**Chapter 12.3: Atomic Spectroscopy**

**Introduction**

Scientists often are asked for answers to important analytical questions, such as what is the chemical composition of a particular sample, whether a sample is a mixture or a pure substance, and how much of each component is present in a sample? Luckily, spectroscopic methods can often quickly and easily provide answers to these types of questions. Using the basic understanding of spectroscopy developed in the previous section, we begin by exploring what are often the simplest of these problems: what is the elemental composition of a substance. Knowing the elemental composition of a sample provides useful insight into the origins, identity, and uses of materials.

There are two main types of analytical information that can be determined for an unknown sample: quantitative and qualitative data. As we discussed in Chapter 11, quantitative analysis provides information about how much of a component is present in the sample while qualitative analysis identifies whether something is present or absent in a sample. If the sample is a pure substance, we can use quantitative information to determine its empirical formula (Chapter 11.3) and, in so doing, move towards a definitive identification of the material. Sometimes, simply determining the presence of a particular element in the sample qualitatively is all that’s needed: finding arsenic in food suggests poisoning, identifying lead in paint suggests legal problems with the product, or discovering iron in certain inks suggest a forgery. In other instances, we need to know quantitatively exactly how much of each component is present: is the alloy found in a bullet recovered from a crime-scene identical to that found in the chamber of a suspect’s gun, how much cocaine is contained in a seized sample, or what is the concentration of beryllium in a tissue sample to aid in a cause of death determination.

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Figure 12.3.1. Schematic drawing of atomic emission spectroscopy (top) and atomic absorption spectroscopy (middle). A comparison of the output from these two similar types of spectroscopy is shown at bottom (www.green-planet-solar-energy.com/atomic-emission-spectrum.html).
As the name implies, atomic spectroscopy deals with the identification and quantification of the different elements, rather than the molecules, that make up a sample. Each element, under the right conditions, either absorbs or emits light of different energies, allowing us to gain valuable information about the elemental composition of the substance. In this section, we will focus on light and atoms.

**Atomic Absorption Spectroscopy (AAS)**

Atomic absorption spectroscopy, based on the discoveries first made in the late 19th century, measures the light absorbed by the atoms of a sample and provides both quantitative and qualitative elemental information. In this method, the atoms, in the form of a gas (Figure 12.3.1), absorb light energy which excites the atom’s electrons from their lowest energy state, called the ground state, to a higher energy, called the excited state. This type of energy transition is shown schematically in Figure 12.3.2. The energy of the photon that is absorbed by the atom must match *exactly* the energy needed to excite the electron from a lower to the higher level. Just as when you walk up stair steps, you must put in exactly the right amount of energy to make it to the next step – too little energy and you don’t make it to the next step, and too much energy does not put you on the next step either. Also, you can’t step only ½ way or ¾ the distance to the next step – you must put in just enough energy to make it *exactly* to the next quantized step. In atoms, the photon absorbed must likewise provide exactly the right amount of energy to promote an atom’s electron to a higher energy level.

**Useful Terms in Spectroscopy**

- **Ground state** - the lowest energy state of an atom or molecule.
- **Excited state** – states with more energy than the ground (lowest energy level) in an atom or molecule.
- **Emission** - When an electron in an excited energy state (excited state) returns to the a lower energy state, the transition energy is emitted as light.
- **Absorption** - When electrons become excited from a lower to a higher energy state by absorbing light energy.

![Figure 12.3.2.](www.answers.com/topic/energy-level)

**Figure 12.3.2.** Electron transitions from absorbing light in atomic absorption spectroscopy

![Figure 12.3.3.](http://faculty.sdmiramar.edu/jgarces/LabMatters/Instruments/AA/AAS_Instrument/AASInstruments.htm)

**Figure 12.3.3.** (Left) Three electronic transitions for the sodium atom showing the wavelengths for each transition. (Right) The three sodium atomic transitions show up as different wavelengths of light absorbed by the sodium atoms with energy exactly equal to the energy difference between the two levels involved in the transition.

