Radiochemistry Webinars
Actinide Chemistry Series
- *Sample Dissolution*

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Meet the Presenter...   *Ralf Sudowe*

Dr. Ralf Sudowe has extensive experience in the areas of nuclear and radiochemistry, particularly in the development of radioanalytical separations for actinide and transactinide elements, as well as fission products. He is currently an Associate Professor of Health Physics and Radiochemistry at the University of Nevada Las Vegas. He received a M.S. degree in Chemistry from the Philipps-University Marburg in Germany in 1995, and a Ph.D. in Nuclear Chemistry from the same institution in 1999. Dr. Sudowe spent two years as Visiting Postdoctoral Fellow in the Nuclear Science Division at Lawrence Berkeley National Laboratory and then worked for five years as Staff Scientist in the Nuclear Science and Chemical Sciences Division at LBNL before joining the faculty at UNLV in 2006. He is a member of the American Chemical Society, the American Nuclear Society, and the Health Physics Society.

At UNLV, Dr. Sudowe teaches courses in radioanalytical chemistry, radiation detection, environmental health physics and radiation biology, as well as laboratory courses in radiochemistry and radiation detection instrumentation. His research focuses on the development and optimization of advanced radioanalytical methods for environmental monitoring, nuclear forensics and safeguards, and emergency response. The goal is to make radioanalytical methods available that have lower detection limits for the radionuclides of interest, facilitate the fast analysis of a large number of samples, and allow assay of unusual sample matrices such as urban rubble and process streams. The research utilizes a variety of modern analytical tools to obtain a better understanding of the fundamental properties of the separation process and to elucidate the role that interfering elements have on the technique. In addition, Dr. Sudowe studies the chemical and nuclear properties of transactinide elements and is involved in target preparation and cross section measurements for stockpile stewardship science.

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Sample Dissolution

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TRAINING AND EDUCATION SUBCOMMITTEE

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- The use of these commercial products and manufacturers for this presentation does not imply a recommendation or endorsement.

Introduction

Sample Dissolution

- In order to dissolve a sample completely, each insoluble component must be converted into a soluble form.

- Several different chemical methods may need to be employed to dissolve a sample completely.

Sample Dissolution

- Initially, the sample may be treated with acids, yielding an insoluble residue.

- The residue may need to be dissolved using fusion or hydrofluoric acid (HF) and then combined with the original mixture or analyzed separately.

Techniques for Sample Dissolution

- Wet Ashing
  - Leaching
  - Acid Digestion
- Fusion
- Microwave Digestion
  - Low-Pressure, Closed-Vessel Systems
  - High-Pressure, Closed-Vessel Systems
  - Focused Open-Vessel Systems
- Sequential Extraction

Addition of Tracers

- The tracer is usually added to the sample at the time of sample dissolution.

- Independent of the means of dissolution, it should be added to the sample during the first step of chemical change.

- This will ensure that the yield for the entire process can be determined accurately.

Acid Digestion

Wet Ashing

- "Wet ashing" and "acid dissolution" utilize hot, concentrated acids for sample decomposition.

- The digestion of geological or ceramic samples can be particularly challenging.

- Many inorganic matrices such as oxides, silicates, nitrides, carbides, and borides can be difficult to dissolve completely.

Wet Ashing

- Different acids are therefore used either alone or in combination to decompose specific compounds that may be present in the sample.

- Almost no single technique can be used to decompose all types of samples completely.

- Many decomposition procedures use wet ashing to dissolve the major portion of the sample.

- A minor fraction is, however, often left behind as residue.

Wet Ashing

- The remaining residue may require additional treatment (by wet ashing or fusion), depending on:
  – The amount of residue
  – Whether it is expected to contain the radionuclides of interest

- The residue should not be discarded until all of the results have been reviewed and determined to be acceptable.

Acids Used for Wet Ashing

Acid	Typical Uses
Hydrofluoric Acid (HF)	Removal of silicon and destruction of silicates; dissolves oxides of Nb, Ta, Ti, and Zr, and Nb, and Ta ores
Hydrochloric Acid (HCl)	Dissolves many carbonates, oxides, hydroxides, phosphates, borates, and sulfides; dissolves cement
Hydrobromic Acid (HBr)	Distillation of bromides (e.g., As, Sb, Sn, Se)
Hydroiodic Acid (HI)	Effective reducing agent; dissolves Sn^{4+} oxide and Hg^{2+} sulfide
Sulfuric Acid (H_2SO_4)	Dissolves oxides, hydroxides, carbonates, and various sulfide ores; hot concentrated acid will oxidize most organic compounds
Phosphoric Acid (H_3PO_4)	Dissolves Al_2O_3, chrome ores, iron oxide ores, and slag
Nitric Acid (HNO_3)	Oxidizes many metals and alloys to soluble nitrates; organic material oxidized slowly
Perchloric Acid ($HClO_4$)	Extremely strong oxidizer; reacts violently or explosively to oxidize organic compounds; attacks nearly all metals

Acid Digestion Methods

Method	Title	Matrix	Goal	Reagents	Summary
EPA 200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements	Water Sludge Sediment Soil	Incomplete Dissolution	HNO_3 HCl	Sample mass: 100 mL • 2 mL conc. HNO_3 + 1 mL conc. HCl are added to the sample. • Sample volume is reduced to 20 mL by heating to 85 °C. • Sample is then refluxed in a beaker for 30 min. • Sample is then either centrifuged or allowed to settle overnight.
EPA 3050A	Acid Digestion of Sediments, Sludges, and Soils	Sediment Sludge Soil Oil	Incomplete Dissolution	HNO_3 H_2O_2	Sample mass: 1 g • 10 mL 1:1 HNO_3 is added to the sample • Sample is refluxed at 85 °C for 10-15 min. • 5 mL conc. HNO_3 is added to the sample • Sample is refluxed at 85 °C for 30 min. • 2 mL of water and 3 mL of 30% H_2O_2 are added to the sample. • Sample is heated and additional 30% H_2O_2 is added (1 mL portions). • Sample volume is reduced to 5 mL.

