Low Resolution Emission Spectroscopy of AA Flames

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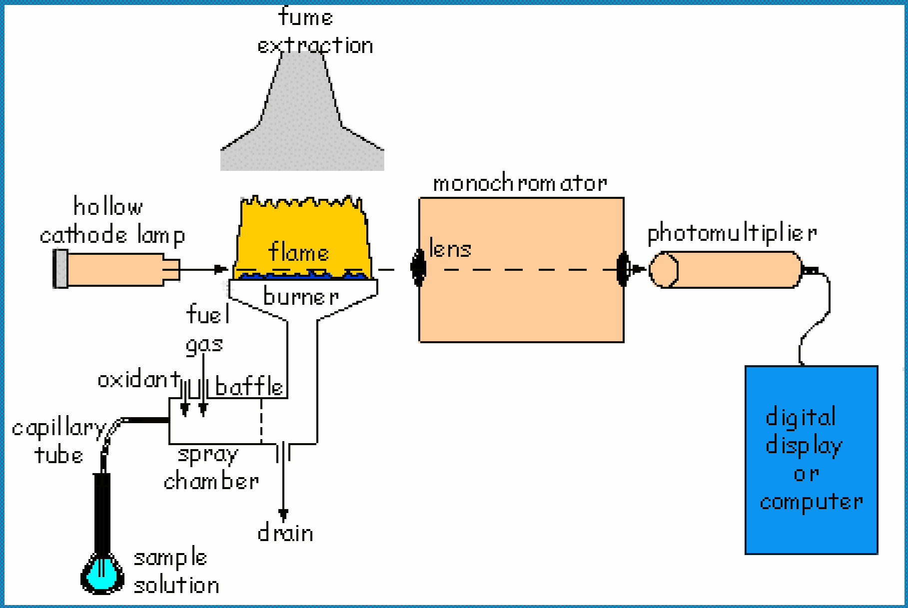
Motivation

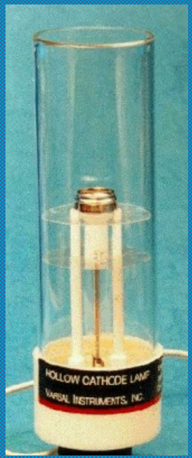
- AAS and AES as tools in analytical chemistry typically involve monitoring absorption or emission intensity at a particular λ value.
- Monitoring of the whole spectrum during AAS/AES leads to additional information regarding the presence and nature of interferent species, long-lived mantle impurities, etc.
- To understand such effects it is important to characterize the emission spectra found in flames typical of AA burners.

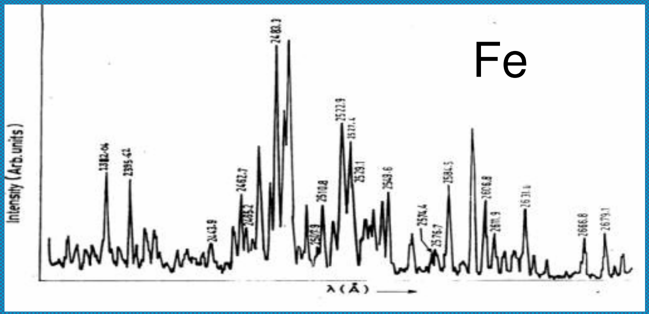
Outline

- Overview of AA method
- Overview of flame chemistry
- Experimental approach
- Flame spectra – Swan bands
- Flame T profiles and effects during sampling
- Lamp spectra – Na, K, and Fe lines
- Impurity effects
- Summary and conclusions

Flame atomic absorption:







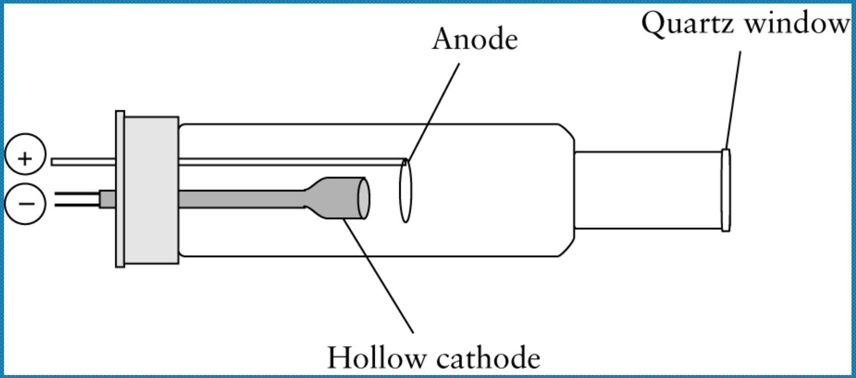
Light from a hollow cathode lamp passes through sample being vaporized in a flame.

The lamp has the atomic emission spectrum of the particular chosen element under analysis (sharp lines).

In theory, the only species in the sample absorbing at that wavelength is the analyte.

However, molecular band spectra from the flame itself, and interference effects from e.g. complex anions can cloud the issue.