When white light, containing a continuous spectrum of all the visible wavelengths, is used to excite the atoms in the sample, the wavelengths of light that the atoms absorb show up as “missing” wavelengths, or dark lines in the spectrum. These “missing” wavelengths correspond exactly to the energy required for the electronic
“steps” between energy levels in the atom. For example, shown in Figure 12.3.3 are four important energy levels in the sodium atom (labeled 3s, 3p, 4p and 5p). Three transitions (or “steps”) are possible between these four different levels, each requiring a different amount of energy to cause them to happen (shown by the blue arrows). These three transitions give rise to the sodium absorption spectrum (shown at right in Figure 12.3.3) consisting of the three missing wavelengths corresponding to the three different energy steps or transitions.

Since each element in the periodic table has its own uniquely different set of energy levels, measuring the wavelengths of the light absorbed by a sample can tell us which elements are present (called the characteristic wavelengths for that element). Using atomic absorption, it is possible to quickly determine most of the elements that are present in a sample, such as shown in Figure 12.3.4. Additionally, the area under a peak for an element in the spectrum can give information on how much of the element is present in the sample (vide infra). This means that, under the right conditions, atomic absorption analysis can be both qualitative and quantitative.

In the AAS method, the compounds present must be broken down into individual atoms and placed into the vapor phase. This can be done in a variety of ways but, most commonly, the sample is dissolved in a solvent that is then dispersed into a flame, plasma, or other hot reactor. This provides enough energy to decompose the compounds into charged atoms but not enough to electronically excite the electrons to a higher energy level – the vast majority of atoms remain in the ground electronic state.

Once the sample is atomized, light, typically covering the spectrum from the ultraviolet (~200 nm) to the near infrared (~900 nm), is then shone through the relatively cool, gaseous sample (by cool we mean on the order of only 2,000 – 3,000° C). The various elements in the vaporized sample each absorb light at their characteristic wavelengths, based upon their individual atomic energy levels. A special detector is then used to determine which wavelengths of light have been absorbed and, therefore, which elements are present. This method works well for the qualitative detection of the elements present and can detect the majority of the elements in the periodic table, as shown in Figure 12.3.5.

**Figure 12.3.4.** Typical atomic absorption spectrum showing absorption peaks for a variety of elements including sodium (Na), Aluminum (Al), Potassium (K) and iron (Fe). (http://faculty.sdmiramar.edu/fgarces/LabMatters/Instruments/AA/AAS_Instrument/AASInstruments.htm).

**Figure 12.3.5.** Elements detectable in atomic absorption spectroscopy (red) (http://weather.nmsu.edu/teaching_material/soil698/student_reports/spectroscopy/report.htm).
Atomic absorption spectroscopy can also be used to quantitatively measure how much of each element is present in the sample. When this is done, the amount of light absorbed at a particular wavelength is compared with the previously measured absorptions of a set of standard solutions of that element made at different concentrations but measured at the same wavelength. When this is done, the absorptions from the set of known concentration solutions are plotted to form a calibration curve, shown in Figure 12.3.6. Then, the amount of light absorption measured for the unknown solution is plotted against the calibration curve to determine from the plot how much of the element is present in the unknown sample. The relationship of the concentration of an element in the unknown sample and the amount of light it will absorb is given by a rather simple equation (called the Beer-Lambert Law) that says: \( A = abc \). This equation means that the amount of absorption by the sample (\( A \), absorbance) is equal to a constant for the element (\( a \), called the absorptivity) times the length of the sample that the light has to go through (\( b \), path length) times the concentration (\( c \)).

**More Terms in Spectroscopy**

- **Absorbance** – a measure of the amount of light of a specific wavelength that is absorbed by sample.
- **Characteristic Wavelengths** – the wavelengths of light absorbed by atoms of a particular element. The wavelengths depend upon the energies of the different levels in the element.
- **Transmission** – the amount of light passing directly through a sample that is not absorbed.

**Uses of Atomic Absorption in Forensic Science:** Atomic absorption spectroscopy has found its way into forensic investigations as a valuable tool in a variety of analyses including gunshot residue, food, environmental, and medicolegal investigations.

One of the major uses of atomic absorption spectroscopy is in firearms investigations. When a weapon is fired, there is an instantaneous, but significant, burst of vaporized material coming from the bullet, gunpowder, and casing materials that is expelled from the weapon. Often, this vapor is transferred to the hands and

![Figure 12.3.6. Use of a calibration curve to find the concentration of an unknown in solution](www.hitachi-hitec.com/global/science/trv_vis/uv_basic_4.html).

