LA-12952-MS

Determination of Plutonium Activity Levels and $^{240}Pu/^{239}Pu$ Isotope Ratios in Bone Collected from Nonoccupationally-Exposed Individuals Living in Colorado

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LA-12952-MS

UC-700 and UC-707
Issued: April 1995

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by

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ABSTRACT

Los Alamos scientists measured $^{239+240}Pu$ alpha activities and $^{240}Pu/^{239}Pu$ atom ratios in bone tissues collected from Colorado residents who were not occupationally exposed to this type of radioactivity. Bone tissues from 519 individuals were collected from 1975 to 1979 as part of an Environmental Protection Agency directed project to determine the effect of plutonium on people who live in areas surrounding the Rocky Flats Plant. Los Alamos selected 59 individuals who were suspected of having high plutonium body burdens based on the plutonium content of their livers. The plutonium activity level in the subset of bones analyzed in this study contained 7.8 ± 9.4 pCi $^{239+240}Pu$/10 kg wet weight. The average $^{240}Pu/^{239}Pu$ atom ratio was 0.182 ± 0.068; this ratio suggests that the plutonium detected in these individuals originated predominately from global fallout.

Introduction

Senator Haskell (US Senator from Colorado) requested that the Environmental Protection Agency (EPA) initiate a study to determine the presence, extent, and potential effect of plutonium on people living in areas surrounding the Rocky Flats Plant (RFP). The study, directed by R. Train, EPA Administrator, was designed to compare levels of plutonium in human autopsy tissues from individuals who lived near the Rocky Flats Plant with tissues from individuals who lived in Denver and Pueblo, Colorado, with the intent of determining the source of plutonium found. No decedents who might have been occupationally exposed to plutonium were chosen

for the study. The EPA's Environmental Monitoring Systems Laboratory in Las Vegas, Nevada, designed the study in consultation with the staff from the University of Colorado Medical Center (UCMC) and the Colorado State Health Department. The original design specified tissue specimens from human autopsies in each of three collection areas: Area A encompassed the area up to 25 km from the RFP; Area B included the area between 25 and 50 km from the RFP; and Area C (originally defined as the vicinity of Pueblo, Colorado) was later expanded to include all areas outside a 50-km radius of the RFP and east of the Continental Divide.

In June 1975, the EPA awarded a contract to the UCMC to collect tissue samples in each of the three collection areas and to obtain epidemiological data. Each set of samples usually included

- one whole lung,
- approximately 750 g of liver,
- both gonads, if available,
- both adrenals, if available, and
- a sample of rib.

Fifteen hospitals in the vicinities of Denver, Pueblo, and Colorado Springs agreed to collect tissue samples for the study. Tissues were collected from 519 separate autopsies. Tissue sampling required several steps.

(1) The hospital staff was asked to obtain an informed consent from the next of kin specifically for the study.

(2) The pathology staff of each cooperating hospital recorded information about the decedent according to established protocol.

(3) The UCMC staff picked up the sets of the tissue specimens from individual hospitals and brought them to UCMC, where each tissue was assigned a number, weighed, logged, and frozen.

The US Air Force's McClellan Central Laboratory (MCL) in Sacramento, California, analyzed liver and lung samples for plutonium in accordance with the EPA/US Air Force interagency agreement. Plutonium activity levels and $^{240}Pu/^{239}Pu$ atom ratios were measured in liver and/or lung tissues from 473 individuals, and the results of the study were published in 1982.[1] Some of the samples originally collected for the EPA study were expended during the initial research and development activities at MCL. The remaining tissue samples were shipped to Los Alamos National Laboratory (LANL) for storage and possible future analyses.

In 1991, at the request and direction of J. Chavez, Chief Counsel's Office, US Department of Energy (DOE), Albuquerque, and W. Wicker, Colorado State University (CSU), we agreed to analyze approximately 50 bones from the EPA's original study for plutonium content and $^{240}Pu/^{239}Pu$ atom ratios. After we

completed our measurements of plutonium in bone, all remaining tissue samples from the EPA study that had been stored at LANL were transferred to W. Wicker at CSU.

