FINGER PRINTING THE ATOMIC WORLD

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All of us are aware of the unique nature of the human finger print. That is the finger print of one person is different from that of another person. It will be a very rare incident that the finger print of two persons to be alike. We can identify a criminal by the finger prints left by him. Even in the unusual situation where two people are found with the same finger print, we may still have some other finger print (there are many fingers) information to identify the criminal.

Different atoms, molecules, minerals (naturally occurring material on earth), chemical compounds all have some unique character by which we can identify them. This unique character may be called a finger print or signature. There are many signatures for any atom, molecule or compound. Some signatures are macroscopic, eg. density, melting point, thermal conductivity etc. When the property considered (that is the signature) depends on a large number of atoms, or molecules it is a macroscopic property.

Recently we are interested in the signatures from the atomic world. That is signatures given by individual atoms or molecules or a group of them. I shall present to you now some of the most commonly used signatures to identify atoms, minerals or chemical compounds.

1. The Bragg spacings (d-spacings) on crystals as a finger print

Most of the chemical compounds are crystalline. However there are some compounds that are amorphous. In crystalline materials (crystals) the atoms are arranged in a systematic way. While in amorphous material the atoms are arranged in random. In the crystal of sodium chloride (NaCl), each Na atom is surrounded by six Cl atoms and each Cl atom is surrounded by six Na atoms to give a crystal lattice (fig 1).

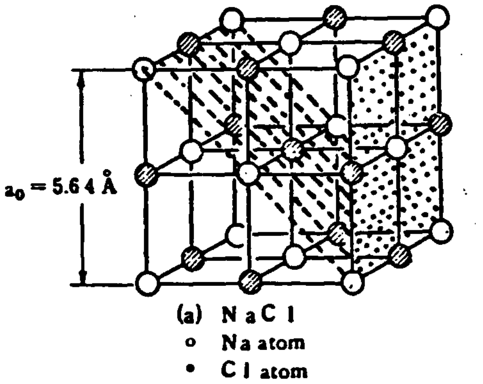

Fig (1). Nacl crystal lattice & bragg plances.

In the crystal lattice we can identify atomic planes. Some atomic planes have more atoms while some atomic planes have less atoms. A given set of atomic planes have a unique spacing. It is named as the Bragg Spacing in memory of their discoverers Sir William Henry Bragg and his son Sir William Lawrence Bragg (1917). Some call it the d-spacing. You would have realized that there can be many d-spacings in a crystal as there are many different sets of Bragg planes (fig. 1).

d-spacings of crystals are unique to a crystal and we can identify a material (or mineral) by its d-spacings. The instrument used to measure d-spacings is called an X-ray diffractometer.

In the X-ray diffractometer we reflect a beam of X-rays from different sets of Bragg planes. By observing the different reflections from Bragg planes we can calculate d-spacings. We have a data bank where d-spacings of all known compounds are stored. When we get an unknown compound, we can measure its d-spacings and compare with the information in the data-bank and identify the unknown compound(s) or mineral(s).

2. Characteristic emission wavelength (or frequency) as a finger print

You are very familiar with the flame test for sodium (Na) and potassium (K) etc. Sodium salts when heated in a Bunsen flame gives yellow light and potassium salts emits red light. Here we notice that colour is a finger print of different elements. The colour depends on the wavelength of light. A given atom is associated with its characteristic emissions wavelengths which are its finger prints. By heating the sodium salt we impart energy to the sodium atoms. By accepting energy, orbiting electrons of atoms can enter into higher orbits. Electrons in higher orbits pocess more energy than in lower orbits. However these excited atoms (as they are called) quickly get de-excited and return to the former state - the ground state. In doing so, energy is released as a packet of radiation (fig.2). We call such an energy packet as a photon. The energy of a photon is hf. h is the Phlank constant and f is the frequency of radiation. We can also write the energy of a photon as hc/λ where C is the speed of radiation ($=3x10^8$ ms^{-1}) and λ the wavelength of emitted radiation. If E_i is the energy of electron in the excited state and E_f is the energy in the lower energy state, then

$$E_f - E_i = hf \quad \text{or} \quad E_f - E_i - hc/\lambda$$

Ex

An atom is to emit short wavelength radiation, consider the energy difference between excited and de-excited state. Should this be high or low when compared with an emission in the long wawelength range?

Different ways to excite an atom

Atoms can be excited in may ways.

(1) We can heat them in a hot flame.

(2) We can bombard them with energetic (fast moving) electron beams.

(3) We can bombard them with X-ray or γ-ray photons.

