

A Laser-Pointer-Based Spectrometer for Endpoint Detection of EDTA Titrations

Christopher E. Dahm* and James W. Hall

Department of Chemistry and Physics, Wingate University, Wingate, NC 28174; *cdahm@wingate.edu

Brian E. Mattioni

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

One of the most common multidentate ligands used for the analysis of metal-ion standards is ethylenediaminetetraacetic acid (EDTA). *Reagent Chemicals* (1) ranks EDTA complexation titrations as the preferred method for 10% of the listed compounds. Besides all of its laboratory application, EDTA is also present in many commercial products. In the mid-1980s, Hart (2, 3) compiled a list of commodities that contain EDTA, such as cleaning compounds (shampoos, liquid soaps, and tile cleansers) and foods (mayonnaise and salad dressings).

Because of the prevalence of EDTA as the multidentate ligand of choice, EDTA titrations of metal ions are invariably incorporated into the undergraduate analytical laboratory. As a result of its stability over time and its sharp color change at the endpoint, Calmagite is a common indicator chosen for these titrations. In a basic solution, Calmagite changes color from wine red, to purple, to sky blue; the endpoint is defined as the precise moment when all of the red color has disappeared from the solution. Since each student's color perception is slightly different, it can be difficult for the untrained eye to ascertain the exact point when all of the red color has disappeared. This ambiguity in the detection of the endpoint can lead to a large standard deviation in endpoint volumes, which can cause the student to become frustrated. It was these types of results that led us to design a spectrophotometric determination of the endpoint.

Morssman, Kooser, and Welch (4) reported the successful development of a laser photometer for endpoint detection of an EDTA titration of calcium or magnesium ions. Endpoint volumes were achieved by the addition of titrant until the photodiode reached a certain voltage. Their setup incorporated the use of a He-Ne laser, a photodiode, and an A/D connection to a computer to monitor the results. One of the stated emphases was the incorporation of modern chemical technology into the classic EDTA titration.

Because of the cost of the instrumentation used in the aforementioned article, we were motivated to build a less expensive laser spectrometer. In the present work we have developed a laser spectrometer for the EDTA titration of magnesium or calcium ions that is designed around a handheld laser pointer as the source and a photoresistor as the detector.

Indicator Characteristics

For spectrometric detection of EDTA titrations to succeed the indicator has to have a color change that can be exploited. The absorption spectra for both complexed and free Calmagite are shown in Figure 1. Lindstrom and Diehl (5) developed Calmagite as a replacement indicator for Eriochrome Black T. It is stable in aqueous solutions over an extended period of time and has a much sharper color change than that of Eriochrome Black T. In a pH 10 buffer, Calmagite complexed with magnesium has a maximum absorbance at 537 nm, as seen in trace A of Figure 1. When enough EDTA has been added to complex all of the magnesium the Calmagite becomes a free ligand; this results in a red shift in the absorbance maximum to the range of 610–670 nm (Figure 1, trace B). Most handheld laser pointers emit radiation with a wavelength of light between 630–670 nm. Before the endpoint the spectrum resembles trace A and no absorption of light from the laser pointer will occur. However, once enough EDTA has been added, the spectrum changes to trace B and light will be absorbed.

Detector Characteristics

A simple and inexpensive device that responds to light is a photoresistor. Resistance in a photoresistor is inversely proportional to the number of photons that strike the surface. With the addition of the voltage-divider circuit shown in Figure 2 a pH-volt meter can be used to measure the voltage drop across the photoresistor.

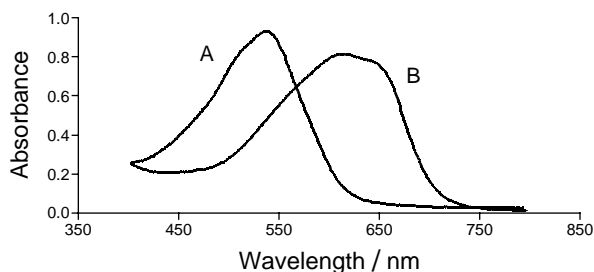


Figure 1. Visible spectra of the Calmagite indicator in an aqueous ammonia buffer at a pH of 10 containing magnesium ions: (A) without EDTA present and (B) with EDTA added to the solution.

