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Selection of titration indicators in Analytical Chemistry

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Resumen

La selección de indicadores para titulación en Química Analítica. Los libros de texto de química analítica se centran en trazar curvas de titulación y solo se calcula el error de titulación. No se enfocan en seleccionar indicadores para una titulación dada, una situación que los profesionales podrían enfrentar en el trabajo. Los ejemplos sobre este tema están incompletos y la teoría no cubre el material necesario. En este estudio se resuelven ejemplos de selección de indicadores para valoraciones ácido-base, complexométricas y oxidación-reducción. Se muestran los fundamentos teóricos de estos ejemplos y se resuelven algunos problemas. Las valoraciones clásicas son precisas y exactas a altas concentraciones, no necesitan calibración, tienen un alto valor didáctico y constituyen muchos métodos estandarizados.

Palabras claves: Indicadores ácido-base; indicadores de iones metálicos; indicadores redox; enseñanza; educación universitaria

Abstract

Analytical chemistry textbooks are focused on plotting titration curves and only the titration error is calculated. They do not focus on selecting indicators for a given titration, a situation that professionals might face at work. Examples on this topic are incomplete and the theory does not cover the necessary material. In this study, examples of indicator selection for acid-base, complexometric, and oxidation-reduction titrations are solved. The theoretical foundations of these examples are shown and some problems are solved. Classical titrations are precise and accurate at high concentrations, do not need calibration, have a high didactic value, and make up many standardized methods.

Keywords: acid-base indicators; metal ion indicators; redox indicators; teaching; university education

Introduction

Indicators are substances used to determine the endpoint of titrations in classical analytical chemistry. One of the first indicators used was phenolphthalein, to determine the endpoint in acid-base titrations. Other indicators, such as methyl orange, soon followed[1,2]. The establishment of the pH scale by Sorensen (1909) provided a rigorous means for comparing visual indicators[3]. The determination of acid–base dissociation constants made the calculation of theoretical titration curves possible, as outlined by Bjerrum in 1914[4]. For the first time, a rational method existed for selecting visual indicators, establishing acid–base titrimetry as a useful alternative to gravimetry[2].

There are fast and efficient instrumental methods for the determination of the endpoint of a titration that dominate today in analytical laboratories. These methods include electrochemical, spectrometric[5,6], and thermometric[7] endpoints, among others. Classical methods of analysis have disadvantages such as low sensitivity and throughput for which they can be rarely used with analyte solutions <1.00 mM and are time-consuming when there are many samples. Also, indicators cannot be used by color-blind analysts. However, knowledge of the classical methods is important for their application in small laboratories where a limited number of samples is analyzed or when electrochemical, spectroscopic, or similar instruments are not available for endpoint detection. Other reasons why classical titrations remain part of the chemistry curriculum are that[8]:

- Yield high precision and accuracy results at high concentrations (> 1.00 mM), where instrumental methods have a lower performance.
- Do not need a calibration If a primary standard is used as titrant; if not, standardization of the titrant is required. That is why they are called primary or absolute methods. This represents an advantage of simplicity and speed if there are few samples.
- Have a high didactic value in the teaching of chemical balances.
- Make up many important standardized methods.

The selection of indicators must be carried out in a systematic way including explanations (theory), solved examples, and proposed problems. Kahlert *et al.* recognized that the available textbooks study indicator selection in an incomplete or disjointed manner, with rules of thumb that fail in many cases[8]. The theory should cover what is necessary for students to learn the selection of indicators. The problems proposed in these books regarding indicators only calculate

the titration error but not which indicator is suitable for a certain titration. Most of these texts do not solve examples on selecting an indicator for a given titration, a situation that professionals might face at a laboratory when performing at work. In these situations, the aim is not only to calculate a titration curve but also to determine which indicators are suitable for it depending on the reagents used and their concentration. This is the kind of theory, examples and problems that are rarely, if ever, found in textbooks.

For example, in Skoog's Analytical Chemistry textbook[5], the chapter on metal ion titrations has no examples on indicator selection, but there is a solved example where the error when using a certain indicator is calculated. However, that example does not mention that the formation constant of the metal-ligand complex must be more than 10,000 times greater than that of the metal-indicator complex[9] nor is it requested to select an indicator from a list.

