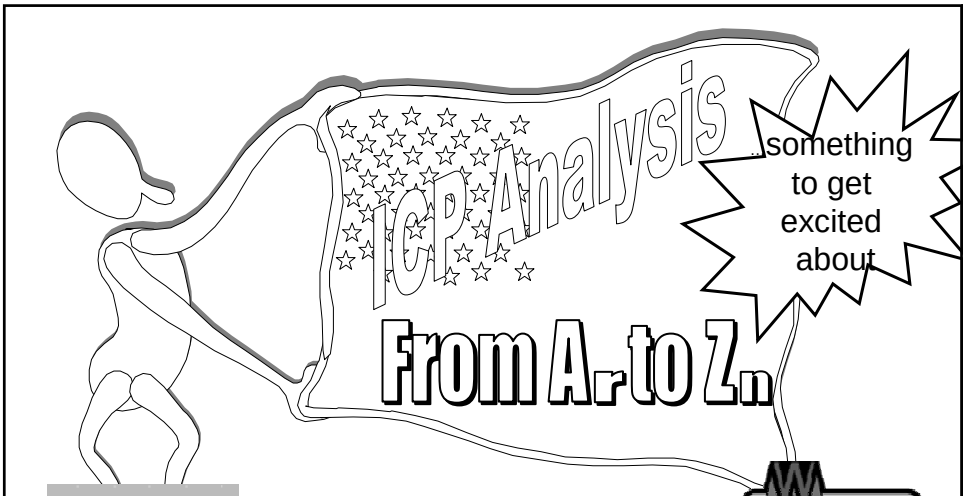

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WSLH WISCONSIN STATE LABORATORY OF HYGIENE

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With additional support from: **Perkin-Elmer, Jobin-Yvon, Leeman Labs**

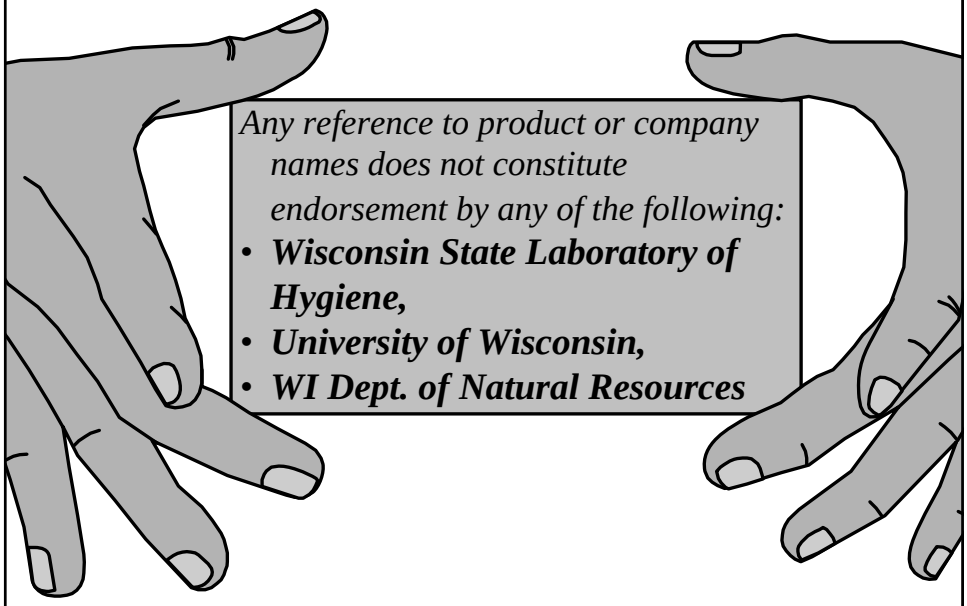
ICP Analysis:

FROM 18 Ar 39.95 **TO** 30 Zn 65.39

	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18
								------- VIII -------										
								------- 8 -------										
1	H 1.008																	He 4.003
2	Li 6.941	Be 9.012											B 10.81	C 12.01	N 14.01	O 16.00	F 19.00	Ne 20.18
3	Na 22.99	Mg 24.31											Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45	Ar 39.95
4	K 39.10	Ca 40.08	Sc 44.96	Ti 47.88	V 50.94	Cr 52.00	Mn 54.94	Fe 55.85	Co 58.47	Ni 58.69	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.59	As 74.92	Se 78.96	Br 79.90	Kr 83.80
5	Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc (98)	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	Xe 131.3
6	Cs 132.9	Ba 137.3	La* 138.9	Hf 178.5	Ta 180.9	W 183.9	Re 186.2	Os 190.2	Ir 190.2	Pt 195.1	Au 197.0	Hg 200.5	Tl 204.4	Pb 207.2	Bi 209.0	Po (210)	At (210)	Rn (222)
7	Fr (223)	Ra (226)	Ac~ (227)	Rf (257)	Db (260)	Sg (263)	Bh (262)	Hs (265)	Mt (266)	--- 0	--- 0	--- 0		--- 0		--- 0		--- 0

Lanthanide Series*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinide Series~	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Disclaimer



Any reference to product or company names does not constitute endorsement by any of the following:

- ***Wisconsin State Laboratory of Hygiene,***
- ***University of Wisconsin,***
- ***WI Dept. of Natural Resources***

Warm-up

- T/F ICP/AES can quantitate Fe+3 and Fe+2 separately
- T/F Approved EPA methods require calibration with more than a blank and a single level standard
- T/F A “Radial” torch requires the torch to be oriented vertically
- T/F Using default 75-125% matrix spike control limits is acceptable
- T/F Interference Check Samples do not need to contain target analytes (in addition to interferent elements).
- T/F Interference checks must be run at the beginning AND end of each analytical sequence
- T/F Approved methods require analysis of a solution containing 10 ppm each of As, Pb, Se and Tl each day.

Warm-up

- T/F The ICP torch burns hotter than an F-16 exhaust in 8th stage afterburner
- T/F Samples that are not digested must be matrix (acid) matched or use an internal standard
- T/F Interference Correction Factors can be either positive or negative
- T/F Interelement Correction Factors are mandatory

Why ICP Training? - Common Deficiencies

NOT establishing IECs

- The laboratory has not determined the extent of spectral interferences; interelement correction factors are not employed.
- Although the laboratory analyzes only drinking water samples, interelement correction factors have not been established and spectral interference check solutions are not analyzed to support the absence of correction factors.
- Correction factors on the ICP are only established when the apparent signal of an analyte resulting from an interfering element is at or above the limit of quantitation (LOQ) of the analyte.

Only establishing IECs for **limited** # of analytes

- Interelement correction (IEC) factors have only been established for the four major cations (aluminum, iron, calcium, and magnesium).

ICS data shows inadequate IECs

- Current interelement correction factors do not provide acceptable correction for ….

Why ICP Training? - Common Deficiencies

NOT analyzing ICSs

- Interference check samples (ICS) are not analyzed
- The laboratory does not check the validity of the ICP interelement correction factors using appropriate interference check standards.
- Although interference check samples are analyzed with each batch of samples, analysts do not evaluate the results of these determinations.
- Interference check samples are not properly evaluated.

NOT establishing LDR

- The linear dynamic range for each element has not been established.
- The linear dynamic range is not performed every six months for those analytes that approach the upper limit.

Other

- The laboratory evaluates all matrix spikes against acceptance criteria of 70-130%.

Session Goals

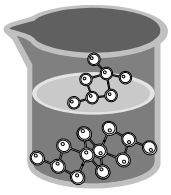
- **Simplify the technology**
- **Share the knowledge**
- **Increase understanding**
- **Provide explanations supported by data**
- **Offer logical/defensible solutions**
- **Generate new thinking**

Discussion Topics

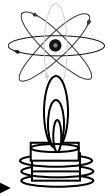
1. ICP theory and principles of operation
2. Operational differences by ICP type
   - *sequential vs. simultaneous*
   - *direct readers,*
   - *solid state detection,*
   - *axial v. radial v. Dual View*
3. Instrument prep prior to analysis
4. Calibration
   - *Sample preparation concerns*
   - *Standard preparation*
   - *Levels & Concentrations*
5. Initial Demonstration of Capability
   - *LOD (not IDL)*
   - *Background Correction*
   - *Interference Correction*
   - *Linear Dynamic Range*
6. Basic Quality Control
   - *Blanks*
   - *LCS*
   - *Spikes*
   - *Duplicates*
   - *Internal Standards*
   - *Verifying IECs*
7. Record keeping
8. Troubleshooting
9. Overview of ICP/MS
10. Which configuration is for you?

☆ Panel Discussion: Q&A Forum ☆

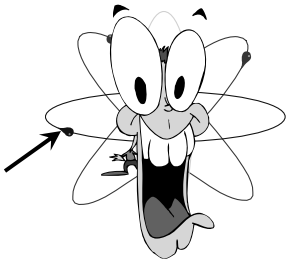
Basic theory



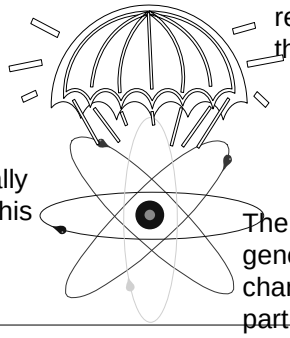
Sample, containing infinite numbers of molecules, is aspirated into the ICP torch



Inside the plasma, the sample is initially vaporized. At this point all molecules are atomized.



Then, atoms collide with electrons and Argon ions causing the atoms to become excited



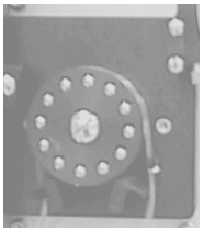
The atoms naturally drop back to ground state, releasing energy in the form of light

$+ \lambda$

The wavelength generated is characteristic of the particular element

Sample aspiration

First step is to transport the sample into the ICP system...

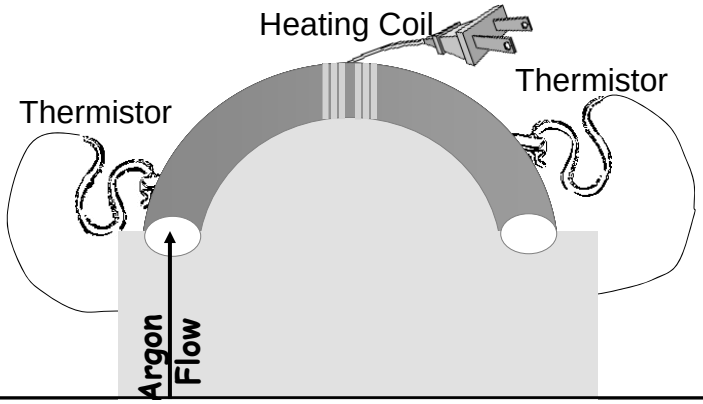


Peristaltic pump is critical

- the flow rate of the solution into the nebulizer is fixed
- eliminates variability due to sample viscosity and surface tension.
- allows for more rapid rinse-through of the nebulizer and spray chamber.

Mass Flow Controller

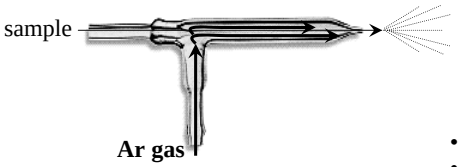
Provides absolute control of gas flow
Eliminates “pulsing” in the nebulizer or spray chamber
“Pulsing” can result in result variability (high %RSD).
Used for plasma, auxiliary, carrier and any optional gas lines.
Help with viscosity problems



The Nebulizer

The sample can only be introduced into the plasma as an ultra-fine mist of small droplets (aerosolized). This is accomplished using a nebulizer.

Glass concentric (Meinhard type)

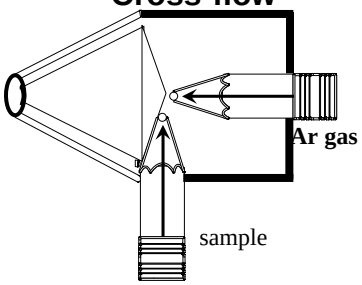


low flow (vs. AA) requires minute orifice sensitive to clogging, so salt solutions should be kept below 1% concentration glass can be corroded by acidic solutions

Micro-concentric

- ability to run small samples (100 µL/min).
- inert construction and low memory effects, e.g., B, Hg.
- minimizes small drop formation
- less sensitive to acids

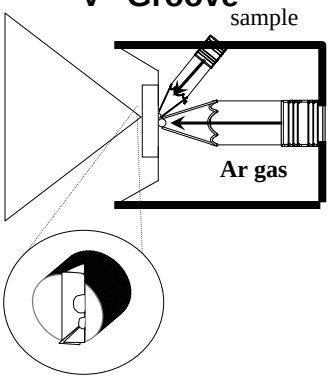
Cross-flow



- **perpendicular vs. parallel gas flow**
- less clogging than a concentric nebuliser (larger diameter capillary, longer distance)
- generally not as efficient at creating the small enough droplets needed for ICP analyses.
- generally more rugged and corrosion-resistant than glass concentric nebulizers.

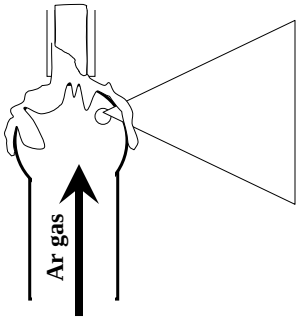
The Nebulizer

"V" Groove



- Sample flows down a groove which has a small hole in the center for the nebulizing gas.
- being used increasingly for nebulization of solutions containing high salt and particulate concentrations.

Babington (modified"V" Groove)



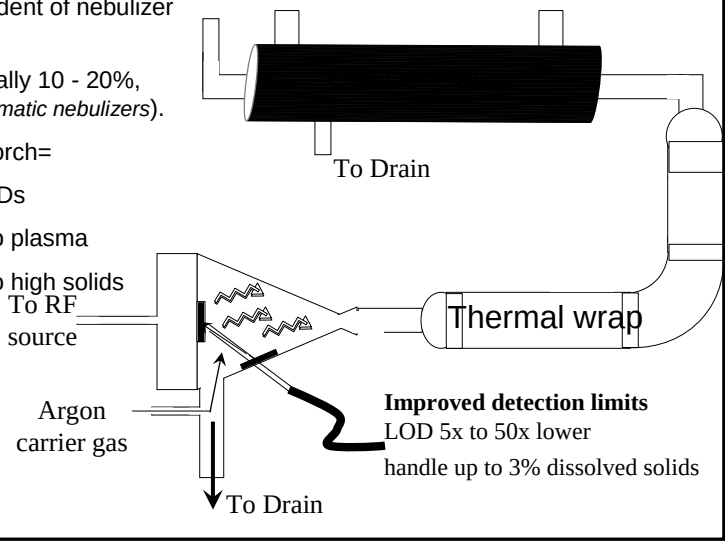
- originally developed to aerosolize fuel oil for industrial burners.
- liquid sample flows over a smooth surface with a small orifice
- High-speed argon gas emanating from the orifice shears the sheet of liquid into small drops.
- least susceptible to clogging
- can nebulize very viscous liquids.

The Nebulizer

- Liquid sample pumped onto an piezoelectric transducer.
- Ultrasonic waves aerosolize the sample - independent of nebulizer gas flow.
- Efficiency is typically 10 - 20%, (≥ *10X typical pneumatic nebulizers*).
- More sample to torch=
  - •10X lower LODs
  - • more water to plasma
- Still susceptible to high solids

Ultrasonic nebulizers

Greater efficiency = more water in the torch
Post-nebulizer desolvation unit removes water



Improved detection limits
LOD 5x to 50x lower
handle up to 3% dissolved solids

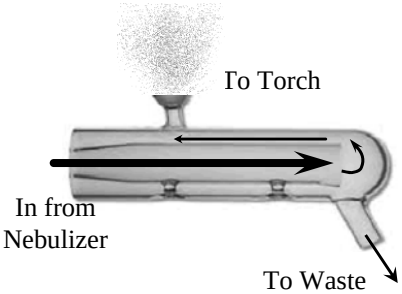
Spray Chamber

Two main functions:

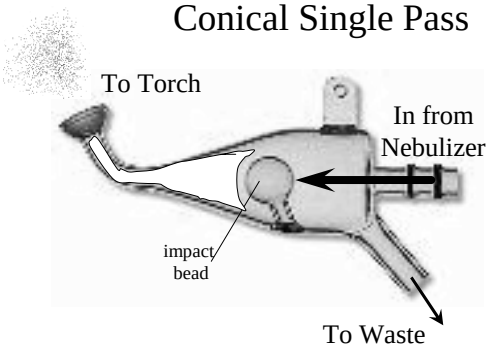
1. **Filter large droplets from the aerosol coming out of the nebulizer**
   The aerosol entering the torch must be limited to minuscule sized droplets (~ 10 µm) or either the plasma will be interrupted or the torch will be extinguished.
2. **Smooth out any "pulses".** often due to pumping of the solution.

- For most systems, only about 1-5% of the sample is converted into the requisite droplet range. The rest goes to drainage.
- Spray chamber component material can be an important consideration. Need to be corrosion-resistant materials to allow introduction of matrices containing such as hydrofluoric acid

Scott Double Pass

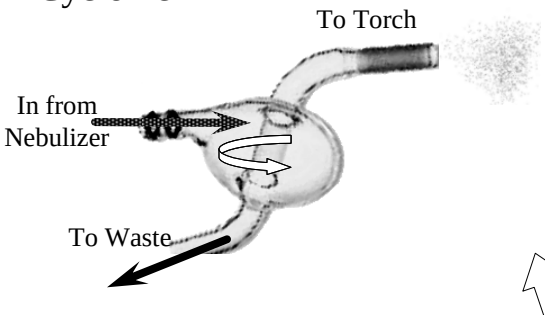


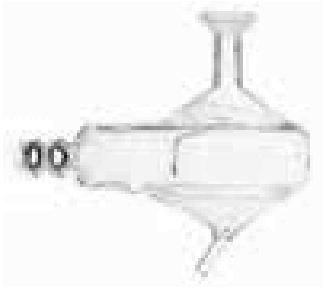
Conical Single Pass



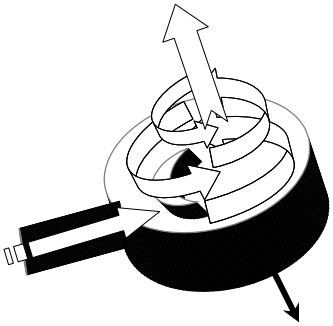
Spray Chamber

Cyclonic





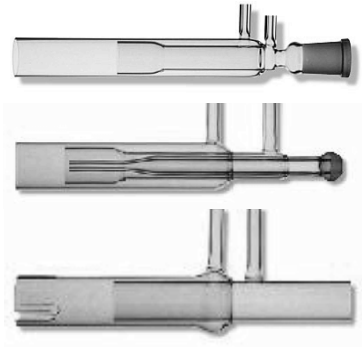
This design provides optimal separation of droplet sizes which translates to better precision.



The Torch

The "classic" ICP torch = a one-piece torch.
3 concentric quartz tubes sealed together.
good plasma stability and easy to use.
Disadvantages of the one-piece torch:

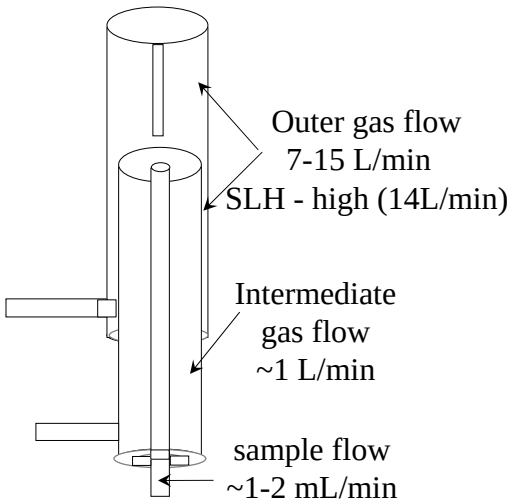
1) not resistant to corrosion by HF
2) if damaged, replace entire torch
3) difficult to manufacture



Demountable types now most popular.
Replace individual tubes without replacing entire torch.
The main advantages

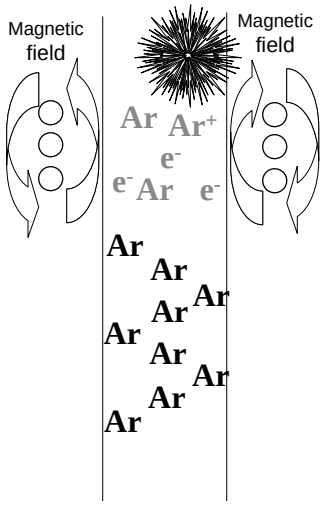
1) lower torch replacement costs,
2) can use a variety of injector tubes
   A. corrosion-resistant ceramic
   B. narrow-bore injectors for organic solvents, and
   C. wide-bore for hi TDS samples

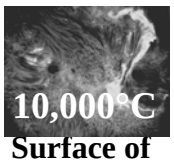
The Torch



The Torch

- Upper portion of torch surrounded by a water-cooled induction coil
- Induction coil connected to RF supply
- RF operates at either 27 or 41 MHz
- Argon flows through outer torch ring at ~ 5 -20 L/min.
- Spark from a Tesla coil initiates ionization of Argon
- The electrons and ions interact with the magnetic field produced by the induction coil-generating more electrons.
- Once the argon conducts, the plasma is formed spontaneously if the flow patterns inside the tube are proper. The ions and the electrons low in the closed annular paths.
- Ohmic heating develops as a result the resistance of the ions and electrons to this movement.

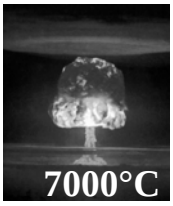




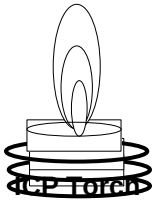
Surface of the sun?

molten lava?

Candle flame molten steel?



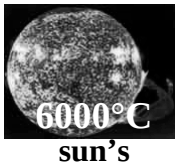
A Nuke?
(dominant thermal pulse)



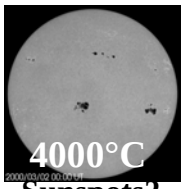
8000-10000°C

lightning?

An F-16 in full afterburner?



sun's photosphere?



Sunspots?

The Plasma

…is partially ionized gas

...is generated from radio frequency (RF) magnetic fields induced by a copper coil which is wound around the top of a quartz torch.

… is less susceptible to interferences.

Temperatures such that all chemical bonds are broken---causing complete atomization of the analyte solution

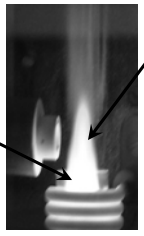
If the charged particles flow through the field, cutting the magnetic lines of force, ohmic heating results.

The standard radio frequency used is either 27 or 41MHz.

Excitation region

The bright, white, donut shaped region at the top of the torch. (base of the plasma)

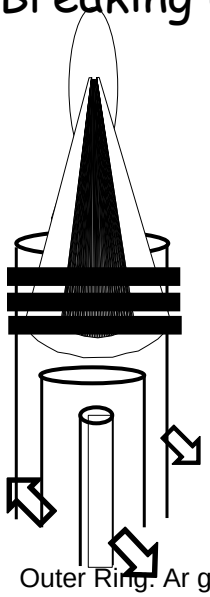
Radiation : continuum w/ Ar line spectrum superimposed.
Temperature: 8000-10000K



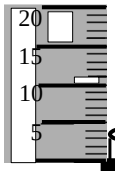
Observation region

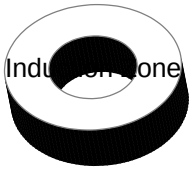
The bluish flame shaped region above the torch
Radiation: A spectrum consisting of emission lines from the analyte plus lines from ions in the torch
Temperature: 1000-8000K

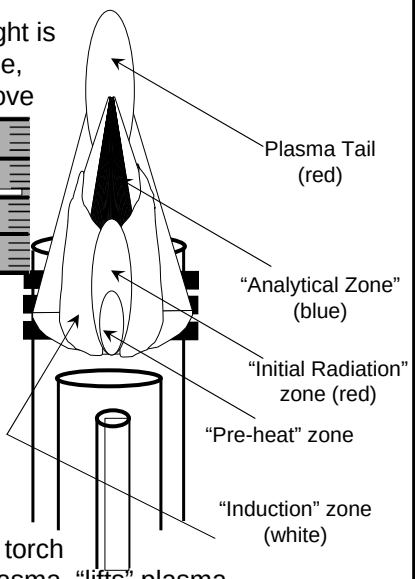
Breaking down the Plasma



Optimal viewing height is in the Analytical Zone, about 15-18 mm above the load coil.