Hollow cathode lamp

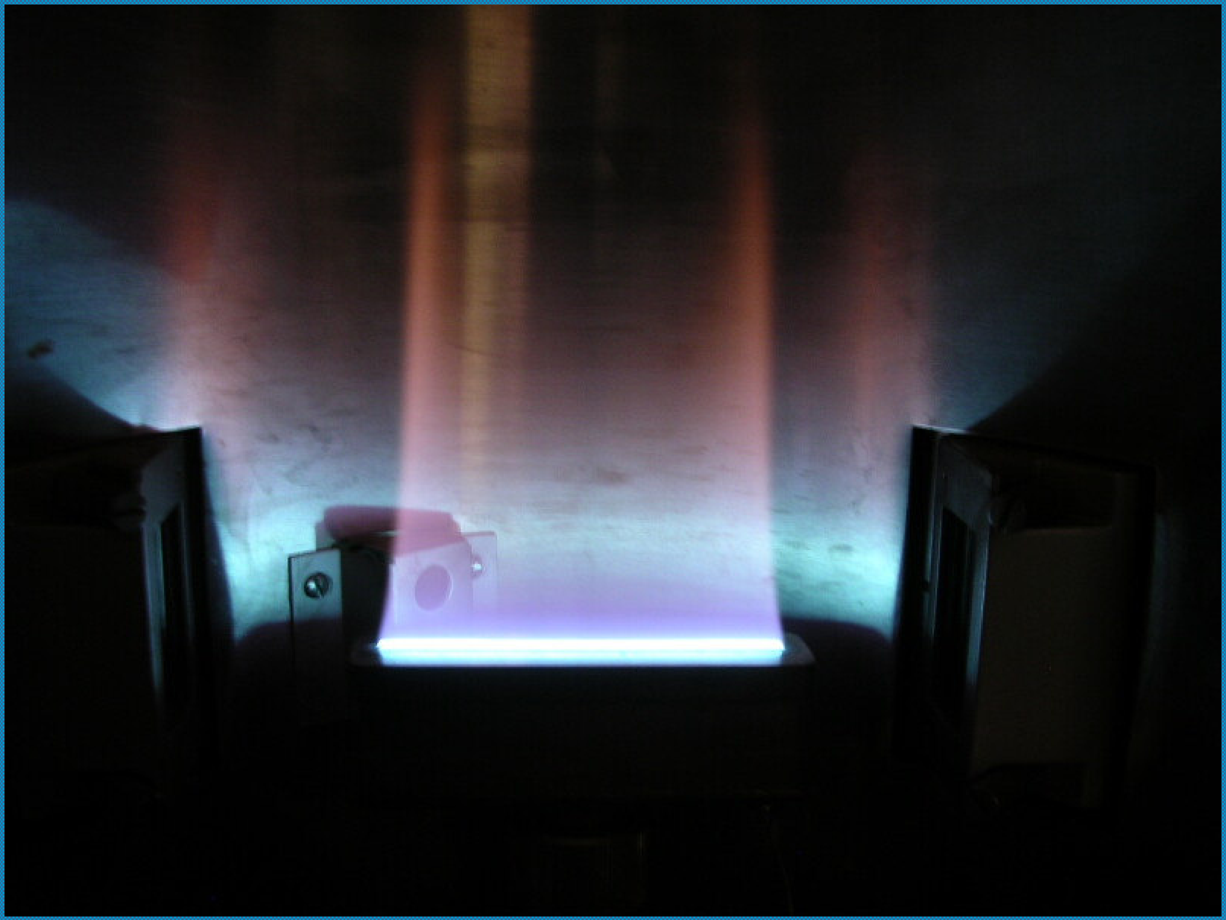


- Inert gas-filled (1-5 torr) tube with tungsten anode and cathode of metal to be studied
- 300 V potential across electrodes
- Cations from ionized gas dislodge metal atoms from surface by *sputtering*
- Doppler broadening of emission lines is lower than that for equivalent absorption lines in flame (lower temperature)

Flame chemistry

- Typical flame is acetylene/air (sometimes acetylene/N_2O)
- Acetylene combustion chemistry produces C_2 among its intermediates
- Product species (CO_2, H_2O) do not have transitions in vis/uv range used – emission spectra dominated by molecular bands from reactive intermediates of acetylene combustion process.

Oxidizing flame



Oxygen-rich mixture

Spectrum contains molecular emission bands from intermediates formed in the reaction zone

Reducing flame

Fuel-rich mixture

High carbon content

Lower temperature?

Higher luminosity

Spectrum is a mixture of band and continuum components

Combustion of C_2H_2

- Acetylene/air mixtures studied since 1895 (Le Chatelier)
- Mechanism is complex and depends on flame temperature

Some significant processes:

