Certified-sterile Centristar™ Corning® polypropylene centrifuge vials were used exclusively for sample containment due to their consistently negligible elemental background levels.

Data Handling for ICP-MS Measurements

The ICP-MS instrument output in units of counts per second for each measured peak was exported to a Microsoft® Excel® workbook so it could be readily manipulated to refine the dead-time correction being applied, to implement corrections for background or interference signals, and to calculate mass-bias corrections from ratios obtained with isotopic standards interspersed among the samples in a given analysis sequence. The first operation applied in treating the data was to remove the dead-time correction that the instrument had applied to the output data so the data set included only detector count rates with no dead-time corrections applied. Then, the data were corrected for background contributions to individual peaks, especially those from Xe isotopes, and the corrected peak-intensity data for barium standards analyzed during the run were fit to a model that provided a best-fit evaluation of linearity- and mass-bias-correction parameters for the ICP-MS run. The model we used was derived in-house to address shortcomings that were encountered when a simpler mass-bias correction routine was applied to our data. The model that was applied to evaluate and correct for the non-linearity and mass-bias effects on the measured isotopic signals is described elsewhere[6].

Measuring Cesium and Barium Isotopes by ICP-MS

Samples for the ICP-MS determination of cesium and barium were prepared within the context of a purposeful analysis strategy intended to reduce random and systematic error contributions to the analysis results by closely controlling additions of internal standard,

using ratio-based data reduction and calibration formulas, and employing mass-based measurements throughout, as recommended by Salit and coworkers at NIST.[12-14] Calibration standards for concentration measurements were prepared by mixing weighed amounts of Cs and Ba spectroscopic standard solutions (1000 μg/g diluted by mass to nominally 2 μg/g) with a weighed amount of a nominally 1 μg/g solution of praseodymium, designated as internal standard. The amounts of Cs and Ba standards were selected to produce concentrations of 0, 10, 20, and 30 ng/g when the Pr was diluted to 10 ng/g. In preparing an unknown sample for comparison to these standards, a portion of the sample was transferred to or collected in a weighed tube that contained a weighed portion of the same Pr solution that was used in making the standards, and the mass of the added sample was measured. Samples were then diluted by mass to produce a concentration close to 10 ng/g for the Pr internal standard. By following this protocol, one does not have to know the concentration of the Pr internal standard because the amount of Pr is proportional to the known mass of internal standard solution and, if calibrations and calculations are based on the internal standard solution mass, the concentration cancels between standards and samples. Operations in any given test were laid out ahead of time to specify amounts of internal standard, sample, and diluent to give final concentrations within a narrow range of values comparable to the standards. Most often, the sample tubes were set up to contain 0.5 g of the Pr solution and were brought to a nominal value of 50 g solution after being diluted for analysis. The mass of Pr solution, mass of added sample, and final dilution mass were recorded for every sample. We also monitored the mass of the Pr internal standard stock solution to ensure that its concentration was not changing as a result of evaporation during storage as this would spoil the comparability between samples and standards on which the analysis strategy depends. We did not see any evidence of evaporation over the period of interest but mention that corrections can be applied for small changes in the internal standard solution if evaporation were to be noted.

Each analysis run was set up in a sequence that included the cesium and barium standard solutions. Barium isotopes in the standards were used for evaluating non-linearity and mass-bias effects. The run sequence typically prescribed running the standards, a set of analytical samples, the standards, more samples, and so on, such that every group of

analytical samples was bracketed by the standards. The entire standard sequence was usually repeated at least three times during a run so at least three replicate measurements of each desired signal ratio were produced. Blank samples consisting of the 2% HNO_3 diluent were analyzed before and after every sample and standard to ensure complete washout of the sample and prevent carryover of analyte from one sample to the next.

Peaks located at m/z 129(Xe), 130(Xe,Ba), 131(Xe), 132(Xe,Ba), 133(Cs), 134(Xe,Ba), 135(Ba), 136(Xe,Ba), 137(Ba), 138(Ba), and 141(Pr) were measured. The signal at m/z 129 (^{129}Xe) was used to monitor the level of xenon impurity in the argon plasma gas and to allow correction for contributions by xenon isotopes to the signals for ^{130}Ba, ^{132}Ba, ^{134}Ba, and ^{136}Ba. Corrections for the xenon isotopes were made using the ratios to ^{129}Xe observed in the blanks that bracketed each sample and the ^{129}Xe observed for a specific sample because both the level of xenon impurity and its isotopic composition might have varied both within each run and between runs. This variation was a concern because xenon concentrates in the argon supply tank as the argon is used and the xenon isotopes evaporate at slightly different rates, which could cause the xenon isotopic composition to change due to isotope fractionation as evaporation occurs.

