HIGH-PURITY™ STANDARDS

Quantifying the Efficiency of Different Solid Sample Digestion Methods: A Comparison of Time, Cost, and Accuracy

Connie Hayes

Selection of Digestion Procedures

- Digestion is used to convert solid samples into liquid extracts to quantify the concentrations of metallic elements in soils
- Methods in common use vary from total digestion to leach methods, depending upon the analytical goal
- The digestion is principal factor contributing to the uncertainty
- Numerous combinations of reagents
  - Nitric Acid
  - Hydrochloric Acid
  - Sulfuric Acid
  - Hydrogen Peroxide
  - Perchloric Acid
  - Hydrofluoric Acid
  - Aqua Regia

Confidential & Proprietary | High Purity Standards © 2018

Digestion Methods: EPA 3050B, 3052 and 3051

- EPA 3050B and 3051A
  - Extraction of elements of interest using acids (HNO_3 + HCl)
    - Provides high recovery for most base elements (Cd, Cu, Pb, Zn)
    - Elements bound to silicate matrix and elements of a refractory nature are poorly extracted
- EPA 3052
  - Total digestion of soil matrix using HNO_3 + HCl + **HF**
  - Improvement in the recovery of silicate-bound elements

Confidential & Proprietary | High Purity Standards © 2018

Choosing the Right Method

Factors to Consider:

- Contractual requirements
- Target analytes
- Major physical characteristics of the sample (soil type)
- Number of samples, frequency of digestion
- Availability of equipment, resources and budget
- Skill level of the analyst

Confidential & Proprietary | High Purity Standards © 2018

Equipment Comparison

	HotBlock® (Environmental Express® SC154)	Microwave (Milestone Ethos Up)
Cleaning Method Required	None	Yes
Maximum # of samples	54	15
Lab Requirements	Fume Hood	None
Risk of sample loss	Volatilization Boiling	None
Market Price	~$4,200	~$30,000

Confidential & Proprietary | High Purity Standards © 2018

Method Requirements

Method Number	Special Equipment Required	Reagents
EPA3050B (A)	HotBlock®	HNO_3 H_2O_2 HCl
EPA3051A	Microwave	HNO_3 (HCl)
Total Digestion	Microwave (3052) Hot Plate (In-house)	HNO_3 HF (HCl/H_2O_2) $HClO_4$

Confidential & Proprietary | High Purity Standards © 2018

Methods Comparison

EPA3050B	EPA3051A	EPA3052	Total Digestion (In-house)
Pros		**Pros**	
• Large digestion batches • High recovery for most elements	• Rapid Digestion • Low risk of sample loss • Simple set up & handling • Temperature monitoring	• Good recovery for Si bound elements	• Good recovery for Si bound elements
Cons		**Cons**	
• Higher risk of loss • High risk of contamination • Low recovery for Si bound elements	• Max. of 15 in a batch • Low recovery for Si bound elements	• Higher level of skill • Single acid mixture/quantity per batch	• Higher level of skill • Addition of $HCLO_4$, dangerous • Lengthy digestions

Confidential & Proprietary | High Purity Standards © 2018

Digestion Time Estimates

3051 (Microwave)	3052 (Microwave)	3050B (Hot Block)	Total Digestion (In-house)
3 hours	3 - 8 hours	16 hours	20 hours*

* Does not include additional hours for digestion study

Confidential & Proprietary | High Purity Standards © 2018

Total Digestion/Hot Plate Method

- General Methodology used for National Bureau of Standards (NBS)/NIST soil SRMs
- EPA Methods developed to address a range of material
  - Accuracy of some elements will be compromised
- To meet goal of most complete digestion, process must be tailored for specific sample
  - Digestion Study may be required
  - Minimizing any precipitate will result in more accurate values
    - Volatile elements may be sacrificed
  - Requires experienced chemists
  - Final values accepted as “true”