An indicator that is suitable for a certain titration must transition within the inflection of the equivalence point and the titrant must react with the indicator only at the equivalence point. The latter implies that the indicator must:

- be much weaker than the analyte in acid-base titrations. This is true if the pKa value of the indicator is within the pH values of the inflection of the titration curve,
- form a complex with the analyte with a formation constant 10,000 times lower, at least, than the titrant-analyte complex (metal ion titrations)[9] or
- have a standard potential that allows a color transition within the inflection (redox titrations).

To minimize a given titration error, the entire pH range of the indicator must be within the rapid pH change near the equivalence point. Harvey has a solved acid-base exercise on this, exercise 9.2.5, but it only gives approximate calculations[2].

This information on indicator selection, although scarce, can be found in scientific journals. Gorin (1956) describes the method for selecting appropriate indicators and the teaching of this subject[10]. Kalbus *et al*. (1976) propose an experiment where students are presented with the problem of selecting a suitable indicator for specific acid-base titrations. Two methods to accomplish this are discussed.[11] Also, an experiment to evaluate four indicators for a strong acid-strong base titration using conductivity is presented[12]. Other approaches have been used to select indicators for a given titration. Kahlert *et al.* used color maps to show how a suitable color indicator has to be chosen, and what color changes happen at the inflection point of a titration[8]. pH-logc_i diagrams (Hagg or Sillen diagrams) have been used to determine the equivalence points of different acid-base titrations and thus select a suitable indicator for them[13]. Expressions to calculate the indicator error in redox titrations and examples of the use of these expressions have been published[14]. It has been shown that the pH and potential calculation at the equivalence point in acid-base and redox titrations, respectively, are not required to choose the titration indicator but calculating points immediately after and before the curve inflection. Also, those complexometric and precipitation curve calculations are not required to select indicators for complexometric and precipitation titrations. Finally, methods to calculate titration errors in complexometric and precipitation titrations that are simpler than those in the literature are presented[15].

Most analytical chemistry textbooks are focused on teaching the construction of titration curves and, sometimes, the errors made when using a certain indicator. However, in real life, not only must the error of an indicator be calculated, but the procedure to select an indicator for a given titration must be known. In this study, we solve examples of indicator selection for acid-base, metal ion, and oxidation-reduction titrations. We also demonstrate that the selection of indicators mainly involves the calculation of the titration curve inflection and checking that the color transition of the indicator falls exactly within this zone. In addition, we recommend the theoretical treatment related to this topic and propose some problems.

Methods

Recent editions of the most widely used and popular Analytical Chemistry textbooks were reviewed. Skoog's Analytical Chemistry book was chosen since its first edition dates from 1963 and, at this moment, it is in its tenth edition and in these almost 40 years it has been significantly improved. An internet search of the text "best analytical chemistry textbooks" was carried out. From these results, the selections of the textbooks of Analytical Chemistry recommended by academic websites such as Research gate and Chemistry Hall were chosen.

Chemistry Hall[16] included, among its top four, the books by Skoog *et al.*[5], Fifield and Kealey[17], Christian[18] and Harris[6]. In Research gate[19], 112 responses were recorded to the question "What is the best book for understand the basic analytical chemistry?" (sic). The responses came from teachers and researchers in this area of chemistry and suggested the following as the best five books: Fundamentals of Analytical Chemistry by Skoog *et al.*[5] 52 votes, Analytical Chemistry by Christian[18] 24 votes, Quantitative Chemical Analysis by Harris[6] 20 votes, A textbook of Quantitative Chemical Analysis by Vogel[9] 12 votes, and Modern Analytical Chemistry by Harvey[2] 12 votes. The difference between these and the following ones was large in terms of the number of votes obtained, so only these five books were selected in this way.