Non-linearity (τ) and mass-bias (F) correction factors as defined in Ref. 6 were determined separately for every run using results from the barium standards analyzed during the run and reference ratios for 130/138, 134/138, 136/138, and 137/138 based on the IUPAC abundances for the barium isotopes.[15] We found that, due to the very low abundance of ^{132}Ba (0.1012%) and the high abundance of ^{132}Xe (26.89%), corrected ^{132}Ba/^{138}Ba ratios were not very precise; consequently they were not used in modeling the data to determine corrections. In every ICP-MS run that was carried out as part of this task, the fit of data to the model was excellent with corrected ratios of the Ba isotopes to ^{138}Ba deviating not more than 0.2% from the reference values.

Calibration of the ICP-MS signal response *vs* concentrations of standards was established from the simple straight-line relationship between the isotope/internal standard signal ratio and the amount ratio of the isotope to internal standard solution in the calibrants. The standard uncertainties of the ICP-MS concentration measurements of Cs (based on

^{133}Cs) and Ba (based on ^{138}Ba) were estimated directly by pooling standard deviations from analysis runs carried out on seven different days during the study. Values for u_{Noise} and u_{Prop} for Cs and Ba are shown in Table 1. The proportional uncertainties include contributions from not only sample-to-sample variations, but also from long term drift in the calibration slopes over the several hour duration of the ICP-MS runs. In the case of Cs, this long term drift is a substantial component of the variance while for Ba it is much less significant.

Table 1. Figures of Merit for Concentration Measurements by ICP-MS; Random Error Components Expressed as Standard Deviations for a Single Measurement.

Analyte	u_{Noise}, standard uncertainty, ng/g	u_{Prop}, relative uncertainty, ng/g per ng/g
Cesium Isotopes	0.005	0.51%
Barium Isotopes	0.006	0.33%

Procedure for Surrogate Preparation

A high-purity (99.95% metals basis, Pfaltz and Bauer) sodium aluminum silicate was chosen as the base material for fabrication of the ceramic surrogate. This material was chosen because the sodium cation is easily replaced with cesium or barium by ion exchange and the material is a likely starting material in a manufacturing process due to its low cost and abundant availability. Individual portions (nominally 0.1 g) of the sodium aluminum silicate were weighed into 30-mL, pre-cleaned, PTFE beakers. Next, equal weighed portions of cesium and barium spectroscopic standard solutions (High Purity Standards, Charleston, SC; Inorganic Ventures, Christiansburg, VA; or SCP Science, Champlain, NY) were dispensed into each beaker. The mixtures were gently swirled and placed under a laminar-flow hood to air dry overnight. This process allowed ample time for the cesium and barium ions to exchange with the sodium ions present in the aluminosilicate and create the cesium-containing ceramic surrogate. With this preparation, each portion of surrogate is expected to contain accurately known amounts of cesium and barium determined by the mass of standard solution that was added. A sodium aluminum silicate blank was prepared (by adding deionized water in place of the element solutions) and similarly air-dried overnight to allow assessment of barium contamination that might have been introduced during handling of the samples or from

the reagents used in the synthesis. After drying, each beaker containing the synthesized ceramic-surrogate solids was covered with Parafilm™ and placed in storage for subsequent use as test samples for evaluating the dissolution and separation procedures.

Dissolution Procedure

Given the similarity in chemical composition between the silica-based glass material that was studied in our past work [6] and the aluminosilicate ceramic surrogate, we applied a comparable dissolution method. Silicates in the sample are decomposed with HF and silicon is evolved as SiF_4 gas in the first step of the dissolution, which involved adding 2 mL of reagent water, 2 mL of concentrated nitric acid (Optima™ grade, Fisher), 1 mL of concentrated hydrochloric acid (Optima™ grade, Fisher), and 1 mL of concentrated hydrofluoric acid (Optima™ grade, Fisher), covering the beaker with a Teflon® watch glass, refluxing the solution on a hotplate at medium heat for 0.5 h, and then taking each sample to dryness. This step is repeated to ensure that all silicates are decomposed and all silicon is expelled from the sample. Residual fluoride is evolved as BF_3 gas by adding 2 mL of a 2% solution of H_3BO_3 (Puratronic, 99.9995% metals basis, Alfa Aesar®) and an additional 2 mL of concentrated nitric acid, taking to dryness, and repeating to ensure all excess fluoride is removed. Excess boric acid is evolved as gaseous trimethyl borate to limit the amount of total dissolved solids introduced into the ICP-MS plasma when samples are ultimately analyzed. To remove the boric acid, 5 mL of Optima™-grade methanol (Fisher Scientific) is added; then, the beaker is covered with a Teflon® watch glass and the liquid is refluxed on a hot plate at 70 °C for a short time (15 min), at which time the watch glass is removed and the solvent allowed to evaporate to dryness. This step is then repeated once more to ensure complete removal of the boric acid. We note that previous development work on this procedure showed that heating the methanol/boric acid mixture at too high a temperature (> 80 °C) or in the presence of water can cause disintegration of the trimethyl borate and impede complete boron removal [16]. Salts in each beaker are finally dissolved in 3 M nitric acid, with no visible residues of undissolved solids.