Acid Digestion Bombs

- Some materials that cannot be totally dissolved by acid digestion in an open vessel on a hotplate, can be completely dissolved in an acid digestion bomb.

- These pressure vessels hold strong mineral acids or alkalis at temperatures well above normal boiling points.

- This enables complete digestion or dissolution of samples that would react slowly or incompletely at atmospheric pressure.
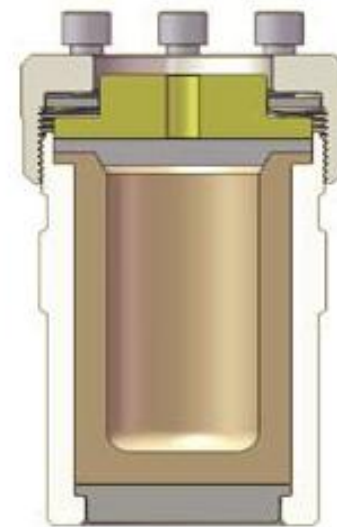
Acid Digestion Bombs

- The use of a digestion bomb prevents the loss of volatile elements during digestion.

- Ores, rock samples, glass and other inorganic samples can be dissolved quickly using strong mineral acids such as:
    - HF
    - HCl
    - H_2SO_4
    - HNO_3
    - Aqua regia (HCl/HNO_3 3:1)

Acid Digestion Bombs

- The sealed pressure vessels are typically lined with Teflon.

- This provides resistance to attack by HF.

- It also prevents cross-contamination between samples.

Acid Digestion Bombs

Source: PARR Instrument Company, http://www.parrinst.com/products/sample-preparation/acid-digestion/
        Retrieved December 6, 2012

Acid Digestion Bombs

- The digestion bomb should never be completely filled.

- Adequate space needs to always be reserved above the contents for vapors generated.

- When working with inorganic materials, the total volume of sample plus reagents should never exceed 2/3 of the capacity of the bomb.

Acid Digestion Bombs

- Acid digestion bombs can also be used to treat many organic materials satisfactorily.

- However, critical attention must be given to the nature of the sample as well as to possible explosive reactions with the digestion media.

Acid Leaching vs. Total Digestion

- Mineral acids are often not able to completely dissolve all components of a given sample.

- In comparison, other techniques such as fusion can result in complete dissolution of the sample.

- The validity of results obtained by acid leaching compared to values acquired after total dissolution is therefore under constant debate.

- It is important to be aware of the limitations of both methods.

Acid Leaching vs. Total Digestion

"In many cases, the mono-, di-, and small tervalent elements can be leached fairly completely from simple solids by boiling with concentrated hydrochloric or nitric acids. However, even these elements cannot necessarily be guaranteed to be dissolved completely by selective leaching. If they are included in a refractory matrix, they will not be removed completely without dissolution of the matrix. If the samples have been exposed to water over long periods of time, such as with sediments in a radioactive waste pond, small ions such as divalent cobalt will have diffused deeply into the rock lattice from which they cannot be removed without complete dissolution of the host matrix. In contrast, because of its large size, ionic cesium has a marked tendency to undergo isomorphous replacement in the lattice of complex silicates from which it too cannot be removed completely."

Source: Sill, C.W., Sill, D.S., *Sample Dissolution*, Radioactivity and Radiochemistry **6**, 8 (1995)

Acid Leaching vs. Total Digestion

- Mineral acids have proven to be effective leaching solvents for metals, oxides, and salts in many samples.

- Leaching typically requires fewer chemicals and less time to accomplish than complete sample dissolution.

- Acid leaching allows processing of multiple samples simultaneously using a hotplate or microwave system.

Acid Leaching vs. Total Digestion

- Excess reagents can be removed through evaporation.

- Complete dissolution of a sample is not necessary if it can be shown that the nuclide of interest is completely leached from the sample.

Fusion Digestion

Fusion Techniques

- Sample decomposition through fusion is often used for samples that are difficult to dissolve in acids.

- These types of samples include:
    - Soils
    - Sludges
    - Silicates
    - Some metal oxides

Fusion Techniques

- The mixture is heated to a temperature above the melting point of the salt.

- The sample is then allowed to react in the molten mixture.

- When the reaction is completed, the mixture is allowed to cool to room temperature.

- The fused sample is then dissolved, and the analysis is continued.

Fusion Techniques

- Any residue remaining may be treated by:
  - Repeating the fusion with the same salt
  - Performing a fusion with a different salt
  - Acid treatment
  - Any combination of the three

Fusion Techniques

- Decomposition of the sample matrix depends on the high temperatures required to melt a flux salt and the ratio of the flux salt to the sample.

- For a fusion to be successful, the sample must contain chemically bound oxygen as in oxides, carbonates, and silicates.

- Samples that contain no chemically bound oxygen, such as sulfides, metals, and organics, must be oxidized before the fusion process.

Fusion Techniques

- Samples to be fused should be oven-dried to remove moisture.

- Samples with significant amounts of organic material are typically dry ashed or wet ashed before fusion.

- Solid samples are typically ground to increase the surface area.

- This allows the fusion process to proceed more readily.

Fusion Techniques

- The sample must be mixed thoroughly with the flux in an appropriate ratio.

