

# Analytical techniques

(Equipments in grey boxes are present at U.S.)

## **I. X-Ray fluorescence (XRF)**

- Sample is excited by (primary) X-rays; electrons “jump” to higher energy level.
- Electrons return to their original level and emit (secondary) X-rays whose energy (or wavelength) is characteristic of the element
- Energy or wavelength spectrum; height of the peaks correspond to concentration.

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<ul style="list-style-type: none"> <li>- Cheap</li> <li>- Fast</li> <li>- Large concentration range (80% - 10 ppm)</li> </ul>	<ul style="list-style-type: none"> <li>- Not usable for light elements (&lt; 11 = Na)</li> <li>- Detection limit too high for some useful trace elements (REE)</li> <li>- Questionable accuracy</li> </ul>
Still the most cost-efficient and most common system for major elements (and some traces).	

## **II. Inductively Coupled Plasma (ICP)**

“Flame” spectrometry (6000 – 10000 C)

- Sample solution nebulized into an Argon plasma, heated by sparks and contained in a magnetic field
- Sample dissociates into single ions (ionic plasma)

### **A. Atomic Emission Spectrophotometry ICP (ICP-AES)**

- Excited atoms in the plasma emit light in specific wavelengths
- The peak size is proportional to the concentration

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<ul style="list-style-type: none"> <li>- Low detection limits ( 1 ppm)</li> <li>- Good precision</li> <li>- Can analyze light elements</li> </ul>	<ul style="list-style-type: none"> <li>- Needs a “clean” chemistry</li> <li>- Less precise for major elements</li> </ul>
Once the standard instrument for traces; is now being replaced by ICP-MS.	

### **B. Mass Spectrometry ICP (ICP-MS)**

- Mass spectrometry takes advantage of the fact that ions in a magnetic field follow circular trajectories, radius is a function of the charge/mass ratio
- Ions are extracted from the plasma, accelerated and pumped into a magnetic field onto the mass detector

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<ul style="list-style-type: none"> <li>- Very low detection limits (down to 1 <i>ppb</i> for modern instruments)</li> <li>- Good precision</li> <li>- Can analyze light elements</li> <li>- Limited isotopic capacity</li> </ul>	<ul style="list-style-type: none"> <li>- Needs a “clean” chemistry</li> <li>- Can’t do major elements</li> <li>- Expensive and hi-tech (1-5 millions ZAR)</li> </ul>
Becoming the de facto standard for trace elements.	

### C. Laser Ablation ICP (LA-ICP-MS)

- The plasma is here generated by shooting a high energy laser on the sample

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Same as “normal” ICP-MS, plus...	
<ul style="list-style-type: none"> <li>- In situ analysis of individual minerals, etc.</li> <li>- No chemistry needed</li> <li>- Now routinely built by the industry and commonly used, relatively robust and simple to use once installed</li> </ul>	<ul style="list-style-type: none"> <li>- Additional complexity (coupling the laser and the ICP)</li> <li>- <i>Very expensive!</i></li> </ul>
<p>Getting increasingly common; most instrument are able to function with or without the laser, depending on the needs.</p> <p>Increasingly used for isotopic work (e.g. geochronology)</p>	

### **III. Isotopic Dilution and Thermo-Ionization Mass Spectrometry (ID-TIMS)**

- Samples are put in solution, generally chemically separated to keep only the elements of interest
- A “spike” of known concentration and isotopic composition is added
- Mass spectrometry takes advantage of the fact that ions in a magnetic field follow circular trajectories, radius is a function of the charge/mass ratio
- Isotopic *ratios* are measured (no need for calibration, so less error)
- Ratios are commonly interpreted; spiking allows to calculate the concentrations.

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<ul style="list-style-type: none"> <li>- Very low detection limits</li> <li>- Excellent precision</li> <li>- Can do isotopes</li> </ul>	<ul style="list-style-type: none"> <li>- Needs a “ultra-clean” chemistry</li> <li>- Can not do all elements</li> <li>- Time consuming and difficult</li> </ul>
Normally not used for trace elements, but still common for isotopes. Slowly concurred by LA-ICP-MS.	

#### ***IV. Electron microprobe***

- Very similar to XRF
- Sample is excited by a beam of electrons; electrons (from the sample) “jump” to higher energy level.
- Electrons return to their original level and emit X-rays whose energy (or wavelength) is characteristic of the element
- Energy or wavelength spectrum; height of the peaks correspond to concentration.

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<ul style="list-style-type: none"><li>- Non-destructive</li><li>- In-situ, very small spatial resolution</li></ul>		<ul style="list-style-type: none"><li>- High detection limits and poor precision for anything other than majors</li><li>- Light elements are difficult to analyze</li><li>- Use and maintenance not that easy</li></ul>	
Still the main tool for mineral chemistry. Modern studies couple EM with LA-ICP-MS for a complete analysis.			

#### ***V. Ion microprobe***

- A beam of O ions is fired at the sample
- The sample is ionized in a small volume (actually drilling a small hole) and secondary ions are emitted
- Secondary ions are analyzed by mass spectrometry

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<ul style="list-style-type: none"><li>- Very low detection limits</li><li>- Excellent precision</li><li>- Can do isotopes</li><li>- In situ analysis</li></ul>		<ul style="list-style-type: none"><li>- Very expensive</li><li>- Very complex and difficult to use</li><li>- Likely to be replaced by LA-ICP-MS in the next few years</li></ul>	
Very popular during the 90's, became the standard for Pb geochronology. Its cost and complexity always restricted its use (no more than 10-20 machines worldwide in Earth sciences), and it is now replaced by LA-ICP-MS.			