$$O + C_2H_2 \longrightarrow CO + CH_2$$ production of methylene radical

$$O + C_2H_2 \longrightarrow OH + C_2H$$ production of ethynyl radical

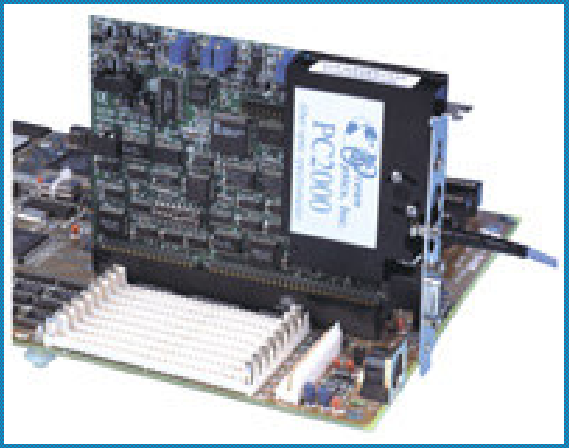
$$O_2 + C_2H \longrightarrow 2CO + H$$

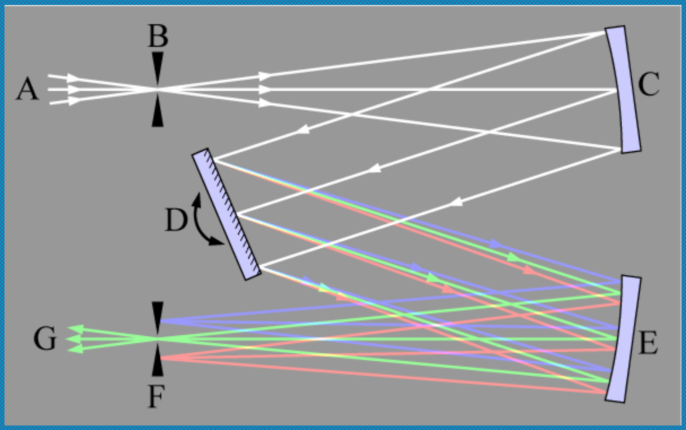
$$CO + OH \longrightarrow CO_2 + H$$

A. Williams and D. B. Smith, *Chem. Rev.* **70** (1970) 267

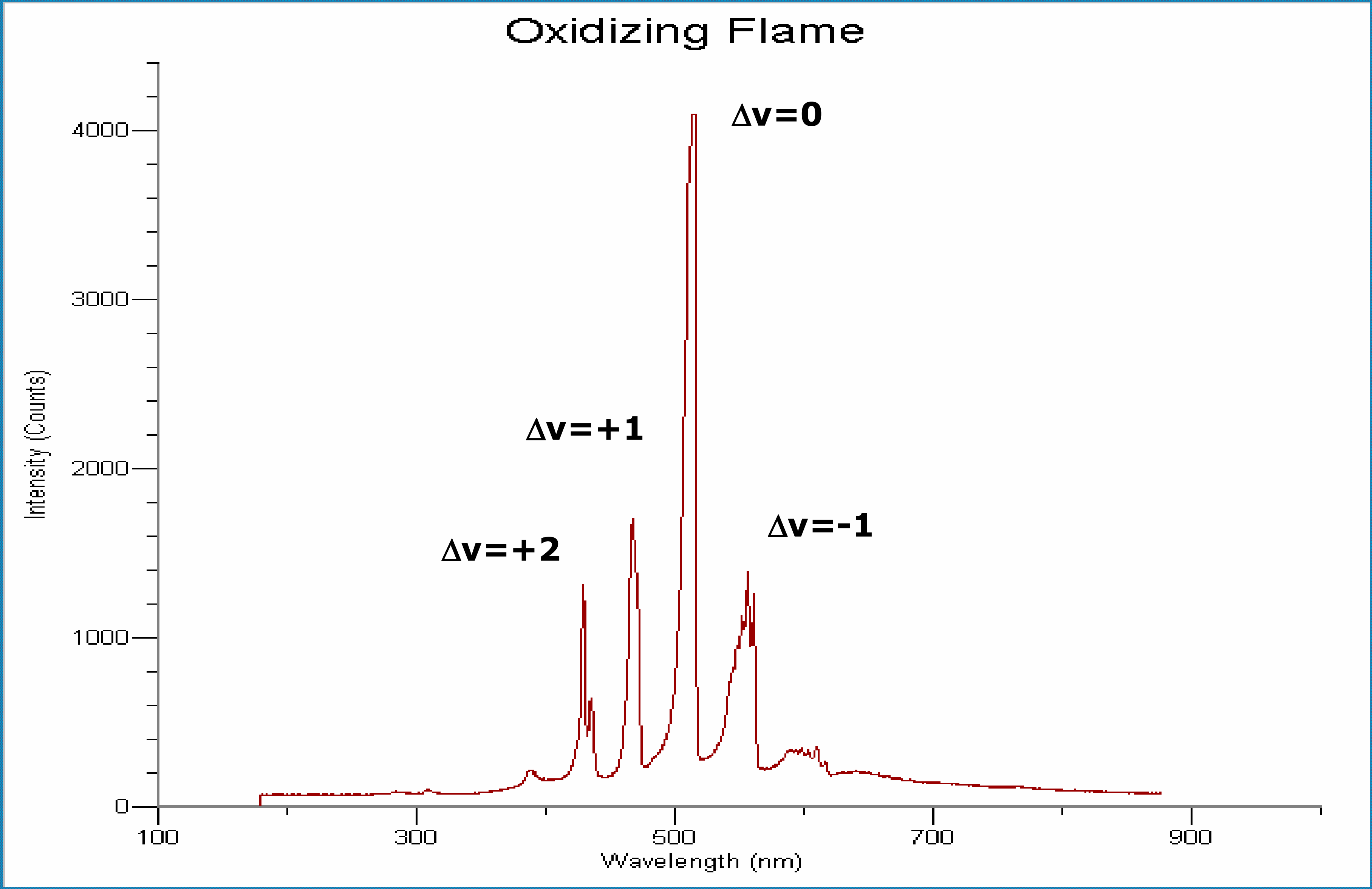
The Spectrometer

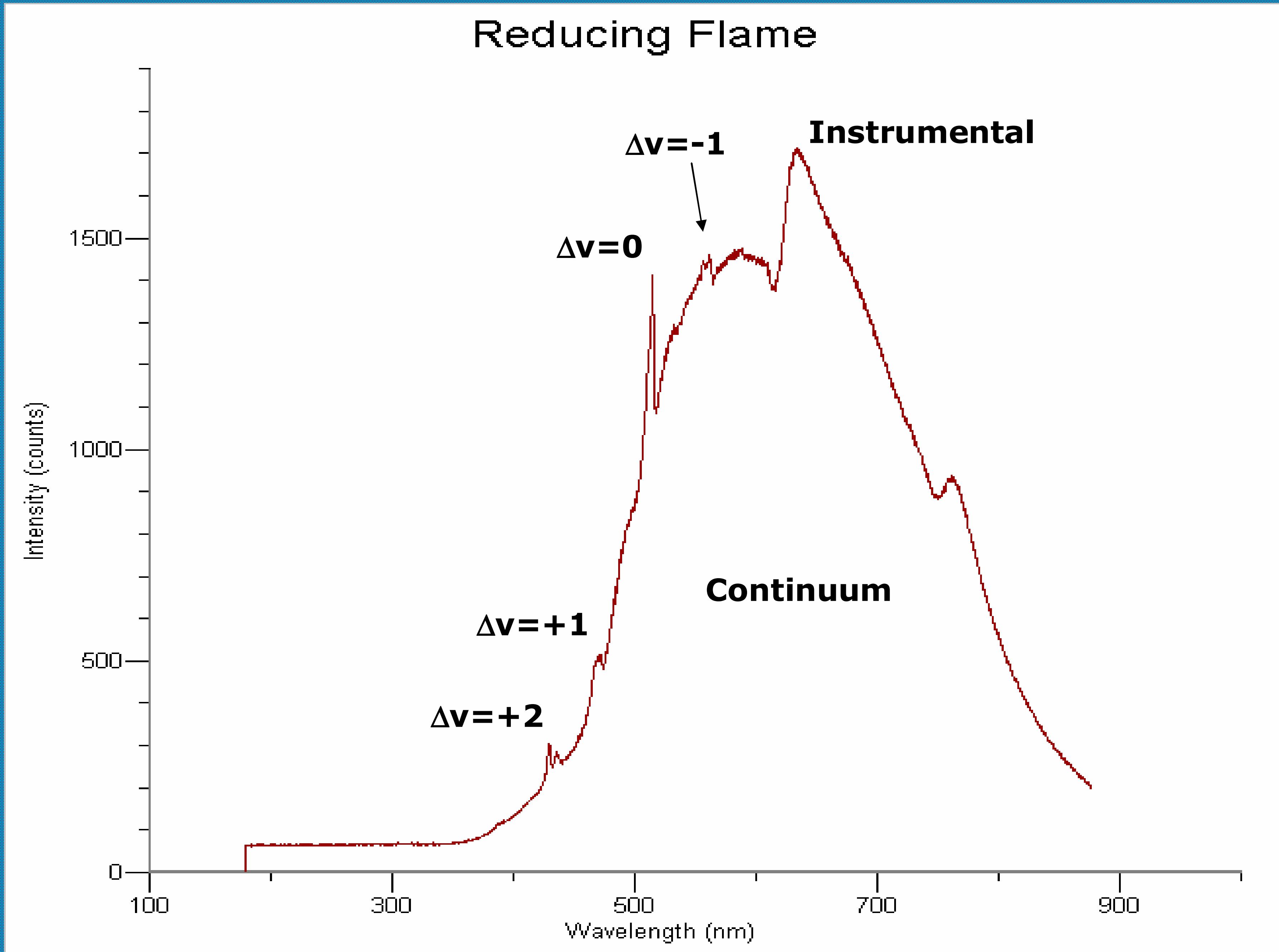
- Ocean Optics PC2000
- ISA bus mounted miniature spectrometer
- Crossed Czerny-Turner monochromator
- 2048 element linear Si CCD array
- Groove density 600/mm
- Coupled to optical fiber (solarization-resistant, 300 or 600 μm core)
- Resolution dependent on groove density and entrance aperture - nominally around 2 nm FWHM



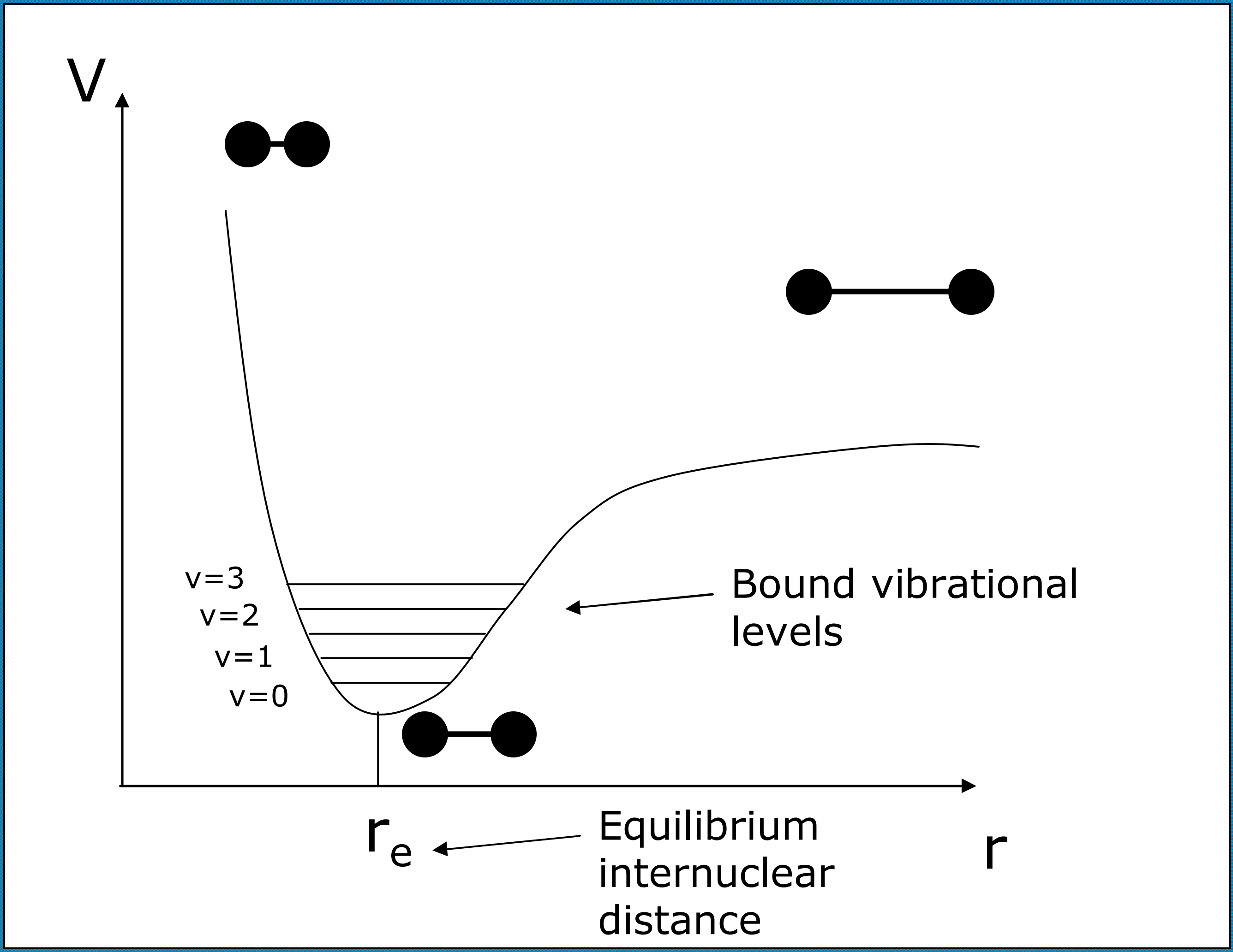


Dominant feature in oxidizing acetylene flames – Swan bands of diatomic carbon.