- The crucible used should never be more than half-filled at the outset of the fusion process.

Fusion Techniques

- Fusions may be performed using sand or oil baths on a hot plate, in a muffle furnace, or over a burner.

- Platinum, zirconium, nickel, or porcelain are used as material for the crucibles.

- The choice of heat source and crucible material generally depends on the salt used for the fusion.

Fusion Techniques

Source: Claisse, http://www.claisse.com/fusion-apparatus-m4-fluxer.php
         Retrieved December 6, 2012

Heating

- During fusion, samples are heated slowly and evenly to prevent ignition of the sample before the reaction with the molten salt can begin.

- It is especially important to raise the temperature slowly when using a gas flame.

- The evolution of water and gases is a common occurrence at the beginning of the fusion.

- This can lead to spattering and sample loss.

- The crucible can be covered with a lid as an added precaution.

Heat Sources

Source	Advantages	Disadvantages
Sand/oil bath	• Most even source of heat • Readily available	• Difficult to maintain at high temperatures
Gas burner	• Convenient heat source • Readily available	• Difficult to heat the sample evenly
Muffle furnace	• Even source of heat	• Difficult to monitor progress of the reaction • Impossible to work with the sample during digestion

Heating

- The maximum temperature employed can vary and depends on the sample and the flux.

- Excessive temperatures should be avoided to prevent decomposition of the flux and to minimize attack of the crucible.

- Once the salt has melted, the melt is swirled gently to monitor the reaction.

- The fusion is continued until visible signs of reaction, such as formation of gases, foaming, fumes, are completed.

Heating

- It is often difficult to decide when exactly the heating should be stopped.

- In ideal cases, the flux will have turned into a clear melt.

- This indicates complete sample decomposition.

- In other cases, it is not as obvious, and the analyst must base the heating time on past experience.

Cooling

- The melt sometimes is swirled during cooling to spread it over the inside of the crucible.

- Thin layers of salt on the sides of the crucible often will crack and flake into small pieces during cooling.

- These small fragments are easier to remove and dissolve.

Dissolution

- After the sample has returned to room temperature, the fused material is dissolved.

- Usually warm water or a dilute acid solution is used as solvent, depending on the salt.

Dissolution

- The aqueous solution from the dissolution of the melt should be examined carefully for particles of undissolved sample.

- If undissolved particles are present, they need to be separated from the solution by centrifugation or filtration.

- In some cases, a second fusion needs to be performed.

Crucibles

- Several types of materials are used for crucibles.

- The most common ones are:
    - Platinum
    - Graphite
    - Nickel
    - Zirconium
    - Silver

Crucible Materials

Source	Advantages	Disadvantages
Graphite	• Cost effective • Disposable • No cross contamination • Chemically inert • Heat resistant	• Oxidize slowly at temperatures above 430 °C • Not recommended for lengthy fusion reactions • Not recommended for reactions where the sample may be reduced
Platinum	• Expensive • Chemically inert	• Attacked by concentrated phosphoric acid & sodium carbonate • Dissolves readily in Aqua Regia • Sodium peroxide, free elements (C, P, S, Ag, Bi, Cu, Pb, Zn, Se, and Te), ammonium, chlorine and volatile chlorides, sulfur dioxide, and gases with carbon content should be avoided.

Fluxes

- Many kinds of salts are used in fusions.

- The lowest melting flux capable of reacting completely with the sample is usually the optimum choice.

- Basic fluxes, such as the carbonates, the hydroxides, and the borates, are used to attack acidic materials.

Fluxes

- Sodium or potassium nitrate should be added to furnish an oxidizing agent when needed.

- This is the case for sulfides, certain oxides, ferroalloys, and some silicate materials.

Fluxes

- The most effective alkaline oxidizing flux is sodium peroxide.

- It is both a strong base and a powerful oxidizing agent.

- Because it is such a strong alkali, sodium peroxide is often used even when no oxidant is required.

- Alternatively, acid fluxes are the pyrosulfates, the acid fluorides, and boric acids.

Common Fusion Fluxes

Flux (mp, °C)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
$Na_2S_2O_7$ (403°) $K_2S_2O_7$ (419°)	Up to red heat	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples, particularly those of Al, Be, Ta, Ti, Zr, Pu, and the rare earths.
NaOH (321°) KOH (404°)	450-600°	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides.
Na_2CO_3 (853°) K_2CO_3 (903°)	900-1,000°	Ni, Pt for short periods (use lid)	For silicates and silica-containing samples (clays, minerals, rocks, glasses), refractory oxides, quartz, and insoluble phosphates and sulfates.
Na_2O_2	600°	Ni; Ag, Au, Zr; Pt (<500 °C)	For sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals.
H_3BO_3	250°	Pt	For analysis of sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels.
$Na_2B_4O_7$ (878°)	1,000-1,200°	Pt	For Al_2O_3; ZrO_2 and zirconium ores, minerals of the rare earths, Ti, Nb, and Ta, aluminum-containing materials; iron ores and slags.
$Li_2B_4O_7$ (920°) $LiBO_2$ (845°)	1,000-1,100°	Pt, graphite	For almost anything except metals and sulfides. The tetraborate salt is especially good for basic oxides and some resistant silicates. The metaborate is better suited for dissolving acidic oxides such as silica and TiO_2 and nearly all minerals.
NH_4HF_2 (125°) NaF (992°) KF (857°) KHF_2 (239°)	900°	Pt	For the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of Nb, Ta, Ti, and Zr.

Disadvantages

- Fusions are frequently more labor intensive than the leaching approach.

- Large quantities of the flux are generally required to decompose most substances, often 5 to 10 times the sample weight.

