Appendix I
A Brief Chronology

NOTE: Texts are date of first publication. Instruments and processes are approximate date of first commercial introduction unless otherwise noted.

METALLURGY	INORGANIC ANALYTICAL CHEMISTRY
14th century BC—Reduction of iron ore	14th century BC—Babylonians use fire assay to test the purity of gold
700 BC—Iron displaces bronze	
14th Century AD—Blast furnace for pig iron	
1530—*De la Pirotechnia* (Vannocio Biringuccio)	
1556—*De re Metallica* (Georg Agricola)	
	1574—*Beschreibung allerfurnemisten mineralischen Ertzt und Bergwercksarten* (Lazarus Ercker)
1600—Wrought iron, cementation process for steel	
1613—Reverberatory furnace	
	1661—*The Sceptical Chymist* (Robert Boyle)
	1681—Phlogiston theory
1709—precoking for ironmaking	
1722—*On the Art of Converting Iron to Steel* (R. A. F. de Réaumur)	
	1729—Bouguer's Law
1734—*Treatise on Copper* (E. Swedenborg)	
1742—Crucible process for steel	
	1768—Lambert's Law
	1774—Joseph Priestley discovers oxygen
1780—Role of carbon in steelmaking discovered	
1784—Puddling process for wrought iron	
1808—Widmanstätten structure discovered in meteorites	1808—*New System of Chemical Philosopy* (John Dalton)
	1811—Avogadro's Theory
	1828—Berzelius: table of atomic weights
	1832—Gay-Lussac titrates silver with chloride
1836—Hot dip galvanizing	
1856—Bessemer (Kelley) process	1856—*Lehrbuch der chemisch-analytischen Titrirmethode* (K. F. Mohr)
	1859—Beer's law
	1862—First issue: *Zeitschrift für Analytische Chemie* (Fresenius)
1863—Sorby: microscopic metallography	
	1871—Mendeleev: periodic table
	1877—synthetic acid/base indicators
1882—Hadfield steel (high manganese)	
1886—Hall/Heroult electrolytic process for aluminum	
	1887—Arrhenius equation
1888—Open hearth (Siemens) process; thermocouple (Le Chatelier)	

METALLURGY	INORGANIC ANALYTICAL CHEMISTRY
1889—Nickel steels	1889—Nerst equation
	1894—*Die wissenschaftlichen Grundlagen der analytischen Chemie* (W. Ostwald)
1898—Tempered high-tungsten tool steel	
1899—Electric arc furnace	
1900—Silicon-iron	
	1903—Conductivity titrations
1904—Vanadium steels	
1905—Monel alloys	
1906—Age hardening of aluminum alloys discovered	
	1909—Sorensen: pH concept
1910—Direct reduction of iron ore (Hoganas process)	
1913—Stainless steel	1913—Moseley: X-ray spectra of the elements
	1914—*Rapid Methods for the Chemical Analysis of Special Steels . . .* (C. M. Johnson)
1915—Nickel-iron high-permeability alloys	
	1920—Glass pH electrodes
1922—Galvannealing process	
	1923—Fluorescent indicators; Debye-Hückel theory; Brønsted theory
	1925—Redox indicators
1926—Type 310 stainless steel	
1927—High-frequency induction furnace; cobalt-iron high-saturation alloys	
1928—Type 304 stainless steel	
	1929—*Applied Inorganic Analysis*, 1st ed. (Hillebrand, Lundell, and Hoffman)
1931—Alnico magnet alloys	1931—*Chemical Analysis of Iron and Steel* (Lundell, Hoffman, and Bright)
1932—Cobalt-base alloys (vitallium)	
1933—High-strength low-alloy steels	
	1934—Ion exchange resins
1935—Electroslag remelting process (developed)	
	1938—Coulometric titrations; *Outlines of Methods of Chemical Analysis* (Lundell and Hoffman)
	1940—UV/visible spectrophotometer; *Fire Assaying* (Shepherd and Dietrich)
	1942—Direct reading spectrophotometer
1943—Precipitation-hardening austenitic stainless steel	
	1944–46—Analytical chemistry of the Manhatten Project (published, 1950)
1945—Vacuum arc remelting furnace	
1949—Sintered aluminum powder	
1950—Type 201 stainless steel; Sendzimer mill	1950—Direct-reading optical emission spectrometer
1951—Titanium alloys	
1952—Basic oxygen process (L-D)	
	1953—*Applied Inorganic Analysis*, 2nd ed. (Hillebrand, Lundell, Bright, and Hoffman)
	1955—X-ray fluorescence spectrometer
1960—Rapid solidification processing; maraging steel; vacuum degassing	1960—Flame atomic absorption spectrophotometer
1962—Basic oxygen process (Stora-Kaldo)	
1963—Continuous casting	

