GENERAL ATOMIC SPECTROSCOPY

ENERGY LEVELS, ABSORPTION, EMISSION, ATOMIZATION

ATOMIC ABSORPTION: FLAME, FURNACE, HYDRIDE, COLD VAPOR

BOOKS

ICPs in Analytical Atomic Spectrometry Montaser, Ed., VCH, 1992.

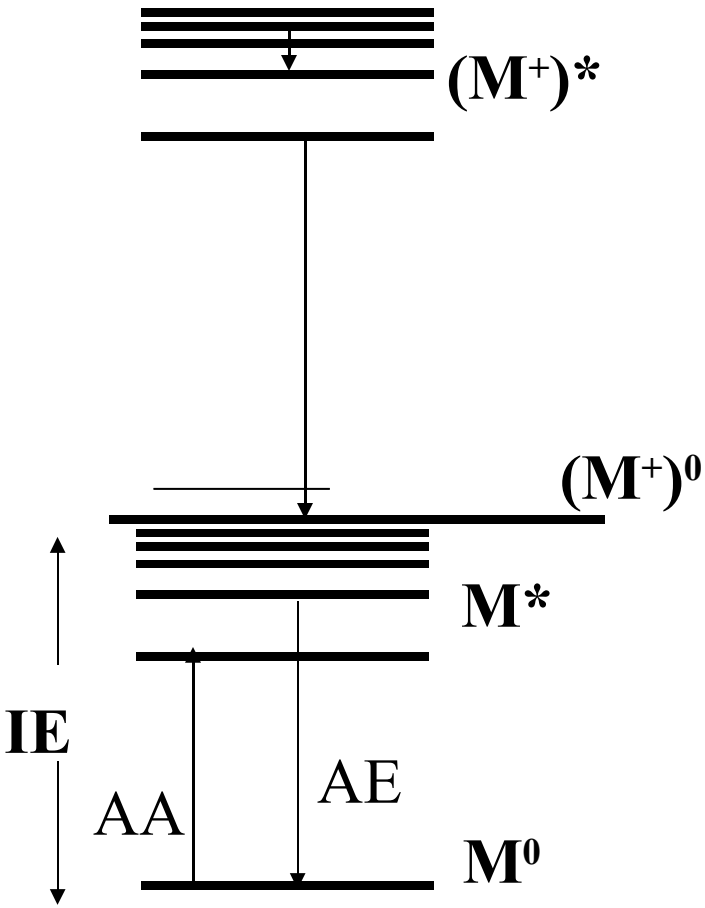
Handbook of ICP-AES, Thompson & Walsh Viridian Publishing, reprinted 2003.

Winge, Fassel et al. ICP-AES: An Atlas of Spectral Information, Elsevier, 1985.

Ingle & Crouch, Spectrochemical Analysis, Prentice Hall, 1988

Also NBS, MIT Wavelength Tables

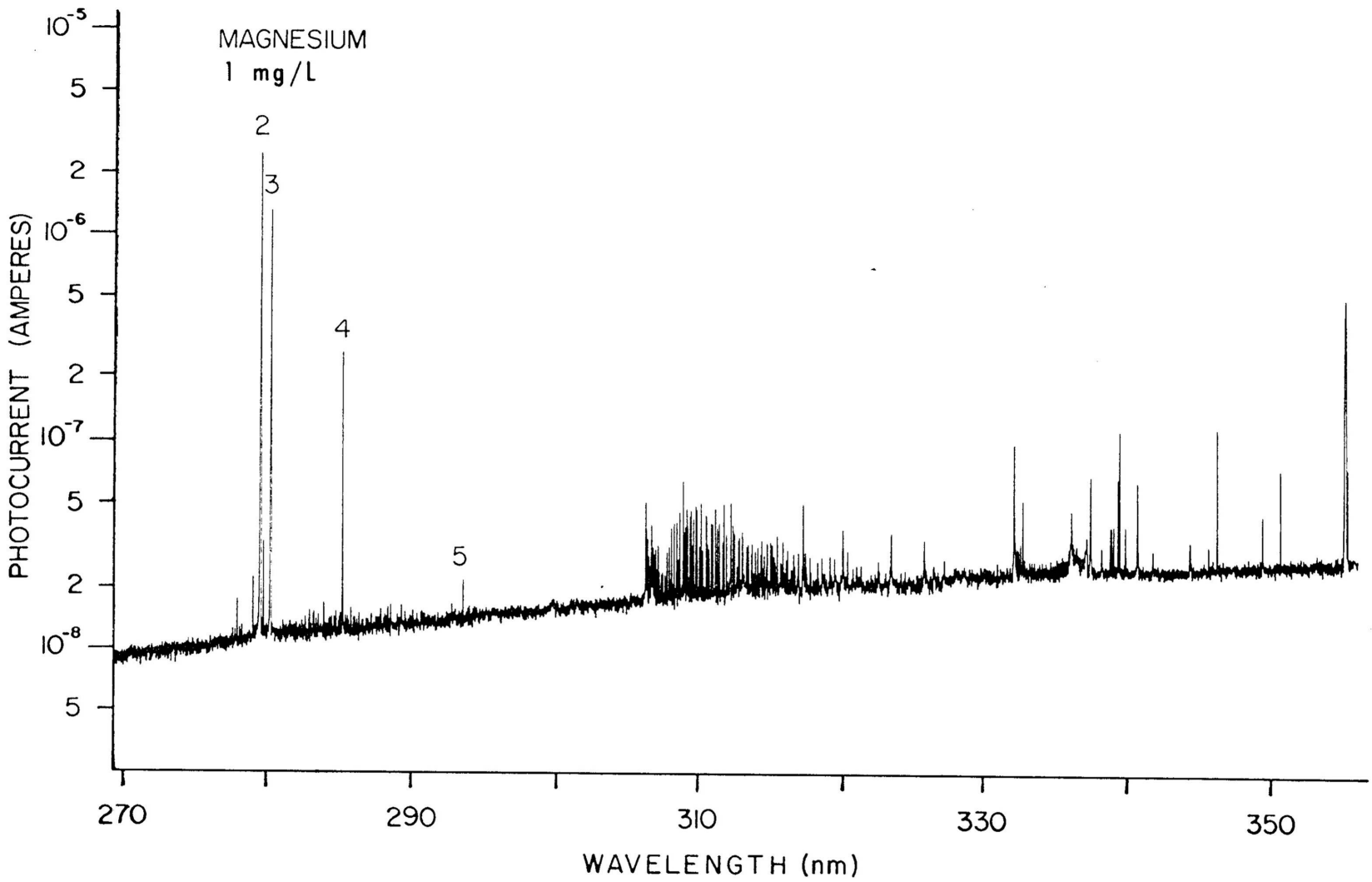
ATOMIC SPECTROSCOPY



ATOMIC LEVELS
NO VIB - ROT SUBLEVELS
SHARP LINES
<u>HIGH SELECTIVITY(+)</u>
ONLY DETERMINE ELEMENT
NOT COMPOUND (-)

PRODUCE FREE ATOMS
FROM SAMPLE ?
EXCITE EMISSION (AE)

WITH ADDITIONAL SOURCE:
-ABS. (AA) FROM LOWER STATE
(USUALLY GROUND STATE)
-FLUORESCENCE (AF)



2	Mg	II	279.553	4	Mg	I	285.213
3	Mg	II	280.270	5	Mg	II	293.654

Winge, ICP-AES, An Atlas of Spectral Lines

C. E. MOORE ATOMIC ENERGY LEVELS

Mg I

Config.	Desig.	J	Level	Interval
$3s^2$	$3s^2$ ^1S	0	0.00	
$3s(^2S)3p$	$3p$ $^3P^o$	0	*21850.368*	20.058
		1	*21870.426*	40.714
		2	*21911.140*	
$3s(^2S)3p$	$3p$ $^1P^o$	1	*35051.36*	
$3s(^2S)4s$	$4s$ ^3S	1	41197.37	
$3s(^2S)4s$	$4s$ ^1S	0	43503.0	
$3s(^2S)3d$	$3d$ ^1D	2	46403.14	
$3s(^2S)4p$	$4p$ $^3P^o$	0, 1	*47847.7*	4.1
		2	*47851.8*	
$3s(^2S)3d$	$3d$ ^3D	3	47957.035	0.017
		2	47957.018	−0.029
		1	47957.047	
$3s(^2S)4p$	$4p$ $^1P^o$	1	*49346.6*	
$3s(^2S)5s$	$5s$ ^3S	1	51872.36	
$3s(^2S)5s$	$5s$ ^1S	0	52556.37	
$3s(^2S)4d$	$4d$ ^1D	2	53134.70	

TRANSITIONS TO GROUND STATE

Triplet → singlet
Forbidden, no lines

Singlet → singlet allowed
P → S allowed
One line
35051 cm^{-1} = 285.3 nm

C. E. MOORE ATOMIC ENERGY LEVELS

Mg II

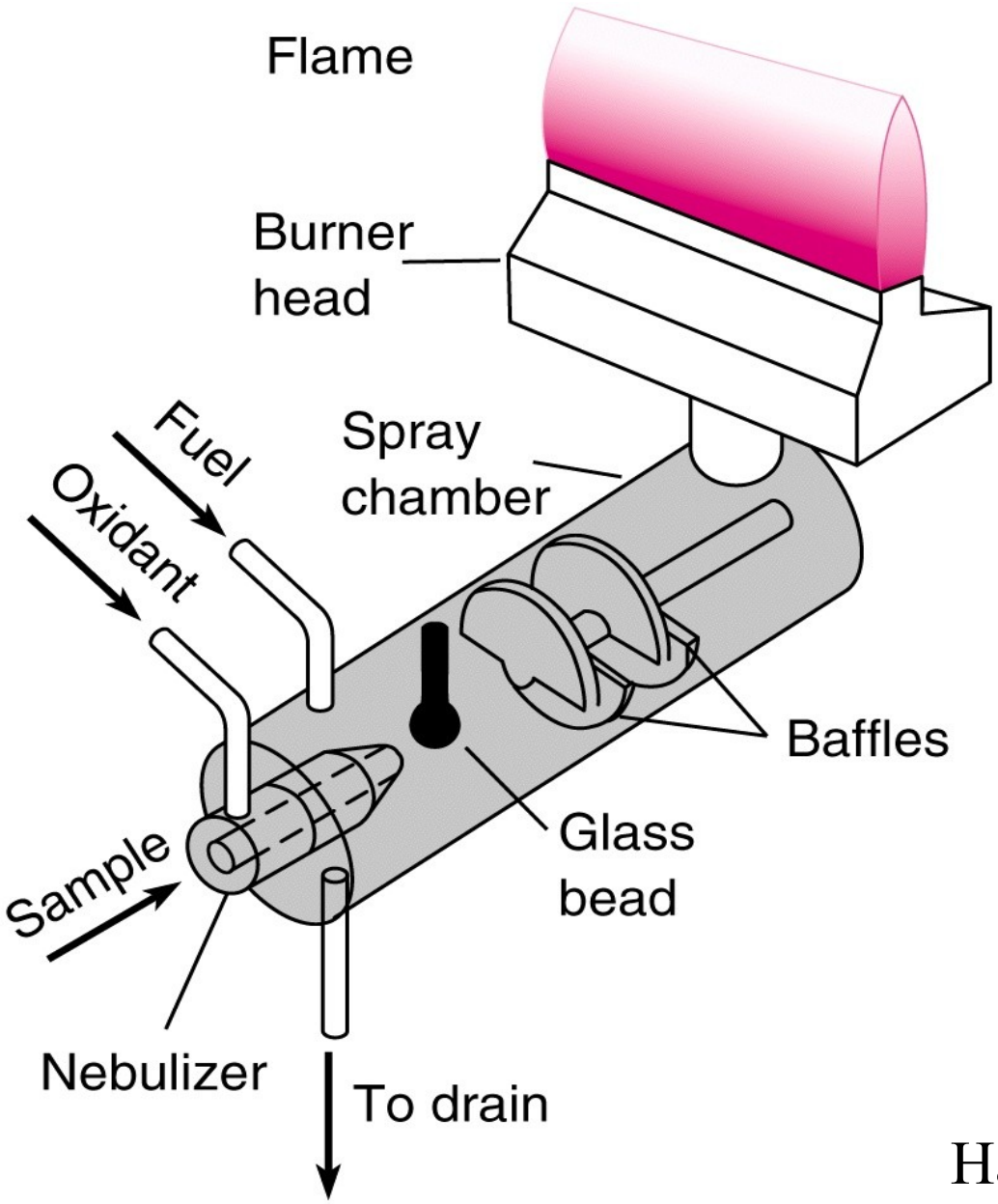
Config.	Desig.	J	Level	Interval
3s	3s ^{2}S	½	0. 00	
3p	3p ^{2}P°	½ 1½	*35669. 42* *35760. 97*	91. 55
4s	4s ^{2}S	½	69805. 19	
3d	3d ^{2}D	2½ 1½	71490. 41 71491. 32	[−1. 000]
4p	4p ^{2}P°	½ 1½	*80620. 8* *80651. 3*	30. 5
5s	5s ^{2}S	½	92786. 2	
4d	4d ^{2}D	1½ 2½	93312. 1	
4f	4f ^{2}F°	2½ 3½	*93800. 0*	
5p	5p ^{2}P°	½ 1½	*97454. 9* *97469. 0*	14. 1
6s	6s ^{2}S	½	103198. 1	
5d	5d ^{2}D	1½ 2½	103421. 1	
5f	5f ^{2}F°	2½ 3½	*103690. 2*	

TRANSITIONS TO GROUND STATE

Doublet → doublet allowed
P → S allowed
Two J values in upper state,
Two lines

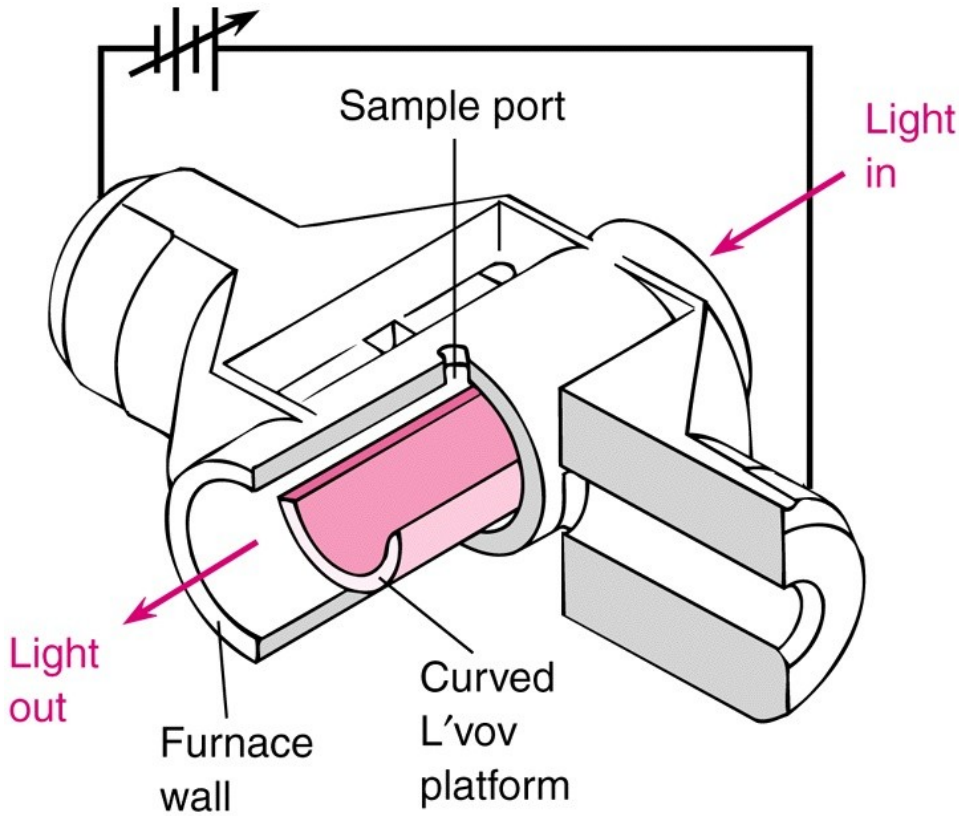
35760 & 35669 cm^{-1}
279.63 & 280.36 nm