The list of the 25 most cited books in analytical chemistry (1980-1999)[20] includes only the textbook by Vogel. Finally, in the Amazon bestseller list in analytical chemistry[21] only the books by Harris and Skoog *et al.* appear in the first 24

positions. However, out of these 25 books only these two are textbooks of analytical chemistry. For all these reasons, the books by Harris, Skoog *et al.*, Christian, Harvey, Vogel, and Fifield and Kealey, among others, were selected for this study. These texts were searched for theory, examples, and problems on how to find the right indicator to perform a given titration. The same was done by searching Google Scholar in the titles of the results for the terms "metal ion indicator", "metallochromic indicator", "complexometric indicator", "acid-base" indicator, "redox" indicator, "oxide

tion-reduction" indicator, and EDTA indicator. In addition, acid-base, complexometric, and redox titration problems were solved by determining the feasibility of the titration using a given indicator or by selecting one from a table.

Results and discussion

Analytical chemistry textbooks undertaking a systematic and coherent study of the selection of indicators for classical titrations with problems and exercises on this subject are required. Table S1 evaluates the content of the most popular and best-selling analytical chemistry textbooks. It details the explanations, problems, or examples of the general procedure of indicator selection for acid-base, metal ion, or redox titrations. Some of these books have solution manuals that may contain additional information but they were not reviewed.

To determine that an indicator is suitable for a certain titration, it must be shown that its color transition lays within the inflection of the equivalence point and that the titrant reacts with the indicator only at this point. The latter implies that the indicator must be weaker than the titrant so that no appreciable errors occur due to consumption of the titrant by the indicator before the equivalence point.

Acid-base Titrations

Indicators are generally selected with their pKa matching the titration pH at the equivalence point[18]. This is correct for the titration of concentrated strong acids and bases. However, with dilute solutions and weak acids or bases, errors can be made because the color transition of the indicator can occur outside the inflection of the titration curve even though its pK_a is at this inflection.

To select an indicator for an acid-base titration, it should be checked that the transition range of the indicator does not go beyond the inflection of the equivalence point. This implies that the titrant reacts with the indicator only at the equivalence point (the indicator must be weaker than the analyte).

Harris states referring to acid-base titrations: "we seek an indicator whose transition range overlaps the steepest part of the titration curve as closely as possible"[6]. We have to determine the inflection to verify that this transition does not fall outside of it. The inflection is delimited by calculating the pH 0.10 ml before and 0.10 ml after the equivalence point in a 25-ml-titration or less, in the case of autotitrators or microburettes. This procedure can lead to a maximum error of 0.5% in a titration that consumes 20 ml of the titrant. This is illustrated in the following example:

Example 1. Choose acid-base indicators for the titration of 50.00 ml of chloroacetic acid, HA, 0.100 M, with 0.200 M NaOH, at 25°C. K_a chloroacetic acid = $1.36x10^{-3}$

Here we must A) look for the pH range of the inflection of the titration curve and B) an indicator whose color transition occurs completely in this range.

The number of moles, n, of the titrant is calculated: n = 50.00 ml x 0.100 M = 0.500 mmol and the volume of titrant at the equivalence point, V = 50.00 ml x 0.100 M / 0.200 M = 25.00 ml.

A) To find the pH range of the titration inflection, the pH 0.1 ml before and 0.1 ml after the equivalence point is calculated, corresponding to 24.90 ml and 25.10 ml of titrant, respectively.

A1) pH 0.1 ml before the equivalence point, when adding 24.90 ml of NaOH:

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

$$Ka = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+]C_{A^-}}{C_{HA} - [H_3O^+]}$$

Where C stands for the initial concentration before dissociation. Because $\frac{C_{HA}}{K_a} < 1000$, $[H_3O^+]$ in the denominator cannot be neglected and a quadratic equation must be solved returning $[H_3O^+] = 5.35x10^{-6}$ M and pH 5.271.

A2) pH 0.1 ml after the equivalence point when 25.10 ml of NaOH is added

At this point there is an excess of 0.10 ml of NaOH in the solution:

$$[OH^-] = \frac{0.100 \text{ ml x } 0.200 \text{ M}}{75.1 \text{ ml}} = 2.66x10^{-4} \text{ M}$$

This concentration returns a pOH of 3.575 and pH of 10.422. Then, the inflection of the titration curve goes from pH 5.271 to 10.422.