METALLURGY	INORGANIC ANALYTICAL CHEMISTRY
	1964—Ion selective electrodes
	1965—d-c plasma emission spectrometer
	1968—Grimm glow discharge lamp
1970—Electroslag remelting widely used; argon-oxygen decarburization (AOD); rare earth-cobalt magnet alloys	1970—Graphite furnace atomic absorption spectrophotometer
1975—Amorphous metals	1975—ICP emission spectrometer
1978—Metal-matrix composites	
	1979—Dual-beam diode array spectrophotometer
1980—Large-scale ladle refining	1980—Total reflection X-ray fluorescence spectrometer
1982—Single crystal alloys	
	1983—Glow discharge mass spectrometer; single-beam diode array spectrophotometer
1984—Neodymium-iron-boron magnet alloy	1984—ICP-mass spectrometer
1985—Ductile-ordered alloys (intermetallic compounds)	1985—Glow discharge atomic absorption spectrophotometer (solids sampling)
1987—Ion implantation; beam processing; metallurgy of surfaces	1987—Laser ablation-ICP-MS
	1989—Early robot labs for steel control
	1990—Echelle-CID optical emission spectrometer
1992—*Nano-Structured Materials* (journal) begins publication	1992—ICP-OES-MS system

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Appendix II

The Chemical Behavior of Analytes

NOTE: Element name and symbol are followed by atomic number, atomic weight, and common aqueous oxidation states with the most stable state underlined. Abbreviations—(s): solution; (p): precipitate; (o): organic; (a): aqueous; RT: room temperature.

Element	Aluminum (Al) 13 26.982 +3	Antimony (Sb) 51 121.757 +3 , +5, −3	Arsenic (As) 33 74.922 +3, +5, −3
Useful precipitations	NaOH: (s) NH_4OH: (p) 8-hydroxyquinoline: (p)	Acid sulfide: (p) Basic sulfide:(s) Accompanies Fe + NH_4OH: (p)	Acid sulfide: (p) Basic sulfide: (s) Accompanies Fe + NH_4OH: (p)
Useful solvent extractions	Ethyl ether/ HCl— from Mo, Fe: (a); 8-hydroxyquinoline-$CHCl_3$/pH 9: (o)	Ethyl acetate/1.5 *M* HCl—Sb(V): (o) TOPO/ MIBK: (o)	
Useful volatilizations/ distillations		SbH_3 (gas at RT) $SbCl_3$ (b.p. approx. 200°C)	AsH_3 (gas at RT) $AsCl_3$ (b.p. 108°C)
Other useful separations/ comments	Amphoteric Mercury cathode: (a)		Highly toxic
Best methods at high concentrations	Volum: Titr. with standard acid after AlF_3 precip. at pH 10 Grav.: 8-hydroxyquinoline	Volum.: Titr. with BrO_3^- Grav.: as Sb_2S_3	Volum.: Titr. with BrO_3^- Grav.: as As metal
Best methods at low concentrations	FAA: 309.3 nm ICP-OES: 369.1 nm (Intf.: Mo) Color: 8-hydroxyquinoline	FAA/GFAA: 217.6 nm ICP-OES: 206.8 nm (Intf.: Cr) Color: Brilliant Green; Rhodamine B	FAA/GFAA: 193.7 nm ICP-OES: 193.7 nm (Intf.: Al) Color: AsH_3 + pyridine + Ag-diethyldithiocarbamate; arsenomolybdate

Element	Barium (Ba) 56 137.327 +2	Beryllium (Be) 4 9.0122 +2	Bismuth (Bi) 83 208.980 +3, (+5)
Useful Precipitations	Sulfate: (p) Chromate: (p)—from Sr Ammonium phosphate (ammoniacal): (p)	NaOH: (s) NH_4OH: (p)	Acid sulfide: (p) Basic sulfide: (p)
Useful Solvent Extractions			Dithizone - $CHCl_3$: (o) TOPO-MIBK: (o)
Useful Volatilizations/ Distillations			
Other Useful Separations/ Comments	Yellow-green flame test Mercury cathode: (a)	Highly toxic Mercury cathode: (a)	
Best Methods at High Concentrations	Volum.: EDTA (ind.: Eriochrome Black T) Grav.: as the sulfate	Grav.: as BeO after NH_4OH precip.; Photoneutron emission	Grav.: as BiOCl or $BiPO_4$
Best Methods at Low Concentrations	FAA: 553.6 nm ICP-OES: 493.4 nm	FAA: 234.9 nm ICP-OES:313.0 nm Color: Aluminon; Fluorimetric: quinalizarin; morin	FAA/GFAA: 223.1 nm (pk. ht. best) ICP-OES: 223.0 nm (Intf.: Cu, Ni) Color: dithizone

