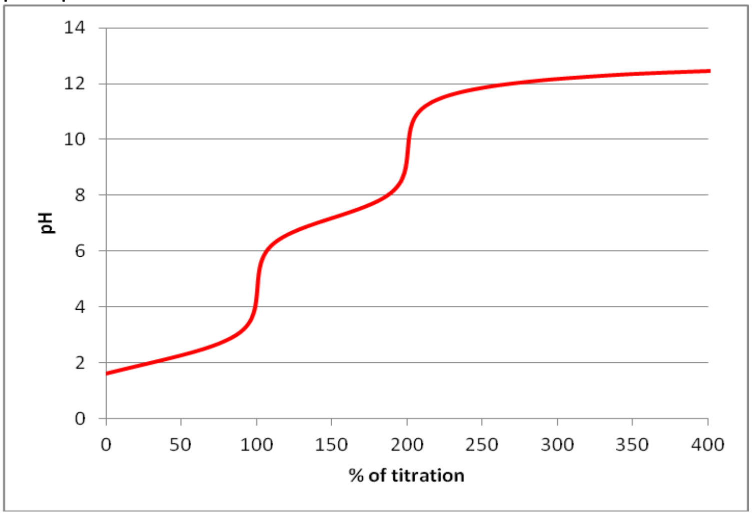
15. Determination of H_3PO_4 or citric acid using volumetric and pH-metric titrations

Titration of the polyproton acids, for example phosphoric acid H_3PO_4 or citric is not trivial. Although often listed together with strong mineral acids (hydrochloric, nitric and sulfuric), the phosphoric acid is relatively weak, with pK_{a1}=2.15, pK_{a2}=7.20 and pK_{a3}=12.35. That means titration curve contains only two inflection points and phosphoric acid can be titrated either as a monoprotic acid or as a diprotic acid. In the first case acid has to be titrated against indicator changing color around pH 4.7 (for example Bromocresol Green or Methyl Orange), in the second case - against indicator changing color around pH 9.65 (for example Thymolphthalein). Phenolphthalein should not be used, as it starts to change color around pH 8.2, when phosphoric acid is titrated in about 95%.

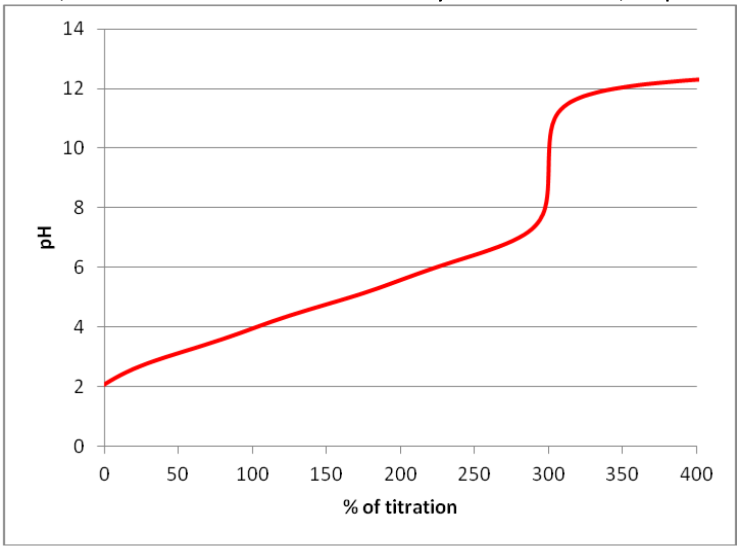


If the sample is pepsi, one cannot titrate it classically (using dyes as indicators, procedure no. 1 below). For pehametric titration of pepsi using 0.1M NaOH, student should measure exactly 50 mL of this beverage to a beaker, degas it mixing vigorously few minutes, add water to the total volume 150 mL of and then titrate (procedure 2).

Titration curve calculated for 0.1M solution of phosphoric acid titrated with 0.1M solution of strong base.

As explained above, during titration of phosphoric acid can be used either Methyl Orange or Bromocresol Green and detect first end point around pH 4.7, or Thymolphthalein and detect second end point around pH 9.6. Decision which indicator should be used can be based on the approximate concentration of phosphoric acid and titrant and on personal preferences - some find it easier to detect change of the Methyl Orange from red to yellow or Bromocresol Green from yellow to blue color than the appearance of a blue hue of Thymolphthalein. We will however use both the end points (pH 4.7 and 9.6); the results of them will be averaged – see below.

