



Radiochemical Separations for “Unusual” Sample Matrices

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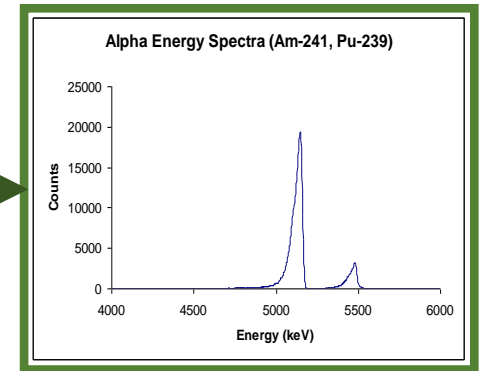
U.S. Transuranium Registry Scientific Advisory Committee Meeting

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Radioanalytical Chemistry



Time & Effort Investment



**Activity:
Total or per
Radionuclide**

➤ Traditional Uses

- Regulatory monitoring
- Environmental restoration and surveillance
- Nuclear materials processing
- Basic science, etc.

Common Sample Matrices

- Sample media analyzed in routine monitoring:
 - Air
 - Water
 - Drinking water
 - Surface water (lakes, rivers)
 - Ocean water
 - Soil
 - Vegetation



Emergency Response Analytics

- Fast identification and quantification of nuclides becomes crucial.
- Rapid and reliable identification of radionuclides is necessary for source attribution.
- A significantly larger number of samples (~30,000) will have to be analyzed.
- A high-confidence level is required for decision making.
- Results will need to meet standards for law enforcement and stand up in court.

Emergency Response Analytics

- Prior to 9/11 the most likely emergency response scenarios were:
 - Nuclear reactor accidents
 - Accidents involving nuclear weapons
 - Transport accidents involving radioactive material
- Radioanalytical emergency response techniques were developed to respond to a “Chernobyl-type” event.



Source: The Atlantic, <http://www.theatlantic.com/infocus/2011/03/the-chernobyl-disaster-25-years-ago/100033/>, retrieved July 2, 2014



Source: Wikipedia, http://en.wikipedia.org/wiki/1966_Palomares_B-52_crash, retrieved July 2, 2014

Emergency Response Analytics

- Post-2001: An inherent paradigm shift occurred
 - New types of “incidents” had to be considered.
 - Source attribution became as important as risk assessment.
 - Both require quick turn-around-time, intermediate phase decision making
- New radioanalytical procedures need to be developed:
 - Methods have to be rapid, reliable and accurate.
 - Techniques have to be able handle high sample throughput.
 - Methods for non-standard matrices are needed.

Challenge: Sample Matrix

- Bioassay, Bone ash
- Urban rubble
 - Molten glass
 - Steel
 - Concrete
 - Asphalt
- Nuclear process streams
- Nuclear waste streams
- ?????



Source: NASA ARS Disaster Assistance & Rescue Team
<http://dart2.arc.nasa.gov/Deployments/NYC-WTC2001/LER049.JPG.html>
Accessed May 24, 2012

Research Goals

- Develop radioanalytical methods for analysis of samples with “unusual matrices”.
 - Rapid and reliable procedures
 - Capable of handling post-detonation samples
- Understand the effects of complex matrices on radiochemical separations.
- Test methods using real-world samples.
- Develop and characterize simulated matrix materials.

Unusual Matrix: Urban Debris

➤ Steel

- Wide range of composition, but defined

➤ Cement

- Defined composition
- Compounds

➤ Concrete

- Cement with aggregate
- Aggregate from local mines

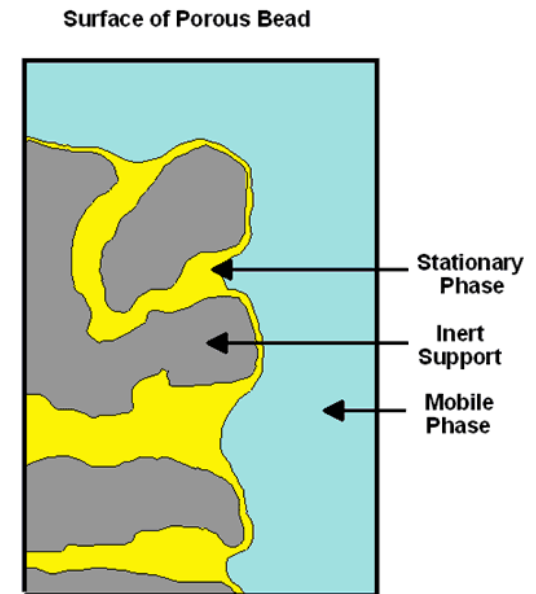
Extraction Chromatography

➤ Extraction Chromatography (EC)

- Mobile phase
 - Diluents and analytes
- Stationary phase
 - Extractant in solvent
 - Inert support
- $k' = \text{FCV to peak maximum}$

$$D_w = \left(\frac{A_0 - A_{aq}}{m_r} \right) \cdot \left(\frac{V_{aq}}{A_{aq}} \right)$$

$$k' = \frac{D_w}{\left(\frac{\text{FCV}}{m_r} \right)}$$

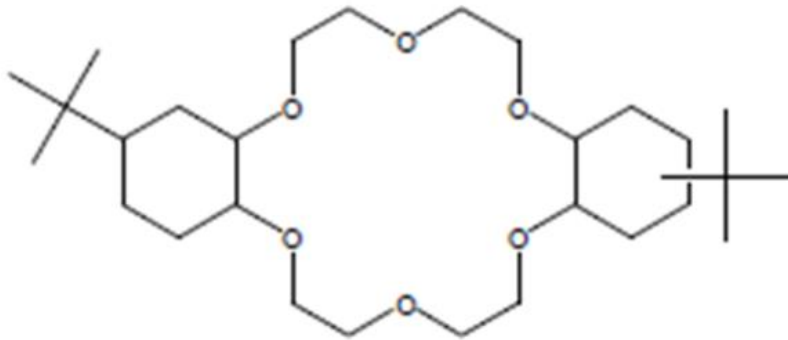


Source: Eichrom Technologies, LLC
<http://www.eichrom.com/products/extraction.aspx>
 Accessed May 24, 2012