Element	Boron (B) 5 10.811 +3	Cadmium (Cd) 48 112.411 +2	Calcium (Ca) 20 40.078 +2
Useful precipitations		Acid sulfide: (p) Basic sulfide: (p) NaOH: (p) NH_4OH: (s)	Oxalate: (p)—from Mg Chromate: (s)—from Ba
Useful solvent extractions	$CHCl_3$—BF_3: (o) (tetraphenyl arsonium chloride; methylene blue)		
Useful volatilizations/ distillations	$B(OCH_3)_3$ (b.p. 68.7°C) BF_3 (b.p. −99°C) BCl_3 (b.p. 12.4° C)		
Other useful separations/ comments	Mercury cathode: (a) Ion exchange (remove other cations and anions) Borates: yellow-green flame test	Highly toxic	Mercury cathode: (a) Yellow-red flame test
Best methods at high concentrations	Volum.: Mannitol complex—titr. released H^+ with standard NaOH. ICP-OES: 249.6 nm (Intf.: Co)	Grav.: as $Cd_2P_2O_7$; as Cd metal (electrolytic) ICP-OES: 226.5 nm	Volum.: EDTA (ind.: Eriochrome Black T) Grav.: as CaC_2O_4
Best methods at low concentrations	ICP-OES: 249.6 nm (Intf.: Co) Color: curcumin (after methyl borate distillation); dianthrimide (direct)	FAA/GFAA: 228.8 nm ICP-OES: 226.5 nm Color: dithizone	FAA: 422.7 nm ICP-OES: 317.9 nm (Intf.: Cr)

Element	Chromium (Cr) 24 51.996 +2, <u>+3</u>, +6	Cobalt (Co) 27 58.933 <u>+2</u>, +3	Copper (Cu) 29 63.546 +1, <u>+2</u>
Useful precipitations	NaOH: Cr(III)(p), Cr(VI)(s) NH_4OH: Cr(III)(p); Cr(VI)(s) Na_2O_2 fusion /H_2O leach: (s) Ag^+,Hg_2^{2+}, Ba^{2+}, Pb^{2+}: (p)—Cr(VI)	ZnO: (s)—from Fe; NaOH:(p) NH_4OH:(s), but Fe and Al coprecip.	Acid sulfide: (p) Basic sulfide: (p) $(NH_4)_2S$: (p) NaOH:(p) NH_4OH: (s)
Useful solvent extractions		Tetraphenylarsonium chloride-$CHCl_3$: (o)	Neocuproine-$CHCl_3$: Cu(I):(o)
Useful volatilizations/ distillations	CrO_2Cl_2 (b.p. 117°C)		
Other useful separations/ comments	Mercury cathode is slow to remove Cr (VI)	Ion Exchange (Cl^-) from Ni, Cu, Fe; Co^{2+}: pink/ Co^{3+}: blue	Ion exchange(Cl^-)— from Ni, Co, Fe
Best methods at high concentrations	Volum.: oxidize with persulfate, titr. with ferrous ammonium sulfate	Volum.: oxidize with excess $K_2Fe(CN)_6$, back titr. with Co^{2+} Grav.: electroplate as metal	Grav.: electrolytic as metal Volum.: iodometric
Best methods at low concentrations	FAA: 357.9 nm ICP-OES: 267.7 nm Color: diphenylcarbazide	FAA: 240.7 (D_2 arc); 242.5 (Zeeman) ICP-OES: 228.6 nm (2nd order) Color: nitroso-R salt, tetraphenyl arsonium chloride	FAA: 324.8 nm ICP-OES: 324.7 nm Color: diethyldithiocarbamate; neocuproine

Element	Gallium (Ga) 31 69.723 +3	Germanium (Ge) 32 72.61 +4	Gold (Au) 79 196.967 +3
Useful precipitations	NH_4OH: (p) NaOH: (s) Cupferron: (p) 8-hydroxyquinoline: (p)	Acid sulfide: (p) Basic sulfide: (s)	$NaNO_2$: (p), as metal from the Pt group Acid sulfide: (p) Basic sulfide: (p)
Useful solvent extractions	Ethyl ether/HCl: Ga(o); Al(a)		Isopropyl ether/dil. HBr: (o) Ethyl ether/HCl: (o)
Useful volatilizations/ distillations		$GeCl_4$ (b.p. 83.1°C)	
Other useful separations/ comments	Metal melts at 29.75°C , boils at 1980°C (widest liquid range)	Highly toxic	Gold salts are strong oxidizing agents ($Au^{3+} + 3e^- \rightarrow Au^o$)
Best methods at high concentrations	Grav.: as Ga_2O_3, after precip. with NH_4OH	Grav.: acid sulfide precip., diss. in NH_4OH, oxidize with H_2O_2, ignite to GeO_2	Fire assay Grav.: as metal. after reduction with oxalic acid, SO_2, $NaNO_2$, or hypophosphorous acid
Best methods at low concentrations	FAA: 287.4 nm ICP-OES: 294.4 nm Color: 8-hydroxyquinoline-$CHCl_3$	FAA: 265.1 nm ICP-OES: 209.4 nm Color: phenylfluorone	FAA: 242.8 nm ICP-OES: 242.8 nm