Different case is citric acid (HOOC-CH_2-C(OH)(COOH)-CH_2-COOH), with pK_{a1}=3.15, pK_{a2}=4.77 and pK_{a3}=6.40. Here, the titration curve exhibits only one inflection, at pH=9.25.



If the sample is citron juice, measure exactly 4 mL of it to a beaker, add water to the total volume 150 mL and then titrate (procedure 2).

It is clear that for citric acid one should use Thymolphthalein (the reasons are the same as for H_3PO_4), but here the third inflection is detected, influencing the stoichiometry factor, here equal to three, used in calculation of the final result.

Titration curve calculated for 0.1M solution of citric acid titrated with 0.1M solution of strong base

Thus, the classical volumetric titration of polyproton acids requires first determination of the titration curve, to know the stoichiometry of the neutralization reaction. The curve can be easily determined by titrating a sample of acid using strong base and simultaneous measurement of pH. One has to note the volume of titrant added together with respective value of pH as read on the device.*/

Procedure 1 (volumetric titration)

1. Dilute the sample in the volumetric flask to the mark with distilled water and shake carefully.
2. Pipette 20 lub 25 mL (H_3PO_4 sample from teacher) or 50 mL (pepsi) or 4 mL (citron juice) into Erlenmayer flask.
3. Dilute with distilled water to 150 mL total volume.
4. (only if sample is pure H_3PO_4): Add 2-4 drops of Bromocresol Green (preferred) or Methyl Orange and titrate with NaOH solution till the color change completely from yellow to blue (red to yellow with Methyl Orange). Note the volume of titrant. Repeat points 2-4. Calculate the average titrant volume.
5. (both acids) Perform ps. 2-4 two or three times, but using Thymolphthalein and titrating till the blue color appears.

Result calculation

Depending on the indicator used reaction is:

either $H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$ or $H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$

However, for citric acid only the following reaction is useful in quantitative analysis:

$C_3H_5O(COOH)_3 + 3NaOH \rightarrow C_3H_5O(COONa)_3 + 3H_2O$

Consequently, the stoichiometric ratio of sodium hydroxide and phosphoric acid is either 1:1 or 2:1, but that for citric acid is 3:1..

Calculate the mass of phosphoric acid in the initial sample independently for these two series and, finally, calculate the arithmetic average of these two results. If the sample contains **citric acid**, skip point 4 and calculate the results from the mean of 2-3 titrations using Thymolphthalein only.

Procedure 2 (pH-metric titration)

Attention: this part can be performed simultaneously with procedure 1 or separately.

1. Dilute the sample in your volumetric flask to the mark with distilled water and shake carefully.
2. Pipette 20 lub 25 mL (H_3PO_4 sample from teacher) or 50 mL (pepsi) or 4 mL (citron juice) into Erlenmayer flask.
3. Dilute with distilled water to 150 mL total volume.
4. Place the beaker on magnetic stirrer, insert the magnet in it, as well as pH-electrode. Ask the assistant to control the correctness of the installation and some advices.
5. Measure and note pH. Repeat this adding small portions of the titrant base (few drops each), noting also the actual volume of titrant added (total). Finish titration when pH exceeds ca. 12.

Processing the results

Using a computer data-sheet, plot the titration curve obtained and determine as exactly as possible the volume of titrant corresponding to the inflection points (two for phosphoric acid, one for citric acid). Calculate the respective contents of acids in the initial sample, independently for every inflection.

For more aspiring students: The preciseness of determination of the inflection point can be very improved if calculating the second derivative of the titration curve. Ask your teacher for details if want to try this procedure.

REPORT: should contain all the results obtained (the titration curves In form of plots only) and a short interpretation.

Sources: Wikipedia, http://www.titrations.info/acid-base-titration-phosphoric-acid (2012-02-10) and others, also textbooks.

*/ For Reader's information: the curves shown here in Figures were calculated using the following formula:

$$v_{titr} = -\frac{v_0\ [H^+]^5 - c_a[H^+]^3K_{a1} + [H^+]^4K_{a1} - 2\cdot c_a[H^+]^2K_{a1}K_{a2} + [H^+]^3K_{a1}K_{a2} - 3\cdot c_a[H^+]K_{a1}K_{a2}K_{a3} + [H^+]^2K_{a1}K_{a2}K_{a3} - [H^+]^3K_w - [H^+]^2K_{a1}K_w - [H^+]K_{a1}K_{a2}K_w - K_{a1}K_{a2}K_{a3}K_w}{(c_{titr}[H^+] + [H^+]^2 - K_w)([H^+]^3 + [H^+]^2K_{a1} + [H^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3})}$$