Analytical Chemistry 2.1: An Open-Access Digital Resource for Undergraduate Education in Analytical Chemistry

DePauw University Est. 1837

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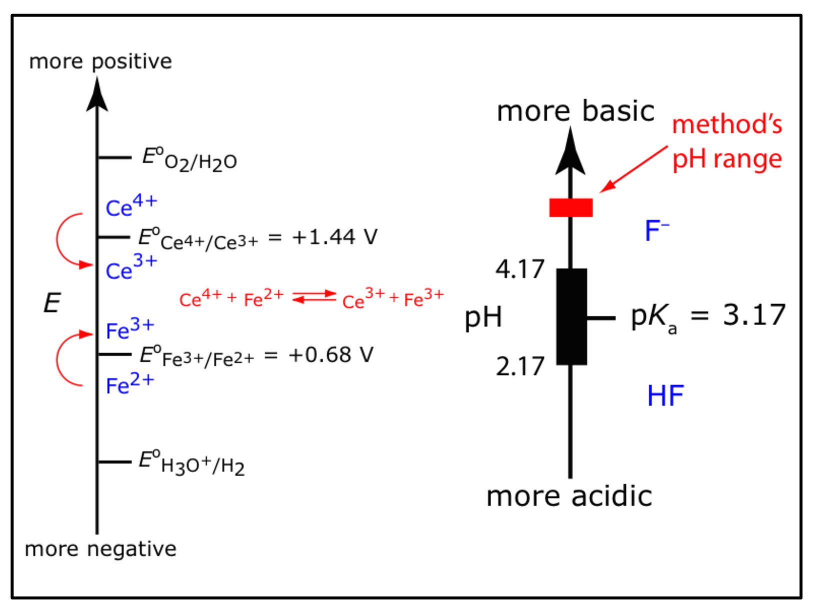
Textbook and Solutions Manual

Analytical Chemistry 2.1 is an open-access, digital textbook and accompanying solutions manual for undergraduate courses in analytical chemistry, released under a Creative Commons BY-NC-SA license and available in PDF format at no cost to faculty and students.

The topics covered in *Analytical Chemistry 2.1* (see TOC on right) include those common to introductory, undergraduate courses in analytical chemistry with an additional emphasis on topics such as sampling and method development.

The textbook's art work includes illustrations and photographs, all in color, which are available separately either as .png or as editable .ai files.

Examples of some of the textbook's features are highlighted in this panel.



A central feature of *Analytical Chemistry 2.1* is the use of ladder diagrams to help students think intuitively about the importance of controlling equilibrium chemistry when developing an analytical method. Two examples are shown on the left: one that illustrates how a mediator works in constant-current coulometry, and one that illustrates the need to control pH when using a fluoride ISE.

Examples that illustrate the development of analytical methods are highlighted throughout the textbook, either using representative methods, such as the determination of quinine in urine by fluorescence spectroscopy (shown on the right), or using experimental data, such as the optimization of an HPLC separation by controlling the mobile phase's pH (shown below).

Representative Method 10.3

Determination of Quinine in Urine

Description of Method

Quinine is an alkaloid used to treat malaria. It is a strongly fluorescent compound in dilute solutions of H_2SO_4 ($\Phi_f = 0.55$). Quinine's excitation spectrum has absorption bands at 250 nm and 350 nm and its emission spectrum has a single emission band at 450 nm. Quinine is excreted rapidly from the body in urine and is determined by measuring its fluorescence following its extraction from the urine sample.

Procedure

Transfer a 2.00-mL sample of urine to a 15-mL test tube and use 3.7 M NaOH to adjust its pH to between 9 and 10. Add 4 mL of a 3:1 (v/v) mixture of chloroform and isopropanol and shake the contents of the test tube for one minute. Allow the organic and the aqueous (urine) layers to separate and transfer the organic phase to a clean test tube. Add 2.00 mL of 0.05 M H_2SO_4 to the organic phase and shake the contents for one minute. Allow the organic and the aqueous layers to separate and transfer the aqueous phase to the sample cell. Measure the fluorescent emission at 450 nm using an excitation wavelength of 350 nm. Determine the concentration of quinine in the urine sample using a set of external standards in 0.05 M H_2SO_4, prepared from a 100.0 ppm solution of quinine in 0.05 M H_2SO_4. Use distilled water as a blank.