Element	Hafnium (Hf) 72 178.49 +4	Indium (In) 49 114.818 +3	Iridium (Ir) 77 192.22 +3, +4, +6
Useful precipitations	NaOH: (p); NH_4OH: (p); p-Bromomandelic acid: (p); Cupferron: (p); $(NH_4)_2HPO_4$: (p) In all cases Zr accompanies.	NaOH: (p) NH_4OH: (p) Dilute (pH 2-3) acid sulfide: (p) Ammonium oxalate (pH 8): (p)	Acid sulfide: (p) Basic sulfide: (s)
Useful solvent extractions	TOPO-Cyclohexane/HNO_3: (o) Zr accompanies.	Ethyl ether/HCl: (o)	Ethyl ether/HCl: (o)
Useful volatilizations/ distillations			
Other useful separations/ comments	Mercury cathode: (a) Hf and Zr can be separated by ion exchange		$IrCl_4$: dark brown
Best methods at high concentrations	Grav.: as HfO_2 after cupferron precip. and ignition; as HfP_2O_7 after $(NH_4)_2HPO_4$ precip. and ignition (do not overwash).	Grav.: as In_2O_3 after precip. with NH_4OH Volum.: Titr. with $K_2Fe(CN)_6$	Grav.: as metal after precip. with 2-mercaptobenzothiazole followed by reduction in H_2
Best methods at low concentrations	ICP-OES: 273.8 nm (Intf.: Fe, Mo) Color: Pyrocatechol Violet; Xylenol Orange	FAA: 325.6 nm ICP-OES: 451.1 nm Color: dithizone	ICP-OES: 224.3 nm

Element	Iron (Fe) 26 55.847 +2, +3	Lead (Pb) 82 207.2 +2, +4	Magnesium (Mg) 12 24.305 +2
Useful precipitations	NH_4OH: (p) NaOH: (p) Cupferron (as Fe^{3+}): (p)	Acid sulfide: (p) Basic sulfide: (p) Sulfate: (p) Chromate: (p)	$(NH_4)_2HPO_4$: (p) NaOH: (p) 8-Hydroxyquinoline (ammoniacal sol.): (p)
Useful solvent extractions	Cupferron-$CHCl_3$/10% HCl: (o) Ethyl ether/HCl: (o) Acetylacetone-$CHCl_3$ (as Fe^{3+} at pH 1): (o)	Dithizone-$CHCl_3$: (o) TOPO-MIBK: (o)	8-Hydroxyquinoline-$CHCl_3$/ pH 10: (o)
Useful volatilizations/ distillations			
Other useful separations/ comments	Ion exchange (Cl^- system)—from Ni, Co, Cu	Highly toxic	Mercury cathode: (a)
Best methods at high concentrations	Volum.: Reduce with $SnCl_2$, then titr. with $K_2Cr_2O_4$ or Ce (IV)	Grav.: as $PbSO_4$; Electrolytic (as PbO)	Volum.: EDTA (ind.: Eriochrome Black T) Grav.: as $Mg_2P_2O_7$ after precip. with $(NH_4)_2HPO_4$ and ignition.
Best methods at low concentrations	FAA: 248.3 nm ICP-OES: 259.9 nm Color: o-phenanthroline; thiocyanate; 2, 2′-bipyridyl	FAA: 283.3 nm ICP-OES: 220.3 nm (Intf.: Co, Ni, Al) Color: dithizone	FAA: 285.2 nm ICP-OES: 279.0 nm (Intf.: Mn, Cr, Fe)

Element	Manganese (Mn) 25 54.938 +2, +3, +4, +6, +7	Mercury (Hg) 80 200.59 +1, +2	Molybdenum (Mo) 42 95.94 +3, +5, +6
Useful precipitations	Acid sulfide: (s) Basic sulfide: (p) $(NH_4)_2HPO_4$: (p) NaOH: (p)	Acid sulfide: (p) (insol. HNO_3) Basic sulfide: (p)	NH_4OH: (s) NaOH: (s) Acid sulfide: (p) Basic sulfide: (s) α-Benzoinoxime:(p)
Useful solvent extractions			Ethyl ether/HCl: (o)
Useful volatilizations/ distillations		Hg^o (b.p. 356.58°C) $HgCl_2$ (b.p. 302°C)	MoO_3 (loss begins at approx. 600°C)
Other useful separations/ comments		Highly toxic Liquid at R.T. Forms amalgams with many metals	Cl^-/F^- System anion exchange—from W, Ti, Nb, Ta, etc.
Best methods at high conc.	Volum.: oxidize with persulfate, titr. with arsenite (visual or potentiometric) Volum.: complex with pyrophosphate, titr. with $KMnO_4$ (potentiometric)	Volum.: Titr. with thiocyanate (Fe^{3+} ind.) Grav.: as HgS after precip. with $(NH_4)_2S$ from basic sol.	Grav.: as MoO_3 after precip with α-Benzoinoxime and ignition Volum.: Pass through Jones reductor, collect in excess std. ferrous ammonium sulfate, titr. excess with $KMnO_4$
Best methods at low concentrations	Color: meta-periodate (as MnO_4^-) FAA: 279.5 nm ICP-OES: 257.6 nm	Cold vapor AA/ FAA/GFAA: 253.7 nm ICP-OES: 435.8 nm	FAA: 313.3 nm ICP-OES: 202.0 nm Color: thiocyanate; toluene-3,4-dithiol

