Atomic Spectroscopy

Types of atomic spectroscopic techniques

Atomic absorption (in a hot gaseous medium)
Resonance lines (3s to 3p in Na) (see Fig 6.17a or equiv)

Atomic emission (excited first by the heat of a flame, a plasma, an electron arc or spark)
Resonance lines (3p to 3s in Na)
Non-resonance lines (e.g. 4d to 3p in Na)

Atomic fluorescence (excited first by irradiation)
Resonance lines ($Mg = 3s \xrightarrow[2852\overset{o}{A}]{} 3p \xrightarrow[2852\overset{o}{A}]{} 3s$)

Non-resonance lines ($Na = 3s \xrightarrow[3303\overset{o}{A}]{} 4p \sim\sim\sim 3p \xrightarrow[5890/5896\overset{o}{A}]{} 3s$)

Energy level diagram

For one electron system (doublet) S = 1/2
The lowest energy electronic transition of both Na and Mg^+ are between 3s and 3p (Fig. 8-1).
The splitting of two p orbitals leads to 2 closely-spaced emitted lines (e.g. Na - 5896, 5890 (yellow), Mg^+ - 2803, 2796 nm.
For $2e^-$ system (singlet [S=0] or triplet [S=1]) e.g. (Mg: 2852 nm (singlet), 4571 nm (triplet))
Triplet excited state is of lower energy (Fig. 8-2).

Although correlation of atomic spectra with energy level diagrams for light element (e.g. Na and Mg) is relatively straightforward, the same is not applicable to heavier elements (e.g. Ca or transition metals).
For instance, the number of lines in neutal atoms and singly changed ion are Li(30), Mg(173), Ca(662), Fe(4757).
But fewer lines are excited in low-temperature atomizers, e.g. flame.

Atomic Line Width

Although an atomic line should theoretically contain only a single wavelength with zero line width, several phenomena cause line broadening. These include (1) uncertainty effect (2) Doppler effect (3) pressure or collisional effect and (4) electron and magnetic effects.

(1)   According to the uncertainty principle, finite uncertainty in transition state lifetime leads to finite uncertainty in frequency or wavelength (i.e. line broadening). For instance, lifetime of 2 x 10^{-8} s leads to 10^{-4} Å natural line width ($\Delta\lambda\frac{1}{2}$)

(2)   According to the Doppler effect, the wavelength of radiation emitted or absorbed by a rapidly moving atom (in a flame) decreases if the motion is toward the detector or increases if away from it (Fig. 8-7). This leads to lines that are about 2 orders of magnitude greater in linewidth as compared to $\Delta\lambda\frac{1}{2}$

(3)   This arises from collisions of the emitting or absorbing species with others in a heated medium. This pressure effect results in broadening that is 2 or 3 orders of magnitude greater than $\Delta\lambda\frac{1}{2}$

The effect of temperature on atomic spectra

The number of atoms in the excited (Nj) and ground states (N_0) is related as follows:

$$\frac{Nj}{No} = \frac{Pj}{Po} \exp\left(-\frac{Ej}{kT}\right)$$

$$\overline{\lambda} = 5893\,\text{Å}$$

For example (Fig.8-2 or R1* Table 9.5), for Na   3s $\rightarrow$ 3p at 2500 K and at 2510 K.

$$\frac{Nj}{No} = \frac{6}{2} \exp\left(-\frac{3.37 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{JK}^{-1}\quad 2500\text{K}}\right)$$

$$= 1.72 \times 10^{-4} = 0.0172\%$$

Similarly, at 2510 K, $\dfrac{Nj}{No} = 1.79 \times 10^{-4} = 0.0179\,\%$

So a temperature increase of 10 K results in a 4% increase in the number of excited Na atoms, leading to an increase in emitted radiation.

Therefore, analysis based on atomic emission, which depends on Nj, requires close control of atomization temperature. This observation can be employed to determine flame temperature.

