Current State of Extraction—Don’t Be Deceived!

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Overview

- Factors
- Purpose of Dissolution
- Quality Objectives of Program
- Effectiveness of Dissolution Technique
- Safety Considerations
- Cost &/or Time Efficiency
- Generation of Waste
- Interferences
- Method of Detection

But First—Remember!

- Support of AOAC 2017.02
- Fertilizer Subgroup of the Agricultural Materials Community in AOACI
- History of Methods Forum
- Most using methods deriving from environmental methodologies
- Fertilizer matrices—high salts, spectral interferences, uncontrolled ionization effects
- IRON
- SUIP No. 25
- AOAC 2006.03

Method Requirements

- Equipment & instrumentation common in state fertilizer laboratories
- ICP-OES (not ICP-MS)
- Detection limits to meet SUIP #25
- Digestion equipment & cross contamination requirements
- Extension of AOAC 2006.03 for nutritive metals
- Simple acid mixture, not perchloric acid
- Include wide variety of metals & fertilizer matrices, some sacrifices worth the expanded scope

Techniques

- Fusion
- Wet Ashing
- Acid Leaching
- Microwave Digestion
- Dry Ashing

Considerations

- Solubility Rules
  - g/100 mL solvent
  - Soluble, slightly soluble, insoluble
- Solubility Constant: K_{sp}
  - As K_{sp} ↓, insolubility ↑
- Exchange, decomposition, & Rearrangement Reactions
- Oxidation-Reduction
- Complexation

Fusion

- Combine flux (a salt) & sample
  - Organic material ashed prior to this
  - Crucibles: Pt, Zr, Ni, or porcelain
  - Sand or oil baths on hot plate, furnace or burner
- Heat above melting point of salt, sample reacts with molten salt
- Dissolved cool fused sample
- Multiple times
- Multiple salts, acids, or combination
- Sample must contain chemically bound oxygen
- Moisture removed

Common Fluxes & Crucibles

Flux (mp, °C)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
$Na_2S_2O_7$ (403°) or $K_2S_2O_7$ (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°) or KOH (404°)	450-600°	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides.
Na_2CO_3 (853) or 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°) or $LiBO_2$ (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°) or 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.

Source: Dean (1995) and Bock (1979).

- Sulfate: Ignited oxides to sulfates
- Alkali-OH: Silicates, oxides, phosphates, fluorides, actinides in soils
- Na_2CO_3: silicates, refractory oxides, phosphates, & sulfates (K_{sp} is high)
- Boron: Sand, slag, Al silicates, alumina, Fe, rare earth ores, Zirconium dioxide, Ti, niobium, Tantalum (Pt crucible) nasty
- Fluoride: silicon, destruction of silicates, rare earth metals; oxides of niobium, tantalum, Ti, Zi (Pt crucible)
- NaOH: Fe in soil
- Wet/Dry Ash: may leave oxides, silicates, nitrides, carbides, borides—if looking for radionuclide

Common & Nasty Acids

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.

Remember the Acids

- Oxidizing acids: metals whose $E^0 > E^0_H$

Half-Reaction	E^0 (volts)	Half-Reaction	E^0 (volts)
$Ag^{2+} + e^- \rightarrow Ag^+$	1.980	$I^-_3 + 3e^- \rightarrow 3I^-$	0.536
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	1.96	$I_2 + 2e^- \rightarrow 2I^-$	0.536
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.72	$Cu^+ + e^- \rightarrow Cu$	0.53
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 (s) + 2H_2O$	1.70	$4H_2SO_3 + 4H^+ + 6e^- \rightarrow S_4O_6^{2-} + 6H_2O$	0.507
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	1.630	$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	0.449
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	1.604	$2H_2SO_3 + 2H^+ + 4e^- \rightarrow S_2O_3^{2-} + 3H_2O$	0.400
$NiO_2 + 4H^+ + 2e^- \rightarrow Ni^{2+} + 2H_2O$	1.593	$UO_2^+ + 4H^+ + e^- \rightarrow U^{4+} + 2H_2O$	0.38
Bi_2O_4 (bismuthate) $+ 4H^+ + 2e^- \rightarrow 2BiO^+ + 2H_2O$	1.59	$Cu^{2+} + 2e^- \rightarrow Cu$	0.340
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$	0.337
$2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$	1.478	$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O$	0.32
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.468	$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	0.27
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.36	$Hg_2Cl_2 (s) + 2e^- \rightarrow 2Hg + 2Cl^-$	0.2676
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.3583	$AgCl (s) + e^- \rightarrow Ag + Cl^-$	0.2223
$2HNO_2 + 4H^+ + 4e^- \rightarrow N_2O + 3H_2O$	1.297	$SbO^+ + 2H^+ + 3e^- \rightarrow Sb + H_2O$	0.212
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23	$CuCl_3^{2-} + e^- \rightarrow Cu + 3Cl^-$	0.178
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.158
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO^-_3 + H_2O$	1.201	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 3H_2O$	1.19	$CuCl + e^- \rightarrow Cu + Cl^-$	0.121
$N_2O_4 + 2H^+ + 2e^- \rightarrow 2HNO_2$	1.07	$TiO^{2+} + 2H^+ + e- \rightarrow Ti^{3+} + H_2O$	0.100
$2ICl^-_2 + 2e^- \rightarrow 4Cl^- + I_2$	1.07	$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	0.08
$Br_2 (aq) + 2e^- \rightarrow 2Br^-$	1.065	$2H^+ + 2e^- \rightarrow H_2$	0.0000