Variable	Definition
FCV	Free Column Volume (mL)
D_w	Weight Distribution
V_{aq}	Aqueous Phase Volume (mL)
m_r	Mass Resin (g)
A_{aq}	Final Activity In Aqueous Phase (Bq)
A_0	Initial Activity in Aqueous Phase (Bq)

Strontium Resin

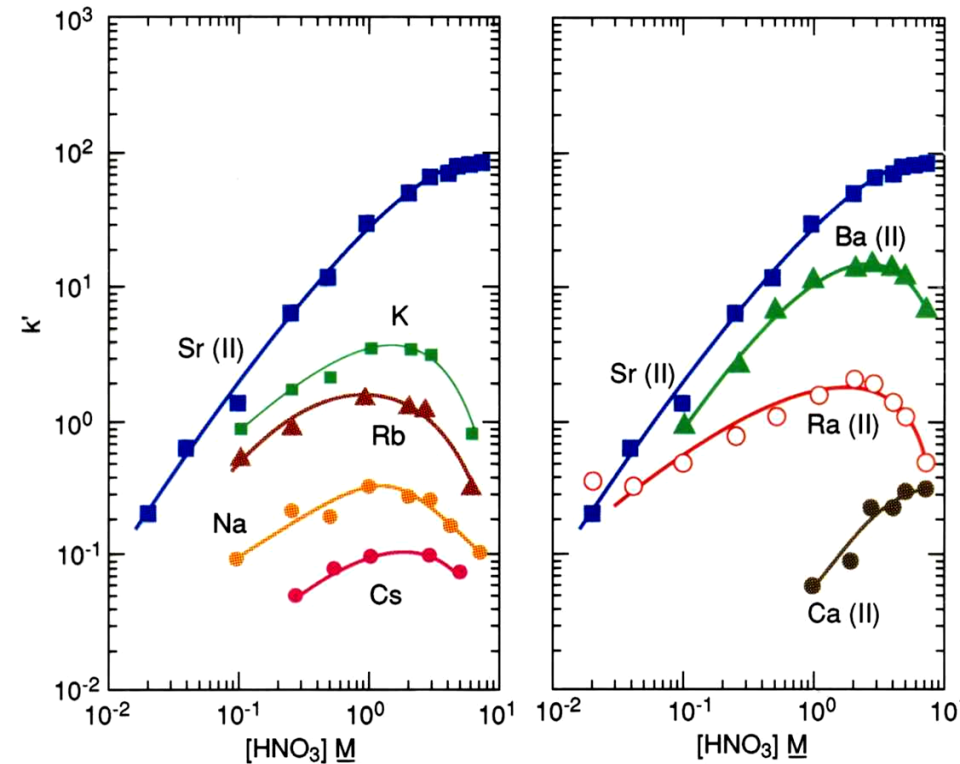
- 4,4', (5')-di-(t-butylcyclohexano)-18-crown-6
 - 1.0M solution in octanol
 - Coated onto polymer beads
 - 40% weight loading



Strontium Resin

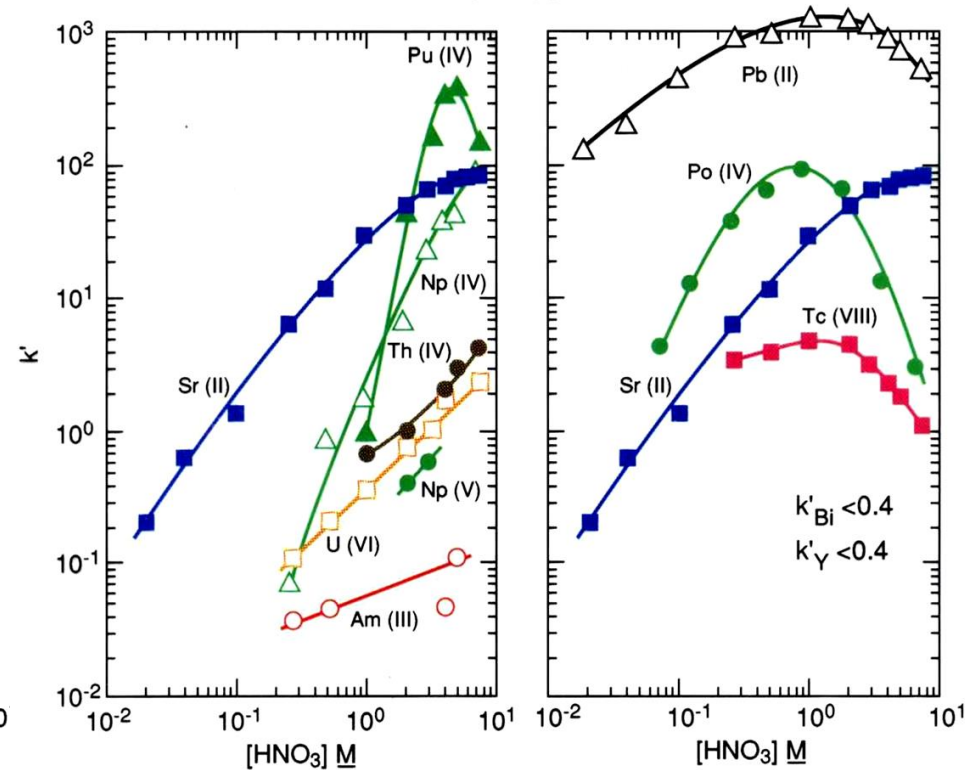
Acid dependency of k' for various ions at 23-25°C.

Sr Resin



Acid dependency of k' for various ions at 23-25°C.