Element	Nickel (Ni) 28 58.693 +2	Niobium (Nb) 41 92.906 (+3), +5	Osmium (Os) 76 190.23 +4 , +6, +8
Useful precipitations	Dimethylglyoxime: (p) NaOH: (p) NH_4OH: (s) Basic sulfide: (p)— after removal of acid sulfide group	NaOH: (p) NH_4OH: (p) Cupferron: (p)	Acid sulfide: (p) Basic sulfide: (p)
Useful solvent extractions	Dimethylglyoxime-$CHCl_3$: (o)		
Useful volatilizations/ distillations			OsO_4 (b.p. 130°C)
Other useful separations/ comments	Ion Exchange (Cl^- system)— from Fe, Co, Cu	Mercury cathode: (a) Ion exchange (Cl^-/F^- system)— from Mo, Ti, W, Ta, etc.	$OsCl_4$: yellow Highly toxic, especially as oxide vapor
Best methods at high concentrations	Grav.: as dimethylglyoximate Volum.: excess EDTA, back titr. with $Bi(NO_3)_3$	Grav.: as Nb_2O_5 , after precip. with cupferron and ignition	Grav.: as the metal after distillation of OsO_4 and reduction in H_2
Best methods at low concentrations	FAA: 232.0 nm ICP-OES: 231.6 nm (Intf.: Co) Color: Ni-dimethylglyoxime complex (in presence of I_2)	Color: H_2O_2 in conc. H_2SO_4; hydroquinone in conc. H_2SO_4 ICP-OES: 309.4 nm (Intf.: V)	Color: thiourea; ephedrine-HCl ICP-OES: 225.6 nm

Element	Palladium (Pd) 46 106.42 +2, +4	Phosphorus (P) 15 30.974 +3, +5, -3	Platinum (Pt) 78 195.08 +2, +4
Useful precipitations	Dimethylglyoxime: (p)—from weak acid sol. Cupferron: (p)	NaOH: (s) NaOH + Na_2O_2: (s) Accompanies Fe + NH_4OH: (p)	Acid sulfide: (p) Basic sulfide: (s)
Useful solvent extractions	Pd-dimethylglyoximate—$CHCl_3$: (o)	Phosphomolyddate complex—N-butanol: [ox.—yellow: (o); reduced—blue: (a)]	
Useful volatilizations/ distillations		PCl_3 (b.p. 76.1°C)	
Other useful separations/ comments	PdI_2: black precipitate (soluble in NH_4OH + iodide)	Highly toxic volatile compounds Ion exchange (alumina column)	Pt^0 appears as a red colloid if reduced with $SnCl_2$, or as a black precip. if reduced with formaldehyde in basic sol.
Best methods at high concentrations	Grav.: as Pd-dimethylglyoximate from weak acid sol.	Grav.: as $Mg_2P_2O_7$ after precip. with $MgCl_2$ + NH_4OH Volum.: Precip. as ammonium phosphomolybdate, add excess std. NaOH and backtitr. with std. HCl	Grav.: as Pt metal after acid sulfide precip. and ignition to the metal Fire Assay
Best methods at low concentrations	ICP-OES: 229.7 nm FAA: 247.6 nm Color: α-furfuraldoxime; bromide after extraction of phenylthiourea complex	Color: phosphomolybdate; phosphomolybdovanadate ICP-OES: 214.9 nm (Intf.: Cu)	ICP-OES: 214.4 nm FAA: 265.9 nm Color: p - nitrosodimethylaniline

Element	Rhenium (Re) 75 186.207 +4, +6, +7	Rhodium (Rh) 45 102.906 +3, +4	Ruthenium (Ru) 44 101.07 +3, +4, +6, +8
Useful precipitations	Nitron: (p) Tetraphenylarsonium chloride: (p) α-Benzoinoxime: (s)— from Mo	Acid sulfide: (p) Basic sulfide: (p)	Acid sulfide: (p) Basic sulfide:(p) Bismuthiol: [Ru(III)] (p)
Useful solvent extractions	Ethyl ether/HCl: (o)		
Useful volatilizations/ distillations	Re_2O_7 (b.p. 362°C)— from Mo		RuO_4 (decomp. 108°C) RuOF (b.p. 184°C)
Other useful separations/ comments	Ion exchange—from Mo Yields yellow-brown precip. with HCl + $SnCl_2$ + KCNS	$RhCl_3$: red Yields yellow color with thiocyanate	Highly toxic volatile compounds $RuCl_3$: dark brown
Best methods at high concentrations	Grav.: as tetraphenylarsonium perrhenate; as nitron perrhenate ICP-OES: 197.3 nm	Grav.: as Rh metal after precip. as the acid sulfide and reduction in H_2 ICP-OES: 233.5 nm	Grav.: as Ru metal after precip. as the acid sulfide and reduction in H_2 ICP-OES: 240.3 nm
Best methods at low concentrations	ICP-OES: 197.3 nm	ICP-OES: 233.5 nm FAA: 343.5 nm Color: sodium hypochlorite	ICP-OES: 240.3 nm FAA: 349.9 nm Color: p-nitrosodimethylanaline; rubeanic acid