Standard reduction potentials of ½ reactions at 25 °C

$Br_2\,(aq) + 2e^- \rightarrow 2Br^-$	1.065	$2H^+ + 2e^- \rightarrow H_2$	0.0000
$N_2O_4 + 4H^+ + 4e^- \rightarrow 2NO + 2H_2O$	1.039	$Hg_2I_2\,(s) + 2e^- \rightarrow 2Hg + 2I^-$	-0.0405
$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$	0.996	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.125
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.957	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$	0.94	$AgI\,(s) + e^- \rightarrow Ag + I^-$	-0.1522
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.911	$V^{3+} + e^- \rightarrow V^{2+}$	-0.255
$Cu^{2+} + I^- + e^- \rightarrow CuI\,(s)$	0.861	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.257
$OsO_4\,(s) + 8H^+ + 8e^- \rightarrow Os + 4H_2O$	0.84	$Co^{2+} + 2e^- \rightarrow Co$	-0.277
$Ag^+ + e^- \rightarrow Ag$	0.7991	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.3505
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.7960	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.4025
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.424
$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O$	0.739	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$HN_3 + 11H^+ + 8e^- \rightarrow 3NH_4^+$	0.695	$H_3PO_3 + 2H^+ + 2e^- \rightarrow HPH_2O_2 + H_2O$	-0.499
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695	$U^{4+} + e^- \rightarrow U^{3+}$	-0.52
$Ag_2SO_4 + 2e^- \rightarrow 2Ag + SO_4^{2-}$	0.654	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.7626
$Cu^{2+} + Br^- + e^- \rightarrow CuBr\,(s)$	0.654	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$2HgCl_2 + 2e^- \rightarrow Hg_2Cl_2\,(s) + 2Cl^-$	0.63	$Al^{3+} + 3e^- \rightarrow Al$	-1.67
$Sb_2O_5 + 6H^+ + 4e^- \rightarrow 2SbO^+ + 3H_2O$	0.605	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.356
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2\,H_2O$	0.560	$Na^+ + e^- \rightarrow Na$	-2.714
$TeOOH^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O$	0.559	$K^+ + e^- \rightarrow K$	-2.925
$Cu^{2+} + Cl^- + e^- \rightarrow CuCl\,(s)$	0.559	$Li^+ + e^- \rightarrow Li$	-3.045
		$3N_2 + 2H^+ + 2e^- \rightarrow 2HN_3$	-3.1

Standard reduction potentials of ½ reactions at 25 °C

Remember the Acids

- HNO_3: most commonly used
- HCl: most commonly used; insoluble silicates, ignited oxides of Al, Be, Cr, Fe, Ti, Zr or Th; oxides of Sn, Sb, Nb, Ta; Zr phosphate; sulfates of Sr, Ba, Ra, or Pb; alkaline earth fluorines; sulides of Hg; ores of Nb, Ta, U, or Th
- Aqua Regia: (1:3, HNO_3:HCl)—oxidizing effect of N^{+5} & Cl^- coupled with catalytic effect of Cl_2 & NOCl—acidity meets complexing power of Cl^-!
- H_2SO_4: silicates—not good for high concentrations of Ca, Sr, Ba, Ra, Pb
- HF: Dissolves silica & other silicates—loves complexing; dissolves compounds of elements from IV to VI groups. Very NASTY!
- $HClO_4$: hot, concentrated to be effective; attacks all metals but Au & Pt group metals; violent reactions; DANGEROUS—higher probability to explode! Not contact organic material! No cotton!

