PHOTOMETRIC TITRATION OF A MIXTURE OF Ca$^{+2}$ AND Cu$^{+2}$

In this experiment a standard solution of EDTA will be used to titrate an unknown mixture of Ca$^{+2}$ and Cu$^{+2}$. The transmittance of the reaction mixture will be monitored throughout the titration so that a plot of absorbance vs. volume of titrant added can be constructed. The graph will yield linear sections of the curve that intersect at equivalence points. An attractive feature of this approach is the fact that the titration can be made fairly quickly without the need to record data carefully near the equivalence point(s).

However, the choice of the analytical wavelength used merits some special care. Even in a simpler experiment where only one substance in the sample is to be determined there are at least three components present which may absorb light: the original substance, the titrant, and the resulting product or products. The usual procedure is to select some wavelength at which only one component absorbs. However, the mere fact that only one component absorbs at a particular wavelength does not necessarily mean that particular wavelength is the optimum choice. For example, if the solution is very darkly colored initially, the %T readings may be limited to the 0 to 20 %T region of the scale where the relative uncertainty of the %T (and therefore, absorbance) is large. Sometimes there is no other choice but a situation in which more than one species absorbs. Occasionally, as in case II below, such a choice actually makes the detection of the endpoint more distinct. Here are some typical photometric titration curves for the reaction

$$X + T \rightarrow P$$

where $T$ = titrant

$X$ = component to be determined

$P$ = product(s) of the reaction

Case 1: $X$ and $P$ both absorb and $P < X$

Case 2: $X$ and $T$ both absorb.

Case 3: only $T$ absorbs.

Case 4: one (or more) of the products, $P$, absorbs.

Case 5: one (or more) of the products, $P$, absorbs.

Case 6: $P$ and $T$ absorb and $T > P$. 

Case 6: $P$ and $T$ absorb and $T < P$. 

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[Graphs showing absorbance vs. volume for different cases]
In this experiment only the Cu(NH$_3$)$_4^{2+}$ complex and the Cu(EDTA) complex have a significant absorbance. The spectrum for each of these two complexes is shown below. In the presence of the NH$_3$ buffer the stability constant of the Cu(EDTA) complex is less than that for the Ca(EDTA) complex which means that the Ca$^{2+}$ ion will be titrated first. **Before coming to the lab** think about what wavelength to choose to give the most distinct endpoint (greatest change in slope). Sketch the shape of the titration curve that you would expect for the Ca$^{2+}$ and Cu(NH$_3$)$_4^{2+}$ mixture. Discuss this and the choice of wavelength with the instructor before starting.

![Absorbance vs Wavelength](image)

There is one other subtle point to consider here. Consider case 2 after the equivalence point. The maximum amount of colored product is produced at the equivalence point. The absorbance also should reach a constant level here except for the effect of dilution. This graph does not show a drop in absorbance beyond the equivalence point because it has been corrected for dilution. In fact, the absorbance at any point along the titration curve (for any of these cases) must be corrected for dilution, otherwise it will cause the straight-line segments to curve. This can throw off the process of establishing the true equivalence point. The corrected absorbance can be calculated as follows:

\[
A_{corr} = A_{obs} \cdot \frac{(V_{initial} + V_{titrant})}{V_{initial}}
\]

or

\[
A_{corr} = A_{obs} \cdot (1 + \frac{V_{titrant}}{V_{initial}})
\]

where $A_{obs}$ is the observed absorbance ($A_{obs} = -\log T$).

**Prelab Assignment**

Determine the best wavelength for the determination.
**SOLUTIONS**

- Standard 0.025 M Cu$^{2+}$ (prepared for you)
- pH 10, 8 M Ammonia buffer (570 mL concentrated ammonia, 70 g NH$_4$Cl diluted to 1L)
- 0.05 M EDTA (prepared for you)
- Ca$^{2+}$ and Cu$^{2+}$ unknown (both ions about 0.025 M)

**PROCEDURE**

A. Installing the photometer.

Attach the output leads from your photometer to the input leads of the pH meter. Start up the Titratio2004 LabView application. Check to see that your pump is running properly. Block the light path in the photometer and record the dark current that corresponds to 0% T. Place water in your cuvette and record the 100% T reading.

B. Standardization of the Stock EDTA Solution.

Rinse and fill your buret with the stock EDTA solution which is roughly 0.10 M. Place a small magnetic stirring bar in your cuvette. Pipet 5.00 ml of standard Cu solution (provided for you) and add 10 ml of 8 M ammonia buffer to the cuvette. Start the stirrer and mix the solution. Titrate your solution. Proceed efficiently to avoid loss of ammonia.

Continue the titration until at least twenty-five points have been recorded past the endpoint.

C. Titration of Unknown Ca-Cu Solution Mixture.

After cleaning out the apparatus repeat the procedure with a 5.00 ml sample of unknown solution. If time allows do the standardization and unknown determination in duplicate.

**Calculations**

Transfer your data to Excel. Convert your readings to absorbance (just like you did for last weeks lab). Do the volume correction for the absorbance using Eq. 1 or 2. Find the intersection of lines fitted to the straight portions of the titration curve.

**REPORT**

Use the titration version of the standard report form. Also, provide a plot of the corrected absorbance vs. the volume of EDTA added for the standardization and unknown titrations. Label the endpoints on the graphs. Report the concentrations for Ca$^{2+}$ and Cu$^{2+}$ in your unknown.