B) Looking at a table of acid-base indicators (Table 14.1 from Skoog *et al.*[5], see Appendix 3), we find that phenolphthalein has a pK_a of 9.4 and changes in the pH range ~8.3 to ~10.0. This transition range is effectively within the pH range of the inflection, 5.271 to 10.422 so phenolphthalein can be used in this titration. Thymolphthalein has a higher pK_a and a transition range between pH ~9.3 to ~10.5. This indicator could produce an endpoint determination error since 10.5>10.422 and it could be observed after the equivalence point when there is an excess of NaOH. The error made if thymolphthalein is used in this titration is 0.5% (Appendix 1). Other indicators with more basic pK_a cannot be used because they produce larger errors.

In the table of acid-base indicators, with a pK_a less basic than phenolphthalein, we find bromothymol blue (pK_a 7.10), which changes in the pH range of ~6.2 to ~7.6. This range falls within the inflection of the titration curve so this indicator can be used in this titration. Bromothymol violet has a more acidic pK_a, in the pH range ~5.2 to ~6.8. This indicator could produce an error in the determination of the endpoint since 5.2 is lower than 5.271, the lowest limit of the titration curve inflection. Therefore, this endpoint could be observed when the equivalence point has not yet been reached. However, the error made if bromothymol violet is used in this titration is only 0.1% (Appendix 2) and, therefore, could be used in the titration. Other indicators with more acidic pK_a cannot be used because they produce larger errors. Indicators with pK_a between those of bromothymol blue and phenolphthalein (between 9.4 and 7.10) can be used for this titration and include thymol blue, phenol red, and cresol violet.

Harris´ problem 11-J [6], which was used to solve this example, approaches an adequate treatment of the selection of an acid-base indicator. It asks to find the indicator error for a titration curve using thymol blue as the indicator, which changes between pH 8.0 and 9.6. Harris calculates the titration error from the difference between the volume of titrant to reach the equivalence point, 10.00 ml, and the volume needed to reach pH 9.6. However, he did not take into account that the color transition of the indicator is between 8.0 and 9.6, and that pH 8.0 appears to be outside the inflection. Because of this, an early transition might be observed. However, when solving as in problem 11Jb[6], an error of only 0.006% is found, but one should not forget to check the pH change of the indicator at both limits of the inflection.

Metal Ions Titrations

The selection of metallochromic indicators can be done by checking that:

- The formation constant of the titrant-analyte complex is at least 10 000 times higher than that of the indicator-analyte complex. In this way, the titrant does not displace the indicator from the complex before the equivalence point giving an early color transition. However, the indicator-analyte formation constant should not be too weak ($<10^4$) to prevent an early or diffuse endpoint.[18]
- The amount of untitrated analyte when the indicator changes should be negligible. This implies that the indicator transition is within the inflection of the equivalence point. This could also be checked assuring that the color transition of the indicator falls exactly within the inflection of the titration curve. However, the color transitions of these indicators are not reported in most textbooks.
- The metallochromic indicator meets other properties such as strong absorbance, stability and more.

These principles are applied in the following example.

Example 2. A sample of 25.00 mL of 0.00987 M copper (II) chloride is titrated with 0.0198 M EDTA (Y). Find the error of the titration at pH 11.000 and show that the indicator HIn^{2-} is suitable for the titration, at 25°C. Dissociation constant of the indicator, K_a, $10^{-11.41}$. Metal-indicator formation constant (K_{fCuIn}) $10^{7.6}$.

The following should be checked:

A) $K_{fCuY} >> K_{fCuIn}$ (Conditional formation constants)

B) The indicator-analyte constant should not be too weak

C) The amount of untitrated Cu(II) when the indicator changes is negligible.

A) $Kf_{CuY} >> Kf_{CuIn}$: $6.3\text{x}10^{18} >> 10^{7.6}$. Therefore, EDTA displaces In^{3-} from the complex only at the equivalence point.