FLAME ATOMIC ABSORPTION
PREMIX SLOT BURNER

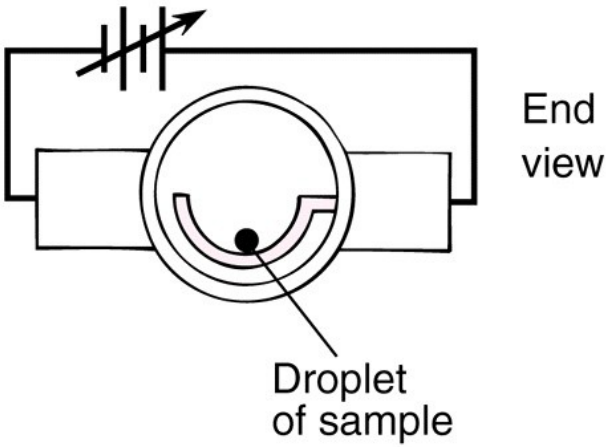


Harris

FURNACE ATOMIC ABSORPTION



(*a*)



Harris

COLD VAPOR AAS FOR Hg

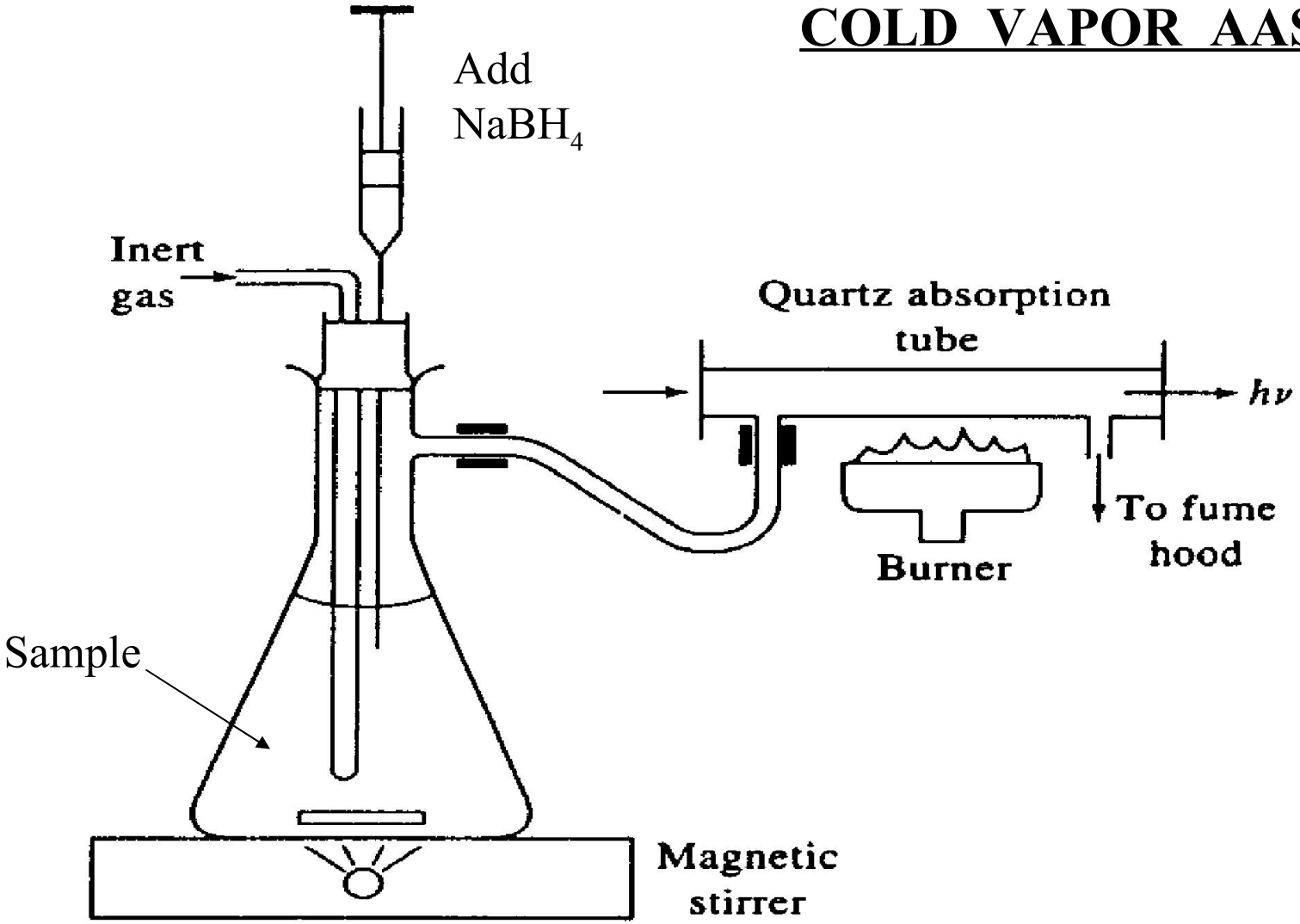


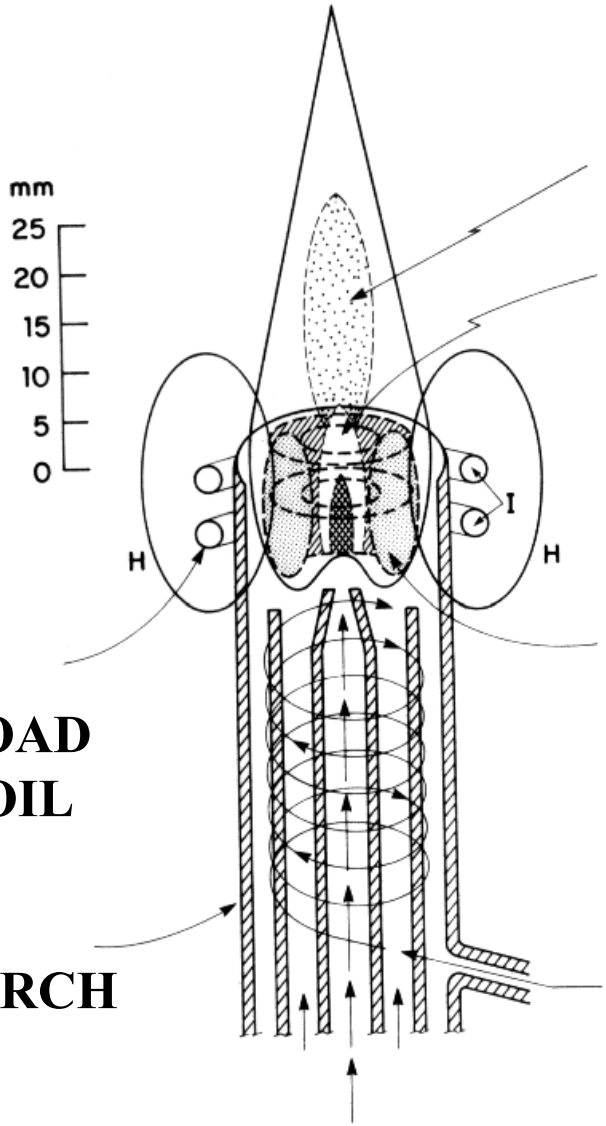
Figure 9-9 A hydride generation and atomization system for atomic absorption spectrometry.

Skoog et al., 5th ed.

INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROMETRY

ICP-AES

INDUCTIVELY COUPLED PLASMA (ICP)



NORMAL ANALYTICAL ZONE (blue)

INITIAL RAD. ZONE (red)

INDUCTION REGION

LOAD COIL

TORCH

OUTER GAS FLOW

AEROSOL GAS FLOW INTO AXIAL CHANNEL

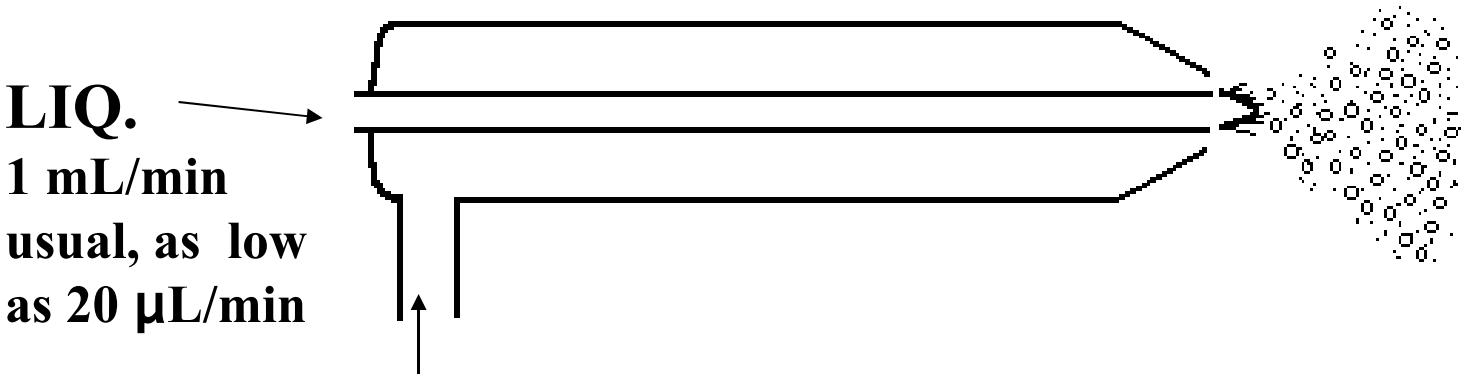
NEBULIZATION

Browner & Boorn, Anal. Chem. 1984, 56, 786A, 875A.
Sharp, J. Anal. Atomic Spectrom. 1988, 3, 613, 939.
Sneddon, Sample Intro in Atomic Spectroscopy, Elsevier, 1990.

Not req'd.

Pneumatic Nebulizer - liquid disrupted by gas flow

CONCENTRIC NEB., MEINHARD NEB.



GAS

ICP - Ar, ~ 1 L/min

Flame - oxidant, ~ 5 L/min

air, O_2, N_2O

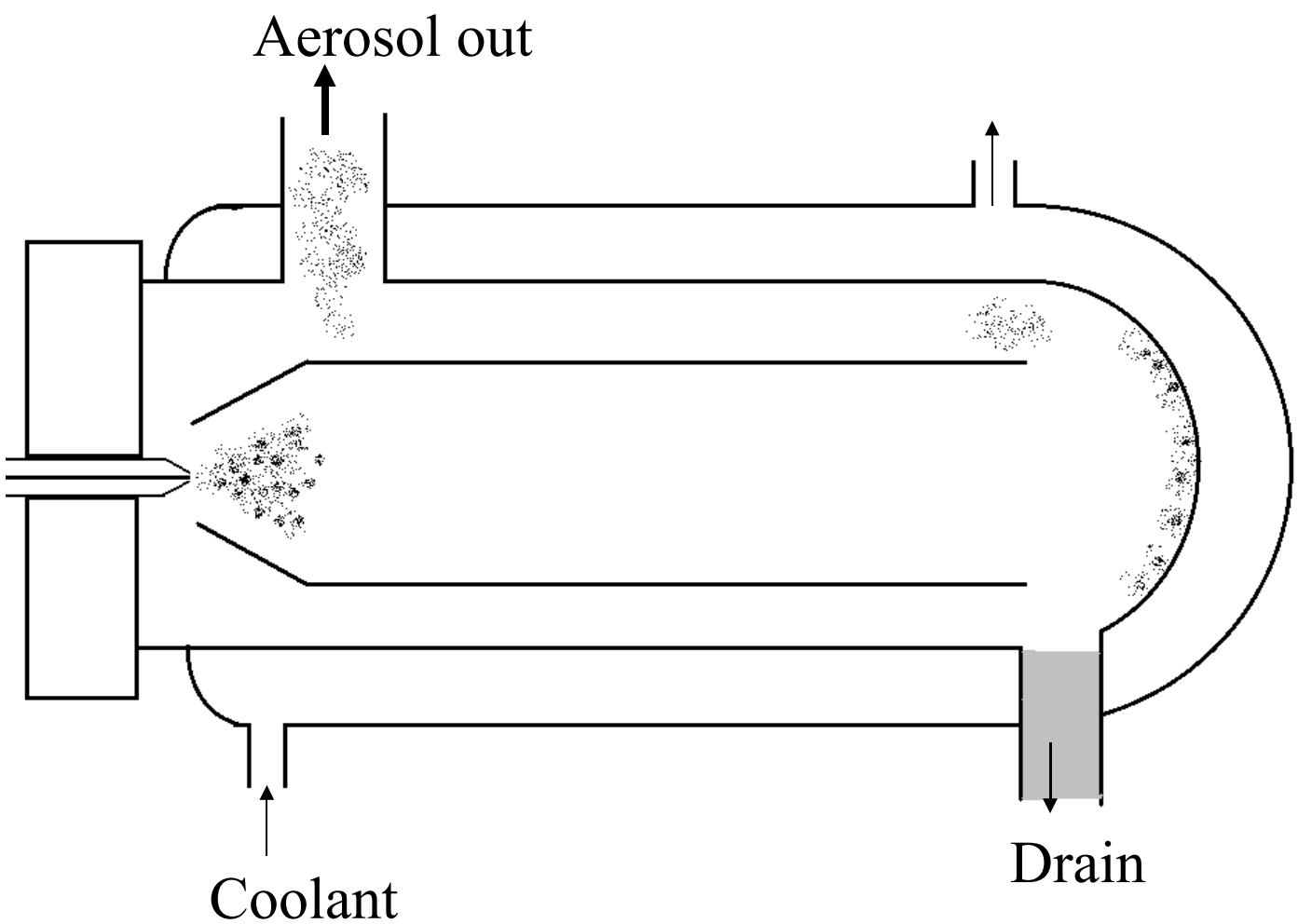
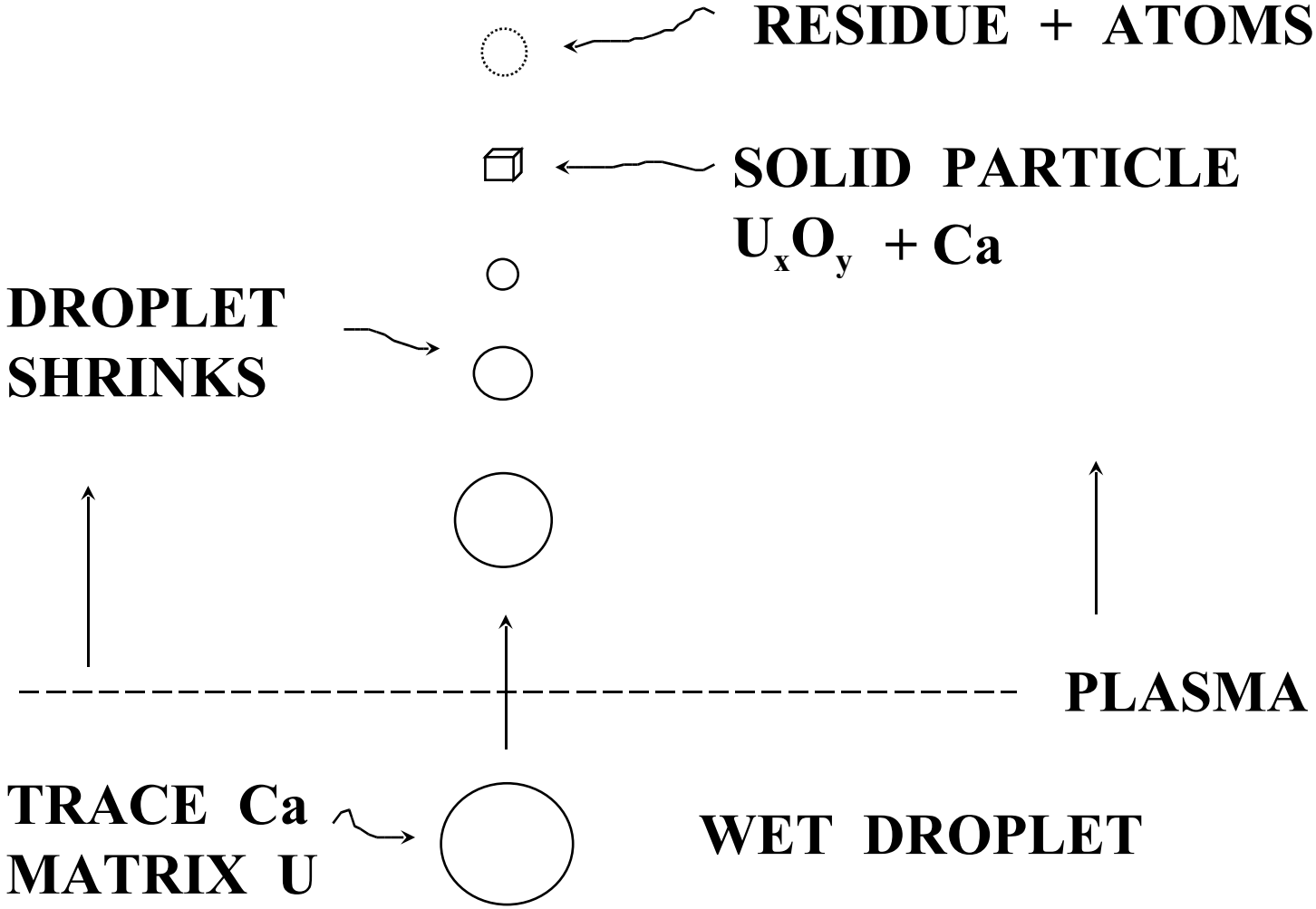


Fig. 21. Cooled spray chambers for solvent removal. a) cooled double pass Scott chamber b) Cyclone chamber, side and top views. In both chambers, most of the large droplets are deposited at the bends, while fine droplets pass out to the plasma.