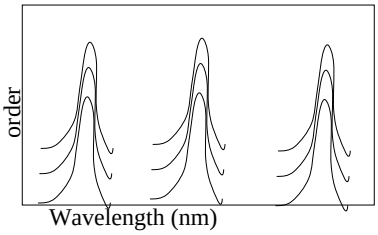




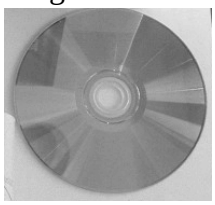


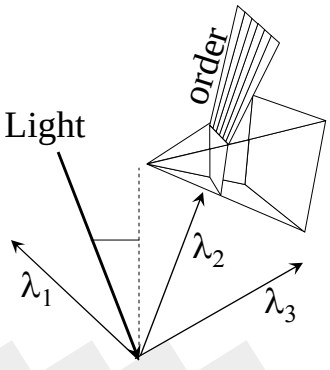
Outer Ring: Ar gas is fuel for plasma, cools torch
Inner Ring: Ar gas facilitates sample into plasma, "lifts" plasma
Sample Injector: Sample "punches" hole through plasma

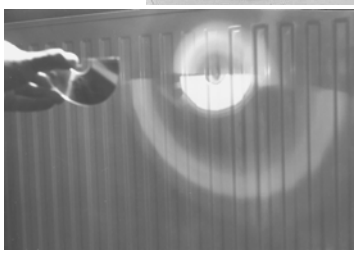
Splitting Light: Diffraction Gratings



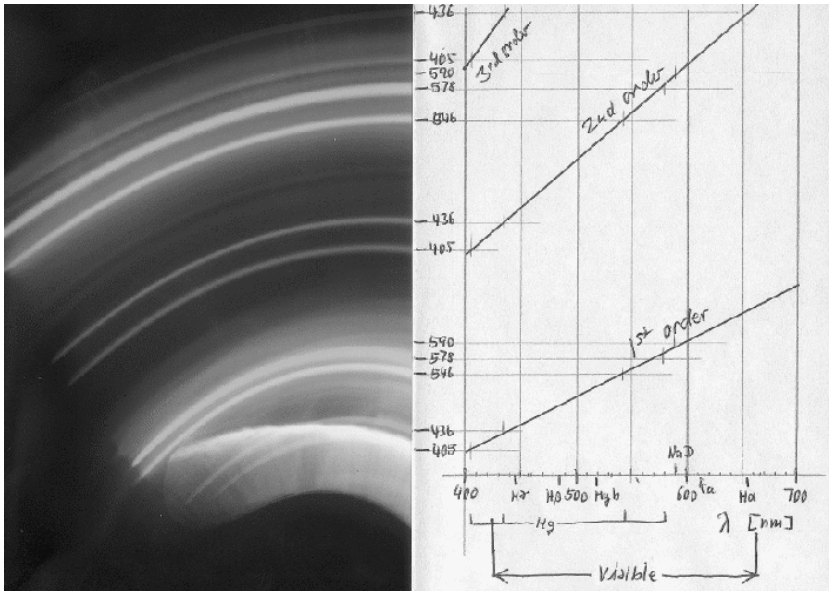
Echelle gratings plus a prism provide 2-D separation of light. The echelle grating separates the polychromatic emission into wavelengths, the prism then separates the wavelengths into orders. A similar effect can be seen as light flashes off a compact disc.







Orders of Light: CD-ROM example



Obtained via the Internet…site no longer "live"

Detection Systems

Monochromator vs. polychromator

Sequential vs. simultaneous

Diffraction grating systems

PMT vs. PDA vs. CCD vs. CID vs. SCD

Photomultiplier Tubes

Photo-Diode Arrays

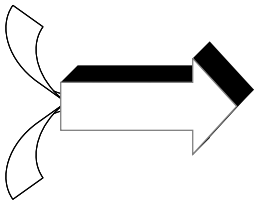
Charge-Coupled Devices

Charge-Injected Devices

Segmented-Array CCD

Operational differences by ICP type

Sequential — Monochromator



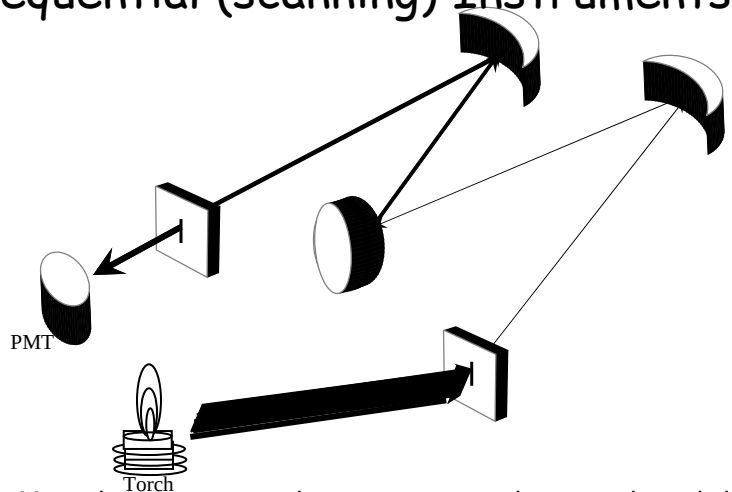
Hybrid Systems
(offering sequential + simultaneous)

Simultaneous

Polychromator — PMT (Direct Reader) — Multiple PMTs (~30)- each set to a fixed λ

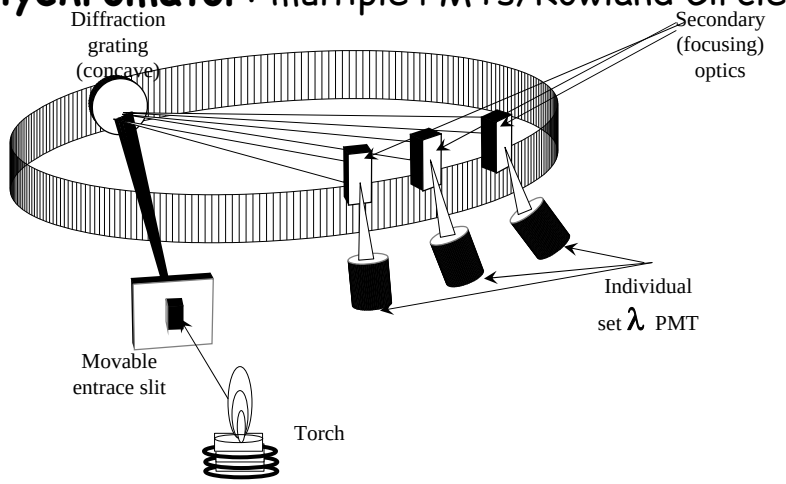
Solid State detectors (microchips)

Sequential (scanning) Instruments



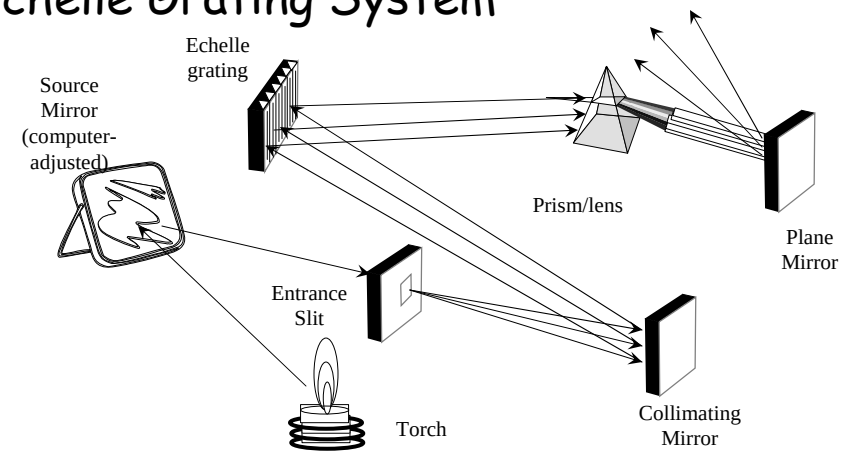
- Monochromator scans the spectrum, pausing at each analytical wavelength long enough to achieve desired signal-to-noise ratio.
- Theoretically, no limit to the number of wavelengths analyzed per sample.
- Real world: the number of wavelengths is limited by the volume of sample, sample pumping rate, and time required at each wavelength.

Polychromator: multiple PMTs/Rowland Circle



- Up to 60 photomultiplier tubes (PMT) placed directly in the curved focal plane of a concave diffraction grating.
- Multi- "channel" system allows simultaneous acquisition from each PMT.
- Up to 60 elements can be analyzed in the same amount of time that it takes to analyze one element on a scanning instrument.
- Saves time, sample, and money.

Echelle Grating System

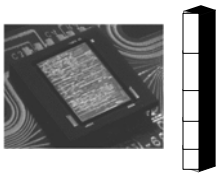


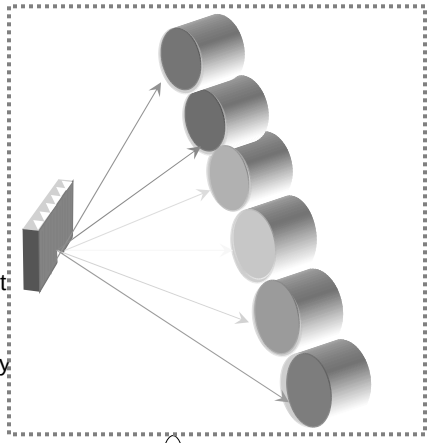
- Low resolution grating disperses the radiation onto a prism.
- The one-dimensional radiation that hits the prism is further dispersed into a two dimensional spectrum that is focused on an aperture (slit) plate that is fitted with either PMTs or diode arrays.
- Provides much better resolution than a single dispersing monochromator and allows simultaneous detection of several elements.

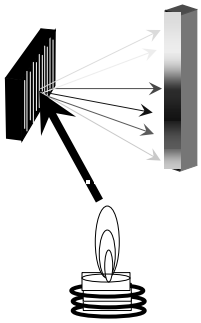
Solid State Detectors

PhotoDiode Arrays **PMT Polychromator** **vs. 1-D PDA detection**

PDA







- 1-dimensional vs. 1-pt
- PMT: instantaneous light energy
- PDA: total light energy over integration time
- smaller so more (~1024) can be put in an instrument.
- more elements or multiple "lines" per element

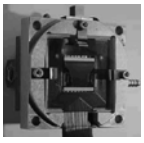
Key advantage: smaller size!
Microchip vs. multiple PMTs
PMT size limits the # of "lines"

Solid State Detectors

State-of-the-Art: 2-Dimensional detection

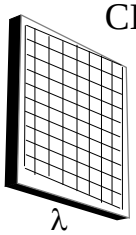
Charge-Coupled Device

CCD



Charge-Injected Device

CID

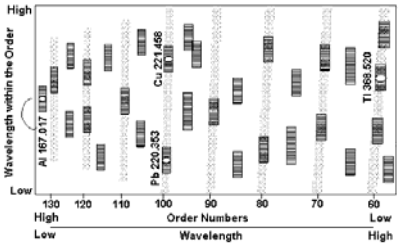


Segmented-array CCD Detector

SCD

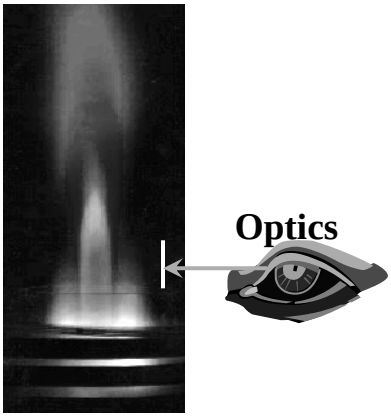
- Pixels at locations of preferred λs.
- 70 most common elements
- 236 most common lines
- ~200 subarrays placed in 2-D
- Subarrays=20-80 pixels each
- Pixels=12.5 um x 80-170 um high--depending on wavelength

- Introduces 2-dimensional technology
- Light split into wavelengths AND orders
- Records data from >95% of spectrum
- Allows 2-D background correction
- The two types differ only in how they are "read" by the electronics.
- CIDs suffer less from **blooming**



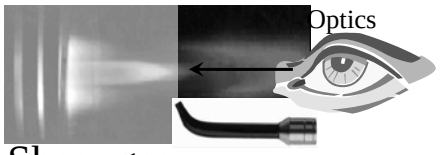
From: Perkin-Elmer, 1999. Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry

Radial Torch Alignment



- **Conventional ICP**
- **Radial or “side-on” viewing**
- **Focused on the “analytical zone”**
- **Region of least amount of interference**
- **More stable, lower detection in challenging matrices**

Axial Torch Alignment

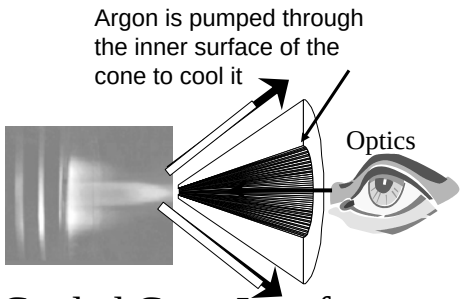


Shear gas

A “shear gas” can be used to “blast away” the tail plume... giving the optics a clear shot

Use of a “cooled cone interface” is another way to deflect the tail plume (although this can be subject to build-up)

While axial or “end-on” view “sees’ more emission from elements, it also “sees” more interference.
Heat from tail plume also interferes with optics and must be dealt with.

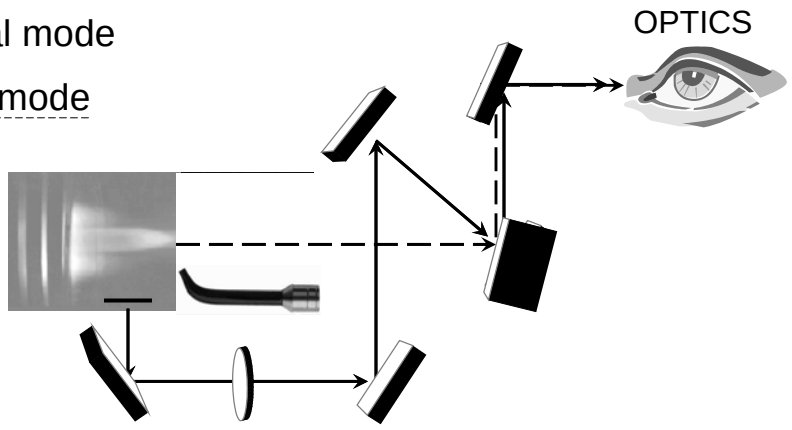


Cooled Cone Interface

"Dual View" Systems

Radial mode

Axial mode



It would be cool if: they just put 2 torches in it (but they don't)

So… how do they do it?: A system of mirrors allows the user to select either radial or axial viewing.

Daily Instrument Preparation

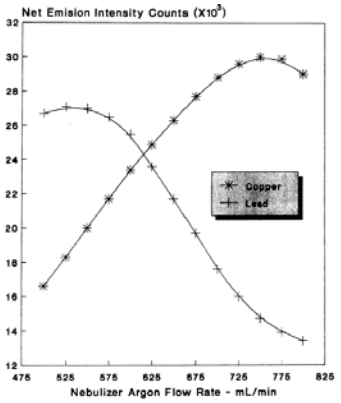
Adjust pump "windings" to eliminate "mist" in spray chamber when pump is off

Optimize Viewing Height
(Plasma Solution)

Adjust nebulizer pressure to setpoint
(Yttrium Bullet Test)

Verify sample flow

Profile the instrument



Mist in the Spray Chamber

Method Comparison - Plasma Optimization

	200.7	=	6010		SM3120B
10.2.1	Allow ICP to warm up 30-60 min	10.1	Allow ICP to warm up ≥ 30 min	4.c.	Allow ICP to warm up ≥ 30 min
10.2.1	Aspirate 1000 ppm Y solution.	10.1.3.1	Aspirate 1000 ppm Y solution.	4.c.	For polychromators, perform optical alignment using the profile lamp or solution
10.2.1	Adjust aerosol carrier gas flow rate (thru the nebulizer) so a definitive blue emission region extends 5-20 mm above the top of the work coil	10.1.3.1	Adjust aerosol carrier gas flow rate (thru the nebulizer) so a definitive blue emission region extends 5-20 mm above the top of the work coil	4.c.	Check alignment of plasma torch
				4.c.	Check alignment of spectrometer entrance slit
10.2.2	Aspirate known volume of calibration blank ≥ 3 mins.	10.1.3.2	Aspirate known volume of calibration blank ≥ 3 mins.		
10.2.2	Divide volume used by time (mins).	10.1.3.2	Divide volume used by time (mins).		
10.2.2	Set peristaltic pump to deliver this rate in a steady/even flow.	10.1.3.2	Set peristaltic pump to deliver this rate in a steady/even flow.		

200.7/6010: Y "bullet" test v. SM open ended
200.7/6010: set peristaltic pump v. SM no discussion

Method Comparison - Plasma Optimization

200.7 6010

10.2.3 7.15	10.1.3.3	Aspirate plasma solution. 10 ppm each: As, Pb, Se, Tl. *Can also use V, Cr, Cu, Li, Mn*
10.2.3	10.1.3.3	Collect intensity data at the λ peak for each analyte at 1 mm intervals from 14 to 18 mm above the top of the work coil.
10.2.3	10.1.3.3	Repeat with Calibration blank
10.2.3	10.1.3.3	Subtract CB response from each element
10.2.3	10.1.3.3	Choose the height (mmm above coil) for viewing plasma that providers the largest intensity ratio for the least sensitive element.
10.2.5	10.1.3.3	**REPEAT when:** Incident power or nebulizer gas flow rate are changed. Or when a new torch injector tube w/ differnent internal diameter is installed.

200.7/6010: Plasma solution (As, Pb, Se, Tl)

vs.

SM 3120B: vague reference to making a Cu/Mn "or similar" intensity ratio adjustment

This data should be available to an auditor

Be sure to repeat as necessary

Establishing the Viewing Height

			April '03					
ELEM	**18mm**	**17mm**	**16mm**	**15mm**	**14mm**	**13mm**	**12 mm**	
AS	1640	1907	2150	2437	2731	2963	3122	
blank	126	131	135	154	168	189	206	
ratio	**13.02**	**14.56**	**15.93**	**15.82**	**16.26**	**15.68**	**15.16**	15.77
PB	4642	5447	6189	7069	7823	8358	8689	
blank	394	426	463	542	586	700	809	
ratio	**11.78**	**12.79**	**13.37**	**13.04**	**13.35**	**11.94**	**10.74**	12.49
SE	1523	1758	1994	2216	2529	2749	2944	
blank	192	203	220	238	246	286	308	
ratio	**7.93**	**8.66**	**9.06**	**9.31**	**10.28**	**9.61**	**9.56**	9.57
			Selenium is the least sensitive analye					
TL	880	1032	1222	1442	1645	1770	1901	
blank	85	87	100	111	120	137	155	
ratio	**10.35**	**11.86**	**12.22**	**12.99**	**13.71**	**12.92**	**12.26**	12.82

Viewing height set at 14 mm

Establishing the Viewing Height

			Feb '01					Mar '02		
ELEM	18mm	17mm	16mm	15mm	14mm	18mm	17mm	16mm	15mm	14mm
AS	4334	4679	5012	5338	5528	3065	3502	3921	4374	4825
blank	223	249	274	327	386	172	189	199	224	250
ratio	**19.43**	**18.79**	**18.29**	**16.32**	**14.32**	**17.82**	**18.53**	**19.70**	**19.53**	**19.30**
PB	12460	13120	13670	13960	13740	8935	10010	11060	12080	12910
blank	846	976	1104	1343	1657	584	636	716	826	954
ratio	**14.73**	**13.44**	**12.38**	**10.39**	**8.29**	**15.30**	**15.74**	**15.45**	**14.62**	**13.53**
SE	4168	4460	4828	5232	5513	2911	3291	3731	4201	4610
blank	334	369	398	470	558	240	258	288	317	357
ratio	**12.48**	**12.09**	**12.13**	**11.13**	**9.88**	**12.13**	**12.76**	**12.95**	**13.25**	**12.91**
TL	3214	3455	3690	3894	3954	2103	2392	2693	3040	3292
blank	162	182	210	240	299	117	123	139	157	184
ratio	**19.84**	**18.98**	**17.57**	**16.23**	**13.22**	**17.97**	**19.45**	**19.37**	**19.36**	**17.89**
			viewing height set at:		**18mm**			viewing height set at:		**15mm**

Optimal height DOES change!

Re-establish viewing height with major instrument changes.

Effect of Sample Uptake Rate

Nominal = 2.0 mL/minute

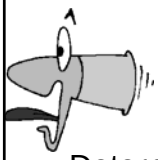
When changed to = 1.0 mL/minute:

- ~ 20% less emission
- raises effective LOD
  - *attempts to read back LOQ standard failed*
- required longer flush time
  - *translates to longer analytical run time*
  - *and higher analytical cost per sample*
- uses more argon
- %RSD of replicate integrations ↑ significantly

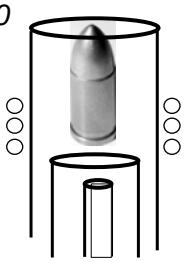
When changed to = 3.0 mL/minute:

- No significant difference vs. 2.0 mL/min

Initial Set-up of an ICP



- Determine sample uptake rate. Use a small graduated cylinder and a timer (*200.7 suggests 1.0 to 1.8 mL/min is optimal*).
- Aspirate an Yttrium standard (**≥200 ppm**). Adjust nebulizer pressure to place the "bullet tip" at the edge of the outer tube
- Optimize viewing height using the "Plasma Solution"
- "Profile" to correctly align the center of analyte peaks. Choose an analyte with a λ in the middle of the target λ range (*SLH uses Cu 324.754 nm*).



Calibration - Standard Preparation

Compatibility Issues

Solubility concerns
Spectral interferences
Stability (Ag)

How many groups?

Driven by compatibility
Plan on at least 5

Vendor	#Elements /#solutions
Spex	25 in 5
XAXO	25 in 5
Radian	25 in 6
Inorganic Ventures	31 in 6
High Purity Stds	26 in 4
RTC	31 in 2
SLH	24 in 5

Purchase vs. Prepare

Time, Cost, Errors associated with manual prep.

Other Concerns

Standard Codes - Traceable back to stocks
Expiration Dates.

Method Comparison - Standard Mixes

		200.7		6010		SM3120B
Instrument Optimization	7.9	Mixed calibration standards NOT prepared from primary standards must be initially verified using a certified reference solution	7.4	For all intermediate and working solutions (especially those < 1 ppm) stability MUST be demonstrated prior to use	3.e.	Before preparing mixed standards, analyze each stock standard separately to check for interferences/impurities. Verify calibration standards initially w2/ QCS; monitor weekly for stability.
	7.9	Acid content = 2% HNO_3 / 2% HCl	10.4.11	Calibration standards should be prepared with the same acid combination/concentration as samples.	3.e.	Mixed calibration standard acid content = 1% HNO_3 / 5% HCl
Suggested standard mixes	7.9	**Std I**: Ag, As, Ba, B, Ca, Cd, Cu, Mn, Sb, Se	7.4	**Std I**: Be, Cd, Mn, Pb, Se, Zn	3.e.	**Std I**: Be, Cd, Mn, Pb, Se, Zn
	7.9	**Std II**: K, Li, Mo, Na, Sr ,Ti	7.4	**Std II**: Ba, Co, Cu, Fe, V	3.e.	**Std II**: Ba, Co, Cu, Fe, V
	7.9	**Std III**: Co, P, V	7.4	**Std III**: As, Mo	3.e.	**Std III**: As, Mo, Li, Si, Sr
	7.9	**Std IV**: Al, Cr, SiO_2, Sn, Zn	7.4	**Std IV**: Al, Ca, Cr, K, Na, Ni, Li, Sr	3.e.	**Std IV**: Al, Ca, Cr, K, Na, Ni
	7.9	**Std V**: Be, Fe, Mg, Ni, Pb, Tl	7.4	**Std V**: Ag, Mg, Sb, Tl	3.e.	**Std V**: Ag, B, Mg, Sb, Tl

Agree that mixed standards should be verified….disagree on "how"

Much variation on standard acid composition. 6010 makes best sense

Agree that 5 standard mixes are needed….disagree on composition

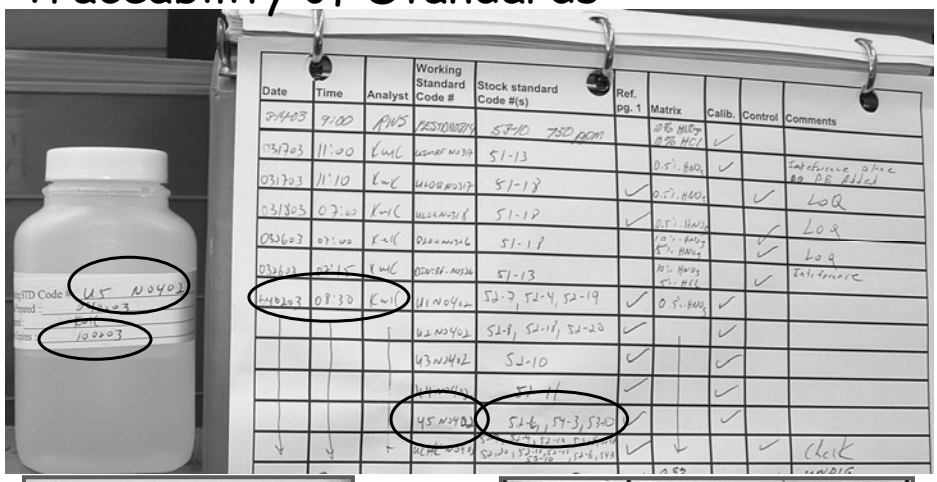
Method Comparison-Calibration Concentrations

Calibration Standard Concentrations

		200.7	3120B
Suggested standard concentrations	7.9	**Std I**:0.5 (Ag),1.0 (Ba), 2.0(B,Cd,Cu,Mn) 5.0 (Sb,Se), 10 (As,Ca)	**Std I**: 1.0 (Be), 2.0 (Cd, Mn), 5.0 (Se, Zn), 10 (Pb)
	7.9	**Std II**: 1.0 (Sr), 5.0 (Li), 10 (Mo,Na), 20 (K), ? (Ti)	**Std II**: 1.0 (Ba, Cu, V), 2.0 (Co), 10 (Fe)
	7.9	**Std III**: 2.0 (Co,V), 10 (P)	**Std III**: 1.0 (Sr), 5.0 (Li) 10 (As, Mo), 21.4 (Si)
	7.9	**Std IV**: 4.0 (Sn), 5.0 (Cr,Zn), 10 (Al,SiO_2	**Std IV**: 2.0 (Ni), 5.0 (Cr), 10 (Al, Ca, K, Na)
	7.9	**Std V**: 1.0 (Be), 2.0 (Ni), 5.0 (Tl), 10 (Fe,Mg,Pb)	**Std V**: 1.0 (B), 2.0 (Ag), 10 (Mg, Sb, Tl)

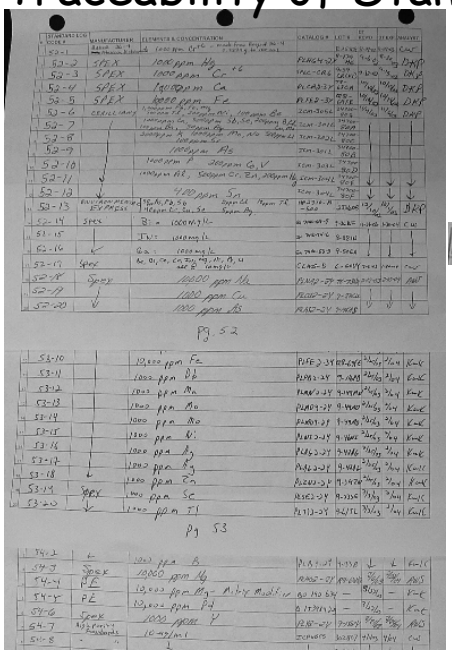
0.5ppm	1ppm	2ppm	5ppm	10ppm	20ppm
Ag	Ba,Sr, Be	Cd,Co,Mn, Ni B,Cu,V,	Cr,Li,Se,Zn Sb,Tl	Al,As,Ca,Fe, Mg,Mo,Na,Pb, Si	K
---	Ba,Sr, Be, Cu,V,B	Cd, Co, Mn,Ni, Ag	Cr,Li,Se,Zn,	Al,As,Ca,Fe, Mg,Mo,Na,Pb, Si, K, Sb, Tl	---

Traceability of Standards



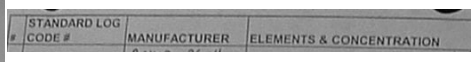
1. Trace the solution label to the standards prep logbook
2. To determine its composition...
3. Who made it (and when)...
4. …and the expiration date

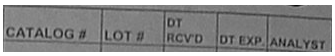
Traceability of Standards



A Stock Standards Logbook is maintained.