![Figure 12.3.7. Atomic absorption spectroscopy can be used very effective in the analysis of food components, such as looking for toxic cadmium in chocolate. AA is especially good for this type of analysis since there are very few things that interfere with this analysis](www.rsc.org/chemistryworld/Issues/2010/August/MarketPlace.asp).
clothing of both the shooter and victim. If someone is suspected of firing a weapon, their hands and clothing can be swabbed and analyzed by AAS to determine the presence of unusual amounts of lead, antimony, and bismuth in the sample – all elements found in bullets, gunpowder and casings. Additional clues as to what happened can come from where the different gunshot residues are found. For example, if residues are found mostly on the back of a person’s hands or on their non-firing hand in the case of a rifle shot (the hand used to steady a rifle), then that person is likely the shooter. If, instead, the residues are found primarily on a person’s palms or forearms, it suggests either a defensive position of the person, possibly the intended victim, or else of someone who has handled the weapon. While positive findings are valuable corroborating evidence, failure to find such evidence does not exonerate someone – the method has a significant false negative rate. Additionally, the sampling needs to be performed soon after the firing and before a person has had a chance to wash their hands, eliminating the residue.

AA analysis is also commonly used for soil and environmental analysis. When soil samples are found on evidence or directly on a suspect, such as on clothing, adhered to shoes or tires, or coating plant materials, investigators often try to trace the soil to its geographical source. One way to do this is to measure the elemental composition of the sample and compare it to known soil compositions measured from various locations.

Atomic absorption is also quite useful in analyzing biological samples. Trace elements, such as As, Ca, Fe, Hg, Pb and others, can be readily determined in hair, blood, skin, under fingernails, and in body organs and fluids. Recently, for example, AA was used to show that an injury was caused by an electrical discharge by identifying trace amounts of copper and aluminum in wounds on the skin.

**Advantages and Limitations of Atomic Absorption Spectroscopy:** AAS allows for the rapid detection of very small quantities of over 60 elements of the periodic table, with very few interferences (something in the sample that gets in the way of the desired measurement of an element). The instrumentation is relatively simple and straightforward to operate.

The technique has a few disadvantages, however. Probably chief among these is the need to construct a calibration curve when doing a quantitative analysis for each element. Quantitative analysis also limits the method to the determination of one element at a time, requires the use of special light sources (usually made of the element being detected), and cannot readily measure non-metals. Nonetheless, AAS remains a very useful forensic tool in specific circumstances.

**Atomic Emission Spectroscopy (AES)**

Atomic emission spectroscopy (AES) can be thought of as the exact compliment to atomic absorption spectroscopy. In AES, electrons start in a higher level, excited energy state and then fall down into an empty lower energy state. When this happens, the atom must emit a photon of light to...
“shed” the “extra” energy that is exactly equal to the size of the energy step, shown in Figure 12.3.8. This is precisely the opposite of what happens in atomic absorption where the electrons start at the lower energy state and then absorb a photon to become excited and move to a higher energy level. Since the energy levels involved in both of these processes (absorption and emission) are exactly the same, the energy differences between these possible “steps” or transitions are also the same. This means that the wavelengths of the emission lines are at the same wavelengths as the absorption lines, as illustrated in Figure 12.3.9.

In many ways, we are already well familiar with the phenomenon that is behind atomic emission spectroscopy. For example, fireworks, the aurora borealis (“northern lights”), and the glowing colors from “neon” electric signs are all examples of excited atoms losing their energy by the emission of visible light. In fireworks, a very energetic explosion puts atoms from the different elements present into an excited energetic state. These atoms then quickly lose their energy by emitting the beautifully colored lights that we see: sodium produces yellow,
calcium produces orange, strontium produce red, and blue comes from copper - each element emitting light at its own characteristic wavelengths, in a process that is the exact reverse of atomic absorption (Figure 12.3.10). In essence, the emission spectrograph simply allows a fireworks-like process to happen inside the instrument while we measure the wavelengths of the light generated. If, while watching fireworks, you were to look through a prism that spread out the spectrum, you would see the many emission lines from all of the elements present in the explosion – these emission lines correspond exactly to the characteristic energies of those elements that are displayed through atomic emission spectroscopy.

