Chapter 9

Textbook questions

Question 9-2

Describe the effects that are responsible for the three different absorbance profiles in Figure 9-4 and select three additional elements you would expect to have similar profiles.

Cr 的吸光度隨火焰高度的增加而降低，因為隨著 Cr 在火焰中的上升，氧化鉻的形成程度越來越大。

隨著銀在火焰中的上升，原子化化程度越高， Ag 的吸光度也會增加，氧化銀不易形成。

相較於 Cr, Ag 鎂表現出中間值。

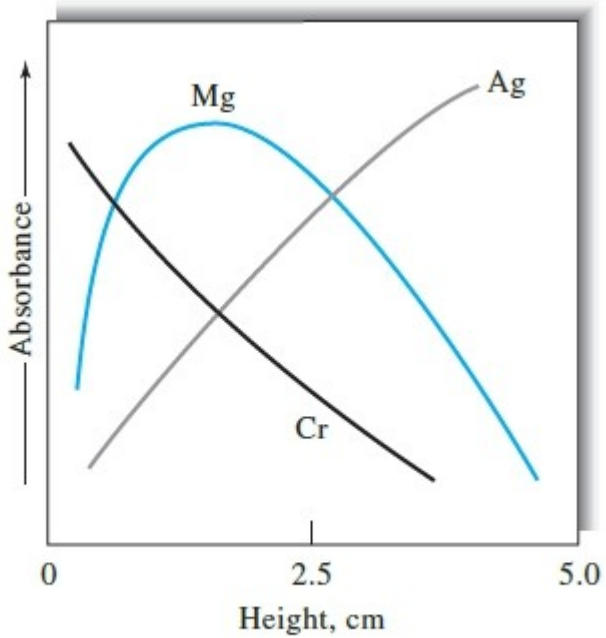
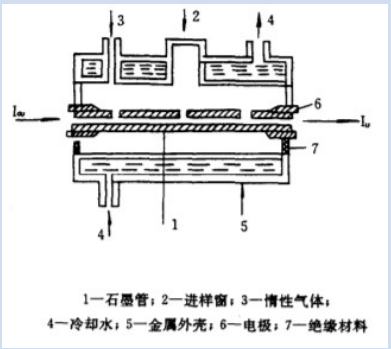


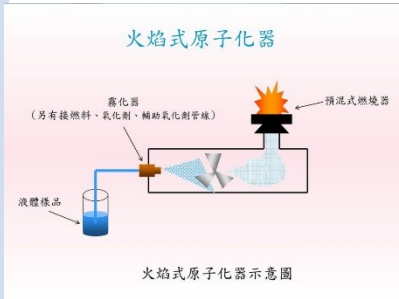
FIGURE 9-4 Flame absorption profiles for three elements.

Question 9-3

Why is an electrothermal atomizer more sensitive than a flame atomizer?

	Electrothermal atomizer 電熱式原子化器	Flame atomizer 火焰式原子化器
過程	管式石墨爐 1. 乾燥 2. 灰化 3. 原子化 4. 淨化	1. 液體樣品由毛細管進入霧化器 2. 經氧化劑霧化分散成微小顆粒 3. 與燃料混合 4. 以一系列檔板除去較大顆粒的粒子 5. 樣品進入預混式燃燒器中，在火燄中加熱形成自由原子
優點	1. 靈敏度與偵測及現優於火焰是原子化器 2. 樣品用量極少	1. 火焰頭不易阻塞 2. 產生火焰長度較長且安靜、增加靈敏度 與再現性
缺點	1. 較易受化學干擾 2. 精準度較差 3. 有些元素會和此法作用，進而無法用此法分析	1. 測定精密度較低 2. 基質干擾比火焰原子化法大 3. 背景干擾比較嚴重，一般都需要校正背景。





電熱式原子化器 (石墨爐 AA) 靈敏度較高原因 :