Element	Selenium (Se) 34 78.96 +4, +6, -2	Silicon (Si) 14 28.086 +4	Silver (Ag) 47 107.868 +1
Useful precipitations	Hydrazine sulfate: as the element (p) Accompanies Fe + NH_4OH: (p)	Fuming with $HClO_4$ or H_2SO_4: as silicic acid (p)	NaOH: (p) NH_4OH: (s) Chloride: (p) Acid sulfide: (p) Basic sulfide: (p)
Useful solvent extractions		Silicomolybdate-N-butanol: [ox.: yellow(o); red.: blue (a)]	
Useful volatilizations/ distillations	$SeOCl_2$ (b.p. 175.5°C) H_2Se (gas at R.T.)	SiF_4 (gas at R.T.) H_2SiF_6 (b.p. 300°C)	
Other useful separations/ comments	Highly toxic	Carries down B as it precipitates as SiO_2	Pb^{2+}, Hg_2^{2+}, Tl^+, Bi^{3+}, Sb^{3+} may contaminate AgCl
Best methods at high concentrations	Grav.: as the element, reduced by H_2SO_3, $SnCl_2$, or hydroxylamine-HCl	Grav.: as SiO_2 after dehydration with $HClO_4$ and/ or H_2SO_4	Fire Assay Volum.: titr. with thiocyanate Grav.: as AgCl (protect from light); as metal— electroplate out of oxalate or persulfate sol.
Best methods at low concentrations	ICP-OES: 196.0 nm (Intf.: Al, Co, Fe, Mn, Mg) FAA:/GFAA: 196.0 nm Color: 3, 3′-diaminobenzidine	Color: silicomolybdate FAA: 251.6 nm ICP-OES: 251.6 nm	FAA/GFAA: 328.1 nm ICP-OES: 328.1 nm

Element	Strontium (Sr) 38 87.62 +2	Sulfur (S) 16 32.066 +4, +6, -2	Tantalum (Ta) 73 180.948 +5
Useful precipitations	Oxalate: (p)—from Ba and Mg NaOH fusion/H_2O leach: (p) Sulfate: (p)	$BaCl_2$: as $BaSO_4$: (p)	Cupferron: (p) NH_4OH: (p) NaOH: (p) Hydrolysis with H_2SO_3 after fuming with $HClO_4$: as hydrous Ta_2O_5: (p)
Useful solvent extractions			
Useful volatilizations/ distillations		H_2S (gas at R.T.)	
Other useful separations/ comments	Mercury cathode: (a) Scarlet red flame test	H_2S is highly toxic Ion exchange (alumina column)	F^-/Cl^- system anion exchange No color with H_2O_2 (unlike Nb in H_2SO_4 and Ti in dilute acid)
Best methods at high concentrations	ICP-OES: 407.8 nm Grav.: as oxalate	Grav.: as $BaSO_4$— first oxidize S with Br_2—reduce Fe before adding $BaCl_2$ Volum.: Ignite in O_2 to SO_2, titr. iodimetrically	Grav.: as Ta_2O_5 after ion exchange separation, cupferron precipitation and ignition
Best methods at low concentrations	FAA: 407.8 nm ICP-OES: 407.8 nm	IR abs: ignite to SO_2 Color: pararosaniline (after ignition to SO_2)	Color: pyrogallol ICP-OES: 240.0 nm (Intf.: Co, Fe)

Element	Tellurium (Te) 52 127.60 +4, +6, -2	Thallium (Tl) 81 204.383 +1, +3	Thorium (Th) 90 232.038 +4
Useful precipitations	Hydrazine sulfate or sodium hypophosphite: as the element (p) Accompanies Fe + NH_4OH: (p) Acid sulfide: (p) Basic sulfide: (s)	Chromate: as Tl_2CrO_4: (p); Iodide: as TlI (p); Chloride : as TlCl (p); Weak acid sulfide: (p); Basic sulfide: (p)	NH_4OH: (p) NaOH: (p) Fluoride: (p) Oxalate (pH 3-4): (p) Iodate: (p) $(NH_4)_2HPO_4$: (p)
Useful solvent extractions	TOPO-MIBK: (o)	Ethyl ether/ HCl: (o) TOPO-MIBK: (o)	Cupferron-butyl acetate/ 0.5M H_2SO_4: (o)
Useful volatilizations/ distillations	$TeCl_2$ (b.p. 328°C) H_2Te (gas at R.T.)		
Other useful separations/ comments	Highly toxic; Se can be distilled away from Te (HCl/H_2SO_4)	Highly toxic; Imparts emerald-green color to colorless flame; Fluoresces in NaCl under short λ UV	Highly toxic; H_2O_2: (p) in HNO_3 medium
Best methods at high concentrations	Volum.: titr. with $K_2Cr_2O_7$ (diphenylamine ind.) Grav.: as the element (H_2SO_3 + hydrazine · HCl reduction)	Grav.: as Tl_2CrO_4 from NH_4OH sol. Volum.: Titr. with Ce(IV) ICP-OES: 190.9 nm	Grav.: as ThO_2 after precip. with oxalic acid ICP-OES: 283.7 nm
Best methods at low concentrations	FAA/GFAA: 214.3 nm ICP-OES: 214.3 nm Color: iodine complex	FAA/GFAA: 276.8 nm ICP-OES: 190.9 nm	ICP-OES: 283.7 nm