B) The indicator-analyte constant should not be too weak ($<10^4$): $Kf_{CuIn} = 10^{7.6} >> 10^4$

C) The amount of untitrated Cu(II) when the indicator changes and the indicator error are calculated:

$$HIn^{2-} + H_2O \leftrightarrow In^{3-} + H_3O^+,$$

$$K_a = \frac{[In^{3-}][H_3O^+]}{[HIn^{2-}]} = 10^{-11,41}$$

$$Cu^{2+} + In^{3-} \leftrightarrow CuIn^-,$$

$$K_{f\,CuIn} = \frac{[CuIn^-]}{[Cu^{2+}][In^{3-}]} = 10^{7.6}$$

Let us say $CuIn^-$ is red and HIn^{2-} is blue. Before the equivalence point, the color of the solution is red due to the presence of $CuIn^-$ and after the equivalence point, EDTA releases In^{3-} from the complex with the analyte giving the solution a blue color due to the formation of HIn^{2-}.

$$K_a x K_{f\,CuIn} = \frac{[In^{3-}][H_3O^+]}{[HIn^{2-}]} x \frac{[CuIn^-]}{[Cu^{2+}][In^{3-}]}$$

$$= \frac{[H_3O^+]}{[HIn^{2-}]} \frac{[CuIn^-]}{[Cu^{2+}]} = 1.55\text{x}10^{-4}$$

$$[Cu^{2+}] = \frac{[CuIn^-]}{[HIn^{2-}]} \frac{[H_3O^+]}{1.55\text{x}10^{-4}}$$

An average human being can detect the color of an indicator species when that species has a concentration 10 times higher than the other one. Then, the solution will be red if $[CuIn^-]/[HIn^{2-}] \geq 10$ and blue if $[CuIn^-]/[HIn^{2-}] \leq 0.1$. Replacing these values and $[H_3O^+]$ by $1.00\text{x}10^{-11}$ M in the copper concentration expression, we obtain the concentrations of Cu (II) at which the color transition is observed:

$$[Cu^{2+}] = 10x\frac{1.00\text{x}10^{-11}}{1.55\text{x}10^{-4}} = 6.46\text{x}10^{-7}\text{M}$$

red solution before the end point

$$[Cu^{2+}] = 0.1x\frac{1.00\text{x}10^{-11}}{1.55\text{x}10^{-4}} = 6.46\text{x}10^{-9}\text{M}$$

blue solution after the end point

The titration error, calculated as the percent difference between the original Cu(II) concentration and 6.46×10^{-7} M, is 0.0065%.

Because the two factors gave positive results, the indicator can be used for this titration. However, there are other factors to check: the analyte should not precipitate at the titration pH, the indicator-analyte reaction must be reversible, the indicator concentration must be negligible, and more. Under these conditions, other factors would dictate the uncertainty of the titration: uncertainty in reading burette volumes, burette calibration tolerances, droplet volume, etc. These are also missing from the discussion in modern texts, but that does not detract from their significance.

From this example, it follows that the concentration of metal (M^{n+}) remaining when the indicator (In) changes color is calculated as:

$$[M^{n+}] = 10 \text{ x } \frac{[H_3O^+]}{(K_{a\,HIn})(K_{f\,MIn})}$$

Using this equation, the problems on the selection of metal ion indicators in Appendix 3 were solved.

Although indicators can be selected in this way, it is still a less simple procedure than in the case of acid-base titrations. There is a visual guide for selecting conditions of EDTA titrations[5,22] that is addressed to those inexperienced in the use of EDTA. It shows a chart that guides the selection of proper conditions for EDTA titrations of metal ions, the pH range where EDTA reacts quantitatively with metal ions, the pH range where a specific metal indicator may be used, and the pH range where an auxiliary complexing agent is required to avoid metal ion precipitation as hydroxide[22]. However, when using the procedure in this section, some metals that can be titrated with EDTA according to the chart gave the opposite result. This is the case with barium, calcium, and magnesium metal ions. A confirmation of this result is found in Skoog *et al.* where Figure 17.9 shows that calcium cannot be titrated with eriochrome black T[5]. This demonstrates the need for further research in this field. Therefore, for metal ion titrations is better to rely on experience rather than only on calculations or literature reports.