Tests of the dissolution procedure verified that it was effective for bringing the simulated ceramic matrix of cesium aluminosilicate into solution. Salts remaining in the beaker

after treatment dissolved readily in 3N HNO_3 with no apparent residue. It was noted that the quantity of salts observed with the aluminosilicate samples was somewhat greater than the amounts present after dissolving glass samples in our earlier work. This was not surprising since the elemental composition of the aluminosilicate includes a lower fraction of silicon, which is removed during the process, and higher amounts of elements like aluminum and alkali metals, which are converted to nitrate salts and remain in the beaker.

Separations using Sr Resin in an Omnifit® Column Assembly

For our separation tests with the Omnifit® column assembly, a Benchmark 3-mm i.d. x 100-mm long "microbore" Omnifit® column kit was procured. The size of the column was selected based on capacity specifications for the Sr Resin (Eichrom Technologies website) and a projected loading of 1 ug Cs and 1 μg Ba for mixtures to be tested. The Omifit® column consists of a glass column tube with fritted, screw-on fittings at each end. Both end fittings connect to narrow bore polyethylene tubing used for bringing solution to and away from the column. The column was mounted in a clamp on a ring stand and connected the tube from the bottom of the column to a small peristaltic pump with a reverse switch that allowed moving liquid through the column in either the top-to-bottom or bottom-to-top direction. The setup is shown in Figure 1.

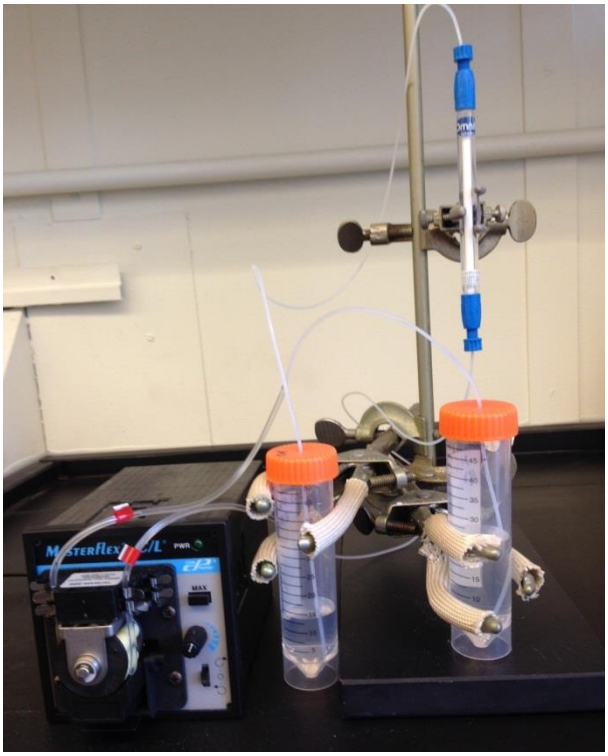

Figure 1. Omnifit® Column Assembly with 3-mm x 100-mm Column

To pack the column, Sr resin (50-100 µm particle size) was slurried in reagent water and the slurry added to the top end of the glass column with the top fitting removed. The resin was allowed to settle and supernatant liquid was pumped out the bottom of the column. Then, more slurry was added and the process was repeated until the entire length of the column was packed. The top fritted fitting was then attached, completing the column preparation. The bed volume was calculated as approximately 0.35 mL.

Prior to use, the column was washed by pumping through it (bottom to top) 10 mL of reagent water, 10 mL of 3N HNO_3, and 10 mL of 1% acetic acid. Then the column was conditioned with another 5 mL of 3N HNO_3. When the column was not in use, it was flushed with DI water and left filled with water. It was reconditioned with 5 mL of 3N HNO_3 just prior to using it for each subsequent separation. Except for packing the column where solutions were pumped top-to-bottom through the column, all operations were done with the pump set for bottom-to-top liquid flow.

Starting with a 2 µg/g sample solution (3N HNO_3) in a centrifuge cone, 0.5 mL of the solution from the tube was pumped through the column, stopped the pump, moved the

input tube to a tube containing 3N HNO_3, and continued the elution. We determined the exact amount of sample solution transferred to the column by weighing the sample tube before and after the sample was removed. After the sample was loaded, 5 mL of 3N HNO_3 was pumped through the column and then put the input tube in a container of 1% acetic acid and pumped 5 mL of that solution through. Pumping was regulated at 0.5 mL/min. Analogous to the first test, 0.5 mL fractions of the column effluent were collected into centrifuge cones that contained previously measured portions of Pr internal standard. Each tube was weighed to determine the exact amount of eluent collected in each fraction and then diluted the fractions for ICP-MS determination of their Cs and Ba contents. Results of these measurements are plotted as elution profiles for Cs and Ba in Figure 2.

