

# AS Techniques for the Analysis of Environmental Samples

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Riccardo Magarini ICPMS /ICPOES /AAS specialist

riccardo.magarini@perkinelmer.com

# Summary



- Poredenje različitih spektroskopskih medoda u analizi metala
- Comparison of Atomic Spectroscopy Techniques and Performances
  - Flame-AAS, GF-AAS, ICP-OES, ICP-MS
  - DLs, speed, interferences, easy of use
- Analytical Factors
  - Sample preparation, pre-analytical factors, official methods
- The analysis process
  - Method development
  - Calibration
  - Performances evaluation
  - Interferences
  - QC



#### **Atomic Absorption**



**ICP-OES** 



#### **Sample Preparation**



**ICP-MS** 



#### Atomic spectroscopy techniques A quick review









### **Detection Limits (ug/L)**





### **Detection Limits (ug/L)**



Elem	Flame AA	Hg/ Hvdride	GFAA	ICP-OES	ICP-MS	Elem	Flame AA	Hg/ Hvdride	GFAA	ICP-OES	ICP-MS
Aa	1.5		0.005	0.6	0.002	Mo	45		0.03	0.5	0.001
Al	45		0.1	1	0.005 <sup>a</sup>	Na	0.3		0.005	0.5	0.0003 <sup>c</sup>
As	150	0.03	0.05	2	0.0006 <sup>b</sup>	Nb	1500			1	0.0006
Au	9		0.15	1	0.0009	Nd	1500			2	0.0004
В	1000		20	1	0.003 <sup>c</sup>	Ni	6		0.07	0.5	0.0004°
Ba	15		0.35	0.03	0.00002 <sup>d</sup>	Os				6	
Be	1.5		0.008	0.09	0.003	Р	75000		130	4	0.1ª
Bi	30	0.03	0.05	1	0.0006	Pb	15		0.05	1	0.00004
Br					0.2	Pd	30		0.09	2	0.0005
C					0.8°	Pr	7500			2	0.00009
Са	1.5		0.01	0.05	0.0002 <sup>d</sup>	Pt	60		2.0	1	0.002
Cd	0.8		0.002	0.1	0.00000 <sup>d</sup>	RЬ	3		0.03	5	0.0004
Ce				1.5	0.0002	Re	750			0.5	0.0003
CI					12	Rh	6			5	0.0002
Co	9		0.15	0.2	0.0009	Ru	100		1.0	1	0.0002
Cr	3		0.004	0.2	0.0002 <sup>d</sup>	s				10	28 <sup>J</sup>
Cs	15				0.0003	Sb	45	0.15	0.05	2	0.0009
Cu	1.5		0.014	0.4	0.0002°	Sc	30			0.1	0.004
Dy	50			0.5	0.0001 <sup>r</sup>	Se	100	0.03	0.05	4	0.0007 <sup>b</sup>
Er	60			0.5	0.0001	Si	90		1.0	10	0.03 <sup>a</sup>
Eu	30			0.2	0.00009	Sm	3000			2	0.0002
F					372	Sn	150		0.1	2	0.0005 <sup>a</sup>
Fe	5		0.06	0.1	0.0003 <sup>d</sup>	Sr	3		0.025	0.05	0.00002
Ga	75			1.5	0.0002	Та	1500			1	0.0005
Gd	1800			0.9	0.00089	Tb	900			2	0.00004
Ge	300			1	0.001 <sup>h</sup>	Te	30	0.03	0.1	2	0.0008 <sup>k</sup>
Hf	300			0.5	0.0008	Th				2	0.0004
Hg	300	0.009	0.6	1	0.016 <sup>1</sup>	Ti	75		0.35	0.4	0.003
Ho	60			0.4	0.00006	TI	15		0.1	2	0.0002
1					0.002	Tm	15			0.6	0.00006
In	30			1	0.0007	U	15000			10	0.0001
Ir	900		3.0	1	0.001	v	60		0.1	0.5	0.0005
К	3		0.005	1	0.0002 <sup>d</sup>	W	1500			1	0.005
La	3000			0.4	0.0009	Y	75			0.2	0.0002
Li	0.8		0.06	0.3	0.001°	Yb	8			0.1	0.0002 <sup>m</sup>
Lu	1000			0.1	0.00005	Zn	1.5		0.02	0.2	0.0003 <sup>d</sup>
Mg	0.15		0.004	0.04	0.0003°	Zr	450			0.5	0.0003
Mn	1.5		0.005	0.1	0.00007 <sup>d</sup>						

### Linear Dynamic Range







Factor	Flame AA	GFAAS	Radial ICP-OES	Axial ICP-OES	ICP-MS
Detection Limits	0	$\odot$	0	$\odot$	•
Accuracy/Precision	۲	0	0	0	0
Concentration Range	$\odot$	•	0	0	•
Sample Volume	0	•	0	0	0
Elements per sample	$\overline{ullet}$	•	0	0	•
Operator Expertise	•	$\odot$	0	0	$\odot$
Purchase price	•	$\odot$	0	0	۲
<ul> <li>Much better</li> </ul>	<ul> <li>Better</li> </ul>	O-Average	<ul> <li>Poorer</li> </ul>	<ul> <li>Much pool</li> </ul>	orer



