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Analysis of copper(II) using the ascorbate/oxygen system – a valuable undergraduate resource

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ABSTRACT

In deionised water, ascorbic acid (AH^-), through oxidation by oxygen in the presence of copper(II), was found to degrade with zero-order kinetics. The magnitude of the reaction rate varied directly with the copper(II) concentration. At a higher pH (7.4), the same reaction was found to be pseudo-first order. Once again, the magnitude of the rate increased linearly with copper(II) concentration at a micromolar level. Dissolved oxygen levels, in excess AH^- and trace copper(II), displayed similar kinetics under both conditions. Monitoring of either AH^- levels or dissolved oxygen concentration was found to be a useful novel undergraduate practical laboratory for trace copper(II) determination. Students can measure the kinetics for standards and their unknown copper solution and quantitate the unknown copper.

Keywords: ascorbic acid, copper, kinetics.

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Introduction

Ascorbic acid (AH_2) is an effective hydrophilic antioxidant. With a pKa of 4.17, it typically exists as an anion AH^- : ascorbate. It is widely used as such in preserved foods^[1,2] and it is an important vitamin for humans. The two-electron oxidation of AH^- by oxygen catalysed by transition metals has been investigated for more than 80 years^[3]. There have been kinetic studies of the rate of this reaction, catalysed by Cu^{II} or Fe^{III} , particularly as a function of pH, and a review has appeared.^[4] AH^- has recently been studied as a marker for oxidative potential in the assessment of air quality.^[5] There is a protective level of AH^- in the epithelial fluid lining the lungs and if particulates loaded with Cu^{II} are breathed in, a catalytic reaction ensues. Thus, the oxidative potential, through the presence on AH^- , is seen as a good indicator of air quality.^[5] This system has also been employed for the spectroscopic determination of ascorbic acid^[6] and the present work is the first report of the system used for copper(II) detection. The AH^- oxidation reaction has seldom found its way into undergraduate laboratories. However, in Technological University (TU) Dublin, it has been a standard second year analytical/physical chemistry practical for over 20 years. In addition, it has formed the basis of final year undergraduate projects. There are some valuable learning outcomes from this particular system as this paper will describe. The aim of the work is to demonstrate a linear relationship between kinetic measurements and Cu^{II} concentration and to use this to determine the concentration of an unknown sample.

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Results and discussion

Following the AH^- concentration change by spectroscopy

Initially, a spectrum of AH^- (0.2 mM in deionised water) was recorded using a quartz cuvette and the λ_{max} was determined to be 257 nm. The challenge is to locate deionised water of good enough quality so that the absorbance at 257 nm is constant for 10 min. This is dependent on the cleanliness of the glassware and the quality of the water. Next, a

series of stock solutions were prepared. By serial dilution of the 100 ppm Cu^{II} stock solution, Cu^{II} was added to the 0.2 mM AH^- solution in deionised water at micromolar levels as shown in Fig. 1.

The absorbance of the AH^- decreased more rapidly with increasing Cu^{II} concentrations. It will be apparent to the student that Cu^{II} is present at very low concentration levels. As can be seen, the slope of the plots follows a zero-order rate of decrease of AH^- . It can also be seen that there is a slight decrease in the intercept, even though each solution was freshly prepared. By plotting 'minus the slope' against the copper concentration, (Supplementary Fig. S1) a linear relationship ($y = 5.7 \times 10^{-5}x + 2.5 \times 10^{-4}$, $R^2 = 0.98$, $n = 6$, $\text{LOD} = 8.3 \mu\text{M}$) was found. Thus, using safe readily available chemicals and a UV-vis spectrometer, it is possible

to obtain linear behaviour for a range of micromolar copper concentrations. Students are encouraged to bring in samples from their home for analysis. Students are asked to calculate the LOD of each method, and to quantitate their copper sample. The LOD was determined as outlined in the Supplementary material. The typical pH of a deionised water solution in equilibrium with air is 5.7 owing to CO_2 dissolution into the water.^[7] The pH of the deionised water was measured to be 6.0 ± 0.5 and that of 0.2 mM ascorbic acid was 4.1 ± 0.1 . The conductivity of the deionised water was between 65 and 95 $\mu\text{S}/\text{cm}$.