- Therefore, contamination of the sample by impurities in the reagent is quite possible.

Disadvantages

- Aqueous solutions resulting from the fusions will have a very high salt content.

- This may lead to difficulties in subsequent steps of the analysis.

- The high temperatures during the fusion process can cause loss of analytes by volatilization.

- In addition, the crucible itself may be attacked by the flux.

- This can also introduce possible contamination.

Microwave Digestion

Microwave Digestion

- Microwave energy as a heat source for sample digestion was first described in 1975.

- It is considered faster, cleaner, more reproducible, and more accurate than hot-plate digestion.

- However, until recently, this technology has had limited application in radioanalytical chemistry due to constraints on sample size.

- This restriction resulted from vessel pressure limitations.

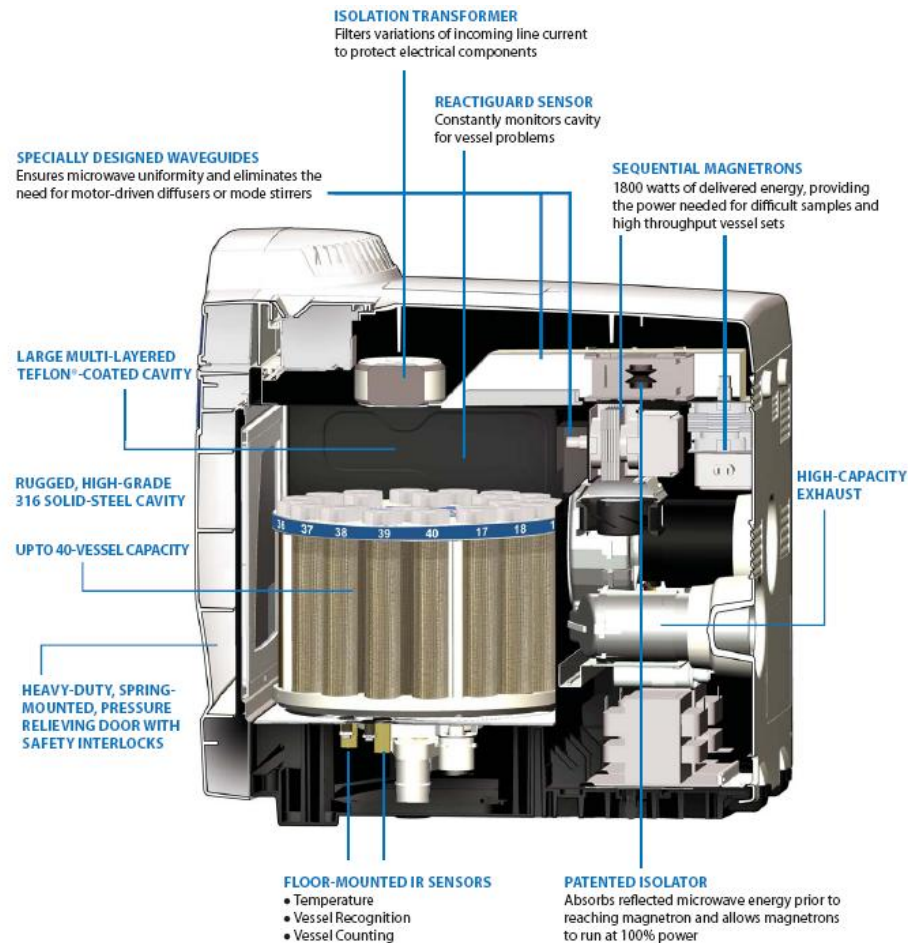# Microwave Digestion

- Microwave dissolution was not practical for procedures where larger sample sizes were necessary to meet required detection limits.

- However, recent advances in vessel design, as well as improved detection methods (e.g., ICP-MS) have eliminated this disadvantage.

- Microwave dissolution is now considered an important radiochemical tool.

Closed-Vessel Digestion Systems

Closed-Vessel Digestion Systems

ISOLATION TRANSFORMER
Filters variations of incoming line current
to protect electrical components

REACTIGUARD SENSOR
Constantly monitors cavity
for vessel problems

SPECIALLY DESIGNED WAVEGUIDES
Ensures microwave uniformity and eliminates the
need for motor-driven diffusers or mode stirrers

SEQUENTIAL MAGNETRONS
1800 watts of delivered energy, providing
the power needed for difficult samples and
high throughput vessel sets

**LARGE MULTI-LAYERED
TEFLON®-COATED CAVITY**

**RUGGED, HIGH-GRADE
316 SOLID-STEEL CAVITY**

UP TO 40-VESSEL CAPACITY

**HIGH-CAPACITY
EXHAUST**

**HEAVY-DUTY, SPRING-
MOUNTED, PRESSURE
RELIEVING DOOR WITH
SAFETY INTERLOCKS**

FLOOR-MOUNTED IR SENSORS
• Temperature
• Vessel Recognition
• Vessel Counting

PATENTED ISOLATOR
Absorbs reflected microwave energy prior to
reaching magnetron and allows magnetrons
to run at 100% power

Source: CEM Corporation, http://cem.com/mars6.html, retrieved December 6, 2012

Pressure & Temperature Control

Direct Fiber Optic Temperature Sensor of the Reference Vessel

The fiber optic temperature probe is the gold standard in temperature measurement. Unlike metal thermocouples, which can self-heat in the microwave and give imprecise readings, CEM's fiber optic temperature probe provides accurate measurement every time. An optional NIST-traceable fiber optic temperature probe is also available.