The following information is recorded for each standard:



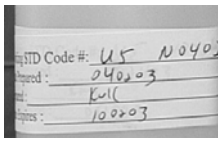


Each stock standard is given a code which can be traced back to the specific Page and Line # in the Standards Log.

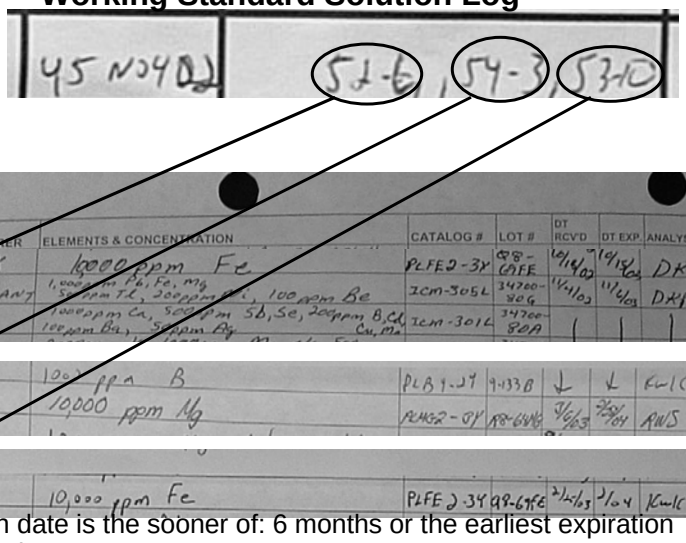
These standards can then be referenced in the Working Standards Logbook

Traceability of Standards

Std Label



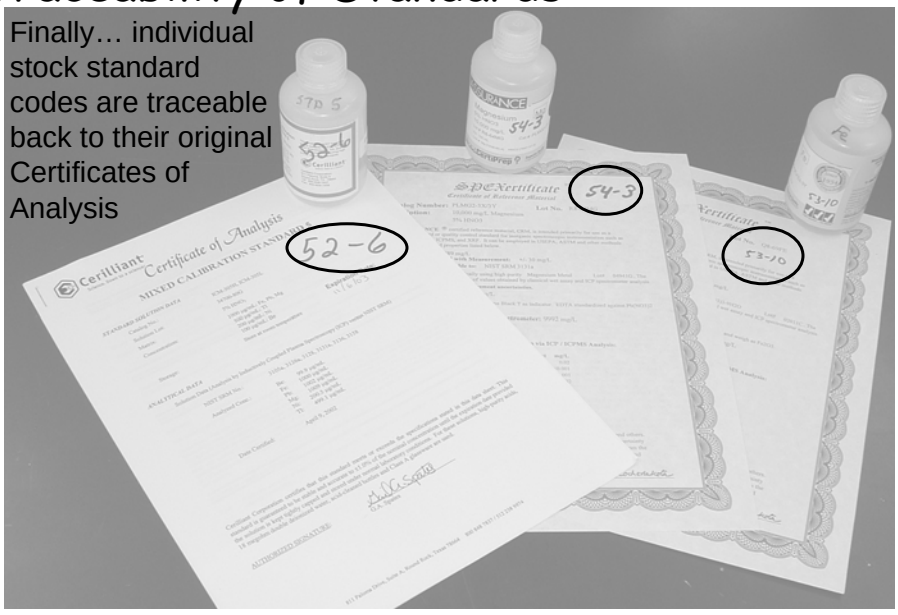
Working Standard Solution Log



The expiration date is the sooner of: 6 months or the earliest expiration of any standard component

Traceability of Standards

Finally… individual stock standard codes are traceable back to their original Certificates of Analysis



Calibration - Sample Preparation Issues

Waters

200.7	2% HNO3, 2% HCl
EPA Diss/6010	1% HNO3
TR	1% HNO3, 0.5% HCl
3005	2% HNO3, 5% HCl
3010	5% HNO3, 5% HCl
3120B	1% HNO3, 5% HCl
3030E	5% HNO3

Soils

EPA	2% HNO3, 2% HCl
3050	5% HNO3, 10% HCl

Microwave

3015, 3051/SM 3030K 10% HNO3

Significant variability exists between method recommended acid content for calibration standards.

Variability in acid concentration between samples and standards DOES affect precision and accuracy.

Effect of Non-Acid Matched Standards

Calibration with 0.5% HNO_3……reading back an ICV in….

		ICV	2.5% HNO3	ICV	10% HNO3	ICV	10% HNO3	ICV	10% HNO3
			5% HCl		5% HCl		no HCl		10% HCl
Element	TV	± 10%	± 5%	± 10%	± 5%	± 10%	± 5%	± 10%	± 5%
Al	5000	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Sb	2500	pass	* FAIL *	pass	-barely-	pass	* FAIL *	pass	* FAIL *
As	5000	pass	* FAIL *	pass	-barely-	-barely-	* FAIL *	pass	pass
Ba	500	pass	pass	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Be	500	pass	pass	pass	pass	pass	pass	pass	pass
B	1000	pass	pass	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Cd	1000	pass	* FAIL *	pass	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *
Ca	**75**	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	* FAIL *	* FAIL *
Cr	2500	pass	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *
Co	1000	pass	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *
Cu	3000	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	* FAIL *	* FAIL *
Fe	**75**	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Pb	5000	pass	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *
Mg	**50**	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	* FAIL *	* FAIL *
Mn	1000	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	* FAIL *	* FAIL *
Mo	5000	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Ni	1000	pass	-barely-	pass	* FAIL *	pass	* FAIL *	* FAIL *	* FAIL *
K	**10**	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Se	2500	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Na	**75**	pass	pass	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Tl	2500	pass	pass	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
V	1000	pass	-barely-	pass	* FAIL *	pass	* FAIL *	pass	* FAIL *
Zn	2500	pass	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *
Ag	250	pass	pass	pass	* FAIL *	* FAIL *	* FAIL *	* FAIL *	* FAIL *
% pass criteria		100%	33%	83%	13%	75%	4%	54%	8%

Effect of an Internal Standard

Calibration with 0.5% HNO_3; all samples adjusted by IS (Y)

			Y-adjusted		Y-adjusted		Y-adjusted
		ICV	2.5% HNO3	ICV	10% HNO3	ICV	10% HNO3
			5% HCl		5% HCl		no HCl
Element	**TV**	**± 10%**	**± 5%**	**± 10%**	**± 5%**	**± 10%**	**± 5%**
Al	5000	pass	pass	pass	pass	pass	pass
Sb	2500	pass	pass	pass	pass	pass	pass
As	5000	pass	pass	pass	pass	pass	pass
Ba	500	pass	pass	pass	pass	pass	pass
Be	500	pass	pass	pass	~ FAIL ~	pass	pass
B	1000	pass	pass	pass	pass	pass	pass
Cd	1000	pass	pass	pass	pass	pass	pass
Ca	**75**	pass	pass	pass	pass	pass	pass
Cr	2500	pass	pass	pass	pass	pass	pass
Co	1000	pass	~ FAIL ~	pass	pass	pass	pass
Cu	3000	pass	pass	pass	pass	pass	pass
Fe	**75**	pass	pass	pass	pass	pass	pass
Pb	5000	pass	* FAIL *	pass	pass	pass	pass
Mg	**50**	pass	~ FAIL ~	pass	pass	pass	pass
Mn	1000	pass	pass	pass	pass	pass	pass
Mo	5000	pass	pass	pass	pass	pass	pass
Ni	1000	pass	pass	pass	pass	pass	pass
K	**10**	pass	pass	pass	pass	pass	pass
Se	2500	pass	pass	pass	pass	pass	pass
Na	**75**	pass	pass	pass	pass	pass	pass
Tl	2500	pass	* FAIL *	pass	pass	pass	* FAIL *
V	1000	pass	pass	pass	pass	pass	pass
Zn	2500	pass	pass	pass	pass	pass	pass
Ag	250	pass	* FAIL *	pass	~ FAIL ~	pass	pass
		100%	**79%**	**100%**	**92%**	**100%**	**96%**
Simulates		Total Recoverable		Digestion		Tissues	

Calibration - Sample Preparation Issues

The use of a **"block" digestion system** is highly recommended.

These systems provide even heating throughout the sample set…which is difficult to achieve with conventional "hot plate" digestions.

Disposable digestion tubes minimize the potential for contamination during digestion or sample transfer. *Be sure you can substantiate the accuracy of these vials if used to measure sample volume.*

Calibration…2 Schools of thought

Blank
+1 standard

Blank +
Multiple standards

Manufacturers recommend Blank + 1 standard.

SLH calibrates with 2 standards plus a blank to meet NELAP requirements:

Calibrate with Blank, mid-range and top standard
"Read back" an LOQ level (for each element) std.

Either is fine as long as you can demonstrate linearity and obtain acceptable results upon "reading back" an LOQ standard.

Method Comparison - # of Calibration Levels

	200.7		6010C		3120B	
Initial Calibration - # stds	7.4.4	Calibration should consist of minimum of calibration blank + high standard.	10.4.2	**Calibration option A:** A calibration curve MUST be prepared daily with a minimum of a calibration blank + 3 standards. **This calibration MUST have an r ≥ 0.995**	4.c.	Calibrate according to manufcturer's recommended procedure using calibration standards and a blank.
			10.4.2	**Calibration option B:** OR... Initial curve may be prepared daily with a minimum of a blank + 1 high standard. **Must verify calibration with a low-level and mid-level standard. Criteria ± 20% for each**		Use multiple integrations for standards/samples.

Calibration with blank and one standard acceptable for all 3

6010 incorporates stricter criteria when 1-pt calibration is used

Verify the calibration at low and mid-level, but…

…± 20% criteria is quite forgiving for a mid-level standard

…but may be difficult at LOQ level regardless of calibration

Note that only SM touches on the need for multiple integrations

Method Comparison -Calibration Check Solutions

	200.7		6010C		3120B	
1° source std	7.11	**IPC** solution prepared from calibration stock IPC: **Ag < 0.5, K/Si 10;others 2 ppm**	10.4.4	**CCV solution** should be the same source as calibration standards **at or near midrange** concentration	3.h.	Instrument Check Standard (ICS) - prepare to contain **all elements at 2 ppm**
2nd source std	7.12	**QCS** solution must be from 2nd source	7.6	**ICV solution** must be from 2nd source	3.i.	**QCS** solution must be from 2nd source
	7.12	**QCS**: Ag < 0.5, all others SHOULD be 1 ppm	7.6	**ICV solution** should be at a concentration near the midpoint of the calibration range		
	9.2.3	Analyze **QCS:** with IDC, quarterly, after preparation of calibration standards				
Other Standard Solutions			10.4.5	**Low Level CCV (LLCCV)** is required: ● when calibrating with blank+1 std ● at the LOQ for each element.		
			10.3.3	**MDL Check Sample (MCS)** is spiked into reagent water at 2-3 times the MDL.		
			10.3.3	Analyze **MCS**: after determining MDL, and quarterly to demonstrate detectability Goes through any digestion		

Both 200.7 & 3120B set absolute levels for a calibration standard
2nd source standard is required by all
6010: LOQ std required (2-3X MDL level)…if cal w/ blank+1std
6010: Also requires digested LOQ std (2-3X MDL) to verify LODs

Method Comparison - Initial Calibration Criteria

	200.7		6010C		3120B	
Initial Calibration Verification (Standard)	9.3.4	Analyze IPC immediately after calibration: must be: ● ± 5% True Value (TV), and ● RSD ≤ 3% of ≥ 4 replicate integrations 1° source	10.4.3	Analyze ICV immediately after calibration: must be ± 10% TV. *Else determine cause and re-calibrate before sample analysis* 2° source	4.c.	Before analyzing samples, analyze the Instrument Check Standard (ICS). Concentration should be within (*whichever is more stringent*) ● ± 5% from True Value (TV) or ● established limits 2° source
			10.4.5	**If calibrate w/ a blank and ≥3 stds,** then correlation MUST be ≥ 0.995		
(Blank)	9.3.4	Analyze CB after calibration: must be < IDL, > mean - 3sd of CB			4.d.	Begin each sample run with an analysis of the **calibration blank (CB)**, then analyze the **method blank (MB)**
(Additional Standards)	9.2.3	**QCS acceptance criteria**: Mean of triplicates ± 5% TV	10.4.2	**If Calibrate w/ blank + 1 std: Must verify calibration with a low-level and mid-level standard. Criteria ± 20% for each**		Tough to meet for LOQ standard

All 3 require calibration verification prior to sample analysis.
200.7 & 3120B require ± 5%; 6010C more flexible w/ ± 10%
Very different initial blank criteria:

no discussion as a requirement (6010), to
…analyze it but no criteria given (SM3120B), to…
…must be < the IDL but > -3x SD of a blank

Only 200.7 established precision limits for replicate integrations

Method Comparison - Continuing Calibration Verification

	200.7		6010C		3120B	
Continuing calibration verification	9.3.4	Analyze IPC + CB (CCV/CCB) - after every 10th sample	10.4.4	Analyze IPC + CB (CCV/CCB) - after every 10th sample	4.e.	Analyze ICS (CCV) - after every 10th sample
	9.3.4	CCV must be ± 10% or else re-analyze. If re-analysis fails, stop; correct the problem; re-calibrate	10.4.4	CCV must be ± 10% or else re-analyze. If re-analysis fails, stop; correct the problem; re-calibrate	4.e.	ICS must be ± 5% *[or established limits]* or else re-analyze. If re-analysis fails, stop; correct the problem; re-calibrate
	9.3.4	CCB must be < IDL, > mean - 3sd of CB	10.4.4	CCB must not contain elements > 2-3 x MDL. All samples following the last acceptable CCV/CCB must be re-analyzed		
		NOTE: This assumes one has determined mean and sd for a calibration blank				

All 3 agree that calibration must be checked every 10 samples
Split on evaluation criteria:200.7 & 6010C= ± 10% ; 3120B = ± 5%

200.7 & 6010C agree that blanks needed every 10 samples;

Very different continuing blank criteria: requires multiple analysis of the CB

3120B sets no criteria,

…200.7 requires < IDL and > -3xSD of the CB, while

… 6010C requires < 2-3x MDL (~ LOQ)

Method Comparison - End of Run Calibration Criteria

	200.7		6010C		3120B	
Final calibration verification	9.3.4	Analyze IPC + CB (FCV/FCB) - at the end of each analytical sequence	10.4.4	Analyze CCV + CB (FCV/FCB) - at the end of each analytical sequence	4.e.	Reanalyze one or more samples analyzed just before termination of the analytical run.
	9.3.4	FCV must be + 10% or else re-analyze. If re-analysis fails, stop; correct the problem; re-calibrate	10.4.4	FCV must be ± 10% or else re-analyze. If re-analysis fails, stop; correct the problem; re-calibrate	4.e.	Results should agree to within ± 5%, else all samples since last acceptable ICS must be reanalyzed
	9.3.4	FCB must be < IDL, > mean - 3sd of CB	10.4.4	FCB must not contain elements > 2-3 x MDL. All samples following the last acceptable CCV/CCB must be re-analyzed		

All 3 agree that calibration must be checked before the run ends

200.7 & 6010C require ± 10% as evaluation criteria

3120B specifies 5% *for agreement of a re-analyzed sample* with the original result…

...although it's a "should"

Initial Demonstration of Capability (IDC)

BGC Determine Background Correction Points

LDR Determine Linear Dynamic Range (each element)

LOD Determine Limit of Detection (each element)

IEC Determine Inter-Element Correction Factors

- **Must know what your LODs are to properly set/evaluate IECs…**
- **Must use the same IECs to establish LODs as you would for sample**
- **The concentration used for the single element standards must be w/in the LDR to properly establish IECs**

Recommended IDC Sequence

- Select BackGround Correction (BGC) points based on peak definition and any spectral interference from adjacent wavelengths.
- Analyze standards to determine Linear Dynamic Range (LDR)
- Calibrate with a blank + "an appropriate number" of standards
- Using EPA 200.7 (or 6010C) estimated MDLs , analyze single element standards [*at multiple levels*]. Determine initial Interelement Correction Factors (IEC).
- Re-calibrate, Determine actual MDLs. [40 CFR Part 136, App. B]
- Re-determine IECs, based on actual MDLs
- Analyze a quality control sample [QCS]. Mean of 3 results should be $\pm$ 5% of true value.

Background Correction

6010C
10.1.1 Before using this procedure to analyze samples, data must be available documenting the initial demonstration of performance. The required data **document the selection criteria for background correction points**; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. These data must be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data must be kept on file and be available for review by the data user or auditor.

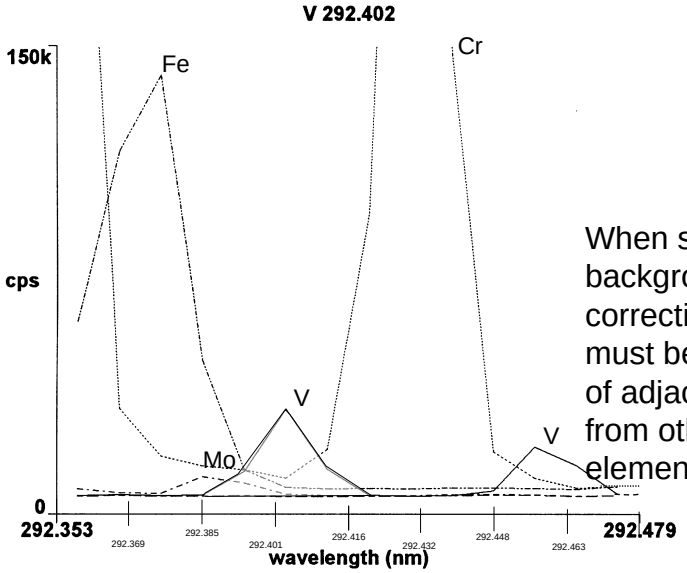
6010C4.1.2 AND 200.7 4.1.4
4.1.2 To determine the appropriate location for off-line background correction, **the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes**. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations.

200.7
4.1.4 If a wavelength other than the recommended wavelength is used, the **user must determine and document both the on-line and off-line spectral interference** effect from all method analytes and provide for their automatic correction on all analyses.

Bottom Line: What BGC points were selected and why?

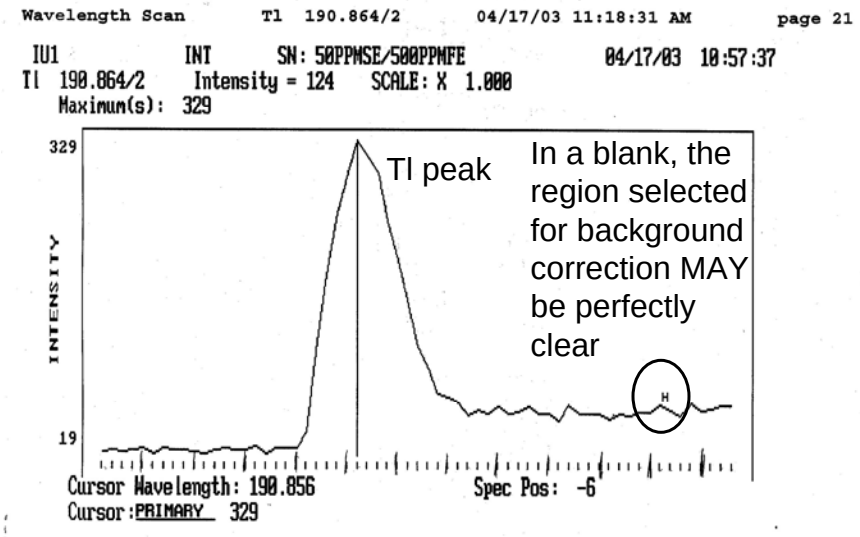
Background Correction

Where would you set background correction here?



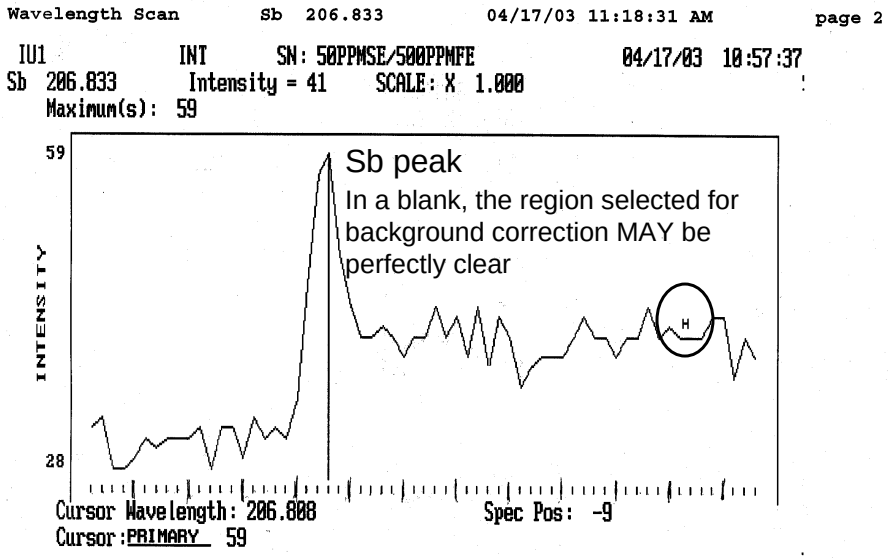
When setting background correction points, must be aware of adjacent lines from other elements

Background Correction - Tl example



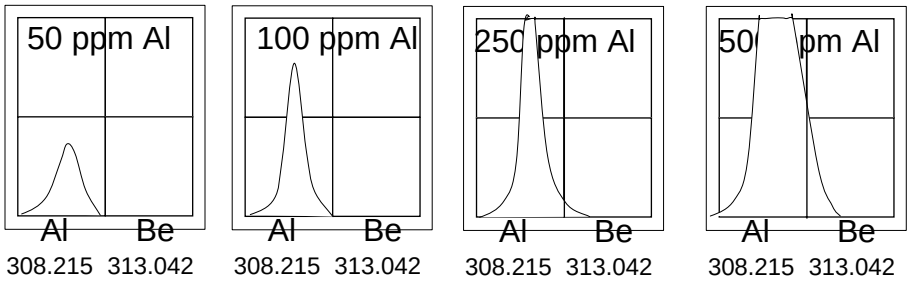
Solution of 50 ppm Se + 500 ppm Fe…scanning at Tl λ

Background Correction - Sb example



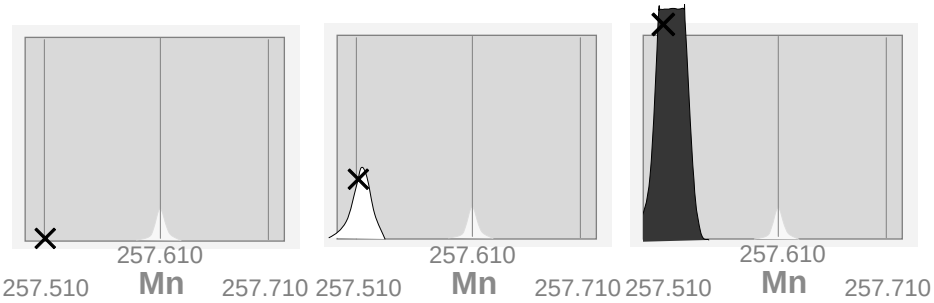
Solution of 50 ppm Se + 500 ppm Fe…scanning at Sb λ

Spectral Overlap? Background Correction?