Redox Titrations

Redox indicators present fewer selection problems than indicators for acid-base titrations since their color transition is within a very small range of potentials compared to the large size of the equivalence point inflection of most titrations. For example, in the titration of a 0.1 M weak acid with a 0.1 M strong base, the pH change at the equivalence point inflection is ~2, ~4, and ~6 units if the pK_a of the acids is 6, 4, and 2, respectively, compared to the ~2 pH units of the indicator color transition, a ratio (inflection pH range)/(two pH units) of 1, 2, and 3, respectively. In redox titrations, this ratio is ~13.3 when the difference in standard potentials of the titrant and analyte is one volt. This ratio can be higher as these potential differences can be greater than 2 V, leaving a wide variety of indicators that can work for one of these titrations.

To determine that an indicator is suitable for a certain titration, it must be shown that:

- The indicator changes within the inflection of the equivalence point (the indicator undergoes oxidation/reduction only at the equivalence point). This implies that the oxidation-reduction potential of the indicator must be at the inflection of the analyte´s titration curve.
- The potential range of the color transition of the indicator does not fall outside the inflection of the titration curve.

Example 3. Find the appropriate indicator for the titration of 20.00 ml of 0.009018 M sodium thiosulfate with triiodide ion, I_3^-, 0.02001 M at a neutral pH and 25°C. Explain why the chosen indicator is appropriate.

In the standard potential tables,[5] we find:

$$S_4O_6^{2-} + 2e^- \leftrightarrow 2S_2O_3^{2-}, E^0 = 0.0800 \text{ V}$$

$$I_3^- + 2e^- \leftrightarrow 3I^-, E^0 = 0.536 \text{ V}$$

Then, the global reaction is:

$$I_3^- + 2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 3I^-$$

Initial moles of thiosulfate, $n^i_{S_2O_3^{2-}}$ = 20 ml x 0.009018 M = 0.1804 mmol

Volume at the equivalence point =

$$0.1804 \text{ mmol } S_2O_3^{2-} \text{ x } \frac{1 \text{ mmol } I_3^-}{2 \text{ mmol } S_2O_3^{2-}} \text{ x } \frac{\text{ml } I_3^-}{0.02001 \text{ mmol } I_3^-} = 4.51 \text{ ml } I_3^-$$

A) To verify that the indicator changes within the inflection of the equivalence point, we calculate the potential 0.1 ml before and after the equivalence point, this is at 4.41 ml and 4.61 ml, respectively. Then, we compare these values to the range of potentials of the color transition of the indicator.

A1) Potential 0.1 ml before the equivalence point (at 4.41 ml), sf: stoichiometric factor:

$$n_{S_2O_3^{2-}} = \left(n^i_{S_2O_3^{2-}}\right) - \left(n_{I_3^-}\right)sf$$

$$= 0.1804 \text{ mmol} - 4.41 \text{ ml x } 0.02001 \text{ M x } \frac{2}{1}$$

$$= 4.00 \times 10^{-3} \text{ mmol}$$

$$n_{S_4O_6^{2-}} = \left(n_{I_3^-}\right) sf = 4.41 \text{ ml x } 0.02001 \text{ M x } \frac{2}{1} = 0.1764 \text{ mmol}$$

$$E = E^0_{\frac{S_4O_6^{2-}}{S_2O_3^{2-}}} - \frac{0.0592}{n} \log \frac{[S_2O_3^{2-}]}{[S_4O_6^{2-}]}$$

$$= 0.0800 - \frac{0.0592}{2} \log \frac{\left(\frac{4.00 \times 10^{-3}}{24.41}\right)^2}{\left(\frac{0.1764}{24.41}\right)} = 0.241 \text{ V}$$

A2) Potential 0.1 ml after the equivalence point (at 4.61 ml).

$$n_{I_3^-} = V_{I_3^- \text{ excess}}[I_3^-] = (4.61 - 4.51) \text{ ml x } 0.02001 \text{ M} = 2.001\text{x}10^{-3} \text{ mmol}$$

$$n_{I^-} = n^{i}_{S_2O_3^{2-}} \text{x sf} = 0.1804 \text{ mmol} \text{x} \frac{3}{2} = 1.680 \text{ mmol}$$

$$E = E^0_{\frac{I_3^-}{I^-}} - \frac{0.0592}{n} \log \frac{[I^-]^3}{[I_3^-]} = 0.536 - \frac{0.0592}{2} \log \frac{\left(\frac{1.680}{24.61}\right)^3}{\left(\frac{2.001\text{x}10^{-3}}{24.61}\right)}$$

$$= 0.518 \text{ V}$$

The inflection goes from 0.241 V to 0.518 V.