Results and discussion

3.1 Quantitative Evaluation of Dissolution Performance

Quantitative performance of the dissolution procedure was tested by analyzing solutions prepared by dissolving a set of surrogate ceramic samples and comparing results of the analysis with values expected from data recorded when the surrogate samples were prepared. Four surrogate samples were made according to the procedure given in Section 2.4 using a nominal mass of 100 mg of sodium aluminosilicate (99.95% metals basis, Pfaltz and Bauer) and spectroscopic standard solutions from Inorganic Ventures (Christiansburg, VA). Components of each surrogate are listed in Table 2.

Table 2. Surrogate Ceramic Samples for Dissolution Tests

Sample ID	$Na_2Al_2SiO_6$ Added, g	Cs Standard Solution[a] Added, g	Ba Standard Solution[b] Added, g	Cs Added, µg	Ba Added, µg
Ceramic 1	0.10075	0.99480	0.99670	995 ± 5	993 ± 5
Ceramic 2	0.10298	0.99740	0.99792	997 ± 5	994 ± 5
Ceramic 3	0.09957	0.99863	0.99781	999 ± 5	994 ± 5

Ceramic 4	0.10090	None	None	None	None

[a] Inorganic Ventures Lot F2-CS02015; 1,000 ± 5 µg Cs/mL; density = 1.000 g/mL at 20 °C.
[b] Inorganic Ventures Lot F2-BA02076; 996 ± 5 µg Ba/mL; density = 1.000 g/mL at 20 °C.

Each of the four surrogate samples was then dissolved using the procedure in Table 1. Each of the resulting solutions was transferred from the dissolution beaker to a weighed 50-mL centrifuge cone (Corning,™ certified sterile polypropylene vial) using 3N HNO_3. The solution in each vial was brought to a mass of approximately 50 g using additional 3N HNO_3, and the vials were weighed again to determine the total solution mass. Each of the stock solutions prepared in this way was serially diluted by mass to provide a final concentration on the order of 2 µg of Cs or Ba per g of solution for samples to which Cs and Ba had been added; the same dilutions were applied to the unspiked sample, Ceramic 4. Next, 0.5 g of each 2-µg/g solution was weighed into a pre-weighed 50-mL centrifuge cone containing a weighed portion (0.5 g) of a 1 µg/g solution of Pr internal standard. The Pr solution was from the same batch that was used in preparing Cs and Ba calibration standards for ICP-MS determination of the elements. These operations produced analysis solutions containing roughly 20 ng/g concentrations of Cs and Ba, and 10 ng/g Pr.

The solutions spiked with internal standard and the corresponding calibration standards were analyzed in four ICP-MS runs carried out on separate days. The data from each run were processed using Microsoft Excel® based spreadsheets to correct the data for background signals from xenon isotopes that contribute to the mass spectrum, and to apply Argonne's model formulas that account for non-linearity and mass discrimination in the ICP-MS data [8]. Each run provided a value for the concentration of Cs and the concentration of Ba in the solution. Results of these measurements are shown in Table 3.

Table 3. Measured Concentrations for Cs and Ba in Ceramic Surrogate Solutions

	Cesium Concentrations, ug Cs/g Solution						
Sample ID	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Average**	**Std dev.**	**%rsd**
Ceramic 1	2.014	2.008	2.019	2.012	2.012	0.007	0.35
Ceramic 2	2.064	2.056	2.065	2.068	2.063	0.005	0.25
Ceramic 3	2.042	2.043	2.043	2.047	2.043	0.002	0.11
Ceramic 4	<0.001	<0.001	<0.001	<0.001	<0.001	NA	NA

					pooled %rsd for Cs:		0.26
	Barium Concentrations, ug Ba/g Solution						
Sample ID	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Average**	**Std dev.**	**%rsd**
Ceramic 1	2.019	2.022	2.029	2.015	2.021	0.006	0.29
Ceramic 2	2.063	2.066	2.059	2.053	2.061	0.006	0.27
Ceramic 3	2.060	2.054	2.051	2.045	2.052	0.006	0.31
Ceramic 4	0.031	0.031	0.031	0.032	0.031	0.001	
					pooled %rsd for Ba:		0.29

The precision of the concentration measurements was quite good, having a pooled rsd of 0.26% for Cs and 0.29% for Ba. This level of precision for measurements with the quadrupole ICP-MS reflects the effectiveness of the experimental design and data-reduction process incorporated into our operations.