Classic Spectral Overlap

Spectral Overlap? Background Correction?

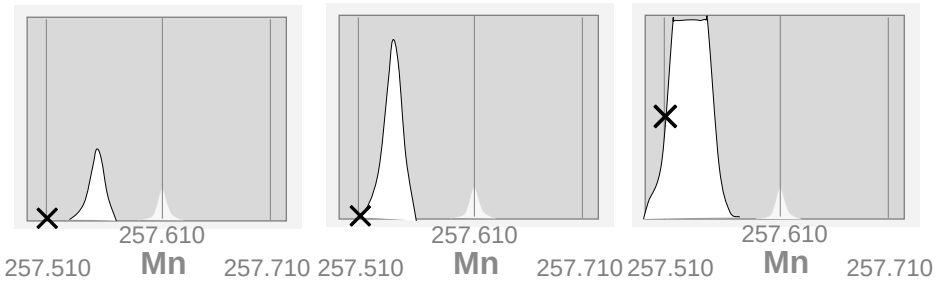


Background Correction Scenario A

- Minor (relatively uncommon) element has a line right on the background correction point.
- Background correction is only adequate when the element is not present.

How will you know if this situation is occurring?

Spectral Overlap? Background Correction?



Background Correction Scenario B
Minor (common) element has a line adjacent to the background correction point.

As concentration (and intensity) increases, there is bleed into the background correction point wavelength.

How will you know if this situation is occurring?

Method Comparison - LDR

	6010C [10.3.4]	200.7 [9.2.2]
	The upper limit of the LDR must be established for each wavelength	
Quanitate by	A standard at the upper limit must be ...quantitated against the normal calibration curve.	Must be determined from a linear calibration prepared in the normal manner
Procedure	...by determining responses from a minimum of three, preferably five, different concentration standards across the range. A standard at the upper limit must be prepared, and analyzed.	The LDR should be determined by analyzing succeedingly higher standard concentrations
Criteria	The calculated value must be within 10% (±10%) of the true value.	... until the observed concentration is ≤ 10% **below** the true concentration...
Reporting	Report results up to the LDR	Sample concentrations > 90% of the determined upper LDR limit must be diluted and reanalyzed.
Frequency	New upper range limits **should** be determined whenever there is a significant change in instrument response. At a minimum, the range **should** be checked every six months.	The LDRs **should** be verified annually or whenever, in the judgement of the analyst, a change in analytical performance (I.e., hardware or operating conditions) would dictate they be redetermined.
Documentation	The data, calculations and rationale for choice of range should be documented....	Determined LDRs must be documented and kept on file.

Linear Dynamic Range

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Required for each emission wavelength used to report analytical results

- ⊙ Establish a valid linear calibration curve (exactly as for samples)
- ⊙ Analyze solutions of progressively higher known concentrations until one yields a recovery below 90%.
  LDR = highest standard with recovery ≥90%.
- ⊙ At least six known concentrations (counting calibration standards) must be analyzed.
  - 1 pt + blank: need at least 5 standards for LDR
  - 3 pts + blank: need at least 3 standards for LDR
- ⊙ Any sample concentration > 90% of the instrument's linear dynamic range for that element must be diluted & reanalyzed.
- ⊙ Linear dynamic ranges must be kept on file
- ⊙ Verify annually or whenever a significant change in the system

Linear Dynamic Range

What if a lab chooses to use the highest calibration standard as its "LDR"?

Those choosing to report results from the LOD up to the LDR or 90% LDR limit…..

…would need to perform a "full" LDR determination

Those choosing to report only those results between the LOD and the highest calibration standard…..

…could analyze a single standard at least 11% higher than the upper calibration standard (± 10%) to demonstrate the calibration range does not exceed 90% of the LDR

IDC- Determination of LOD

"Instrument" Detection Limits (IDL) vs. true "Method" Detection Limits (MDL or LOD)

When deciding whether to purchase an ICP...

…Get the following answers

Does ICP literature indicate IDLs or MDLs?
What matrices will these be valid for?

…Consider the following...

When do I have to report down to the LOD?
What LOD demands do various programs have?
Will my ICP *realistically* achieve the LODs I need?

Capability: Results of 1998 LOD Survey

	%age of labs reporting LOD at/below			
Cadmium (150)	25%	50%	75%	100%
FLAA	3.2	4.8	8.9	19
GFAA	0.08	0.1	0.2	0.5
ICP (Radial)	**1.5**	**2.5**	**3.6**	**9.6**
ICP/MS	0.04	0.06	0.1	0.2
ICP-Trace	**0.3**	**0.4**	**0.6**	**2.9**
Lead (170)				
FLAA	28	38	62	100
GFAA	0.7	0.9	1.4	3.3
ICP (Radial)	**18**	**29**	**37**	**87**
ICP/MS	0.078	0.1	0.2	0.6
ICP-Trace	**1.3**	**1.6**	**2.1**	**17**
Thallium (90)				
FLAA	NA	NA	NA	60
GFAA	0.7	1	1.4	5
ICP (Radial)	**22**	**50**	**85**	**330**
ICP/MS	0.015	0.04	0.05	0.5
ICP-Trace	**2.8**	**3.8**	**5**	**9.7**

**All units are in ug/L*

Reporting to the LOD

When labs are required to report data down to the LOD:

1. If a **client requests** it.
2. **Groundwater or Landfill Program samples:** report all analytes to the LOD.
3. **WPDES permit-required samples** (NR105): report all analytes to the LOD.
4. **Drinking Water Program samples**: report each element for which an MCL has been promulgated to the LOD
5. If (1), (2), (3) & (4) do not apply to the sample, report **any substance on the "NR 149 Compounds of Concern" reporting list** to the LOD

Compounds of Concern [Metals]		
Antimony	Beryllium	Cadmium
Lead	Thallium	

6. **If (1), (2), (3), (4) or (5) do not apply, then it is not necessary to report to the LOD.**

LOD "Demands" / Detection Claims (all values in ug/L)

	NR140 PAL	SDWA MDL	P-E axial	J-Y HR*	Thermo radial*	Thermo axial*
Ag	10	xxxxxx	1	0.9	---	---
As	5	5→1	20	1.8	8	4
Ba	400	200	0.1	0.03	---	---
Cd	**0.5**	**1**	**1**	**0.14**	**0.6**	**0.4**
Cr	10	10	2	0.23	---	---
Pb	**1.5**	**1.5**	**10**	**2.3**	**6**	**4**
Se	10	5	60	2.3	10	6
Cu	130	130	0.4	0.27	4	2
Zn	2500	xxxxxxxx	1	0.23	0.4	0.3
Be	**0.4**	**0.4**	**0.1**	**0.08**	**---**	**---**
Sb	**1.2**	**0.6**	**10**	**2.3**	**10**	**10**
Tl	**0.4**	**0.2**	**30**	**1.5**	**10**	**6**

underlined text = ICP not an approved technology for SDWA

Red text= NR 149 req'ment to report to LOD * "guaranteed" detection limits

NR 140 PALs for metals

Public Health Standards (ug/L)

	ES	PAL
Antimony	6	1.2
Arsenic	50	5
Barium	2000	400
Beryllium	4	0.4
Boron	960	190
Cadmium	5	0.5
Chromium	100	10
Cobalt	40	8
Copper	1300	130
Lead	15	1.5
Nickel	100	20
Selenium	50	10
Silver	50	10
Thallium	2	0.4
Vanadium	30	6

ES=
Enforcement Standard
PAL=
Preventive Action Limit

Public Welfare Standards (Aesthetics) [ug/L]

	ES	PAL
Iron	300	150
Manganese	50	25
Zinc	5000	2500

1. Determine a spike concentration (close to the expected LOD)
2. Analyze at least 7 spiked replicates of reagent water at this spike level that have been taken through the entire sample preparation procedure.

NOTE: Be aware that some older permits may specifically require the LOD to be determined in effluent.
Ideally, it may be best to determine your LOD in effluent.
Practically, however, by doing so, may not be able to achieve a valid LOD.

3. Calculate the mean (**X**) and standard deviation (**SD**)
4. Obtain the "**t**"-value associated with the number of replicates
5. Calculate the LOD: **SD** times **t**
6. Perform the "5-point check" of the LOD

Lead Example

Spike level = 5.0 ug/L

Blank	-0.8
Rep. 1	4.9
Rep. 2	4.7
Rep. 3	4.6
Rep. 4	4.5
Rep. 5	4.7
Rep. 6	4.8
Rep. 7	4.8
mean	**4.7**
st dev.	**0.13**
t-value	**3.143**

# replicates	t-value
7	3.143
8	2.998
9	2.896
10	2.821

t-value **3.143** = from table based on # replicates

LOD= 0.41 = t-value x std deviation

LOQ= 1.3 = 3.333 x LOD

(these first 3 are mandatory checks) **LOD= 0.41**

1. Is LOD greater than 10% of the spike level? **NO**

Spiked at **5.0**, so LOD should be > 0.5
If LOD < 10% of spike level, re-do at lower spike level

2. Is the spike level greater than the LOD? **yes**

Common sense: if LOD > spike level, couldn't detect it

3. Is the LOD below any relevant regulatory limit? **yes**

(if there is one) SDWA requires ≤1.5 ug/L

(additional checks)

Though not specifically required by the EPA method....
these checks help you obtain the best estimate of the LOD.

4. Is the signal-to-noise ratio (S/N) between 2.5 and 10? **NO**

S/N = Mean/std dev. S/N= 36.1

5. Is mean recovery within reasonably expected limits? **yes**

Mean recovery= mean/spike level x 100 = 94.3%
Expected range is approximately 80 to 120%

6. Is the blank within ± LOD? **NO**

Suggests contamination or the LOD is unrealistically low

IDC- Interference Correction

Determining what Interferences exist

Spectral overlap? Or background correction?

Do NOT subtract blank response

Generating correction factors

Deciding NOT to use CFs

Verifying adequate correction
- what the methods require
- CLP approach
- common sense approach
  - cal blk
  - ICS-A….1º interferents
  - ICS-B?? 2º interferents
  - ICS-AB

Problems with Interelement Correction (IEC) Factors

1. (*older instruments*) "Auto-correction" was based on measured concentration (*rather than TRUE concentration*) of the interferent. ***Is this acceptable?***

2. Establishing IECs based on analysis of single-element solutions at a single concentration

   A. assumes linear interference.

   B. assumes that a lack of interference at the selected level means that there will not be an interference at higher concentrations.

3. Corrections made for interference due to an inappropriate background correction point may not provide adequate correction.

Problems with Interelement Correction (IEC) Factors

4. Correction factors may not accurately represent synergistic effect of multiple interferents.

5. Interference correction MUST be "turned off" - for all elements-- before analyzing single element standards.

6. Corrections based on values very close to acceptable variation for a blank (LOD...vs. LOQ) may not be adequate.

7. Making corrections based on only ONE analysis may not be sufficient (doesn't consider normal analyte "bounce")

"Synergistic" Interference Example

This lab analyzed single element standards for Al, Ca, Mg (250 ppm each) and Fe (100 ppm)
Then a mixed solution (ICS-A) consisting of all 4 elements at these concentrations was prepared

	Elem	As 1890	Cr2677	Mn 2576	Zn 2138
	Units	ppm	ppm	ppm	ppm
Al250	**Avge**	**0.00000**	**0.0018**	**0.0000**	**0.0000**
Al250	#1	-0.00090	0.0018	0.0000	0.0000
Al250	#2	0.00090	0.0018	0.0000	0.0000
Ca250	**Avge**	**-0.00075**	**0.0000**	**0.0003**	**0.0050**
Ca250	#1	-0.00084	-0.0002	0.0003	0.0050
Ca250	#2	-0.00066	0.0002	0.0002	0.0049
Mg250	**Avge**	**0.00000**	**0.0000**	**0.0000**	**0.0000**
Mg250	#1	0.00001	0.0001	0.0000	-0.0001
Mg250	#2	-0.00001	-0.0001	0.0000	0.0001
Fe100	**Avge**	**0.00000**	**0.0000**	**0.0000**	**0.0000**
Fe100	#1	-0.00079	-0.0003	0.0000	0.0000
Fe100	#2	0.00079	0.0003	0.0000	0.0000
	LOD=	0.0036	0.0007	0.0003	0.0013
ICS-A	Avge	0.00995	0.0107	-0.0027	-0.0346
ICS-A	#1	0.00850	0.0107	-0.0027	-0.0345
ICS-A	#2	0.01139	0.0106	-0.0027	-0.0346

Determining Interelement Correction Factors

Analyze <u>high purity</u>, single-element standards

Determine the concentration of apparent analyte per unit concentration of interferent.

Do NOT subtract blank response

What "interferents" need to be tested?

What concentration of interferent should be tested?

Is only a single concentration of interferent enough?

Method Comparison -What Elements Must be Tested?

		200.7		6010C		3120B
Option A: Interference Correction using method wavelngths	4.1.4	Interferences must be evaluated for each instrument. When using method suggested λ, analyst must determine and document for each λ the effect of interferences in Table 2 (and use a computer routine for auto-correction	4.1.4	Interferences must be evaluated for each instrument. When using method suggested λ, analyst must determine and document for each λ the effect of interferences in Table 2		Determine interelement CFs by analyzing single element stock solutions of appropriate concentration under conditions matching as closely as possible those of samples.
	Table 2	Requires evaluation of interference from 17 elements: Al,Fe,Cu,Ni,Cr,Mn,V,Be,Ba,Co,Mo,Sn,Ti, Cd,Tl,Si,Ce	Table 2	Requires evaluation of interference from 10 elements: Al, **Ca**, **Mg**, Fe, Cu, Ni, Cr, Mn, V, Ti 1000 ppm: (Al, Ca,Fe,Mg) used by EPA 200 ppm: all others used by EPA		
		NOTE what's missing: Ca, Mg, Na		*NOTE what's missing: Na only*		

200.7 (4.1.4)
6010C (4.1.2)
If a wavelength **other than the recommended wavelength is used**, the user must **determine and document both the on-line and off-line spectral interference** effect **from all method analytes** and provide for their automatic correction on all analyses.

Interferents to be tested: 6010C

1000 mg/L: Al, Ca, Fe, Mg

Analyte	Wavelenth (nm)	Interferant Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

200 mg/L: Cu, Mn, Ni, Ti, Cr, V

Interferents to be tested: 200.7

TABLE 2: ON-LINE METHOD INTERELEMENT SPECTRAL INTERFERANCES ARISING FROM INTERFERANTS AT THE 100 mg/L LEVEL

Analyte	Wavelength (nm)	Interferant*
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

*These on-line interferences from method analytes and titanium only were observed using an instrument with 0.035 nm resolution (see Section 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

7.13.1 SIC solutions containing
(a) 300 mg/L Fe;
(b) 200 mg/L Al;
(c-q) 50 mg/L each of Ba; Be; Cd; Ce; Co; Cr; Cu; Mn; Mo; Ni; Sn; SiO2; Ti; Tl; and V
should be prepared in the same acid mixture as the calibration standards. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Table 1.
Other solutions could achieve the same objective as well. (*Multielement SIC solutions may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution.*)

Method Comparison -Levels to be Tested

	200.7		6010	
Option B: Interference Correction using alternate wavelengths	4.1.4 If using **other than** method suggested λ, users must determine/document both on & off-linespectal interference (SI) effect from all method analytes and provide correction.			
	4.1.4 Tests to determine the SI must be done at concentrations sufficient to describe the interference (usually 100 ppm). interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit.		4.1.2 Tests to determine the SI must be done at concentrations sufficient to describe the interference (usually 100 ppm). However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range	

200.7 and 6010 both suggest 100 ppm, but caution that "elements found at high concentration"[e.g., Fe] may need to done at a level near the LDR *(look at the levels they used)*

3120B: no guidance

Interferent Levels to be Tested

200.7/6010: Tests to determine the spectral interference (SI) must be done at concentrations sufficient to describe the interference (usually 100 ppm). However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range

SM 3120 B: If using a polychromator, verify absence of SI from an element that COULD occur in a sample but for which there is no channel in the array by analyzing single element solutions of 100 ppm and noting for each element channel the apparent concentration from the INT that is > element IDL.

CLP SOW ILMO 5.2 (December 2001)12.11.1
NOTE: Depending on sample matrix and interferences, it may be necessary to analyze interelement correction factors at a frequency greater than quarterly and/or at multiple concentrations comparable to the sample interferent levels.

"...When operative and uncorrected, interferences will produce false positive or positively biased determinations…"

A "-" IEC can result where an interfering line is encountered at the background correction λ rather than the peak λ

Evaluating Interelement Correction Factor Data

Review IEC Data against some evaluation criteria
When does an *apparent* interference warrant correction?

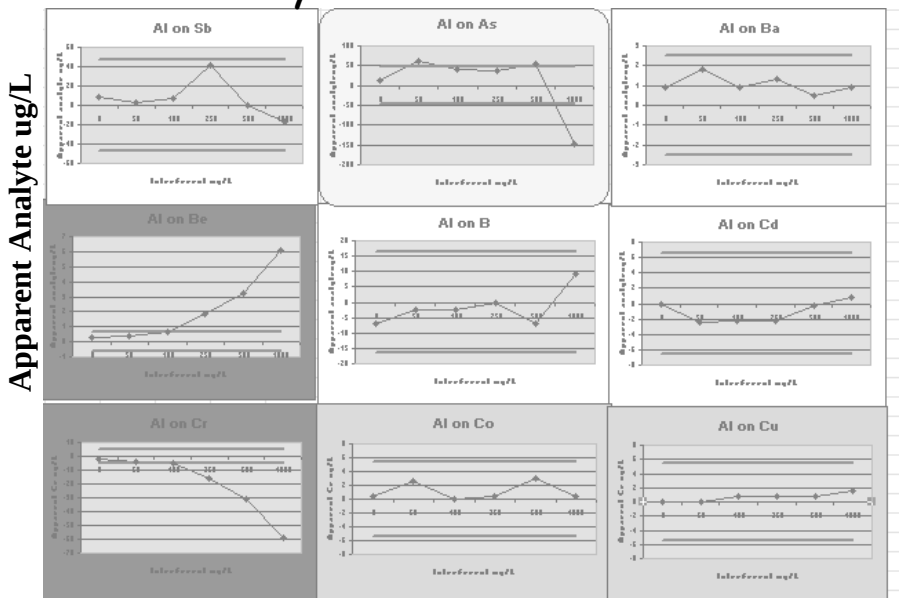
While it is never *clearly* stated in EPA methods,
it would seem appropriate to base corrections on LODs:

If an apparent analyte concentration (i.e. interference) exceeds the analyte's LOD,
it would result in a false positive

Optimal approach…for major cations(Al, Ca, Fe, Mg)

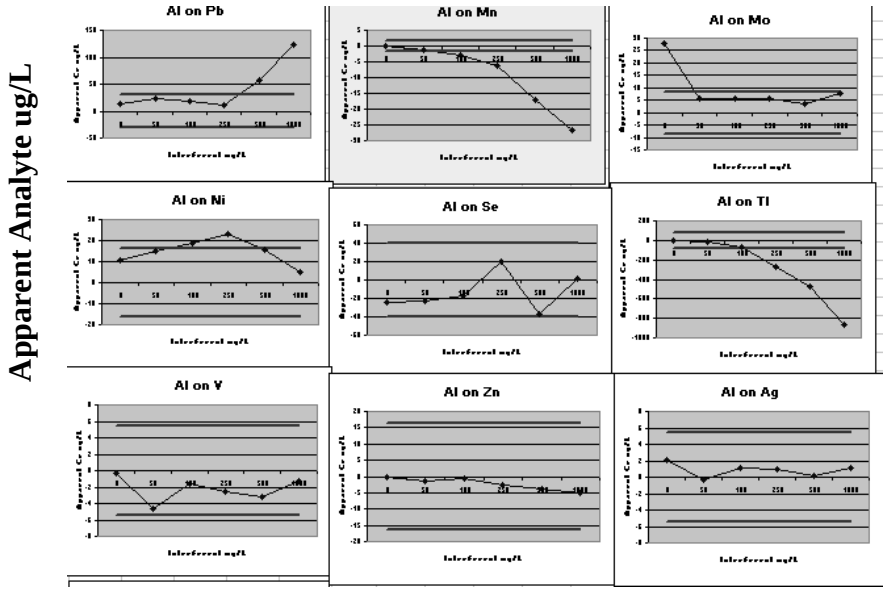
Test a series of increasing concentrations of each
Plot apparent analyte (ug/L) vs. interferent (mg/L)
Add plot lines of + LOD and -LOD
Identify those needing an IEC vs. BGC concerns

Plots of Analyte Interference: Al



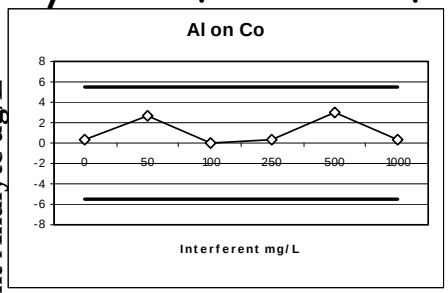
Interferent Concentration: 0, 50, 100, 250, 500, 1000 ppm

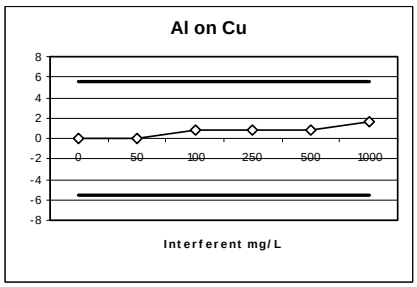
Plots of Analyte Interference: Al



Interferent Concentration: 0, 50, 100, 250, 500, 1000 ppm

Key interferences from Al

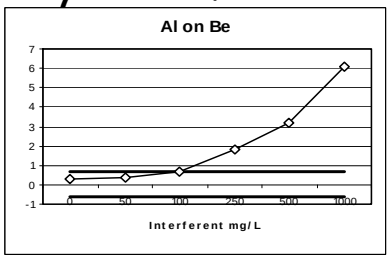




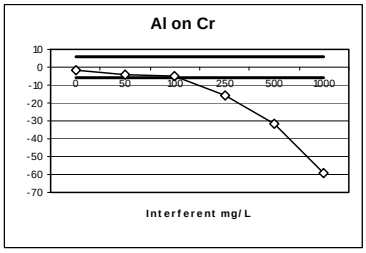
No correction required for those elements that fluctuate within +/- LOD

Interferent Concentration: 0, 50, 100, 250, 500, 1000 ppm

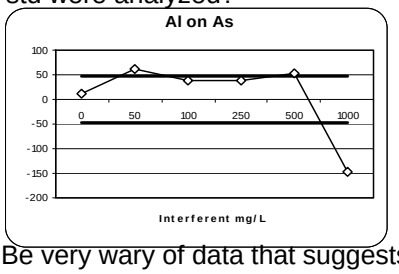
Key interferences from Al

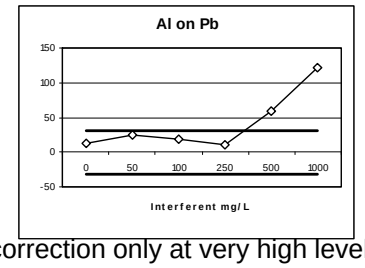


Definitely requires Correction
…but would it if only a 100 ppm std were analyzed?



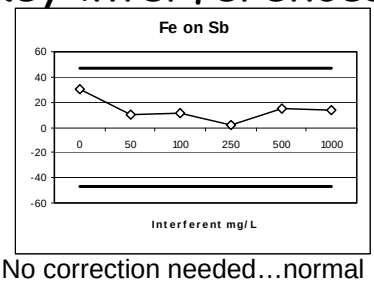
Is correction required?
Or is something else going on?



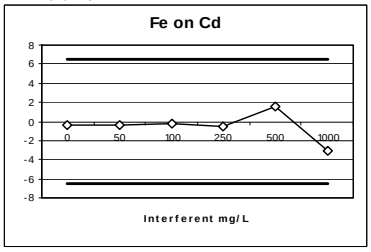


Be very wary of data that suggests a correction only at very high levels or data in which the apparent correction seems to change direction.

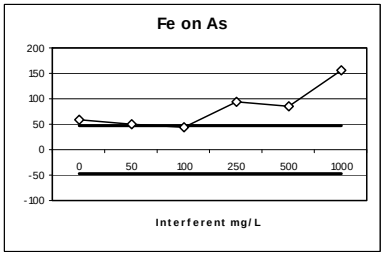
Key interferences from Fe



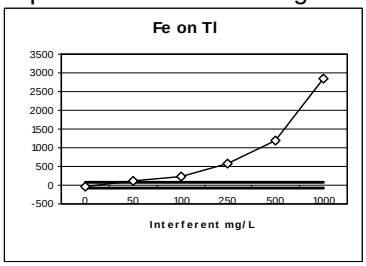
No correction needed…normal fluctuation



Normal fluctuation as well…although last point should be investigated

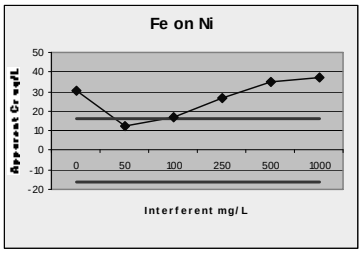


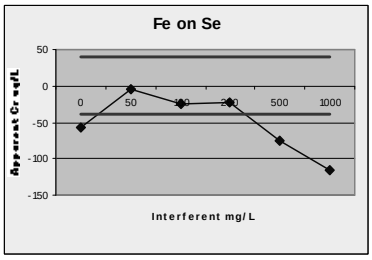
Correction required above 100 ppm…but doesn't look linear.