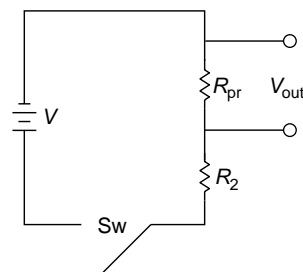
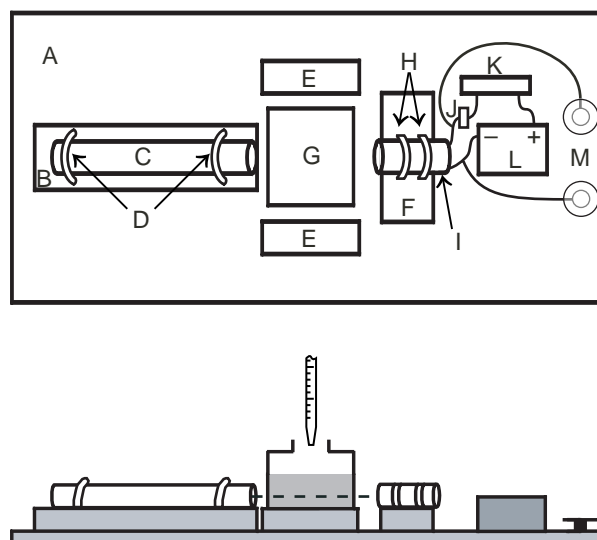


Figure 2. Schematic of the detector circuit: V—1.5-V battery, R_{pr} —photoresistor, R_2 —1000-ohm resistor, and Sw—single-pole, single-throw switch.

Figure 3. Diagram of laser spectrometer. (Top) Top view layout of laser pointer spectrometer. (Bottom) Side view of laser spectrometer.

- A—spectrometer board (poplar wood)
- B—laser-pointer base (poplar wood)
- C—laser-pointer holder and alignment PVC pipe
- D—plastic clamps
- E—titration vessel support (poplar wood)
- F—detector base (poplar wood)
- G—square titration vessel
- H—plastic clamps
- I—detector alignment PVC pipe
- J—1000-ohm resistor
- K—C-type battery holder
- L—single-pole, single-throw switch
- M—voltage out screws



Instrumentation

A layout of the spectrometer is shown in Figure 3. Twelve of these were constructed on site with material available at any hardware and electronics store. Detailed instructions are given in the Supplemental Material.^W

Procedure

Alignment of the Spectrometer

Prior to any readings the laser spectrometer must be aligned. This involves rotating the laser pointer so that the maximum quantity of light strikes the detector.

Beer's Law Test

To demonstrate that the spectrometer gives a linear response between absorption and concentration, a Beer's law plot with copper(II) chloride (or any solution that absorbs between 630–670 nm) can be constructed. Two key measurements, V_0 and V_{100} , must be recorded before data for a Beer's law plot can be obtained. V_0 is the voltage when no light reaches the detector and is found by covering the PVC pipe that contains the photoresistor. V_{100} , which is similar to a 100% T setting, is found by placing water in the titration bottle and recording the voltage. Once V_{100} is found, the water is replaced with 50 mL of a 5.6×10^{-2} M solution of copper(II) chloride and the voltage is recorded. Water is then added to the titration vessel from a buret and the voltage recorded after each addition.

Titration

Before the titration begins a known quantity of magnesium solution and 3 drops of Calmagite indicator are added to the titration vessel. EDTA is added in 10-mL increments until the solution begins to turn dark red, at which point the aliquot of EDTA is decreased to 0.2 mL. Once the solution has turned blue, four additional 1-mL portions of EDTA

are added from the buret into the bottle. Voltages are recorded after each addition of EDTA.

Results and Discussion

Beer's Law

To generate a Beer's law plot the data have to be transformed into an absorbance. A detailed explanation of the transformation is given in the Supplemental Material.^W The data plotted in Figure 4 show that the laser spectrometer responds in a Beer's law fashion with a R^2 value of 0.9965. A plot of the mV from the spectrophotometer versus the mL of EDTA for the titration of a magnesium sample is shown in Figure 5. At the beginning of the titration the solution is red, the absorbance of the laser light is minimal, and the mV from the spectrophotometer is low (area A). As the moles of EDTA added to the solution become equal to moles of magnesium in the solution, the EDTA removes the magnesium from the Calmagite indicator, the solution turns from red to blue, the light from the laser is absorbed, and the millivolts increase dramatically (area B). As more EDTA is added to the solution, the concentration of the free Calmagite decreases, and the absorbance correspondingly goes down (area C).

