

# Everyone talks about ICP why not talk about AAS as a change

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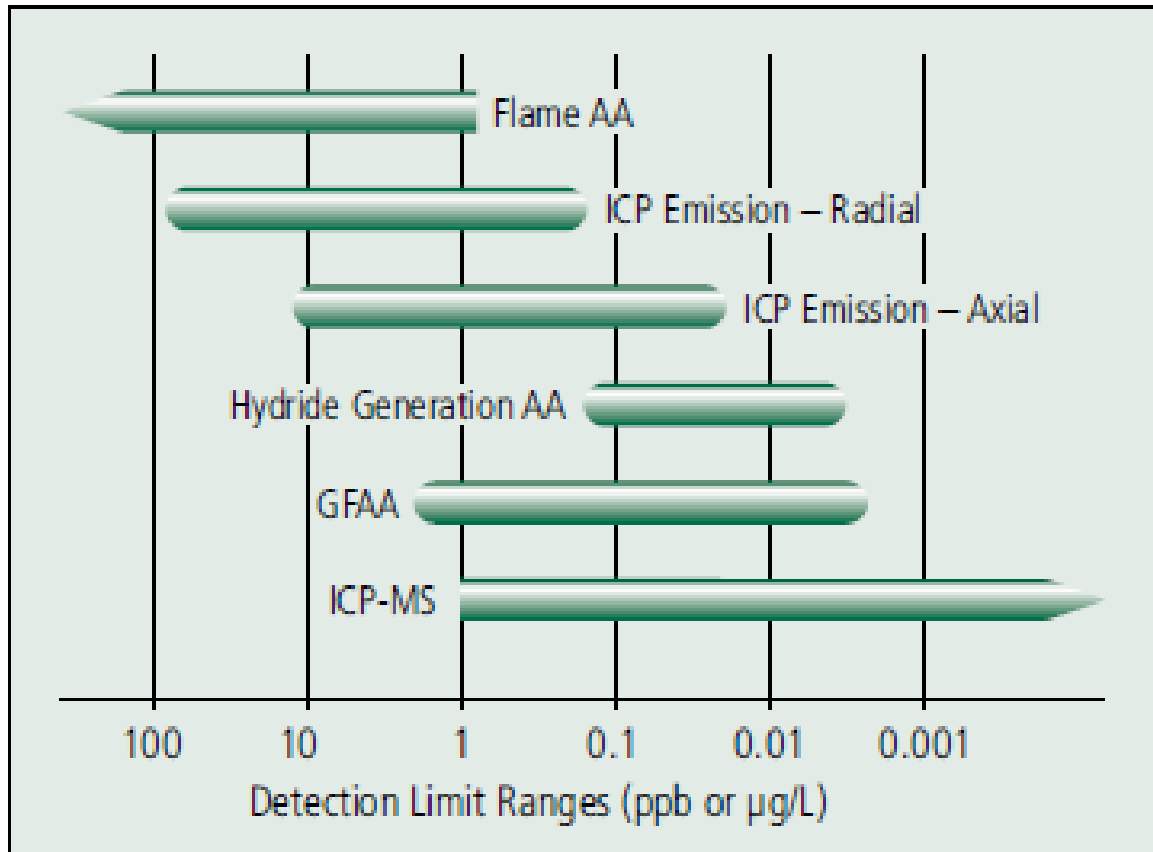
# Customer requirements

- ▶ Easy to handle
  - Many operators
- ▶ Few samples
  - <10/day
- ▶ Few elements
  - Mn on daily basis
  - Al weekly
  - NPE monthly