Clear case of correction required. Appears linear from 50 to 1000 ppm

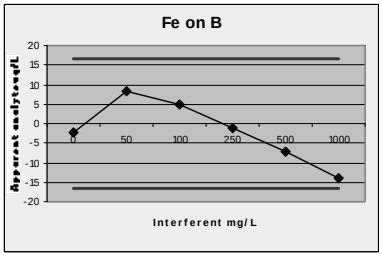
Key interferences from Fe





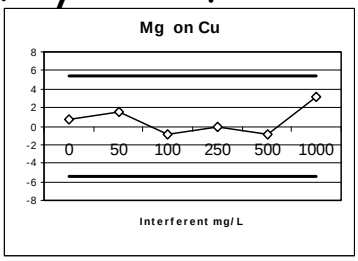
Ni: Innate high bias. correction…but would it if only a 100 ppm std were analyzed?

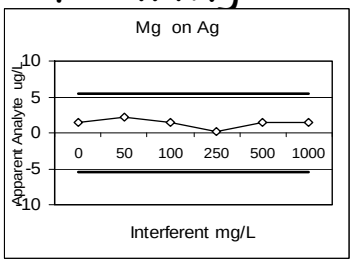
Se: Looks to be an interference above 250 ppm. Blank point suggests possibility that LODs are unrealistically low.



B: Unique data. Clearly an interference exists, but it is insignificant relative to the blank at/below 1000 ppm.

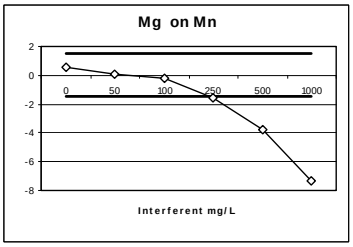
Key interferences from Mg

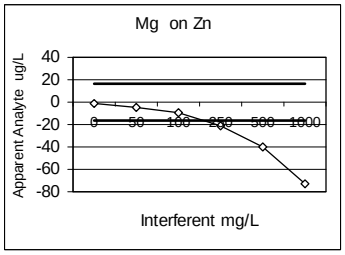




Cu: Ok up to 1000 ppm

Ag: No observed interference

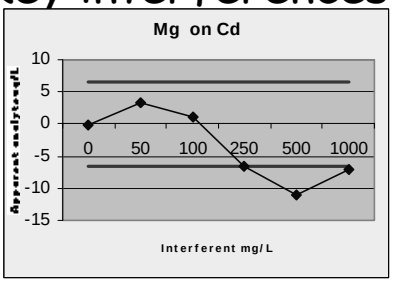




Mn: Clear "suppression" at/above 250 ppm. Likely a BGC issue

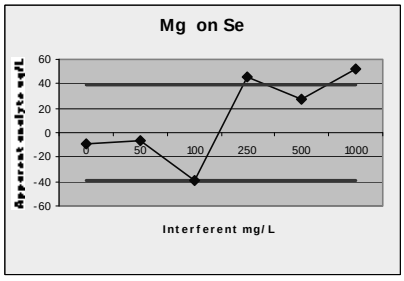
Zn: Clear "suppression" at/above 250 ppm. Likely a BGC issue

Key interferences from Mg

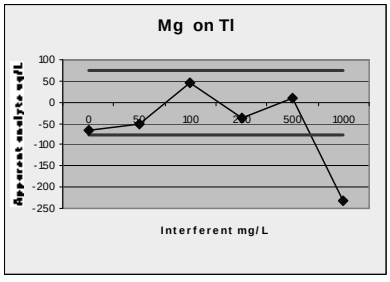


50-500 ppm appear to be a supression (BGC issue) but the 1000 ppm level alters the sequence.

Need to look at BGC set point

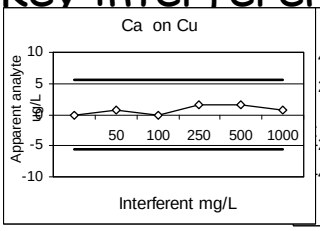


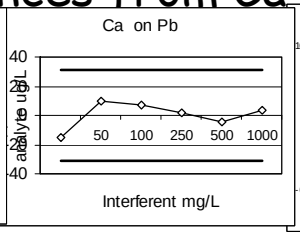
Need to look more closely… but could be an LOD issue



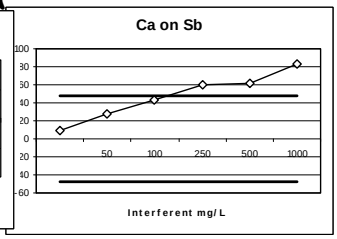
Need to look more closely at the 1000 ppm level

Key interferences from Ca

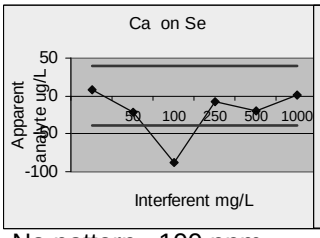




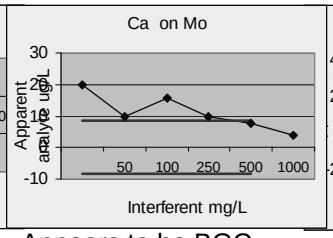
Clear lack of relationship



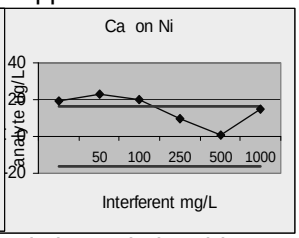
Distinct relationship, but only affects results above 100 ppm



No pattern. 100 ppm level may suggest LOD is unrealistically low.



Appears to be BGC issue but high "0" level suggests an LOD issue.



Distinct relationship, Another potential BGC concern

Calculating Inter-element Correction Factors (IECs)

$$\frac{5.991\ \text{ug/L}}{250\ \text{mg/L}} = \frac{0.023964\ \text{ug/L}}{1\ \text{mg/L}}$$

Actual **Fe**	Apparent **Co**		
0	2.355		
50	1.39	1.39 ppb per 50 ppm	= 0.0278 ppb per ppmFe
100	1.089	1.089 ppb per 100 ppm	= 0.0109 ppb per ppmFe

Co LOD = 5.0 **Should values within ± LOD be used for correction?**

250	5.991	5.991 ppb per 250 ppm	= 0.0240 ppb per ppmFe
500	11.24	11.24 ppb per 500 ppm	= 0.0225 ppb per ppmFe
1000	18.47	18.47 ppb per 1000 ppm	= 0.0185 ppb per ppmFe

Avg CF 50-1000 =0.0207 ppb per ppmFe
LSR 50-1000 slope= -1.97E-06 intercept =0.0215

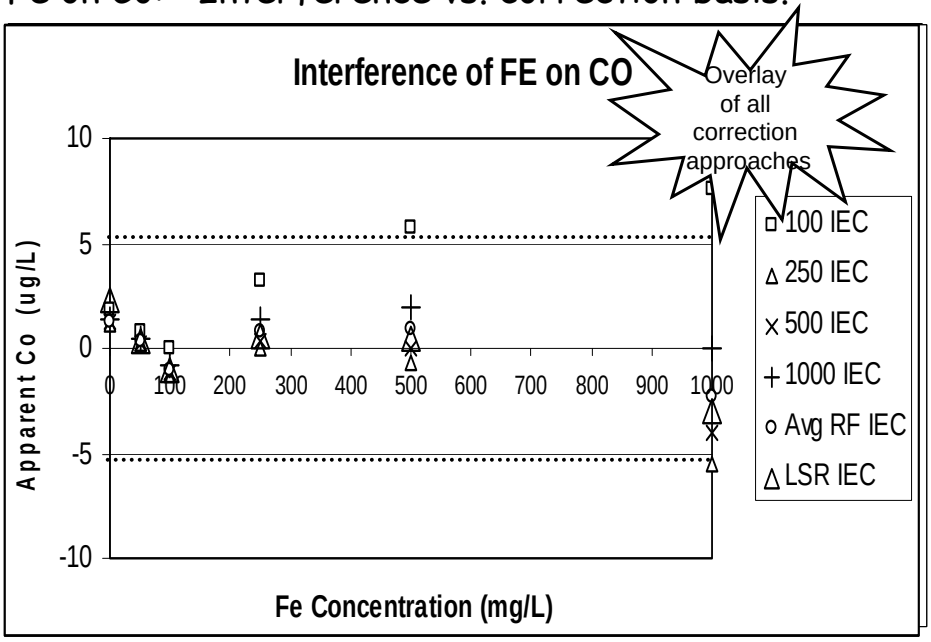
Avg CF 250-1000 =0.0216 ppb per ppmFe
LSR 250-1000 slope= -1.97E-06 intercept =0.0260

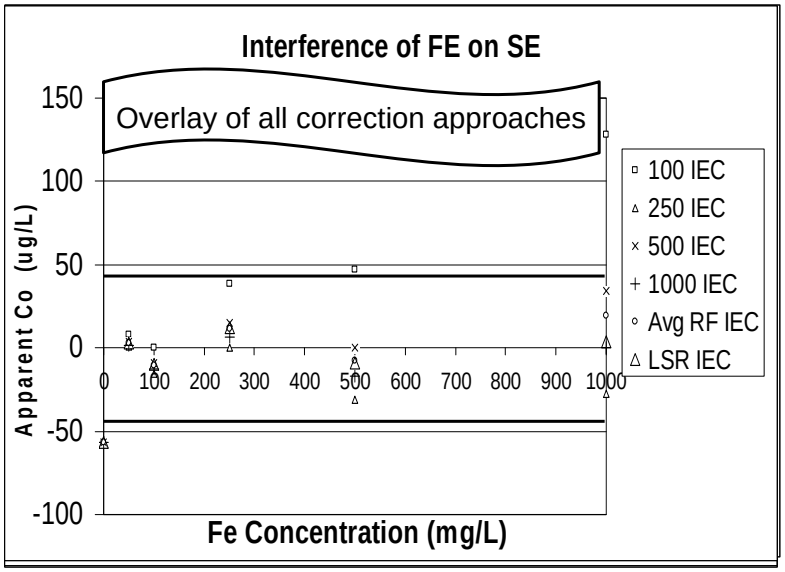
Manual vs. "auto" correction

Things to consider before establishing IECs

- Is blank level reasonable?
- Is the standard deviation reasonable?
- Is there any evidence of carryover?
- Use your judgment
- Document your reasoning

Fe on Co: Interference vs. correction basis.





Multi-Component Spectral Fitting (MSF)

Proprietary algorithm for correction of spectral interferences

Relies on multi-dimensional multiple linear regression vs. one or more discrete data points from an interferent.

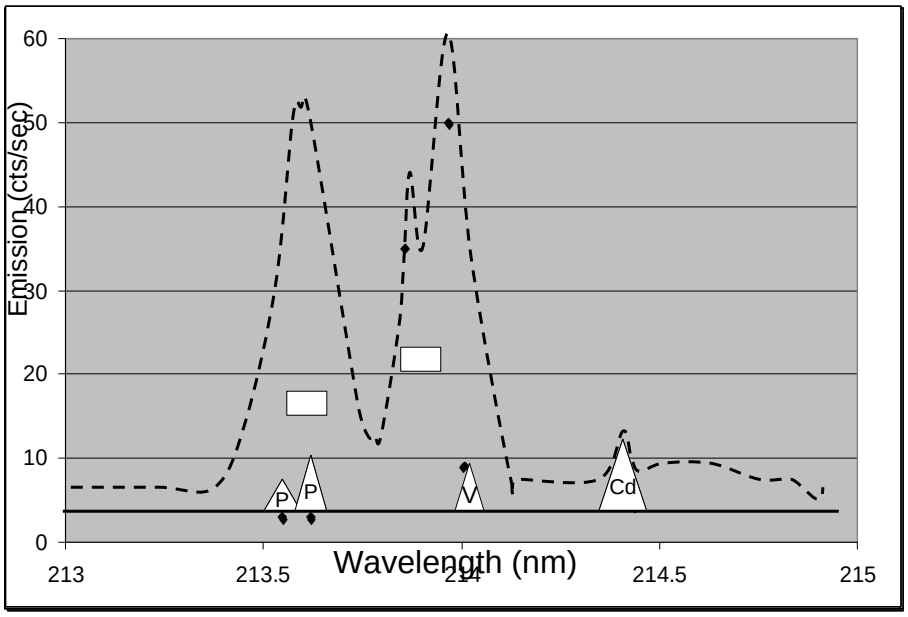
If appropriate information is considered, represents the most mathematically accurate interference correction.

Requires user to identify (in the software) what corrections are made:

correction for blank response
correction for sample matrix
correction for any spectral concerns (BGC and overlap)

Result is to effectively separate analyte signal from all other noise.

MSF Example…a rough neighborhood



Method Comparison - Physical Interference & Memory Effects

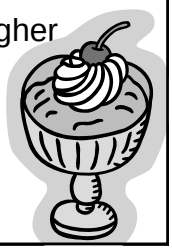
Don't forget about these problems!!!

		200.7		6010
Physical Interferences	4.2	Physical interference= effects associated with nebulization & transport: changes in viscosity + surface tension can cause significant inaccuracy--especially in samples w/ hi TDS or hi acid. MUST reduce w/: high solids nebulizer, dilution, peristaltic pump, or internal std (IS)	4.2	Physical interference= effects associated with nebulization & transport: changes in viscosity + surface tension can cause significant inaccuracy--especially in samples w/ hi TDS or hi acid. MUST reduce w/: high solids nebulizer, dilution, peristaltic pump, or internal std (IS)
Memory effects	4.4	Memory effects - The length of time required to reduce analyte signals to **+ 2xMDL** should be noted. Until the req'd rinse time is established, method **requires** ≥ 60 secs. b/w sample/std		Memory effects - The length of time required to reduce analyte signals to **≤ LOD** should be noted. Until the req'd rinse time is established, method **suggests** ≥ 60 secs. b/w sample/std

Note that 200.7 does not seem reasonable if the CCB is required to be ± LOD

Inter-element Correction Factors: Conclusions

- One size does not fit all
- Use at least one concentration level
- Best information obtained from multiple concentration levels
- Method recommended 100 mg/L level is not suitable for major cations
- Best overall correction obtained from average CF over multiple levels OR average of replicates at one level.
- One level probably appropriate for 2° interferents
- Watch for carryover when analyzing 100 ppm or higher
- Spectral overlap yields positive bias
- IECs can be based on ***either*** TRUE ***or*** observed interferent concentration
  ("The proof is in the pudding")



Basic Quality Control

Blanks (Method, Calibration, Rinse)

LCS

MS/MSD

Duplicates

Internal Standards

Interference Checks

Method Comparison - Blanks

		200.7		6010		SM3120B (& 3020B)
Blank term	9.3.1	**LRB** (Lab Reagent Blank)	9.3	MB (Method Blank)	3020B3a	MB (Method Blank)
Blank Frequency	9.3.1	Must analyze **at least one** LRB with each batch of 20 or fewer samples of the same matrix	9.3	Must analyze **at least one** MB with each batch of 20 or fewer samples processed	3020B3a	Must analyze **at least one** MB with each batch of 20 or fewer samples processed
Blank criteria	9.3.1	LRB must be ≤ [*greater of*] - 10% of sample concentration or - 2.2 X MDL	9.3	MB must be ≤ [*greater of*] - 5% of MDL Check Sample - 5% of Regulatory Limit, or - 5% of least [sample] in batch	3020B3a	MB must be < MDL
Blank corrective action	9.3.1	Resolve contamination; fresh aliquots of samples must be prepared and analyzed for affected analytes	9.3	Rerun once; if still unacceptable, all samples back to the last acceptable MB must be re-prepared/analyzed along with associated QC samples.	3020B3a	Take immediate corrective action

All agree that a method blank is required per batch of ≤ 20

Broad span on acceptance criteria.

Will have to meet method specific criteria AND NR 149

NR 149.14 (3)(d) The method blank results exceed control limits when results are higher than the highest of any of the following.

1. The limit of detection.
2. Five percent of the regulatory limit for that analyte.
3. Five percent of the measured concentration in the sample.

Method Comparison - LCS

		200.7		6010		SM3120B (& 3020B)
LCS term	9.3.2	**LFB** (Lab Fortified Blank)	9.4	LCS (Lab Control Sample)	3020B3b	**LFB** (Lab Fortified Blank) or Blank Spike
LCS composition	7.10.3	Reagent blank spiked with: Ag ≤ 0.1 ppm, K: 5.0 ppm; all others 0.2 ppm or 100XMDL (whichever is greater)	9.4	Should spike at the action level or at a level between the low and mid-point standards	3020B3b	Spike at the midpoint of the calibration curve or lower. **Prepare from a source separate from that used for calibration.**
LCS Frequency	9.3.2	Must analyze at least one LFB with each batch of samples	9.4	Must analyze **at least one** LCS with each batch of samples	3020B3b	Must analyze at least one LFB with each batch of 20 or fewer samples
LCS criteria	9.3.2	**85-115**% can use statistical control limits (mean ± 3 sd) but must be equal to or better than 85-115	9.4	Should be historical/statistical based, but no greater than **80-120**%	3020B3b	Ensure that the LFB meets "the performance criteria for the method"
LCS corrective action	9.3.2	If recovery is outside 85-115%, identify and correct problem before continuing	9.4	Rerun once; if still unacceptable, all samples back to the last acceptable LCS must be re-prepared/analyzed.	3020B3b	Establish corrective actions to be taken in the event the LFB does not satisfy acceptance criteria.

Preparation according to 200.7 will meet the needs of all 3

Clear requirement is one LCS per batch of samples

Variable LCS acceptance criteria, but 85-115% suitable for all 3

Method Comparison - Spikes

		200.7		6010		SM3120B (& 3020B)
Spike term	9.4.1	**LFM** (Lab Fortified Matrix)	9.5	MS/MSD (Matrix Spike/Matrix Spike Duplicate)	3020B3d	**LFM/LFMD** (Lab Fortified Matrix/Lab Fortified Matrix Duplicate)
Spike composition	9.4.2	Waters: same level as LCS Solids; LCS level expressed as mg/kg		Same as LCS: Should spike at the action level or at a level between the low and mid-point standards	3020B3d	Prepare addition concentrations to approximately double the concentration present in the original sample. Limit addition volume to ≤ 5% of sample volume
Spike Frequency	9.4.2	Lab must add a known amount of each target analyte to a minimum 10% of routine samples	9.5	Must analyze **at least one** MS/MSD with each batch of samples processed **NOTE**: ***An MS + DUP can be substituted for MS/MSD***	3020B3d	Must analyze **at least one** LFM/LFMD with each batch of samples processed
Spike criteria	9.4.3	70-130% or 3-sigma designated range based on Table 9	9.5	Should be historical/statistical based, **but no greater than 75-125% for accuracy and 20% RPD** for precision	3020B3d	Ensure that the LFB meets "the performance criteria for the method"
Spike corrective action	9.4.4	If the LFM fails but LFB passes decision is that matrix effect is involved.	9.5	If either the accuracy or precision exceed acceptance criteria, the tests for intereferences should be performed.		

6010& 3120B focus on MS/MSD; 200.7 on MS + Duplicate
Frequency is MS/MSD per batch of (*20 or less*) samples
Variable acceptance criteria, but 75-125% (6010) are most strict
NR149: calculate limits; use tighter of: 75-125% or statistical limits

Method Comparison - Replicates (Duplicates)

200.7 doesn't address precision (but NR 149 does)

6010 relies on MS/MSD to evaluate precision.

In addition to MS/MSD, Std Methods (3020B 3.c.) requires an actual duplicate per batch of 20 or fewer samples.

Control Limit Reminder

NR 149.14 (3) (g)

Quality control limits
for replicate sample and spiked sample analysis
shall be calculated for each matrix type
using a method from an authoritative source
[NR 149.03 (5) (a - w)].

.....

NR 149.05 (28) "Sample matrix" means the general physical–chemical makeup of the sample.
Note: Wastewater samples, water supply samples, waste samples, surface water samples, groundwater samples, sediment samples, and soil samples may have different physical–chemical makeups.

.....

When quality control data
shows a dependency on concentration,
the laboratory **shall** calculate separate control limits
to address the concentration dependency.

Method Comparison -Analytical Run Sequence

200.7	6010	SM3120B (& 3020B)
Calibration	**Calibration**	**Calibration**
IPC ± 5%, 4 reps < 3% RSD	**ICV + 10%** *[2nd source]*	**ICS ± 5%** *[2nd source]*
ICB	***LLCCV + 20% (if cal w/ 0, 1std)***	**LFB (stat. CLs)**
LRB	***Mid-Level CCV(if cal w/ 0, 1std)***	**Duplicate (stat. CLs)**
LFB 85-115%	**LCS 80-120%**	**LFM (stat. CLs)**
		LFMD (stat. CLs)
10 samples	**10 samples**	**10 samples**
IPC ± 10%	**CCV ± 10%**	**ICS ± 5%** *[2nd source]*
CCB	**CCB**	
LFM 70-130%	**MB**	
	MS 75-125%	
	MSD 75-125%, 20% RPD	
10 samples	**10 samples**	**10 samples**
IPC ± 10%	**CCV + 10%**	**Re-analyze ≥ 1 sample (± 5%)**
CCB	**CCB**	

	200.7	6010	SM3120B (& 3020B)
Initial Demonstration of Proficiency / Capability	Determine LDR	Determine MDLS	Determine MDLS
	QCS (3 reps ± 5%)	MDL check sample (≥ LOD)	Determine LDR
	Determine MDL	Determine LDR	Analyze 4 LFBs; compare P&A
	Establish IECs	Establish IECs	

Internal Standards

6010C 1.1 Samples which are not digested **require** either an **internal standard** or should be matrix-matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards.

6010C 4.2 If *physical interferences* are present, they **must be reduced** by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. [*200.7 section 4.4*]

6010C 4.3.2 An alternative to using the method of standard additions is to use the internal standard technique. Add one or more elements that are not found in the samples. [*200.7 section 11.5*]

SLH: uses Y adjustment for all TCLP extracts, soils, & tissues
Calibration standards are always acid-matched
%RSD of replicates must be < 2%
± 10% of emission from calibration seems reasonable for IS

	ICV	2.5% HNO3	ICV	10% HNO3	ICV	10% HNO3
		5% HCl		5% HCl		no HCl
	± 10%	± 5%	± 10%	± 5%	± 10%	± 5%
Acid Matching	100%	33%	83%	13%	75%	4%
Internal Standard	100%	79%	100%	92%	100%	96%

Verifying Adequacy of Interelement Correction Factors

We need criteria to determine whether correction is effective
EPA provides the following guidance (in 200.7 & 6010C)

7.13.2 For interferences from iron and aluminum, only those correction factors (positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

?

What does THAT mean???

7.13.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

Method Comparison - Are IECs operating properly?

	200.7		6010
7.13.4	If correction is operating properly, the determined target analyte concentrations from analysis of SICs A thru Q should fall within a concentration range bracketing the CB	4.1.8	If correction routine is operating properly, the determined target analyte concentrations from each SIC should fall within a concentration range bracketing the CB

7.13.4	$Range_x = [INT_x] \times CF_x / 10$	4.1.8	$Range_x = [INT_x] \times CF_x / 10$
7.13.4	If the apparent analyte concentration ([AA]), *after subtraction of the calibration blank* (CB) is outside of this "Range", then a 10% or greater change in the CF has occurred	4.1.8	If the apparent analyte concentration ([AA]), *after subtraction of the calibration blank* (CB) is outside of this "Range", then a 10% or greater change in the CF has occurred
7.13.4	If $[AA_x]$ - CB > ± $Range_x$ ... expect a 10%... or greater... change in CF	4.1.8	If $[AA_x]$ - CB > ± $Range_x$ ... expect a 10%... or greater... change in CF

Method Comparison - Interference Check Solutions (ICS)

	200.7		6010
Spectral Interference Check (IC, SIC) solutions	7.1.3 When ICs are applied, SICs are needed containing interfering elements at levels that will provide an adequate test of CFs	7.8	The ICS contains levels of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements at 0.5 to 1 mg/L
	7.13.1 Solutions A-Q (17) should be prepared in same acid mix as std.	10.1.3.6	After optimizing and before analyzing samples, the lab must establish and initially verify an interelement SI correction routine to be used during sample analysis. The criterion for determining that an interelement SI is present = an apparent "+" or [analyte] beyond 0 ± RL (- RL to +IDL).
	7.13.1 Fe (300 ppm), Al (200) ppm. 50 ppm each: Ba,Be,Cd,Ce,Co,Cr,Cu,Mn,Mo,Ni,Sn, SiO2,Ti,Tl,V		
	NOTE: other solutions could achieve objectives. Also...if other wavelengths are used, other solutions beyond these may be req'd		

Method Comparison - Guidance when no IECs are used

	4.1.5	… either on-going SIC solutions must be analyzed to verify absence of interelement SI	
7.14 **200.7**	For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., >10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data.	4.1.10.2 **6010**	Analyze an ICS w/ similar concentrations of sample analytes (>10 mg/L). If ICS confirms interference that is ± 20% of the [analyte], the analyte must be determined using (1) analytical and background correction wavelengths free of the interference, (2) by an alternative wavelength, or (3) by another test procedure.
	4.1.5	…OR… software must be used that will identify when a potential interferent is present at interfering levels:	
	4.1.5 4.1.5	- will produce a false "+" > analyte IDL. - will produce a false **"-"** < 99% LCL of the CB,	
	4.1.5	When the interference accounts for > 10% of analyte concentration, MUST use - alternate **λ** free of interference, OR - another approved test procedure	

Why isn't this used for cases when IECs ARE used?

