

## A Copper(II) Aspirinate Project for the General Chemistry Laboratory

A successful general chemistry laboratory course not only instructs the students but also captures their interest. To create an informative, stimulating course, single projects which extend over a semester with a logical sequence of experiments and with the challenge of unknowns have been used successfully at Brandeis University (1). One project is the synthesis and analysis of aspirin and of copper(II) aspirinate.

A study of aspirin as a series of experiments in a general chemistry laboratory is not novel (2), but the focus of the course at Brandeis University has been shifted away from the usual concerns of organic chemistry (isolation of aspirin from commercial tablets, melting point, and ultraviolet, infrared, and nmr spectra) to quantitative methods of analysis. Students determine the percent of acetylsalicylic acid in the aspirin they synthesized by three titrimetric methods—phenolphthalein endpoint, conductometric (3), and potentiometric (4), and by a spectrophotometric analysis (5).

A significant extension of the aspirin project introduced at Brandeis University is the synthesis and analysis of copper(II) aspirinate. By this addition, students have dealt with inorganic systems, as well as organic, and have tested out more analytical methods. Furthermore, students are intrigued by the idea that the interaction of copper(II) and aspirinate ions may be related to the pain relieving effect of aspirin. J. Schubert has suggested that the shift of copper(II) ions from cells to the blood which occurs in several human disorders may be reversed by the chelating of the copper(II) ion by aspirin (6).

The preparation of copper(II) aspirinate from copper(II) acetate and aspirin is straightforward (7), but it allows students to check their synthetic techniques. Most percent yields were between sixty and seventy percent. As part of their reports, students were asked which reagent, copper(II) acetate or acetylsalicylic acid, was used in excess and why, and they were asked by what chemical tests and physical measurements could they distinguish between the starting material, blue copper(II) acetate, and the product, blue copper(II) aspirinate.

The weight percent of copper in the student-prepared copper(II) aspirinate was then measured by complimentary methods of analysis: electrogravimetric, spectrophotometric, and titrimetric.

Equipment for the electrodeposition of copper need not be expensive. Electrodes of copper screening and graphite rod may be used. Any source of dc power yielding 10–15V and a current between 0.5 and 1.0 A suffices. During an hour, with

Sample Student Results			
Weight Percent Cu in $\text{Cu}(\text{C}_9\text{H}_7\text{O}_4)_2$ , theoretical 15.06%			
Student	Electro- gravimetric	Spectro- photometric	Titrimetric
1.	14.87	14.1	15.12
2.	15.01	15.4	15.28
3.	15.04	15.0	14.77
4.	15.25	14.9	16.05
5.	15.26	15.1	15.07

constant stirring, a gram of copper(II) aspirinate is quantitatively reduced from an aqueous solution of nitric and sulfuric acid. The observed weight percent copper generally ranged from 14 to 15.3%, the theoretical value being 15.06%.

For a spectrophotometric analysis of copper, suitable colorimetric reagents are tetraethylenepentamine (8) and ethylenediamine. The absorptivity (that is the extinction coefficient) of the former is about twice that of the latter, but the latter has an interesting extra feature. In a solution of excess copper(II) ion, the principal chelate is the blue  $\text{Cu}(\text{en})^{2+}$  ion ( $\lambda_{\text{max}} = 670 \text{ m}\mu$ ,  $\log K_1$  stability = 10.75) whereas in excess ethylenediamine, it is the purple  $\text{Cu}(\text{en})_2^{2+}$  ion ( $\lambda_{\text{max}} = 550 \text{ m}\mu$ ,  $\log K_2$  stability = 9.28). The students investigated the formation of both chelates by the method of continuous variation with 0.02 M copper(II) sulfate and 0.02 M ethylenediamine before they used ethylenediamine to analyze their copper(II) aspirinate. Values of the weight percent copper in copper(II) aspirinate obtained spectrophotometrically ranged from 14.0 to 15.5%.

The copper(II) ion in copper(II) aspirinate may be titrated with EDTA (ethylenediaminetetraacetic acid). The procedure followed at Brandeis University involves dissolving the copper(II) aspirinate in 1:1 water:ethanol acidified with sulfuric acid and titrating aliquots of the solution. To each aliquot is added a known volume of EDTA solution, some pH = 4.8 buffer, and a few drops of the indicator, PAN, which is 1-(2-pyridylazo)-2 naphthol. The excess of EDTA is then titrated with a standard solution of copper(II) ion. The standard Cu(II) solution is prepared by oxidizing copper wire with nitric acid, and the solution is used initially to standardize the EDTA solution. The advantages of this procedure are: only 0.1 g copper(II) aspirinate is needed for a series of titrations, the concentration of the EDTA solution is small, 0.005 M, so that excessive time is not spent dissolving the dihydrate of the disodium salt of EDTA, and the EDTA solution is standard-

ized by the same procedure used to determine the weight percent copper in copper(II) aspirinate. The weight percent copper measured by the EDTA titrations, 14.0 to 16.5%, varied more than those recorded by the other two analytical methods. This variation may be due to errors in preparing the two copper(II) solutions and in pipeting the copper(II) aspirinate and EDTA portions. The results reported by five students are shown in the table.

Having completed the analyses, the students are able to intelligently compare the alternative methods. The advantage of the electrogravimetric procedure is that it is the most accurate but it requires the largest weight and time per sample. The spectrophotometric analysis may require the smallest size sample and least time per sample, but it is the least accurate and most expensive. The titration experiment was a compromise on accuracy, size of sample, and time and involved the least expensive equipment. A final question asked each student was, "if you were to analyze a sample of copper(II) aspirinate by only one method, which method would you choose and why?"

Some students measured the magnetic susceptibility of copper(II) aspirinate using a Faraday Balance (Cahn #7600). They found that acetylsalicylic acid is diamagnetic while the three copper(II) compounds: the aspirinate,  $\text{Cu}(\text{C}_9\text{H}_7\text{O}_4)_2$ , the acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , and the sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , are paramagnetic. Furthermore, of the three copper(II) sub-

stances, the first two have magnetic susceptibilities of about the same value which is less than that of the third by about a factor of 2. The known crystal structures of the three copper(II) compounds were presented to the students. The aspirinate and acetate monohydrate are dimeric, while the sulfate pentahydrate is not (9). The students were able to attribute the lower magnetic susceptibilities of the first two compounds to the interaction between the odd electrons on two neighboring copper(II) ions of each dimer.

The copper(II) aspirinate project constituted a successful general chemistry laboratory course. It introduced students to syntheses and a variety of analytical methods. Furthermore, the coherent aspect of the unifying project was more acceptable and reasonable to the students than isolated exercises, and the research flavor inspired student interest.

#### Literature Cited

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