Fig. 2 is a similar experiment to that presented in Fig. 1, but with the solution buffered to pH 7.4 using $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (0.066 M). It can be seen that the rate of oxidation of AH^- is much faster. It can be seen that even with no Cu^{II}

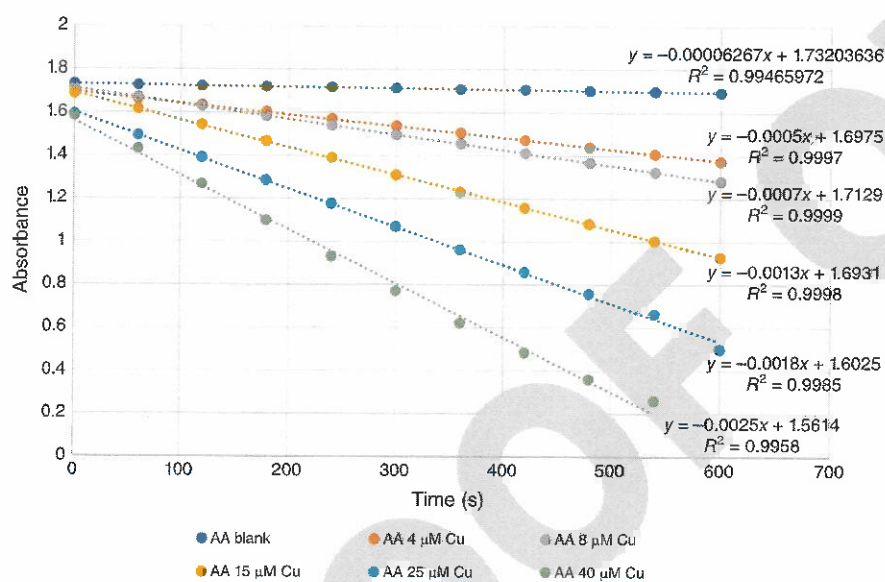


Fig. 1. A plot of 0.2 mM ascorbic acid (AA) degradation using absorbance with various copper (Cu) concentrations (0, 4, 8, 15, 25, 40 μM) vs time (s) in deionised water.

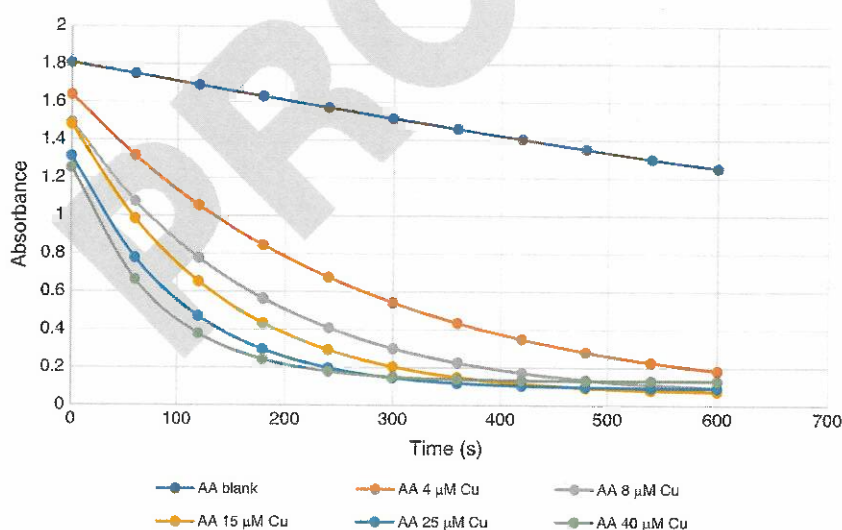


Fig. 2. A plot of 0.2 mM ascorbic acid (AA) degradation using absorbance with various copper (Cu) concentrations (0, 4, 8, 15, 25, 40 μM) vs time (s) in phosphate buffer at pH 7.4.