1. Inert gas (帶走干擾物)
2. Less sample lose

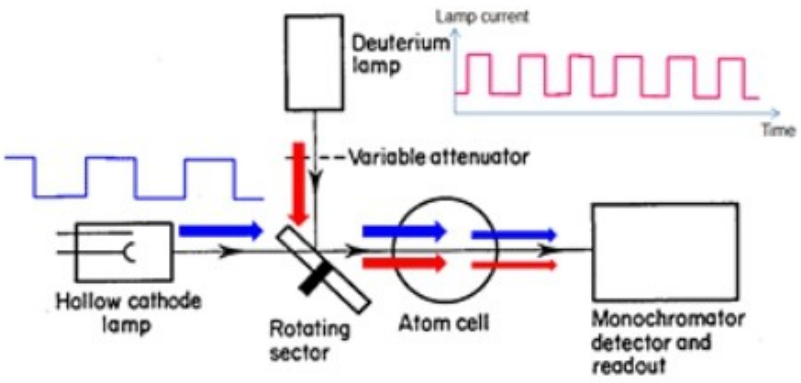
所需樣品較少，可將原子留在管中時間較長

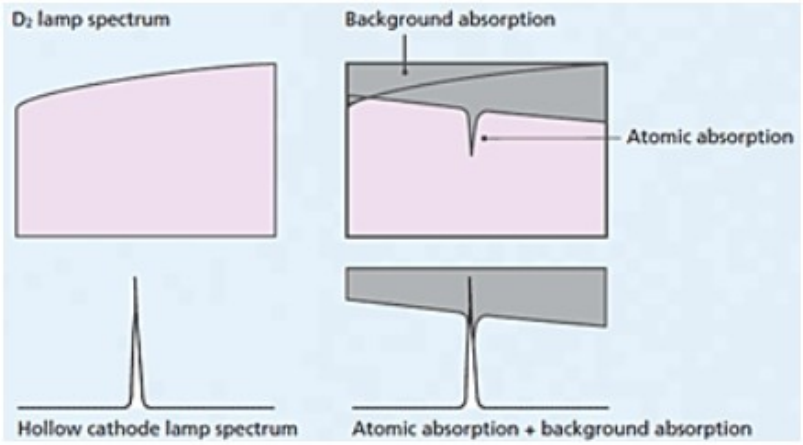
https://slidesplayer.com/slide/15026499/

Question 9-4

Describe how a deuterium lamp can be used to provide a background correction for an atomic absorption spectrum.

D_2 法是一種連續光源校正法 (Continuum-Source Correction Method) 。將 D_2 燈與中空陰極燈管 (HCL) 產生的光以旋轉式遮斷器 (chopper/sector) 快速切換，利用 D_2 燈產生的連續光譜絕大部分為分子光譜吸收或基質產生散射的特性，將中空陰極燈管的吸收光譜與 D_2 燈的吸收光譜相減，即可得到經過背景校正後的正確吸收度值。但由於 D_2 燈在 350 nm 以後的可見光段強度很弱，因此此法無法完全涵蓋 185 nm ～ 900 nm 的波長範圍。





http://www.shimadzu.com.tw/products/aa6880/aa6880_4.html

Question 9-5

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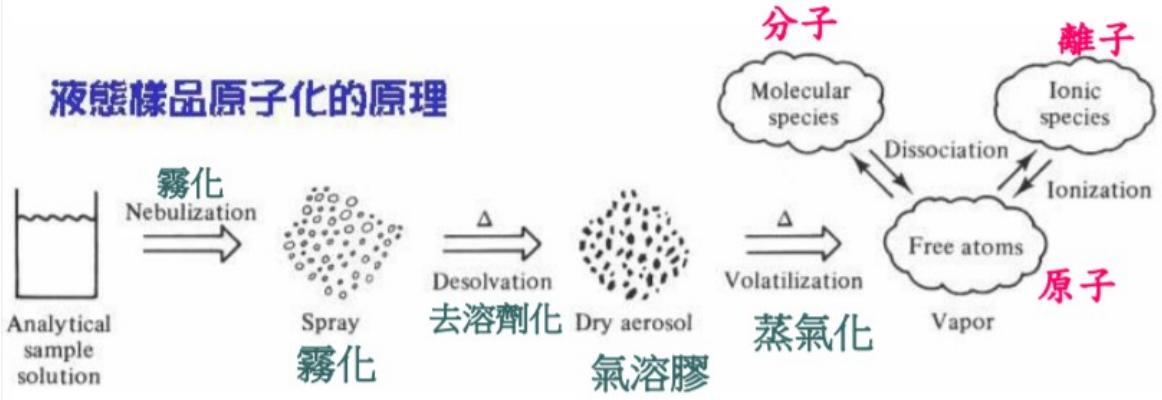
Why is source modulation used in atomic absorption spectroscopy?

- 可用 source modulation 來區分原子吸收（交流信號）和火焰發散（直流信號）。
- High pass filter 過濾

Question 9-6

For two solutions containing the same concentration of nickel, the atomic absorption at 352.4nm was about 30% greater for a solution that contained 50% ethanol than for an aqueous solution that contained no ethanol . Explain

- 酒精會**降低溶液的表面張力**，導致液滴變小。並且改變**溶液的粘度**，使得霧化器的接收效果較好。
- 與冷卻火焰的水相比，**酒精的燃燒熱更大**，從而導致溫度比純水高。