Method Comparison - Instrument printout capability & ICS

	200.7		6010
7.13.6	If instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%.	4.5	If instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 0.5-1 mg/L. Results should be w/in ± 20% of TV or dilution of the sample is necessary

Virtually all instruments in use today are capable of displaying negative values.

…so…why add target analytes to the ICS ????

Recovery at least 95% (200.7) [allows - 50 ppb]
or as low as 80% (6010) [allows ± 100 to 200 ppb]

Method Comparison - IEC Frequency

200.7		6010		SM3120B (& 3020B)	
10.4	Once established, **the entire routine must be** initially and periodically **verified annually**, or whenever there is a change in instrument operating conditions.	4.1.9	All **interelement spectral correction factors** or multivariate correction matrices **must be verified and updated every six months** or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions.	5.c.	Unless analysis conditions can be reproduced accurately from day to day or for longer periods, determine interference CFs found to affect results significantly each time samples are analyzed.
10.4	Only a portion of the correction routine must be verified more frequently or on a daily basis.	10.1.3.6	Only a portion of the correction routine must be verified more frequently or on a daily basis.		

Best advice is to repeat IEC determination at least every 6 months…

...and more frequently if change are made to the instrument that will effect correction factors.

Method Comparison - Interference Check Summary

OK….so there's no crystal clear guidance on how to verify adequacy of correction factors...

Some Assistance from the CLP Program

Interference Correction - CLP approach

CLP = the EPA's Contract Lab Program

- enacted in early 80's in response to Superfund (CERCLA)
- goal was to provide data of "*known and documented* quality"
- How? By having ALL CLP labs do things exactly the same way (*the Stepford Lab Program-SLP???)*

Introduced a 2-part "Interference Check Standard (ICS)

- **ICS-A = 4 major interferents only (Al, Ca, Fe, Mg)**
- **ICS-AB = ICS-A + 0.5-1.0 ppm of each target analyte**

CLP Solutions & LOD Requirements

ILM05.2
December 2001

TABLE 1: Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS)

Analytes		CLP ILMO 3.0 ('93) (mg/L)		Interferents		CLP ILMO 3.0 ('93) (mg/L)	
Ag	**Ag**	**1.0**	0.2	Al	**Al**	**500**	250
As	**As**	**---**	0.1	Ca	**Ca**	**500**	250
Ba	**Ba**	**0.5**	0.5	Fe	**Fe**	**200**	100
Be	**Be**	**0.5**	0.5	Mg	**Mg**	**500**	250
Cd	**Cd**	**1.0**	1.0				
Co	**Co**	**0.5**	0.5				
Cr	**Cr**	**0.5**	0.5				
Cu	**Cu**	**0.5**	0.5				
Mn	**Mn**	**0.5**	0.5				
Ni	**Ni**	**1.0**	1.0				
Pb	**Pb**	**1.0**	0.05				
Sb	**Sb**	**---**	0.6				
Se	**Se**	**---**	0.05				
Tl	**Tl**	**---**	0.1				
V	**V**	**0.5**	0.5				
Zn	**Zn**	**1.0**	1.0				

NOTE: ICS Solution A (ICSA) contains the interferents at the indicated concentrations. **The ICSA may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample**. ICS Solution AB (ICSAB) contains all of the analytes and interferents listed above at the indicated concentrations.

Analyte	ICP-AES CRQL for Water[1,2], MDLs (µg/L)	
Aluminum	100	200
Antimony	30	60
Arsenic	7.5	15
Barium	100	200
Beryllium	2.5	5
Cadmium	2.5	5
Calcium	2500	5000
Chromium	5	10
Cobalt	25	50
Copper	12.5	25
Iron	50	100
Lead	5	10
Magnesium	2500	5000
Manganese	7.5	15
Mercury	0.1	0.2
Nickel	20	40
Potassium	2500	5000
Selenium	17.5	35
Silver	5	10
Sodium	2500	5000
Thallium	12.5	25
Vanadium	25	50
Zinc	30	60

[1]The CRQLs are the minimum levels of quantitation acceptable under the contract Statement of Work (SOW).

[2]Subject to the restrictions specified in Exhibit D, any analytical method specified in ILM05.2 Exhibit D may be utilized as long as the documented Method Detection Limits (MDLs) are less than one-half the CRQLs.

Original CLP Procedure
Interference Check Sample (ICS)

Analyze & report all target elements and interferents in the ICS
- at the beginning of each analysis run,
- not less than once per 20 analytical samples per analysis run,
- at the end of each analysis run,

Solution A = interferents
Solution AB = analytes + interferents.
An ICS analysis = ICS-A + ICS-AB

Analytes in both the ICSA and ICS-AB shall fall within the greater of:
- ICS-A: ± 20% of the true value for each interferent
- ICS-AB: ± 20% of the true value: for each interferent and target analyte

If the results of either the ICSA or ICS-AB do not fall within the control limits,
- Stop analytical sequence
- correct problem
- recalibrate
- re-analyze all samples since last compliant ICS-A

Updated CLP Procedure
ILM05.2
December 2001

Interference Check Sample (ICS)

Example: Arsenic [As]
CRQL = 15 µg/L,
ICSA true value = 0 µg/L

ICSA result = 29 µg/L,
Criteria = ± 30 ug/L
so it passes

Analyze & report all target elements and interferents in the ICS
- at the beginning of each analysis run,
- not less than once per 20 analytical samples per run,
- at the end of each analysis run,

Solution A = interferents
Solution AB = analytes + interferents.
An ICS analysis = ICS-A + ICS-AB

Analytes in both the ICSA and ICS-AB shall fall within the greater of:
- ± 2 times the CRQL of the analyte's true value or
- ± 20% of the analyte's true value, whichever is greater
- (the true value shall be zero unless otherwise stated)

If the results of either the ICSA or ICS-AB do not fall within the control limits,
- Stop analytical sequence
- correct problem
- recalibrate
- re-analyze all samples since last compliant ICS-A

Problems with the CLP Procedure

"Known and documented" quality $\stackrel{?}{=}$ good quality

± 20% is pretty forgiving at 250-500 ppm levels

± 20% for target analytes means:

± 100-200 ppb for all analytes (in earlier SOWs)

NOTE: earlier SOWS did not allow ICP for As, Sb, Se, or Tl

± 200 ppb for Cd, Ni & Zn (= ± 10 to 100 x MDL)

± 120 ppb for Sb (= ± 4 x MDL)

± 100 ppb for Ba, Be, Cr, Cu, Mn & V (= ± 1 to 50 x MDL)

± 40 ppb for Ag (= ± 8 x MDL)

± 20 ppb for As & Tl (= ± 1.5 to 2.5 x MDL)

± 10 ppb for Pb & Sb (= ± 0.5 to 2 x MDL)

Breaking New Ground...

Task *(since it's not clear in the methods):*
Identify an Interference Check Solution(s)…
and a set of evaluation criteria
that ensures adequacy of IECs and BGC points

Objective: Apply the...

... Principle

Devising an Appropriate ICS

Take what we have (CLP) and update it

ICS-A — Major interferent analytes only

This is critical

Add a simple, but overlooked evaluation step

ICB — No analytes of interest

Consider substituting an evaluation step

ICS-A+ (*aka ICS-AB*) — Major interferents spiked with all analytes

vs.

ICS-B — Secondary interferents only

Re-evaluate acceptance criteria (QA)
Re-think analytical frequency

Devising an Appropriate ICS

Analyze & report all target elements and interferents in the ICS

- at the beginning of each analysis run,
- ~~not less than once per 20 analytical samples per analysis run,~~

Instrument conditions should certainly not change after 20 sample analyses

- ~~at the end of each analysis run,~~

If instrument conditions have not changed, then neither should correction factors

Solution A = major interferents only

~~*Solution AB = analytes + interferents*~~

Former "ICS-AB" is not <u>required</u>

An ICS analysis = ICS-A ~~*+ ICS-AB*~~ **+ * *optional* * ICS-B**

Solution B = minor interferents

200.7 7.13.6 <u>If the instrument does not display negative concentration values</u>, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

It could be of value to spike the target analytes, but if--and only if-- the analytes are spiked at or near the LOQ, and acceptance criteria are equivalent to those for blanks (or unspiked analytes)

6010C 7.8 Spike the [ICS] with the elements of interest, particularly those with known interferences, at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. <u>If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary</u>.

Devising an Appropriate ICS

ALL Analytes in both the blank, ICSA, & ICSAB shall fall within the greater of

- ± 2 times the LOD or CRQL
- ± 20% 10% of the analyte's true value, whichever is greater
  (± 10% represents a more realistic measure of ICP bias)
- (the true value shall be zero unless otherwise stated) for unspiked analytes

If the results of either the ICSA or ICS-AB do not fall within the control limits,

- Stop analytical sequence
- Correct problem
- Re-calibrate
- Re-analyze all samples since last compliant ICS solution

Example: Arsenic [As]
LOD = 50 µg/L,
ICSA true value = 0 µg/L

ICSA result = 29 µg/L,
Criteria = ± 50 ug/L
so it passes

Initial Calibration Blank (ICB): ± LOD

Elem	LOD	Avg	#1	#2	%RSD	
Ag 328.068	**0.0005**	**0.0009**	0.0009	0.0008	**8.32%**	**Blank fluctuates at the LOD**
Al 308.215	**0.013**	**0.2974**	0.2837	0.3111	**6.51%**	**Blank significantly greater than LOD**
B 249.773	**0.100**	**0.0655**	0.0665	0.0645	**2.16%**	**OK**
Ba 233.527	**0.001**	**-0.0001**	-0.0001	0.0000	**-141.42%**	**OK**
Cd 226.502	**0.001**	**-0.0021**	-0.0012	-0.0029	**-58.64%**	**Blank fluctuates at -1-2X LOD**
Cr 205.560	**0.002**	**-0.0041**	-0.0038	-0.0043	**-8.73%**	**Blank fluctuates at -2X LOD**
Cu 324.754	**0.001**	**0.0049**	0.0043	0.0055	**17.32%**	**Blank fluctuates at 4-5X LOD**
Fe 259.940	**0.008**	**-0.0068**	-0.0056	-0.0079	**-24.09%**	**OK**
Mn 257.610	**0.003**	**-0.0017**	-0.0016	-0.0017	**-4.29%**	**OK**
Mo 203.844	**0.008**	**0.0012**	0.0037	-0.0013	**294.63%**	**OK**
Ni 231.604	**0.003**	**0.0044**	0.0049	0.0039	**16.07%**	**Blank slightly greater than LOD**
Pb 220.353	**0.008**	**-0.0128**	0.0081	-0.0336	**-231.27%**	**Blank fluctuates widely: 1X to -4X**
Zn 213.856	**0.007**	**0.0037**	0.0042	0.0031	**21.31%**	**OK**
Sc 361.384		**1.0550**	1.0520	1.0580	**0.40%**	
As 193.696	**???**	**0.0144**	0.0069	0.0219	**73.66%**	**Lab does not report As from its ICP**
Be 313.107	**0.001**	**0.0012**	0.0012	0.0011	**6.15%**	**OK**
Co 228.616	**0.002**	**0.0023**	0.0004	0.0042	**116.83%**	**Blank fluctuates at -1-2X LOD**
Sb 206.833	**???**	**0.0151**	0.0222	0.0079	**67.19%**	**Lab does not report Sb from its ICP**
Se 196.026	**???**	**-0.0474**	0.0121	-0.1069	**-177.52%**	**Lab does not report Se from its ICP**
Si 251.611	**0.026**	**0.0027**	0.0024	0.0029	**13.34%**	**OK**
Sn 189.933	**0.010**	**-0.0026**	-0.0014	-0.0037	**-63.78%**	**OK**
Sr 421.552	**0.002**	**-0.0002**	-0.0001	-0.0002	**-47.14%**	**OK**
Tl 190.800	**???**	**-0.0126**	0.0141	-0.0393	**-299.68%**	**Lab does not report Tl from its ICP**
Ti 334.941	**0.010**	**-0.0008**	-0.0006	-0.001	**-35.36%**	**OK**
V 292.402	**0.002**	**0.0002**	0.0002	0.0002	**0.00%**	**OK**

Compare the ICB to the ICS-A (for unspiked)

Element	LOD	BLANK Avg	Al 50 + Fe 20 ppm Avg	
Ag 328.068	0.0005	0.0009	-0.0024	Significant ↓ (-4X LOD)
Al 308.215	0.013	0.2974	49.1400	----------
B 249.773	0.100	0.0655	0.1035	Significant ↑ …needs IEC
Ba 233.527	0.001	-0.0001	0.2967	Significant ↑ …needs IEC
Cd 226.502	0.001	-0.0021	-0.0033	Significant ↓ … may need IEC
Cr 205.560	0.002	-0.0041	-0.0042	No change… but still -2X LOD
Cu 324.754	0.001	0.0049	0.0042	No change… but still 4X LOD
Fe 259.940	0.008	-0.0068	19.4050	----------
Mn 257.610	0.003	-0.0017	-0.0040	Significant ↓ … may need IEC
Mo 203.844	0.008	0.0012	-0.0049	Δ Direction, but still +/- LOD
Ni 231.604	0.003	0.0044	0.0063	Slight further↑ …may need IEC
Pb 220.353	0.008	-0.0128	-0.0089	Looks OK, LOD probably low
Zn 213.856	0.007	0.0037	-0.0175	Significant ↓ … needs IEC
Sc 361.384		1.0550	1.145	Internal Standard
~~As 193.696~~	~~???~~	~~0.0144~~	~~0.0368~~	
Be 313.107	0.001	0.0012	0.0015	Blank fluctuates at -1-2X LOD
Co 228.616	0.002	0.0023	0.0025	Blank fluctuates at -1-2X LOD
~~Sb 206.833~~	~~???~~	~~0.0151~~	~~-0.0038~~	
~~Se 196.026~~	~~???~~	~~-0.0474~~	~~-0.1010~~	
Sn 189.933	0.026	-0.0026	0.1039	OK Significant ↑ …needs IEC
Sr 421.552	0.010	-0.0002	-0.0853	OK
~~Tl 190.800~~	~~0.002~~	~~-0.0126~~	~~0.0179~~	
Ti 334.941	???	-0.0008	-0.0008	OK
V 292.402	0.010	0.0002	-0.0018	OK

Too low a level for Fe and Al.

This does not even consider Ca or Mg…the main cations.

Compare the ICB to the ICS-B (for unspiked)

Element	LOD	BLANK Avg	Cr,Cu,Mn,Ni, Ti, V 10ppm Avg	
Ag 328.068	0.0005	0.0009	-0.0167	Significant further ↓
Al 308.215	0.013	0.2974	0.7383	Significant ↑ …needs IEC
B 249.773	0.100	0.0655	0.0439	OK
Ba 233.527	0.001	-0.0001	-0.0095	Δ Direction
Cd 226.502	0.001	-0.0021	0.0003	maybe OK
Cr 205.560	0.002	-0.0041	10.1800	----------
Cu 324.754	0.001	0.0049	9.8095	----------
Fe 259.940	0.008	-0.0068	0.0107	Fe LOD maybe too low
Mn 257.610	0.003	-0.0017	10.0200	----------
Mo 203.844	0.008	0.0012	0.0103	IEC? Or LOD issue?
Ni 231.604	0.003	0.0044	10.0400	----------
Pb 220.353	0.008	-0.0128	-0.0086	maybe OK
Zn 213.856	0.007	0.0037	-0.0139	still an apparent suppression
Sc 361.384		1.0550	1.1065	Internal Standard
~~As 193.696~~	~~???~~	~~0.0144~~	~~0.0177~~	
Be 313.107	0.001	0.0012	0.0050	Now 5X LOD
Co 228.616	0.002	0.0023	0.0074	Significant ↑ above LOD
~~Sb 206.833~~	~~???~~	~~0.0151~~	~~0.0023~~	
~~Se 196.026~~	~~???~~	~~-0.0474~~	~~-0.0136~~	
Sn 189.933	0.026	-0.0026	0.1873	Significant ↑…needs IEC
Sr 421.552	0.010	-0.0002	-0.0002	OK
~~Tl 190.800~~	~~0.002~~	~~-0.0126~~	~~-0.0995~~	
Ti 334.941	???	-0.0008	10.4650	----------
V 292.402	0.010	0.0002	10.4050	----------

Probably an effective level for these analytes.

Adding this sample provides substantiation that your correction factors work for more than just the typical cations.

ICS Recommendations

Analyze & Evaluate Initial Calibration Blank (ICB)
All target analytes must be within ± LOD

Analyze & Evaluate an ICS-A standard
ICS-A = Al, Ca, Mg, and Fe only
Levels appropriate to cover 99% level of expected concentration
May use different ICS-A levels for different matrices
ex. Soils: Al, Ca, Mg, Fe all at 500 ppm
ex: drinking water: Al, Ca, Mg, Fe all at 50 ppm
Interferents must be within ± 10% of true value
All unspiked target analytes must be within ± LOD

Optimally, checks should be made with each run
(Methods allow weekly if control is demonstrated)

ICS Conclusions **(OPTIONAL)**

Analyze & Evaluate an ICS-B standard
ICS-B = 2° interferents only (Be,Ba,Cd,Co,Cr,Cu,Mn,Ni,V)
Levels appropriate to cover 99% level of expected concentration
Suggest 10-50 ppm for each
Interferents must be within ± 10% of true value
All unspiked target analytes must be within ± LOD

~~Analyze & Evaluate an ICS-A+ *[or ICS-B+]* standard~~
~~ICS-A+ = Interferents at regular level + all target analytes~~
~~Target analyte spike levels appropriate to detect bias near LOD~~
~~Suggest 10 x LOD for each analyte~~
~~**All** analytes must be within ± 10% of true value~~
~~At 10 x LOD, target analyte recovery must be ± LOD~~

Record-Keeping - Method Development

- Analytes to be Reported
- Wavelength Selection
- Background correction points
- Interferents and Levels Tested
- Interelement correction factors
- LOD determinations
- Linear Dynamic Range determination (each analyte)
- Standard traceability (also for spikes)

Record-Keeping - Digestion

Records required for a given batch of samples

- What samples (including standards &QC) were digested?
- Who performed the digestion?
- When was the digestion performed?
- What digestion procedure was used?
- Initial and final weight(s)/volume(s)
- Documentation that digestion criteria fulfilled (temp/time)
- Standard tracking numbers for acids & reagents
- Standard tracking numbers for any standards solutions

Record-Keeping - Analysis

Records required for a given batch of samples

What samples (including standards &QC) were analyzed?

Is calibration verification frequency adequate?

Is QC sample (blanks, QCS, etc,) frequency adequate?

What authoritative source procedure was referenced?

Who analyzed the samples?

When were the samples analyzed?

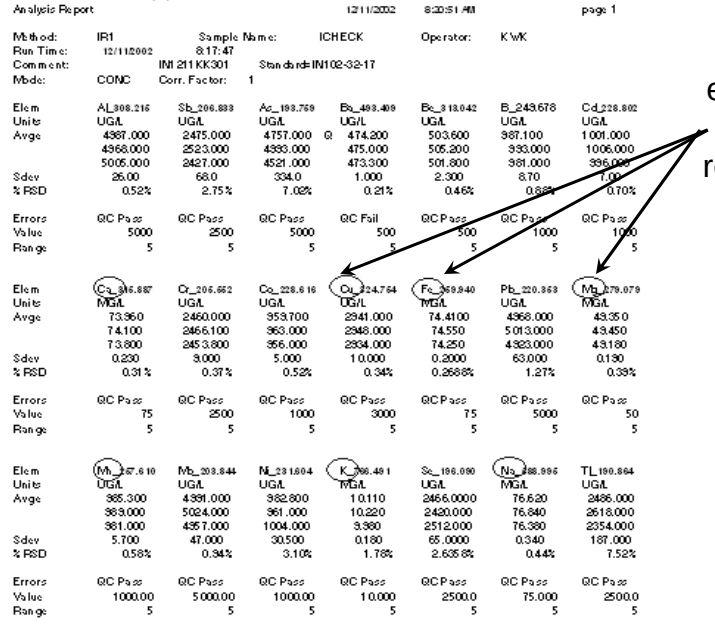
Are elements not required clearly labeled?

Standard tracking numbers for any standards solutions

Raw data for all analyses

- How is “raw data” defined?
- How many replicate “integrations” are required?

Instrument Printout Considerations



Analysis Report 12/11/2002 8:20:51 AM page 1

Method: IR1 Sample Name: ICHECK Operator: KWK
Run Time: 12/11/2002 8:17:47
Comment: INI 211 KK301 Standards IN102-32-17
Mode: CONC Corr. Factor: 1

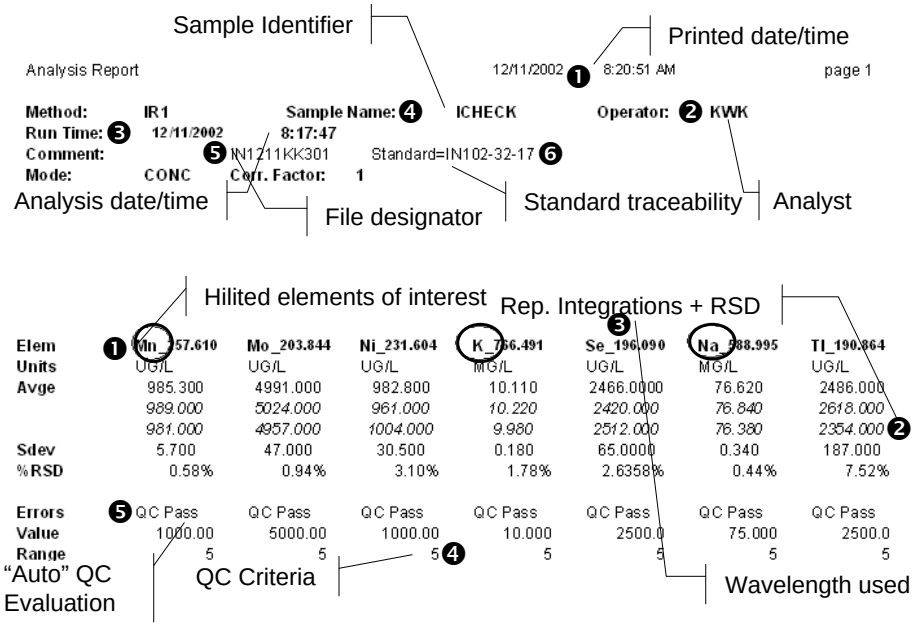
Elem	Al_308.215	Sb_206.833	As_193.759	Ba_493.409	Be_313.042	B_249.678	Cd_228.802
Units	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Avge	4987.000	2475.000	4757.000	Q 474.200	503.600	987.100	1001.000
	4968.000	2523.000	4983.000	475.000	505.200	983.000	1006.000
	5005.000	2427.000	4521.000	473.300	501.800	981.000	996.000
Sdev	26.00	68.0	334.0	1.000	2.300	8.70	7.00
% RSD	0.52%	2.75%	7.02%	0.21%	0.46%	0.88%	0.70%
Errors	QC Pass	QC Pass	QC Pass	QC Fail	QC Pass	QC Pass	QC Pass
Value	5000	2500	5000	500	500	1000	1000
Range	5	5	5	5	5	5	5

Elem	Ca_396.847	Cr_205.552	Co_228.616	Cu_324.754	Fe_259.940	Pb_220.353	Mg_279.079
Units	MG/L	UG/L	UG/L	UG/L	MG/L	UG/L	MG/L
Avge	73.360	2460.000	953.700	2941.000	74.4100	4968.000	49.350
	74.100	2466.100	963.000	2948.000	74.550	5013.000	49.450
	73.800	2453.800	956.000	2934.000	74.250	4923.000	49.180
Sdev	0.230	3.000	5.000	10.000	0.2000	63.000	0.130
% RSD	0.31%	0.37%	0.52%	0.34%	0.2688%	1.27%	0.39%
Errors	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass
Value	75	2500	1000	3000	75	5000	50
Range	5	5	5	5	5	5	5

Elem	Mn_257.610	Mo_203.844	Ni_231.604	K_766.491	Se_196.090	Na_588.995	Tl_190.864
Units	UG/L	UG/L	UG/L	MG/L	UG/L	MG/L	UG/L
Avge	385.300	4981.000	982.800	10.110	2466.0000	76.620	2486.000
	383.000	5024.000	961.000	10.220	2420.000	76.840	2618.000
	381.000	4957.000	1004.000	9.380	2512.000	76.380	2354.000
Sdev	5.700	47.000	30.500	0.180	65.0000	0.340	187.000
% RSD	0.58%	0.34%	3.10%	1.78%	2.635%	0.44%	7.52%
Errors	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass
Value	1000.00	5000.00	1000.00	10.000	2500.0	75.000	2500.0
Range	5	5	5	5	5	5	5

Which elements are to be reported from this batch?

Instrument Printout Considerations



Instrument Printout Considerations

Elem	Cd_228.802	As_193.759	Tl_190.864
Units	UG/L	UG/L	UG/L
Avge	**1001.000**	**4757.000**	2486.000
	1006.000	*4993.000*	*2618.000*
	996.000	*4521.000*	*2354.000*
Sdev	7.00	334.0	187.000
%RSD	0.70%	7.02%	7.52%
Errors	QC Pass	QC Pass	QC Pass
Value	1000	5000	2500.0
Range	5	5	5
	-4 to +6 ppb	-7 to -479 ppb	-146 to +118 ppb

All the RSD tells you is that replicates are "bad"
Having actual replicate values helps define "bad"

What Is "Raw Data"?