- Detection Limits
- > Accuracy
- Precision





**Detection Limit = 0.06 mg/L** 

- Detection Limit can be defined in many ways
- Most often it is approximated as the concentration of an analyte that produces a signal that is 3x the standard deviation of the noise level
- It is often calculated using 3x the standard deviation of a blank or a suitable low-level standard



- Instrument Detection Limit (IDL)
  - Defined as the concentration of analyte which equals three times the standard deviation of ten replicates of the calibration blank
- Method Detection Limit (MDL)
  - The minimum concentration of analyte determined to be different from the blank at a confidence level of 99%.
     Error of carrying a sample through the entire analysis process is built into the calculation.
- Practical Quantitation Limit (PQL)
  - Lowest level that can reliably be achieved within specified limits of precision and accuracy during routine operating conditions; often defined as 5 or 10x the standard deviation of the noise level; from: SW846, 1986.

Calculation of MDL: From EPA Method 200.9 (1 of 2)

- 1. Prepare a suitable amount of sample spiked with the element(s) of interest at a level two to three times the IDL.
- 2. Split the sample into a minimum of seven aliquots and process through the entire analytical procedure (e.g., reagent addition, digestion, replicates, etc.).
- 3. Perform all calculations as described in the method and calculate the standard deviation of the results of the seven aliquots.

Calculation of MDL: From EPA Method 200.9 (2 of 2)