Microwave Digestion

- Faster
- Cleaner
- More reproducible
- More accurate
- Time Efficient

- Open-Vessel Systems
- Low-Pressure, Closed Vessel System
- High-Pressure, Closed Vessel System
- Use up to 3 grams

AOAC Method		Title--Solvents	Matrix or element
965.09		Nutrients (Minor) in Fertilizers	
	a	HCl	Inorganic materials & mixed fertilizers
	b	Char, HCl	Organic
	c	$HClO_4$/HF or HCl/HF	Fritted trace elements
	d		Mn: 972.02, 940.02, 941.02, 972.03
	e	H_2O, EDTA	Fe, Zn
949.02		Boron (Acid-Soluble) in Fertilizers	
		~17:1 H_2O:HCl	
949.03		Boron (Water-Soluble) in Fertilizers	
		H_2O	ppt SO_4 & PO_4, boil out NH_3 titrate
			*NA >5% urea or urea-formaldehyde
982.01		Boron (Acid-and Water-Soluble)	
	a	4:1 H_2O:HCl	
	b	H_2O, HCl added	(1 mL HCl/95 mL H_2O)
945.03		Calcium (Acid-Soluble) in Fertilizers	
		3:1 HNO_3:HCl	ppt Ba & Sr
965.10		Calcium (Acid-Soluble) in Fertilizers	
		945.03	Filter from Mg method (CaC_2O_4) 937.01
945.04		Calcium (Acid-Soluble) in Fertilizers	
		965.09	
965.11		Cobalt in Fertilizers	
		H_2SO_4, HNO_3, $HClO_4$	
975.01		Copper in Fertilizer	
		965.09	
941.01		Copper in Fertilizer	
		HNO_3 & H_2SO_4	~1.5:1
942.01		Copper in Fertilizer	
		HNO_3 & H_2SO_4	2:01
		NH_4HF_2	
967.01		Iron in Fertilizers	
		957.02B(e)	HNO_3, $HClO_4$
		HCl	
980.01		Iron in Fertilizers	
		965.09	

AOAC Method		Title--Solvents	Matrix or element
984.01		Magnesium (Acid-Soluble)	
		965.09	
964.01		Magnesium (Acid-Soluble)	
	a	2:1 HNO_3:HCl, $HClO_4$	organic materials
	b	2:1 HNO_3:HCl, $HClO_4$	Inorganic materials & mixed fertilizers
937.01		Magnesium (Acid-Soluble)	
		3:1 HNO_3:HCl	
940.01		Magnesium (Acid-Soluble)	
		937.01	filtrate
		H_2SO_4	
937.02		Magnesium (Water-Soluble)	
	a	H_2O	$KMgSO_4$, $MgSO_4$, kieserite
	b	H_2O	Other material, mixed fertilizers
	c	a or b extract	
		964.01D	
972.02		Manganese (Acid-Soluble)	
	a	940.02	Mn^{2+} only
		965.09D	
	b	965.09C	Mn^{2+} & Mn^{4+}
		965.09D	
940.02		Manganese (Acid-Soluble)	
		3:1 HNO_3:H_2SO_4, HNO_3, H_3PO_4	
941.02		Manganese (Acid-Soluble)	
		7:1 H_2SO_4:HNO_3, HNO_3	
972.03		Manganese (Water-Soluble)	
		ROH, H_2O, H_2SO_4	Mn^{2+} only
974.01		Sodium in Fertilizers	
		955.06	H_2O & $(NH_4)_2C_2O_4$
983.04		Sodium in Fertilizers	
		H_2O & $(NH_4)_2C_2O_4$	
942.02		Zinc in Fertilizers	
		~1:5 H_2SO_4:HNO_3, HNO_3, H_2O	
942.03		Zinc in Fertilizers	
		1:1 HNO_3:H_2SO_4, HNO_3, H_2O	
975.02		Zinc in Fertilizers	
		965.09	
973.01		Zinc in Fertilizers	
		1:2 HNO_3:HCl, HCL	
2006.03		As, Cd, Co, Cr, Pb, Mo, Ni, & Se	
		HNO_3, Microwave	
2017.02		As, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn,Mo, Ni, & Se in Fertilizers	
		3:1 HNO_3:HCl	

Acid Leaching or Total Dissolution?

- How much dissolution determines the data
- Fusion is more labor intensive
- Large quantities of flux required up to 5 to 10 times the sample weight
- Possible contamination from large amounts of flux
- Higher temperature requirements increases safety concerns
- Mineral acids are effective for metals, oxides and salts in most fertilizers

Questions/Comments?