Tissue Selection Criteria

Plutonium, once it reaches the blood, deposits primarily in the liver and the skeleton. We concluded that we would have the best chance of measuring plutonium in the bones of individuals who had the highest concentrations of plutonium in their livers. We reviewed the results of lung and liver analyses in the 1982 report[1] and organized the cases in order of decreasing liver concentration for each of the geographical divisions specified in the original study. We then picked the 68 tissue sets that corresponded to the highest liver concentrations in samples available at LANL. In addition, we selected 10 samples from individuals who lived close to RFP. We analyzed two separate bone samples from 6 of the individuals as part of our quality assurance/quality control procedures. Processing blanks were also run.

Sample Preparation and Analyses

The bones were traced with ^{242}Pu, ^{232}U, ^{243}Am, and ^{229}Th, ashed at 450°C, and dissolved in mineral acids.[2] The plutonium fractions, isolated by ion exchange chromatography, were electroplated on stainless steel disks and analyzed by alpha spectroscopy.[3,4,5] Alpha spectroscopy analyses indicated the presence of extraneous alpha-emitting radionuclides whose energies corresponded to those of uranium and its decay products. We submitted the samples for thermal ionization mass spectrometric (TIMS) analyses to determine both the plutonium activity levels and the $^{240}Pu/^{239}Pu$ atom ratios. All of the plutonium data reported in this manuscript were derived from the TIMS analyses.

A chemical purification procedure was used to convert samples from a form suitable for alpha spectroscopy analyses to the form suitable for TIMS analyses (see Appendix A). After the plutonium samples were purified, they were electroplated on rhenium filaments and overplated with platinum to produce a surface ionization diffusion-controlled (SID) ionization source for TIMS analyses.[6] The major steps used to produce the SID source are summarized below.

- Purified plutonium samples were dissolved in 100 μℓ of 1.5 M NH_4Cl and 20 μℓ of 1.5 M HCl.
- The solutions were placed on rhenium filaments and electrolyzed at 3.5 V for 20 min.
- The plating voltages were then reduced to 3 V.
- Dinitrito-sulfato-platinous acid diluted with 1.5 M HCl was added to the solutions.
- The samples were electrolyzed for 20 min, rinsed, dried, and inserted into the mass spectrometer for analyses.

The mass spectrometer used in this study is a modified version of the 30.5-cm-radius, 90°-deflection thermal ionization instrument developed at the National Bureau of Standards (now the National Institute of Standards and Technology).[7] This spectrometer is equipped with a 17-stage electron multiplier with a gain of 10^8, a 250-MHz scalar, and a discriminator-amplifier capable of supplying 1-V, 7-ns-wide output pulses when triggered by input pulses between 6 mV and 2 V. The dark current of the counting system is 0.05 counts per second; its deadtime is 11 ± 1 ns. The system's overall linearity and deadtime were verified by analyzing National Bureau of Standards' reference materials U-100, U-500, and U-900.[8] Automatic data acquisition is controlled by an IBM Personal Computer. The spectrometer is equipped with a sample turret that holds 5 SID filaments.[9]

Table I summarizes the plutonium data obtained during this study. The UCMC Case Numbers used in Table I were assigned during the original EPA study. The epidemiological data, residence history, smoking history, plutonium activity levels, and $^{240}Pu/^{239}Pu$ atom ratios in the livers of these individuals have been previously reported.[1]

Ash weight refers to the weight remaining after the bones were heated to 450°C. We were not able to directly determine the wet weight of the bones used in this study because they had become desiccated during years of storage.

Calculated wet weights for ribs collected from both males and females were derived by dividing the ash weights by 0.28.

An ash weight/wet weight ratio of 0.15 was used for sternum samples collected from males, and a ratio of 0.11 was used for sternum samples collected from females. (These ratios are typical for bones analyzed at LANL for efforts that support the US Transuranium Registry.[10])

The $^{240}Pu/^{239}Pu$ atom ratios were measured by TIMS. Standard deviations associated with the $^{240}Pu/^{239}Pu$ atom ratios include the uncertainties associated with measuring the count rate of each plutonium isotope and the measurement backgrounds, as determined at the half-mass positions. Data have been corrected for processing blanks. The uncertainty associated with measurements of the processing blanks is included in the uncertainty term reported for the $^{240}Pu/^{239}Pu$ atom ratios.

Average ^{239}Pu content of the five processing blanks was (6.2 ± 2.3) x 10^7 atoms. The average ^{240}Pu content of the processing blanks was (6.6 ± 2.1) x 10^6 atoms. An additional 4.74% error is propagated as a result of uncertainties in the volume and concentration of the ^{242}Pu spike.