**Single Vessel Reference Pressure Sensor**

Accurate and simple to use, the ESP-1500 Plus is a simple pop-in device that can be immediately removed from the cavity after the run for fast processing of multiple vessel racks. It measures and controls pressure up to 1500 psi.

Contactless Pressure Sensor

CEM's UPS Sensor provides pressure control for every vessel by monitoring the exhaust system. This controller is not limited to NO_x fumes, but can identify small quantities of all acid vapors. It will automatically reduce power or turn off the magnetron based upon the concentration of gas in the cavity.

Contactless All-Vessel Temperature Sensors

The MARS 6 features patented, NIST-traceable, calibrated, dual IR sensors with the shortest path length to the vessel, ensuring more accurate readings and better control than systems with side-mounted IR sensors.

Source: CEM Corporation, http://cem.com/mars6.html, retrieved December 6, 2012
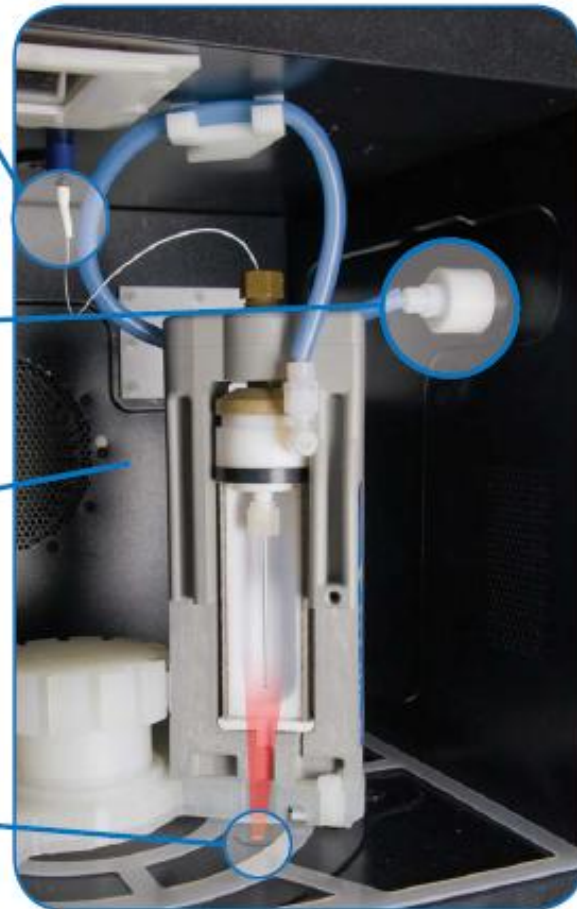
Low-Pressure Closed-Vessel Systems

- These systems consist of a microwave oven equipped with a turntable, a rotor to hold the sample vessels, and a pressure-control module.

- The PFA vessels used with these systems are limited to approximately 225 °C.

- Therefore, only low-boiling reagents or mixtures of reagents should be used.

- Waste is minimized in these systems because smaller quantities of acid are required.

Low-Pressure Closed-Vessel Systems

- Very little or no acid is lost during the digestion.

- This often means that additional portions of acid are not required.

- In addition, typical blank values are minimized.

Low-Pressure Closed-Vessel Systems

- However, the sealed vessels are typically limited to 100 to 300 psi (689 to 2,068 kPa).

- This limits the size of organic samples that can be used.

- Inorganic materials such as water and most soils and sediments can, however, easily be digested.

- Typical sample sizes are:
  - 0.5 g for solids
  - 45 mL for aqueous samples

Low-Pressure Closed-Vessel Systems

- Vessel pressure is monitored to regulate the digestion cycle.

- The pressure is kept constant at different levels for specified time periods.

- This allows complete dissolution and precise recoveries in a minimum amount of time.

- As the samples are irradiated, temperatures in the vessels rise, thereby increasing the pressure.

Low-Pressure Closed-Vessel Systems

- The pressure transducer will cycle the magnetron to maintain sufficient heat to hold the samples at the programmed pressure level for a preset dwell time.

- The vessels are designed to vent safely in case of excessive internal pressure.

High-Pressure Closed-Vessel Systems

- Recent advances in vessel design have produced microwave vessels capable of withstanding pressures on the order of 1,500 psi (10 MPa).

- These vessels can be utilized for larger sample sizes.

- Samples sizes of 1 to 2 g for soil or 0.5 to 3 g for vegetation can be digested safely.

- This increase in sample size results in lower detection limits.

High-Pressure Closed-Vessel Systems

- High-pressure vessels can also be used to digest organic and inorganic substances, such as coals, heavy oils, refractories, and ceramic oxides.

Closed-Vessel Digestion Rotors

SK-10 High Pressure Rotor
Max. temp.: 300°C, Max. press.: 100 bar

Q-20 Quartz Rotor
Ultratrace analysis, high sample throughput
Max. temp.: 250°C, Max. press.: 40 bar

PRO-16 Medium Pressure Rotors
High sample throughput
Max. temp.: 260°C, Max. press.: 30 bar

NOVA-8 High Temperature Rotor
Max. temp.: 300°C, Max. press.: 100 bar

Source: Milestone Inc., http://milestonesci.com/index.php/product-menu/digestion/ethos-ez/vessels-a-rotors/closed-vessel.html
Retrieved December 6, 2012

Focused Open-Vessel Systems

- A focused open-vessel system has no oven.

- Instead, it consists of:
  - A magnetron to generate microwaves
  - A waveguide to direct and focus the microwaves
  - A cavity to contain the sample

- Because of the open-vessel design, pressure does not build up during processing.

- In addition, the system allows for the addition of reagents during the digestion cycle.

Focused Open-Vessel Systems

- These systems are quite universal.