From these measured concentrations and dilution factors calculated from the solution mass data recorded during the dissolution and serial dilutions, we calculated values for the amounts of Cs and Ba recovered from the dissolution process and compared these to the amounts that were added when the surrogate ceramics were prepared. Pertinent data are shown in Table 4.

Table 4. Cs and Ba Recovered from Dissolution of Surrogate Ceramic Samples

		Cesium Recovery			**Barium Recovery**		
Sample	**Dilution Factor**	**Added, µg**	**Found, µg**	**Recovery, %**	**Added, µg**	**Found, µg**	**Recovery, %**
Ceramic 1	497.2	995	1000	100.5	993	1005	101.2
Ceramic 2	483.7	997	998	100.1	994	997	100.3
Ceramic 3	480.8	999	983	98.4	994	987	99.3
Ceramic 4	505.7	None	< 1	--	None	16	--
			Average:	99.7		Average:	100.3
			Std dev:	1.1		Std dev:	1.0

Examination of the data in Table 4 shows that 98% or more of the cesium in each dissolved sample was transferred out of the beaker for measurement. In addition, it is seen that the barium and cesium recoveries are correlated, with the sample showing the highest cesium recovery also showing the highest barium and the sample with the lowest cesium recovery giving the lowest recovery for barium. This relationship between the cesium and barium recoveries is sensible insofar as one would expect the recoveries to be influenced not only by completeness of dissolution but also by the degree to which the analyst was able to wash the solution from the beaker to the dilution vessel. If dissolution and mixing of the solution in the beaker is complete, one would expect the barium-to-cesium ratio to be unaffected by the extent of transfer, particularly if the fraction of sample transferred is high. The observation that more than 98% of the Cs in every sample was recovered indicates that the transfer fraction was satisfactory in these tests.

3.2 Cesium/Barium Separation

To evaluate the separation performance of the column, an elution profile was created in which we loaded 0.5 mL of a test solution containing nominally 2 ug/g of Cs and Ba, 40 ug/g Na and 50 ug/g Al in 3N HNO3. Next, 3N HNO_3 was passed through the column to elute Cs and 7 mL 1% acetic acid to elute barium. Separated fractions were collected containing 1-mL increments of the solution that flowed out of the system. The profile obtained with the 100-mm Omnifit® column is shown in Fig. 3.

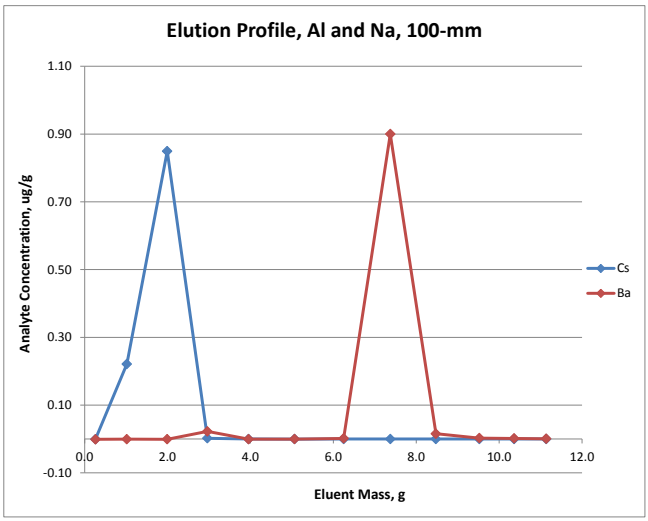

Figure 3. Profiles of Cesium and Barium Elution with Sodium and Aluminum Present in Sample: 0.5 mL sample in 3N HNO_3; Wash with 5 mL 3N HNO_3 and then 7 mL 1% HOAc.

The column performed as expected and retained barium throughout the entire wash with 3N HNO_3 (the single point showing an elevated Ba concentration at about 3 g of eluent in the plot is attributed to a spurious contamination and is not considered real). Cesium eluted from the longer column almost as fast as it did from the shorter one; this is not surprising since the cesium washout is essentially determined by the system dead volume and doubling the column bed volume from 0.35 mL to 0.70 mL only increases the dead volume by 0.60x0.35mL = 0.21 mL based on Eichrom's value of 0.60 for the free volume fraction of a packed Sr resin bed.

To test the Cs and Ba separation efficiency from the prepared ceramic surrogates , a nominal 0.5 mL of each ceramic sample solution (actual amounts ranged from 0.5 to 0.8 g of solution) was loaded onto the column washed with 3 additional mL of 3N HNO_3 to complete the Cs fraction, and then washed with 7 mL of 1% acetic acid to produce the barium fraction. Results of these tests are given in Table 5.