TABLE I

PLUTONIUM ACTIVITY LEVELS AND $^{240}Pu/^{239}Pu$ ISOTOPE RATIOS IN BONE

UCMC Case Number	*Tissue Type*	*Ash Weight (g)*	*Calculated Wet Weight*	*$^{240}Pu/^{239}Pu$*	*Sigma (%)*	*Skeletal Burden (pCi/10 kg)*	*Sigma (%)*
7	Rib	8.58	30.64	0.369	25.0	38.65	14.7
9	Rib	8.52	30.43	0.214	76.1	9.81	33.9
21	Rib	11.5	41.07	0.114	39.5	38.53	13.5
39	Rib	14.75	52.68	0.152	6.1	7.20	5.5
46	Rib	1.63	5.82	0.155	40.9	4.85	23.2
47	Rib	6.62	23.64	0.047	13.5	6.26	6.5
49	Rib	2.61	9.32	0.186	45.8	2.73	25.5
53	Rib	8.22	29.36	0.154	22.5	3.27	11.0
62	Rib	5.85	20.89	0.306	25.4	4.01	13.2
71	Rib	6.52	23.29	0.234	118.3	8.57	55.0
85	Sternum	11.54	76.93	0.155	6.8	4.52	5.6
85	Rib	3.59	12.82	0.143	13.7	6.71	8.8
90	Rib	11.88	42.43	0.086	22.2	34.11	7.7
91	Rib	4.45	15.89	0.222	21.5	6.82	11.5
106	Sternum	2.02	18.36	0.227	46.9	23.85	22.2
118	Rib	3.08	11.00	0.099	79.9	2.63	28.9
118	Rib	11.09	39.60	0.130	12.4	8.94	6.7
119	Sternum	12.74	84.93	0.189	7.1	2.05	6.1
151	Sternum	1.49	13.55	0.234	26.7	3.57	14.7
151	Rib	2.81	10.04	0.064	4.2	120.46	4.9
155	Rib	7.02	25.07	0.125	12.9	3.90	8.3
163	Rib	2.79	9.96	0.115	29.6	4.19	16.1
164	Rib	3.29	11.75	0.258	103.4	26.44	50.7
168	Rib	5.25	18.75	0.244	14.8	9.17	8.6
180	Rib	4.87	17.39	0.150	15.4	5.40	8.9
185	Rib	4.01	14.32	0.191	50.2	1.52	28.4
186	Rib	6.61	23.61	0.159	22.3	2.43	12.5
200	Sternum	32.76	117.00	0.178	9.9	1.79	6.4
220	Rib	17.53	62.61	0.102	6.6	6.85	5.4
251	Rib	5.93	21.18	0.100	65.9	20.10	19.3
256	Rib	21.19	75.68	0.178	8.4	5.57	5.9
289	Rib	3.43	12.25	0.131	28.2	8.38	12.6
309	Rib	6.01	21.46	0.186	11.7	6.44	7.4
318	Rib	14.34	51.21	0.127	7.5	2.93	6.3
321	Rib	10.25	36.61	0.107	30.0	8.95	10.5
328	Rib	13.26	47.36	0.204	10.9	2.96	7.4
336	Rib	10.38	37.07	0.187	15.0	2.38	9.1
343	Rib	14.05	50.18	0.182	9.8	2.47	7.2
345	Rib	14.77	52.75	0.201	12.6	1.71	8.4