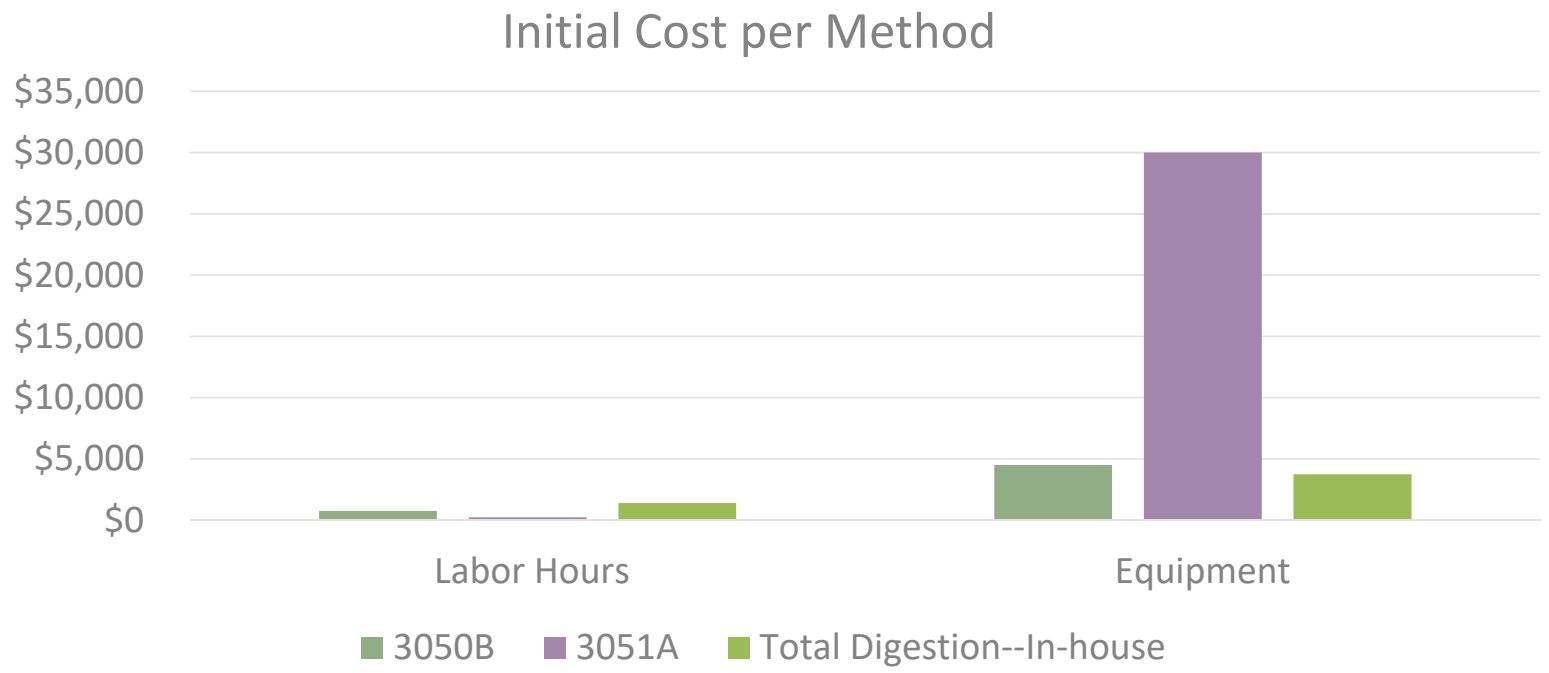
Confidential & Proprietary | High Purity Standards © 2018

Sample Descriptions

Part Number	Description: Major Elements	Digestion Methods
CRM-S-I	Industrial Sludge: Ca, Fe	3050B Total Digestion (In-house)
CRM-S-D	Domestic Sludge: Al, Fe	3050B Total Digestion (In-house)
CRM-LO-B	Loam Soil: Al, Fe	3050A 3050B Total Digestion (In-house)
CRM-MS-S	Marine Sediment: Al, Ca, Fe	3050A 3050B Total Digestion (In-house)