- A number of different reagents and various types of vessel can be used.

- Available vessels include:
  - Glass
  - Quartz
  - Perfluoroalcoholoxil [PFA]

# Focused Open-Vessel Systems

- The waveguide ensures that energy is directed only at the portion of the vessel that lies in the path of the focused microwaves.

- The neck of the vessel and the attached refluxer remain cool.

- Vapors are trapped in the refluxer, condensed and returned to the solution.

- This ensures that even volatile elements such as selenium or mercury are kept in the system.

Focused Open-Vessel Systems

- The focused microwaves cause solutions to reach temperatures quicker compared to conventional hotplates or block-type digesters.

- This method also improves the reproducibility of the heating process.

- An aspirator removes excess acid vapors and decomposition gases.

- Depending on the system, up to 20 g of solids or 50 to 100 mL of liquids can be digested within 10 to 30 minutes on average.

Focused Open-Vessel Systems

Source: CEM Corporation, http://www.cem.com/star-technology.html
Retrieved December 6, 2012
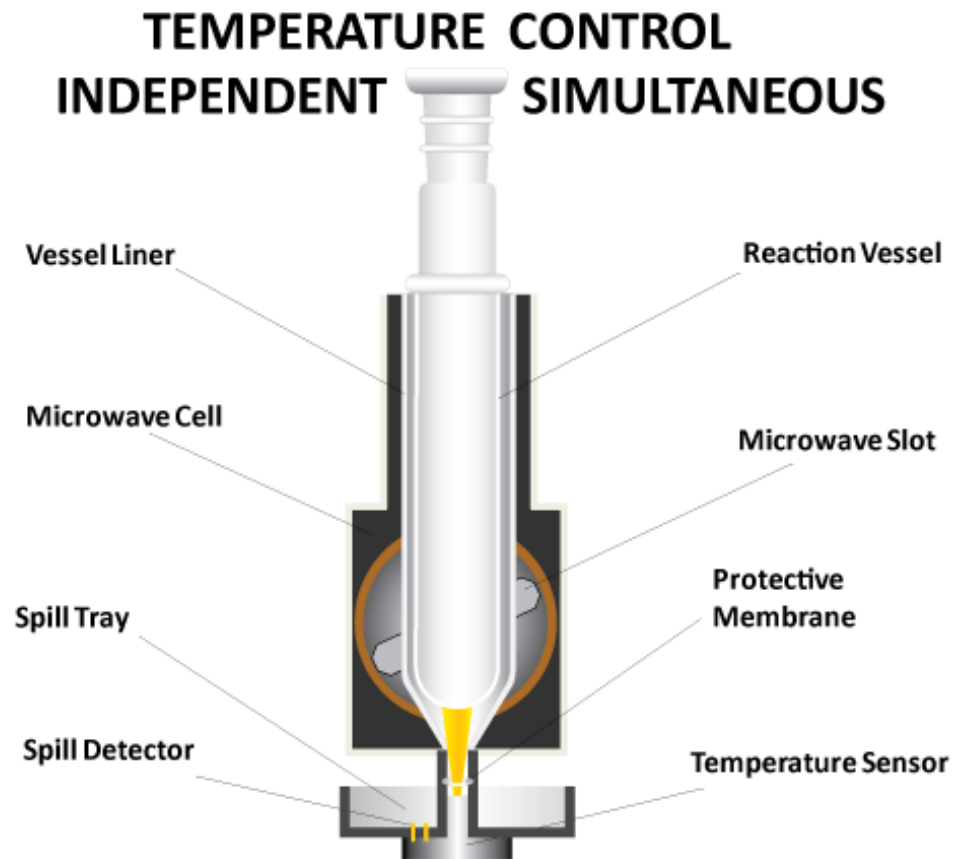
Digestion Methods

Method	Title	Matrix	Goal	Reagents	Summary
EPA 3015A	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	Water	Incomplete Dissolution	HNO_3, HCl	Sample mass: 45 mL Temperature: 170 °C Ramp time: 10 min Holding time: 10 min
EPA 3051A	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils	Sediments Sludges Soils Oil	Incomplete Dissolution	HNO_3, HCl	Sample mass: 0.5 g Temperature: 175 °C Ramp time: 5.5 min Holding time: 4.5min
EPA 3052A	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices	Siliceous, organic and other complex matrices	Complete Dissolution	HCl, HF, HNO_3	Sample mass: 0.5 g Temperature: 180 °C Ramp time: 5.5 min Holding time: 9.5min

Reagent Selection for EPA 3052A

Matrix	HNO$_3$	HF	HCl
NIST SRM 2710 -Highly Contaminated Montana Soil	9 mL	3 mL	0-2* mL
NIST SRM 2711 -Moderately Contaminated Montana Soil	9 mL	3 mL	0-2* mL
NIST SRM 2704 -Buffalo River Sediment	9 mL	3 mL	0-2* mL
NIST SRM 1566a - Oyster Tissue	9 mL	0 mL	0 mL
NIST SRM 1577a - Bovine Liver	9 mL	0 mL	0 mL
NIST SRM 1515 - Apple Leaves	9 mL	0 mL	0 mL
NIST SRM 1547 - Peach Leaves	9 mL	0 mL	0 mL
NIST SRM 1572 - Citrus Leaves	9 mL	0.5 mL	0 mL
NIST SRM 1084a - Wear-Metals in Lubricating Oil	9 mL	0.5 mL	0-2* mL

* HCl is added to stabilize elements such as Ag and Sb during analysis.