Ex. **How can you get γ-rays?**

Ex. **How can you get a beam of energetic electrons?**

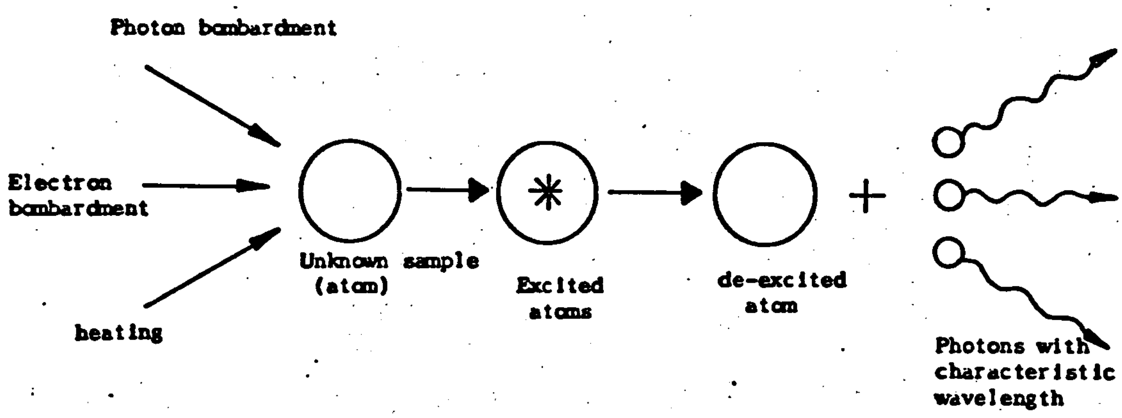

Fig. 2 - Generation of Photons

Heating generally excites atoms to lower energies compared to electron bombardment and (specially) photon bombardment. When atoms are heated the characteristic wavelengths emitted are normally in the visible (~400 nm in violet to 700 nm in the red) the infrared-IR (>700 nm) or ultraviolet-UV (< 400 nm) region. Excitation of atoms with high energy electrons or photons generally gives characteristic wavelengths in the X-ray region (0.01 ~ 10 nm) see fig 3.

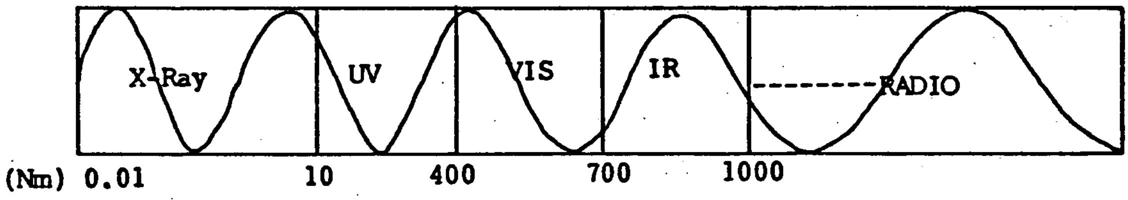

Fig. 3 The wavelength spectrum of Electro Magnetic radiation

Characteristic emission wavelengths of all atomic species are documented and stored in data banks. When we want to identify atoms in an unknown sample we excite their atoms and observe their characteristic wavelengths. Next we compare these wavelengths with those of the data bank and identify the unknown atoms. There are a number of devices that identify atoms (elements) by observing the emission lines, eg.

(1) UV-VIS spectrometer for ultraviolet and visible emissions (detection limit in ppm range).

(2) I.C.P.S (inductively coupled plasma spectrometer) UV-VIS emissions (detection limit in ppb range).

(3) X.R.F. (X-ray fluorescence spectrometer) X-ray emissions (detection limit in ppm range).

3. Absorption wavelengths as a finger print

It is interesting to note that photons emitted by an excited atom have the correct energy to be absorbed by a fellow atom. So the emission wavelengths can also be absorbed by a ground state atom. For example light emitted by a neon lamp (eg. those in street advertisements) can be absorbed by a neon gas that is not excited. This principle is employed in the atomic absorption spectrometer (AAS). The AAS has a number of lamps that emit different wavelengths. Typical lamps consist of Cd, Mg, Na, Ca, K, Li, Mn etc. Imagine we let light from one lamp (cadma) fall on a liquid that is vaporized (see fig. 4).

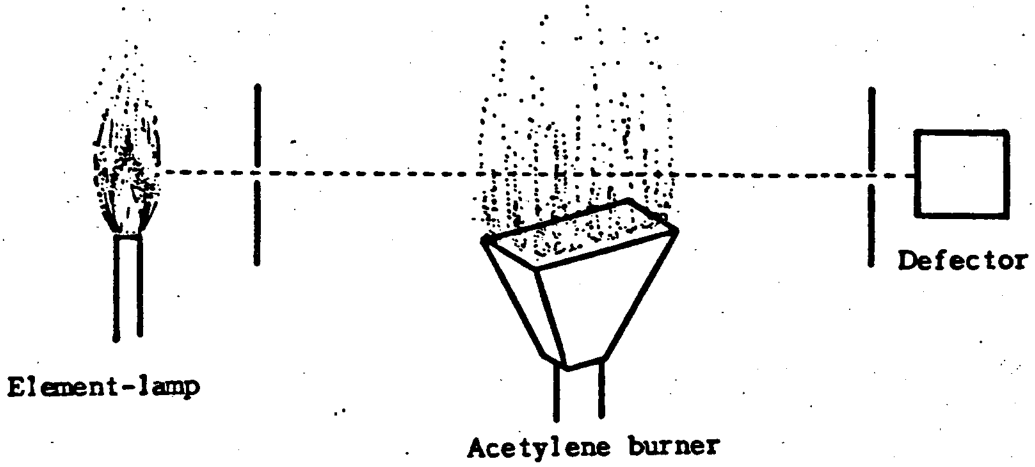

Fig. 4 A schematic diagram of an Atom absorption spectrometer

If the light received at the detector is reduced when the sample is sent in, we know that cadmium is present in our sample. Water quality is routinely tested for pollutants in this manner.

There are many more finger printing techniques such as Mossbauer spectroscopy. Nuclear magnetic resonance spectroscopy; Auger electron (NMR) spectroscopy, IR spectroscopy, etc. They all work on similar ideas. That is samples emit characteristic signals by which we can identify an element or compound.