On the other hand, the temperature effect on analysis based on atomic absorption and fluorescence, which depends on N_o, is, in theory, minimal. In reality, this is not the case because an increase in temperature usually increases the atomization process, line broadening due to Doppler effect, and ionization interference.

Sample atomization techniques.

Flame atomization and (optional) electrothermal atomization are widely used.

Flame atomization
In a flame atomizer, a solution of the sample is nebulized (formed into a fine mist or aerosol) by a flow of gaseous oxidant (e.g. air), mixed with a gaseous fuel (e.g. C_2H_2), and carried into a flame when atomization (formation of gaseous atoms) occurs.

Various complex processes occur in a flame, leading to the formation of molecules, atoms ions and their excited states (Fig. 9-1 or R1* Fig 9.4)

Table 9-1 (or R1* Table 9.3) lists the common fuels and oxidants employed in atomic spectroscopy. At 1700°C, only easily decomposed sample are atomized when air is the oxidant. Higher flame temperature (2500 - 3100°C), which is obtained when O_2 or N_2O is the oxidant, is needed to decompose refractory samples.

To obtain a stable flame, the burning velocity must be equal to the flow rate of the fuel/oxidant mixture. If the former is higher flashback will occur, otherwise the flame is blown off the burner.

The important regions (Fig. 9-2 or R1* Fig 9.5) of a flame (e.g. hydrocarbon flame) including the primary combustion zone (blue color due to C_2, CH and other radials, not in thermal equil), interzonal region (rich in free atoms) and secondary combustion zone (formation of stable molecular oxides to be dispersed into the surroundings)

The interzonal region just above the primary combustion zone is the location for use in atomic spectroscopy (as adjusted by the burner height settings) because the flame temperature is the highest here (Fig. 9-3).

Oxide formation (e.g. $Cr_2O_3 > MgO > Ag_2O$) will lead to a decrease in the number atoms, and hence a lower absorbance or emission (Fig. 9-4).

A commonly used flame atomizer is a laminar flow burner (Fig. 9-5 or R1* Fig 23-4b). The aerosol is formed at the nebulizer by the flow of oxidant (e.g. air). It is then mixed with fuel and enters a series of baffles that allow only the finest solution droplets to pass through. The mixture is then burn at the slotted burner. The large droplets are collected in the mixing chamber and drain to a waste container.

The laminar flow burner provides a relatively quiet flame, and a long optical path length which enhance sensitivity and reproducibility. However, the burner should be equipped with pressure relief vents to avoid explosion if flashback occurs.

Close control of flow rates of oxidant and fuel is required to provide optimal atomization conditions. For determination of metals that form stable oxides, a fuel-rich flame is desired.

Flame atomizers are superior to produce reproducible results. But because of a low sampling efficiency or nebulization rate (e.g. 20%) and short sample residence time ~10^{-4}s), the sensitivity of flame atomizers is inferior to other methods (e.g. electrothermal atomization).

Atomic absorption.

Instruments for atomic absorption spectroscopy (AAS) consist of a radiation source (hollow-cathode lamp), a sample holder (the atomizer), a wavelength selector, a detector, and a signal processor and readout (see R1* Fig 9-15).

Hollow cathode lamp
This commonly used source consists of a tungsten anode and a cylindrical cathode (made of or consisting of a metal or a metal alloy which are sealed in a glass tube filled with an inert gas (e.g. Ne or Ar at 1-5 torr), see Fig 9-11 (or R1* Fig 9-18).

When a potential of 300 V is applied, ionisation of the inert gas occurs. A current of 5-15 mA is normally generated. When the gaseous cations are energetic enough, sputtering (formation of an atomic cloud due to dislodgement of metal atoms) around cathode occurs. Some metal atoms are in the excited states and they then emit the characteristic radiation.

The hollow cathode configuration enables the redeposition of metal atoms (after sputtering) back to the cathode, and this also help concentrate the radiation.

Higher potentials, and thus higher currents, lead to greater intensity. But Doppler broadening of emission lines occurs because of increased temperature. Self-absorption, particularly at the centre of the emission band, will also result because of the presence of a greater number of unexcited atoms in the cloud (Fig 9-16).