In AES, samples must first be put into the form of a gas of atoms, just as in atomic absorption methods. This is usually done using high-energy sources such as electrical discharge, plasmas or laser beams. Once in the beam, the high-energy process rips apart any molecules present and puts the individual atoms from the molecules into a gaseous form in a highly excited state. Then, just as in fireworks, the excited atoms quickly lose energy by emitting a characteristic photon of light to drop into a lower energy state. Using AES, it is possible to simultaneously detect the presence of about 60 different elements in the sample.

It is important to note the difference between the AAS and AES experiments. In absorption spectroscopy, a bright white light is used to shine through the sample to excite the atoms. The resulting spectrum shows black lines at wavelengths that are absorbed by the sample. In emission spectroscopy, no light source is used; the sample is energized by adding heat to excite the electrons in the atoms. The light that is then emitted from the sample itself as the electrons fall back to lower energy levels is measured and appears as bright lines on a black background at the energy levels characteristic of the elements in the sample. Because light emission is weaker than absorption in these experiments (mainly because, even at high energy, most of the atoms are not excited above the ground state so relatively few atoms emit light at any given moment), the atomic absorption method is more sensitive than emission.

The intensity of the light emitted in AES is proportional to the number of atoms present in a sample. This provides the ability to quantitatively determine how much of a given element is in the material. Emission spectroscopy has a number of advantages including a high throughput rate (many samples can be analyzed in a relatively short amount of time), high resolution (providing the ability to measure elements separately), good stability (the results are reproducible), and relative ease of operation of the instrument.
Uses of Atomic Emission in Forensic Science: Atomic emission spectroscopy is a reliable, simple, and inexpensive method for determining the elemental composition of an unknown sample. It is used in forensic analysis to provide accurate composition information about soil, environmental, glass, biological, metal alloy and other samples.

It is occasionally necessary to measure the composition of metallic and glass samples to determine whether they are similar to a known reference or standard, such as comparing a piece of glass found on a victim with that taken from a suspect’s car. When glass is manufactured, very small amounts of trace elements (the tiny amounts of other elements besides silicon, oxygen and boron found in glass) can be inadvertently incorporated in the glass from the raw materials, furnace, or handling technique used in the process. This unintended inclusion of very small amounts of impurities can easily vary significantly from batch to batch and between manufacturers. Measuring the amounts of these trace elements in a glass sample can help to show that a particular sample was or was not produced by a specific manufacturer or with a specific batch of glass. This type of information might be quite helpful in differentiating between glass samples produced by various manufacturers and even pinpointing which production line at one manufacturer produced the glass. There has even been work to try to determine when a particular sample was made using this trace elemental composition data. Currently, the AES analysis of ten elements in glasses (Al, Ba, Ca, Fe, Mg, Mn, Na, Ti, Sr, and Zr) is employed regularly on very small samples (milligram-sized) with very good analytical precision. Reports have also shown that it is possible using AES to identify the type of a glass sample – window glass, headlight glass, etc.

Similarly, metals, such as steel, aluminum, copper, and others, also typically contain a relatively large number of trace elements resulting from the mining, refining and manufacturing processes. AES data can help, as with glass, to identify the manufacturer or to compare two metal samples in an attempt to show that they came from the same source.

Biological forensic samples have also been analyzed using AED. For example, thallium, arsenic and mercury poisoning have been confirmed by AES data from liver samples recovered at autopsy.

Atomic Fluorescence Spectroscopy (AFS)

Atomic fluorescence (AFS) spectroscopy can be thought of as similar to atomic emission spectroscopy in a number of key ways. In atomic fluorescence, the electrons of atoms are first excited to higher energy levels, just as in atomic emission. Rather than immediately emitting their characteristic wavelength of light to return to a lower-energy state as in emission, however, in fluorescence the atoms first lose some of their energy without emitting light – typically through quantized low-energy vibrations or some other similar non-radiative process (meaning without the radiation of light). This drops the energy of the atom down a small amount but not to the ground state. After it loses a fixed amount of its energy through vibration, the atom can then emit a photon of light – but a photon of lower energy (longer...
wavelength) than what it absorbed. In other words, it absorbs the light energy from a photon and then later emits a lower energy photon of light. This is shown schematically in Figure 12.3.12. This is actually quite similar to the way fluorescent lights used in homes and offices work. By measuring the amount of light later emitted by the atom, it is possible to both qualitatively and quantitatively identify the elements present in the sample that fluoresce.