Element	Tin (Sn) 50 118.710 +2, <u>+4</u>	Titanium (Ti) 22 47.88 +3, <u>+4</u>	Tungsten (W) 74 183.84 (+3), <u>+6</u>
Useful precipitations	Acid sulfide: (p) Basic sulfide: (s) NH_4OH: (p) NaOH: (s) Cupferron: (p)	NH_4OH: (p) NaOH: (p) Cupferron: (p) Na_2CO_3 fusion/ H_2O leach: (p)	NaOH: (s) NH_4OH: (s) Basic sulfide: (s) α-Benzoinoxime (coprecip. with excess Mo only): (p)
Useful solvent extractions	TOPO-MIBK: (o)		
Useful volatilizations/ distillations	$SnCl_4$ (b.p. 114.1°C) SnI_4 (b.p. 364.5°C)		
Other useful separations/ comments	May be electrodeposited from acid oxalate sol.	Ti(III): violet Ti(IV): colorless Phosphate is insoluble	Cinchonine aids precip. of WO_3 by dilute acid hydrolysis
Best methods at high concentrations	Volum.: Titr. with I_2 after reduction with metallic Pb, Ni, Al, or Zn Grav.: as SnO_2 from HNO_3	Grav.: as TiO_2 after ion exchange, NaOH sep. from W, cupferron precip. and ignition Volum.: Jones reductor into excess std. ferric sulfate; back-tir. with $KMnO_4$	Grav.: as WO_3 after ion exchange and precip. with cinchonine (diss. in NaOH and weigh impurities)
Best methods at low concentrations	FAA/GFAA: 286.3 nm ICP-OES: 189.9 nm Color: phenylfluorone	FAA: 364.3 nm ICP-OES: 334.9 nm Color: H_2O_2 in dil. H_2SO_4; diantipyrlmethane; hydroquinone in conc. H_2SO_4	ICP-OES: 207.9 nm (Intf. Al) Color: hydroquinone in conc. H_2SO_4; toluene-3,4-dithiol; thiocyanate

Element	Uranium (U) 92 238.029 +4, <u>+6</u>	Vanadium (V) 23 50.942 +3, +4, <u>+5</u>	Zinc (Zn) 30 65.39 +2	Zirconium (Zr) 40 91.224 +4
Useful precipitations	NaOH: (p); NH_4OH: (p)— must be V & CO_2-free; Cupferron: (p); $(NH_4)_2CO_3$: (s) —from Fe, Al & Cr which precip.	Na_2O_2 + NaOH: (s) Cupferron: (p); Accompanies Fe + NH_4OH: (p) NH_4OH: (s) NaOH: (s)	NH_4OH: (s) NaOH: (s) Acid sulfide: (s) Basic sulfide: (p) $(NH_4)_2HPO_4$: (p)	NaOH: (p) NH_4OH: (p) Cupferron: (p) p-Bromomandelic acid: (p) $(NH_4)_2HPO_4$: (p) In all cases Hf accompanies
Useful solvent extractions	Ethyl ether/HNO_3: UO_2^{2+}— (o)		Dithizone-$CHCl_3$	TOPO-Cyclohexane/ HNO_3: (o) Hf accompanies
Useful volatilizations/ distillations				
Other useful separations/comments	Highly toxic U(VI): yellow U(IV): green Forms soluble complex with CO_3^{2-}	Mercury cathode: (a) III: V^{3+} (blue); IV: $V_2O_2^{4+}$ (blue); VO^{2+} (blue); V: VO_2^+ (yellow); VO_3^- (orange)	Amphoteric Whitish flame test	Mercury cathode: (a) Zr and Hf can be separated by ion exchange
Best methods at high concentrations	Grav.: as U_3O_8 after NH_4OH precip. and ignition Volum.: Titr. with $KMnO_4$	Volum.: Oxidize with boiling HNO_3, titr. potentiometrically with ferrous ammonium sulfate	Grav.: as $Zn_2P_2O_7$ after precip. with $(NH_4)_2HPO_4$ and ignition Volum.: Potentiometric titr. with $K_2Fe(CN)_6$	Grav.: as ZrO_2 after cupferron precip. and ignition; as ZrP_2O_7 after $(NH_4)_2HPO_4$ precip. and ignition (do not overwash)
Best methods at low concentrations	ICP-OES: 386.0 nm Fluorimetry: of fused NaF + sample with UV (<300 nm) excitation	FAA: 318.4 nm ICP-OES: 292.4 nm (Intf.: Mo) Color: H_2O_2 (unlike the Ti complex, not bleached by HF)	FAA: 213.9 nm ICP-OES: 213.9 nm (Intf.: Ni, Cu) Color: dithizone Fluorimetry: benzoin complex	ICP-OES: 339.1 nm Color: Pyrocatechol Violet; Xylenol Orange