4. Calculate the MDL according to this formula:

```
MDL = t \cdot s
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where:

- t = students' t value at the 99% confidence level using n-1 degrees of freedom (t = 3.14 (for seven replicates)
- s = standard deviation of the results of the prepared aliquots



- 1. Repeat steps 1-3 as in 200.9 over three nonconsecutive days
- 2. Average the 'daily' MDL values to obtain the 'rugged' MDL



### Accuracy

The difference between an average value and the true value when the latter is known (from EPA)

### Precision

The degree of mutual agreement among individual measurements made under prescribed conditions (from EPA)







- Fast
  - 3 5" a determination
- Low analytical costs
- Easy to use
- Single element technique







- Selecting the correct instrument parameters
- Determining the range of analysis for each element
  - Working Ranges
  - Sensitivity and Detection Limits
- Setup and Optimization
  - Flame
  - Burner and Nebulizer Adjustments
  - Integration times
- Interferences
  - Non spectral and spectral
- Quality Control

#### **Recommended Conditions from AAWinLab™**



PerkinElmer

precisely



#### Flame Sensitivity











# Nonspectral

Any interference which affects the sample signal in a manner which is different from the calibrating materials

(Matrix; Chemical; Ionization)

Spectral

Occur when the measured absorption in a sample is erroneous due to the presence of another species which is also absorbing light at that wavelength

(Non Specific Absorption, more common in GF-AAS)









Conc



- Example: Certain samples may contain components that form thermally stable compounds that will not decompose with the typical energy available in the flame
  - Temperature of air-C<sub>2</sub>H<sub>2</sub> flame: 2100 2400°C
  - Temperature of N2O-C<sub>2</sub>H<sub>2</sub> flame: 2650 2800°C





- > Add releasing agent to all solutions
- Example: Add Lanthanum to combine with the phosphate and allow the free Ca atoms to be produced in the flame
- > In this example, 0.2-0.5% La is usually added

$$Ca_3(PO_4)_2 \xrightarrow{LaCl_3} CaCl_2 \xrightarrow{air-C_2H_2} Ca^0$$



- > Matrix match all samples, standards, and blanks
- > Analyze using Method of Standard Additions (MSA)











### **Background Correction: Continuum Source**







# Dissolved

- Filtered through 0.45  $\mu$ m membrane filter
- Acidified to pH < 2

# Total recoverable

- Acid preserved drinking water with turbidity < 1 NTU
   <ul>
   no digestion necessary (unfiltered)
- Others, acid digestion

SW-846 Sample Prep Procedures for FL-AAS



### Method 3005A

Acid digestion of waters for total recoverable or dissolved metals for analysis by FLAA or ICP Spectroscopy

### Method 3010A

Acid digestion of aqueous samples and extracts for total metals for analysis by FLAA or ICP Spectroscopy

SW-846 Sample Prep Procedures for FL-AAS



Method 3015 Microwave assisted digestion of aqueous sample and extracts

Method 3031 Acid digestion of oils for metals analysis by atomic absorption or ICP spectrometry

> Method 3040A

Dissolution procedure for oils, greases, or waxes



Method 3050B Acid digestion of sediments, sludges, and soils

Method 3051 Microwave assisted acid digestion of sediments, sludges, soils, and oils

### Method 3052

Microwave assisted acid digestion of siliceous and organically based matrices


Element	Method	Est. Range mg/L *	Oxidant	Bkg. Corr.
Aluminum	7020	>1	Nitrous oxide	Not required
Antimony	7040	> 0.5	Air	Required
Barium	7080A	> 0.4	Nitrous oxide	Not required
Beryllium	7090	> 0.025	Nitrous oxide	Required
Cadmium	7130	> 0.025	Air	Required
Calcium	7140	> 0.08	Nitrous oxide	Not required
Chromium	7190	> 0.25	Nitrous oxide	Not required
Cobalt	7200	> 0.2	Air	Required
Copper	7210	> 0.1	Air	Recommend

\* Based on 0.0044 absorbance



## Barium

- Numerous chemical interferences in air-C<sub>2</sub>H<sub>2</sub> which are virtually eliminated using N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>
- Strong emission of the N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame can lead to excessive noise; try increasing the lamp current and/or reducing the slit
- Barium is ionized 80-90% in a N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame; add 0.2-0.5% of an easily ionizable metal (e.g., K as CI<sup>-</sup>)
- Char. conc. at 553.6 is approx.. 0.4 mg/L; can be improved by concentrating sample and/or changing impact device



## Cadmium

- At the primary wavelength of 228.8 nm, Cd is easily determined in an air-C<sub>2</sub>H<sub>2</sub> flame with a detection limit of about 0.8 ug/L