TABLE I (CONT)
PLUTONIUM ACTIVITY LEVELS AND $^{240}Pu/^{239}Pu$ ISOTOPE RATIOS IN BONE

UCMC Case Number	*Tissue Type*	*Ash Weight (g)*	*Calculated Wet Weight*	*$^{240}Pu/^{239}Pu$*	*Sigma (%)*	*Skeletal Burden (pCi/10 kg)*	*Sigma (%)*
351	Rib	25.92	92.57	0.167	4.7	4.31	5.3
352	Rib	15.13	54.04	0.180	21.2	6.28	9.9
355	Rib	17.50	62.50	0.146	16.7	2.80	8.3
366	Sternum	10.38	69.20	0.160	4.3	3.77	5.3
384	Sternum	8.45	76.82	0.156	11.4	1.32	7.9
384	Rib	3.60	12.86	0.175	40.7	2.48	22.1
386	Rib	19.18	68.5	0.305	34.0	2.98	18.4
395	Rib	10.06	35.93	0.179	10.7	3.49	7.3
396	Rib	8.97	32.04	0.391	39.6	6.74	22.9
398	Rib	7.93	28.32	0.323	44.9	15.69	24.6
403	Rib	9.03	32.25	0.163	10.6	4.52	7.9
404	Rib	15.01	53.61	0.221	21.3	44.13	11.0
405	Rib	13.28	47.43	0.172	11.3	2.86	7.4
413	Rib	8.42	30.07	0.086	26.4	9.36	8.4
427	Rib	10.02	35.79	0.172	43.8	7.49	18.0
473	Rib	10.93	39.04	0.181	33.3	5.63	14.9
473	Sternum	5.53	50.27	0.197	11.7	3.65	7.3
475	Rib	7.23	25.82	0.114	24.0	4.72	9.9
491	Sternum	14.76	98.40	0.193	14.0	1.61	8.0
491	Rib	7.44	26.57	0.376	37.4	2.91	20.7
494	Rib	10.19	36.39	0.144	11.4	2.93	7.8
496	Rib	15.73	56.18	0.193	18.7	5.20	9.3
497	Rib	16.07	57.39	0.185	276.3	3.10	112.8
500	Rib	12.05	43.04	0.208	37.4	5.22	17.1
506	Rib	6.41	22.89	0.186	21.4	2.28	12.8
507	Rib	20.79	74.25	0.148	14.1	1.82	8.3

Skeletal burden is reported in picoCuries of $^{239+240}Pu$ calculated to be present in a 10-kg skeleton. The values are the equivalent alpha activities derived from the TIMS analyses. The method used to calculate the $^{239+240}Pu$ specific activities from the TIMS data is outlined here:

- Each tissue sample was traced with 4.58 ± 0.22 dpm of ultrapure ^{242}Pu.
- The ^{242}Pu alpha activity added to each sample was converted to atoms of ^{242}Pu.
- TIMS measured the $^{239}Pu/^{242}Pu$ and $^{240}Pu/^{242}Pu$ isotope ratios in each sample and calculated the number of atoms of ^{239}Pu and ^{240}Pu present.

- The samples were corrected by the average processing blank value.
- Finally, the atoms of ^{239}Pu and ^{240}Pu were converted to $^{239+240}Pu$ alpha activities and normalized to a 10-kg skeleton.

The standard deviation associated with the plutonium skeleton burdens includes all of the error terms associated with the TIMS measurements and the ^{242}Pu tracer. It does not include any uncertainties associated with the half-lives used to convert atoms to activity rates or the uncertainties associated with converting the ash weights to calculated wet weights. The constants used to convert between specific activities and atoms are listed in Table II.

TABLE II

CONSTANTS USED TO CONVERT BETWEEN ATOMS AND SPECIFIC ACTIVITIES

Isotope	*Half-Life (years)*	*Decay Constant (min^{-1})*
^{242}Pu	376284	3.50233×10^{-12}
^{239}Pu	24118	5.46415×10^{-11}
^{240}Pu	6569	2.00624×10^{-10}

Plutonium body burdens vary from individual to individual. The 59 individuals we selected for this study were expected to be representative of those who had the highest plutonium body burdens among the individuals who donated tissues to the original EPA study (based on the plutonium content of their livers[1] or their proximity to the RFP). Calculations of the plutonium activity level in the bones we analyzed indicated a wet weight of 7.8 ± 9.4 pCi $^{239+240}Pu$/10 kg. The results for skeletal plutonium burden calculated from the analysis of sternum tissue from UCMC case number 151 were excluded from this average for several reasons discussed later in this manuscript. Fox *et al.* calculated that a plutonium skeletal burden of 9.30 pCi $^{239+240}Pu$/10 kg wet weight for females and 14.66 pCi $^{239+240}Pu$/ 10 kg wet weight for males is representative of the 75th percentile for individuals residing in Colorado.[11]

We attempted to determine the plutonium content of the bones corresponding to UCMC case numbers 2, 5, 17, 18, 23, 64, 119, 189, 190, 200, 221, 332, 392, 400, 401, 426, 454, 456, and 519. However, they were lost in analyses; no mass spectrometric results were obtained from these samples.