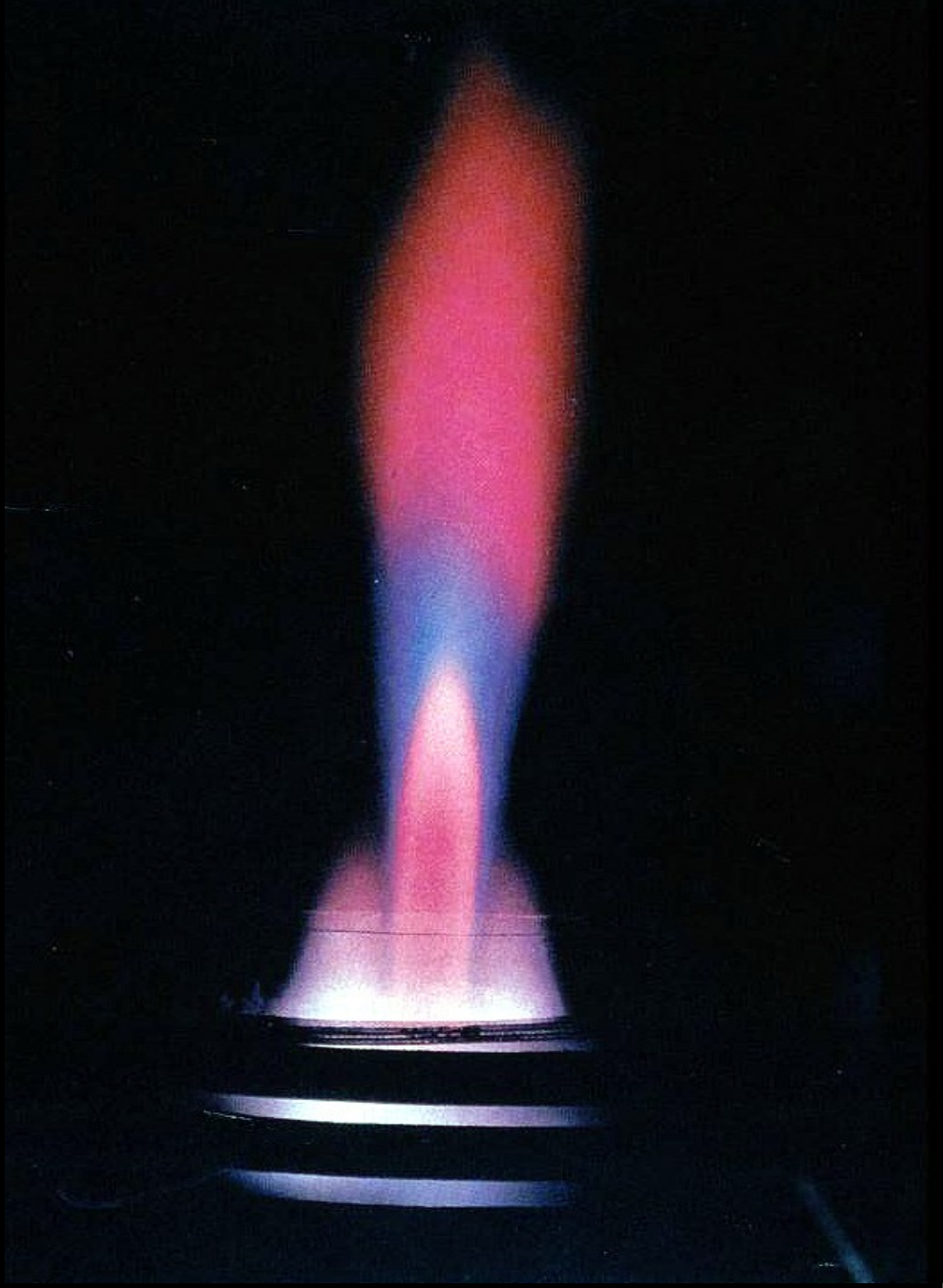
* SOLUTIONS : 1) ADJUST PLASMA CONDITIONS TO ATOMIZE MATRIX

2) SEPARATE Ca FROM U !

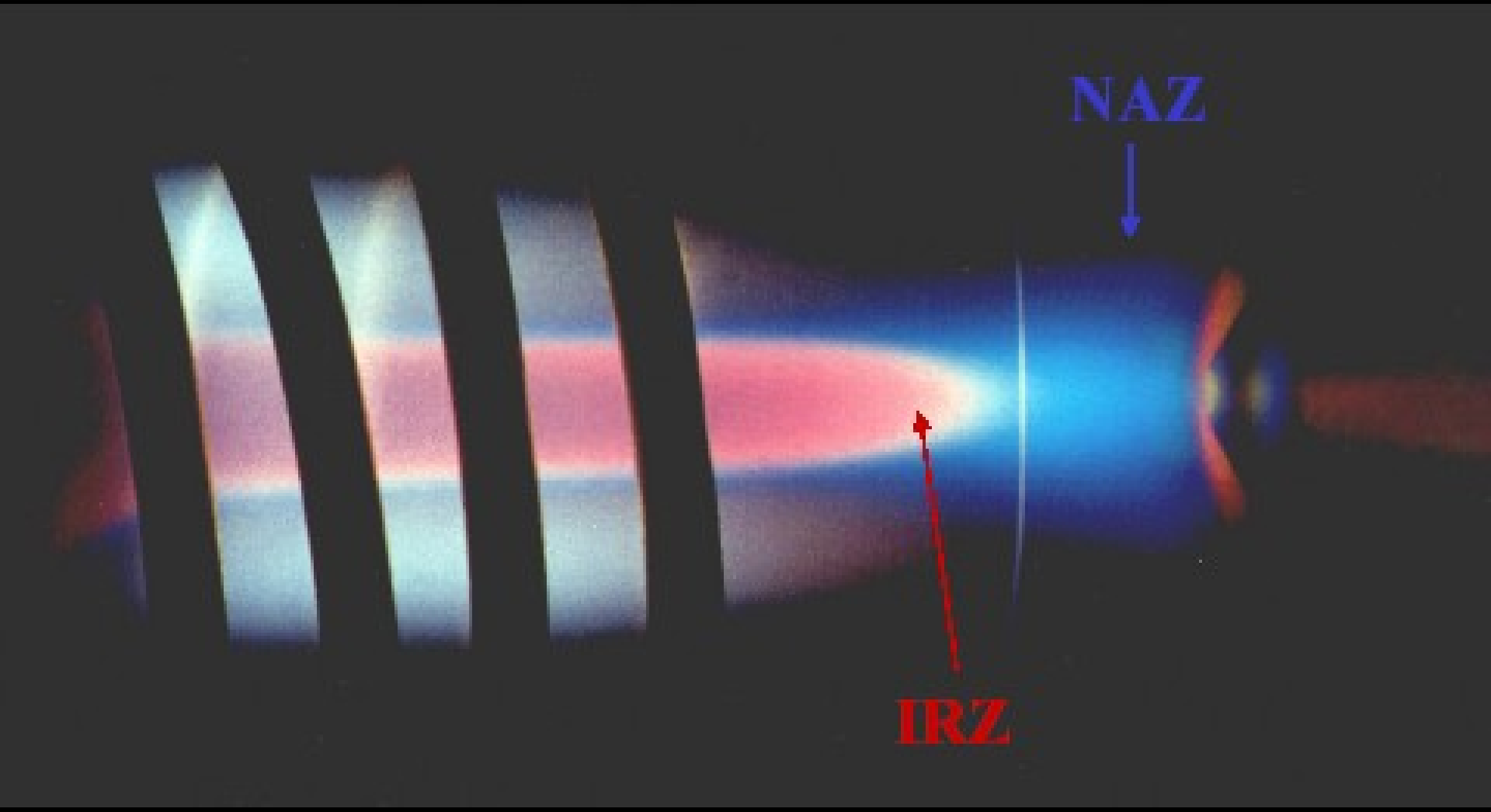
SELECT OBSERVATION POSITION?

SPECTROMETER

LENS

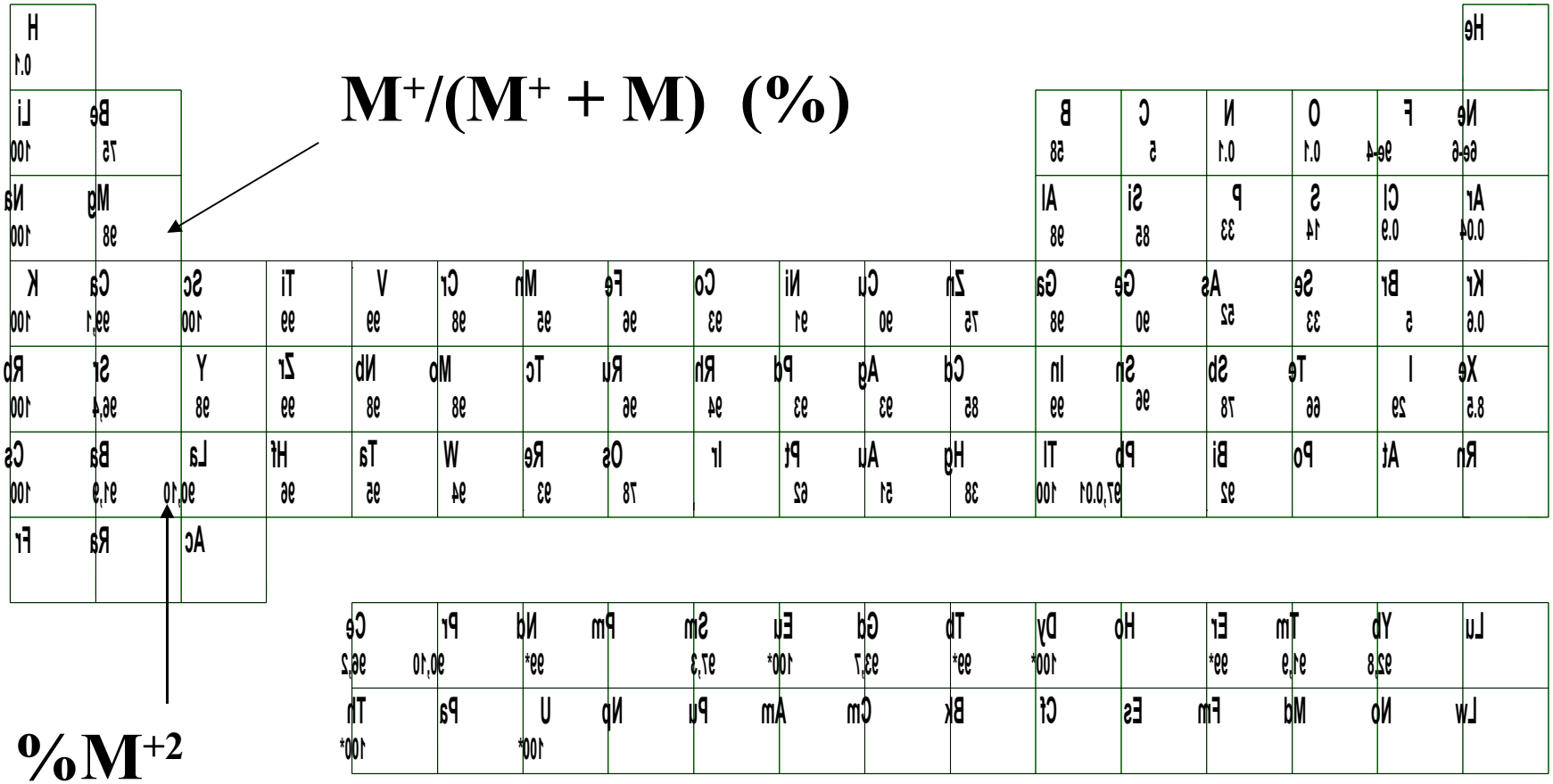


YO, Y(I), Y(II) EMISSION ZONES COURTESY VARIAN



IONIZATION IN ICP

$M^+/(M^+ + M)$ (%)