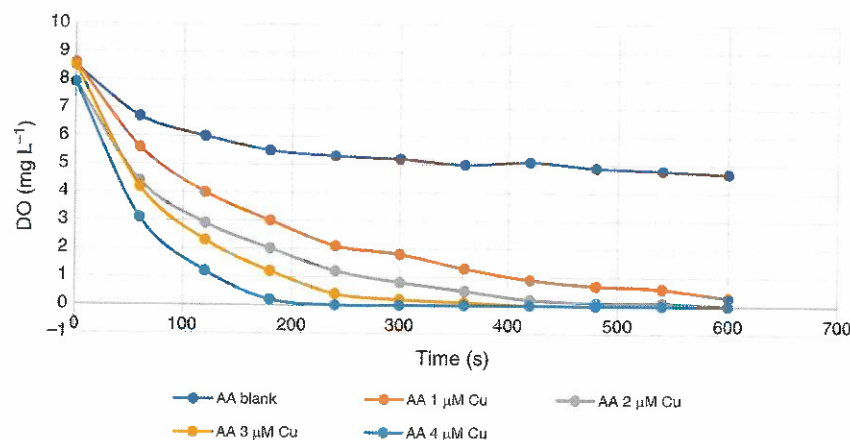


Fig. 3. Degradation of dissolved oxygen (mg L^{-1}) in 10 mM AA with various copper (Cu) concentrations (0, 1, 2, 3, 4 μM) vs time (s) in phosphate buffer at pH 7.4.

added, the blank decreased somewhat. When the \ln (absorbance) was plotted against time (Supplementary Fig. S2), linear plots associated with pseudo-first-order decay resulted. Furthermore, when the slope of these plots was plotted against the Cu^{II} concentration (Supplementary Fig. S3), a line was obtained ($y = 8.6 \times 10^{-5}x + 1.37 \times 10^{-3}$, $R^2 = 0.98$, $n = 4$). Thus, there is a transition from zero-order rate to pseudo-first-order decay at higher pH. It has been reported that the rate of oxidation of ascorbic acid increases by several orders of magnitude with an increase in pH.^[4,8]

Following the dissolved oxygen using a probe

In deionised water with an excess of AH^- (10 mM), when the dissolved oxygen levels are monitored, they also decrease linearly with time, indicating zero-order behaviour (Supplementary Fig. S4), and the magnitude of the slopes of these decays increases with copper concentration as follows: $y = 6 \times 10^{-4}x + 6 \times 10^{-3}$ ($R^2 = 0.99$, $n = 3$). This correlates with the behaviour of the AH^- in Fig. 1.

At higher pH, the behaviour of oxygen concentration as a function of time is pseudo-first order, as can be seen in Fig. 3. Once again, the AH^- is in excess and it is notable that the range of copper concentrations is much smaller than before: from 1 to 4 μM . A plot of \ln (absorbance) against time yields straight lines (Supplementary Fig. S5). A plot of magnitude of the slopes of these lines (Supplementary Fig. S6) yields $y = 1.7 \times 10^{-3}x + 4 \times 10^{-4}$ ($R^2 = 0.99$, $n = 4$, LOD = 0.14 μM). The sensitivity of the latter technique rivals that of flame atomic absorption or graphite furnace atomic absorption spectroscopy in terms of limit of detection for copper.

Conclusion

This is a simple, safe series of experiments with good learning outcomes. The chemicals used are environmentally safe. The novelty is the facile determination of copper at

micromolar levels through the measurement of rate constants. Either of these can be observed spectroscopically or by monitoring dissolved oxygen, which, however, has to be recorded by hand. This series of experiments comprises a demonstration of a zero-order rate of reaction and a pseudo-first-order rate of reaction. The specificity of the technique could be assessed by using other cations; in particular, Fe^{III} does interfere (see Supplementary Fig. S7). The premise may be expanded for the purpose of final year projects through the monitoring of products of the reaction such as hydrogen peroxide^[2,9] or dehydroascorbic acid.

Experimental

Ascorbic acid, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and K_2HPO_4 (Sigma-Aldrich) were analytical grade and used as received. Deionised water was used to prepare the solutions. Fresh AH^- solutions (10 mM) were prepared before each experiment. Spectra were recorded using a Shimadzu UV1900 spectrometer. A Vernier dissolved oxygen probe was calibrated using 2 M sodium sulfite, and using ambient pressure and temperature, a two-point calibration was performed.^[10]

Supplementary material

Supplementary material is available online.

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Data availability. The data from this paper are available from the corresponding author.

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