In order for Beer's Law to be obeyed, the source line width must be narrower than the absorption line width. (Fig. 9-10 or R2 Fi 7-7). This can be achieved by having the source temperature lower (and hence Doppler line broadening is less) than that of the atomizer.

Monochromator
This is designed for λ scanning. A monochromator consists of an entrance slit, a collimator (lens or mirror) a wavelength dispersive element (prism or reflection-grating), a focussing element and an exit slit (Fig 7-16).
A reflection grating linearly disperses λ by diffraction, but a prism disperses shorter λ by diffraction and a prism disperses shorter λ to a greater degree due to refraction. (Fig 7-17). Note the cutoff λ of a glass prism.

The use of minimal monochromator slit width is desirable when the resolution of narrow absorption or emission bands is needed in quantitative work (Fig 7-24). However, this will result in a decrease in the available radiant power and thus resulting in more difficult quantitative analysis.

Radiation Transducers or Detectors
The ideal transducer, which converts the radiant energy into an electrical signal, would have (1) High sensitivity, (2) High SNR, (3) Constant wavelength response, (4) Fast response time, (5) Zero dark current.
A photon (or photoelectric) transducer absorbs the radiation which causes emission of electrons (e.g. PMT) or (optional) enhanced conductivity (e.g. photodiode).

Photomultiplier tube (PMT)
It consists of the photoemissive cathode. Moreover, it contains dynodes which progressively accelerate the electrons, causing additional e$^-$ to emit (Fig 7-29 or equivalent).
Generally, in a 9-dynode PMT, 10^6 - 10^7 e$^-$ can be formed for each incident photon.
PMTs are highly sensitive to UV and visible radiation, and have extremely fast response time.
Thermal dark current can be eliminated by cooling the PMT to a low temp (e.g. -30°C), leading to very low noise. Note that intense light can cause irreversible damage to the photoemissive surface.

Interferences

Spectral interferences

These arise when the absorption or emission of an interfering species either overlays or lies very close to that of the analyte. For instance, the vanadium line at 3082.11 Å overlaps with the aluminum line at 3082.15 Å. This is confirmed after performing a wavelength scan. The interference can be avoided by using a narrower band pass or using another Al line at 3092.7 Å.

Interferences also result from the presence of combustion products that exhibit broadband absorption, or of particulates that scatter radiation. Correction can be made by measuring a blank. However, if the source of absorption or scattering originates in the sample matrix, correction by a blank will not work. For instance, in the determination of Ba (5536 Å) in an alkaline-earth metal mixture, the presence of CaOH interferes (Fig. 8-8). A higher flame temperature (using N_2O as the oxidant) will decompose the interfering CaOH.

(Optional) Various background correction methods (e.g. continuum-source and Zeeman effect) are available to alleviate spectral interferences.

Chemical interferences

These result from various chemical processes occurring during atomization. (e.g. dissociation, ionization, formation of low volatility compounds)

Formation of refractory compounds: Decrease in Ca absorbance with increasing sulfate or phosphate concentration. This effect can be alleviated by using a higher flame temperature or a releasing agent (e.g. excess Sr or La to preferentially react with the interfering phosphate and release Ca) or a protective agent (e.g. EDTA to complex with Ca and protect it from reacting with phosphate).

Ionization: This only becomes important at higher flame temperatures at which less atoms are available.
$$M \Leftrightarrow M^+ + e^-$$
Hence, the presence of other ionizable metals (e.g. alkali metal as ionization suppressor) will shift the above equilibrium to the left (Fig. 9-17.)

Atomic Emission spectroscopy

Atomic emission can be achieved from flame sources or (optional) plasma sources, arc and spark sources. Here the sources are essential both for atomization and excitation of atoms.

Exercises
8-4, 8-5, 8-6, 8-9, 8-10, 8-11, 9-1, 9-2, 9-7, 9-8, 9-9, 9-10, 9-13, 9-14 a, b, 9-20, 9-21, 9-22.