Sr Resin



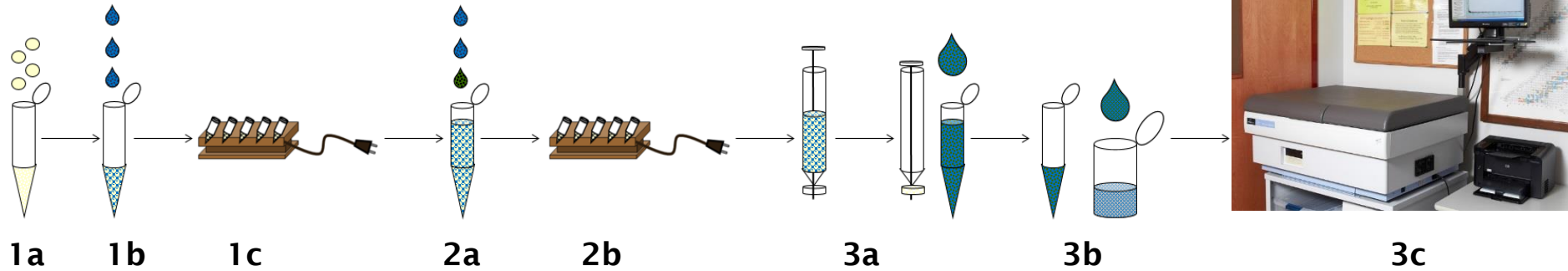
Steel

- Three categories
 - Carbon steel
 - Alloy steel
 - Stainless steel
- Selection
 - Abundance in steel
 - Ionic radius (in pm)

Element	Ionic Radius	Element	Ionic Radius
Ni	69	Co	77
Cr	62	Al	54
Fe	55	Pb	119
Mn	96	Sr	118

Standard Reference Material Components		
Constituent	Carbon Steel % wt. (SRM 14f)	High Tensile Steel % wt. (SRM 361)
Al	0.06	0.021
C	0.753	
Cr	0.07	0.694
Co		0.032
Fe	98.347	96.017
Mn	0.41	0.66
Mo	0.013	0.19
Ni	0.053	2.00
V	0.002	0.011
P	0.009	0.014
Si	0.172	0.222
S	0.039	0.0143
Cu	0.072	0.042