Significance of $^{240}Pu/^{239}Pu$ Atom Ratios

A $^{240}Pu/^{239}Pu$ atom ratio of 0.06 ± 0.01 is indicative of RFP-processed plutonium.[12,13] Global-fallout plutonium is a complicated mixture in which the isotopic composition was influenced by the type of nuclear device being tested, the location of the test (such as the Nevada Test Site, People's Republic of China, the former USSR, etc.), the mechanisms of atmospheric transport, and diffusion processes coupled with various fractionation processes. The $^{240}Pu/^{239}Pu$ atom ratios in global fallout are variable from location to location. Krey *et al.* measured the $^{240}Pu/^{239}Pu$ atom ratio in global fallout at 0.176 with a standard deviation of 0.014 and ranges from 0.12 to 0.21 around the world.[14] Efurd *et al.* measured the $^{240}Pu/^{239}Pu$ atom ratios in 12 soil samples believed to be representative of global fallout in Colorado.[15] The $^{240}Pu/^{239}Pu$ atom ratios in these samples ranged from a low of 0.143 ± 0.003 to a high of 0.170 ± 0.002; the average ratio for the 12 samples was 0.155 ± 0.010. Additional soil samples are now being analyzed to more precisely determine the $^{240}Pu/^{239}Pu$ atom ratios of global fallout in the vicinity of the RFP.

The average $^{240}Pu/^{239}Pu$ atom ratio for the results reported in Table I was 0.182 ± 0.068. This ratio, measured in the bones analyzed during this study, suggests that the plutonium detected in these individuals predominately originated from global fallout.

Results of Replicate Analyses

Replicate samples were analyzed from six individuals. The results are shown in Table III. The $^{240}Pu/^{239}Pu$ atom ratios measured for replicate analyses for UCMC case numbers 85, 118, 384, and 473 are in good agreement. As seen in the ratio of ratios column, they overlap at the 1-sigma uncertainty level. Case number 491 disagrees at the 2-sigma uncertainty, although both analyses are consistent with fallout plutonium at about the same body burden concentration. It is somewhat more difficult to compare the plutonium concentrations for these replicate analyses because the plutonium does not deposit uniformly in bones.[16]

We do not know the reason for the anomalous results obtained for UCMC case number 151. The rib indicates the presence of plutonium for which the $^{240}Pu/^{239}Pu$ atom ratio of 0.065 is similar to that of plutonium processed at the RFP. The plutonium activity level estimated from the rib sample is 120.46 pCi/10 kg skeleton. The $^{240}Pu/^{239}Pu$ atom ratio measured in the sternum was 0.234, which is indicative of global-fallout plutonium. The plutonium content of the sternum sample estimates a skeleton burden of 3.57 pCi/10 kg skeleton. Anomalous results were also obtained in the original analyses of tissues from this individual: a 0.16 $^{240}Pu/^{239}Pu$ atom ratio measured in the liver by MCL is also indicative of global fallout.[1] The $^{240}Pu/^{239}Pu$ atom ratio measured in the lung by MCL was 0.09, indicative of the type of plutonium processed at the RFP. We have no explanation for these results; however, the anomalously large apparent excess body burden concentration in the rib sample may be indicative of an analytical contamination with weapons-grade plutonium.

TABLE III

RESULTS FOR REPLICATE ANALYSES

UCMC Case Number	*Tissue Type*	*Ash Weight (g)*	*Calculated Wet Weight*	*$^{240}Pu/^{239}Pu$*	*Sigma (%)*	*Skeletal Burden (pCi/10 kg)*	*Sigma (%)*	*Ratio of $^{240/239}Pu$ Ratios*
85	Sternum	11.54	76.93	0.155	6.8	4.52	5.6	1.08 ± 0.17
85	Rib	3.59	12.82	0.143	13.7	6.71	8.8	
118	Rib	3.08	11.00	0.099	79.9	2.63	28.9	0.76 ± 0.62
118	Rib	11.09	39.60	0.130	12.4	8.94	6.7	
151	Sternum	1.49	13.55	0.234	26.7	3.57	14.7	3.66 ± 0.99
151	Rib	2.81	10.04	0.064	4.2	120.46	4.9	
384	Sternum	8.45	76.82	0.156	11.4	1.32	7.9	0.89 ± 0.38
384	Rib	3.60	12.86	0.175	40.7	2.48	22.1	
473	Rib	10.93	39.04	0.181	33.3	5.63	14.9	0.92 ± 0.32
473	Sternum	5.53	50.27	0.197	11.7	3.65	7.3	
491	Sternum	14.76	98.40	0.193	14.0	1.61	8.0	0.51 ± 0.20
491	Rib	7.44	26.57	0.38	37.4	2.91	20.7	

CONCLUSIONS

Bone tissues were analyzed from 59 individuals who were suspected of having high plutonium body burdens (based on the plutonium content of their livers). The average $^{240}Pu/^{239}Pu$ atom ratio was 0.182 ± 0.068. The $^{240}Pu/^{239}Pu$ atom ratio measured in the bones suggests that the plutonium detected in these individuals predominately originated from global fallout.