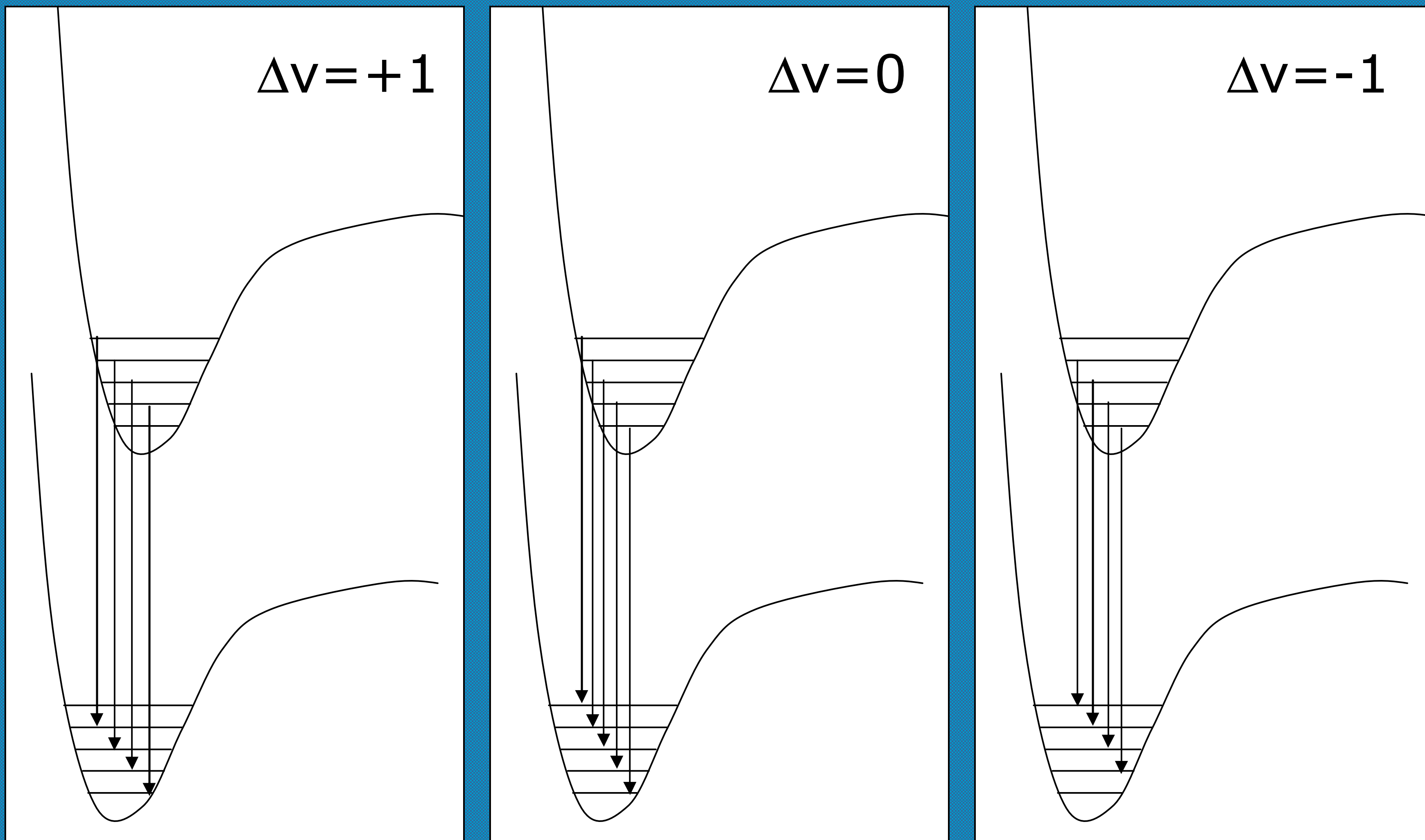



Reducing Flame
Instrumental
Δv=-1
Δv=0
Continuum
Δv=+1
Δv=+2
Intensity (counts)
1500
1000
500
0
100
300
500
700
900
Wavelength (nm)

Bond energy curve for diatomic molecule



Vibronic bands of a diatomic (e.g. C_2 Swan bands)



Swan bands: Background

Among the earliest observed molecular bands (W. Swan, 1856).

Transition is $d^3\Pi_g$<->$a^3\Pi_u$

(old notation: $A^3\Pi_g$<->$X^3\Pi_u$)

(It was originally thought that the triplet state was the ground state – in fact $^3\Pi_u$ lies above $^1\Sigma_g^+$ by about 716 cm^{-1}.)

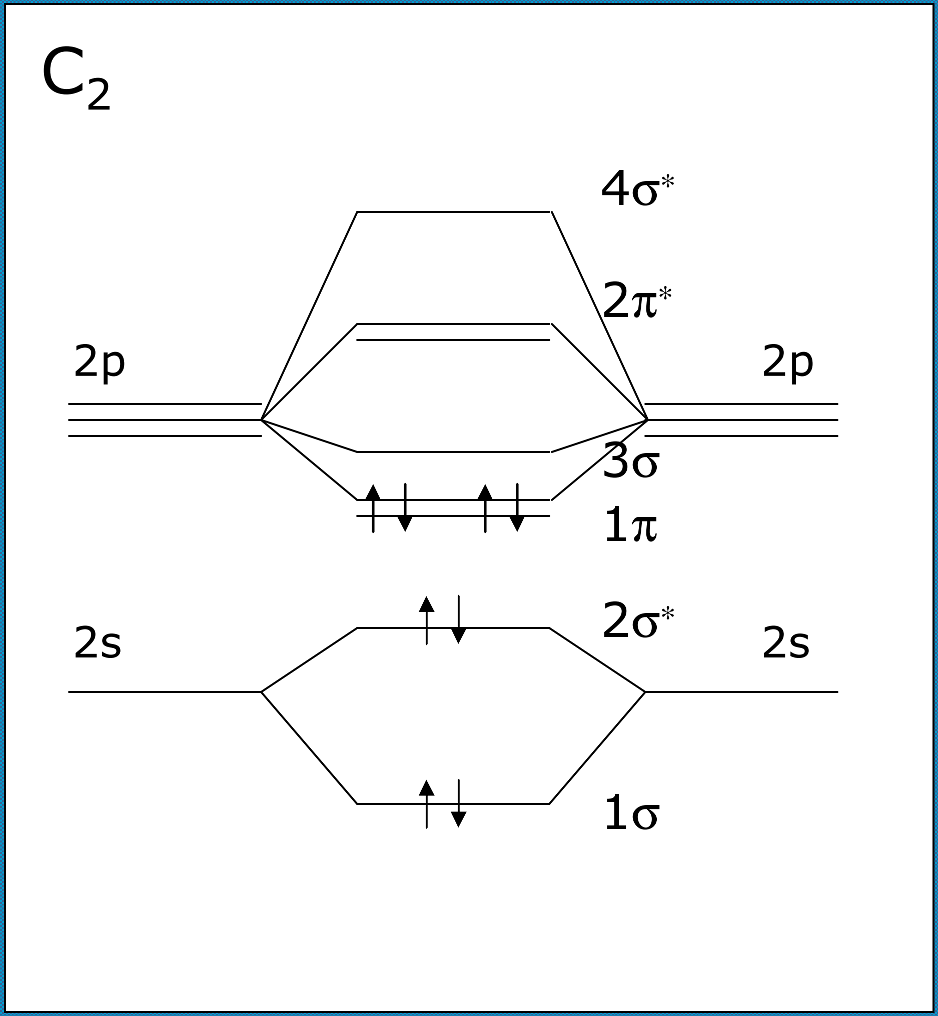
Swan bands are observed in carbon arcs, in the solar spectrum, in comets, white dwarf stars, etc.