Batch Study Procedure



1. Preconditioning

- 50 mg resin
- 0.50 mL desired acid concentration
- Agitate for 1 hour

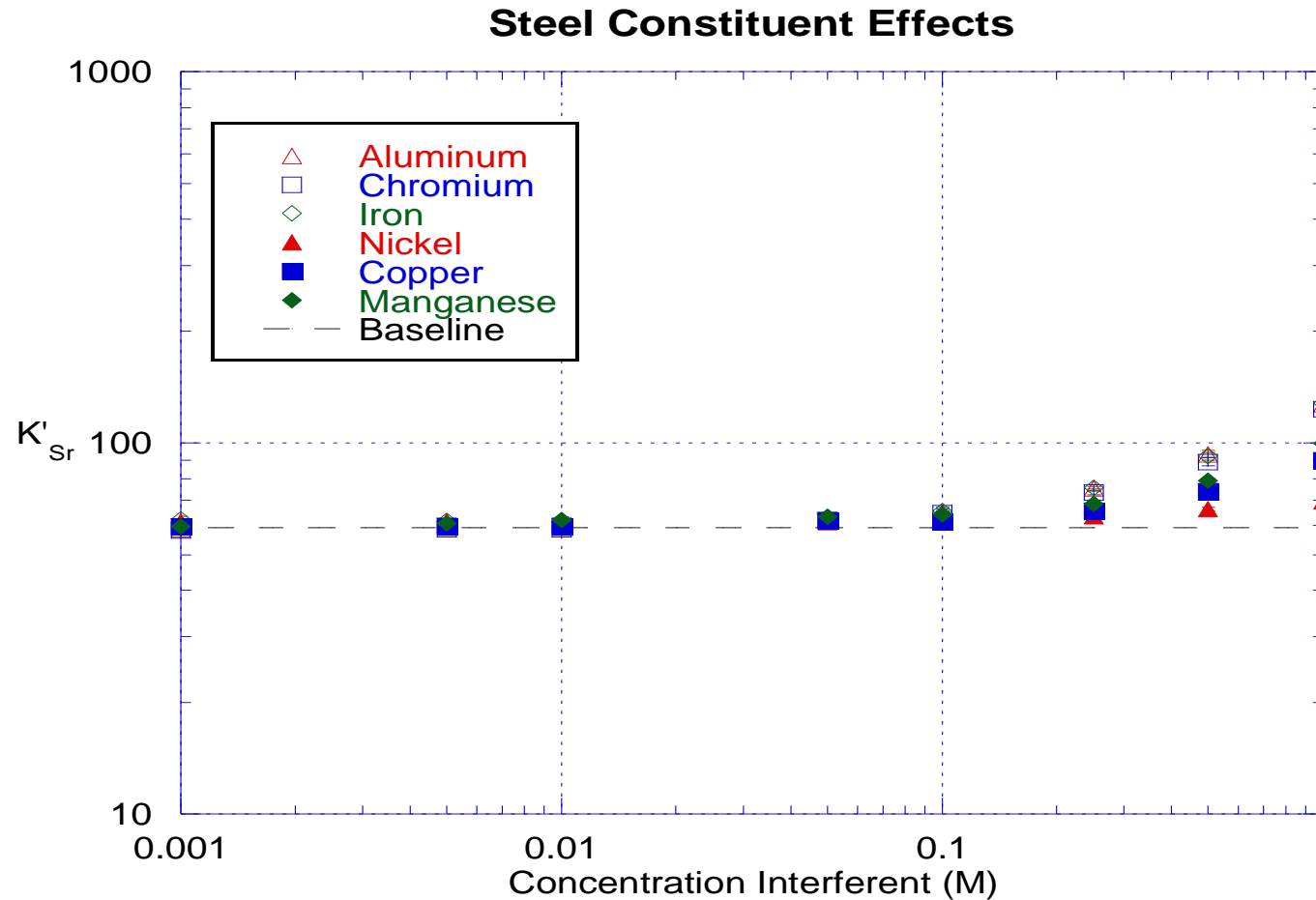
2. Spiking

- 0.50 mL of salt solution
0.50 mL of tracer solution
- Agitate for 1 hour

3. Analysis

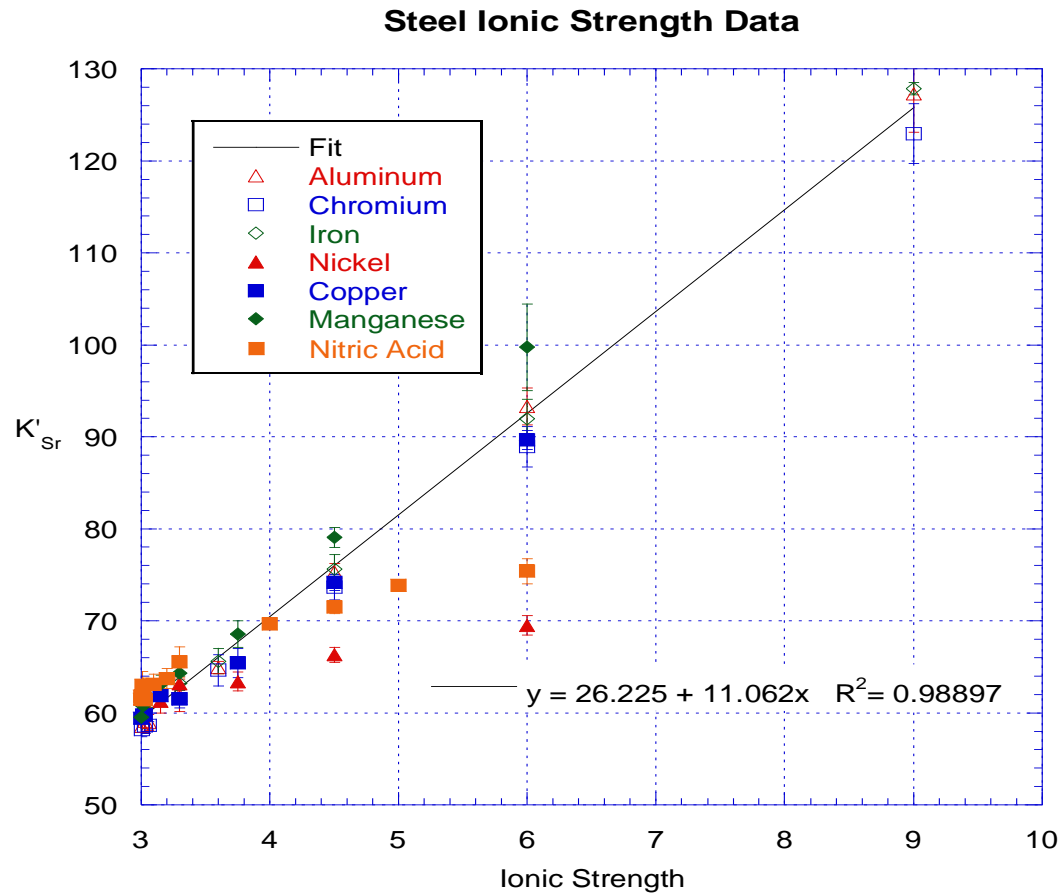
- Filter sample using PTFE syringe filter
- Take aliquot of the filtered eluent for analysis
- Analysis (LSC, Gamma counting, ICP-AES)

Results: Steel Batch Study



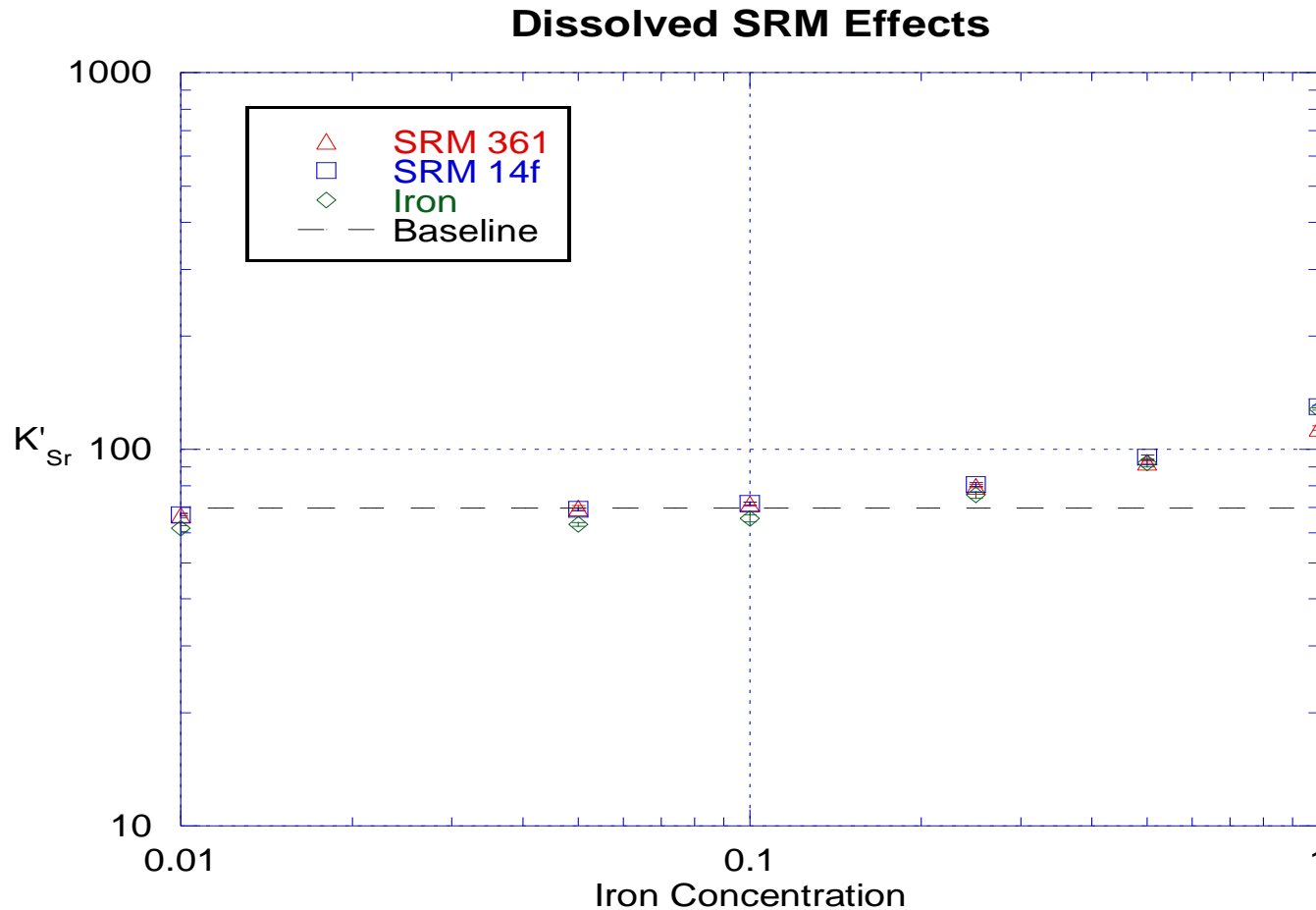
Data represents the mean and standard deviation of five trials