# Technique decision matrix

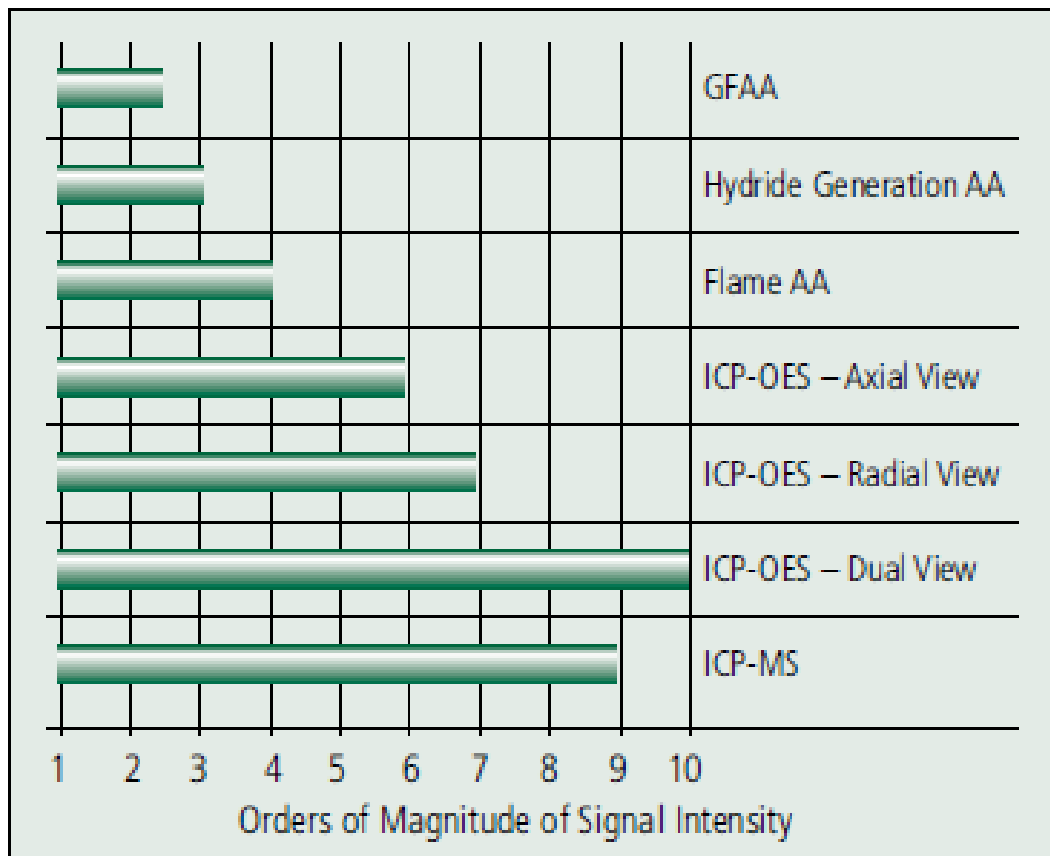
|                    | Flame AA     | GFAA         | ICP-OES  | ICP-MS   |
|--------------------|--------------|--------------|----------|----------|
| Number of elements | Few          | Some         | Many     | Many     |
| Content levels     | ppb-%        | ppb          | ppb-%    | ppt-ppb  |
| Number of samples  | Very few-few | Very few-few | Few-many | Few-many |
| Sample size        | >5 ml        | <1-2 ml      | >5 ml    | >5 ml    |

# Typical detection limit ranges for the major atomic spectroscopy techniques



From PerkinElmer BRO\_WorldLeaderAAICPMSICPMS.pdf

# Typical analytical working ranges for the major atomic spectroscopy techniques



# Analytical techniques Flame-AAS

- ▶ AAS
- ▶ AES
- ▶ Graphite Furnace
- ▶ Cold Vapor
- ▶ Hydride Generation

# Gasblandning och analysteknik

| 1  | 2  | 3   | 4  | 5   | 6   | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|----|----|---|--|-----|-----|----|----|----|----|----|----|----|----|----|----|----|----|
| H  |    |   |  |     |     |    |    |    |    |    |    |    |    |    |    |    | He |
| Li | Be | Air-C <sub>2</sub> H <sub>2</sub>                       | N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> | HVG | MVU |    |    |    |    | B  | C  | N  | O  | F  |    | Ne |    |
| Na | Mg | Color codes denote flame type or measurement technique. |  |     |     |    |    |    |    |    |    | Al | Si | P  | S  | Cl | Ar |
| K  | Ca | Sc  | Ti   | V   | Cr  | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y   | Zr   | Nb  | Mo  | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  | Xe |
| Cs | Ba | La  | Hf   | Ta  | W   | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac  |  |     |     |    |    |    |    |    |    |    |    |    |    |    |    |
|    |    |   | Ce   | Pr  | Nd  | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |    |
|    |    |   | Th   | Pa  | U   | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |    |

HVG=Hydride Vapor Generator  
MVU=Mercury Vapor Unit

# Temperature for different flames

| Oxidant - Fuel                  | Temperature °C |
|---------------------------------|----------------|
| Air - Methane                   | 1850 - 1900    |
| Air - Natural gas               | 1700 - 1900    |
| Air - Hydrogen                  | 2000 - 2050    |
| Air - Acetylene (AAS)           | 2125 - 2400    |
| Nitrous oxide - Acetylene (AAS) | 2600 - 2800    |