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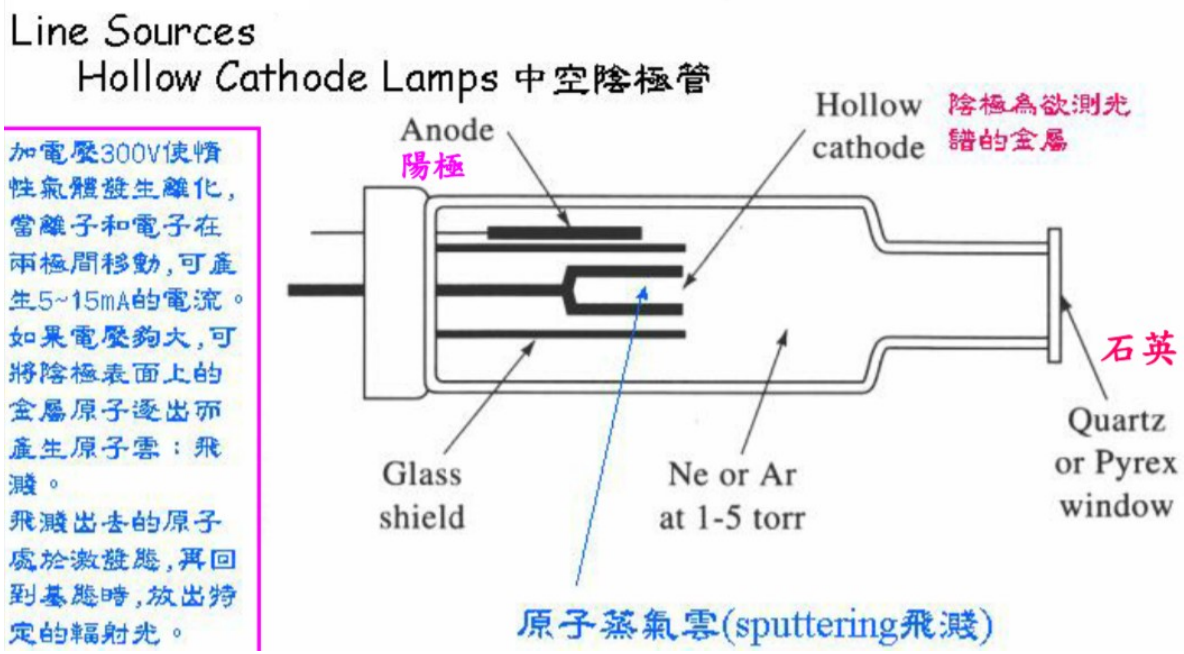
Question 9-7

The emission spectrum of a hollow-cathode lamp for molybdenum has a sharp line at 313.3nm as long as the lamp current is less than 50mA.

At higher currents, however, the emission line develops a cuplike crater at its maximum. Explain

在高電流下，在濺射過程中會形成更多的未激發原子。這些原子通常比激發原子具有更少的動能。其吸收線的多普勒展寬因此而小於運動較快的激發原子的發射線的展寬。

因此，只有中間的吸收線會被自吸收影響。



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Question 9-8

Can analyte attempts to determine **strontium** with an atomic absorption instrument equipped with a nitrous oxide-acetylene burner, but the sensitivity associated with the 460.7nm atomic resonance line is not satisfactory.

Suggest at least three things that might be tried to increase sensitivity.

(1). 嘗試使用**較低溫度的火焰**（空氣 - 氫氣）以減少電離。
(2). 使用含有**乙醇或其他有機物質**的溶劑。
(3). 添加**脫模劑**，**保護劑**或**電離抑製劑**。

Degree of ionization of metals at flame temperatures

- In high temperature flames, ionization becomes important.
- Electrons are produced by the equilibrium:

$$M \Longleftrightarrow M^+ + e^-$$

- The equilibrium constant:

$$K = \frac{[M^+][e^-]}{[M]}$$

- Ionization decreases the concentration of atoms.

Element	Ionization Potential, eV	Fraction Ionized at the Indicated Pressure and Temperature			
		$P = 10^{-4}$ atm		$P = 10^{-6}$ atm	
		2000 K	3500 K	2000 K	3500 K
Cs	3.893	0.01 lower	0.86 higher	0.11	>0.99
Rb	4.176	0.004	0.74	0.04	>0.99
K	4.339	0.003	0.66	0.03	0.99
Na	5.138	0.0003	0.26	0.003	0.90
Li	5.390	0.0001	0.18	0.001	0.82
Ba	5.210	0.0006	0.41	0.006	0.95
Sr	5.692	0.0001	0.21	0.001	0.87
Ca	6.111	3×10^{-5}	0.11	0.0003	0.67
Mg	7.644	4×10^{-7}	0.01	4×10^{-6}	0.09

Data from B. L. Vallee and R. E. Thiers, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, eds., Part I, Vol. 6, p. 3500, New York: Interscience, 1965. Reprinted with permission of John Wiley & Sons, Inc.

Skoog D.A., Holler F.J., Crouch S.R. 2017, *Principles of Instrumental Analysis, 7th Edition*. Cengage.