Results: Steel Batch Study



Data represents the mean and standard deviation of five trials

Results: Steel Batch Study



Data represents the mean and standard deviation of five trials

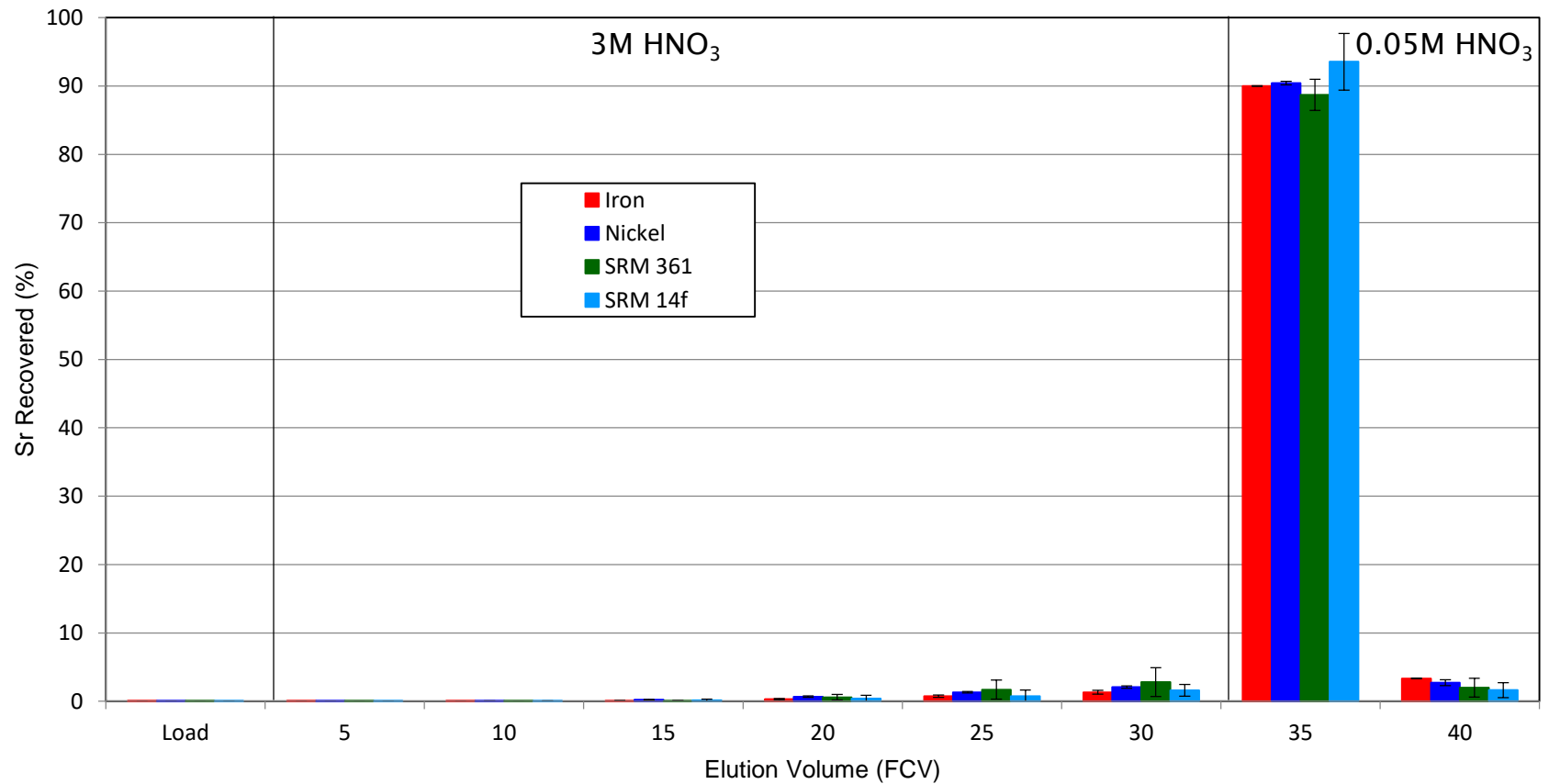
Column Procedure

- Prepacked 2 mL Sr column
- Precondition column:
 - 5 mL of either 3M or 8M HNO₃
- Load column:
 - 600 μL metal salt solution
 - 1M metal in either 3M or 8M HNO₃
 - 600 μL ⁸⁵Sr stock solution
 - 200 Bq/mL in either 3M or 8M HNO₃
- Rinse column:
 - 30 FCV of either 3M or 8M HNO₃
- Rinse column:
 - 10 FCV of 0.05M HNO₃