Questions

1. Chloride ion quenches the intensity of quinine's fluorescent emission. For example, in the presence of 100 ppm NaCl (61 ppm Cl^-) quinine's emission intensity is only 83% of its emission intensity in the absence of chloride. The presence of 1000 ppm NaCl (610 ppm Cl^-) further reduces quinine's fluorescent emission to less than 30% of its emission intensity in the absence of chloride. The concentration of chloride in urine typically ranges from 4600–6700 ppm Cl^-. Explain how this procedure prevents an interference from chloride.

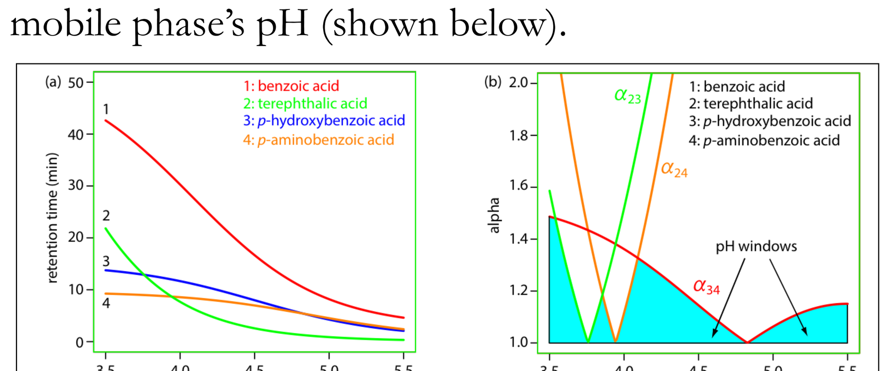


Figure 12.17 Example showing how the mobile phase pH in liquid chromatography affects selectivity: (a) retention times for four substituted benzoic acids as a function of the mobile phase's pH; (b) alpha values for three pairs of solutes that are difficult to separate. See text for details. The mobile phase is an acetic acid/sodium acetate buffer and the stationary phase is a nonpolar hydrocarbon. Data from Harvey, D. T.; Byerly, S.; Bowman, A.; Tomlin, J. "Optimization of HPLC and GC Separations Using Response Surfaces," *J. Chem. Educ.* **1991**, *68*, 162–168.

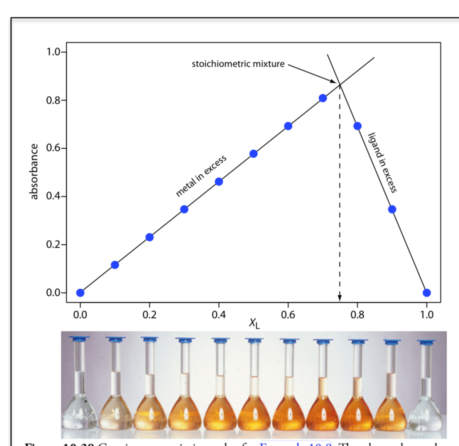


Figure 10.38 Continuous variations plot for Example 10.8. The photo shows the solutions used to gather the data. Each solution is displayed directly below its corresponding point on the continuous variations plot.