Calculation of the Endpoint

At the molecular level, the endpoint occurs once all of the magnesium has become complexed with EDTA and ideally this point correlates with the highest mV reading obtained. In reality it is experimentally very difficult to collect the exact data point at which the Calmagite becomes free. Therefore, the data are divided into areas B and C as shown in Figure 5. A least-squares analysis is applied to the data from both areas, with the intersection between these two regression lines corresponding to the true endpoint of the titration. Typical student titrations with the spectrometer generate a standard deviation in endpoint volume of ± 0.24 mL, com-

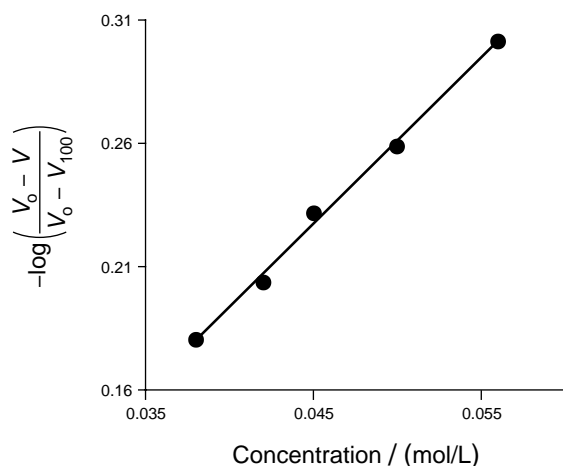


Figure 4. Absorbance versus concentration for 3.8×10^{-2} M to 5.6×10^{-2} M solutions of copper(II) chloride. R^2 value of 0.9965.

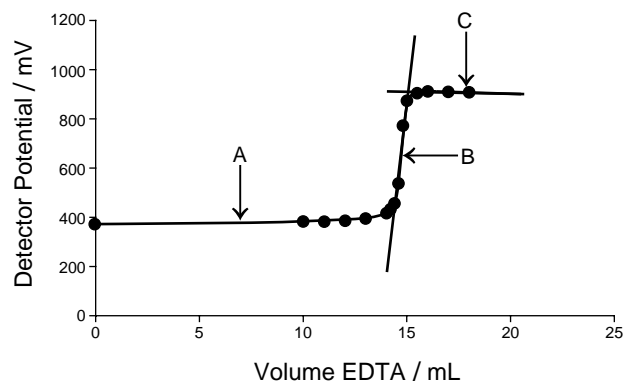


Figure 5. Detector potential versus volume of EDTA for titration of magnesium with EDTA (A) at beginning of titration, (B) near endpoint, and (C) after endpoint.

pared to a standard deviation of ± 0.50 mL in endpoint volumes for a visual based determination.

Hazards

Appropriate MSDS sheets should be available for EDTA, calcium carbonate, magnesium chloride, and copper(II) chloride. No extensive safety procedures are required for the chemicals EDTA, calcium carbonate, magnesium chloride, copper(II) chloride and Calmagite other than those observed in normal laboratory conditions. 6 M hydrochloric is corrosive and should be handled with care. Laser-pointers are a Class IIIa laser product. Care should be taken to avoid direct eye exposure.

Conclusions

Over the three years that this laser spectrometer has been in use, students have responded favorably to the EDTA titration. They enjoy working with the laser pointer and are interested in watching the millivolts change as the color of the solution changes. Since the endpoint is now determined

graphically students do not complain about how hard it is to identify the endpoint. Use of the spectrometer reduces the degree of uncertainty and error in one part of our EDTA titrations, however overall standard deviations are still greatly dependent on the skill of the student and their willingness to be careful and precise.

Supplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

Literature Cited

1. *Reagent Chemicals*, 8th ed.; American Chemical Society: Washington, DC, 1993.
2. Hart, J. R. *J. Chem. Educ.* **1984**, *61*, 1060–1061.
3. Hart, J. R. *J. Chem. Educ.* **1985**, *62*, 75–76.
4. Mossman, D. M.; Kooser, R. G.; Welch, L. E. *J. Chem. Educ.* **1996**, *73*, 82–85.
5. Lindstrom, F.; Diehl, H. *Anal. Chem.* **1960**, *32*, 1123–1127.