- Samples with high dissolved solids, such as wastewater, often require background correction



## Chromium

- For flame AA, most sensitive using a fuel-rich, air-C<sub>2</sub>H<sub>2</sub> flame, but is extremely prone to interferences from Fe, Ni, and other metals; 0.2% Na<sub>2</sub>SO<sub>4</sub> and/or 2% NH4CI have been shown to reduce the effects
- Cr(III) exhibits a higher sensitivity than Cr(VI) in the rich, air-C<sub>2</sub>H<sub>2</sub> flame; a lean flame flame or a N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame will reduce the interference, but also the sensitivity
- For determinations of Cr(VI), EPA Methods 218.3 & 7197 chelate the Cr(VI) with ammonium pyrrolidine dithiocarbamate (APDC) and subsequent extraction with methyl isobutyl ketone (MIBK); extract can be determined by flame or furnace; MDL by flame is approx. 1 ug/L



## > Chromium (cont.)

• For determination of Cr(VI), EPA Method 7195 involves the coprecipitation of Cr(VI) as lead chromate with lead sulfate in an acetic acid solution. The supernate is drawn off and the precipitate is resolubilized. Quantification can be by flame or furnace AA.

## Copper

- Few interferences in an air-C<sub>2</sub>H<sub>2</sub> flame at 324.8 nm
- Sensitivity not affected by many instrument conditions so frequently used as a test for instrument/method



## ≻ Lead

- The resonance line at 217.0 nm is 2.5X more sensitive than the 283.3 nm line, but the DL is slightly degraded because of significantly higher noise
- The 217.0 nm line also suffers from additional background effects
- To improve sensitivity, an extraction procedure can be performed; in EPA 600/4-79-020, Section 9.2 an extraction with APDC in MIBK is recommended for flame determinations where Pb levels are below 200 ug/L

Wastewater Analysis (ERA Wastewater Reference)



- Many metals limits are of sufficient concentration for flame AA determination
- Wastewater standard from ERA Corporation, prepared with EPA Hotplate method 200.2

Element	Result	True Value	Spike Added	Recovery
	(mg/L)	(mg/L)	(mg/L)	%
Ba	0.464	0.469	5.00	98.9
Cd	0.147	0.148	0.50	99.3
Cr	0.790	0.801	0.50	98.6
Cu	0.218	0.221	0.50	98.4
Mn	0.185	0.188	0.50	98.1
Ni	0.351	0.346	0.50	101
Zn	0.108	0.0995	0.50	108

 Spikes and comparison to the true values verify method performance for a representative matrix



- > Low DLs ( $\mu$ g/L) for many elements
- Slower than flame (45-90")
- Little sample consumption (μL)
- Single element technique
- Some experience is needed





Chromium, 10  $\mu$ L of 1  $\mu$ g/L

#### **Selecting Element Parameters**



Element:       Pb (Lead)         Setup Data         Wavelength (nm)         Low Slit (nm)         0.7         Rollover (abs)         Temperatures (°C):         Pyrolysis         850         Atomization Site         Pyro/Platform         Chemical Modifier:         0.050 mg NH4H2P04 + 0.003 mg Mg(N03)2	
Performance Checks         Characteristic Mass: Typical 30 pg/0.0044 A-s         Sensitivity Check	<ul> <li>Recommended Conditions</li> <li>Recommended Conditions</li> <li>Element: Pb (Lead)</li> <li>Significant contamination problems are possible for this element.</li> <li>An electrodeless discharge lamp was used to obtain these data.</li> <li>Rollover occurs above approx. 0.5 Å using 217.0 nm line.</li> <li>Recommended atomization time: 3s.</li> <li>A modifier of 0.005 mg Pd + 0.003 mg Mg(NO3)2 allows a pyrolysis temperature of 1000 C with a characteristic mass of 50 pg. With this modifier a higher atomization temperature of 1900 C is required.</li> <li>Variations of +/- 20% for the characteristic mass under the above conditions are possible.</li> <li>The characteristic mass when using tubes with end caps is 21 pg/0.0044 A-s.</li> </ul>
	Print

#### GF-AAS typical thermal program (Pb) HGA program for 20 uL sample and 5 uL modifier



Step	Temp	Ramp	Hold	Gas Flow	Read
	(°C)	(sec)	(sec)	(mL/min)	
Dry 1	90	1	5	300	
Dry 2	130	10	20	300	
Pyrolysis	700	5	20	300	
Atomization	1600	0	5	0	*
Clean-out	2650	1	5	300	











#### Stabilised Temperature Platform Furnace (STPF)



Parameter/Feature	Benefit	Proof Statements				
Platform atomization						
Integrated platforms THGA (with & without endcaps) Integrated platform HGA tubes Uniform pyrolytic graphite coatings	Isothermal atomization Ease of use (no changing platforms) Reproducible & reliable data All elements from platform Longer tube lifetimes (corrosive samples)	Gas-phase temperature measurements (CARS) Reduced or eliminated chemical interferences Characteristic mass ( <i>m</i> <sub>0</sub> ) stability Lifetime studies Scientific publications				