The color transition of redox indicators, ΔE, is calculated with the standard redox potential of the indicator, E^0, and the number of electrons exchanged by the indicator, n:

$$\Delta E = E^0 \pm \frac{0.0592}{n}$$

Using the redox indicators in Table S2 with n=1, we see that phenosafranine, with an E^0 of 0.28 V, has a ΔE = 0.28 ± 0.0592 ≅ [0.22-0.34] V. Because 0.22 < 0.241V, a premature color transition could be observed. Indigo tetrasulfonate, E^0 = 0.36 V, yields a ΔE of 0.30-0.42 V and can be used in this titration because 0.30 V > 0.241 V and 0.42 V < 0.518 V. This indicates that the indicator changes within the inflection of the equivalence point. Methylene blue (E^0 0.53 V) yields a ΔE of 0.47-0.59 V and cannot be used because 0.59 V > 0.518 V and a late color transition may be observed. This also happens to indicators with a higher standard redox potential such as diphenylamine (E^0 0.75 V), ethoxy-2,4-diaminoazobenzene yellow (E^0 0.76 V), diphenylamine sulfonic acid (E^0 0.85), and indicators #7 to 11.

Precise and approximate expressions for the indicator error have been derived for oxidation-reduction titrations. Examples are given of the use of these expressions to select the best indicator for titrations with ascorbic acid[13].

Vogel estimates that "for a sharp colour change at the endpoint, E^0_{In} should differ by about at least 0.15 volt from the standard (formal) potentials of the other systems involved in the reaction" [9] with no further explanation. Figure S1 explains graphically this statement using the theoretical titration curve for the titration of 50 mL of Fe^{2+} 0.0500 M with Ce^{4+} 0.100 M. The color transitions of indicators A and B are shown. E^0_{In} of indicator A differ by ~0.15 volts from the standard potentials of the Fe^{2+}/Fe^{3+} system. This condition places its color transition into the titration inflection making it acceptable for that titration. This suggestion coincides with Harris who says "If the difference in formal potentials is ≥0.4 V, then a redox indicator usually gives a satisfactory end-point"[6] but only if the indicator pK_a is in the middle of the inflection.

The procedure suggested by Vogel [9] would be an easier way to find an indicator but would leave out of the curriculum the important redox equilibria studied in Example 3. However, teaching this procedure is encouraged to check the results obtained in Example 3. In this example, the standard potentials of the systems involved in the reaction are 0.536 and 0.080 V. For a difference of 0.15 V proposed by Vogel [9] as the difference from these standard potentials and E^0_{In}, a range of useful pK_a from 0.230 to 0.386 V is obtained. Using Table S2 again, we see that indigo tetrasulfonate, E^0 = 0.36 V, can be used in this titration because 0.36 V is within the 0.230-0.386 V range. The other indicators, with a pK_a out of this range, cannot be used in this titration. These results coincide with those obtained in Example 3.

Misleading Statements from Analytical Chemistry Textbooks

Some statements and examples related to indicators that may be erroneous, misleading, or contradictory are discussed in this section.

Vogel considers that "In general, it may be stated that weak acids ($K_a > 5\text{x}10^{-6}$) should be titrated with phenolphthalein, thymolphthalein, or thymol blue as indicators"[9]. However, this depends on the analyte concentrations: the less concentrated the analyte, the smaller the endpoint inflection, complicating the use of chemical indicators.

On the other hand, Harris considers that "If the difference in formal potentials [between the titrant and analyte systems] is ~0.4 V, then a redox indicator usually gives a satisfactory endpoint"[6]. Nevertheless, the indicator standard redox must be near the center of the inflection for this to be true.

