

# Techniques for Metal Analysis at CEST

A CEST Instrument  
Familiarization Seminar

# CEST Instruments

- **Inductively Coupled Plasma Mass Spectrometer**
- Finnigan Delta+ Stable Isotope Spectrometer
- Costech Elemental Analyzer
- Thermo Finnigan Gas Chromatograph Mass Spectrometer
- Agilent Gas Chromatographs
- Varian Gas Chromatographs
- **Varian Atomic Absorption Spectrometer**
- **Dionex Ion Chromatograph**
- Waters High-Pressure Liquid Chromatographs (HPLC)
- Capillary/Nano High-Pressure Liquid Chromatograph
- Triple Quadrupole Liquid Chromatograph Mass Spectrometer
- Shimadzu TOC 5000 Organic Carbon Analyzer
- Shimadzu TOC-V Organic Carbon Analyzer
- **Inductively Coupled Plasma Emission Spectrometer**
- **Scanning UV/Vis Spectrophotometer**
- **Scanning Electron Microscopy- Energy Dispersive X-ray Spectroscopy**
- Purge and Trap Units
- Zeta Potential
- Streaming Potential
- GC-MS

# Purpose

- Introduce instruments ideal for metal analysis
- For each instrument:
  - Inform you of how they work and what type of samples they require
  - Inform you as to which elements and concentrations work best
  - Present the advantages and disadvantages

# ICP-OES

Inductively Couple Plasma –  
Optical Emission Spectroscopy

# What ICP-OES does

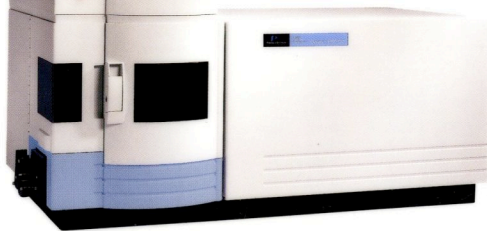
Major technique for elemental analysis –  
mainly heavy metals.

- Can measure about 70 elements in aqueous solutions. It cannot measure H, He, C, N, O, F, Ne, Cl, and some other random elements.
- Total dissolved solids in solutions need to be less than 1.5%.
- Optimum working range for element concentrations is 0.5-100 ppm. Possible to go both lower and higher, but response may become non-linear.
- All sample solutions must be filtered and free of particulates, sediments, precipitates, etc...

# How ICP-OES works

- Liquid sample introduced (usually aqueous)
- Nebulizer blows samples into micro droplets
- Droplets enter plasma and are excited, when they relax light is emitted
- Emitted light is wavelength specific for elements and measured by solid state detector

# What ICP analyzes for ....



<sup>51</sup> **Sb** — Atomic Number, Element  
 206.836 — Wavelength  
 I — Ionization States