Rapid, controlled furnace heating Independent of line voltage, tube parameters ( <i>i.e.</i> , resistance) True Temperature Control (TTC)	Reliable day-to-day performance	Temperature measurements Refractory element performance with different voltages				
Integrated Absorbance (peak area) measurements	More robust measurements Reliable day-to-day performance Independent of matrix changes	Peak area <i>vs</i> peak height studies				
Zeeman-effect Background Correction	No user selection required Wavelength independent method Better detection limits	Interference studies Scientific publications				
'Universal' Chemical Modifier Palladium/Magnesium nitrate	Faster, simpler method development Reproducible & reliable data	Interference studies Recovery measurements Scientific publications				









#### Deuterium bkgd. correction problems (over / under correction)





Interfering lines in slit band-width with D<sub>2</sub> bkgd. correction







- From EPA Monitoring Systems Laboratory (EMSL) in Cincinnati
- Revision 1.2 published in 1991
- Revision 2.2 published in 1994
- Designed primarily for the analysis of waters including: drinking, surface, ground, and wastewaters
- Principles of analysis may also be applied for the analysis of sediments, sludges, and soils



- Drinking water samples where the turbidity is < 1 NTU the sample are analyzed "directly"
- Total Recoverable Metals in aqueous samples require digestion
- Sample preparation for total recoverable elements in water or waste water
  - 1. 100 mL sample + 1 mL HNO<sub>3</sub> + 0.5 mL HCl into a 250 mL beaker
  - 2. Heat at 85 °C until the volume is reduced to 20 mL
  - 3. Cover and reflux for 30 minutes
  - 4. Cool; transfer to a 50 mL volumetric flask and dilute to volume



- Sample preparation for total recoverable elements in solid samples
  - 1. 1 g of well homogenized sample + 4 mL (1+1)  $HNO_3$  + 10 mL (1+4) HCl into a 250 mL beaker
  - 2. Cover and reflux for 30 minutes
  - 3. Cool; transfer to a 100 mL volumetric flask and dilute to volume
  - 4. Allow to stand overnight before analysis



- STPF conditions
- Platform atomization
- Background correction
- Where sample digestion is required a mixed acid digestion using HCI and HNO<sub>3</sub> is used
- Palladium/magnesium nitrate modifier [0.015mg Pd + 0.01mg Mg(NO<sub>3</sub>)<sub>2</sub>]
- A mixture of 95%Ar/ 5% H<sub>2</sub> is used as the internal gas during the dry and pyrolysis steps



AA and Bkgd. signals for As in a drinking water sample

(3.3 µg L<sup>-1</sup>)





		Arsenic			Lead	ead				
Water	Conc.	+Spike	%	Conc.	+Spike	%				
Sample	µg/L	50 µg/L	Recovery	µg/L	25 µg/L	Recovery				
Nist SRM 1643c	77.2		94	35.3		100				
Drinking	<dl< td=""><td>54.5</td><td>109</td><td>2.5</td><td>29.2</td><td>107</td></dl<>	54.5	109	2.5	29.2	107				
Ground	<dl< td=""><td>56.2</td><td>112</td><td>9.8</td><td>37.1</td><td>109</td></dl<>	56.2	112	9.8	37.1	109				
Stream	<dl< td=""><td>57.0</td><td>114</td><td>3.1</td><td>31.1</td><td>112</td></dl<>	57.0	114	3.1	31.1	112				
Pond	1.2	55.3	108	<dl< td=""><td>26.8</td><td>107</td></dl<>	26.8	107				
River	<dl< td=""><td>57.4</td><td>115</td><td>2.5</td><td>29.9</td><td>110</td></dl<>	57.4	115	2.5	29.9	110				

#### Atomic Absorption CV / Hydrides

- > Very low DLs ( $\mu$ g/L), but
  - only useful for Hg; As; Sb; Se; Te; Bi; Sn
- Slower than flame
- Chemistry dependent









#### **Examples of Prereduction:**

<u>Element</u>	<b>Reduction</b>	<u>Method</u>	<u>Time</u>
As	+5 →+3	10% KI +	30 min.
		5% Ascorbic Acid	
As	<b>+5 → +3</b>	L-cysteine	Immediate
Sb	<b>+5 +3</b>	10% KI +	Immediate
		5% Ascorbic Acid	
Bi	+5 +3	6M HCI	Immediate
Se	+6 +4	6M HCI, 90 °C	20 min.
Те	<b>+6</b> → <b>+</b> 4	6M HCI, 100 °C	2 min.



# GF-AAS Data Verification



- > Use furnace conditions optimized for the sample matrices
- Use good QA/QC
- > Examine the peak profiles



- > Make sure the furnace temperatures are OK
- Observe the peaks
  - Is the background peak high or complex?
  - Do either of the peaks go below the baseline?
  - Does the analyte peak come off too fast?
  - Does the analyte peak come off too slow?
  - Is there a BOC error?
- > If necessary, spike the sample to see an analyte peak



- > Run the sample
- Run the spiked (fortified) sample
- > Determine the spike recovery

conc. of fortified sample

- conc. of unfortified sample
- = conc. of addition?



- Post-digestion Spikes
  - Sample is spiked the day of analysis
  - Checks for matrix interferences
- Pre-digestion spikes
  - Sample is spiked prior to digestion
  - Checks for analyte contamination during the sample preparation procedure
  - Checks for analyte losses during sample preparation