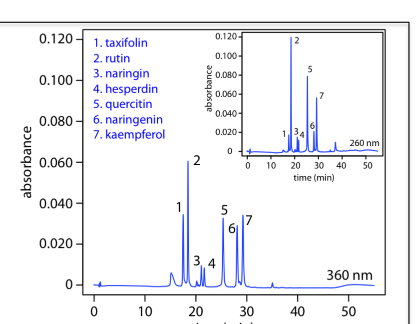


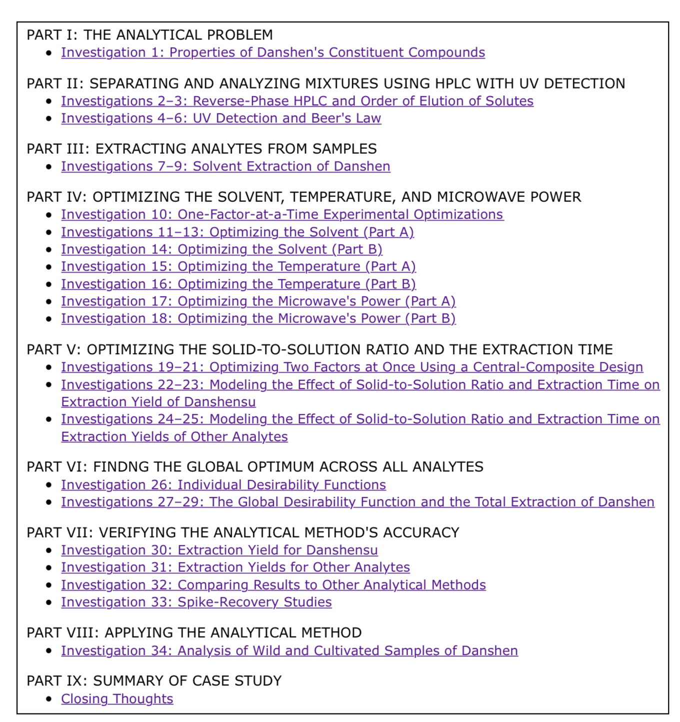
Figure 12.47 HPLC separation of a mixture of flavonoids with UV/Vis detection at 360 nm and, in the inset, at 260 nm. The choice of wavelength affects each analyte's signal. By carefully choosing the wavelength, we can enhance the signal for the analytes of greatest interest. Data provided by Chistopher Schardon, Kyle Meinhardt, and Michelle Bushey, Department of Chemistry, Trinty University.

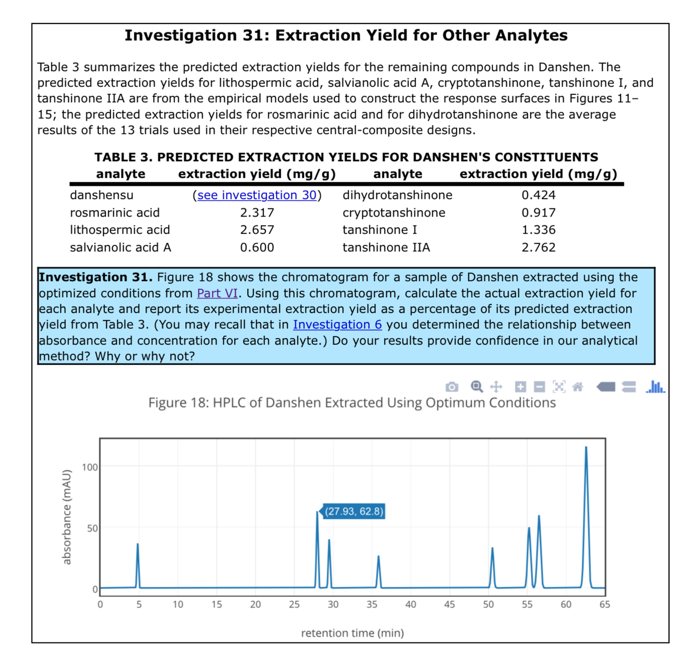
Finally, the textbook's illustrations, worked examples, and end-of-chapter problems draw upon experimental data from the literature and collected in lab, as illustrated on the left for the method of continuous variations and for the HPLC separation of flavonoids.