The experimental set-up for AFS is shown in Figure 12.3.11. In this case, a bright white light (all visible wavelengths) is shone on vaporized atoms and the fluorescence is measured to the side of the direct path of the white light beam. This allows for the accurate measurement of the longer wavelength of the fluorescent emission without interference with the exciting white light beam that also includes the fluorescent wavelength.

Uses of Fluorescence Spectroscopy in Forensic Science: Atomic fluorescence has its place in forensic investigations particularly in the analysis of elements that prove difficult using other methods. Important among these are the analysis of mercury and lead. Additionally, AF is used in microscopy to map elemental compositions in a sample.

Neutron Activation Analysis (NAA)

Some experimental techniques for examining samples on the atomic level techniques involve the emission of light through mechanisms other than those described above. Small particles, such as electrons, neutrons, and even small atoms, can be aimed at the atoms in a sample. These particles can collide with a low-energy electron in the atom, knocking it completely away from the atom. This is similar to the way one ball can knock another ball away through a direct collision. This collision leaves behind a “hole” in the inner electronic structure of the atom that is then filled by the cascading of the higher energy electrons down to lower levels results in the emission of photons of light. 

Figure 12.3.14. Light can be emitted by particles knocking off low-energy electrons through collisions and the resulting “cascade” of the higher energy electrons down to lower levels results in the emission of photons of light. 

Figure 12.3.13. Removing pieces at the bottoms of a stack in this game will ultimately result in pieces falling from higher levels to replace the removed lower pieces, similar to how removal of a lower-energy electron results in a cascade of electrons falling to lower energy levels, in turn producing the emission of electromagnetic radiation.
resulting in the emission of light corresponding to the energy difference between the starting and ending energy levels for each electron in the cascade. The wavelengths and intensity of this emitted light can then be measured to determine what elements are present by their characteristic emitted light. This process is shown schematically in Figure 12.3.14.

One of the analytical techniques that involves this type of light emission from the collision of particles with low-lying electrons in atoms is called neutron activation analysis (NAA). In this method, thermal neutrons (relatively slow, low-energy neutrons) from a nuclear reactor are aimed at a sample of unknown elemental composition. The atoms of the sample can absorb these additional neutrons into their nuclei, each becoming one neutron heavier. This altered nucleus, however, is not very stable and quickly emits a gamma ray to lose some of its added energy. Gamma radiation is a form of very high energy electromagnetic radiation. Each gamma photon carries ~ 10^5 times the energy of a visible photon. This emission results in a somewhat more stable, but radioactive nucleus (see section 12.6 for more about radioactivity). This radioactive nucleus then undergoes a nuclear decay process by first emitting a beta particle (a beta particle is simply an electron) to convert the additional neutron into a proton, and then emitting a second gamma ray to produce a stable, non-radioactive nucleus (one proton heavier than the original atom; e.g., converting As^{33} into Se^{34}). This is shown schematically in Figure 12.3.15.

In neutron activation analysis (NAA), the energy of the second gamma ray that is emitted (the “delayed gamma ray”) can be analyzed to reveal the identity of the original target nucleus – all atoms emit gamma rays with different characteristic energies (the first gamma ray can also be analyzed, but less commonly). It is important to note, however, that the gamma ray emitted in NAA does not come from the movement of electrons between energy levels but arises from energy level shifts within the nucleus itself.

Figure 12.3.15. The processes involved in neutron activation analysis: [from left to right] (1) irradiation of the nucleus with a low-energy thermal neutron, (2) absorption of the thermal neutron into the target nucleus, (3) decay with the immediate release of a gamma ray to form a radioactive nucleus, and (4) radioactive decay to emit a second gamma ray and a beta particle – an electron – to form a stable nucleus.