  - May not pick up volatile compound losses (sample analyte is volatile, spike analyte is stable)



- Spike recoveries are good (85-115%)
  - Proceed with the analysis
- > Spike recoveries are poor
  - Make sure the spike concentrations are not within the precision levels
  - Further method development





## **ICP-OES**







- This multi-element analysis is usually performed by ICP-OES due to its speed and robustness
- National or supra-national regulations are usually applied:
  - EPA 200.7 in USA (! As withdrawal !)
    - Determination of Metals and Trace Elements in Water and Wastes by ICP-AES
  - Method 6010B from SW846
  - ASTM; APHA /AWWA
  - DIN 38 406 E 22 in Germany
  - EN ISO 11885:1998 Europe and global scale
    - Water quality. Determination of 33 elements by ICP-AES

### Method Editor/Spectrometer/Define Elements



🚇 Method E	ditor	: Optima Tr	aining					_		×											
C	Def	fine Elem	ents					ne Elem	ients												
<u>CC</u>	Metł	nod Descriptio	n: Optima	Training			Setti	ngs		L											
32		Symbol	Wavelength (nm)	Name	Function	k	Spec	stral		I.		_	_	_	_	_	_	_	_	_	
$\square$	1	V	292.402	V 292.402	Analyte	Peri	odic T	able												_ [	IJŇ
	2	As	188.979	As 188.979	Analyte			_	2			Jia	. '	T							
	3	Cd	226.502	Cd 226.502	Analyte	1.1	1		<b>-</b> e	<u> </u>	00		,	lā	10		,			Г	
	4	РЬ	220.353	РЬ 220.353	Analyte	1:	Pol								1	P	<u> </u>	N	0	-	No
	5	Se	196.026	Se 196.026	Analyte	LI No	De l										~				An I
	6		190.801	TI 190.801	Analyte	Na	Mg Ca			<u>.</u>	4. 5.		<b>b</b> 11		7	HI	31	F	3 0		Hr
	7	Sb	206.836	SB 206.836	Analyte	к.			<b>v</b>		¶n ⊢e		Ni	UU	Zn	Ga	Ge	HS	se _	Br	Kr
	8		324.752	LU 324.752	Analyte	RЬ	Sr Y	Zr		Mo	C RU	Rh	Pd	A9	Ca	In	Sn	SР	Te	I	Xe
	9	T	360.073	1 360.073	int. sta.	Cs	Ba La	Hf	та	ωl	Re Os	Ir	Pt	Âυ	H9	ΤI	РЬ	Bi	Po	At	Rn
3		Elements a	nd wavelength	is can be selected by	Periodic Table	Fr	Ra Ac	Kull	Ha												
- A		clicking on	one of the but	tons to the right	Fellouic Lable		_												_		
1				<u>`</u>	Wavelength Table		Ce	Pr	ы	Pm 💲	Sm EU	Gd	ΤЬ	Dy	Но	Er	Tm	YЬ	LU		
							ТЬ	Pa	U	Np F	Pu Am	Cm	Βk	Cf	Es	Fm	ЫM	No	Ln		
						_															_
XX Spectron	neter	Sampler		Calibration	hecks OK QC		Active Method	Rowir d Edito	r r		Eleme	ent: [							•		
							10	<u>+</u>		Wa	veleng	jth: [			•	] [	λ	Tabl	e	J	
													E	nter	in M	etho	rd	]			



		NIST 1643d (µg/L)									
Element	λ <b>(nm)</b>	found	±	S.D.	certified	±	S.D.				
A	309	125.3	±	4	127.60	±	3.5				
As	193	56.6	±	0.9	56.02	±	0.73				
Ba	233	506	±	4	506.50	±	8.9				
Be	234	12.4	±	0.03	12.53	±	0.28				
Cd	214	6.4	±	0.2	6.47	±	0.37				
Со	238	24.6	±	0.2	25.00	±	0.59				
Mn	257	37.8	±	0.3	37.66	±	0.83				
Mo	203	113.	±	0.95	112.90	±	1.7				
Ni	231	57.4	±	0.3	58.10	±	2.7				
Pb	220	17.8	±	0.15	18.15	±	0.64				
Sb	217	52.5	±	1.4	54.10	±	1.1				
Se	196	10.9	±	0.8	11.43	±	0.17				
V	309	36.4	±	0.4	35.10	±	1.4				
Zn	206	72.4	±	0.3	72.48	±	0.65				

NIST 1643d, Trace elements in water


Elem.	Wavelength	D.L.
AI	396.152	0.9
As	193.696	3.6
В	249.772	0.25
Be	313.107	0.017
Cd	214.440	0.07
Со	238.892	0.25
Cr	267.716	0.25
Cu	224.700	0.9
Fe	259.939	0.2
Mn	257.610	0.03
Мо	202.031	2
Ni	231.604	0.4
Pb	220.353	1.4
Sb	206.836	4
Se	196.026	4.5
TI	190.801	3.5
V	309.310	0.15
Zn	206.200	0.2

#### Acquired using

- $\checkmark$  10 seconds integration times
- ✓ Cyclonic spray chamber
- ✓ Low-flow GemCone neb.
- ✓3 x Blank SD, ug/L

- Vibrating piezoelectric crystal to generate aerosol
- Would result in introduction of too high amounts of mass into plasma
  - Removal of solvent through vaporization (heating) and condensation (cooling)
- Cannot tolerate high TDS
- Not for HF solutions
- Usually increases sensitivity 5-15 fold
- Can have washout problems due to cooled transfer line
- It is expensive







## Ultrasonic Nebulizer DLs (ug/L, Optima 4x00DV, XL)PerkinElmer

Element	Wavelength (nm)	Pneumatic Nebulizer	U-5000AT+
0		(GemCone)	
Ag	328.068	1	0.03
AI	396.153	2	0.06
As	188.979	3	0.7
Ba	233.527	0.5	0.01
Be	313.107	0.1	0.009
Bi	233.061	2	0.2
Са	317.933	2	0.03
Cd	228.802	0.1	0.02
Co	228.616	0.2	0.02
Cr	267.716	0.2	0.01
Cu	324.754	0.6	0.02
Fe	238.204	0.1	0.02
Mg	285.213	0.5	0.06
Mn	257.610	0.1	0.03
Mo	202.031	0.6	0.3
Ni	231.604	0.4	0.06
Pb	220.353	2	0.2
Sb	206.836	2	0.3
Se	196.026	3	0.5
Sn	189.927	1	0.4
Ti	334.940	0.2	0.006
TI	190.801	2	0.5
V	290.880	2	0.02
Zn	213.857	0.2	0.03
Detect	ion limits are based on	3 sigma, with a 20 sec. inte	gration time.



#### CRM Waste-Water CWW-TM-G Trace Metals in Certified Wastewater (High Purity Standards, Charleston, SC – USA)

Element	Meas.	SD	RSD	Certif.	Accuracy
	[mg/L]	[mg/L]	[%]	[mg/L]	[%]
AI	1.047	0.005	0.51	1.00	4.7