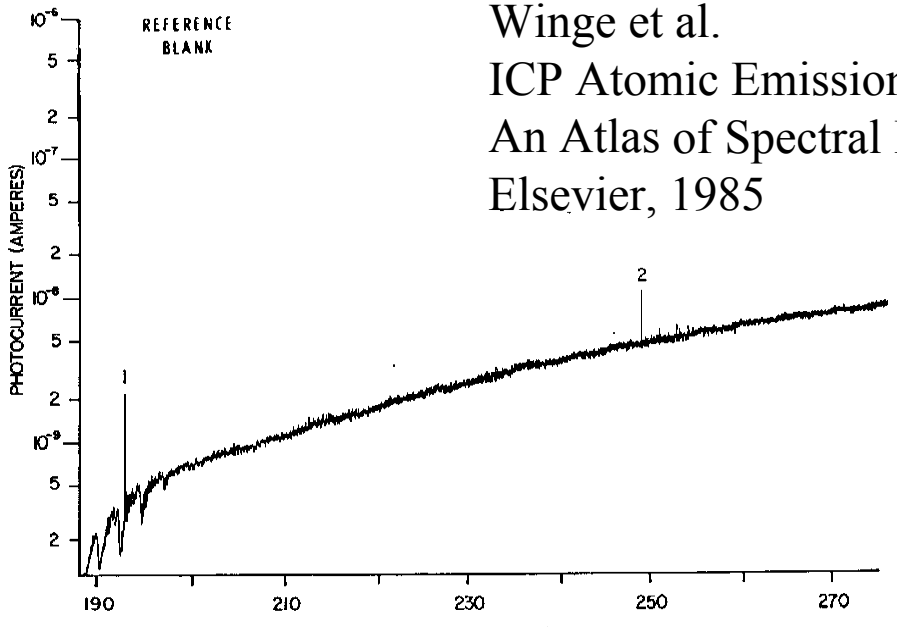


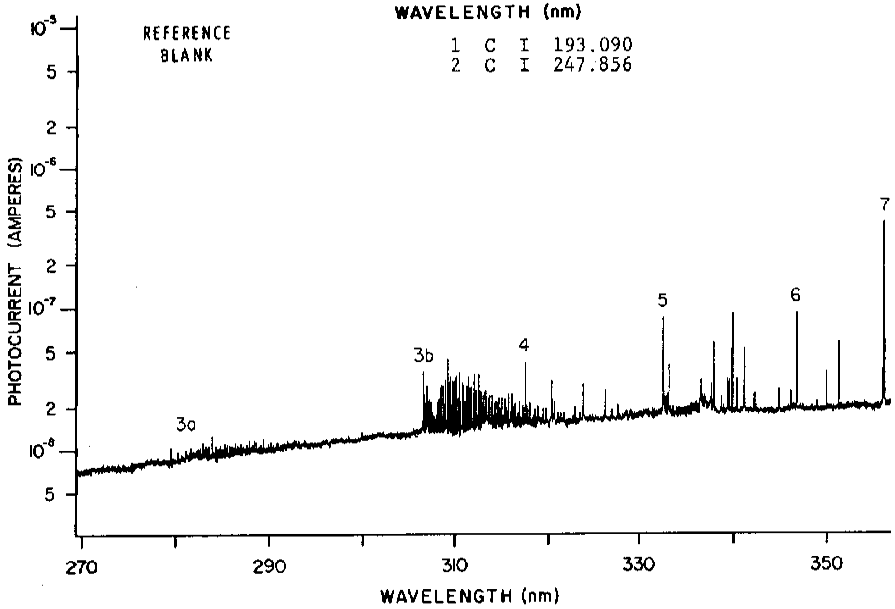
$\%M^{+2}$

T = 7500 K n_e = 1 x 10^{15} cm^{-3}

*These elements also make M^{+2}

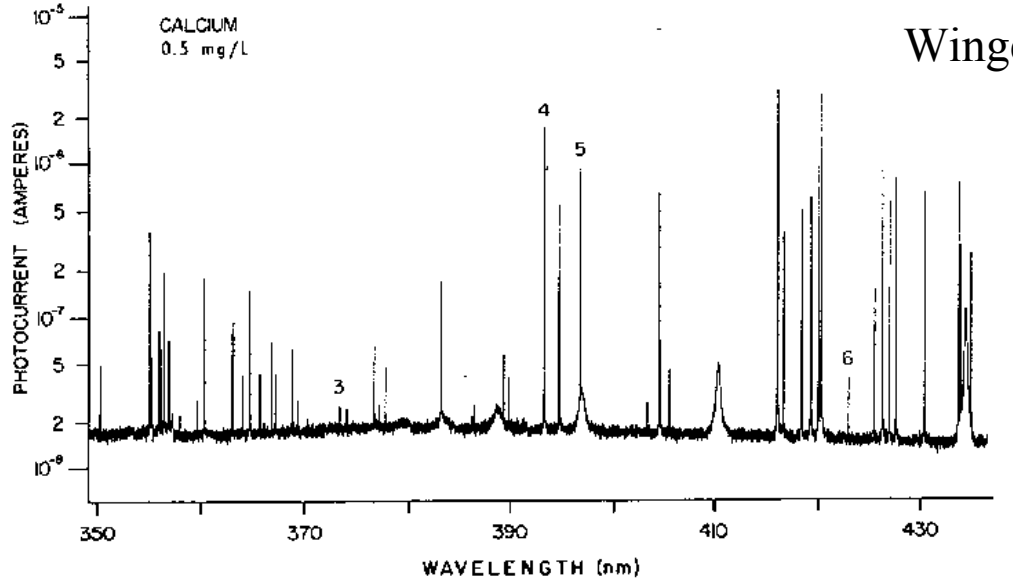
Winge et al.
ICP Atomic Emission Spectroscopy
An Atlas of Spectral Info
Elsevier, 1985



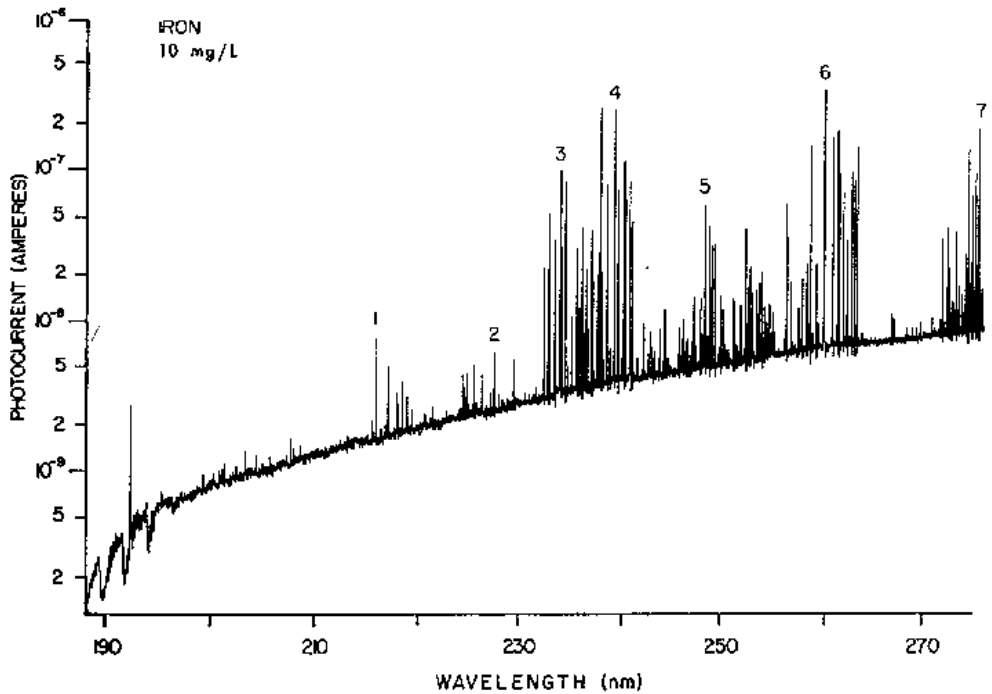


3a	OH	(bh)	281.13	5	Ar	I	331.935
3b	OH	(bh)	306.36	6	Ar	I	346.108
4	Ar	I	317.296	7	Ar	I	355.431

Winge

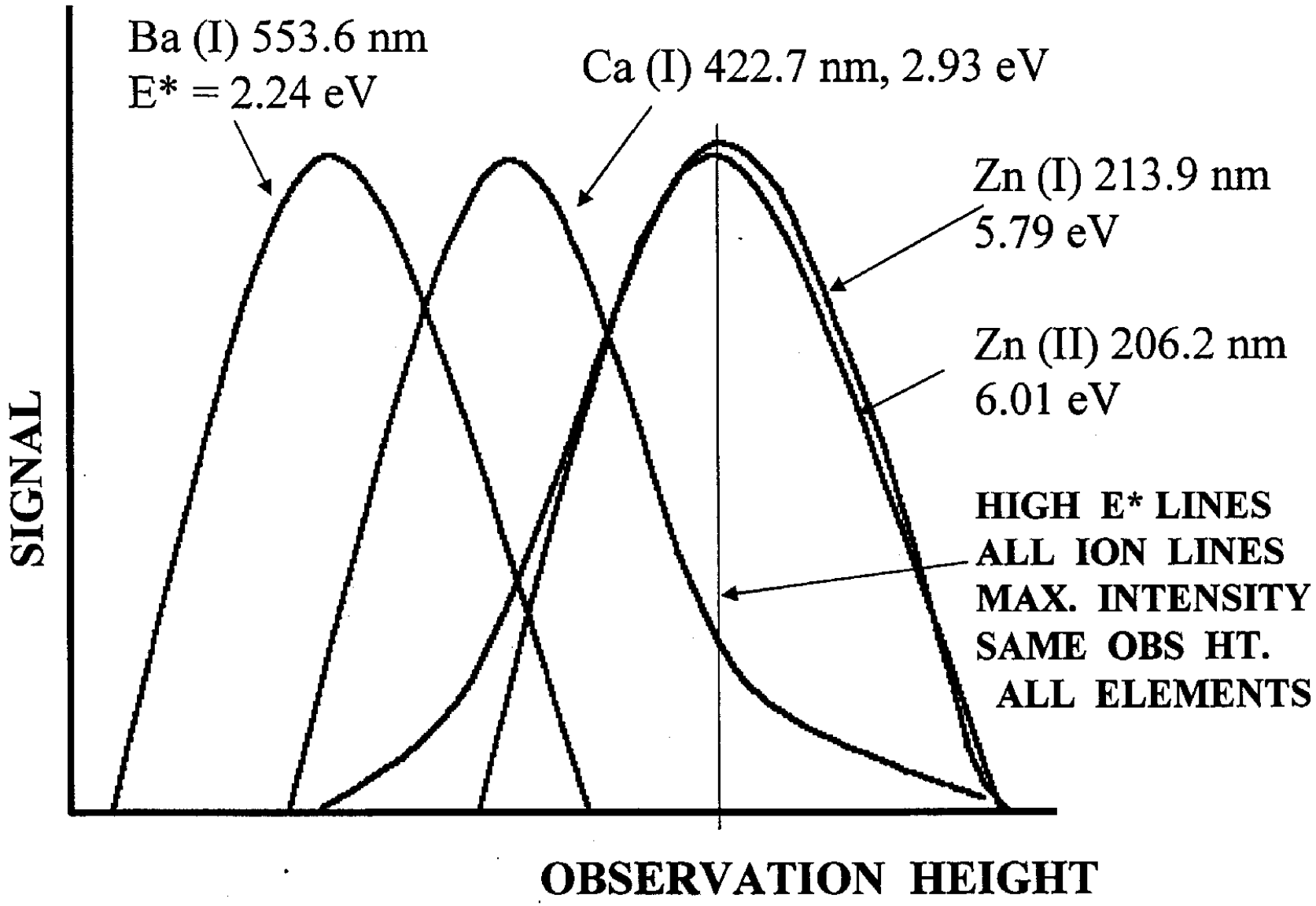


3 Ca II 373.690 5 Ca II 396.847
4 Ca II 393.366 6 Ca I 422.673



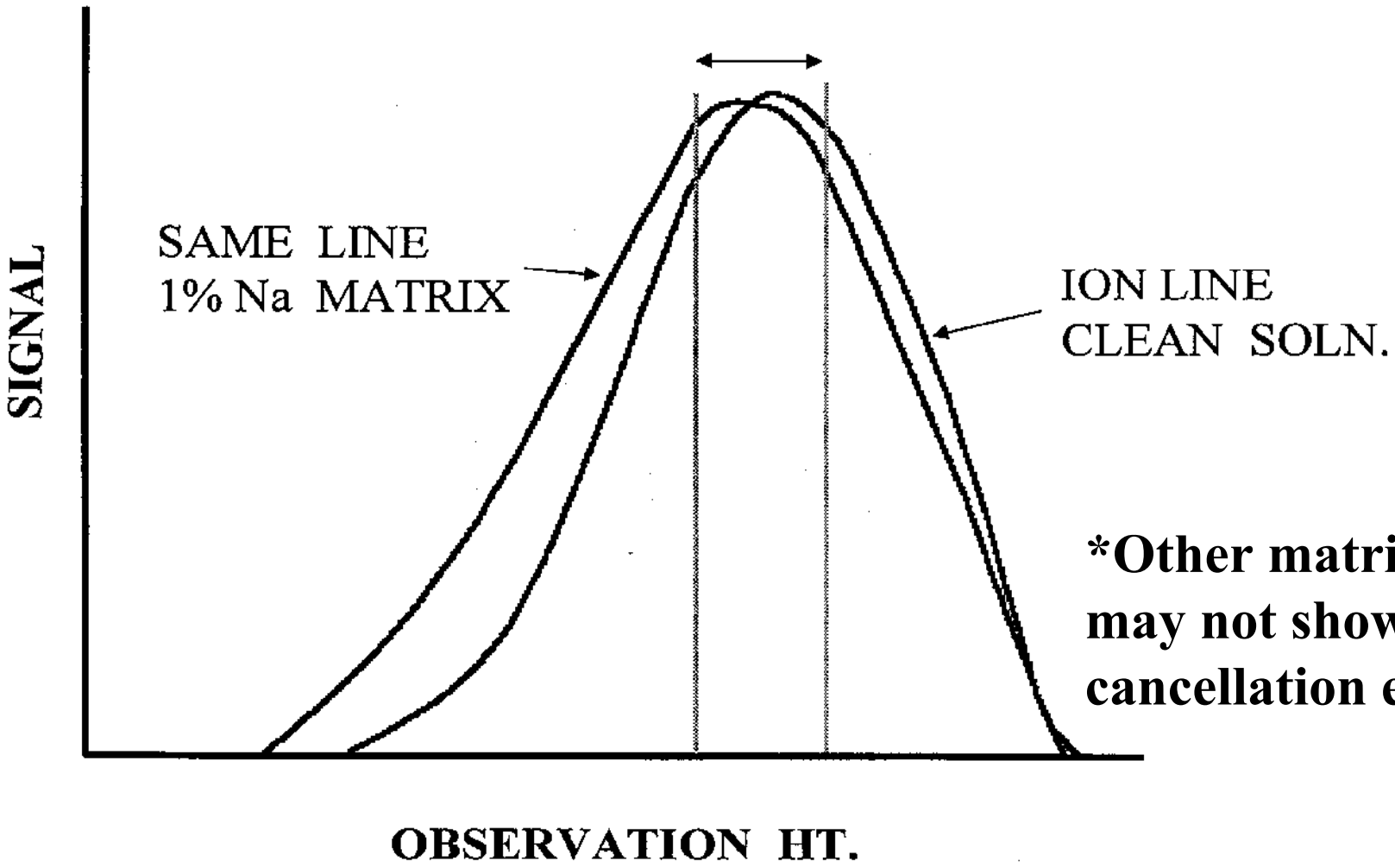
1 Fe I 216.677 5 Fe I 248.327
2 Fe II 227.992 6 Fe II 259.940
3 Fe II 234.349 7 Fe II 274.932
4 Fe II 239.562

VERTICAL EMISSION PROFILES, SELECT OBS. POSITION



MATRIX EFFECTS

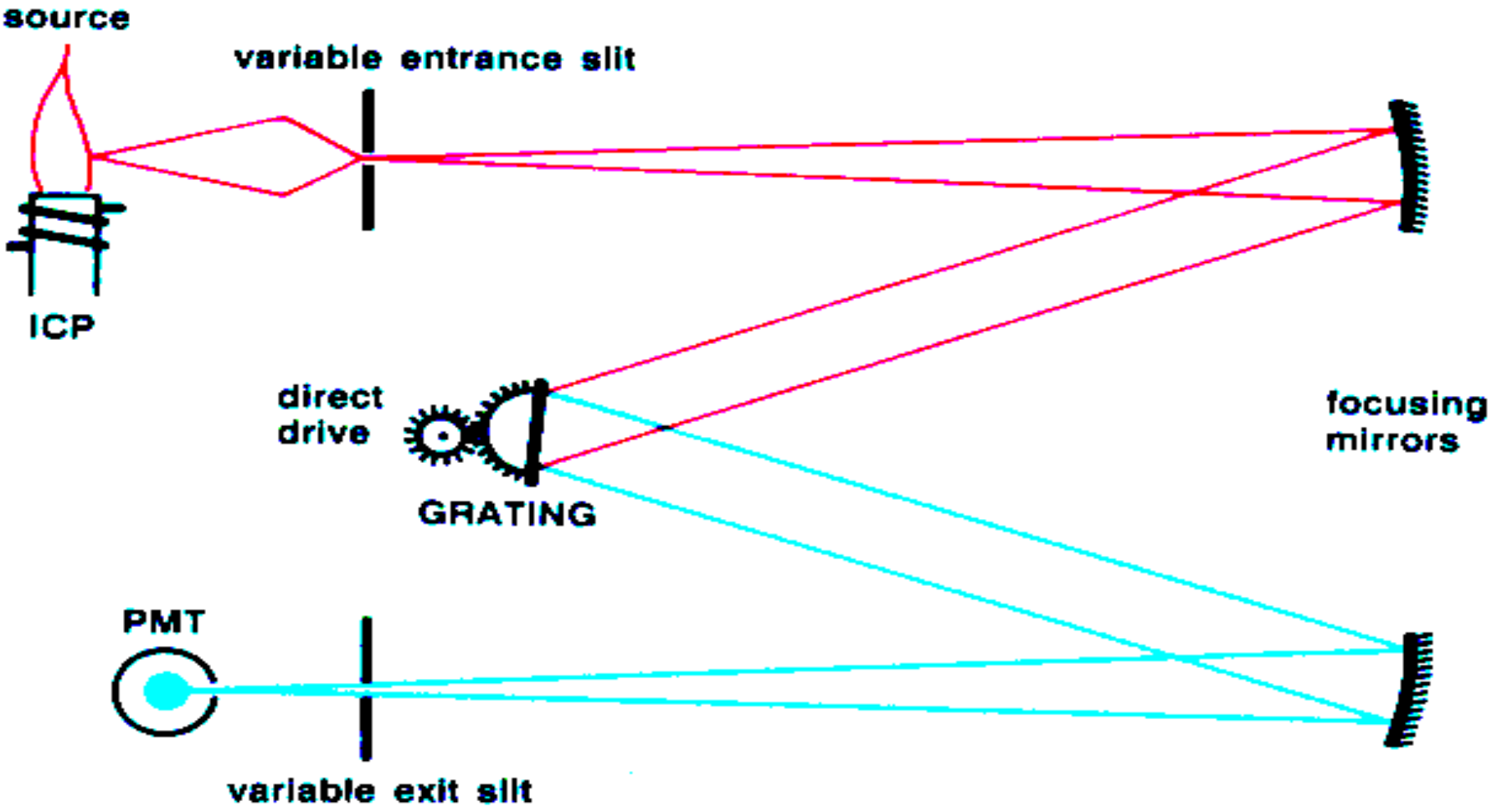
INTEGRATE EMISSION
MATRIX EFFECT CANCELS