Results: Steel Column Study

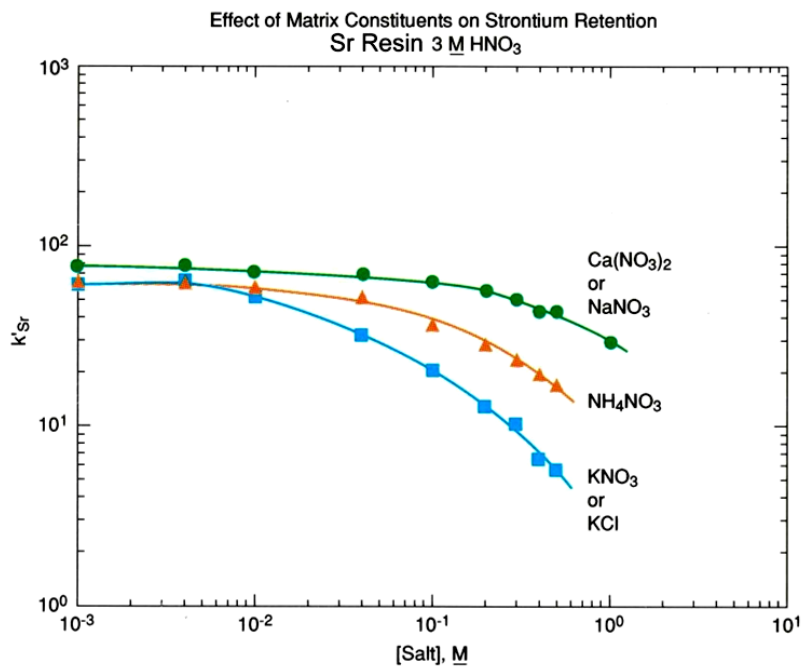
Sr Elution Profiles with Steel Constituents and SRMs



Conclusions: Steel

- Extraction is possible without removing constituents.
 - No constituents have measurable uptake.
 - Sr retention increases with increasing constituent concentrations.
 - Salting out effect

Cement/Concrete



Eichrom Technologies, LLC

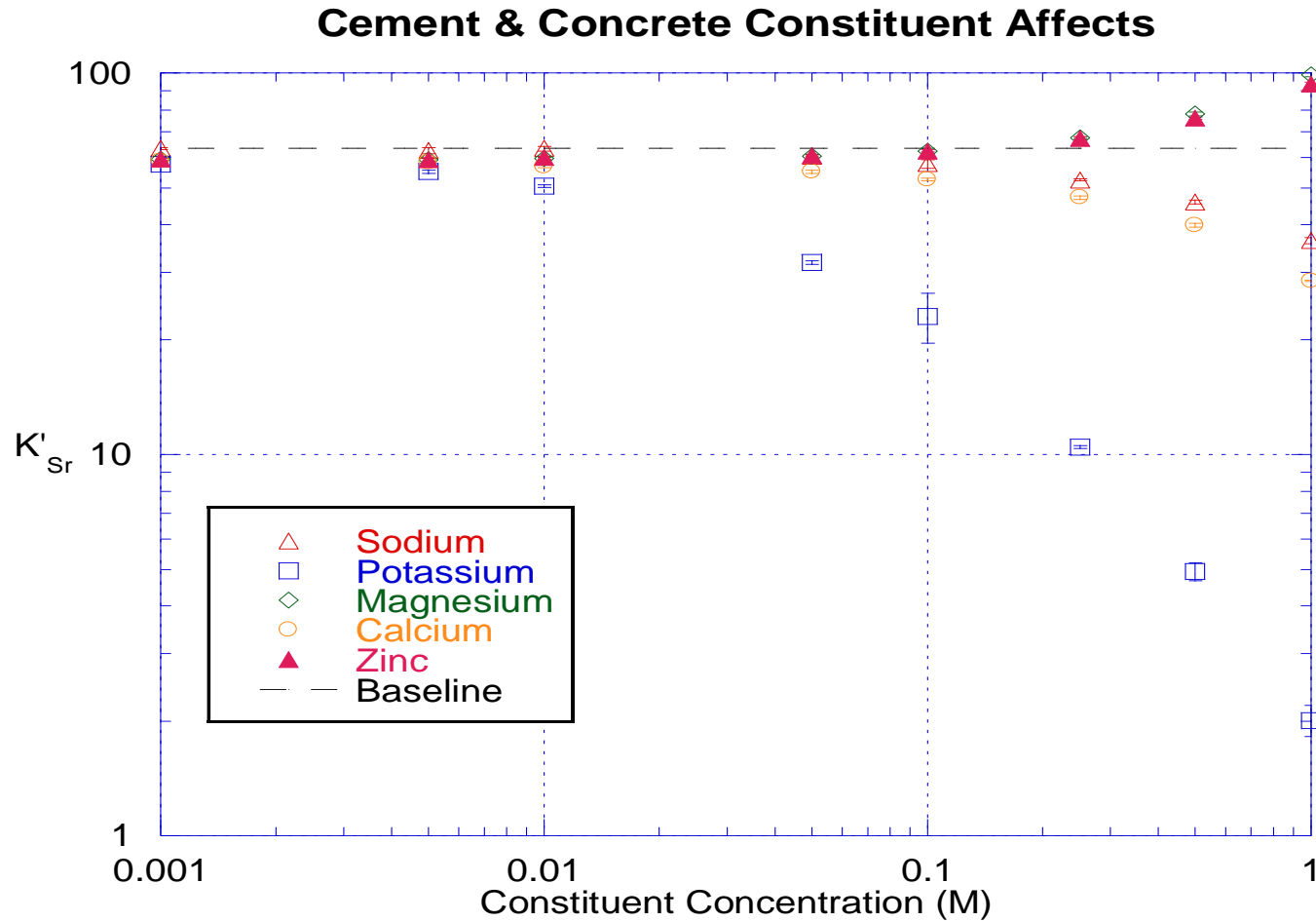
http://www.eichrom.com/products/info/sr_resin.aspx

