Chapter 10: Emission Spectroscopy Using Plasmas, Arcs or Sparks

– Inductively Coupled Plasma (ICP)
– Direct Current Plasma (DCP)
– Arcs and Sparks

Still talking about Optical Atomic Spectrometry
Focus primarily on plasmas as sources
Discuss instrument design and other considerations
<table>
<thead>
<tr>
<th></th>
<th>Desirable Properties of an Emission Spectrometer</th>
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<tbody>
<tr>
<td>1</td>
<td>High Resolution (0.01 nm or λ/Δλ &gt; 100,000)</td>
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<tr>
<td>2</td>
<td>Rapid Signal Acquisition and Recovery</td>
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<td>3</td>
<td>Low Stray Light</td>
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<td>4</td>
<td>Wide Dynamic Range (&lt;10^6)</td>
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<td>5</td>
<td>Accurate and Precise Wavelength Identification and Selection</td>
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<td>6</td>
<td>Precise Intensity Readings (&gt;1% RSD at 500 × the detection limit)</td>
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<td>7</td>
<td>High Stability with respect to Environmental Changes</td>
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<td>8</td>
<td>Easy Background Corrections</td>
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<tr>
<td>9</td>
<td>Computerized Operation: Readout, Store, Data Manipulation, etc.</td>
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</table>

TABLE 10.1
Sources

• In AE the plasma, flame, arc or spark act as the device for atomization and the source to excite the atoms – no light source needed

• High temperatures generate a significant population of excited state atoms from the Boltzmann distribution

• High temp. sources also remove or burn off many potentially problematic molecular species that might result in interferences
ICP Torch with sample introduction system (nebulizer and spray chamber)
ICP Temps.

The viewing area for each element is typically reported as mm above the load coil.
Direct Current Plasma (DCP) Torch Lab will involve use of DCP for multielement analysis.

Figure 10-5  A three-electrode dc plasma jet. (Courtesy of Spectra Metrics, Inc. Haverhill, MA.)
Wavelength Selection Detection

- Same concepts as Molecular Spectroscopy
- Grating and prism based monochromators
- Need very high resolution because atomic lines are narrow & many – overlaps possible
- Can do simultaneous multi-element analysis
- Two types of general approaches:
  - Fixed optical arrangements = direct reading spec
  - Slew scanning or sequential analysis
Aperature plate consisting of multiple exit slits where PMT detectors can be arranged for multi-element detection.

High resolution Echelle Polychromator as used in the DC Plasma AE Spectrometer & other instruments.
Another diagram of an Echelle optical system employing a Charge Injection Transducer (i.e. a 2D array based detector)

Figure 10-9 Optical diagram of an echelle spectrometer with a charge-injection detector.
(From R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., 1990, 44, 1615. With permission.)
Figure 10.11  An echelle spectrometer with segmented array of charge-coupled devices.
Another plasma polychromator system employing the classic Rowland circle design. Entrance slit, grating & exit slits are located in a circular arrangement.

Figure 10-8  Schematic of an ICP polychromator.  (Courtesy of Thermo Jarrell Ash Corp.)
Slew-Scan spectrometer scans rapidly between lines & slowly near lines of interest.
Analytical considerations

- More than one emission line can be used for analytical purposes
  - To avoid interferences
  - To reduce sensitivity
- Calibration curves highly linear – large dynamic range
- Internal standards sometimes used to remove matrix interferences
- Spectrochemical buffers added to samples & standards to control ionization
Figure 10-13

Periodic table characterizing the detection power and number of useful lines. The degree of shading indicates the range of detection limits for the useful lines. The area of useful emission lines of ICP by employing a pneumatic nebulizer.

Detection limit (ng/mL)

Number of lines
ICP Calibration curves for several metals, log-log plots note linearity over at least 2 orders of magnitude.

TI & Nb lines are curved possibly due to improper background correction.

Figure 10-14 Typical calibration curves. (From V. A. Fassel and R. N. Kniseley, Anal. Chem., 1974, 46, 1117A. With permission.)
Four types of samples are compared here to show the lack of any effect for matrix species like Na, Ca & Mg vs. distilled water.
Electrodes for arc & spark emission spectrometry samples are coated on surface or placed wells.

**Figure 10-16** Some typical graphite electrode shapes. Narrow necks are to reduce thermal conductivity.
Eagle Mounting used historically for arc & spark emission with photographic detection.
Photographic detection gives line spectra

Lines can be compared with a densitometer for intensity & semi-quantitative analysis

Figure 10-18  Projected spectra by a comparator-densitometer: (a), (b), and (c) spectra of sample at three different exposures; (d) iron spectrum on the sample plate; (e) and (f) iron spectra on the master plate.
<table>
<thead>
<tr>
<th>Concentration Multiple above Detection Limit</th>
<th>Relative Standard Deviation, %</th>
<th>Recalibration, In</th>
<th>Frequency of Extraneous Frequency on Precision of ICP Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-8</td>
<td>3-7</td>
<td>3-10</td>
<td>8-15</td>
</tr>
<tr>
<td>2-3</td>
<td>1.5-2</td>
<td>2-6</td>
<td>2-10</td>
</tr>
<tr>
<td>1.5-2</td>
<td>1-2</td>
<td>1-3</td>
<td>3-7</td>
</tr>
<tr>
<td>104+ to 10</td>
<td>103 to 103</td>
<td>102 to 102</td>
<td>101 to 102</td>
</tr>
</tbody>
</table>

TABLE 10.2 Effect of Standardization Frequency on Precision of ICP Data
Chapter 11: Atomic Mass Spectrometry (Inorganic MS)

- Mass Spectrometers
- ICP-MS
- Spark Source MS
- Glow-Discharge MS
- Elemental Surface Analysis by MS
- Laser Ablation ICP-MS
Atomic Mass Spec processes

- Atomization (sample intro)
- Conversion to ions
- Separation based on m/z ratio
- Detection

In other forms of MS (GC-MS or MS of organic compounds), sample introduction does not involve making atoms, just getting molecules into the high vacuum system.
Basic MS design components
Note high vacuum