NR 149.05

(22m) "Raw data" means any laboratory worksheets, records, memoranda, notes, or exact copies thereof, that are the result of original observations and activities of an analysis and are necessary for the reconstruction and evaluation of the analysis which may include photographs, microfilm or microfiche copies, computer printouts, magnetic media, and recorded information from automated collection systems.

SW-846 Chapter 1

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, benchsheets, files or other sample tracking or data entry forms. Instrumental output should be

CLP

2.5.2.3.1 Raw data shall contain all instrument readouts and data pertinent to the reconstruction of the analysis and results (e.g., Batch Sheets) used for the sample results. Each exposure or instrumental reading shall be provided, including those readouts that may fall below the Method Detection Limit (MDL). Raw data shall not be corrected for dilutions or volume adjustments. All Atomic Absorption (AA), Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES), and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) instruments shall provide a legible hardcopy of the direct real-time instrument readout (i.e., strip charts, printer tapes, etc.) or a printout of the unedited instrument data output file. A photocopy of the instrument's direct sequential readout shall be included. A hardcopy of the instrument's direct readout shall be included for cyanide if the instrumentation has the capability.

Is THIS Raw Data?

Method:	**IR1**	**Sample Name:**	**ICV**	**Operator:**	**KWK**
Run Time:	**12/11/2002**	**8:20:55**			
Comment:		IN1211KK301			
Mode:	**CONC**	**Corr. Factor:**	**1**		

Elem	**Al**	**Sb**	**As**	**Ba**	**Be**	**B**	**Cd**
Units	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Avge	4703.000	2838.000	4786.000	4853.000	396.400	951.100	492.100
Sdev	37.00	58.0	43.0	40.000	1.800	11.40	10.50
%RSD	0.79%	2.04%	0.90%	0.82%	0.45%	1.20%	2.13%
Errors	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass
Value	5000	3000	5000	5000	400	1000	500
Range	10	10	10	10	10	10	10

Or this? Or this? …and what 'correction' was made?

Elem	**Cd 226.502**	**Cr 205.560**	**Cu 324.754**	**Fe 259.940**	**Mn 257.610**	**Int. Std Sc 361.384**
Units	ppm	ppm	ppm	ppm	ppm	mg/L
Avg	0.9880	11.0300	10.7400	1.0185	10.8750	0.6621
Stddev	0.006010	0.000000	0.014142	0.003536	0.007071	0.008344
%RSD	**0.61%**	**0.00%**	**0.13%**	**0.35%**	**0.07%**	**1.26%**
Mean Corrected Intensity	12977.7	66096.4	614705.7	17872.5	1217528.8	274776.2
#1 ppm	0.9922	11.03	10.73	1.021	10.88	0.6562
#2 ppm	0.9837	11.03	10.7500	1.016	10.87	0.6680
Net Intensity 1	8293.2	43325.1	407507.9	11483.1	799659.8	272323.5
Net Intensity 2	8367.7	44102.5	415501.0	11626.5	812721.6	277228.8
Corr. Intensity 1	13033.8	66098.6	614217.1	17919.9	1218533.6	272323.5
Corr. Intensity 2	12921.6	66094.1	615194.2	17825	1216524	277228.8

Do I need to retain emission data?

LabCert has reviewed this issue and will <u>not</u> require labs to retain emission data.

- Reports will include as a "Recommended Laboratory Practice" that ICP instruments <u>should</u> be capable of providing raw emission data for each wavelength
- Ultimate goal is to be able to reproduce analyte concentrations from raw, uncorrected emission data.
- This decision, as it relates to ICP, is not viewed as an exception, but rather as an interpretation of how the Program enforces sections of NR 149.
- Best parallel situation = GC or GC/MS raw data:
  - Raw data required = peak area
  - peak area is equivalent to ICP emission counts
  - GC: Peak area can be traced to final results
  - ICP: Emissions cannot (easily) be traced to final result

Which Do I Follow? The Code or the Method (or Both?)

1. The code is the law, and in all cases, labs must meet code requirements.

2. Labs can be held to method requirements that are also addressed by code if the method requirements are as or more stringent than the code requirement:

   - If a method is STRICTER than code requirement ---->method
   - If a method is LESS STRICT than code requirement---->code

3. Labs can also be held to specific or unique method requirements if the code is silent on the subject of that particular requirement.

An example: If a given method provides requirements for acceptable blank performance that are more stringent than the blank acceptance criteria listed in NR 149.14(3)(d), the laboratory can be held to the requirement of the method. If, however, the method requirements are less stringent than 149.14(3)(d), the lab will be held to the code requirements regardless of what the method states.

In <u>MOST</u> cases, passages using "should" are considered recommendations, while language using "must" are considered requirements. This is a general rule of thumb, and certain cases may provide justification for alternate interpretations.

Authoritative Sources

200.7

CFR version?

EPA version?

Revision #? (currently rev. 4.4, 1994)

Draft revision 5.0 out since Aug 1998

SW-846

6010--> 6010B --> 6010C

Standard Methods

SM 3120B (18th, 19th, 20th ed.s approved)

+1020…to cover QA/QC

Things to Come?

- Proposed revision to MDL procedure (FR 3/12/03)
- Draft Revision 5 to 200.7 (8/98)
  - an actual IDC
  - new spike acceptance criteria
  - formal use of minimum level (ML) concept
  - new blank criteria: greater of (ML or 1/3 reg. criteria)
  - new calibration requirements
    - *lowest point must be equal to the "ML"*
    - *should include a standard at the LDR*
    - *calculate response factors*
    - *performance criteria to be established "later"*
  - Interferent concentrations must not exceed LDR

Internal audit as a tool for improving data quality

1. Purpose of an Internal Audit: Meet quality goals:

A. Insure that the analysts are following procedures specified in the lab's methods and in the regulatory methods.

B. Promote consistent practices from test to test throughout the laboratory.

C. Insure that the laboratory is meeting requirements of regulating agencies (e.g. NELAC, USEPA, WDNR). Note: internal audits are a NELAC requirement.

2. Who Conducts an Internal Audit?

A. Ideally, a quality control coordinator.

B. Someone who has a *general* knowledge of the procedure and who is independent of the activity to be audited

What Is An Internal Audit

A. Review method documentation to be sure it is up-to-date, complete, and meets regulations.

1. Review the SOP:

- Does the SOP meet requirements of the reference method? Note any deviations.

  Example: 200.7, 9.2.2: verify the LDR annually or when there is a change in operating conditions.

- Does the SOP meet requirements of any applicable NELAC, EPA, or DNR regulations?

  Example: NR149.14(3)(c): analyze a known standard every 20 samples (limit ± 10%). However **200.7, 9.3.4** requires an Instrument Performance Check (IPC) after the calibration (limit ± 5%), every 10 samples (limit ± 10%), and at the end of the run (limit ± 10%). The lab's SOP should follow 200.7.

- Does the SOP follow a standard format for organization and content? A standard format makes items easier to find and insures that all requirements will be included. Corrective action language *(e.g. what action will be taken if a spike fails?)* is important to include.

What Is An Internal Audit

A. Review method documentation to be sure it is up-to-date, complete, and meets regulations.

2. Review analyst training records, DOCs, LOD verifications, LDR verifications, IEC factors, etc.

B. Review PT sample results analyzed by the method and any exceedance reports that may have been filed.

Example: Arsenic by ICP failed an internal blind -- we discovered that the As standard was contaminated (but not at a level that would show in routine QC samples).

C. Review data to insure the analyst followed required procedures.

1. Have the required quality control samples been analyzed and properly recorded?

Note: *the terminology (e.g. Spike vs. Lab Fortified Matrix) that will be used on the bench records should be recorded in the SOP.*

What Is An Internal Audit

C. Review data to insure the analyst followed required procedures.

2. Was the calibration done according to the method?
3. Are data clearly recorded and manipulations clearly marked?
4. Were the data reviewed by a second person before being reported?
5. Were the data properly reported and filed?

D. Check logbooks for proper entries.

Example: Reagent/standard preparation log provides traceability. Instrument log contains items such as dates used, instruments settings, and maintenance performed.

What Is An Internal Audit

E. Interview the analyst.

1. Usually, watch them analyze some samples by the method and ask them a few questions.
2. Is the analyst following the procedure that is documented in the SOP?
3. Does the analyst have any questions or concerns they would like to have addressed?

F. Write an internal audit report.

1. Fill in a standardized template (example provided w/class materials).

G. The supervisor coordinates corrective actions in response to the internal audit and reports back in writing to the QA Coordinator.

1. The supervisor and the analysts responsible for the method work together to decide what changes will be made to their procedures.

Benefits of Internal Audits

4. What are Positive Outcomes of an Internal Audit?

A. Catch simple mistakes.

Example: The analyst may have failed to check and record the solution uptake rate of the nebulizer (200.7, 10.2.2).

B. Catch complicated issues that need to be resolved or streamlined. The analyst is often grateful to get some guidance, and then they feel more comfortable performing the test.

Example: The analyst may need help to develop a method to adequately verify the interelement correction factors (200.7, 10.4).

Benefits of Internal Audits

4. What are Positive Outcomes of an Internal Audit?

C. Create uniformity from one method to another and standardize procedures throughout a section (or the lab).

1. Often issues that are raised during an internal audit for one method also can improve other methods.

D. The keys to achieving a positive outcome from an internal audit:

1. The auditor maintains a helpful, non-authoritarian, and non-defensive attitude.
2. The auditor offers his/her findings in the audit report and summarizes "Action Items".
3. The Quality System should have provisions to ensure that internal audit findings are addressed, resolved, and documented in a timely manner.

Trouble-shooting

- Room temperature variability - Air-conditioning is necessary 21°C ± 3°C (from J-Y literature)
- Consistent low-moderate humidity
- Matrix match calibration standards to acid content (or use an IS)
- Accurate dispensing is critical when using an IS
- Monitor nebulization…be sure you have an even, fine solution in spray chamber
- Monitor day-to-day variability in blank emission counts
- Unexplained drift may be due to Argon leaks
- Monitor RPDs for increasing variability
- BGC or IEC??
- Review Spectrum shifter problem (direct readers)
- Placement of baffle in spray chamber affects precision

YOU be the auditor

Lab X ….."standard" ICS-A

Elem	As1890	Ag3280	Al3082	Al3961	B2497
Units	ppm	ppm	ppm	ppm	ppm
Avg	0.003	-0.006	536.800	702.150	0.013
Stddev	0.077	0.001	0.424	3.465	0.000
%RSD	2895.14%	-25.82%	0.08%	0.49%	2.19%
#1	-0.0516	-0.0047	536.5000	704.6000	0.0127
#2	0.0569	-0.0068	537.1000	699.7000	0.0131
Elem	Ba2335	Be3130	Ca1838	Cd2265	Co2286
Units	ppm	ppm	ppm	ppm	ppm
Avg	-0.027	0.004	496.200	0.021	0.002
Stddev	0.001	0.000	2.121	0.002	0.001
%RSD	-3.91%	8.08%	0.43%	10.72%	55.00%
#1	-0.0279	0.0037	497.7	0.0227	0.0025
#2	-0.0264	0.0033	494.7	0.0195	0.0011
Elem	Cr2677	Cu3247	Fe2493	Fe2599	K7698
Units	ppm	ppm	ppm	ppm	ppm
Avg	0.045	0.016	200.900	221.550	-0.313
Stddev	0.005	0.001	1.273	11.526	0.028
%RSD	12.02%	5.69%	0.63%	5.20%	-9.02%
#1	0.0409	0.0168	201.8	229.7	-0.2927
#2	0.0485	0.0155	200	213.4	-0.3326

YOU be the auditor

Lab X ….."standard" ICS-A

Elem	Mg2790	Mn2576	Mo2020	Na5895	Ni2316
Units	ppm	ppm	ppm	ppm	ppm
Avg	488.000	-0.008	-0.013	0.043	0.003
Stddev	0.990	0.001	0.000	0.000	0.002
%RSD	0.20%	-8.84%	-2.71%	0.98%	61.37%
#1	488.7	-0.0075	-0.0128	0.0437	0.0038
#2	487.3	-0.0085	-0.0133	0.0431	0.0015
Elem	Pb2203	Sb2068	Se1960	Si2881	Sn1899
Units	ppm	ppm	ppm	ppm	ppm
Avg	-0.006	-0.149	0.073	-1.038	-0.047
Stddev	0.064	0.015	0.028	0.047	0.011
%RSD	-1352.63%	-10.18%	38.78%	-4.50%	-22.38%
#1	-0.0655	-0.1593	0.0934	-1.071	-0.0549
#2	0.0531	-0.1379	0.0532	-1.005	-0.0399
Elem	Sr4215	Tl1908	V 2924	Zn2138	
Units	ppm	ppm	ppm	ppm	
Avg	0.003	0.061	0.008	-0.008	
Stddev	0.000	0.033	0.003	0.000	
%RSD	2.48%	54.29%	39.19%	-5.37%	
#1	0.0028	0.0849	0.0106	-0.0076	
#2	0.0029	0.0378	0.006	-0.0082	

YOU be the auditor

Blank (ICB) analyzed by Lab Y 12/4/02

Method: PLASMA **Sample Name:** blank **Operator:**
Run Time: 09/11/1996 9:30:02
Comment:
Mode: CONC **Corr. Factor:** 1

Elem	Ag3280	Al3082	As1936	Ba4934	Ca3179	Cd2265	Cr2677
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	**-0.0072**	**0.0570**	**-0.0311**	**-0.0019**	**0.1084**	**-0.0053**	**-0.0137**
Sdev	0.0011	0.0084	0.0327	0.0004	0.0074	0.0016	0.0039
%RSD	-15.31%	14.64%	-105.17%	-20.90%	6.82%	-29.44%	-28.17%
#1	-0.0078	0.0487	-0.0689	-0.0024	0.1100	-0.0068	-0.0175
#2	-0.0059	0.0654	-0.0107	-0.0017	0.1148	-0.0037	-0.0098
#3	-0.0078	0.0570	-0.0138	-0.0017	0.1003	-0.0053	-0.0137
LOD	**0.0040**	**0.0590**	**0.0420**	**0.0070**	**0.0620**	**0.0070**	**0.0080**

Elem	Cu3247	Fe2599	Mg2790	Mn2576	Ni2316	Pb2203	Se1960	Zn2138
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	**-0.0036**	**0.0140**	**0.0636**	**0.0000**	**-0.0082**	**-0.0232**	**0.0021**	**-0.0007**
Sdev	0.0018	0.0019	0.0214	0.0000	0.0014	0.0192	0.0070	0.0013
%RSD	-50.00%	13.38%	33.57%	#DIV/0!	-17.53%	-82.96%	327.87%	-173.2%
#1	-0.0054	0.0146	0.0513	0.0000	-0.0099	-0.0442	-0.0039	0
#2	-0.0018	0.0155	0.0883	0.0000	-0.0074	-0.0064	0.0005	0
#3	-0.0036	0.0119	0.0513	0.0000	-0.0074	-0.0190	0.0098	-0.0022
LOD	**0.0060**	**0.0810**	**0.0700**	**0.0060**	**0.0110**	**0.0490**	**0.0700**	**0.0140**

YOU be the auditor

ICS-A (Al_{500},Ca_{500},Mg_{500}, Fe_{200} analyzed by Lab Y 12/4/02

Method: PLASMA **Sample Name:** icsa **Operator:**
Run Time: 09/11/1996 10:25:12
Comment: *(The date is off on this instrument….the actual date is 12/4/2002)*
Mode: CONC **Corr. Factor:** 1

Elem	Ag3280	Al3082	As1936	Ba4934	Ca3179	Cd2265	Cr2677
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	**0.0006**	**480.3667**	**0.0408**	**-0.0013**	**440.9333**	**-0.0019**	**-0.0021**
Sdev	0.0018	3.3171	0.0471	0.0004	2.8006	0.0016	0.0020
%RSD	301.39%	0.69%	115.56%	-30.31%	0.64%	-86.16%	-95.59%
#1	0.0023	484.0000	0.0861	-0.0011	443.7000	-0.0001	-0.0007
#2	-0.0013	479.6000	-0.0080	-0.0011	441.0000	-0.0023	-0.0012
#3	0.0008	477.5000	0.0443	-0.0018	438.1000	-0.0033	-0.0044
LOD	**0.0040**	**0.0590**	**0.0420**	**0.0070**	**0.0620**	**0.0070**	**0.0080**

Elem	Cu3247	Fe2599	Mg2790	Mn2576	Ni2316	Pb2203	Se1960	Zn2138
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	**-0.0008**	**175.6000**	**499.5667**	**-0.0003**	**-0.0004**	**-0.0097**	**-0.0009**	**-0.0053**
Sdev	0.0017	1.3115	3.7754	0.0003	0.0027	0.0137	0.0188	0.0004
%RSD	-198.03%	0.75%	0.76%	-75.50%	-671.29%	-142.06%	-2091.64%	-6.7%
#1	0.0008	177.0000	503.7000	-0.0006	0.0027	0.0020	-0.0046	-0.0049
#2	-0.0008	175.4000	498.7000	-0.0003	-0.0020	-0.0062	0.0195	-0.0056
#3	-0.0025	174.4000	496.3000	-0.0001	-0.0019	-0.0248	-0.0176	-0.0053
LOD	**0.0060**	**0.0810**	**0.0700**	**0.0060**	**0.0110**	**0.0490**	**0.0700**	**0.0140**

Follow-up:Lab Y

What changed? (from ICB to ICS-A)

	Ag3280	Al3082	As1936	Ba4934	Ca3179	Cd2265	Cr2677
ICB	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	-0.0072	0.0570	-0.0311	-0.0019	0.1084	-0.0053	-0.0137
ICS-A	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	0.0006	480.3667	0.0408	-0.0013	440.9333	-0.0019	-0.0021

	Cu3247	Fe2599	Mg2790	Mn2576	Ni2316	Pb2203	Se1960	Zn2138
ICB	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	-0.0036	0.0140	0.0636	0.0000	-0.0082	-0.0232	0.0021	-0.0007
ICS-A	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	-0.0008	175.6000	499.5667	-0.0003	-0.0004	-0.0097	-0.0009	-0.0053

Is it significant? (look at overall precision)

	Ag3280	Al3082	As1936	Ba4934	Ca3179	Cd2265	Cr2677
ICB	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	-0.0078	0.0487	-0.0689	-0.0024	0.1100	-0.0068	-0.0175
	-0.0059	0.0654	-0.0107	-0.0017	0.1148	-0.0037	-0.0098
	-0.0078	0.0570	-0.0138	-0.0017	0.1003	-0.0053	-0.0137
ICS-A	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	0.0023	484.0000	0.0861	-0.0011	443.7000	-0.0001	-0.0007
	-0.0013	479.6000	-0.0080	-0.0011	441.0000	-0.0023	-0.0012
	0.0008	477.5000	0.0443	-0.0018	438.1000	-0.0033	-0.0044

YOU be the auditor

ICS-A (Al_{500},Ca_{500},Mg_{500}, Fe_{200} analyzed by Lab Z 6/25/02

Method:	AUTOROU3		**Sample Name:**	ICSAI	**Operator:**			
Run Time:	06/25/2002	8:06:39						
Comment:	ICP-1							
Mode:	CONC		**Corr. Factor:**	1				
					(Pb 1st order)	*(Pb 2nd order)*	*(Se 1st order)*	
Elem	**As 1890**	**Ba 1934**	**Cd2265**	**Cr2677**	**2203/1**	**2203/2**	**1960/1**	**V 2924**
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	0.00995	0.0033	0.0029	0.0107	0.00051	-0.00288	0.00257	0.0064
Sdev	0.00204	0.0000	0.0000	0.0001	0.00370	0.00134	0.00585	0.0004
%RSD	20.55%	0.00%	0.00%	0.66%	732.31%	-46.65%	227.81%	6.63%
#1	0.00850	0.0033	0.0029	0.0107	-0.00211	-0.00193	0.00671	0.0061
#2	0.01139	0.0033	0.0029	0.0106	0.00312	-0.00383	-0.00157	0.0067
LOD=	**0.0036**	**0.0005**	**0.0005**	**0.0007**				**0.0014**
	(Se 2nd order)							
Elem	**1960/2**	**Pb2203**	**Se1960**	**Ag 3280**	**Cu 3247**	**Ni2316**	**Al 3082**	**Zn 2138**
Units	ppm	**ppm**	**ppm**	ppm	ppm	ppm	ppm	ppm
Avge	0.00329	**-0.00176**	**0.00305**	0.0044	-0.0023	-0.0008	587.9500	-0.0346
Sdev	0.00491	**0.00033**	**0.00523**	0.0001	0.0002	0.0001	0.6364	0.0001
%RSD	149.60%	**-18.94%**	**171.61%**	3.21%	-9.43%	-9.43%	0.11%	-0.20%
#1	0.00676	**-0.00199**	**0.00674**	0.0043	-0.0024	-0.0007	588.4000	-0.0345
#2	-0.00019	**-0.00152**	**-0.00065**	0.0045	-0.0021	-0.0008	587.5000	-0.0346
LOD=		**0.0015**	**0.0034**	**0.0009**	**0.0033**	**0.0032**	**0.0281**	**0.0013**
Elem	**Sb2068**	**Be 3130**	**Ca3179**	**Co 2286**	**Fe 2714**	**Mg 2790**	**Mn 2576**	**Tl 1908**
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Avge	-0.0058	0.0012	504.3500	0.0023	187.5500	522.5500	-0.0027	-0.0146
Sdev	0.0003	0.0001	0.4950	0.0001	0.2121	0.4950	0.0000	0.0000
%RSD	-4.88%	6.15%	0.10%	3.14%	0.11%	0.09%	0.00%	0.00%
#1	-0.0056	0.0012	504	0.0023	187.4	522.9	-0.0027	-0.0146
#2	-0.006	0.0011	504.7	0.0022	187.7	522.2	-0.0027	-0.0146
LOD=	**0.004**	**0.0003**	**0.0036**	**0.0029**	**0.0288**	**0.008**	**0.0003**	**0.0019**

YOU be the auditor

Analysis Report 08/12/2002 13:40:09 PM
Method: 08/02/2002 **Sample Name:** ICSA **Operator:**
Comment: QC Criteria +/- LOQ
Run Time: 8/12/2002 13:32 PM **Type:** QC **Mode:** CONC **Corr. Factor:**

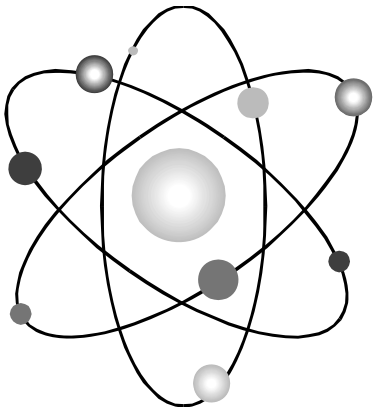
ICS-A (Al_{400},Ca_{400},Mg_{400}, Fe_{160} analyzed by Lab AA 6/25/02

Elem	Ag338.289	Al396.152	As189.042	Ba233.527	Be249.454	Ca184.0062
Units	ppm	ppm	ppm	ppm	ppm	ppm
Avg	0.0011	383.3	-0.0350	0.0031	-0.0015	400.2800
Stddev	0.0023	9.2	0.0295	0.0006	0.0016	1.5054
%RSD	220.05%	2.41%	-84.16%	18.27%	-106.68%	0.38%
Min	-0.0026	377.8000	-0.0836	0.0017	-0.0038	396.6000
Max	0.0045	409.1000	0.0031	0.0036	0.0010	401.6000
Check ?	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass
Value	0.0000	400.00	0.0000	0.0000	0.0000	400.00
Range	0.017	80.0	0.07	0.004	0.0067	80.00

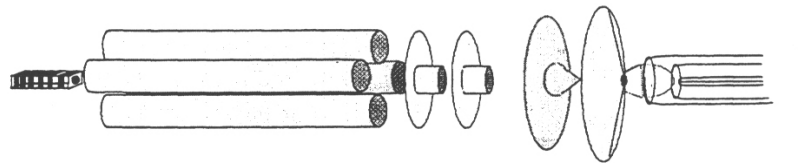
Elem	Cd226.502	Co228.616	Cr267.716	Cu324.754	Fe259.94	Mg293.654
Units	ppm	ppm	ppm	ppm	ppm	ppm
Avg	0.002	-0.0013	-0.0015	0.0003	153.740	433.9100
Stddev	0.001	0.0027	0.0010	0.0007	0.552	1.9134
%RSD	48.15%	-217.39%	-67.51%	250.17%	0.36%	0.44%
Min	0.0007	-0.0042	-0.0035	-0.0007	152.6000	430.0000
Max	0.0040	0.0037	-0.0001	0.0014	154.4000	436.2000
Check ?	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass
Value	0.0000	0.0000	0.0000	0.0000	160.0	400.0000
Range	0.004	0.0073	0.0037	0.0029	32.0	80.0000

Elem	Mn257.610	Ni231.604	Pb220.353	Sb206.833	Se196.090	Zn206.2
Units	ppm	ppm	ppm	ppm	ppm	ppm
Avg	0.000	-0.0029	0.009	-0.0452	0.0159	0.0013
Stddev	0.000	0.0027	0.022	0.0317	0.0268	0.0030
%RSD	311.31%	-94.62%	248.44%	-70.20%	168.66%	227.29%
Min	-0.0005	-0.0075	-0.0170	-0.0954	-0.0201	-0.0043
Max	0.0008	0.0012	0.0445	-0.0029	0.0548	0.0064
Check ?	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass	QC Pass
Value	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Range	0.0140	0.0100	0.0870	0.1400	0.1300	0.0120

An Overview of ICP/MS



Basic Components of an ICP-Mass Spectrometer



detection *filtering* *focusing* *sampling* ***ionisation***

Ref. 4; pg. 4

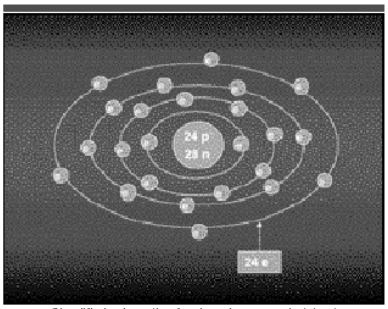


Figure 2. Simplified schematic of a chromium ground-state atom (Cr^0).