# Burner system in a AAS

- ▶ Nebulizer
- ▶ End cap
- ▶ Flow spoiler
- ▶ Spray chamber
- ▶ Burner head

# Interferences

## Spectral interferences

- 1) Background

## Nonspectral interferences

- 1) Matrix
- 2) Chemical
- 3) Ionization

# Recommended conditions

## Flame - AAS (Mn)

| $\lambda$<br>(nm)  | Relative<br>noise | Sensitivity<br>(mg/L) | Linear range<br>(mg/L) |
|--|-------------------|-----------------------|------------------------|
| 279,5  | 1,0               | 0,052                 | 2,0                    |
| 279,8  | 0,77              | 0,067                 | 3,0                    |
| 280,1  | 0,88              | 0,11                  | 5,0                    |
|  |                   |                       |                        |
| Flame  | Air/Ac            | lean, blue            |                        |
| Slit   | 0,2 nm            |                       |                        |
| Flow spoiler   |                   |                       |                        |
| 0,2 % CaCl <sub>2</sub> can be added to overcome interference from silicon |                   |                       |                        |

# Sample types

- ▶ Wood
- ▶ Pulp
- ▶ Board
- ▶ Paper
- ▶ Effluent
- ▶ White Liquor
- ▶ Black Liquor
- ▶ Green Liquor
- ▶ ESP-ash
- ▶ Lime mud
- ▶ Lime

# Which metals

| Element            | AAS-flame                   | AAS-THGA | ICP-OES | ICP-MS |
|--------------------|-----------------------------|----------|---------|--------|
| Fe, Mn, Cu, Zn     | x                           |          | x       | x      |
| Ca, Mg, Al         | La/Cs (N <sub>2</sub> O/Ac) |          | x       | x      |
| Na, K              | Cs (ev. AES)                |          | x       |        |
| Si                 | N <sub>2</sub> O/Ac         |          | x       |        |
| Cd, Co, Cr, Ni, Pb | x                           | x        | x       | x      |
| As, Se, Sb         | Hydride-AAS                 |          | x       | x      |
| Ba, V              | x                           |          | x       | x      |
| Hg                 | CV-AAS                      |          |         |        |

# Metal levels in different sample types

| Element | Wood<br>(mg/kg) | Pulp,<br>bleached<br>(mg/kg) | Board<br>(mg/kg) | White<br>Liquor<br>(mg/L) | Black<br>Liquor<br>(mg/kg) | ESP<br>(mg/kg) |
|---------|-----------------|------------------------------|------------------|---------------------------|----------------------------|----------------|
| Na      |                 | 700                          | 600              | 8-9 %                     | 20 %                       | 31 %           |
| K       |                 | 5                            | 15               | 0,8-0,9 %                 | 2 %                        | 4 %            |
| Ca      | 1000            | 50-100                       | 700              | 20                        | 200-1000                   | 50             |
| Mn      | 150             | 1                            | 30               | 5                         | 50-100                     | 40             |
| Cd      | 0,1             | 0,002                        | 0,01             |                           |                            | 1-5            |

# Comparision AAS - ICP-OES in wood (eucalyptus)

|           | AAS        | ICP         | AAS         | ICP          | AAS        | ICP         | AAS        | ICP        | AAS        | ICP        |
|-----------|------------|-------------|-------------|--------------|------------|-------------|------------|------------|------------|------------|
| Digestion | Fe         |             | Mn          |              | Cu         |             | Ca         |            | Mg         |            |
| mg/kg     | 4,4        | 4,60        | 14,1        | 14,63        | 0,9        | 1,11        | 603        | 635        | 233        | 228        |
|           | 5,9        | 6,23        | 14,3        | 14,95        | 1,0        | 1,38        | 614        | 642        | 239        | 238        |
|           | 3,7        | 3,76        | 14,0        | 14,34        | 0,8        | 1,11        | 599        | 638        | 234        | 231        |
|           | 3,8        | 3,92        | 14,1        | 14,43        | 0,9        | 1,12        | 603        | 647        | 236        | 238        |
|           | 4,1        | 4,02        | 14,2        | 14,70        | 0,9        | 1,11        | 602        | 640        | 237        | 236        |
|           | 7,9        | 8,08        | 14,0        | 14,63        | 0,9        | 1,11        | 592        | 638        | 234        | 234        |
| average   | <b>5,0</b> | <b>5,10</b> | <b>14,1</b> | <b>14,61</b> | <b>0,9</b> | <b>1,16</b> | <b>602</b> | <b>640</b> | <b>236</b> | <b>234</b> |
| std.dev   | 1,64       | 1,72        | 0,12        | 0,21         | 0,06       | 0,11        | 7,14       | 4,15       | 2,26       | 4,02       |

# Conclusion

- ▶ Easy to handle
- ▶ Cheap
- ▶ "Old" technique
- ▶ ?