#### Detection Limit Ranges

- < 0.1 ppb
- 0.1-1 ppb
- 1-10 ppb
- > 10 ppb

#### Wavelength (nm)

Ionization States  
 I = Neutral Atom  
 II = +1 ion

<sup>1</sup> H																	<sup>2</sup> He				
<sup>3</sup> Li 670.784 I	<sup>4</sup> Be 313.107 II															<sup>5</sup> B 249.772 I	<sup>6</sup> C 193.030 I	<sup>7</sup> N	<sup>8</sup> O	<sup>9</sup> F	<sup>10</sup> Ne
<sup>11</sup> Na 589.592 I	<sup>12</sup> Mg 280.271 II															<sup>13</sup> Al 396.153 I	<sup>14</sup> Si 251.611 I	<sup>15</sup> P 213.617 I	<sup>16</sup> S 180.669 I	<sup>17</sup> Cl 725.670 I	<sup>18</sup> Ar
<sup>19</sup> K 766.490 I	<sup>20</sup> Ca 393.366 II	<sup>21</sup> Sc 361.383 II	<sup>22</sup> Ti 334.940 II	<sup>23</sup> V 290.880 I	<sup>24</sup> Cr 267.716 II	<sup>25</sup> Mn 257.610 II	<sup>26</sup> Fe 238.204 II	<sup>27</sup> Co 228.616 II	<sup>28</sup> Ni 231.604 II	<sup>29</sup> Cu 327.393 I	<sup>30</sup> Zn 206.200 II	<sup>31</sup> Ga 417.206 I	<sup>32</sup> Ge 265.118 I	<sup>33</sup> As 188.979 I	<sup>34</sup> Se 196.026 I	<sup>35</sup> Br 863.866 I	<sup>36</sup> Kr				
<sup>37</sup> Rb 780.023 I	<sup>38</sup> Sr 407.771 II	<sup>39</sup> Y 371.029 I	<sup>40</sup> Zr 343.823 II	<sup>41</sup> Nb 309.418 II	<sup>42</sup> Mo 202.031 II	<sup>43</sup> Tc 249.677 II	<sup>44</sup> Ru 240.272 II	<sup>45</sup> Rh 343.489 I	<sup>46</sup> Pd 340.458 I	<sup>47</sup> Ag 328.068 I	<sup>48</sup> Cd 228.804 I	<sup>49</sup> In 230.606 I	<sup>50</sup> Sn 189.927 II	<sup>51</sup> Sb 206.836 I	<sup>52</sup> Te 214.281 I	<sup>53</sup> I 178.215 I	<sup>54</sup> Xe				
<sup>55</sup> Cs 455.531 I	<sup>56</sup> Ba 455.403 II	<sup>57</sup> La 408.672 II	<sup>72</sup> Hf 264.141 II	<sup>73</sup> Ta 226.230 II	<sup>74</sup> W 207.912 II	<sup>75</sup> Re 197.248 I	<sup>76</sup> Os 228.226 II	<sup>77</sup> Ir 224.268 II	<sup>78</sup> Pt 214.423 I	<sup>79</sup> Au 267.595 I	<sup>80</sup> Hg 194.168 II	<sup>81</sup> Tl 190.801 II	<sup>82</sup> Pb 220.353 II	<sup>83</sup> Bi 223.06 I	<sup>84</sup> Po	<sup>85</sup> At	<sup>86</sup> Rn				
<sup>87</sup> Fr	<sup>88</sup> Ra	<sup>89</sup> Ac																			

<sup>58</sup> Ce 413.764 II	<sup>59</sup> Pr 414.311 II	<sup>60</sup> Nd 406.109 II	<sup>61</sup> Pm	<sup>62</sup> Sm 442.434 II	<sup>63</sup> Eu 381.967 II	<sup>64</sup> Gd 342.247 II	<sup>65</sup> Tb 350.917 II	<sup>66</sup> Dy 353.170 I	<sup>67</sup> Ho 345.600 II	<sup>68</sup> Er 337.271 II	<sup>69</sup> Tm 313.126 II	<sup>70</sup> Yb 328.937 II	<sup>71</sup> Lu 261.542 II
<sup>90</sup> Th 283.730 II	<sup>91</sup> Pa 385.958 II	<sup>92</sup> U 385.958 II	<sup>93</sup> Np	<sup>94</sup> Pu	<sup>95</sup> Am	<sup>96</sup> Cm	<sup>97</sup> Bk	<sup>98</sup> Cf	<sup>99</sup> Es	<sup>100</sup> Fm	<sup>101</sup> Md	<sup>102</sup> No	<sup>103</sup> Lr



Courtesy of Perkin Elmer Instruments

# Benefits of ICP-OES

- **Good start off method.**
  - Sample acidified and filtered but nothing else has to be done in order to analyze.
- **Relatively low sample size needed <10mL**
- **Automated analysis**
- **Flexibility of wavelengths and elements.**
  - Plasma excites all atoms in a sample, so you can choose wavelengths for each element and analyze multiple elements at once.

# Disadvantages of ICP-OES

- **Interferences** - Plasma excites all atoms in a sample, so you can choose wavelengths for each element and analyze multiple elements at once.
- **Standards** – Matrix matched standards have to be made for each element of interest.

# SEM-EDS

Scanning Electron Microscopy –  
Energy Dispersive X-ray  
Spectroscopy

# What SEM-EDS Does

- SEM is an **IMAGING** technique.
- EDS is a qualitative / semi-quantitative elemental analysis of a SEM image.

# How SEM-EDS works

- Electron beam is aimed at a sample surface. When the electrons hit the sample, a variety of signals are generated. Most importantly secondary electrons, backscattered electrons, and x-rays.

# Important signals obtained from SEM-EDS

- Secondary electrons
- Backscattered electrons
- **X-rays** -
  - Produced from shell transitions caused by interaction b/t the beam and the sample.
  - The emitted x-ray has an energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis. X-rays may also be used to form maps or line profiles, showing the elemental distribution in a sample surface.