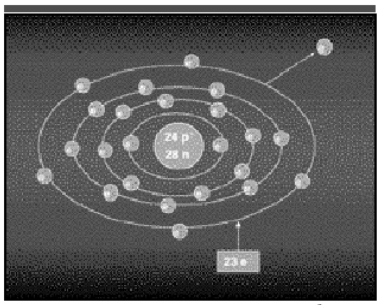
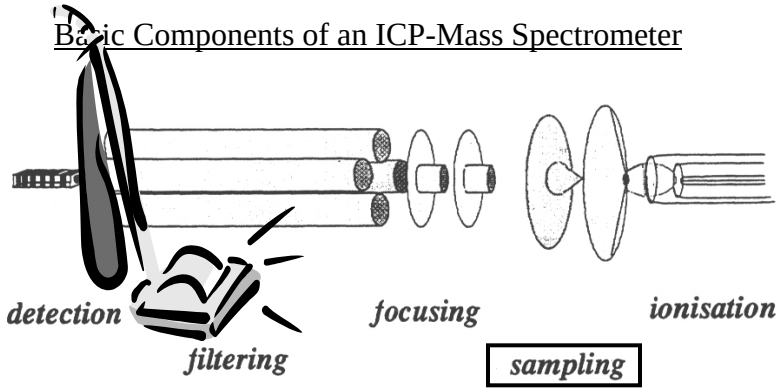


Figure 3. Conversion of a chromium ground-state atom (Cr^0) to an ion (Cr^+).

Ref. 3; pg. 40, Part I

Basic Components of an ICP-Mass Spectrometer



•Two interface cones, each with an orifice size of 0.4-1.2 mm, aid in the transmitting of ions from the atmospheric pressure plasma (at 760 torr) to the low-pressure operating zones of the mass spectrometer (at 10^{-5} -10^{-6} torr).

•The sampling interface is designed to maintain the composition and integrity of the ion stream by limiting the kinetic energy spread of the ions.

Ref. 4; pg. 4

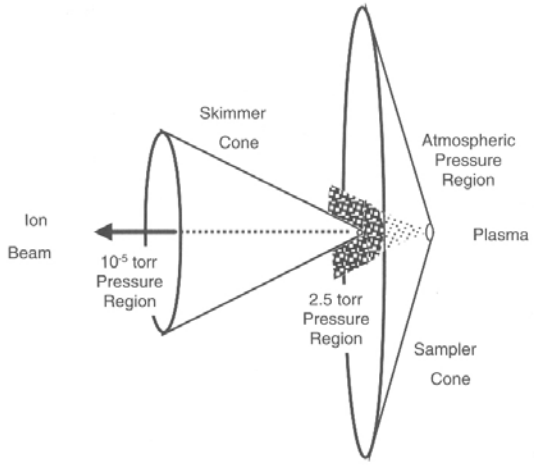
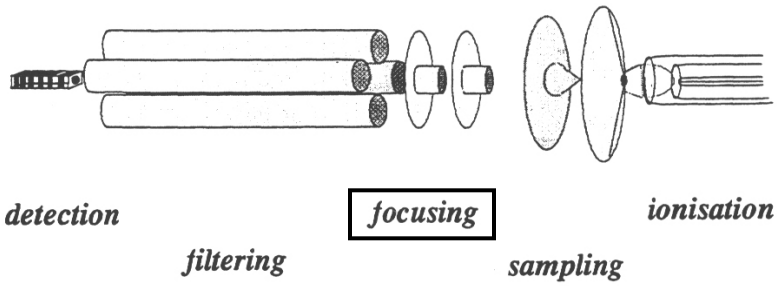


FIGURE 4.2 ICP interface cones, showing the ion beam.

Ref. 2; pg. 31

Basic Components of an ICP-Mass Spectrometer



•The lenses electrostatically steer the maximum number of analyte ions from the sampling region to the mass separation (filtering) device, while minimizing the transport of unwanted non-analyte-based species, such as particulates, neutral species and photons.

Ref. 4; pg. 4

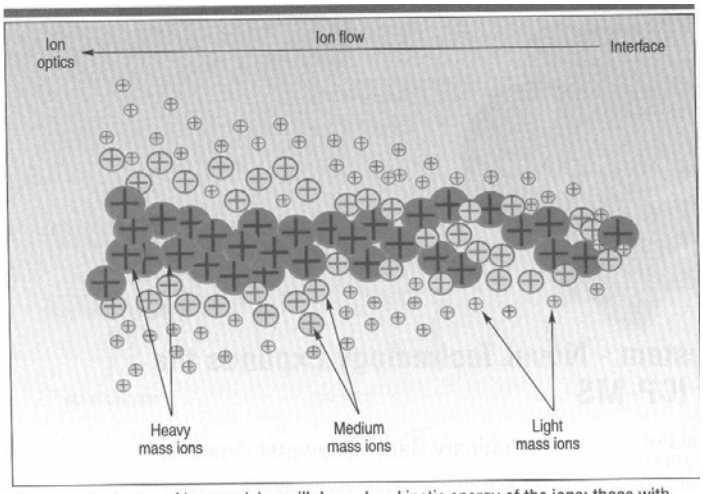
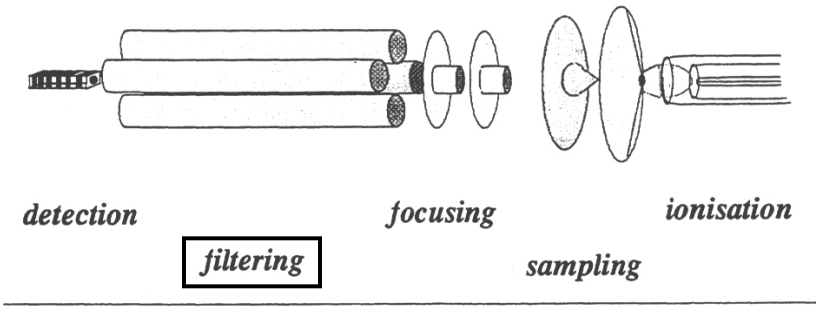


Figure 4. The degree of ion repulsion will depend on kinetic energy of the ions: those with high kinetic energy (green with red +) will be transmitted in preference to ions with medium (yellow with red +) or low kinetic energy (blue with red +).

Ref. 3; pg. 42, Part V

Basic Components of an ICP-Mass Spectrometer



•Quadrupole mass filter is most common (90%) system used in ICPMS.

•Other mass filters used are: Time of Flight, Magnetic Sector, Ion-Trap, Dynamic Reaction Cells.

Ref. 4; pg. 4

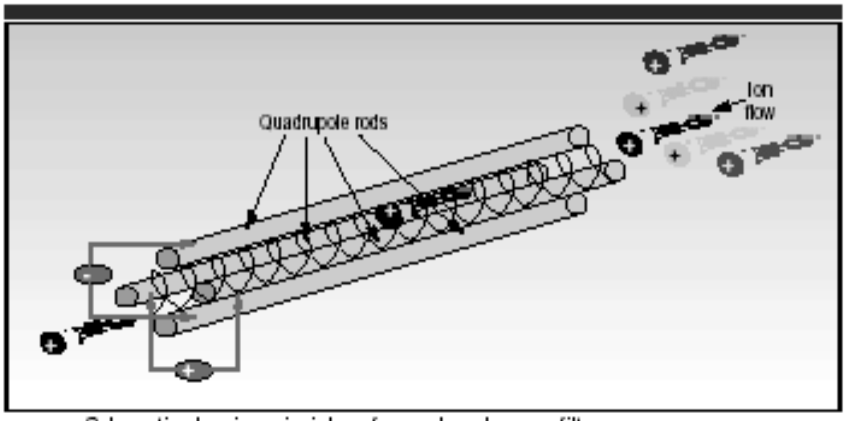
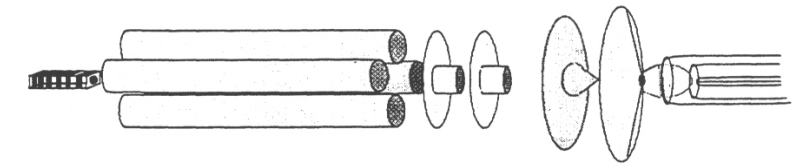


Figure 2. Schematic showing principles of a quadrupole mass filter.

•Separates ions based on their m/z (mass to charge) ratios. Only one mass (m/z) is allowed to reach the detector at any given time.

Ref. 3; pg. 45, Part VI

Basic Components of an ICP-Mass Spectrometer



detection ***focusing*** ***ionisation***

filtering ***sampling***

•Most ICP-MS detection systems use electron multipliers, which convert ion currents into electrical signals.

•The magnitude of the electrical signal is proportional to the number of analyte ions present in the sample.

Ref. 4; pg. 4

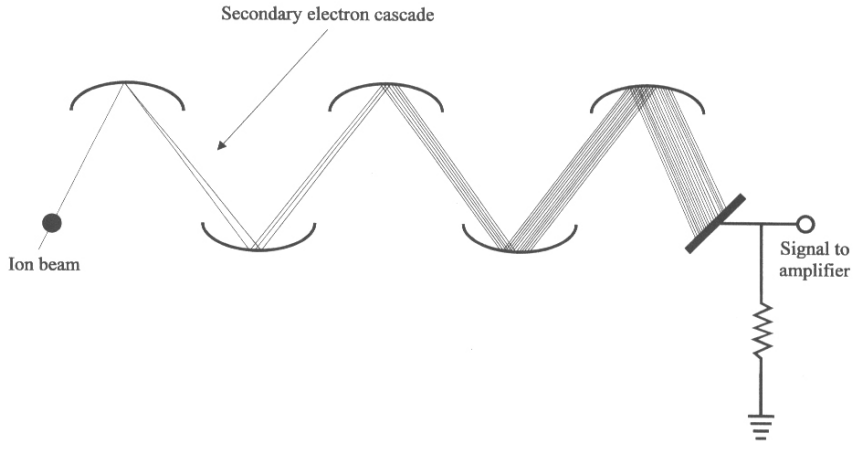
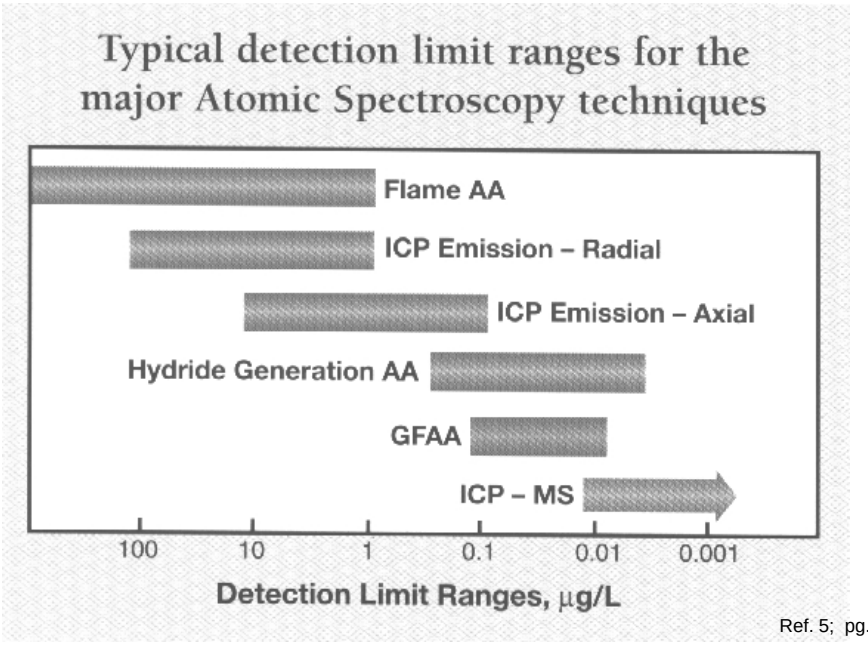


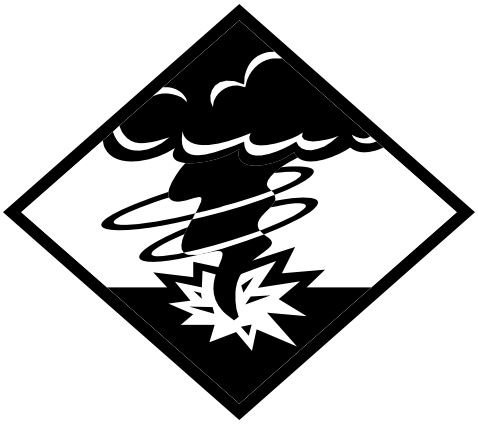
Figure 6.30 Discrete dynode electron multiplier.

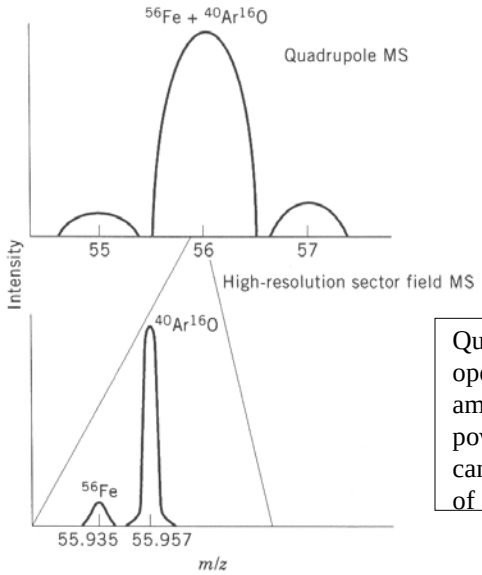
Ref. 1; pg. 481



Ref. 5; pg. 9

HERE COME THE CHALLENGES (QUALIFIED)!!





Quadrupole typically operate at a resolution of 1 amu (approx. 300 resolving power) High resolution can attain a resolving power of approx. 10,000.

Figure 6.34 Comparison of mass spectra of Fe obtained with a quadrupole MS and with a high-resolution magnetic MS.

Ref. 4; pg. 487

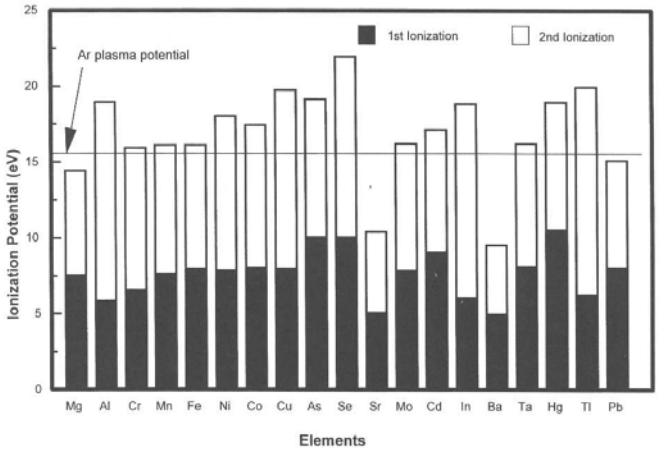
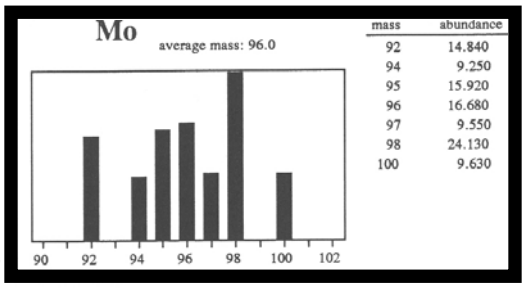
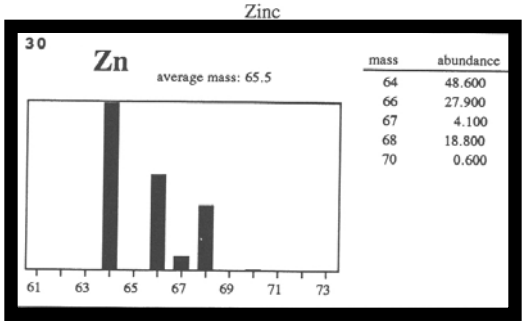


Figure 9.2 First and second ionization potentials of selected metals. (From Reference 16, with permission.)

In ICP-MS, the aim is to maximize singly-charged ions and minimize multiply-charged ions. The instrument measures m/z (mass per unit charge), so a doubly-charged ion will be detected at a mass which is 1/2 that of its singly-charged counterpart. Ref. 1; pg. 684





Natural Isotopes

•Isotopes are atoms of the same element, which have different masses.

•Isotopes have different masses by having varying numbers of neutrons in their nuclei.

•Isotopes of elements that occur in nature have a constant abundance relative to one another, referred to as their *relative natural abundance*.

Ref. 1; pg. 597, 600

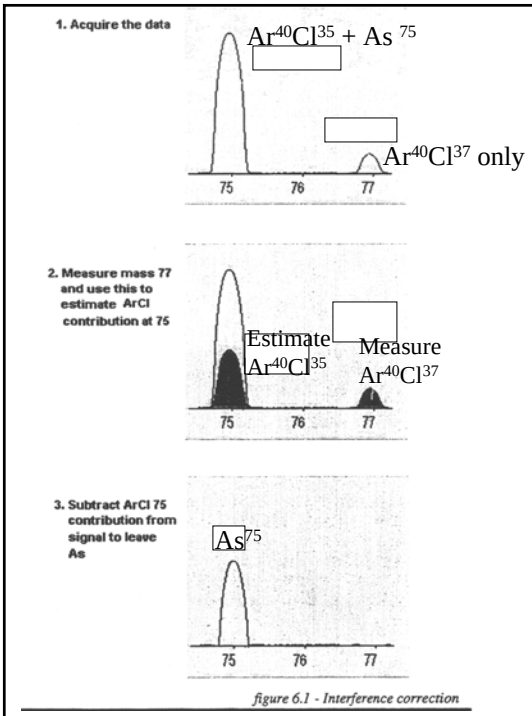


figure 6.1 - Interference correction

Interference Correction Equations

•$Ar^{40}Cl^{35}$ interferes with the analyte of interest, As^{75}, at mass 75.

•Assuming that the other ArCl peak at mass 77 is not itself being interfered with, its peak intensity can be used to estimate the contribution of $Ar^{40}Cl^{35}$ to the peak at mass 75.

•Because Cl^{35} and Cl^{37} are in a fixed natural ratio, the ArCl contribution at mass 75 can be estimated by multiplying the signal at mass 77 by the natural isotope ratio Cl^{35}/Cl^{37}.

•Once the contribution of ArCl at mass 75 is estimated, its intensity can be simply subtracted from the total signal intensity at mass 75, leaving the intensity due to the analyte of interest, As^{75}.

As75=I75-(I77*(75.77/24.23))

Ref. 4; pg. 152

Mass	Element[b]	H_2O (5% HNO_3)	5% H_2SO_4	5% HCl
45	**Sc(100)**	$^{12}C^{16}O^{16}OH$		
46	**Ti(8.01), Ca(0.004)**	$^{14}N^{16}O^{16}$	**$^{32}S^{14}N$**	
47	**Ti(7.33)**		$^{33}S^{14}N$	
48	**Ti(73.81),** Ca(0.187)		$^{34}S^{14}N$, **$^{32}S^{16}O$**	
49	Ti(5.5)		**$^{33}S^{16}O$**	**$^{35}Cl^{14}N$**
50	Ti(5.4), Cr(4.34), V(0.25)	$^{36}Ar^{14}N$	**$^{34}S^{16}O$**	
51	**V(99.76)**			$^{37}Cl^{14}N$, **$^{35}Cl^{16}O$**
52	**Cr(83.79)**	**$^{40}Ar^{12}C$,** $^{36}Ar^{16}O$	$^{36}S^{16}O$	**$^{35}Cl^{16}OH$**
64	**Zn(48.63),** Ni(0.926)		**$^{32}S^{16}O^{16}O$,** $^{32}S^{32}S$	
65	Cu(30.83)		$^{33}S^{16}O^{16}O$, $^{32}S^{33}S$	
66	Zn(27.9)		**$^{34}S^{16}O^{16}O$,** $^{32}S^{34}S$	
67	Zn(4.1)			**$^{35}Cl^{16}O^{16}O$**
68	Zn(18.8)	$^{40}Ar^{14}N^{14}N$	$^{36}S^{16}O^{16}O$, $^{33}S^{36}S$	
69	**Ga(60.108)**			**$^{37}Cl^{16}O^{16}O$**
70	Ge(21.24), Zn(0.62)	$^{40}Ar^{14}N^{16}O$		
71	Ga(39.89)			$^{36}Ar^{35}Cl$
72	Ge(27.66)	$^{36}Ar^{36}Ar$	**$^{40}Ar^{32}S$**	
73	Ge(7.72)		$^{40}Ar^{33}S$	$^{36}Ar^{37}Cl$
74	**Ge(35.94),** Se(0.89)	$^{36}Ar^{38}Ar$	**$^{40}Ar^{34}S$**	
75	**As(100)**			**$^{40}Ar^{35}Cl$**
76	Ge(7.44), Se(9.36)	**$^{36}Ar^{40}Ar$**	$^{40}Ar^{36}S$	

Ref. 1; pg. 523

TABLE 7.5 Calcium Oxide and Hydroxide Species and Other Potential Interferences in the Mass Region for Ni Determination

Mass	Element[a]	Interferences
56	Fe(91.72)	^{40}ArO, ^{40}CaO
57	Fe(2.11)	$^{40}ArOH$, $^{40}CaOH$
58	Ni(68.27), Fe(0.28)	^{42}CaO, NaCl
59	Co(100)	^{43}CaO, $^{42}CaOH$
60	Ni(26.223)	$^{43}CaOH$, ^{44}CaO
61	Ni(1.14)	$^{44}CaOH$
62	Ni(3.634)	^{46}CaO, Na_2O, NaK
63	Cu(69.17)	$^{46}CaOH$, $^{40}ArNa$
64	Ni(0.926), Zn(48.63)	$^{32}SO_2$, $^{32}S_2$, ^{48}CaO
65	Cu(30.83)	$^{32}S^{32}S$, $^{33}SO_2$, $^{48}CaOH$

[a]Natural abundances in parentheses.

Ref. 1; pg. 526

Advantages of ICP-MS

- Detection limits are 10-100 times superior to those of ICP-OES.
- Ability to provide elemental isotopic ratio information.
- Roughly 25 elements can be analyzed in duplicate and with good precision in 1-2 minutes.
- Large linear dynamic working range.
- The effective combination of differing types of ICP-MS instruments coupled with the many varied types of sample introduction allow for customization of techniques for a specific sample type or form of analyte.

Disadvantages of ICP-MS

- The lower-cost ICP-MS systems utilize single-quadrupole mass analyzer systems, which have relatively low mass resolution.
- ICPMS are more costly than ICP-OES.
- Elements such as Ca and Fe are difficult to determine by conventional Ar ICP-MS because of mass spectral interferences by argides.
- If Ni cones are used, can have as much as 5 ppt of nickel being detected as orifice ions. This can be alleviated by switching to more expensive Pt cones.
- Generally requires a clean room environment for ultra-low detection limits.

Disadvantages of ICP-MS

- An outstanding ICP-OES instrument offers a long-term RSD of less than 1% compared to less than 4% for most ICP-MS systems.
- The presence of oxides and doubly-charged ions in the plasma deteriorates the quantitative capability of ICP-MS in ultratrace analysis.
- ICP-MS instruments are more susceptible to instability than ICP-OES intruments when running samples with higher levels of total dissolved solids.
- The relatively cooler sampler and skimmer cones provide direct contact points for sample deposition from the plasma, and can become clogged over time when difficult matrices are analyzed.

References

(1) Montaser, A., Ed., *Inductively Coupled Plasma Mass Spectrometry*, Wiley-VCH, New York, 1998.

(2) Taylor, H.E., *Inductively Coupled Plasma Mass Spectrometry*, Academic Press, San Diego, 2001.

(3) Thomas, R., "A Beginner's Guide to ICP-MS", *Spectroscopy* magazine, April 2001 - February 2003, in 14 parts.

(4) VG Elemental, *PlasmaQuad Software Manual, VG PlasmaQuad 3 User's Guide*.

(5) TJA Solutions, "AAS, FAAS, ICP, or ICP/MS? Which Technique Should I Use?". March 2000.

Which instrument configuration best suits my needs

Flame AA	**No**	Offers no clear advantage
Furnace AA	**Yes**	Can achieve most LODs Need this or ICP/MS for SDWA
Cold Vapor AA	**Yes**	Still the main Hg technique Low level requires MS or fluorescence AA
ICP	**Yes**	Arguably the most versatile Less condition-sensitive and need for training than ICP/MS
ICP/MS	**Maybe**	Provides ultra-trace LODs Can handle unique matrices A good complement to ICP

Which instrument configuration best suits my needs

New technology supplements, not replaces existing technology

(when you buy a snowblower, do you get rid of all your shovels?)

There is no magic bullet

ICP/MS is not the panacea…
nor is dual-view ICP
…or “high resolution” ICP

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