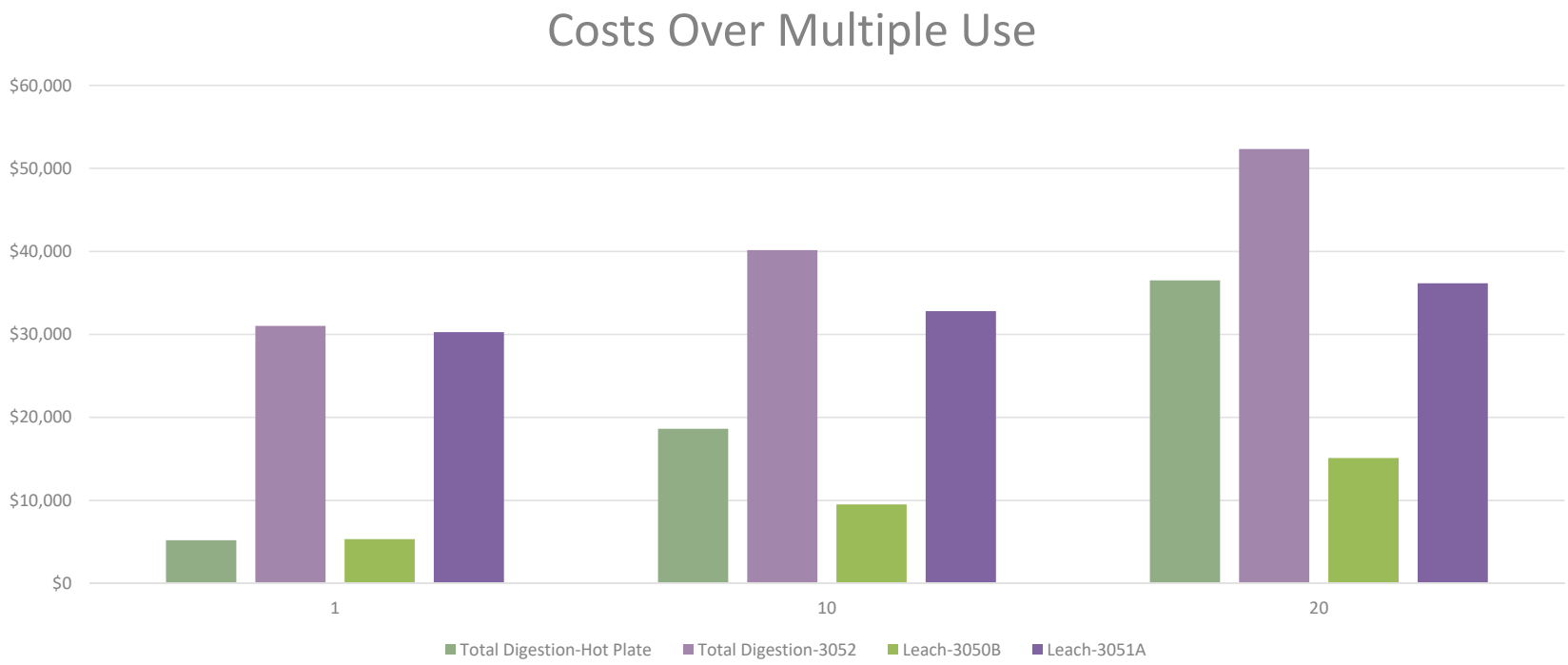
Confidential & Proprietary | High Purity Standards © 2018

Cost Comparison



Confidential & Proprietary | High Purity Standards © 2018

Cost Comparison – Multiple Runs



Confidential & Proprietary | High Purity Standards © 2018

Analyte Recovery Table

Periodic Table of the Elements

Elements Not Analyzed
10 % Comparative Data – All methods
Elements With Varying Results

C	Br	He	Tc
solid	liquid	gas	synthetic

key: element name / atomic number / **symbol** / atomic weight

ydrogen 1 **H** .00794																	helium 2 **He** 4.002602
ithium 3 **Li** 6.941	beryllium 4 **Be** 9.012182											boron 5 **B** 10.811	carbon 6 **C** 12.0107	nitrogen 7 **N** 14.00674	oxygen 8 **O** 15.9994	fluorine 9 **F** 18.9984	neon 10 **Ne** 20.1797
odium 11 **Na** 2.98977	magnesium 12 **Mg** 24.3050											aluminium 13 **Al** 26.981538	silicon 14 **Si** 28.0855	phosphorus 15 **P** 30.97376	sulphur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.984
tassium 19 **K** 9.0983	calcium 20 **Ca** 40.078	scandium 21 **Sc** 44.95591	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.9415	chromium 24 **Cr** 51.9961	manganese 25 **Mn** 54.93805	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.9332	nickel 28 **Ni** 58.6934	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.409	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.64	arsenic 33 **As** 74.9216	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.798
ubidium 37 **Rb** 5.4678	strontium 38 **Sr** 87.62	yttrium 39 **Y** 88.90585	zirconium 40 **Zr** 91.225	niobium 41 **Nb** 92.90638	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.9055	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.8682	cadmium 48 **Cd** 112.411	indium 49 **In** 114.818	tin 50 **Sn** 118.710	antimony 51 **Sb** 121.760	tellurium 52 **Te** 127.60	iodine 53 **I** 126.9045	xenon 54 **Xe** 131.293
aesium 55 **Cs** 2.90545	barium 56 **Ba** 137.327	lutetium 71 **Lu** 174.967	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.9479	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.207	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.217	platinum 78 **Pt** 195.078	gold 79 **Au** 196.96655	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.3833	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.980	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
ancium 87 **Fr** [223]	radium 88 **Ra** [226]	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	darmstadtium 110 **Ds** [271]	roentgenium 111 **Rg** [272]	ununbium 112 **Uub** [285]		ununquadium 114 **Uuq** [289]				

