Atomic (Flame) Emission Spectrometry

The potential of atomic absorption (AA) of radiant energy for qualitative analysis was demonstrated many years ago by Fraunhoffer in his analysis of the sun's elemental composition. However, the modern era of AA began in 1955 when the Australian chemist Walsh designed and built a convenient instrument for measuring the wavelengths and radiant power absorbed by neutral atoms in the vapor state. Walsh also pointed out that the technique is advantageous over its complement, flame photometry, in regard to both sensitivity and selectivity. For these reasons, you don't see much flame photometry being done anymore, but you do see a lot of ICP (Inductively Couple Plasma, which uses the same principle as flame photometry without the flame). We don't have an ICP however, so we'll stick to AA and flame photometry.

In atomic absorption spectroscopy measurement is made of the radiation absorbed by the nonexcited atoms in the vapor state. In emission spectroscopy, measurement is made of energy emitted when atoms in the excited state return to the ground state. Flame emission spectroscopy (what we called flame photometry in the 1st paragraph) is a special area of emission spectroscopy in which a flame is used to excite the atoms.

Flame absorption and flame emission techniques usually involve introduction of a sample solution in aerosol form into a flame. Solvent evaporation and vaporization of the salt occur prior to dissociation of the salt into free gaseous atoms. At the temperature of an air/acetylene flame (~2300°C) atoms of many elements exist largely in the ground state. When a beam of radiant energy that consists of the emission spectrum for the element that is to be determined is passed through the flame, some of the ground state atoms absorb energy of characteristic wavelengths (resonance lines) and are raised to a higher energy state. The radiation not removed by absorption is isolated by a monochromometer and detected by a photomultiplier. For example, at 283.3 nm,
\[ \text{Pb} \rightarrow \text{Pb}^* \text{ by absorption of a photon} \]

The amount of radiant energy absorbed as a function of concentration of an element in the flame is the basis of atomic absorption spectroscopy. The amount of light absorbed is proportional to the elemental concentration, assuming Beer's Law holds.

For a few elements, such as the alkali metals Na and K, an air/acetylene flame is hot enough not only to produce ground state atoms, but to raise some of the atoms to an excited electronic state. The radiant energy emitted when the atoms return to the ground state is proportional to the concentration and is the basis of flame emission spectroscopy. For example, at 589 nm,

\[
\begin{align*}
\text{Na} \rightarrow & \text{Na}^* \text{ (energy from flame)} \\
\text{Na}^* \rightarrow & \text{Na} + h\nu \text{ (at 589 nm)}
\end{align*}
\]

The emitted radiant energy from flame emission is isolated by a monochromator and detected by a photomultiplier. The measured signal may or may not be linearly related to analyte concentration.

Within the flame, there are many more atoms in the ground state than in the excited state. For Zn, for instance, in a 2000K flame, there are \( 7.3 \times 10^{15} \) atoms in the ground state for every excited atom. (You can do these calculations if or when you take 2nd semester P-Chem.) Some 65 elements can be determined with good precision and sensitivity by AA, in contrast to about 10 by conventional flame emission spectroscopy, since a flame provides sufficient energy for only a few elements to have a significant number of atoms in an excited state. The alkali metals are elements with unoccupied atomic orbitals of low enough energy to be sufficiently populated by a flame.

Sodium and potassium ions play an important role in a number of biological systems and their functions. Since these ions form few insoluble compounds and exhibit essentially no acidic or basic properties, they cannot be determined readily by conventional wet chemical techniques and are usually
measured instrumentally. The usual techniques employed in determining these ions include atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and ion selective electrodes (ISE). All of these methods require that the sample exist as, or be converted to, an aqueous form. Choosing between the individual methods is based primarily on the sensitivity of the method required as well as the speed and convenience of the method. Since the detection limit for these ions is lowest by AES and AES is simple, this method is generally used for their determination.

The spectrum obtained with the flame is due to the following order of events. The solution of the metal salt in question is sprayed into the flame and the solvent evaporates leaving the finely powdered salt. The salt is vaporized, atomized, and a valence electron is raised to a higher energy state. The energy emitted when this electron drops down into a vacant lower level is given off as radiant energy of a wavelength determined by the Planck-Einstein relationship:

\[ \Delta E = h\nu = hc/\lambda \]

Flame spectra are mainly composed of ground state transitions, while higher energy sources give rise to transitions between excited states. You will be treated to this sort of thing in the laser laboratory in 2nd semester P-Chem lab.

Flame photometry is largely an empirical method and is sensitive to experimental conditions. The signal intensity from a flame is dependent on the flame temperature, the rate of flow of liquid into the flame, the pressure and rate of flow of fuel gases, and any of many other variables which affect the character of the flame or atomizing of the sample. Thus the compounds in which the ion is found and the viscosity of the solution have a great effect. A consequence of this situation is that reliable results can be obtained only after painstaking attention to details, with repeated checks of reproducibility and the effects of altering conditions.

Atomic emission analyses are most commonly and routinely performed on solutions. Therefore your sample must be converted to liquid form prior to
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analysis. This is most conveniently done using a microwave to digest the sample, leaving a solution that can then be analyzed. There must be a sufficient concentration of analyte for the spectrometer to detect. Prior to performing atomic emission analysis, you will need to determine the minimum detection limit for the element of interest. The minimum quantifiable limit (the lowest concentration of analyte which can be quantitatively determined) is generally 3-5 times the minimum detection limit.

The minimum detection limit is intimately related to the concept of signal-to-noise ratio (S/N) and the standard deviation of a measurement. Noise is conveniently measured as the standard deviation of numerous measurements of the signal. It is possible to detect a signal when the S/N is three or greater. Thus the minimum detection limit is when the S/N = 3. If you measure the standard deviation of a number of measurements you can then calculate the minimum detectable signal. The minimum detection limit is obtained by experimentally determining the concentration of analyte which gives the minimum detectable signal. From the minimum detection limit calculate the minimum quantifiable limit. Check your calculations to see if the AA will detect the analyte concentration you expect in your sample. If you cannot detect that low of a concentration, decide if a preconcentration step is in order.