Method Comparison

Acid Leaching vs. Fusion

Sample Type	Leach Method [a]	Fusion Method [b]	Accepted Value
	$^{239/240}$Pu, pCi/g ($\pm$ 3σ)		
EML Soil	0.034 (0.006)	0.043 (0.006)	0.041 (0.027)
EML Vegetation	0.050 (0.003)	0.058 (0.008)	0.045 (0.003)
NIST SRM 4350B	0.011 (0.006)	0.014 (0.009)	0.014 (0.003)
NIST SRM 4353	0.256 (0.039)	0.266 (0.030)	0.217 (0.015)
High-Fired Soil	0.167 (0.016)	0.256 (0.016)	
	3.363 (0.174)	5.716 (0.288)	
	22.49 (1.12)	23.72 (1.12)	

[a] Samples were boiled in 6 M HCl for 2 hours, then repetitively leached with fresh 6 M HCl, followed by leaching with aqua regia until the color of the leachate clears. Leaching solutions are combined and evaporated.
[b] Samples were digested utilizing a potassium fluoride-pyrosulfate fusion. The residue was then dissolved in dilute HCl.

Source: Smith, L.L., Markun F., TenKate T., *Comparison of acid leachate and fusion methods to determine plutonium and americium in environmental samples*, Argonne National Laboratory, ANL/ACL-92/2 (1992)

Closed-Vessel Microwave Systems

NIST SRM 2704 Buffalo River Sediment	EPA 3051	EPA3050	Certified Values
	μg/g (± SD)		
Cu	89.1 ± 3.6	88 ± 5	98.6 ± 5.0
Pb	153 ± 19	169 ± 8	161 ± 17
Zn	392 ± 19	403 ± 11	438 ± 12
Cr	69.4 ± 3.4	78.9 ± 2.9	135 ± 5
Ni	37.8 ± 3.2	41.8 ± 0.6	44.1 ± 3.0

Source: Kingston H.M., Walter P.J., *Comparison of microwave versus conventional dissolution for environmental applications*, Spectroscopy 7, R103 (1992)

Open-Vessel Microwave Systems

NIST SRM 2704 Buffalo River Sediment	Open Vessel [a]	Hot Plate EPA 3050B	Certified Values
	μg/g (± SD)		
Cu	101.6 ± 4.8	100 ± 2	98.6 ± 5.0
Pb	134 ± 5	146 ± 1	161 ± 17
Zn	407 ± 7.4	427 ± 5	438 ± 12
Cd	3.05 ± 0.65	na	3.45 ± 0.22
Cr	82 ± 8	89 ± 1	135 ± 5
Ni	35.4 ± 7	44 ± 2	44.1 ± 3.0

[a] 10 mL of HNO3 1:1 was added to the sample. Solution was heated to 95 °C in 2 min and maintained at temperature for 5 min. After cooling to 70 °C, 5 mL of conc. HNO3 was added and the solution was heated again to 95 °C in 2 min and held for 5 min. This step was repeated a second time. After cooling to 70 °C, 10 mL of H_2O_2 (30%) was added in 0.5-mL aliquots. The solution was then heated to 95 °C in 6 min, and the temperature was maintained for 5 min. After cooling to 70 °C, 5 mL of conc. HCl in 10 mL of water was added. The solution was then heated to 95 °C in 2 min and held at temperature for 5 min.

Source: Lorentzen, E.M.L., Kingston H.M., *Comparison of microwave-assisted and conventional leaching using EPA method 3050B*, Analytical Chemistry **68**, 4316 (1996)

Naturally Occurring Nuclides

Sample Type	Isotope	Acid Leach [a]	'Total' Acids [b]	Microwave [c]	Certified Values
		Bq/kg			
IAEA 368	^{238}U	14	23	29	31
Pacific Ocean Sediment Mururoa Atoll	^{232}Th	-	-	-	-
IAEA-375	^{238}U	12.1	19.5	21.9	24.4
Top soil Novozybkov, Russia	^{232}Th	9.5	15.9	19.4	20.5
IAEA-326	^{238}U	13.6	22.1	27.6	29.4
Black soil Kursk region, Russia	^{232}Th	18.9	31.1	36.6	39.4

[a] Samples were leached with a mixture of HNO_3 and HCl (1:1) under heating and stirring for 4 h.

[b] Samples were digested and evaporated successively twice with 50mL conc. HF, three times with 50mL conc. HNO_3 and with 50mL conc. HCl + 2g of boric acid.