Accessed June 15, 2017

Standard Reference Material Components

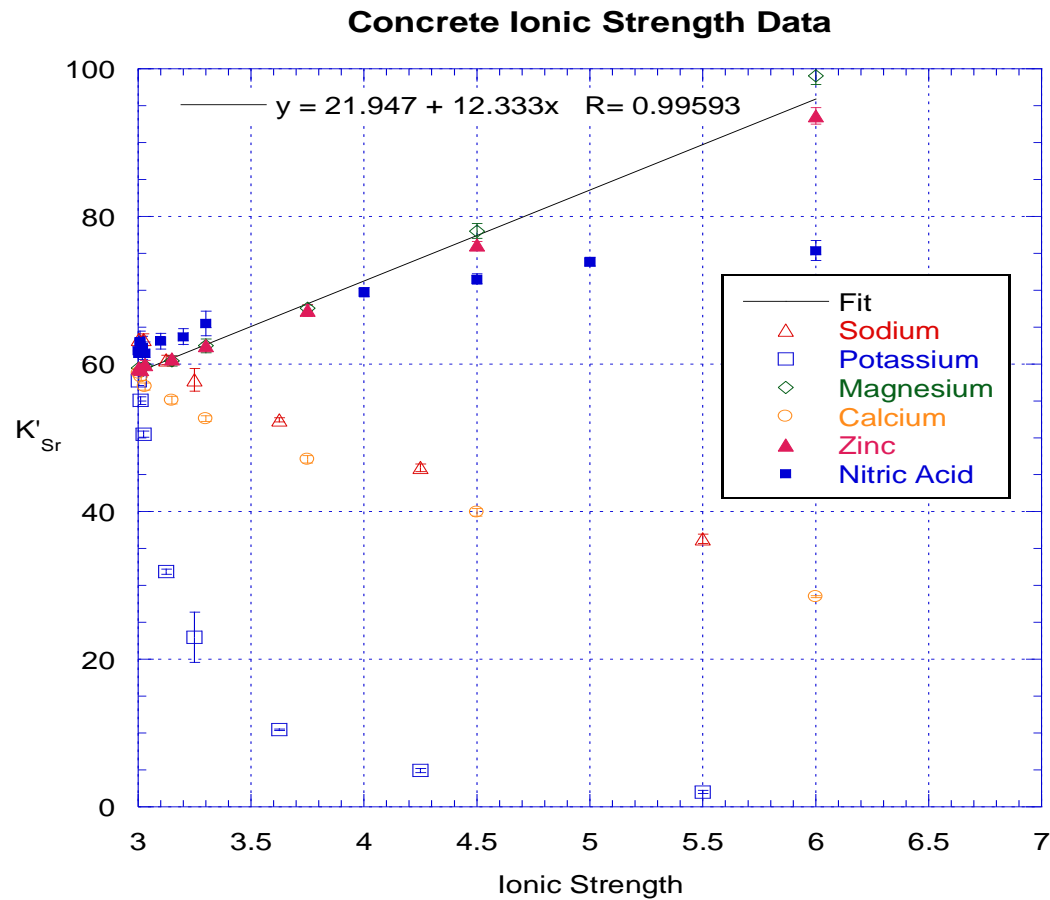
Constituent	Dolomitic Limestone % wt. (SRM 88B)	Portland Cement % wt. (SRM 634)
Al ₂ O ₃	0.336	5.21
CaO	29.95	62.58
CO ₂	46.37	--
Fe ₂ O ₃	0.277	2.84
K ₂ O	0.1030	0.42
MnO*	0.0160	0.13
MgO	21.03	3.30
Na ₂ O	0.0290	0.15
SiO ₂	1.13	20.73
SrO	0.0076	0.12
SO ₂	--	2.21
ZnO	--	0.02