Contextual Case Studies

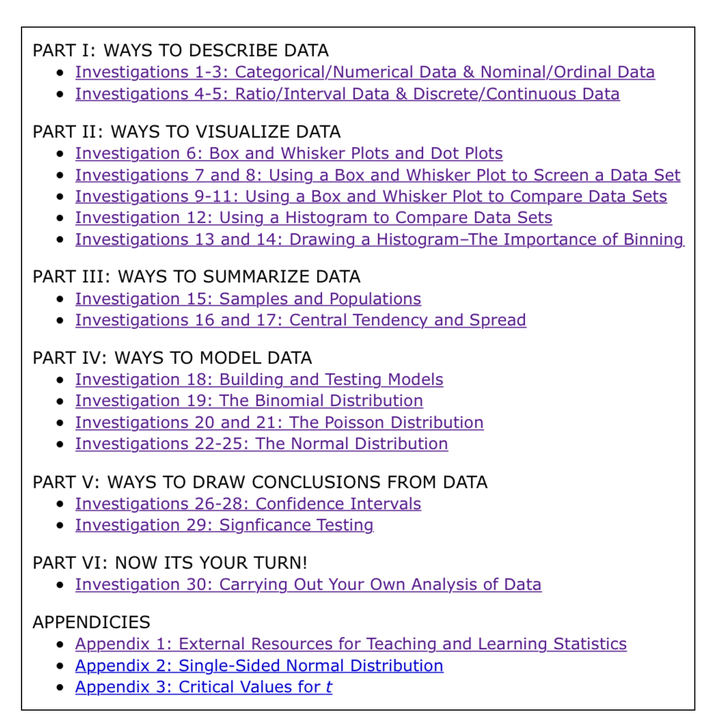
New to this edition of *Analytical Chemistry 2.1* are contextual case studies that illustrate topics covered in the textbook. Each case study is available in two formats: a text file that faculty can use as is or modify to meet local needs, and a web-based version that allows students to interact with the case study's data using figures created with Plotly (https://plot.ly/). Each case study includes an Instructor's Guide, which provides additional background information and suggested responses to the case study's investigations. Two case studies are complete and are highlighted below; additional case studies are in development.

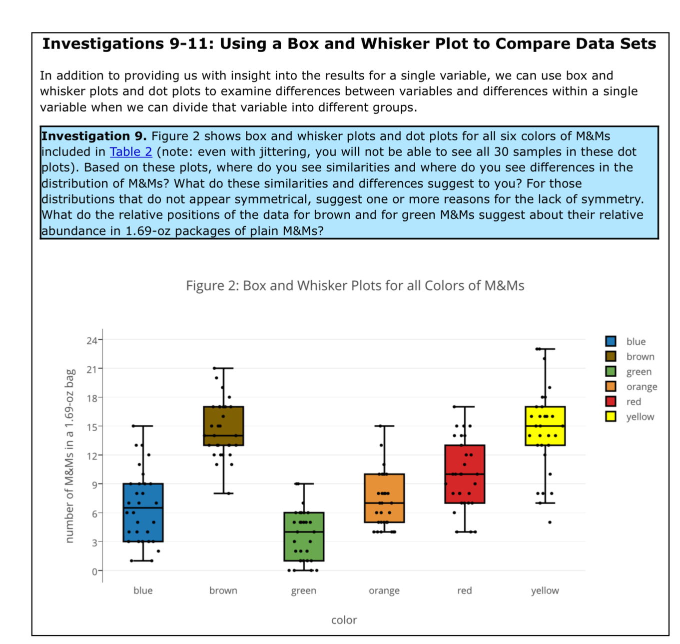
Case Study 1: The first case study introduces method development in the context of the analysis of several pharmacologically important components in a medicinal plant, and is based on results published in the literature as "Simultaneous extraction of hydrosoluble phenolic acids and liposoluble tanshinones from *Salvia miltiorrhiza radix* by an optimized microwave-assisted extraction method," the full reference for which is Fang, X.; Wang, J.; Zhang, S.; Zhao, Q.; Zheng, Z.; and Song, Z. *Sep. Purif. Technol.* **2012**, *86*, 149-156. The topics covered in the module (see below left) include selecting a mobile phase and an analytical wavelength, optimizing the experimental conditions for extracting the analyte, and evaluating the method's accuracy. A typical example of an investigation in its web-based format (see below right) includes data in the form of a chromatogram that students can manipulate to find retention times and peak heights.





Case Study 2: The second case study introduces students to ways of thinking about and working with data using, as an example, the analysis of 1.69-oz packages of plain M&Ms. The module's topics and an example of a typical investigation are shown below.





Case studies in the planning stages will explore topics such as sampling, standardization methods, calibration errors, paper-based assays, proficiency studies, and additional examples of method development.