As	0.258	0.006	2.2	0.25	3.2
Ba	0.0241	0.0001	0.52	0.025	-3.6
Cd	0.255	0.004	1.4	0.25	2.0
Со	1.036	0.002	0.23	1.00	3.6
Cr	0.0249	0.00005	0.20	0.025	-0.4
Cu	0.0250	0.0005	1.8	0.025	0.0
Fe	1.019	0.006	0.56	1.00	1.9
Mn	1.035	0.003	0.29	1.00	3.5
Мо	0.980	0.004	0.38	1.00	-2.0
Ni	0.259	0.001	0.29	0.25	3.6
Pb	0.0252	0.0001	0.40	0.025	0.8
V	1.00	0.007	0.71	1.00	0.0
Zn	0.0249	0.0003	1.2	0.025	-0.4



- Method and instrument performances verified with reference materials (Community Bureau of Reference, Brussels, Belgium)
  - BCR 145 Trace Elements in Sewage Sludge
  - BCR 146 Trace Elements in Sewage Sludge of mainly Industrial Origin
- Sample preparation (as per DIN S7 method)
  - 3 g dried sample and 28 mL of aqua regia were heated under reflux for three hours and diluted to 100 mL. Two digestions were done of each material



#### CRM Sewage Sludge BCR 145 (results are "aqua regia" soluble, while Hg is total)

	Digest 1		Digest 2		CRM	
	Meas.	SD	Meas.	SD	Certif.	Confidence
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	Interval
As	3.5	0.2	3.1	0.2	-	-
Ba	295	3	332	2	-	-
Be	0.203	0.001	0.201	0.002	-	-
Cd	17.7	0.1	17.4	0.1	16.8	1.6
Со	7.7	0.1	7.09	0.02	6.8	1.0
Cr	76.2	0.2	79	1	85.2	16.3
Cu	403	1	401	1	415.9	23.5
Hg	10.65	0.08	10.43	0.06	8.82	0.88
Ni	38.6	0.1	39.0	0.2	38.5	3.6
Pb	364	0.5	350	1	332	22
V	13.5	0.1	13.5	0.1	-	-
Zn	2835	5	2799	11	2772	209



- > Physical
- Spectral
- Chemical
- Ionization



## Physical Interference Kerosene 1% HNO3 5% NaCL 50% H2SO4 2 mg/L Cu



## Corrects for physical interferences

- viscosity variations
- surface tension variations
- Uses a non-analyte element

#### Internal Standardization



- Use element not in samples
- Add precisely to all solutions
- Calibration is on internal standard to analyte ratio as function of analyte concentration
- Software makes correction
- Consider solubility and spectral characteristics





## Any unwanted light that reaches the detector

## > Approaches on dealing with spectral interferences

- Choose another wavelength or use higher resolution, if available
- Simple background correction
- Other correction techniques
  - Multicomponent Spectral Fitting (MSF)
  - Inter Element Correction (IEC)



#### Emission Spectrum = sum of *n* contributions



**Measured Spectrum** 



W StandardAl 1000mg/L



## **Sloping Background**



# Pb StandardAl 1000mg/L



### **Examine Spectra & Setting Background Points**



- Keep background points away from interferences
- Setting points on interferences could result in large negative IECs





The Observed Emission is the Sum of the Emission from the Analyte, the Interfering Element and the Background



Correcting for Interferences (MSF) Cd Corrected for Perkin Elmer\*

Unknown sample with Arsenic interference





#### Wavelength Table

۸V	Wavelength Table									
Γ	Sea	rch Pa	aramet	ers	Metho	od Entry				
	Cen	ter Wa	velengt	h(nm)		50	aroh	Activ Meth	e Row in od Editor	8 ÷
	Way	velengti	h Rang	je (+/-) 0.5			aich			
	-				amente				Enter Selecte Wavelengths	ed sin
	Elen	nents to	) Includ		ements	<u> </u>			Method	
	Way	velengti	ns O	All 🤨 Rec	ommend	ed 🔾	Un Arrays	-		
Γ		Elem	State	Wavelength	Pref.	BEC	DL mg/L	Rel	Sig/Noise	Intensity 🔺
		Elom.	0.0.0	(nm)	Order	(mg/L)	(W, P, &F)	Sens(B)	(S & T)	<u>(W)</u>
	1	Ag		328.068	1	0.26	0.0070	170000	2040.2	4200.0
	2	Ag		338.289	2	0.43	0.0130	82000	1261.2	2200.0
	3	Ag		243.778	3	4.00	0.1200	4200	28.2	23.0
	4	Ag		224.874	4		0.5000	880		3.0
	5	Al		396.153	1	0.95	0.0280	64000	268.4	2050.0
	6	Al	Ι	308.215	2	1.52	0.0450	23000	79.2	780.0
	7	AL	Ι	394.401	3	1.59	0.0470	32000	145.8	1050.0
	8	AL	Ι	237.313	4	1.00	0.0300		28.8	130.0
	9	AL	Ι	309.271	5	0.77	0.0230		141.0	1400.0
	10	Al		167.022	6	0.05				
	11	Ar	Ι	420.069	1				297.2	750.1
	12	Ar	Ι	363.268	2					23.0 💌

#### Continuous flow hydrides kit on ICP









#### **ICP-MS**

#### It is an analytical technique for the

- <u>Determination</u> of
- <u>Elements</u> using
- <u>Mass Spectrometry</u> of
- ons generated by an
- Inductively Coupled Plasma



**PerkinElmerS** 



#### ICP-MS as a routine analytical tool Application Areas (Elan Database)

PerkinElmerSCIEX





- EPA Method 200.8 approved for drinking water and waste water
  - Approved December 5, 1994 (FR 59 (232) p. 62546)
  - 12 metal contaminants approved, including Hg
  - Na, K, Ca, Ba going through approval process

#### EPA Method 6020 - approved for solid waste

- Approved January 13, 1995 (FR <u>60</u> (009) p.3089)
- 15 metal contaminants approved



- > Waters for EPA 200.8 no dilution
  - exception for some waters
- Method 3050 digests for EPA 6020
  - 1:10 dilution