[c] In the first step, samples were treated with conc. HF (15 mL). In the second step, insoluble fluorides were dissolved with HNO_3 (15 mL) saturated with boric acid. Temp.: 250 ◦C, ramp time: 10 min, holding time: 20 min.
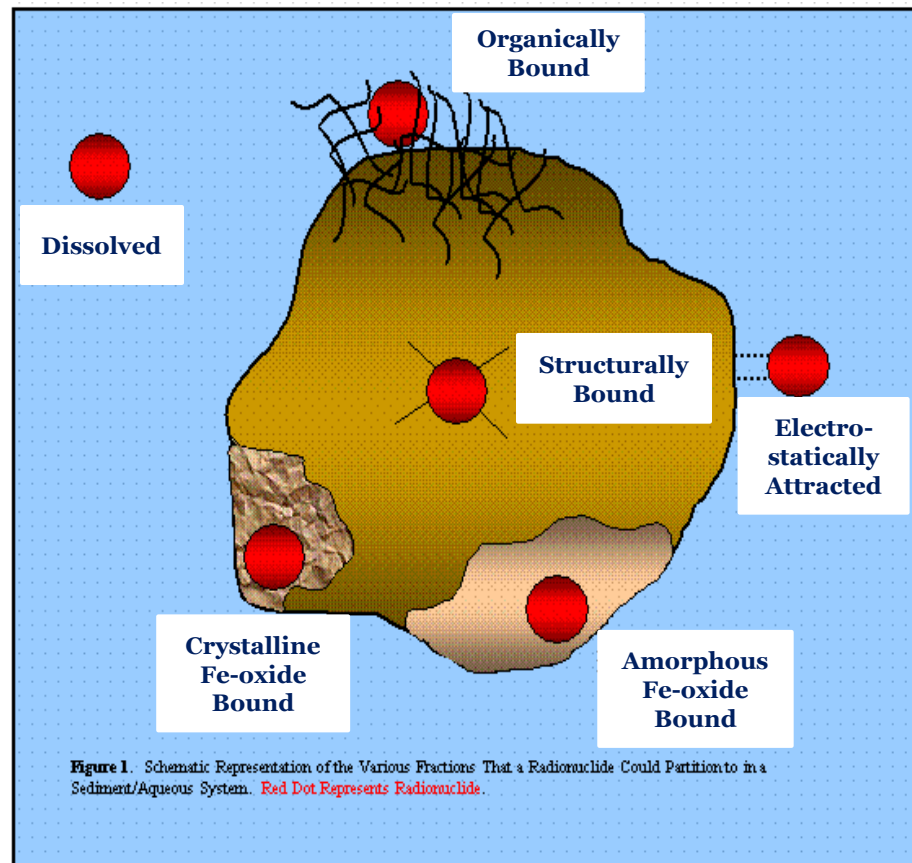
Source: Michel H., Levent D., Barci V., Barci-Funel G., Hurel C., *Soil and sediment sample analysis for the sequential determination of natural and anthropogenic radionuclides*, Talanta **74**, 1527 (2008)

Sequential Extraction

Sequential Extraction

- Sequential extraction is the selective dissolution of soil phases with increasingly aggressive chemical treatment.

- Each extraction is designed to attack a single geochemical phase.

- Furnishes information on:
  - Physicochemical and biological availability
  - Mobilization and transport of contaminants
  - Origin
  - Mode of occurrence

Sequential Extraction

Figure 1. Schematic Representation of the Various Fractions That a Radionuclide Could Partition to in a Sediment/Aqueous System. Red Dot Represents Radionuclide.

Source: Kaplan, D.I., *Quantification of thorium and uranium sorption to contaminated sediments*, Savannah River Site, U.S. Department of Energy, WSRC-MS-2000-00184/Rev.1. AC09-96SR18500 (2000)

Sequential Extraction

- Modern sequential extraction techniques have been in use since at least the 1970s.

- Several different methods have been developed:
  - Tessier (1979)
  - Miller (1986)
  - Schultz (1998)
  - . . .

- Each method has advantages and disadvantages.

Sequential Extraction

- Advantages:
  - Assess the bioavailability of trace elements and radionuclide contaminants
  - Gives an idea of soil and sediment fractionation

- Disadvantages:
  - Does not fully mimic environmental processes
  - Re-adsorption of target phase onto solid particles before separation

Sequential Extraction

Tessier 1979

1	2	3	4	5	6
Exchangeable	Carbonates	Oxides (FeMn)	Organic matter		
1M $MgCl_2$ pH 7	1 M NaOAc pH 5	0.3 M $Na_2S_2O_4$ 0.175 M Na-citrate + 0.025 M citric acid	0.02 M HNO_3 30% H_2O_2 pH 2	30% H_2O_2 pH 2	3.2 M NH_4OAc in 20 % HNO_3

Gimeno-Garcia 1995

1	2	3	4	5
Exchangeable	Organic matter	Carbonates	Oxides (FeMn)	Sulfides
1 M $MgCl_2$ pH 5	0.5 M NaOH	0.05 M Na_2EDTA	Oxalic acid + oxalate pH 3	4 M HNO_3

Sequential Extraction

Schultz 1998

1	2	3	4	5
Exchangeable	Organic matter	Carbonates	Oxides (FeMn)	Residue
0.4 M $MgCl_2$ pH 5	5-6% NaOCl pH 7.5	1 M NaAc in 25% Hac pH 4	0.04 M NH2OH•HCl, pH 2 (HNO3)	NaOH fusion or HNO3/HCl/HF /HClO4

NIST 1998

1	2	3	4	5	6
Exchangeable	Carbonates	Oxides (FeMn)	Organic matter	Acid soluble	Residue
H_2O, $MgCl_2$ pH 4.5	NH_4Ac in 25% Hac pH 4	NH_2OH•HCl in 25% HAc pH 2 (HNO_3)	30% H_2O_2 in 0.02 M HNO_3 pH 2	8 M HNO_3	Total dissolution

Sequential Extraction

Lee 2004

1	2	3	4	5	6
Exchangeable	Carbonates	Oxides (FeMn)	Oxidizable	Acid/Sulfide	Residue
0.4 M $MgCl_2$ pH 4.5 15 mL/g	0.5 M NH_4Ac pH 5 (Hac) 15 mL/g	$NH_2OH \cdot HCl$ in 25% Hac pH 2 (HNO_3) 15mL/g	30% H_2O_2 in 0.02 M HNO_3 15 mL/g	4.0 M HNO_3 15 mL/g	$LiBO_2$/HF fusion

Outola 2009

1	2	3	4	5
Exchangeable	Carbonates	Oxides (FeMn)	Organic matter	Residue
1.0 M $MgCl_2$	2.0 M NH_4Ac in 25% HAc	$NH_2OH \cdot HCl$ in 25% HAc	30% H_2O_2 in 0.05 M HNO_3	16 M HNO_3

Sequential Extraction References

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