***Other matrices may not show same cancellation effect!**

Sequential ICP

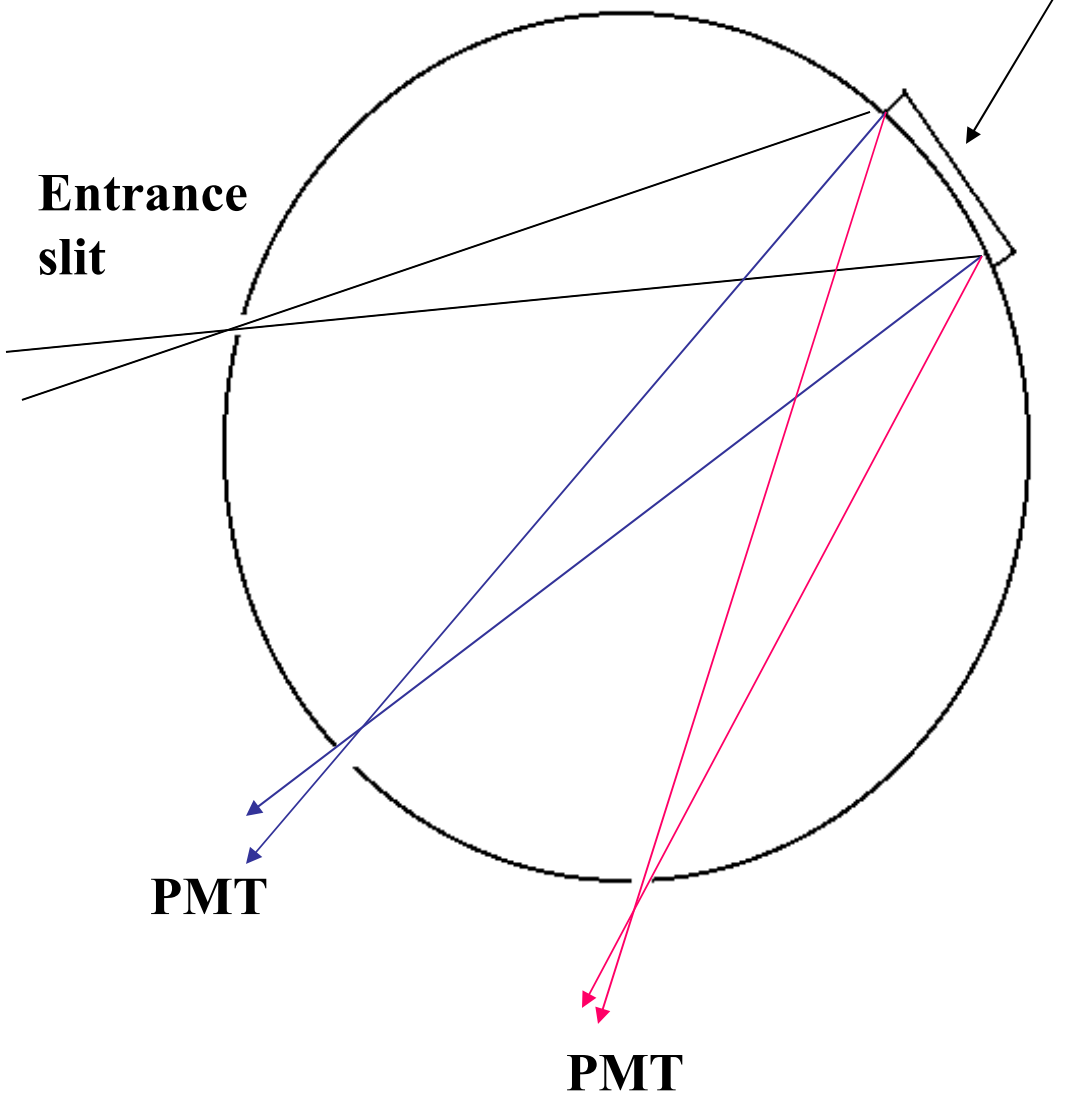
Monochromator



TYPES OF GRATING SPECTROMETER

ROWLAND CIRCLE MOUNT

PASCHEN - RUNGE MOUNT, DIRECT READER

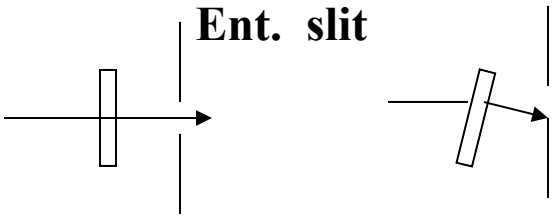


CONCAVE GRATING FOCUSES COMPONENTS ONTO CIRCLE

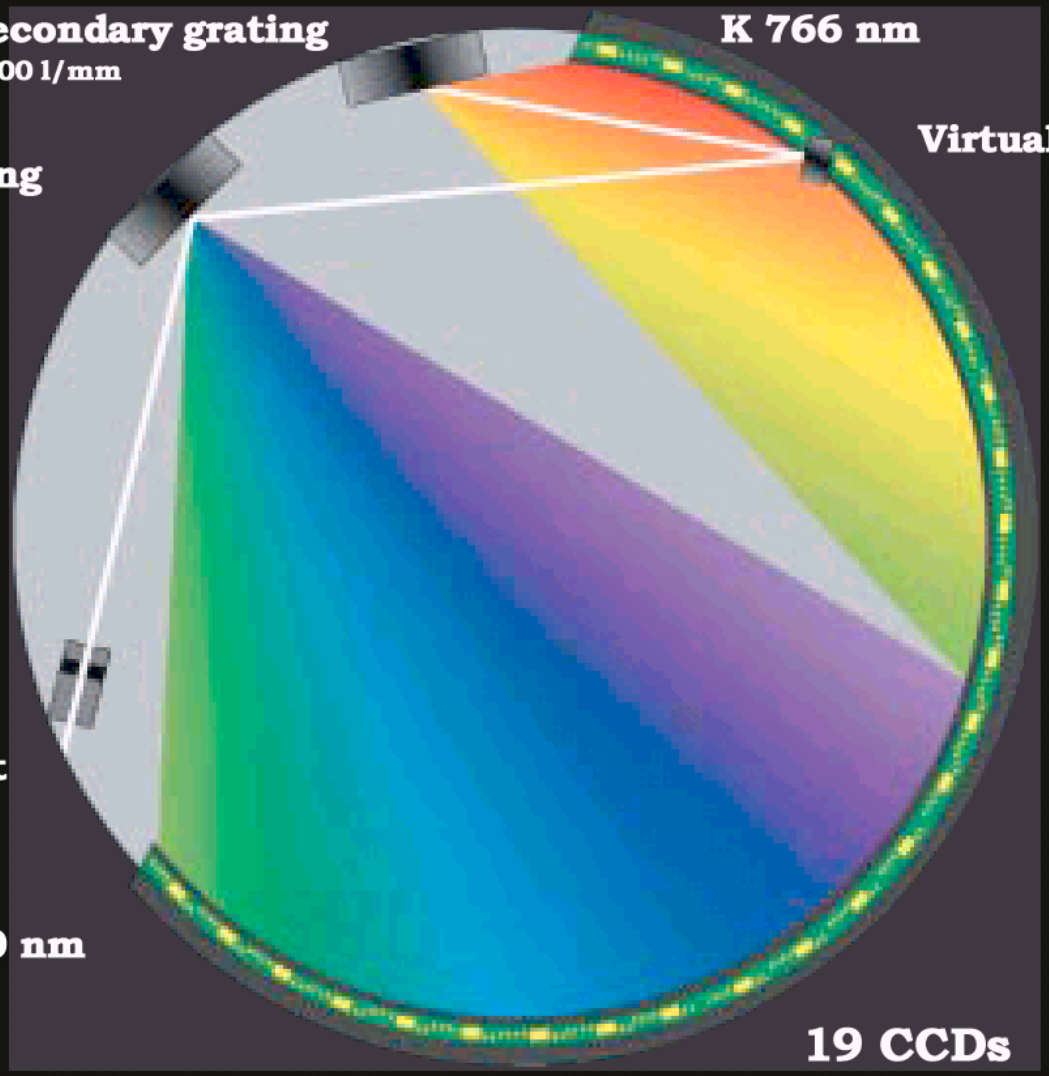
ONE EXIT SLIT & PMT FOR EACH LINE DESIRED, PRESET DIFF. ANGLES

SIMULTANEOUS MEAS. OF AS MANY LINES AS PMTs

SHORT SCAN THRU EACH λ REGION WITH QUARTZ REFRACTOR PLATE



PASCHEN-RUNGE MOUNT, SPECTRO CIROS



HIGH RESOLUTION? <u>LARGE LINEAR DISPERSION</u>

$D_l = f D_a = f |m| / (d \cos \beta$ $\qquad$ $F/n = f/D_p$

$\Omega = A_p / f^2 = \pi /4 (F/n)^2$

1. <u>LARGE f</u> (LARGE f-NUMBER, SMALL Ω LOW THROUGHPUT, LARGER INST. HARDER TO MAKE, LESS STABLE THERMALLY, ...)

2. <u>FINELY-RULED GRATING</u>, <u>SMALL d</u> (MECH. DIFFICULT)

3. <u>LARGE ORDER m</u> (LOW FSR $= \lambda / m$, ORDERS OVERLAP)

4. β 90°, $\cos \beta$ SMALL (DISP. CHANGES WITH λ, λ SCALE NONLINEAR).

SOLUTION:

USE V. LARGE m ~ 50 - 100 β ~ 50° - 70°

MEDIUM f LARGE d

*V. SHORT FSR?

<u>ECHELLE SPECTROMETER</u>

ECHELLE SPECTROMETER

CROSS-DISPERSION
PRISM OR
LOW-RES. GRATING

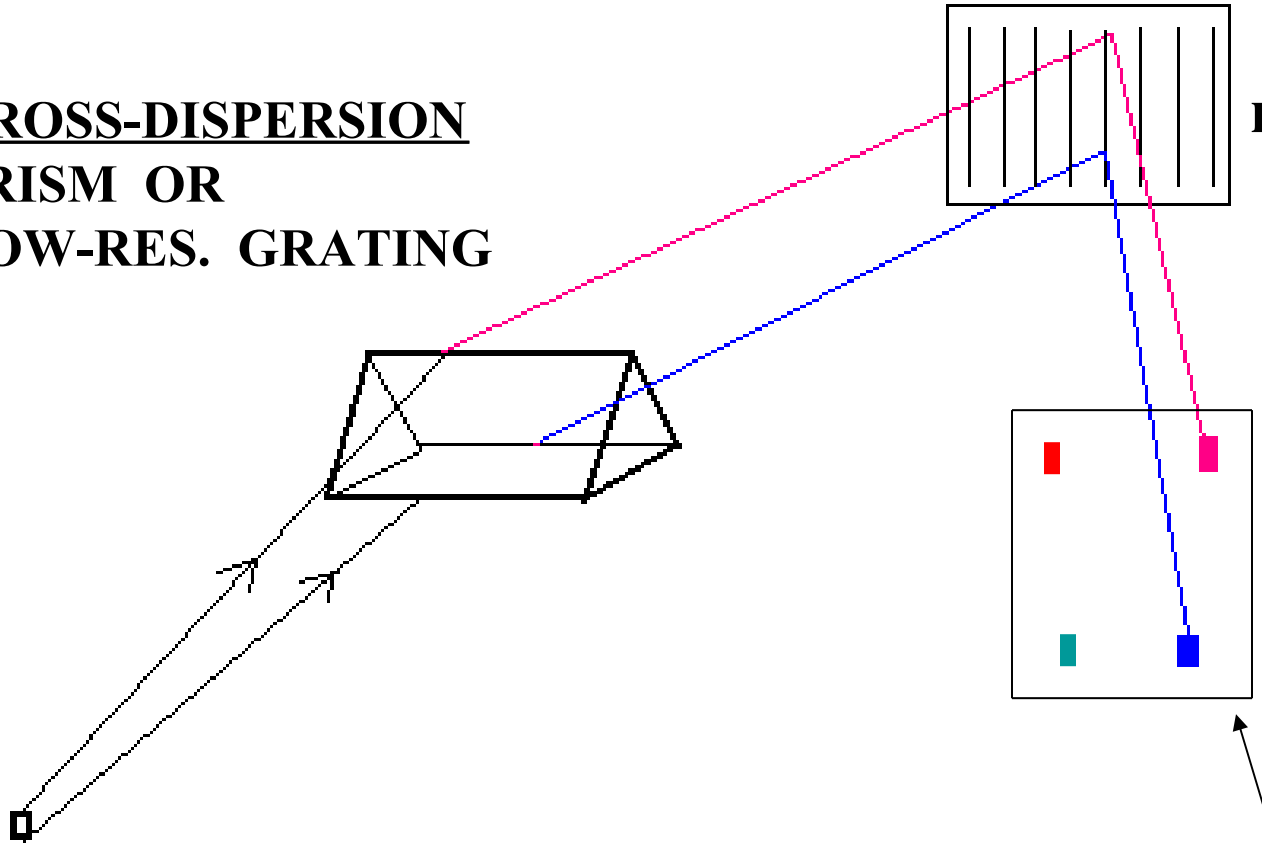
ECHELLE GRATING

$$m\lambda = d \sin(\alpha + \beta)$$

~ CONST.