lanthanum 57 **La** 138.9055	cerium 58 **Ce** 140.116	praseodymium 59 **Pr** 140.90765	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.964	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.9253	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.930	erbium 68 **Er** 167.259	thulium 69 **Tm** 168.934	ytterbium 70 **Yb** 173.04
actinium 89 **Ac** [227]	thorium 90 **Th** 232.038	protactinium 91 **Pa** 231.0359	uranium 92 **U** 238.0289	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Confidential & Proprietary | High Purity Standards © 2018

Analyte Recovery Table

Periodic Table of the Elements

Elements Not Analyzed
20% Comparative Data – All Methods
Elements with Varying Results

C	Br	He	Tc
solid	liquid	gas	synthetic

key: element name / atomic number / symbol / atomic weight

ydrogen 1 H .00794																	helium 2 He 4.002602
ithium 3 Li 6.941	beryllium 4 Be 9.012182											boron 5 B 10.811	carbon 6 C 12.0107	nitrogen 7 N 14.00674	oxygen 8 O 15.9994	fluorine 9 F 18.9984	neon 10 Ne 20.1797
odium 11 Na 2.98977	magnesium 12 Mg 24.3050											aluminium 13 Al 26.981538	silicon 14 Si 28.0855	phosphorus 15 P 30.97376	sulphur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.984
tassium 19 K 9.0983	calcium 20 Ca 40.078	scandium 21 Sc 44.95591	titanium 22 Ti 47.867	vanadium 23 V 50.9415	chromium 24 Cr 51.9961	manganese 25 Mn 54.93805	iron 26 Fe 55.845	cobalt 27 Co 58.9332	nickel 28 Ni 58.6934	copper 29 Cu 63.546	zinc 30 Zn 65.409	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.9216	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798
ubidium 37 Rb 5.4678	strontium 38 Sr 87.62	yttrium 39 Y 88.90585	zirconium 40 Zr 91.225	niobium 41 Nb 92.90638	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.9055	palladium 46 Pd 106.42	silver 47 Ag 107.8682	cadmium 48 Cd 112.411	indium 49 In 114.818	tin 50 Sn 118.710	antimony 51 Sb 121.760	tellurium 52 Te 127.60	iodine 53 I 126.9045	xenon 54 Xe 131.293
aesium 55 Cs .90545	barium 56 Ba 137.327	lutetium 71 Lu 174.967	hafnium 72 Hf 178.49	tantalum 73 Ta 180.9479	tungsten 74 W 183.84	rhenium 75 Re 186.207	osmium 76 Os 190.23	iridium 77 Ir 192.217	platinum 78 Pt 195.078	gold 79 Au 196.96655	mercury 80 Hg 200.59	thallium 81 Tl 204.3833	lead 82 Pb 207.2	bismuth 83 Bi 208.980	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
ancium 87 Fr [223]	radium 88 Ra [226]	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]	ununbium 112 Uub [285]		ununquadium 114 Uuq [289]				

lanthanum 57 La 138.9055	cerium 58 Ce 140.116	praseodymium 59 Pr 140.90765	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.964	gadolinium 64 Gd 157.25	terbium 65 Tb 158.9253	dysprosium 66 Dy 162.50	holmium 67 Ho 164.930	erbium 68 Er 167.259	thulium 69 Tm 168.934	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.038	protactinium 91 Pa 231.0359	uranium 92 U 238.0289	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Confidential & Proprietary | High Purity Standards © 2018

Analyte Recovery Table

Periodic Table of the Elements

Elements Not Analyzed
20% Comparative Data – All Methods
Elements with Varying Results
Elements with Significant Variance