Table 5. Cs and Ba Amounts in Fractions from Ceramics on the 3-mm x 100-mm Omnifit® Column

Sample ID	Cs in Fraction, ng	Ba in Fraction, ng	Ba/Cs Ratio from 50-	Ba/Cs Ratio from	Ba/Cs Omnifit/Unsep.

			mm Omnifit	**Unsep.**	
Blank Ceramic-Cs	<1.5	1.8	--	--	--
Blank Ceramic-Ba	<1.5	19.7			
Ceramic 3-Cs	1417.1	<1.5	0.977	1.004	0.973
Ceramic 3-Ba	<1.5	1384.0			
Ceramic 2-Cs	1097.6	11.1	0.983	0.999	0.984
Ceramic 2-Ba	0.6	1079.			
Ceramic 1-Cs	1538.7	10.6	0.983	1.005	0.978
Ceramic 1-Ba	<1.5	1513.2			
				Average:	0.978
				std dev.:	0.006

Although the element separations with this Omnifit® column appear to be fairly good insofar as only traces of Cs were found in the Ba fractions and traces of Ba in the Cs fractions, the Ba/Cs ratios calculated from the separated fractions are shifted to values lower than the values from analysis of unseparated portions of the same sample solutions. The average Ba/Cs ratio after separation for the three spiked-surrogate ceramic samples relative to the unseparated samples is 0.978 with a standard deviation of 0.006. One possible reason for the low Ba recoveries indicated by this observation is that we did not wash the column with sufficient 1% acetic acid to remove all the Ba from the column. The elution profile data seemed to make this very unlikely, but we could not discount it.

As we continued our investigations, we discovered that the underlying cause is more likely a failure of the Sr resin to completely release barium to the 1% acetic acid eluent. The remarkable pattern of low Ba/Cs ratios after separation observed in these experiments have been reported before. Goldberg, *et al.*,[9] noted in their tests with a ^{137}CsCl source that 1-2% of the barium carried over into the subsequent run and adopted a procedure in which a reagent blank sample was run after each ^{137}Ba/^{137}Cs mixture sample, and the Ba from the blank run was added to that from the sample. Analysts at Idaho National Laboratory (INL) cited variations in recovery of strontium and zirconium from a GPEC system as a substantial contributor to uncertainty in the ^{90}Sr/^{90}Zr ratios measured for ^{90}Sr age dating and proposed an isotope-dilution based procedure [8] to

accommodate them. This history and our observations led us to reconsider an alternative approach for separating Cs and Ba for age dating. It is clear to us that errors amounting to a few percent in the measured element ratio due to the barium (or strontium) not cleanly eluting from the column are not acceptable, particularly as capabilities for measuring the elements of interest in the separated fractions have improved. With our ICP-MS operating and data-reduction procedures, Cs and Ba can be measured with standard deviations of a few tenths percent; this advantage is lost when the separation performance is not at least that good.

We therefore began thinking about ways in which we might improve the effectiveness of removing barium from the resin. On looking at the Eichrom specifications for the Sr resin, we noticed that Eichrom recommends eluting Sr and Ba with dilute (0.01 M) nitric acid. So, we decided we would try 0.01 M HNO_3 in place of the 1% acetic acid. The elution profile and surrogate ceramic separation test data with this system are shown in Figure 4 and Table 6. The average Ba/Cs ratio after separation for the three spiked-surrogate ceramic samples relative to the unseparated samples is 0.968 with a standard deviation of 0.004. Almost no difference is seen between performance with the 0.01 M nitric acid elution of barium and that with 1% acetic acid.

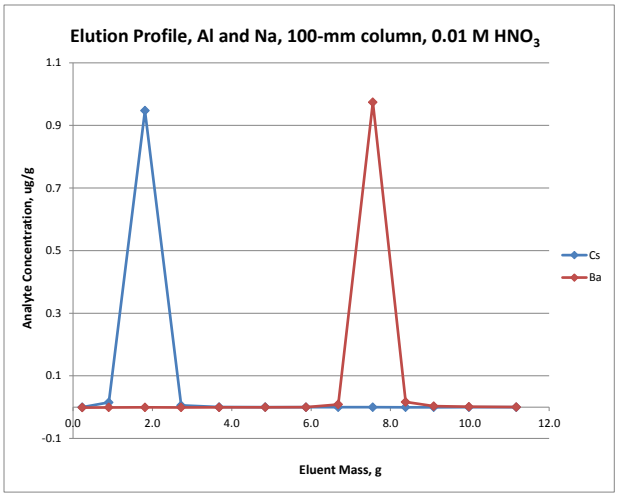

Figure 4. Profiles of Cesium and Barium Elution with Sodium and Aluminum Present in Sample: 0.5 mL sample in 3N HNO_3; Wash with 5 mL 3N HNO_3 and then 7 mL 0.01 M HNO_3.