# Pros and Cons of SEM-EDS

## Advantages

- Environmental SEM
- Small sample needed
- Ability to work with uncoated samples including biologicals
- Adjustable humidity and temperature within chamber
- Windows based system very easy to use

## Disadvantages

- Destructive analysis
  - Biologicals will not be salvageable afterwards
- Qualitative / Semi-quantitative
  - Sample must have relatively high concentration of element
    - several wt. %
- Costly to end user – charged by filament time

# Atomic Absorption

FLAA: Flame AA

GFAA: Graphite furnace AA

# What the AA does

- Determines the concentration of a single element in a sample.
- Can be used for 62 different metals.
- Very sensitive to low concentrations (ie. works best in the ppb range)
- All sample solutions must be filtered and free of particulates, and sediments.

# How the AA works

- The sample is vaporized to a gas.
- A beam of light from a hollow cathode lamp is shot through the sample. (The type of hollow cathode tube is specific to the metal being analyzed.)
- The amount of energy produced is specific to a particular electron transition in a particular element.
- As the quantity of energy put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured and thus get a signal that is proportional to the concentration of the element being measured.

# Pros and Cons of AA

## Advantages

- High sensitivity
- Wide range of elements
- High educational value

## Disadvantages

- Sensitivity limited for refractories
- Single wavelength detection
- Slow
- One lamp per element (can become costly)

# FLAA vs GFAA vs ICP OES

- Flame temperature: 1700 C to 3150 C (N<sub>2</sub>O/acetylene)
- Furnace temperature: 1200 C to 3000 C
- ICP OES temperature: 10,000 K
  
- ICP OES has a significantly greater linear range and can analyze multiple wavelengths simultaneously.
- GFAA has very efficient sample analysis meaning much smaller sample amounts and lower IDLs for some elements.
- ICP OES can take advantage of internal standards addition techniques
- GFAA: modifiers and temperature profiles are available to enhance sensitivity
  
- Some techniques are dependent on interferences and matrix effects.
- All techniques require filtered totally dissolved materials

# Technique and IDLs Comparison

**TABLE 4.19** IDLs for the Most Common Atomic Spectrometric Determinative Techniques in ppb

Element	FIAA	GFAA	HGAA	ICP-AES	ICP-MS
Al	45	0.3		6	0.006
As	150	0.5	0.03	30	0.006
Bi	30	0.6	0.03	30	0.0005
Ca	1.5	0.03		0.15	2
Cd	0.8	0.02		1.5	0.003
Cr	3	0.08		3	0.02
Cu	1.5	0.25		1.5	0.003
Fe	5	0.3		1.5	0.04
Hg	300	15	0.009	30	0.004
K	3	0.02		75	1
La	3000			1.5	0.0005
Mg	0.15	0.01		0.15	0.007
Na	0.3	0.05		6	0.05
Pb	15	0.15		30	0.001
Sb	45	0.4	0.15	90	0.001
Se	100	0.7	0.03	90	0.06
Sn	150	0.5		60	0.002
Tl	15	0.4		60	0.0005
Zn	1.5	0.3		1.5	0.003

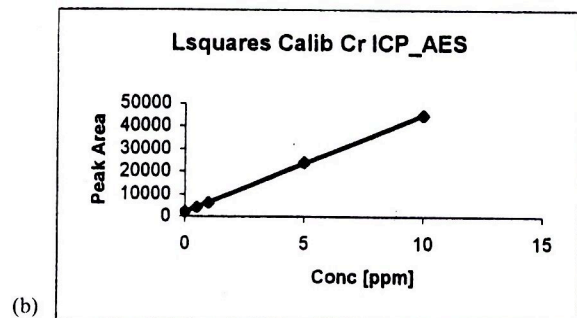
*Note:* Instruments used to generate these IDLs:

- Model 5100 AA (Perkin-Elmer, P-E)
- FIAS-200 flow injection amalgamation (P-E)
- MHS-10 mercury/hydride (P-E)
- Model 5100 PC AA with 5100 ZL Zeeman furnace model (P-E)
- Model 4100 ZL AA
- Plasma 2000 ICP-AES (P-E)
- ELAN 5000 ICP-MS (P-E)

All IDLs are based on a 98% ( $3\sigma$ ) confidence level.