Figure 12.3.16. The neutron activation analysis of a human fingernail showing its trace elemental composition by measuring the energy of the second (delayed) gamma ray emitted.
The gamma ray that is emitted has a much shorter wavelength than visible light (<0.001 nm – remember visible light is ~400 to 750 nm) so special detectors are needed. The amount of radiation given off can also be used to determine how much of each element is present in the sample. For example, an NAA spectrum displaying the trace elemental composition in a human fingernail is shown in Figure 12.3.16.

Neutron activation analysis has some particular advantages and disadvantages over other types of spectroscopic elemental analyses. The advantages include; (1) non-destructive analysis of the sample, (2) extreme sensitivity to low concentrations (up to parts per trillion), (3) simultaneous analysis of many elements to give a total elemental composition of the sample, and (4) insensitivity to any chemical interferences in the sample (e.g., chemical state, molecular form or physical properties). The principal disadvantage of the method is that it requires a source of the thermal neutrons, and this usually means access to a nuclear reactor.

**Uses of Neutron Activation Analysis in Forensic Science:** NA analysis has been used in a variety of forensic cases, primarily when only very small or rare samples are available, to detect extremely low concentrations of trace elements, or when a non-destructive analysis is required.

One forensic application of NAA has been in the identification of explosives. By analyzing the trace components of samples taken after an explosion, NAA has been shown to be a valuable tool in tracking the source of the explosive material back to the original manufacturer. It can also be used in tracking explosive materials found prior to their detonation.

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**Man with the Golden Helmet: But by Who?**

For decades, the painting in the museum in Berlin called the “Man with the Golden Helmet” represented the epitome Rembrandt and was one of the pillars of the museum. But within art circles, experts debated whether it was really the work of Rembrandt – there were some unusual features of the work that helped fuel this debate. Recently, the Rembrandt Project in the Netherlands examined the painting using Neutron Activation Analysis. The results have strongly suggested that the work was not that of the hand of Rembrandt but rather by an unknown contemporary of his.

NAA has an important place in forensic examinations of rare works of art. It provides non-destructive testing for ultra-trace elemental compositions that can be used to support or refute a claim of authenticity of a work of art. How many other great works that we’ve attributed to the masters are really by other artists? Only time may tell.

NAA has been used to examine the ultra-trace elemental compositions of hair, body tissues, soils, paints, plastics, and glass samples. Recent work has also been done on bone samples of...
unidentified people with the idea that the trace elemental composition found in the bones themselves may lead to the geographic region that the person lived in since different places on the earth have different trace element compositions. Food grown and consumed in these areas would be expected to “imprint” their trace elemental composition within the bone, forming a type of geographic “fingerprint” of where the person lived. Measuring this trace elemental composition of the bone sample and comparing it with known geographic trace levels could be used to support the matching of a person that has lived for a period of time in a specific locale.

**Auger, ESCA, and Other Related Forms of Atomic Spectroscopy**

There are many other forms of atomic spectroscopy that have not yet made a significant impact in forensic science but their potential remains to provide valuable information as future needs develop. These forms of spectroscopy are typically conceptually similar to neutron activation analysis. The general process is for a particle, such as an electron, to collide with an inner electron to knock it away from the atom. The higher-level electrons then cascade down to emit characteristic wavelengths of light or an energetic particle that provides an identification of the element present in the sample.

For example, in Auger spectroscopy, a beam of electrons is aimed at a sample. An electron from the beam can collide with an inner electron in a target atom to excite it to a higher energy level. Once in this state, the electron can fall back to the ground state and, in the process, provide enough energy to emit another electron from the atom with a characteristic energy. Information, such as elemental composition at different depths from the surface of the sample, can be readily determined, as shown in Figure 12.3.7. ESCA spectroscopy – or Electron Spectroscopy for Chemical Analysis – is similar to the Auger process in some ways. In the ESCA technique, high-energy photons (rather than electrons) are aimed at the sample and provide enough energy to knock an inner electron away from the atom. The energy of this ejected electron is then analyzed, as in Auger spectroscopy, and similar chemical information can be gained about the compound.

![Auger depth profile of a special (In-Sn-O) film on glass](http://frictioncenter.engr.siu.edu/course/file5.html).