Table 6. Cs and Ba Amounts in Fractions from Ceramics on the 3-mm x 100-mm Omnifit® Column using 0.01 M HNO_3 to Elute Barium

Sample ID	Cs in Fraction, ng	Ba in Fraction, ng	Ba/Cs Ratio from 50-mm Omnifit	Ba/Cs Ratio from Unsep.	Ba/Cs Omnifit/Unsep.
Blank Ceramic-Cs	<1.5	35.6	--	--	--
Blank Ceramic-Ba	<1.5	27.6			
Ceramic 3-Cs	1079.6	<1.5	0.969	1.004	0.965
Ceramic 3-Ba	<1.5	1046.4			
Ceramic 2-Cs	1015.1	12.2	0.972	0.999	0.973
Ceramic 2-Ba	<1.5	986.5			
Ceramic 1-Cs	1083.0	11.5	0.972	1.005	0.967
Ceramic 1-Ba	<1.5	1052.8			
				Average:	0.968
				std dev.:	0.004

The question remained, "how can one improve the desorption of barium from the Sr resin?" Two possibilities came to mind. One would be to decrease the acidity of the solution since the distribution coefficient (K_d) for Ba on the Sr resin is known to decrease exponentially with nitric acid concentration. Just using a pH higher than that of 0.01 M HNO_3 seemed unlikely to be successful. Even going to pure water as eluent did not seem likely to produce the change we desired since this had been reported by Sommers *et al.*,[1] to be less effective than 1% acetic acid in their GPEC operations. The other would be to add a complexant to the barium eluent to promote barium back extraction. On searching the literature for Sr resin applications, we found no reports of complexants having been used for stripping Sr resin columns of Ba or Sr. However, we did find a few references [17-19] that described using a dilute solution of ethylenediaminetetracetic acid (EDTA) or cyclohexylenediaminetetraacetic (CDTA) to strip barium from cation exchange columns in separating it from radium. We selected a dilute solution of EDTA to test the concept of using a complexant in the barium eluent to improve recovery. Because the formation constant for the Ba-EDTA complex is relatively small ($\log K_f \approx 7.9$),[20] complexation is most effective at high pH where H^+ does not compete

effectively with Ba for the complexant. We chose an eluent consisting of 0.05 M disodium EDTA (100 times the anticipated concentration of Ba in the eluent solution) in water, which had a pH of 6.

Using a freshly prepared 100-mm column of Sr resin, the experiments were replicated to separate the Cs and Ba in the four surrogate ceramic sample solutions two times using the EDTA eluent for Ba. Results are shown in Table 7. (We found that our 0.05 M EDTA solution contained a trace impurity of barium, about 0.5 ng/mL, and corrected for it in the barium data shown.) One time, we loaded 0.5 mL of the sample and washed the column with 5 mL of 3N HNO_3 to produce the Cs fraction. Then, we washed the column with 7 mL of 0.05 M EDTA to generate the Ba fraction. The next time, we again loaded 0.5 mL of sample and washed with 7 mL of 0.05 M EDTA to elute barium, but we only used 3 mL of 3N HNO_3 for the wash in the Cs fraction because it appeared some barium might have broken through into the Cs fraction in some of the first-series samples where a 5-mL wash was used. Between samples, we reconditioned the column with 5 mL of 3N HNO_3.

Table 7. Cs and Ba Amounts in Fractions from Ceramics on the 3-mm x 100-mm Omnifit® Column using 0.05 M EDTA to Elute Barium

Sample ID	Cs in Fraction, ng	Ba in Fraction, ng	Ba/Cs Ratio from 50-mm Omnifit	Ba/Cs Ratio from Unsep.	Ba/Cs Omnifit/Unsep.
Series from Day 1: Cs Fraction Wash of 5 mL 3N HNO_3; Ba fraction of 7 mL 0.05M EDTA.					
Blank Ceramic-Cs	<1.5	<1.5	--	--	--
Blank Ceramic-Ba	<1.5	18.4			
Ceramic 3-Cs	1244.4	<1.5	1.001	1.004	0.997
Ceramic 3-Ba	<1.5	1245.8			
Ceramic 2-Cs	1118.5	10.2	0.988	0.999	0.989
Ceramic 2-Ba	<1.5	1104.7			
Ceramic 1-Cs	1033.2	13.4	1.006	1.005	1.001
Ceramic 1-Ba	<1.5	1039.2			
Series from Day 2: Cs Fraction Wash of 3 mL 3N HNO_3; Ba fraction of 7 mL 0.05M EDTA.					