β approx. same for:

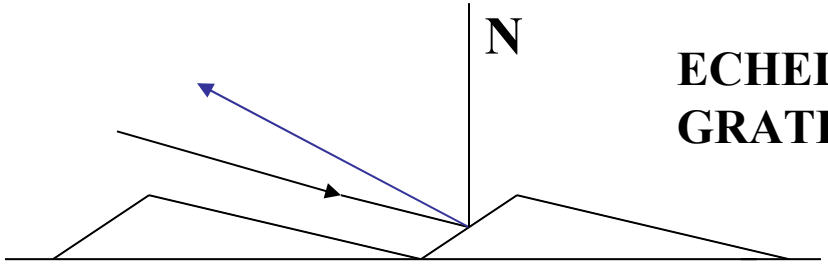
m	λ
60	600
90	400



COARSE RULING
~ 100 grooves/mm

2-D DETECTOR

GROOVE PROFILE
CONCENTRATES LIGHT
INTO HIGH m



ECHELLE GRATING

ECHELLE SPECTRUM

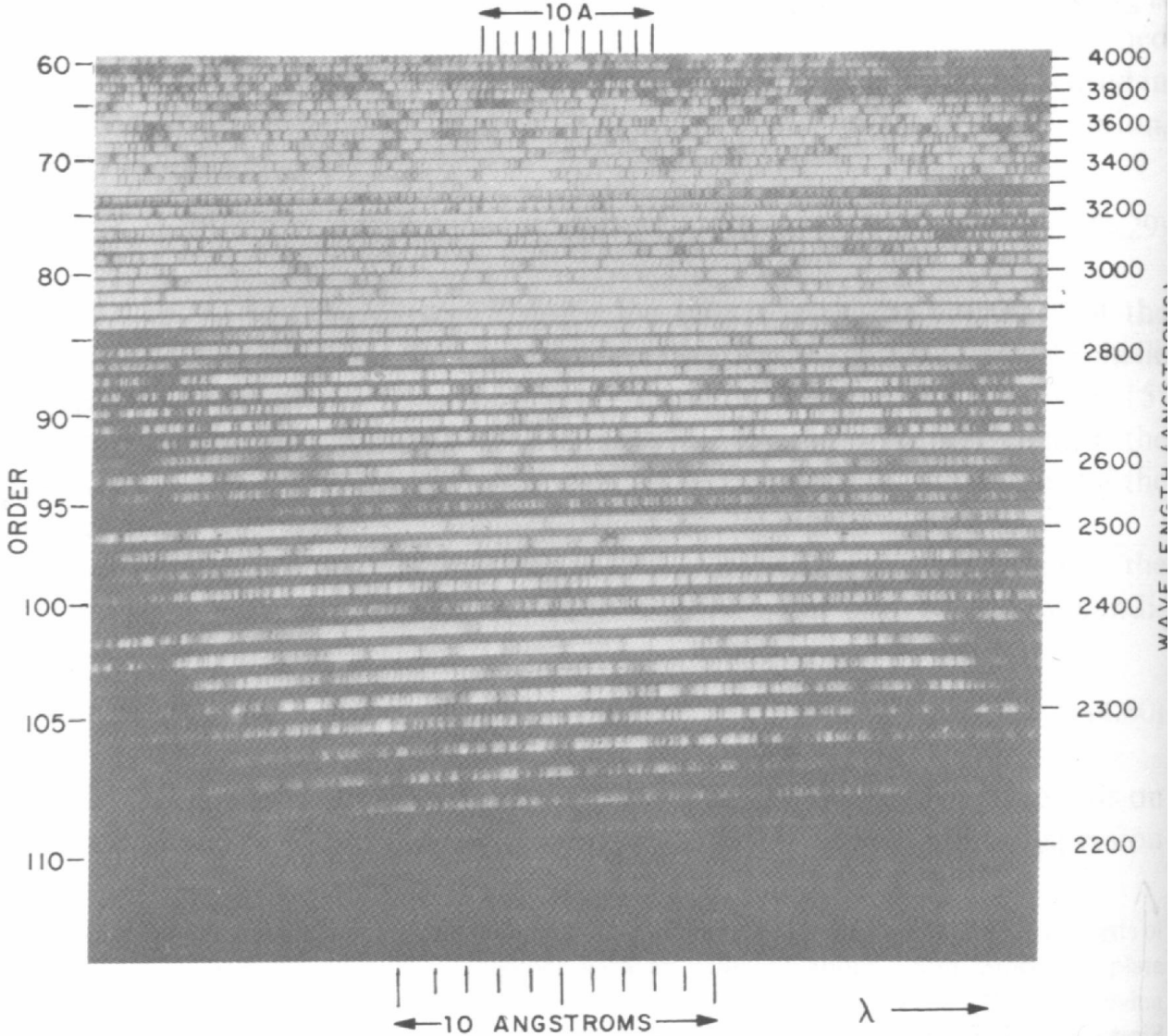


Figure 4.20. High-resolution spectrum from 220 to 400 nm obtained with echelle system and photographed onto film 25 mm square. [Reprinted from D. L. Garrett, S. D. Purcell, and R. Tousey (1962), *Appl. Opt.*, *1*, 726. By permission of the Optical Society of America.]

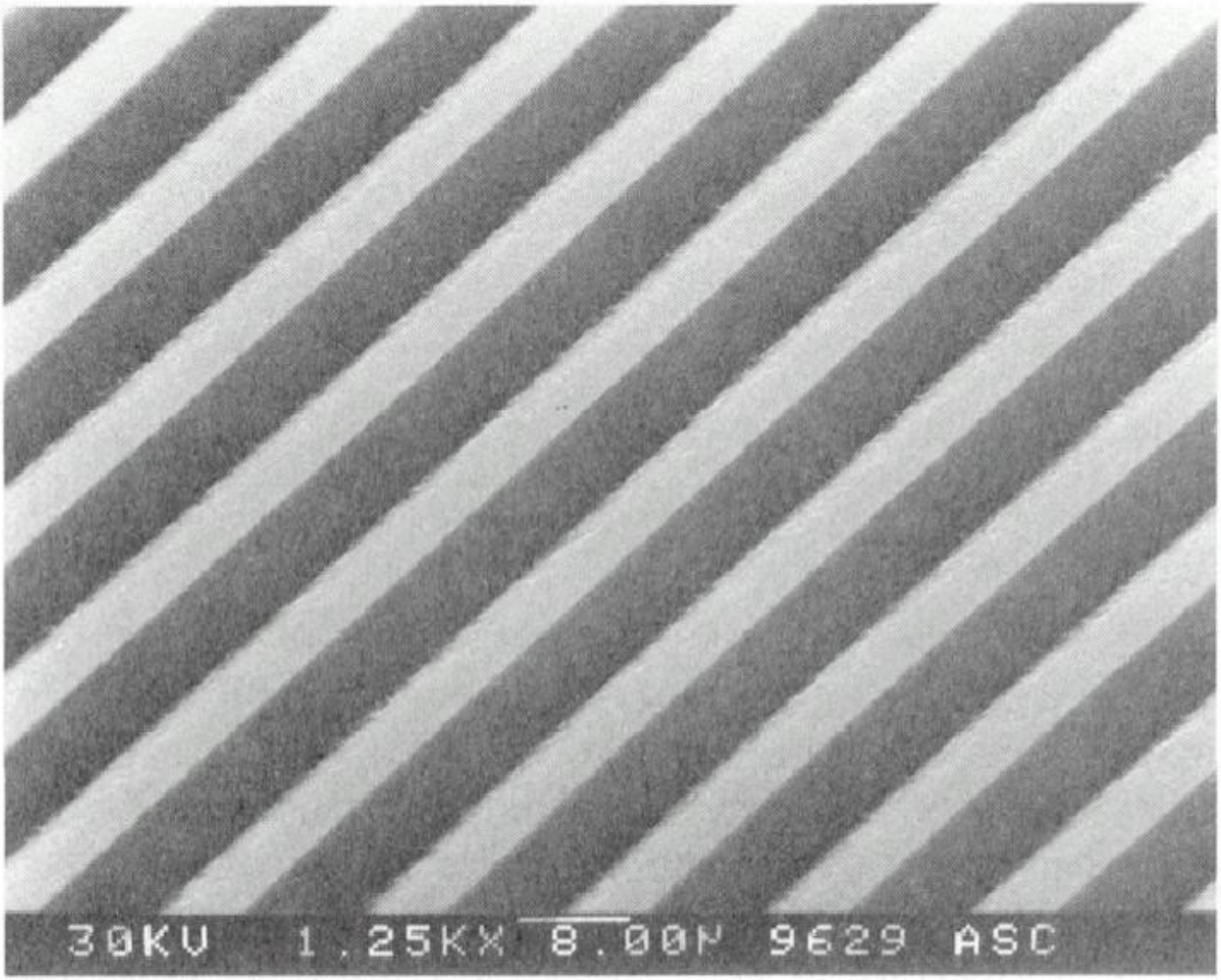


Figure 2. Scanning electron micrograph of the replicated echelle grating surface.

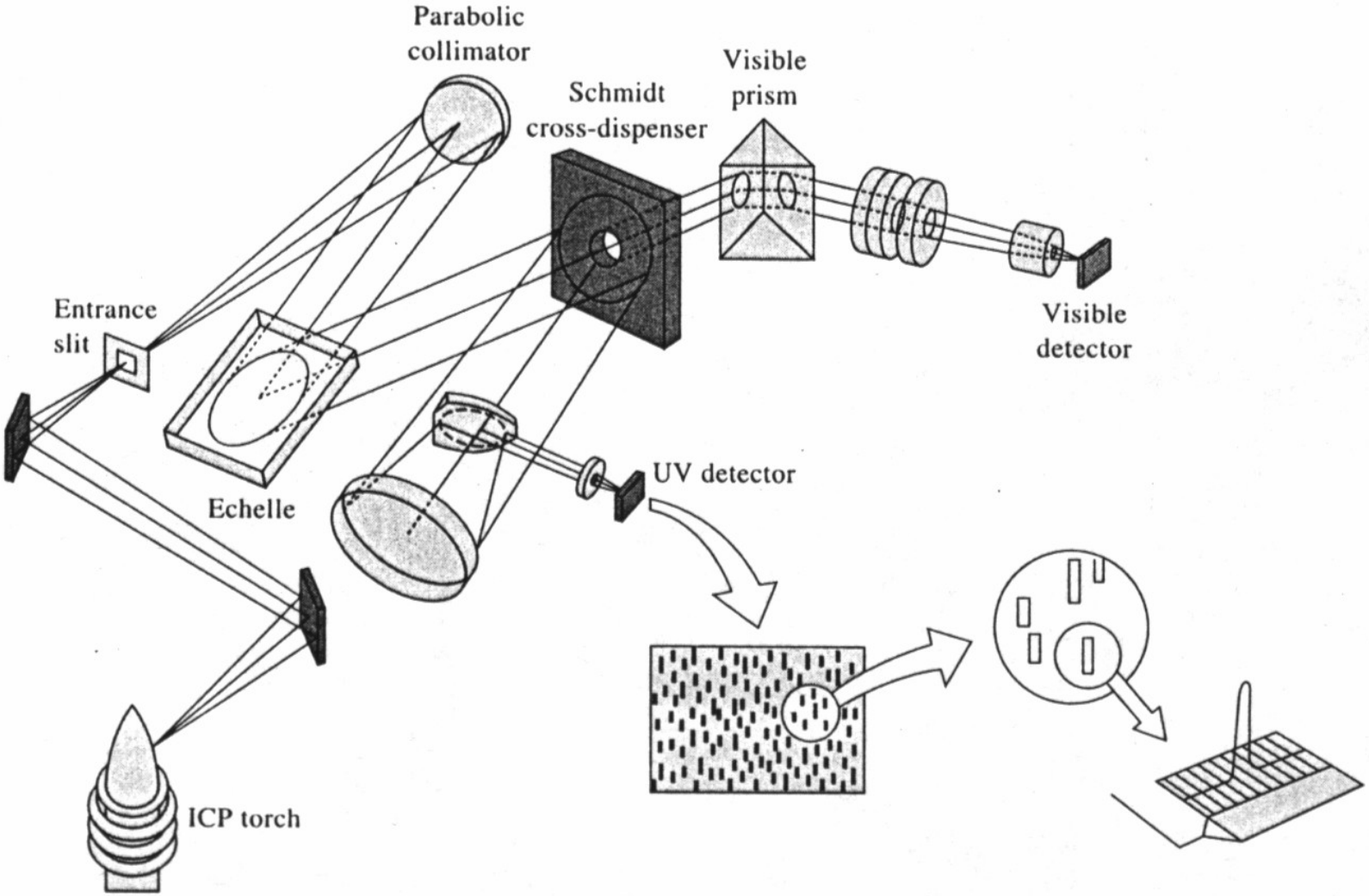
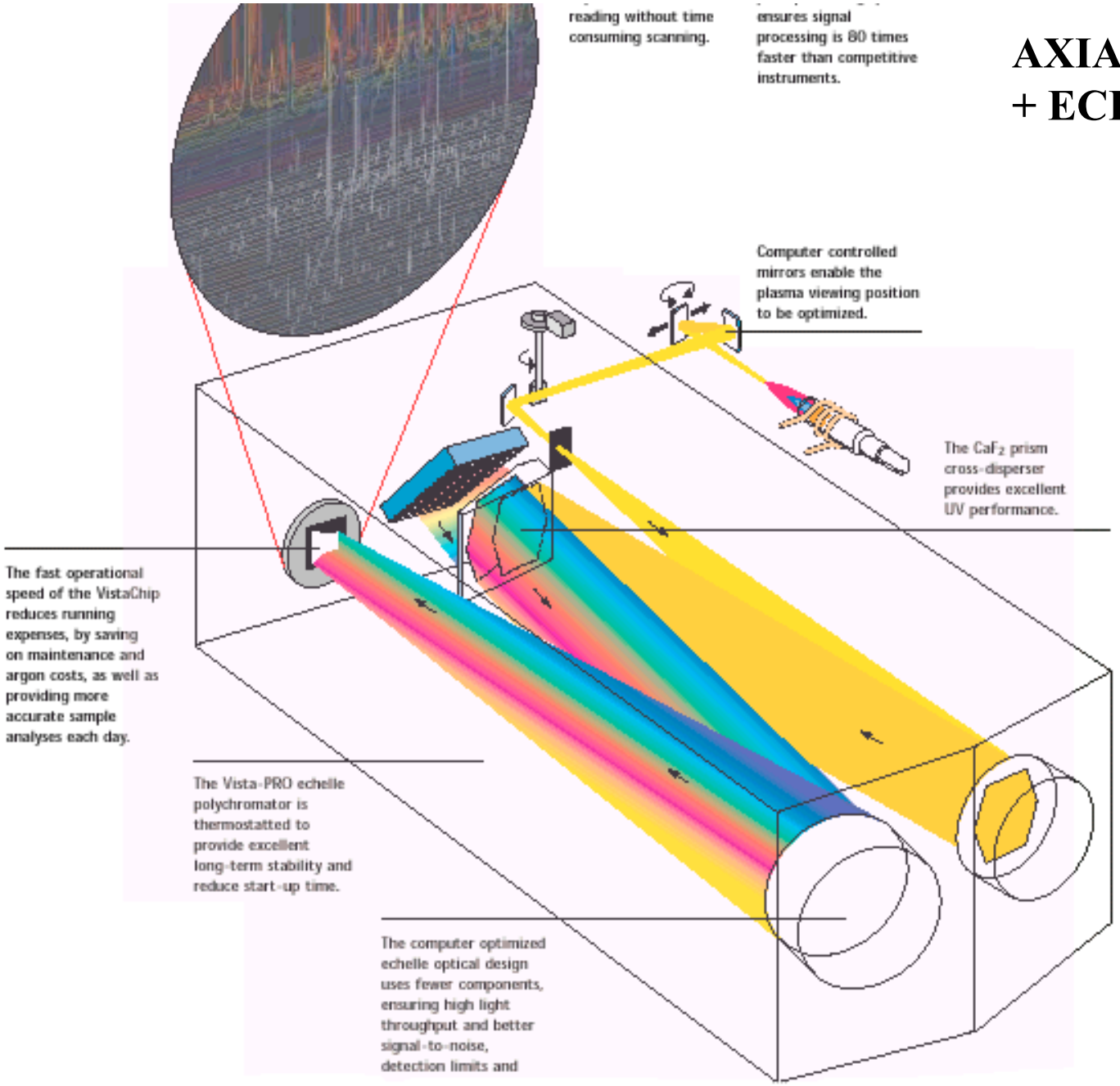
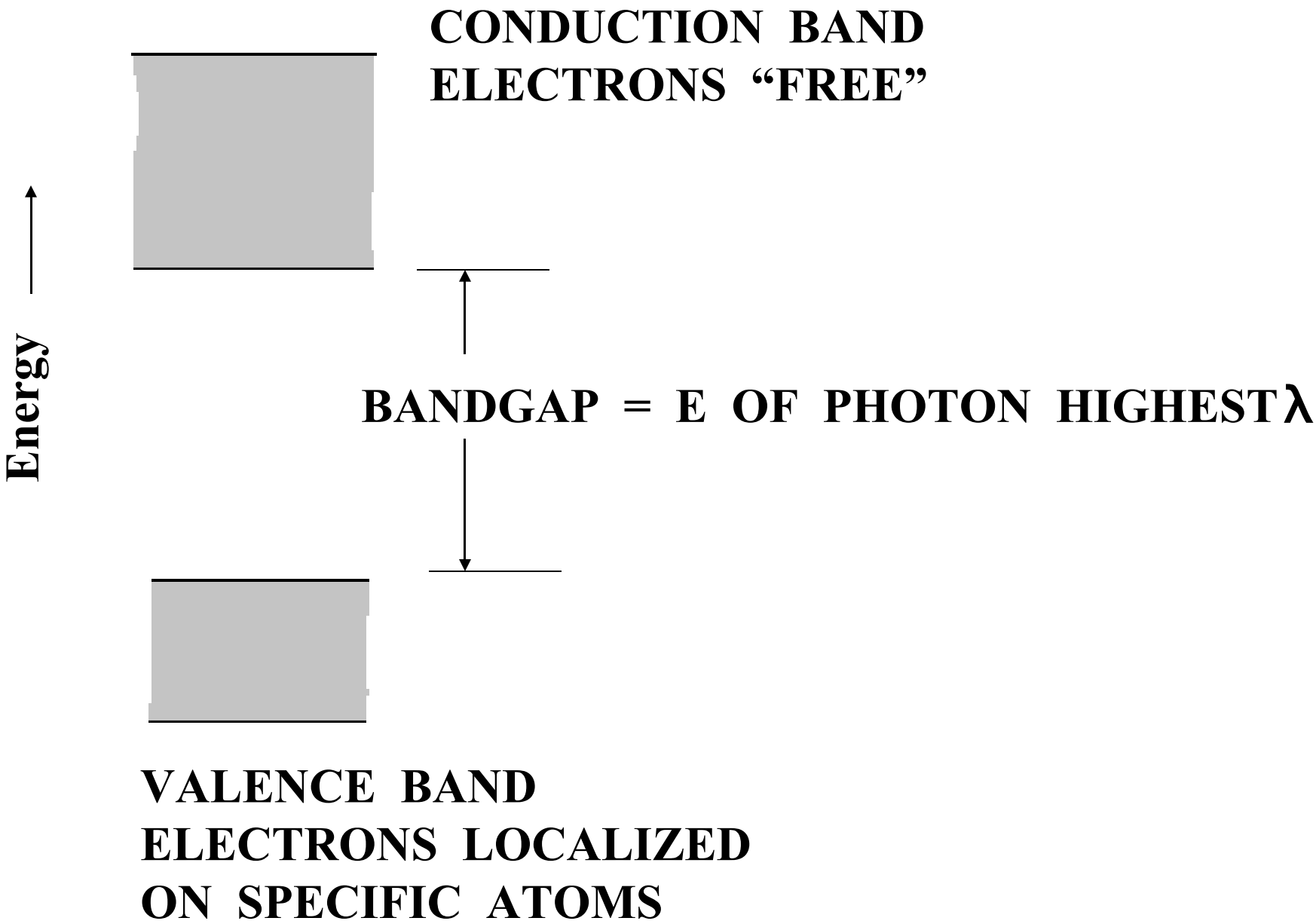