R Functions, Packages, and Shiny Apps

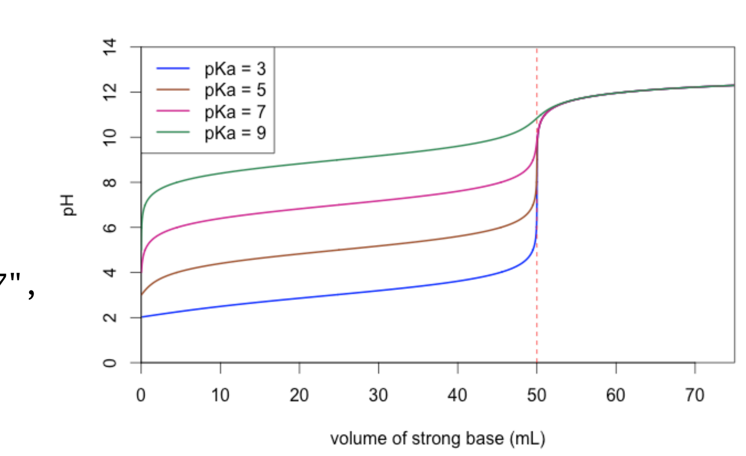
Also new to this edition of *Analytical Chemistry 2.1* are materials developed for use in the R programming environment (https://www.r-project.org/), including functions and packages for generating figures and for simulating data, and learning modules built using the R Shiny package (http://shiny.rstudio.com/).

On the right is an R function that plots the titration curve for a weak acid-strong base titration given the analyte's and the titrant's concentration, the analyte's pK_a, the solvent's pK_w, and the volume of solution. Optional arguments allow for displaying the equivalence point and for overlaying two or more titration curves. An example of the function's output is shown below right with the code shown to the left of the figure.