`Blank Ceramic-Cs	<1.5	<1.5	--	--	--
Blank Ceramic-Ba	<1.5	20.1			
Ceramic 3-Cs	1198.9	<1.5	0.984	1.004	0.980
Ceramic 3-Ba	2.1	1179.4			
Ceramic 2-Cs	1257.6	2.4	0.997	0.999	0.998
Ceramic 2-Ba	2.4	1253.7			
Ceramic 1-Cs	1223.5	<1.5	1.006	1.005	1.001
Ceramic 1-Ba	2.2	1231.1			
				Average:	0.994
				std dev.:	0.008

On looking at the data from these cursory tests of the EDTA-based eluent for barium, the data shows considerable reason to be encouraged that this approach could resolve the shortcomings we observed with 1% acetic acid as eluent. The average Ba/Cs ratio after separation for the six spiked-surrogate ceramic samples relative to the unseparated samples is 0.994 with a standard deviation of 0.008. This is much improved from the corresponding figure of merit with 1% acetic acid, which averaged only 0.98 or less. And, this improvement does not take into account that the EDTA separation conditions are not optimized. One refinement suggested by the data in Table 10 is a fine tuning of the volume used for the 3N HNO_3 wash in the Cs fraction. The data hint that using 5 mL for this wash causes a small amount of Ba to break through into the Cs fraction, while cutting back to 3 mL seems not to completely wash Cs out of the system since a trace of Cs shows itself in the Ba fractions. Some volume between these values is likely to be better. We suspect that some of the variability in the barium recoveries might arise from an insufficient wash with the 0.05 M EDTA eluate. If the 7 mL wash we used were not well beyond the end of the tail of the barium elution peak, then the tail could be cut off in an area where the last little bit of barium is eluting and small run-to-run perturbations of the elution profile could readily result in recovery of only 98% of the barium instead of 100%.

4.Conclusions

The goal of the present task was to investigate whether methodology used for age dating radioactive sources containing ^{137}Cs as chloride salt or glass could be adapted for sources where the ^{137}Cs is incorporated into a ceramic matrix. Although the term "ceramic" was found to encompass a wide variety of substances and materials, an examination of the available literature and specifications from source vendors led us to conclude that the most likely ceramic matrix one might encounter for a ^{137}Cs source would be formulated from a cesium-doped aluminosilicate. Using a surrogate composition based on this material, we evaluated the potential effects that the matrix might have on the individual processes needed for applying the age-dating method, including dissolution of the matrix, separation of the cesium and barium constituents, and measurement of the ^{137}Cs and ^{137}Ba isotopes. As we considered and experimented with each process, we developed several notable insights, which not only clarified potential effects of the ceramic matrix but also exposed some previously underappreciated shortcomings in the methodology applied to age-dating ^{137}Cs in other matrices.

Based on our investigations, we strongly believe that the age-dating methodology for ^{137}Cs can be substantially improved by changes to the procedures for separating the cesium and barium isotopes and for measuring the ^{137}Cs constituent. In prior embodiments of the method, the Cs/Ba separations were done using other apparatus with an expectation that the advantages of that device (small sample requirements, potential for automation) would overcome any drawbacks to its use. Consequently, we investigated an alternative apparatus based on the readily available and inexpensive Omnifit® column kit, a configuration to which we were introduced when we participated in a round-robin exercise for age dating ^{60}Co [7]. We determined that this approach allowed much more convenient operation, better utilization of sample, and a potential for more control over separation conditions. More important, during our studies of the cesium/barium separation with the Omnifit® system, we learned that recovery of barium in a fraction eluted with 1% acetic acid was consistently low by about 2% and varied substantially from one run to another (average recovery was 98.3% with a standard uncertainty of 2.3%); this condition was reported in other studies that used the GPEC apparatus, but was not followed up on in the past. We did a short study of alternative

eluents for the barium fraction and found that adding a complexant such as EDTA in place of acetic acid improved the recovery (99.4 ± 0.8%). This improvement constitutes a major reduction in the overall uncertainty of the age dating method since variability in the barium recovery is the largest single contributor to the combined uncertainty in the measured age, as illustrated in the uncertainty analysis we present.

Consideration of the procedures available for measurement of the ^{137}Cs isotope for the age dating process revealed a serious gap in the chain of comparisons that underlie calibration of the ICP-MS instrument for this nuclide. We noted that, in prior work, assumptions were made regarding identity of responses between ^{137}Cs and ^{133}Cs or ^{137}Ba, which cannot be justified within reasonable uncertainty. This impediment is removed if the ^{137}Cs determination is made radiometrically using gamma counting where suitably traceable standards are available and measurements can be made with predictable uncertainty.

Age dating of ^{137}Cs ceramic sources is shown to be a viable technology for nuclear forensics investigations. The ^{137}Cs age dating method in general, however, could be substantially improved by using radiometric rather than ICP-MS measurement of the ^{137}Cs isotope and by refining the Cs/Ba separation process. With these improvements, uncertainty in the age of a 60-year-old source is < 1 y.

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