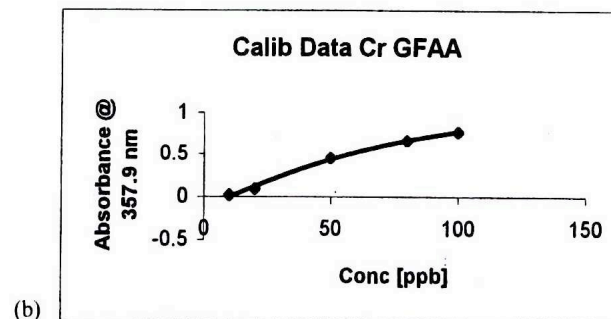
*Source:* Ref. 103.

# Linear Regression ICP OES vs GFAA



**Slope of Least Squares Regression = 4289 counts /ppm Cr**  
**y-intercept of Least Squares Regression = 2075 counts**  
**correlation coefficient = 0.9998**  
**standard deviation in the y-intercept = 193**  
**y(critical) = 2965 counts**  
**x(critical) = 0.21 ppm Cr direct aspiration of aqueous solution**  
**x(detection) = 0.41 ppm Cr direct aspiration of aqueous solution**  
**x(limit of quantitation) = 0.45 ppm Cr direct aspiration of aqueous solution**

**FIGURE 4.73** Calibration plots for the determination of chromium by ICP-AES showing (a) raw data and (b) a least squares regression fit to the raw data and statistical summary using LSQUARES.



**Slope of Least Squares Regression = 0.0087 counts /ppb Cr**  
**y-intercept of Least Squares Regression = 0 counts**  
**correlation coefficient = 0.9905**  
**standard deviation in the y-intercept = 0.0436**  
**y(critical) = 0.1086counts**  
**x(critical) = 18.7 ppb Cr direct injection of aqueous solution**  
**x(detection) = 35.8 ppb Cr direct injection of aqueous solution**  
**x(limit of quantitation) = 69.3 ppb Cr direct aspiration of aqueous solution**

**FIGURE 4.80** Calibration plots for the determination of chromium by GFAA showing (a) raw data and (b) a least squares regression fit to the raw data and statistical summary using LSQUARES.

# ICP MS

Inductively Coupled Plasma  
Mass Spectrometry

# What ICP-MS Does

- Trace element Facility
- Detects all elements except C, N, P, S, O<sub>2</sub>, K and Cl

## How ICP-MS works

- Solids samples by Laser ablation
- Liquid samples by Ultra sonic nebulizer
- IC by Speciation

# Pros and Cons of ICP-MS

## Advantages

- High sensitivity  
ppt to ppq IDL
- Magnetic sector  
1 amu differences to  
fractional amu differences
- Easiest set up for unknowns

## Disadvantages

- Concerns:
  - polyatomic species
  - oxides, hydroxides
  - matrix effects/interferences
- Large concentrations/memory effects
- NOT an endowed facility *ie.* cost per sample

Graduate course available on ICP Technology

# UV-Vis Spectrophotometer

The background is a gradient from dark blue to black. A thin, light blue curved line starts from the top left and curves towards the center. A larger, semi-transparent blue shape is located in the bottom right corner, resembling a stylized 'L' or a corner cutout.

# What UV/Vis Does

- Measures a single wave length from 200-960 nm or scans a range

## Colorimetry

- Color change chemistry
- Some techniques for metals

# Pros and Cons of UV/Vis

## Advantages

- Simple
- “Cook Book” Chemistry
- inexpensive

## Disadvantages

- Slow – larger setup time
- Single analyte vs. many at once
- Regents tend to have short shelf life

The background is a dark blue gradient that transitions to a lighter blue at the bottom. A thin, light blue curved line starts from the top left and curves towards the center. A spotlight effect, represented by a semi-transparent blue cone, originates from the center and points towards the bottom right corner.

IC

Ion Chromatography

# What IC does

- Separates for measurement the anions and cations in an aqueous sample.

# IC Detectors

- Electrochemical
- Absorbance along the UV/Vis Spectrum

# Pros and Cons of the IC

## Advantages

- Well established protocols
- Automated sampling

## Disadvantages

- Expensive – many consumables used
- Transition metals as cations in low concentrations only (2 ppm and lower)
- Reconfiguring the Dionex takes 24 hours
- Complex mobile phase

Look forward to two more CEST  
Instrument Familiarization  
Seminars coming soon to a  
lecture hall near you...

Organic Analysis  
Particle Characteristics