Instrumental Analysis
Problem Set 6—due ~~Friday~~ Monday, November ~~1~~ 4, 2002

1. Skoog 7-15. (21 points) For each of the seven scenarios ((a) through (g)), you should choose an appropriate (i) source, (ii) wavelength selector, (iii) and detector. You do not need to propose appropriate materials.

2. Skoog 7-20 (5 points)

3. Skoog 13-13 (21 points) I don't expect you to write paragraphs for each of these eight comparisons. Just summarize the key points.

4. Skoog 13-19 (4 points)

5. Skoog 14-9 (6 points)

Note: You did not need to note materials for full credit

1. Skoog 7-15

(a) Source: W lamp (continuous throughout visible)
λ selector: Grating (tunable)
Detector: PMT
Material Glass

(b) Source: Globar (SiC)
λ selector: Grating
Detector: Thermocouple
Material: KBr

(c) Source: W lamp
λ selector: filter ← need only 1 λ, and want something portable
Detector: Si Diode (also small)
Material: Glass

(d) Source: Nernst glower
λ selector: interference filter: Like (c), need only 1 λ ("routine determination")
Detector: Photoconductor
Material: ZnSe

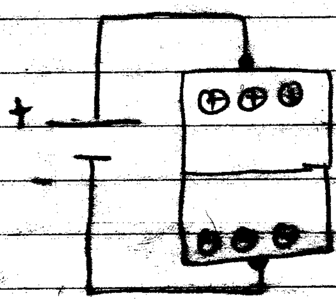
(e) Source: Sample itself ← emission
λ selector: Grating
Detector: Si Diode ← need to cover a wide λ range
Material: Quartz ← not glass

(f) Source: Ar lamp
λ selector: Grating
Detector: Photographic plate ← too high E for PMT's!
Material: KBr

Skoog 7-15 cont.

(g) Source: Nernst Glower
λ Selector: Quartz prism
Detector: Photoconductor
Material: Glass

2. Skoog 7-20



Start w/ a reverse biased diode ⇒ negligible current flow.
Then exposing diode to radiation (w/ the right range of λ's) will create minority carriers which will allow a measurable ~~increase in current~~ flow.
Current is ~ to # of photons.

13-13 (a) *Hydrogen and deuterium lamps* differ only in the gases they contain. The latter produces radiation of somewhat higher intensity.

(b) *Filters* provide low resolution wavelength selection often suitable for quantitative work but not for qualitative analysis. *Monochromators* produce high resolution (narrow bandwidths) for both qualitative and quantitative work.

(c) A *phototube* is a vacuum tube equipped with a photoemissive cathode. It has a high electrical resistance and requires a potential of 90 V or more to produce a photocurrent. The currents are generally small enough to require considerable amplification before they can be measured. A *photovoltaic cell* consists of a photosensitive semiconductor sandwiched between two electrodes. A current is generated between the electrodes when radiation is absorbed by the semiconducting layer. The current is generally large enough to be measured directly with a microammeter. The advantages of a phototube are greater sensitivity and wavelength range as well as better reproducibility. The advantages of the photocell are its simplicity, low cost, and general ruggedness. In addition, it does not require an external power supply or elaborate electric circuitry. Its use is limited to visible radiation, however, and in addition it suffers from fatigue whereby its electrical output decreases gradually with time.

(d) *Phototubes* consist of a single photoemissive surface (cathode) and an anode in an evacuated envelope. They exhibit low dark current but have no inherent amplification (gain). *Photomultipliers* have built-in gain but suffer from somewhat larger dark current.

(e) A *photometer* is an instrument for absorption measurements that consists of a source, a filter, and a photoelectric detector. A *colorimeter* differs from a photometer in the respect that the human eye serves as the detector. The photometer offers the advantage of greater precision and the ability to discriminate between color. The main advantages of a colorimeter are simplicity, low cost, and the fact that no power supply is needed.

(f) *Spectrophotometers* have monochromators for multiple wavelength operation and for procuring spectra while *photometers* utilize filters for fixed wavelength operation.

(g) A *single-beam spectrophotometer* employs a fixed beam of radiation that irradiates first the solvent and then the analyte solution. In a *double-beam instrument*, the solvent and solution are irradiated simultaneously or nearly so. The advantages of the double-beam instruments are freedom from problems arising from fluctuations in the source intensity from drift in electronic circuits; in addition, it is more easily adapted to automatic spectral recording. The single-beam instrument offers the advantages of simplicity and lower cost.

(h) Diode array spectrometers detect the entire spectral range essentially simultaneously and can produce a spectrum in less than a second. *Spectrometers* require several minutes to perform the same task. Accordingly the diode array instruments can be used to monitor processes that occur on very fast time scales. Conventional spectrometers require several minutes to perform the same task.

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4. Skoog 13-19 PMT's can't detect IR because IR photons do not have enough energy to overcome the work function of the metal/coating of the photo cathode.

5. Skoog 14-9

Use result $\frac{s_c}{c} = \pm \left| \frac{s_T}{T \ln T} \right|$ We have case I error: $s_T = k_1 = 0.005$ (not f(T))

(a) $A = -\log T \Rightarrow T = 10^{-A} = 10^{-0.585} = 0.260$

so $\frac{s_c}{c} = \pm \left| \frac{0.005}{(0.260)\ln(0.260)} \right| \times 100\% = \boxed{\pm 1.4\%}$

(b) $\frac{s_c}{c} = \pm \left| \frac{0.005}{0.496 \ln(0.496)} \right| = \boxed{\pm 1.4\%}$

(c) $T = 10^{-A} = 10^{-1.800} = 0.0158$

$\frac{s_c}{c} = \pm \left| \frac{0.005}{(0.0158)\ln(0.0158)} \right| = \boxed{\pm 7.6\%}$

(d) $\frac{s_c}{c} = \pm \left| \frac{0.005}{(0.0592)\ln(0.0592)} \right| = \boxed{\pm 3.0\%}$

(e) $\frac{s_c}{c} = \pm \left| \frac{0.005}{(0.9925)\ln(0.9925)} \right| = \boxed{\pm 67\%}$

(f) $T = 10^{-0.0055} = 0.987$

$\frac{s_c}{c} = \pm \left| \frac{0.005}{(0.987)\ln(0.987)} \right| = \boxed{\pm 40\%}$