Origin of excited C_2 in flames is still not well understood and is the subject of active research.

e.g. G. P. Smith, C. Park, J. Schneiderman, J. Luque, "C_2 Swan Band Laser-Induced Fluorescence and Chemiluminescence in Low-Pressure Hydrocarbon Flames," *Comb. Flame* **141** (2005) 66-77.

(References: G. Herzberg, Spectra of Diatomic Molecules (old notation); NIST Tables (Huber and Herzberg)(new notation))

Molecular Orbitals of C_2



Ground state

(omitting 1s core):

$1\sigma^2 2\sigma^{*2} 1\pi^4$ $X^1\Sigma_g^+$

Swan band states:

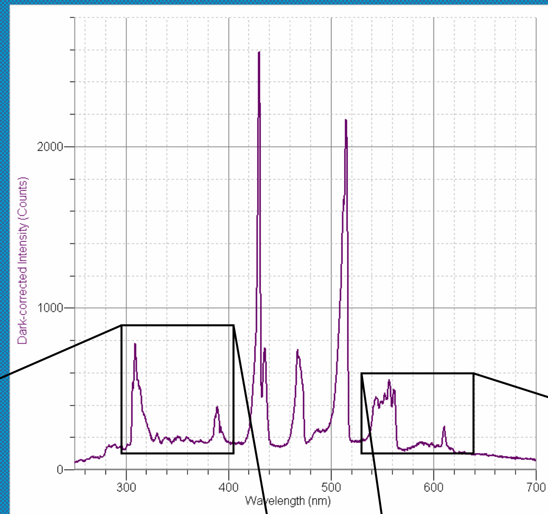
Upper:

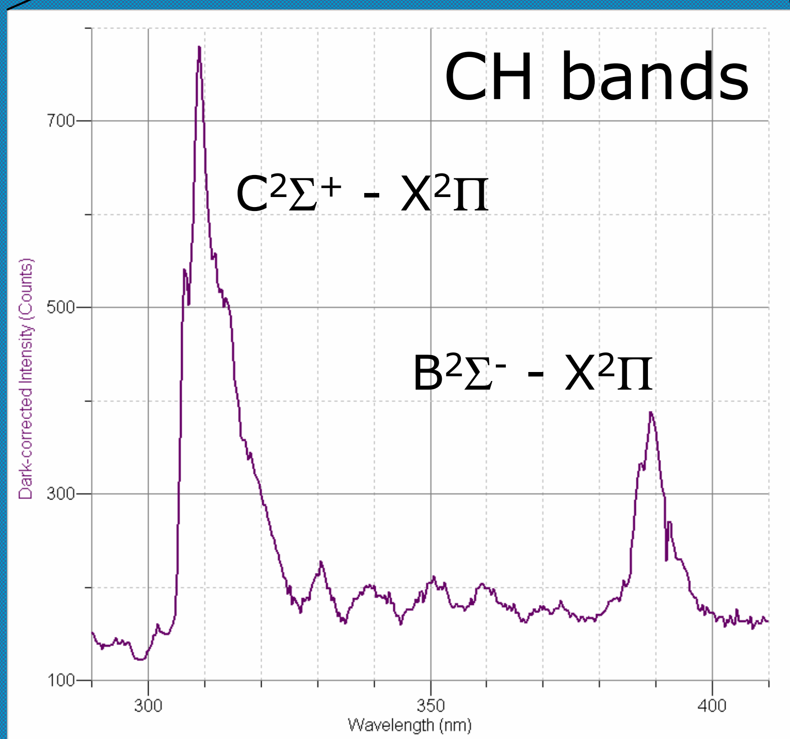
$1\sigma^2 2\sigma^{*2} 1\pi^3 2\pi^{*1}$ $d^3\Pi_g$

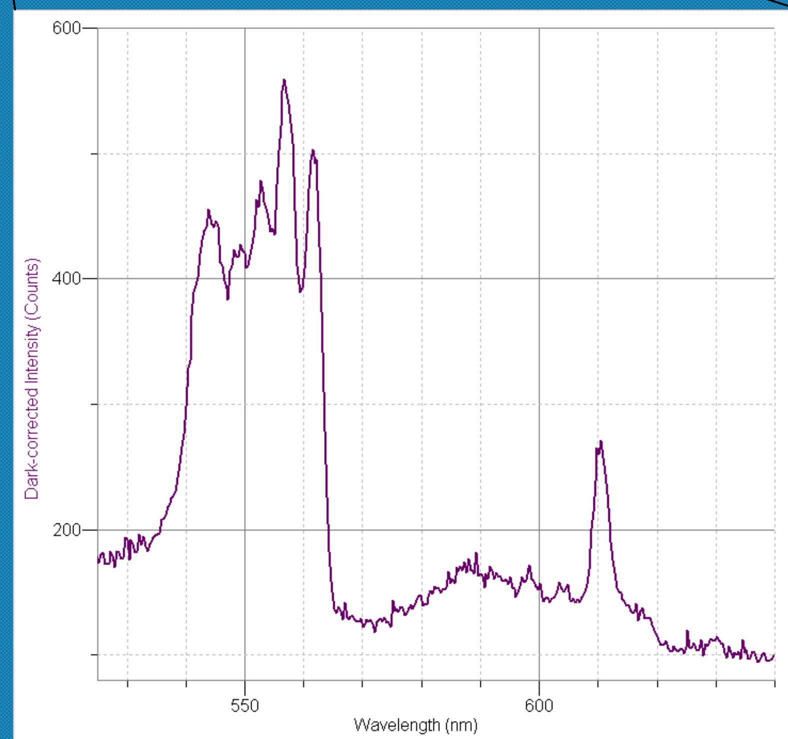
Lower:

$1\sigma^2 2\sigma^{*2} 1\pi^3 3\sigma^1$ $a^3\Pi_u$

Other details from oxidizing flame spectrum

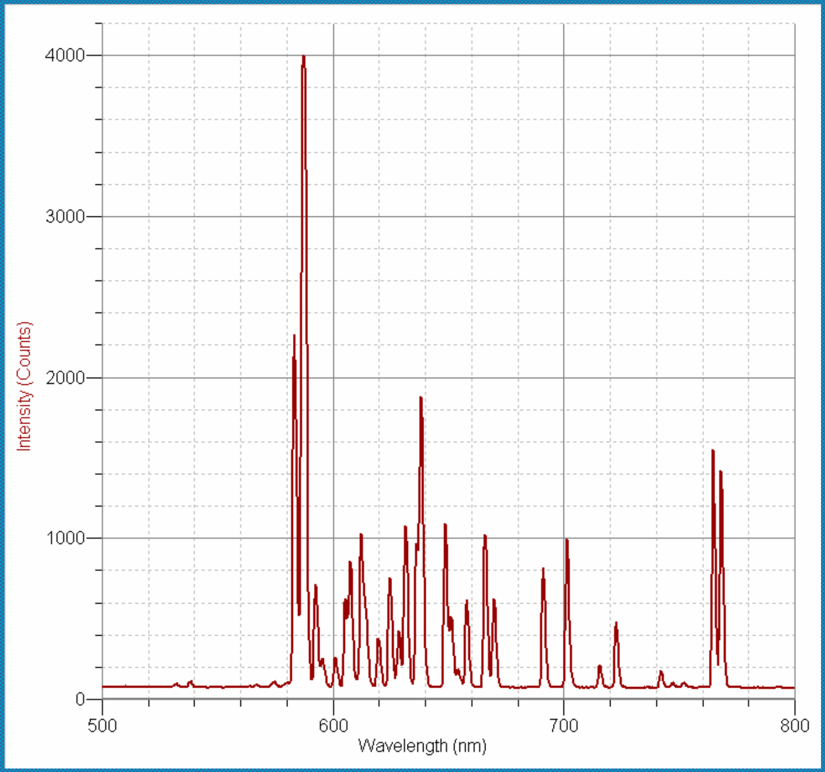




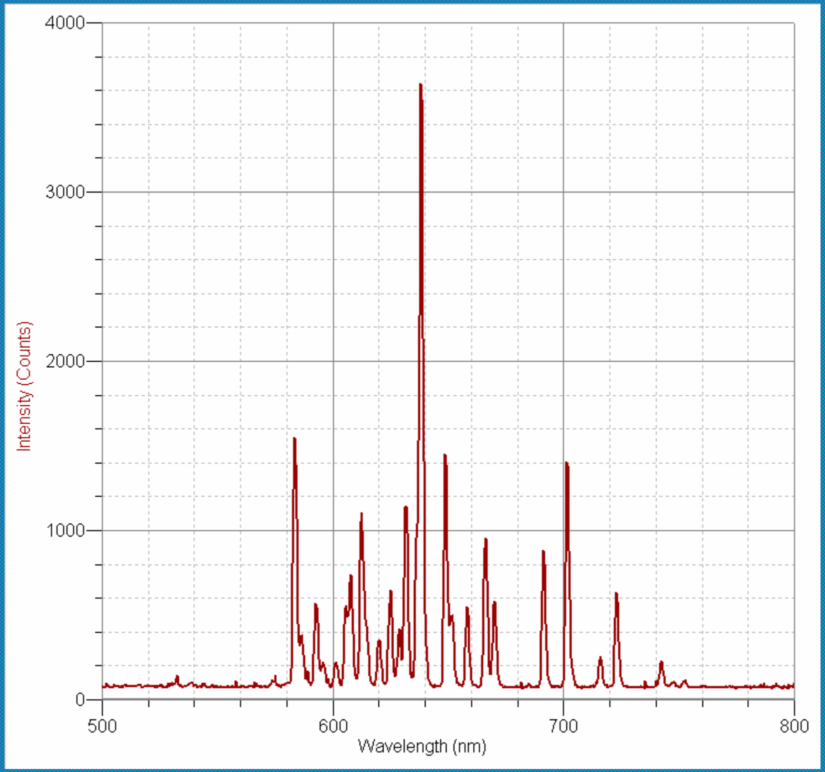


Sample lamp spectra

Na/K (selected region)



Fe (identical region)

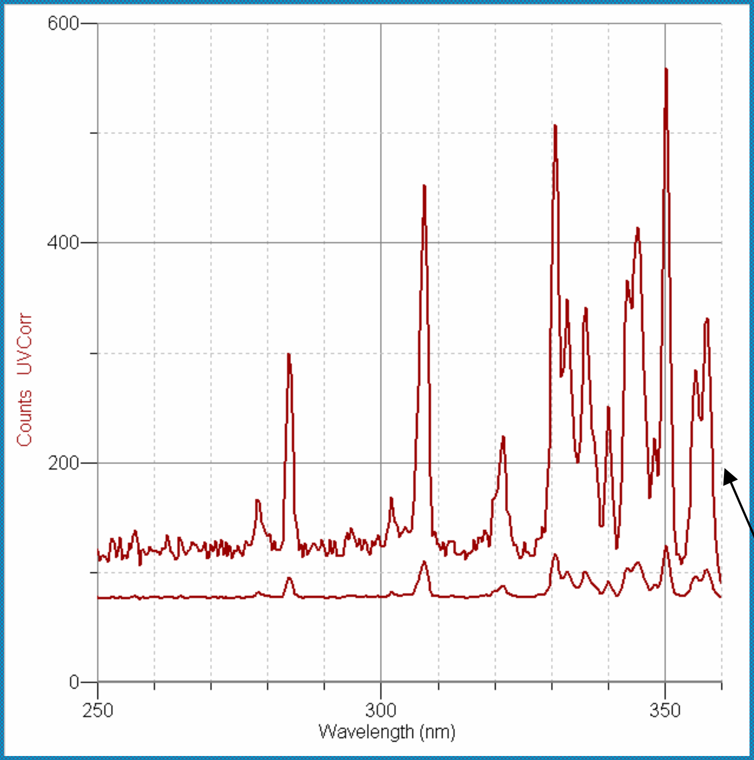


Reducing flames – corrections for instrument function and continuum

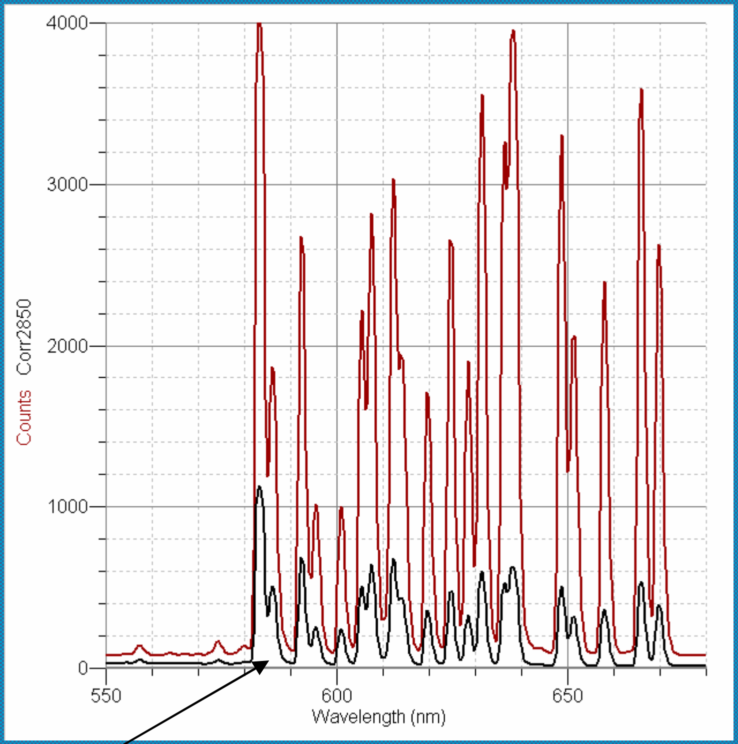
- Detected spectrum (raw counts) = Instrument Function x Spectral Function
- Calibration for Instrument Function – use of BBR source (light bulb = 2850 K)
- Instrument Function = Detected bulb spectrum/ 2850 K BBR
- BBR spectrum calibration – *number* of photons striking each pixel of CCD array

Correction for Instrument Function
(Fe lamp spectrum)