Figure 10-11 An echelle spectrometer with segmented array of charge-coupled devices. *(From T. W. Barnard et al.,* Anal. Chem., *1993,* 65, *1232. With permission.)*

AXIAL VIEWING + ECHELLE + CCD

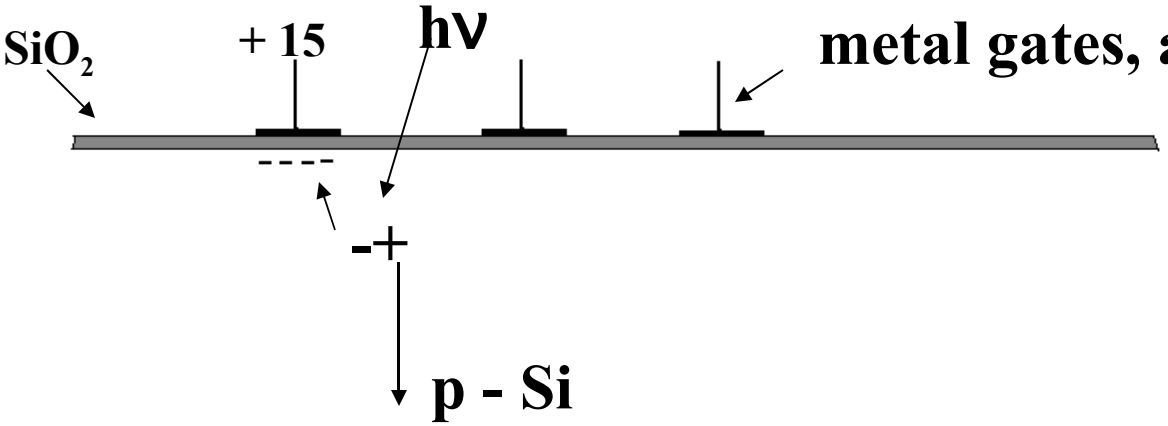


BAND STRUCTURE OF SEMICONDUCTORS



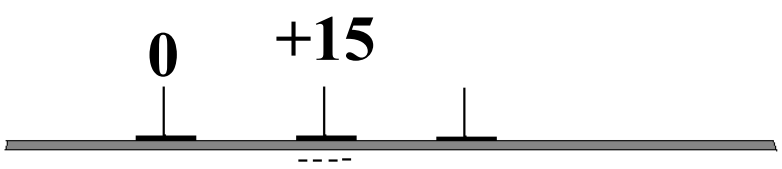
CHARGE TRANSFER DETECTORS

DENTON et al ANAL. CHEM. 1988, 60, 282A, 327A. REQD.



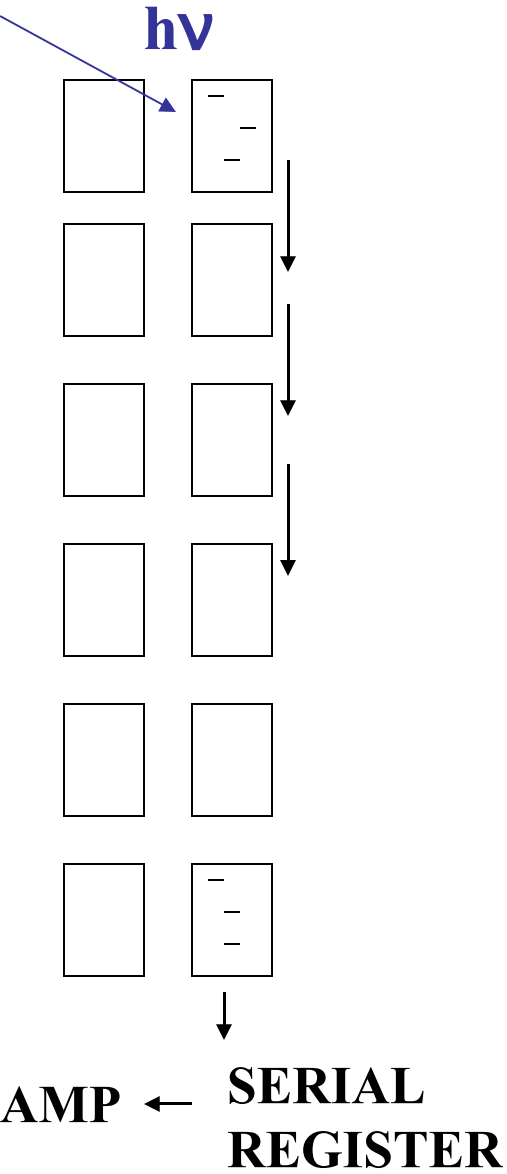
1. INTEGRATE SPECTRUM

 # e^- under gate — Φ each region — t λ



2. READOUT
SHIFT CHARGE
MEASURE CHARGE
EACH PIXEL

CHARGE COUPLED DETECTOR - CCD

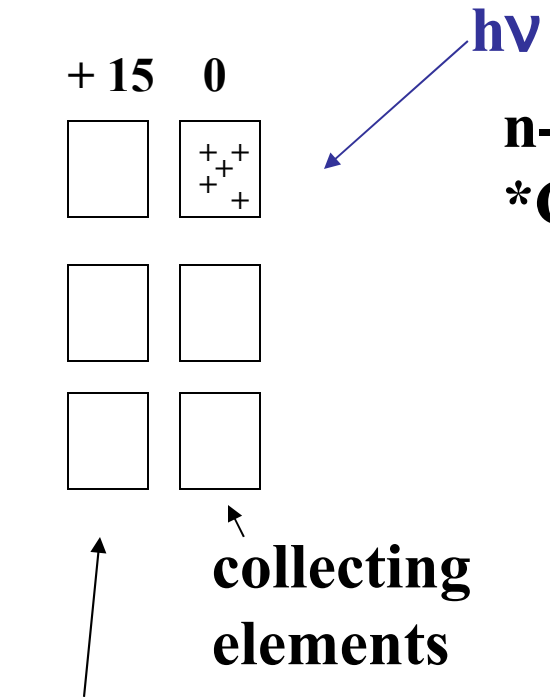


p-doped Si e- collected & shifted
No multiplexing circuitry
Dark current v. low 0.03 to < 0.001 e⁻/s
Shift chg. sequentially down to serial register
Read out WHOLE LINE
Can't read individual detector element

1-D SPECTRUM? USE <u>BINNING</u>:
-sum, read out all charges on single line.
-noise of <u>one read only</u>.

C harge
C onsumed
D

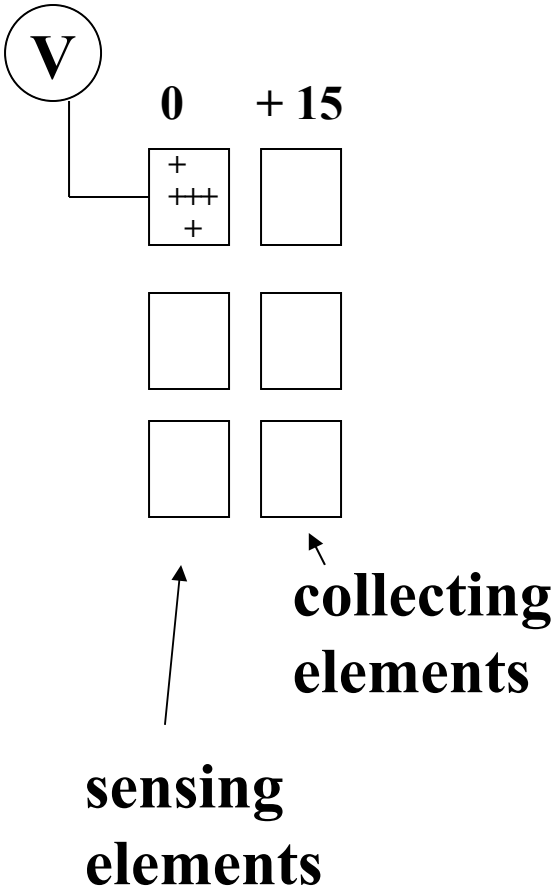
CHARGE INDUCED DETECTOR CID - INTEGRATE STEP



n-doped Si

***Collect <u>holes</u> under collecting element.**

CID READ STEP

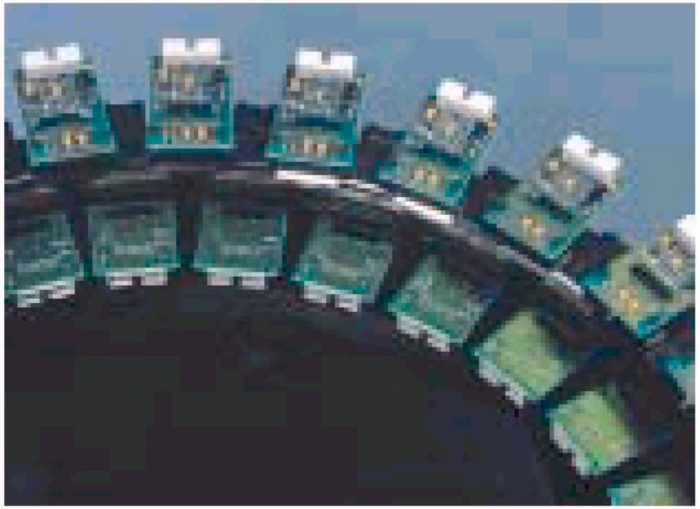


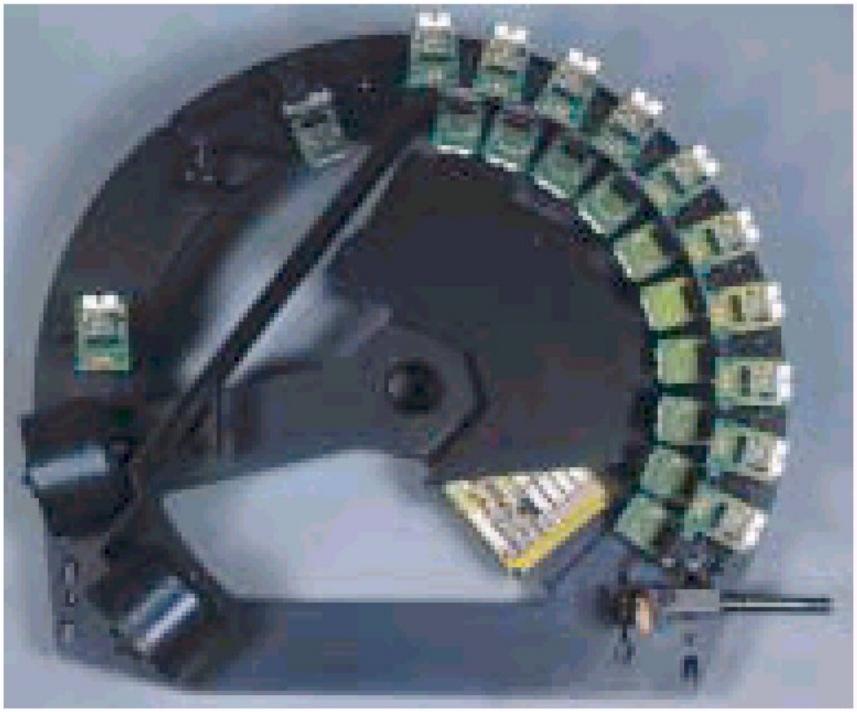
n-doped Si
Transfer chg. from under collector elements to under sensing element.
Meas. voltage induced by chg. under sensing element.

<u>Nondestructive</u>
Charge not consumed during read
Repeat read many times.
Compensate for lower sens. of read process
Random access, read only desired locations.
Dark current < 0.008 e-/s

*Why use n-Si & holes? <u>Less mobile</u> than e-, holes easier to keep under collecting element.