Appendix IIA

The Alkali Metals

NOTE: The only stable aqueous oxidation state is +1. All can be separated by ion exchange/ ion chromatography. Francium has no stable isotopes.

Element	Useful Precipitations	Useful Solvent Extractions	Flame Test	Flame Emission/ ICP Wavelength	FAA Wavelength	Other Methods
Lithium (Li) 3 6.941			Crimson	460.3 nm	670.8 nm	Fluorimetry: 8-Hydroxy-quinoline
Sodium (Na) 11 22.990	Zinc uranyl acetate: (p)		Yellow	330.2 nm (Many intf.)	589.0 nm	
Potassium (K) 19 39.098	ClO_4^-: (p) IO_4^-: (p) $PtCl_6^{2-}$: (p) Tetraphenylborate: (p)	18 - Crown - 6 Ether	Rose/violet	766.5 nm	766.5 nm	X-ray fluorescence: $K\alpha_1$ = 3.7412 Å
Rubidium (Rb) 37 85.468	ClO_4^-: (p) Tetraphenylborate: (p)	18 - Crown - 6 Ether	Rose/violet	420.2 nm	780.0 nm	X-ray fluorescence $K\alpha_1$ = 0.9255 Å
Cesium (Cs) 55 132.905	ClO_4^-: (p) Tartrate: (p) Tetraphenylborate: (p)	21 - Crown - 7 Ether	Red/violet	452.7 nm	852.1 nm	X-ray fluorescence $K\alpha_1$ = 0.4003 Å

Appendix IIB

The Rare Earths

NOTE: This category includes the lanthanides and chemically similar elements. All form precipitates with HF, ammonium oxalate, NH_4OH, NaOH, and Na_2CO_3/H_2O leach. All are left in the aqueous solution on the mercury cathode. All can be separated by ion exchange. All can be determined by X-ray fluorescence. Promethium has been excluded since it has no stable isotopes.

Element	Comments	ICP Wavelength	FAA Wavelength	Other Methods
Scandium (Sc) 21 44.956 +3	Forms complexes more readily than the lanthanides	361.4 nm		
Yttrium (Y) 39 88.906 +3	Properties are half-way between Sc and La	371.0 nm	410.2 nm	
Lanthanum (La) 57 138.906 +3	I_2 + $La(OH)_3$: blue color (no other rare earth exhibits this effect)	398.8 nm		
Cerium (Ce) 58 140.115 +3, +4	Ce^{3+}: colorless Ce^{4+}: orange-red	418.6 nm (Intf.: Zr)		Volum.: oxidize with persulfate, titr. with ferrous ammonium sulfate (potentiometric)
Praseodymium (Pr) 59 140.908 +3	Pr^{3+}: green	390.8 nm		
Neodymium (Nd) 60 144.24 +3	Nd^{3+}: pale violet	401.2 nm		
Samarium (Sm) 62 150.36 (+2), +3	Sm^{2+}: red (decomposes in H_2O) Sm^{3+}: yellow	359.3 nm	429.7 nm	
Europium (Eu) 63 151.965 +2, +3	Eu^{2+}: colorless Eu^{3+}: pale pink	382.0 nm	459.4 nm	Volum.: Jones reductor into excess std. ferric sulfate; back-titr. with $K_2Cr_2O_7$ (Sm and Y *not* reduced and do not interfere)
Gadolinium (Gd) 64 157.25 +3	Gd^{3+}: colorless	342.2 nm		
Terbium (Tb) 65 158.925 +3	Tb^{3+}: pale pink	350.9 nm		
Dysprosium (Dy) 66 162.50 +3	Dy^{3+}: yellow	353.2 nm	421.2 nm	

Element	Comments	ICP Wavelength	FAA Wavelength	Other Methods
Holmium (Ho) 67 164.930 +3	Ho^{3+}: yellow	345.6 nm		
Erbium (Er) 68 167.26 +3	Er^{3+}: pale violet	326.5 nm	400.8 nm	
Thulium (Tm) 69 168.934 +3	Tm^{3+}: green	313.1 nm	371.8 nm	
Ytterbium (Yb) 70 173.04 (+2), +3	Yb^{2+}: only with applied potential (-1.5V) Yb^{3+}: yellow	328.9 nm	398.8 nm	
Lutetium (Lu) 71 174.967 +3	Lu^{3+}: colorless	261.5 nm		