UV region

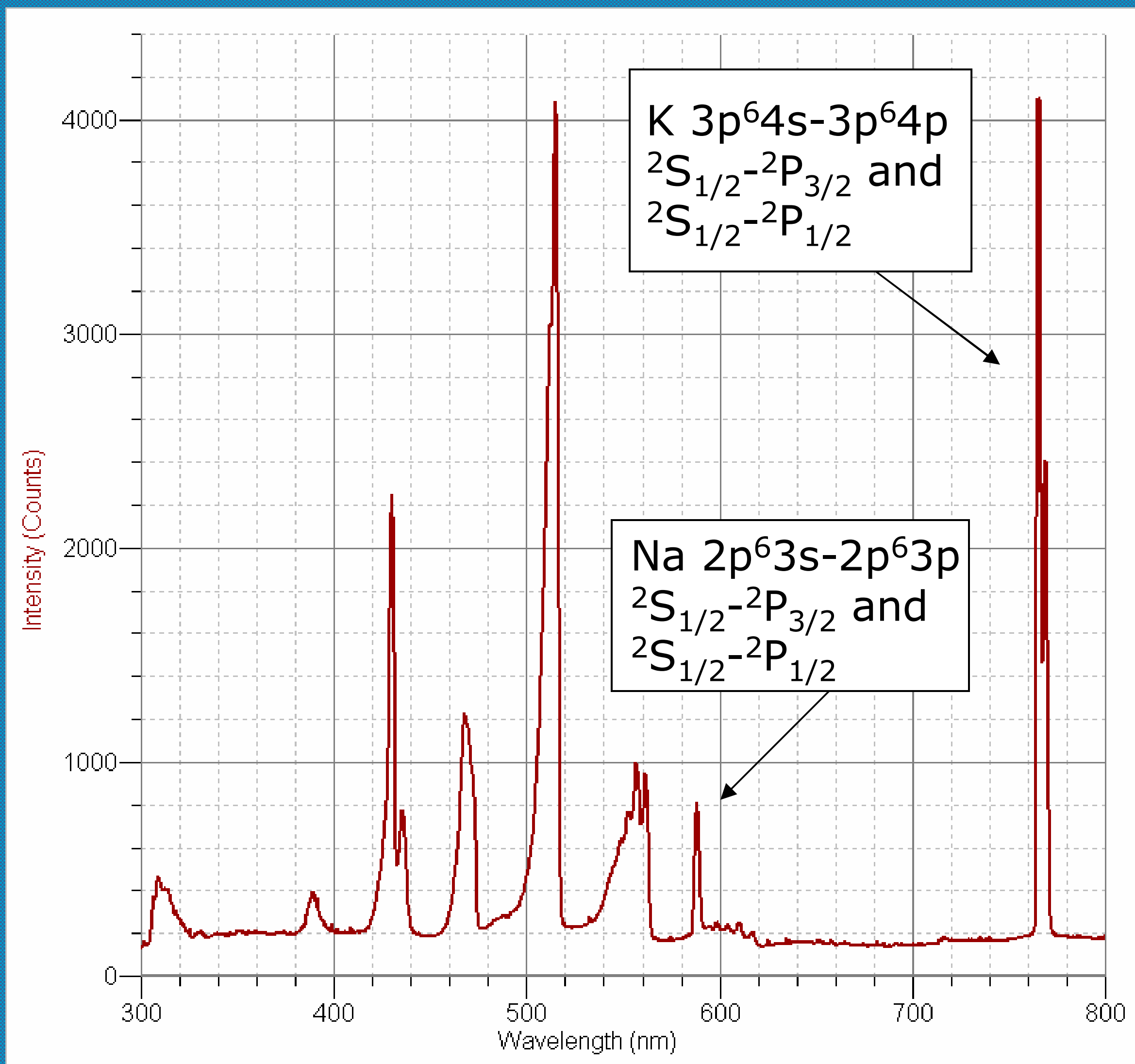


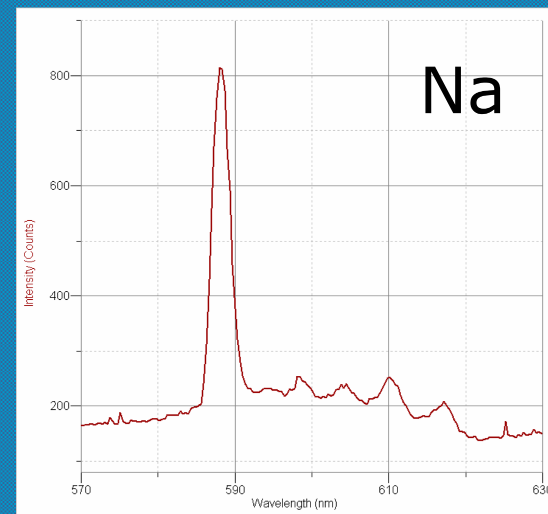
visible region

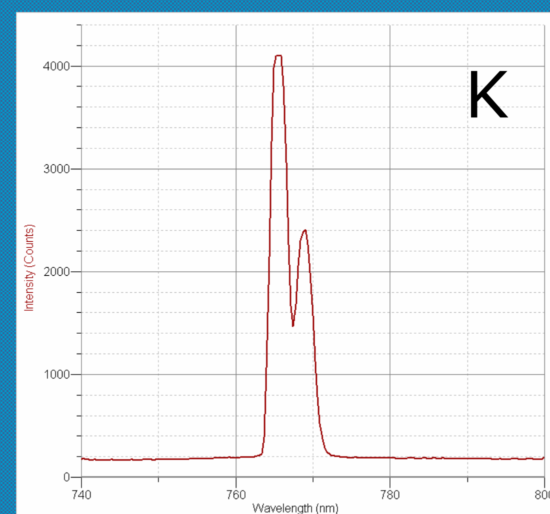


corrected

Na and K are persistent impurities



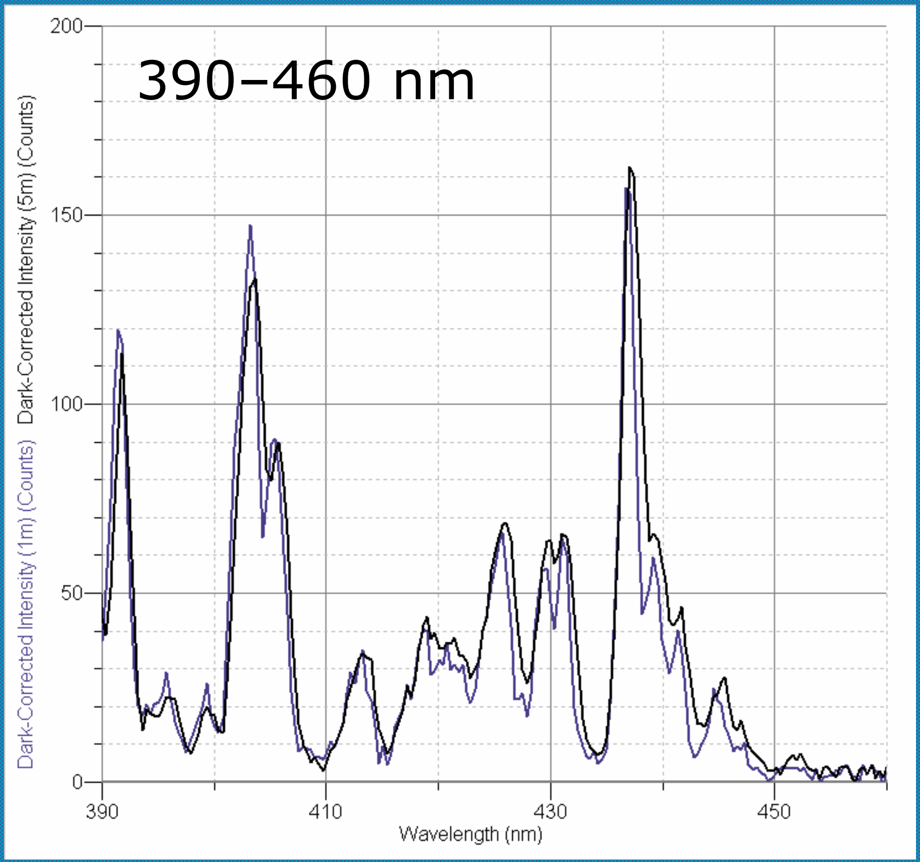


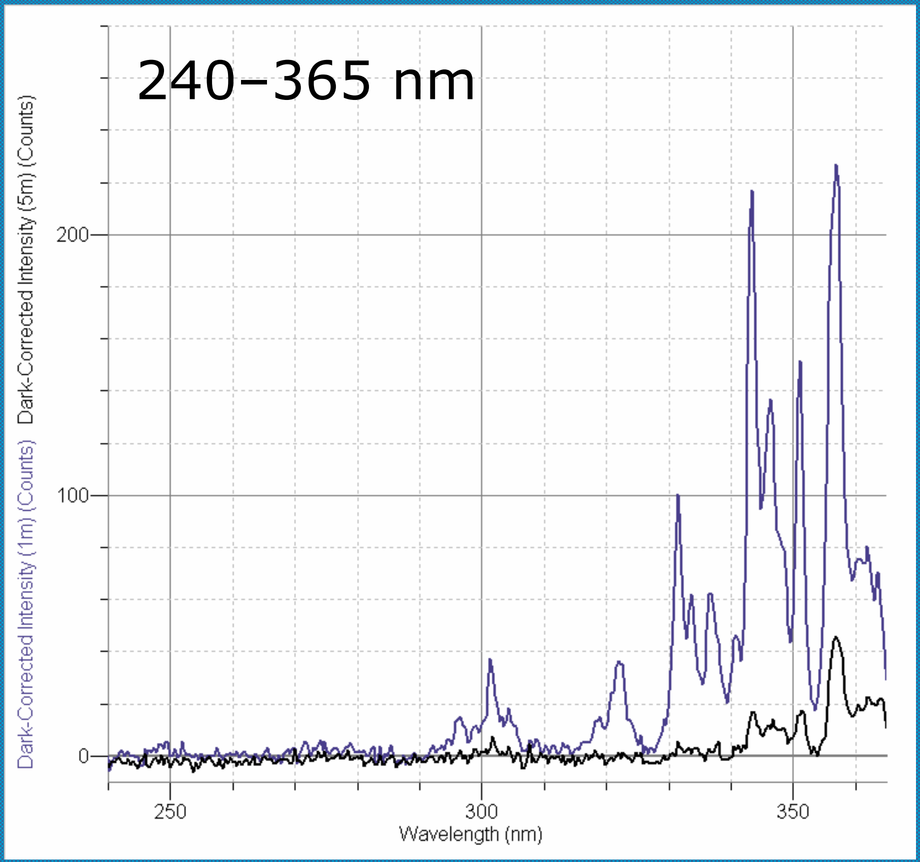


Wavelength sensitivity vs fiber type

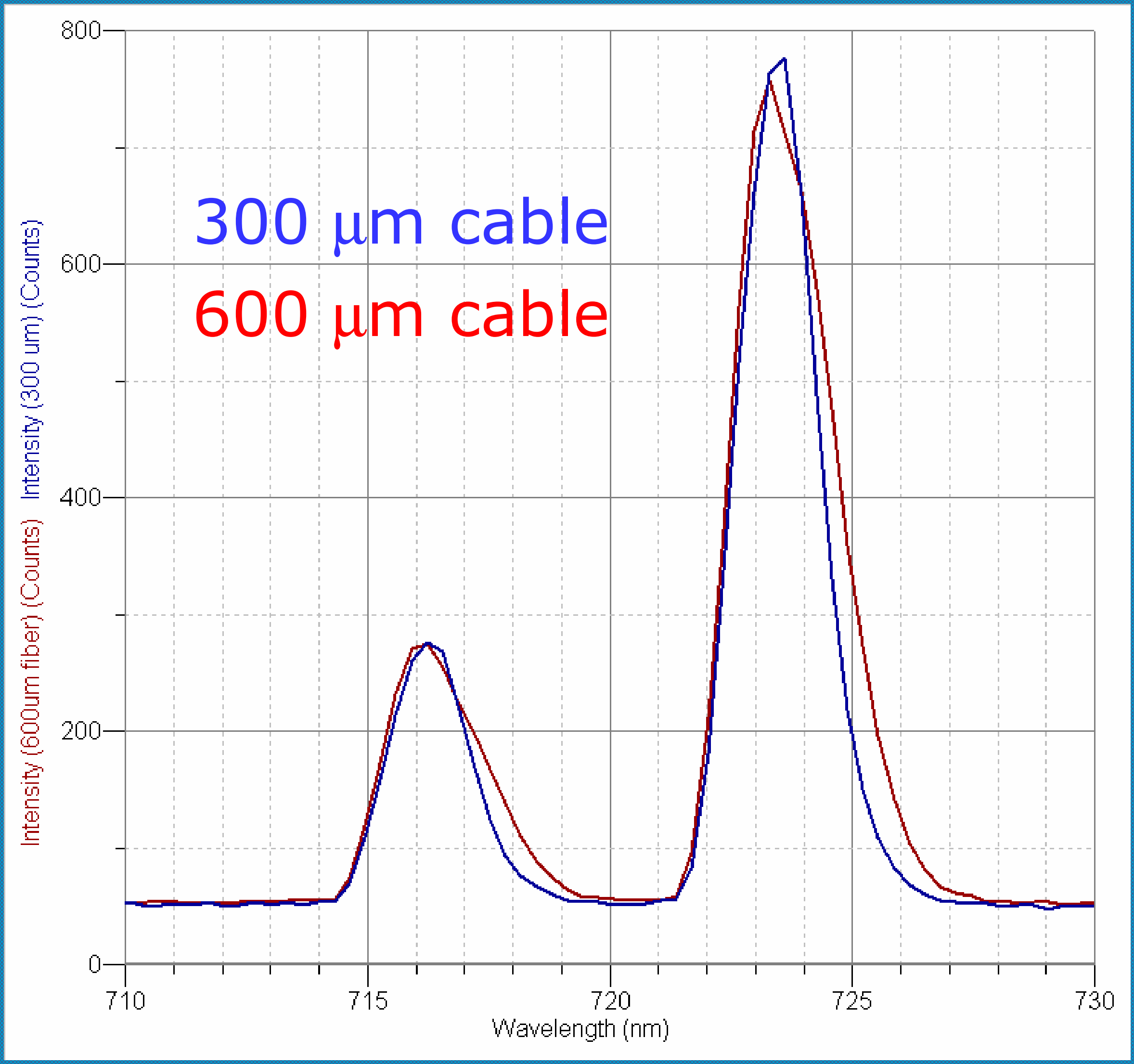
Comparative performance of solarization-resistant fiber (blue spectrum) and ordinary fiber (black spectrum).

Spectra normalized on 390 nm – 460 nm range.





Resolution vs fiber width



Section of Fe lamp spectrum.

(Cable length 1 m in each case.)

Conclusions

- Emission spectra of AA flames were studied using Ocean Optics PC2000 spectrometer
- Flame spectra are dominated by Swan bands (oxidizing flame) and continuum emission (reducing flame)
- Sample spectra - dominated by neutral atom lines - Swan bands weakened
- Persistent impurity lines from Na, K
- Instrument function correction required for absolute intensities (work in progress)
- Resolution limit presently set by entry optics
- Need to improve both resolution and wavelength calibration for more conclusive identification of transitions.