SPECTRO CIROS
PASCHEN-RUNGE MOUNT
DISCRETE CCDs



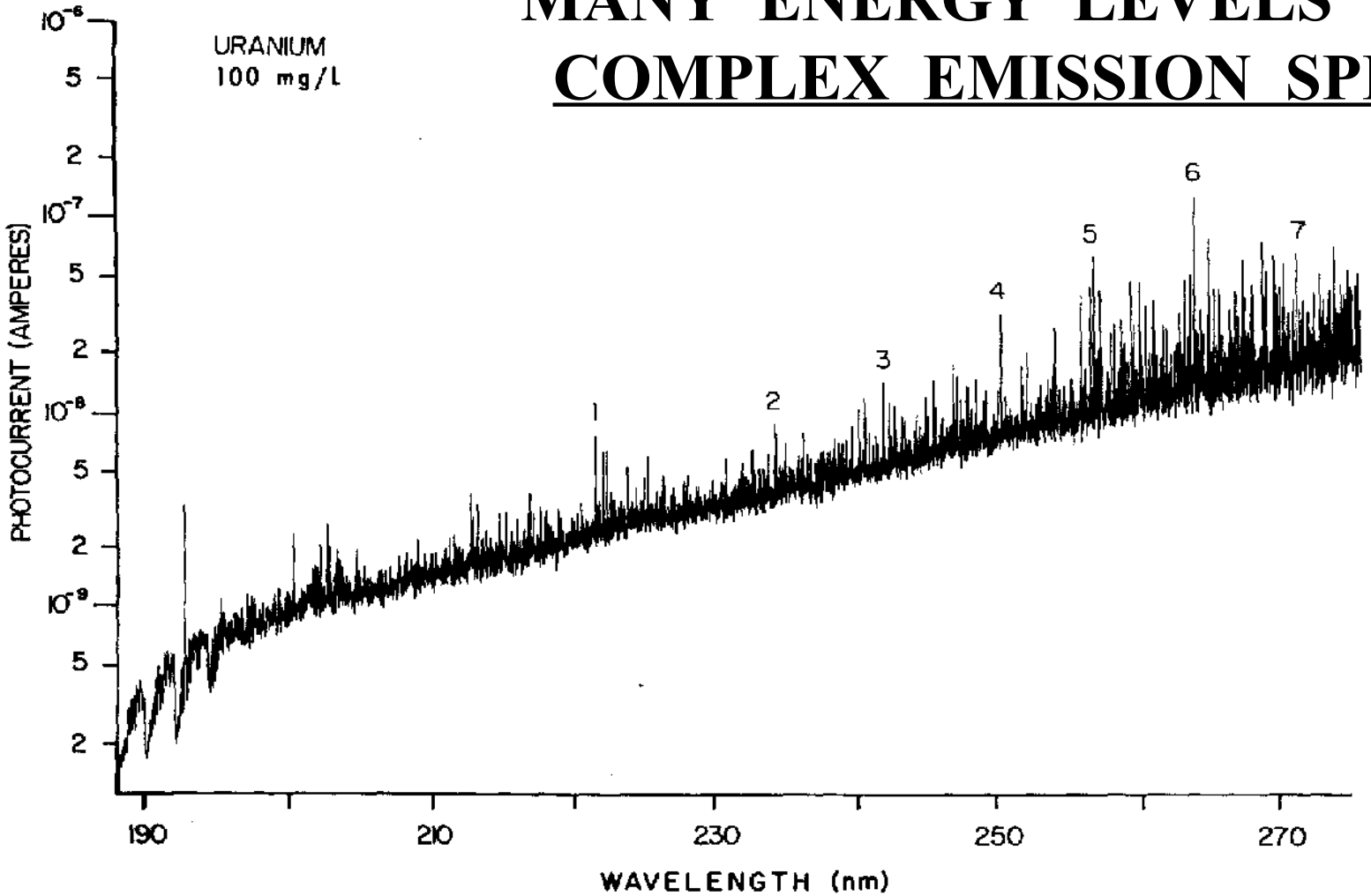


	"RADIAL"	AXIAL
LODs	1-10 ppb	20 – 200 ppt
LINEAR RANGE (FROM LOD)	~1e6	~1e6
SOLUTE LEVEL & MATRIX INTERFERENCE	1% SOLNS. NO PROBLEM	0.1% AT BEST DL 1% OK IF ACCEPT MATRIX EFFECT OR SACRIFICE LOD TO 0.1 – 1 ppb
SPECTRAL INTERFERENCE	SUBSTANTIAL EITHER METHOD	

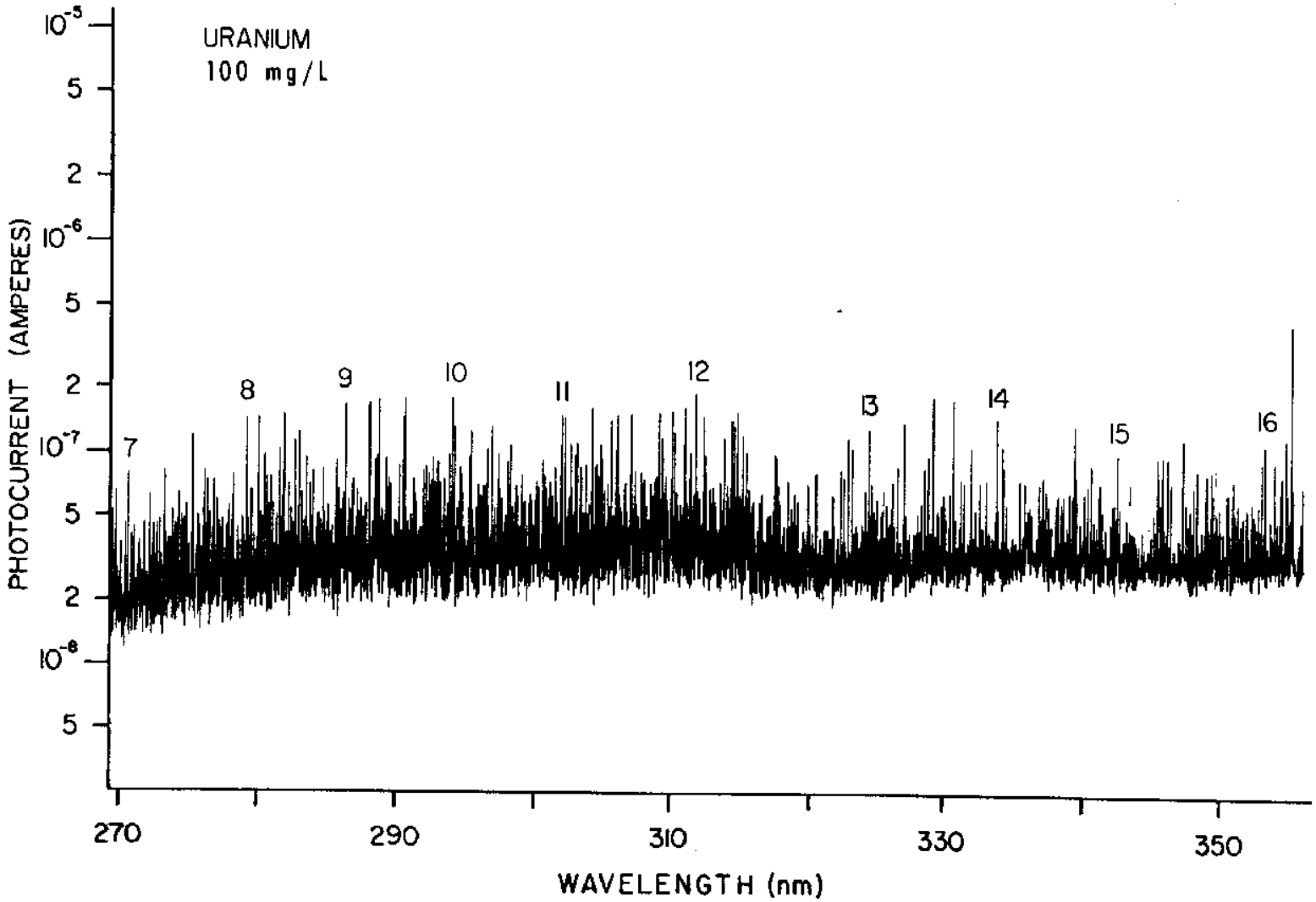
CHALLENGES FOR ICP-AES

- Improving LODs to subppb
- Reduce matrix effects due to EIS, Ca, acids, organics
- Improve precision and accuracy
- On-line sample treatment (preconcentration, matrix elimination, decomposition)
- Direct solids analysis using lasers

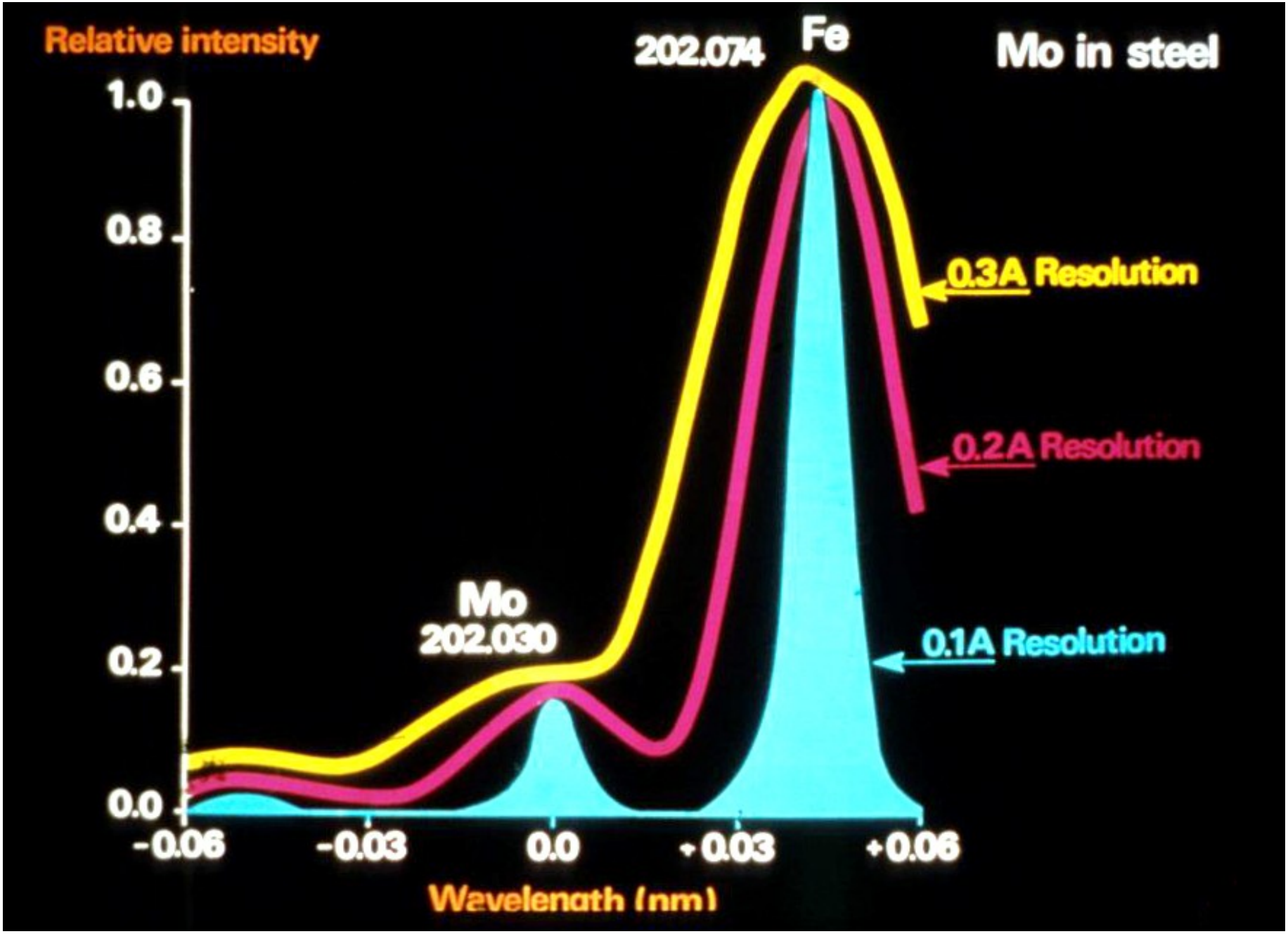
MANY VALENCE ELECTRONS
MANY ENERGY LEVELS
<u>COMPLEX EMISSION SPECTRA</u>



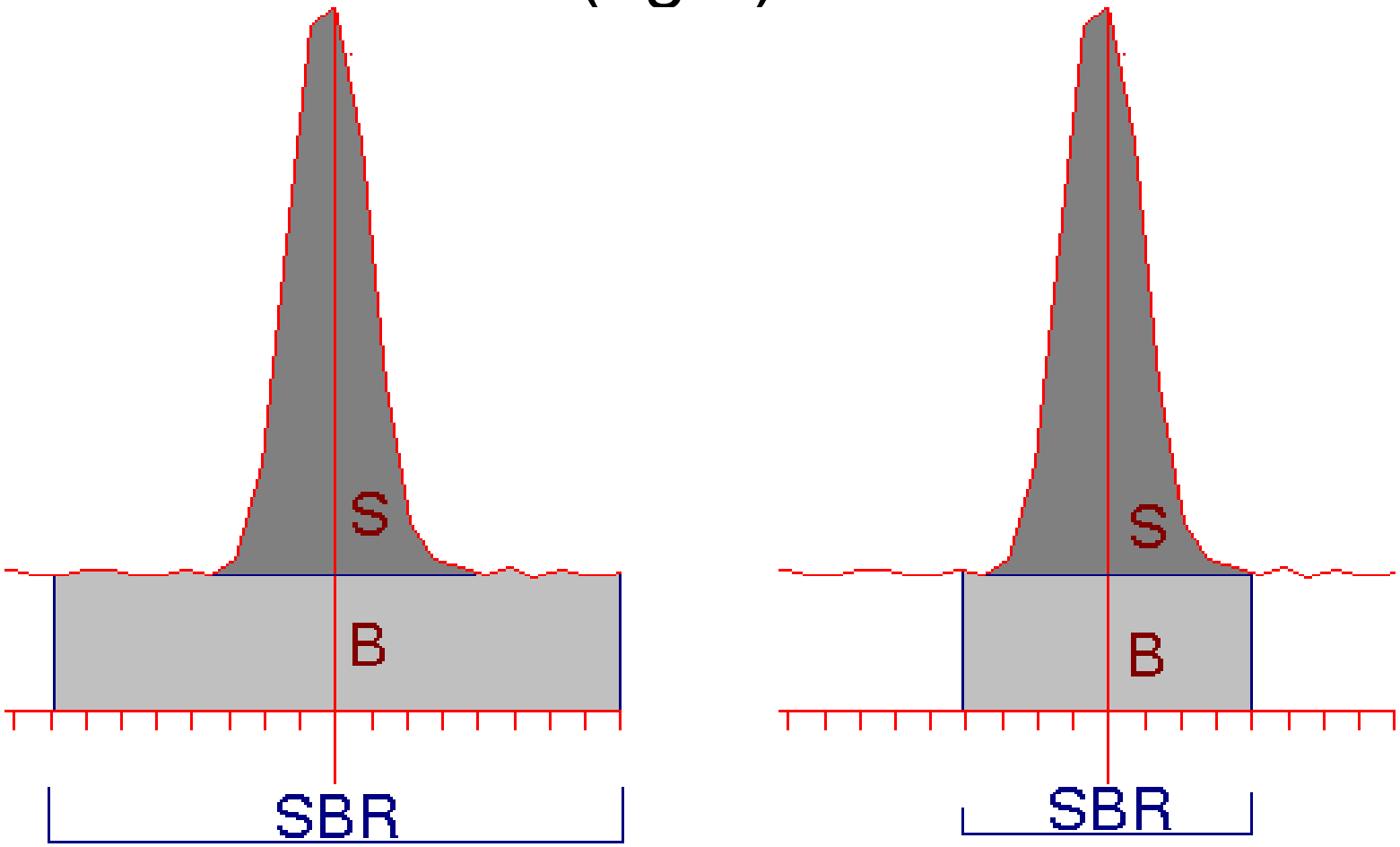
1	U		221.928	4	U	II	250.086	7	U	II	270.695
2	U		234.357	5	U	II	256.541				
3	U	II	241.957	6	U	II	263.553				



7	U	II	270.695	11	U	II	302.221	15	U	II	342.169
8	U	II	279.394	12	U	II	311.935	16	U	II	353.357
9	U	II	286.568	13	U	II	324.417				
10	U	II	294.192	14	U	II	333.779				


Relative intensity
202.074
Fe
Mo in steel
1.0
0.8
0.6
0.4
0.2
0.0
0.3A Resolution
0.2A Resolution
0.1A Resolution
Mo
202.030
-0.06
-0.03
0.0
+0.03
+0.06
Wavelength (nm)

Signal / Background Ratio larger for smaller spectral band pass (right)



Techniques for elemental analysis

	ICP-MS	ICP-AES	FAAS	GFAAS
• Detection Limits	Excellent	Good	Good	Excellent
• Productivity	Excellent	Very good	Good	Low
• LDR	10^{5}	10^{6}/10^{10} HDD	10^{3}	10^{2}
• Precision	1-3 %	0.3-2 %	0.1-1 %	1-5 %
• Spectral interference	Few	Common	Almost none	Very few
• Chemical interference	Moderate	Few	Many	Many
• Ionization	Minimal	Minimal	Some	Minimal
• Mass efffects	High on low	none	none	none
• Isotopes	Yes	none	none	none
• Dissolved solids	0.1-0.4 %	up to 30 %	0.5-3 %	up to 30 %
• No. of elements	~75	~73	~68	~50
• Sample usage	low	medium	high	very low
• Semi-quantitative	yes	yes	no	no
• Isotope analysis	yes	no	no	no
• routine operation	Skill required	easy	easy	skill required
• Method development	skill required	skill required	easy	skill required
• Running costs	high	high	low	medium
• Capital costs	very high	high	low	medium