  - some samples require 1:20 dilution
- TCLP samples
  - 1:20 dilution
    - needed to reduce carbon buildup on cones



		Measured	Certificate
mg/L	Са	37.1	36.8 ± 1.4
	Mg	9.82	<i>9.45 ± 0.27</i>
	Na	12.55	12.19 ± 0.36
	K	2.4	(2.3)
µg/L	Be	19.4	23.2 ± 2.2
	Со	22.0	<i>23.5 ± 0.8</i>
	Pb	34.1	35.3 ± 0.9

#### US EPA ICP-MS Method 6020 NIST 2711 - Contaminated Soil



	Sample	% Rec.	Spike	% Recovery	Spike
	Conc.	Certified	Amount	of	Recovery
Element	(mg/kg)	Value	(mg/L)	Spike	Limits (%)
AI	20,070	111	100	n/a	75-125
Sb	3.9	-	100	198	75-125
As	94.0	104	100	103	75-125
Ba	192.2	96	100	98	75-125
Be	1.1	-	100	104	75-125
Cd	40.0	100	100	102	75-125
Cr	23.7	118	100	97	75-125
Со	8.1	99	100	98	75-125
Cu	104.1	104	100	99	75-125
Pb	1087	99	100	n/a	75-125
Mn	493	101	100	110	75-125
Ni	17.1	107	100	96	75-125
Ag	4.3	108	100	102	75-125
TI	1.2	n/a	100	105	75-125
Zn	315.8	102	100	98.2	75-125

## **Uranium and Thorium determination by ICP-MS**





Elan IDL for U: 0.02 ng/L



Elan IDL for Th: 0.03 ng/L



Natural Uranium (U <sub>3</sub> O <sub>8</sub> )			Depletec	l Uranium (A	ldrich std)
<b>Reading</b>	<u>ratio</u>	RSD	<b>Reading</b>	<u>ratio</u>	<u>RSD</u>
- 1	0.00710	0.99	- 1	0.00318	1.21
- 2	0.00707	0.63	- 2	0.00318	1.25
- 3	0.00708	0.69	- 3	0.00318	1.03
- 4	0.00713	0.43	- 4	0.00316	0.98
- 5	0.00708	1.22	- 5	0.00316	1.08
- 6	0.00712	1.03	- 6	0.00318	1.36

Isotope	Mass	Abundance
U 234	234.0410	0.005500
U 235	235.0440	0.720000
U 238	238.0500	99.274500

	238U
	99.27%
23511	
0	
0.72%	







	Int Std	Analyte (*)	Mass (amu)	Corrections	Potential Interferences
1	Г	Cr	51.9405	-0.000074*Cl35-0.002*C12	ArN, ClO, ArO, SO, ArC, HClO
2		Ni	59.9332	-0.0032*Ca43	CaO
3		Cu	64.9278		PO2, SO2, TiO, Ba++
4		Zn	65.926		TiO, VO, SO2, Ba++
5		Ge	71.9217		ArS, Nd++, Nd++, Sm++
6		As	74.9216	-2.975*(Se77-(0.788*Se82))	ArCl, Sm++, Nd++, Eu++
7	L	Se	81.9167	- 1.007833 * Kr 83	Kr, BrH, Ar2H, Ho++, Dy++, Er++
8		Y	88.9054		
9	1	Rh	102.905		SrO
10		Ag	106.905		YO, ZrO
11	L.	Cd	110.904		MoO
12	1	In	114.904	- 0.014038 * Sn 118	Sn, MoO
13	L	Sb	120.904		
14		Ce	139.905		
15	Γ.	Pb	207.977	+Pb206+Pb207	
16	•	Bi	208.98		
17		U	238.05		

Spectroscopic interferences – Dynamic Reaction Cell





#### **Dynamic Reaction Cell DRC® Operating Principle**







- > Acids
- > Water (use 18 M $\Omega$  or better)
- Pipettes and pipette tips
  - Do not use glass pipettes!
  - Use mechanical pipettes (Eppendorf, etc.)
  - Use only plastic, metal-free tips
- > Sample containers
  - Plastic is preferred (see Spex information)
  - Use pre-cleaned when possible
  - NO lid liners allowed except Teflon!



- > Volumetric ware
  - Glass flasks should be eliminated
  - Use Plastic Volumetrics if necessary
- Your lab environment
  - Dust
  - Paper
  - Rusty hoods
- > YOU!!! (Na, Ti, K, Fe, Cu, Zn, Co, Si, etc....)
  - Your skin in general (Na, Ca, K)
  - Lotions
  - Make-up
  - Hair sprays, gels
  - Deodorant, ....



- Use good clean lab techniques
  - Limit contact with extra devices, containers, etc.
- Wear gloves and lint free labcoat
- Keep any area where samples prepared or opened clean!
  - Hoods, benches, instrument
- Pre-clean vessels for lowest level work
  - Clean in dilute nitric acid and keep in closed containers
- Limit access to clean lab areas



- > Determine Laboratory MDL with normal acids, procedures
  - If good enough no changes are necessary
  - If improvement needed (lower MDLs) need to work on limiting contamination.
- > Use superior acids: Ultrex, Optima, etc..
- Buy ICP or ICP-MS grade standards
  - AA standards contain too many impurities
    - Should not be used for multi-element standards
  - Purchase multi-element standards
    - All elements certified



- Method 200.8 Contained in Method
- Method 6020 Use any preparation procedure
  - 3005
  - 3010
  - 3015 microwave (preferred for lowest level work)
  - 3020
  - 3050 (AA)
  - 3050 (ICP)
  - 3051 microwave (preferred for lowest level work)
- YOU must decide upon sample preparation procedures to meet requirements of ICP-MS (avoid HCI if possible) AND satisfy the regulatory agency you report to.


Material	Major Impurties
Glass test tubes	Si, B, Na
Polypropylene tubes	CI, Mg, Ca (Cr, Zn, Ni)
LDPE	Ca, CI, K
HDPE	Ca, Zn, Si
TCLP Filters	Ba, Si, B



# Speciation

- Allows separation and measurement of forms of an element
  - Oxidation state
  - Organic molecules bound to the element

# > Enviro and toxicology important elements:

- Chromium (Cr3 and Cr6)
- Arsenic (As3; As6; organo-As)
- Selenium
- Mercury
- Platinum, Gold









1 µg/L Mixed Standard on ELAN DRC







> Sn species of concern in marine waters and sediments





#### Hvala

# Grazie

# Thank you