Results: Cement/Concrete Batch Study



Data represents the mean and standard deviation of five trials

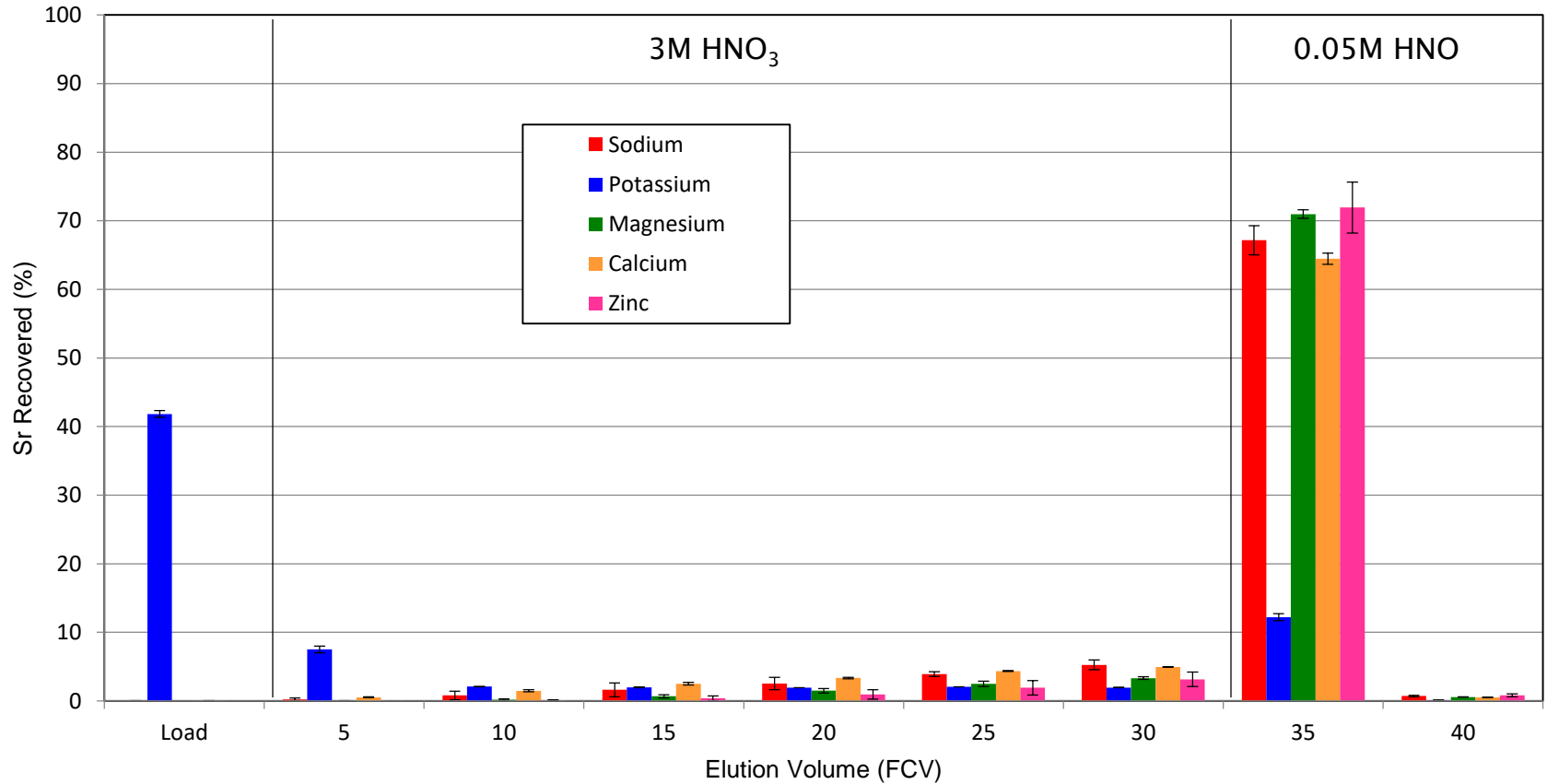
Results: Cement/Concrete Batch Study



Data represents the mean and standard deviation of five trials

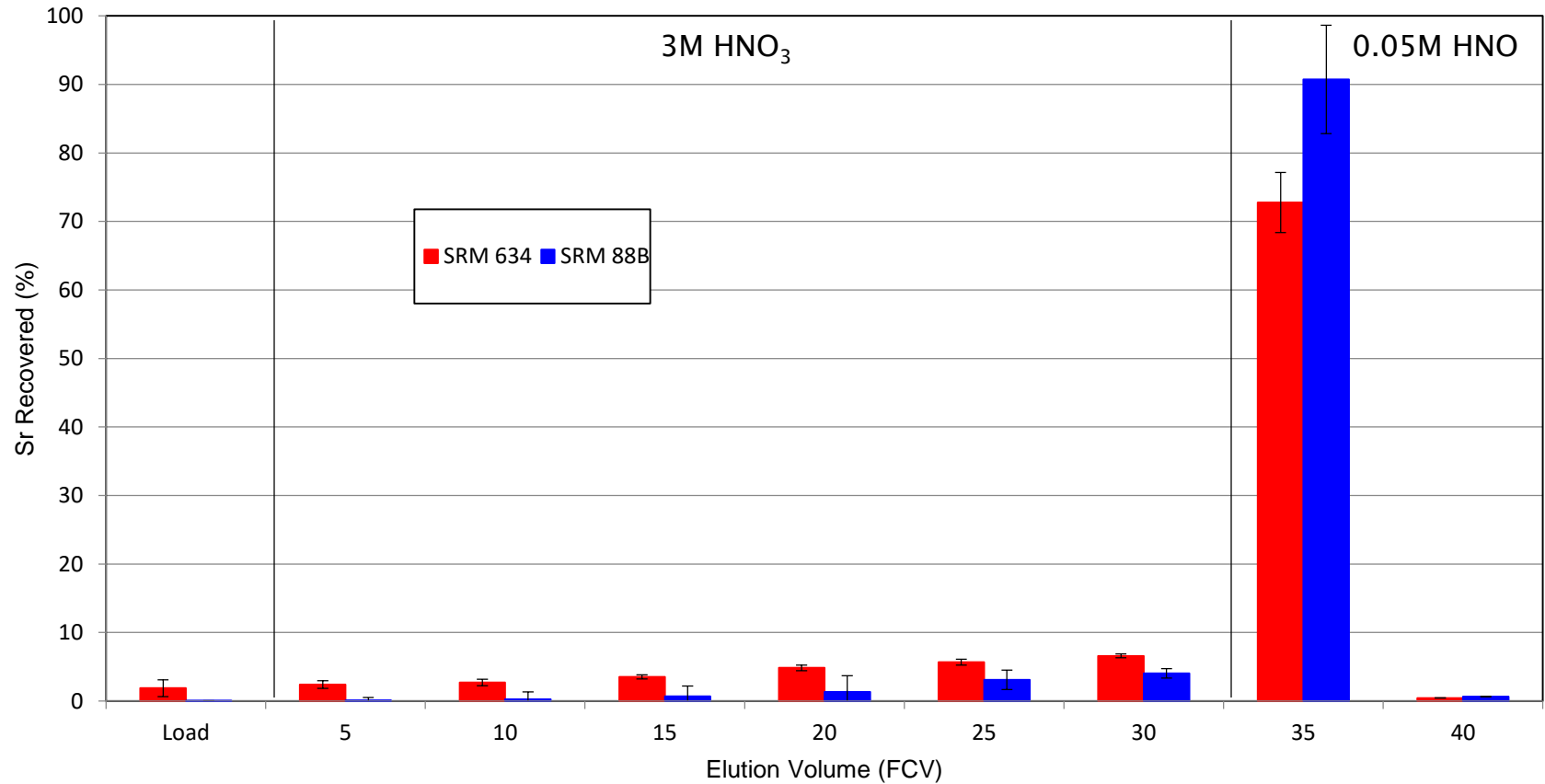
Results: Cement/Concrete Column Study

Sr Elution Profiles with Cement & Concrete Constituents



Results: Cement/Concrete Column Study

Sr Elution Profile with SRM Mixtures



Conclusions: Cement/Concrete

- Some constituents decrease retention:
 - Potassium
 - Calcium
 - Sodium
- Some constituents increase retention:
 - Magnesium
 - Zinc
- SRMs show only little breakthrough
 - SRM 88B shows smaller breakthrough than SRM 634

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