C	Br	He	Tc
solid	liquid	gas	synthetic

key: element name / atomic number / symbol / atomic weight

ydrogen 1 H .00794																	helium 2 He 4.002602
ithium 3 Li 6.941	beryllium 4 Be 9.012182											boron 5 B 10.811	carbon 6 C 12.0107	nitrogen 7 N 14.00674	oxygen 8 O 15.9994	fluorine 9 F 18.9984	neon 10 Ne 20.1797
odium 11 Na 2.98977	magnesium 12 Mg 24.3050											aluminium 13 Al 26.981538	silicon 14 Si 28.0855	phosphorus 15 P 30.97376	sulphur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.984
assium 19 K 9.0983	calcium 20 Ca 40.078	scandium 21 Sc 44.95591	titanium 22 Ti 47.867	vanadium 23 V 50.9415	chromium 24 Cr 51.9961	manganese 25 Mn 54.93805	iron 26 Fe 55.845	cobalt 27 Co 58.9332	nickel 28 Ni 58.6934	copper 29 Cu 63.546	zinc 30 Zn 65.409	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.9216	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798
ubidium 37 Rb 5.4678	strontium 38 Sr 87.62	yttrium 39 Y 88.90585	zirconium 40 Zr 91.225	niobium 41 Nb 92.90638	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.9055	palladium 46 Pd 106.42	silver 47 Ag 107.8682	cadmium 48 Cd 112.411	indium 49 In 114.818	tin 50 Sn 118.710	antimony 51 Sb 121.760	tellurium 52 Te 127.60	iodine 53 I 126.9045	xenon 54 Xe 131.293
aesium 55 Cs 2.90545	barium 56 Ba 137.327	lutetium 71 Lu 174.967	hafnium 72 Hf 178.49	tantalum 73 Ta 180.9479	tungsten 74 W 183.84	rhenium 75 Re 186.207	osmium 76 Os 190.23	iridium 77 Ir 192.217	platinum 78 Pt 195.078	gold 79 Au 196.96655	mercury 80 Hg 200.59	thallium 81 Tl 204.3833	lead 82 Pb 207.2	bismuth 83 Bi 208.980	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
ancium 87 Fr [223]	radium 88 Ra [226]	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]	ununbium 112 Uub [285]		ununquadium 114 Uuq [289]				

lanthanum 57 La 138.9055	cerium 58 Ce 140.116	praseodymium 59 Pr 140.90765	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.964	gadolinium 64 Gd 157.25	terbium 65 Tb 158.9253	dysprosium 66 Dy 162.50	holmium 67 Ho 164.930	erbium 68 Er 167.259	thulium 69 Tm 168.934	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.038	protactinium 91 Pa 231.0359	uranium 92 U 238.0289	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

. This table was downloaded from http://www.science-teachers.com/printable_periodic_tables.htm

Confidential & Proprietary | High Purity Standards © 2018

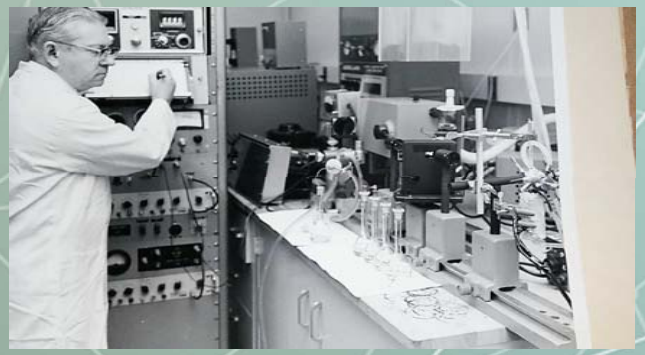
Summary / Conclusions

- **Method 3050B is a Cost-Appropriate Method for Leach Results**
- **Method 3051A maximizes availability of equipment and staff for Leach Results**
- **Equipment and methods may change, but Chemical reactions remain constant**

Confidential & Proprietary | High Purity Standards © 2018

HIGH-PURITY™ STANDARDS

This presentation is the result of decades of research conducted by Dr. Rains, our Founder, from his work at Oak Ridge National Labs, National Bureau of Standards/NIST, and High-Purity Standards



Dr Ted Rains
1925-2017

HIGH-PURITY™ STANDARDS

References

- Shultz, J. I.; Bell, R. K.; Rains, T. C.; Menis, O. Standard Reference Materials: Methods of Analysis of NBS Clay Standards. *Nat. Bur. Stand. (U.S.), Spec. Publ. 260-37* **1972.**
- Epstein, M.S.; Rains, T. C.; Menis, O. Determination of Cadmium and Zinc in Standard Reference Materials by Atomic Fluorescence Spectrometry with Automatic Scatter Correction. *Can. J. Spectrosc.* **1975,** *20,* 22-26
- Mackey, E. A. *et.al.* Certification of Three NIST Renewal Soil Standard Reference Materials for Element Content: SRM 2709a San Joaquin Soil, SRM 2710a Montana Soil I, and SRM 2711a Montana Soil II. Natl. Inst. Stand. Technol. Spec. Publ. *260-172*, **2010.**