30 lines (30 sloc) | 973 Bytes

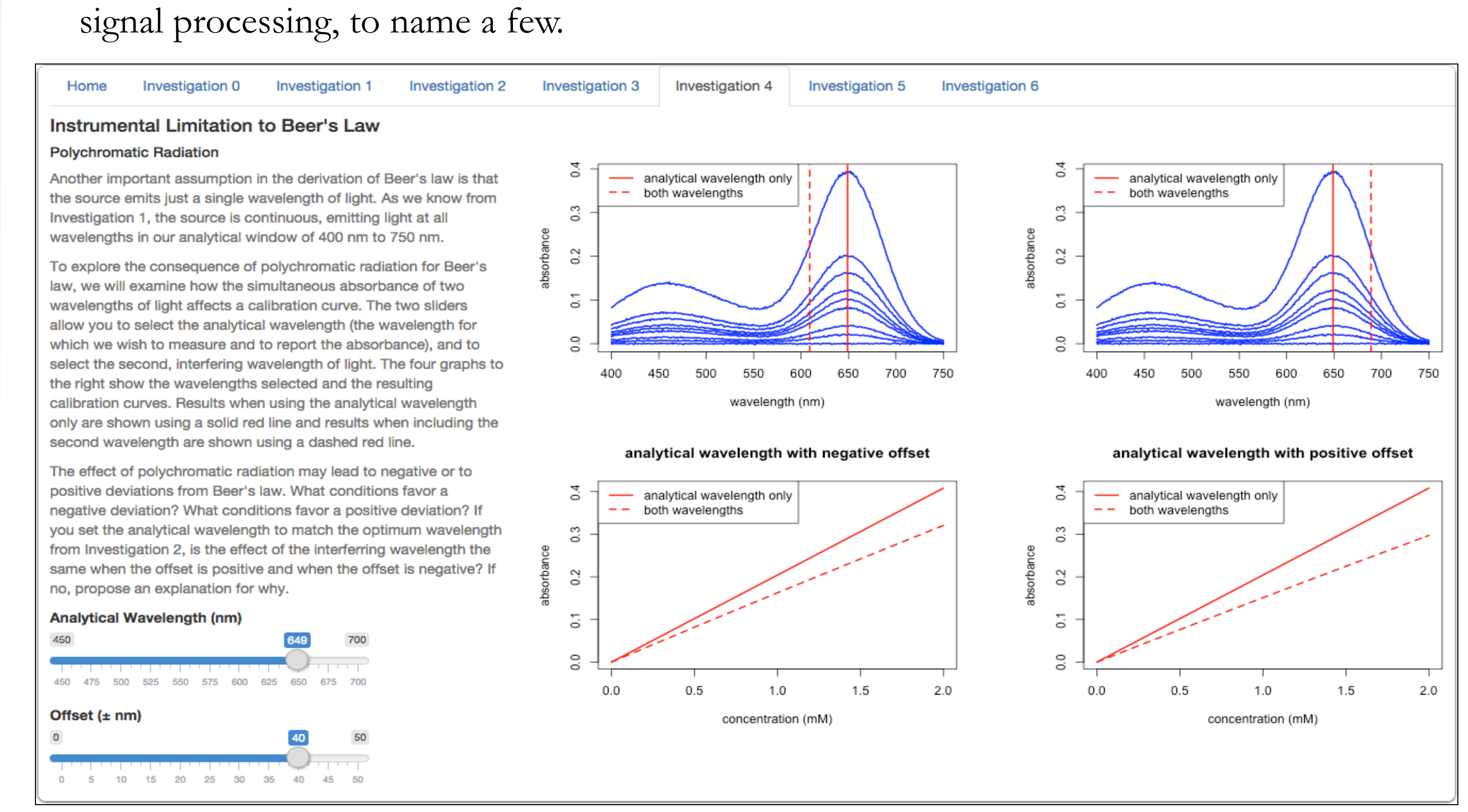
```r
# titration of monoprotic weak acid with a monoprotic strong base
wa_sb = function(conc.acid = 0.1, conc.base = 0.1, pka = 5, pkw = 14,
                 vol.acid = 50, eqpt = FALSE, overlay = FALSE, ...) {
  veq = conc.acid * vol.acid/conc.base
  ka = 10^-pka
  kw = 10^-pkw
  ph = seq(1, pkw, 0.01)
  h = 10^-ph
  oh = kw/h
  delta = h - oh
  alpha = ka/(ka + h)
  volume = vol.acid * (conc.acid * alpha - delta)/(conc.base + delta)
  df = data.frame(volume, ph)
  df = df[df$volume > 0 & df$volume < 2 * veq, ]
  rownames(df) = 1:nrow(df)
  if (overlay == FALSE) {
    plot(df$volume, df$ph, type = "l", lwd = 2, xlim =
           c(0, 1.5 * veq), ylim = c(0, pkw),
            xlab = "volume of strong base (mL)", ylab = "pH",
         xaxs = "i", yaxs = "i", ...)
  } else {
    lines(df$volume, df$ph, type = "l", lwd = 2, ...)
  }
  if (eqpt == TRUE) {
    x = c(veq, veq)
    y = c(0, pkw + 1)
    lines(x, y, type = "l", lty = 2, col = "red")
  }
  invisible(df)
}
```

```r
wa_sb(pka = 3, col = "blue", eqpt = TRUE)
wa_sb(pka = 5, col = "sienna",
   overlay = TRUE)
wa_sb(pka = 7, col = "violetred",
   overlay = TRUE)
wa_sb(pka = 9, col = "seagreen",
   overlay = TRUE)
legend(x = "topleft",
   legend = c("pKa = 3", "pKa = 5", "pKa = 7",
              "pKa = 9"),
   lwd = rep(2, 4),
   col = c("blue", "sienna", "violetred",
           "seagreen"),
   lty = rep(1, 4))
```



The R package titrationCurves includes functions for acid-base, redox, complexation, and precipitation titrations. Additional functions and packages are planned for visualizing topics in the statistical analysis of data, the optimization of experiments, and in equilibrium chemistry, and for generating data sets, to name a few.

Also under development are interactive learning modules, such as the one illustrated below. These learning modules are built using the Shiny package and run locally on a computer with R installed or from a remote server (http://www.shinyapps.io/). Additional Shiny Apps are in development to explore topics such as the central limit theorem, sampling, and signal processing, to name a few.



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Inspiration: participants in summer curriculum workshops sponsored by the Analytical Sciences Digital Library (ASDL); visit http://bit.ly/1QeZ5mb to review other materials.

References: to access, review, and use these materials, visit http://bit.ly/1OYIczn and https://github.com/dtharvey.