ACKNOWLEDGMENTS

The authors are grateful to J. Chavez, Chief Counsel's Office, US Department of Energy, Albuquerque, and W. Wicker, Colorado State University, for their guidance and support. J.C. Cobb provided valuable information that facilitated this study. J. Whiting, EG&G Rocky Flats Plant, provided the soil samples believed to be representative of global fallout in Colorado.

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APPENDIX A

PURIFICATION PROCEDURE USED TO PREPARE SAMPLES FOR TIMS ANALYSES

1. Place the stainless steel disks on top of inverted 50-mℓ Teflon beakers. Add 0.5 mℓ of HF to each disk and evaporate to dryness under a heat lamp.
2. Add 0.5 mℓ of 14 M HNO_3 to the disk and evaporate to dryness under a heat lamp.
3. Rinse the plutonium from the disks with 8 M HNO_3 into 40-mℓ centrifuge tubes. Evaporate the nitric acid solutions containing the plutonium to dryness.
4. Dissolve the samples in 5 mℓ of 8 M HNO_3.
5. Pass the solutions through the large anion exchange columns that have been preconditioned with 10 mℓ of 8 M HNO_3.
6. Rinse the columns with three separate 10-mℓ aliquots of 8 M HNO_3.
7. Elute the plutonium fractions into clean 40-mℓ glass centrifuge tubes by passing 10 mℓ of 0.5 M HCl and 10 mℓ of HI-HCl solution through the columns. Evaporate to dryness.
8. Add 1 mℓ of 0.1 M H_2SO_4 to each tube to dissolve the plutonium.
9. Load the samples onto small anion-exchange columns that have been preconditioned with two 1-mℓ aliquots of 0.1 M H_2SO_4.
10. Rinse the tubes with 1 mℓ of 0.1 M H_2SO_4 and add the rinses to the columns.
11. Rinse the columns with two 1-mℓ portions of the H_2O_2-HCl solution. Rinse the tips of the columns with a stream of deionized water. Discard the eluants.
12. Rinse the columns with two 1-mℓ portions of the HF-HCl solution. Rinse the tips of the columns with a stream of deionized water. Discard the eluants.
13. Rinse the columns with three 1-mℓ portions of 12 M HCl. Discard the eluants.
14. Elute the plutonium into 10-mℓ quartz test tubes with three 0.5-mℓ additions of HI-HCl reagent. Evaporate to dryness.
15. Add 4 drops of 16 M HNO_3 and 4 drops of 12 M $HClO_4$ to each sample. Heat at 130°C for 1 hr. Raise the temperature to 180°C and continue evaporating to dryness.
16. Add 10 drops of 12 M HCl to each sample and slowly heat on a heat block until dry. Cool to room temperature.
17. Submit the samples for TIMS analyses.

REAGENTS

H_2SO_4: 0.1 M
$HClO_4$: 12 M
HNO_3: 16 M, 8 M
HI: 48% (unstabilized)
HF: 29 M
HCl: 12 M, 0.5 M
HI-HCl: 1:9 mixture, by volume, of 48% HI and 12 M HCl
H_2O_2HCl: 2 drops of 30% H_2O_2 to 10 mℓ 12 M HCl
HF-HCl: 0.06 M HF in 12 M HCl

Prepare the large anion exchange chromatography columns by placing 3 mℓ of AG MP-1, 50-100 mesh, anion exchange resin in BIO-RAD Polypropylene Econo-Column Chromatography columns.

Prepare small anion exchange chromatography columns by placing AG MP-1, 50-100 mesh, anion exchange resin in 7-cm-long by 5-mm-diam disposable automatic pipettor tips. Place plugs of prewashed quartz wool in the automatic pipettor tips and add resin to a depth of 2 cm.

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