Also, in example 16-B, Harris asks "Would indigo tetrasulfonate be a suitable redox indicator for the titration of $Fe(CN)_6^{4-}$ with Tl^{+3} in 1 M HCl?" and gives a hint: "The potential at the equivalence point must be between the potentials for each redox couple"[6]. This hint is only an approximation because the potentials of the redox couples are always outside the inflection of the equivalence point, which is where the color transition of the indicator should be found. The hint should say "indicators with a standard potential outside the range between the two standard potentials of redox pairs should be discarded". In example 16-B[6], the redox couples are Tl^+/ Tl^{+3} E^0 = 0.77 V and $Fe(CN)_6^{3-}/ Fe(CN)_6^{4-}$ E^0 = 0.356 V. Any indicator with a standard potential outside the range 0.356-0.77 V will not be useful for this titration. The titration error for those indicators with a standard potential within this range should be calculated. Vogel has a statement similar to Harris´s hint above: "The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated and that of the titrant"[9] which deserves similar observations. However, Vogel has a better statement: "for a sharp color change at the endpoint, E^0_{In} should differ by about at least 0.15 volt from the standard …potentials of the …systems in the reaction"[9]. This will place the indicator transition exactly in the titration inflection.

Conclusions

More time should be devoted to the selection of indicators in chemistry textbooks and more time to the teaching of this subject in the classrooms. Introducing this additional material into the curriculum of a chemistry program would require discarding other topics to make room. This could be done at the expense of determining pH, pM, and the potential at the equivalence point in acid-base, metal ion, and redox titrations, respectively. These calculations are relatively complicated for students, especially in redox titrations, and unnecessary to select an indicator. This is not to suggest that these issues are unimportant. The selection of indicators is mainly required to determine the extent of the inflection at the equivalence point and to check that the color transition of the indicator falls in this zone.

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Supplementary Information

Appendix 1. Calculation of the error made if thymolphthalein is used as the indicator in the titration described in Example 1.

Appendix 2. Error made if bromothymol violet is used as an indicator in Example 1.

Appendix 3. Selected problems with answers.

Table S1. Analytical chemistry textbooks that include explanations, problems, or examples on the general procedure of indicator selection for acid-base, metal ion, or redox titrations.

Table S2. Redox indicators.

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Appendix 1. Calculation of the error made if thymolphthalein is used as the indicator in the titration described in Example 1, 50.00 ml of chloroacetic acid, HA, 0.100 M with 0.200 M NaOH. Titrant volume at the equivalence point: 25.00 ml

Thymolphthalein changes in the pH range ~ 9.3 to ~ 10.5[6]. This indicator could cause an error in the determination of the endpoint since 10.5> 10.422, the upper limit of the inflection of the titration curve. The endpoint could be observed after the equivalence point when there is an excess of NaOH. The error is calculated as follows [Harris (2020), problem 11J][6]. First, V, the volume of NaOH in excess with respect to the pH at the equivalence point to reach pH 10.5 is calculated:

$$[OH^-] = 10^{-(pKw-10.5)} = \frac{n}{V} = \left(\frac{\text{Titrant Concentration x V}}{V_A + V_{pe} + V}\right) = \left(\frac{0.200\ \text{M x V}}{50\ \text{ml} + 25\ \text{ml} + V}\right)$$

Where V_A is the analyte volume and V_{pe} the volume at the equivalence point. This equation returns ~ 0.12 ml for V. Then, the maximum error of the titration with the indicator thymolphthalein is:

$$E = \frac{(25.12-25.0)}{25.0} x100 \cong 0.5\%$$

Appendix 2. Error made if bromothymol violet is used as indicator in Example 1, titration of 50.00 ml of chloroacetic acid, HA, 0.100M with NaOH 0.200 M. Ka = $1.36x10^{-3}$

At the equivalence point:

mmol chloraoacetate: 50.00 ml x 0.100 M = 5.00 mmol

Volume = 50 + 25 = 75 ml

Chloroacetate concentration = 5.00 mmol/75 ml = $6.67x10^{-2}$ M

$[OH^-] = (6.67x10^{-2} \text{ x } 7.43x10^{-12})^{1/2} = 7.04x10^{-7}$ M, pOH = 6.153, pH = 7.844

Bromothymol violet changes in the pH range ~ 5.2 to ~ 6.8[6]. This indicator could produce an error in the determination of the endpoint since 5.2 <7.844, the pH at the equivalence point. The endpoint could be observed when the equivalence point has not yet been reached. To calculate this error, the ratio $[A^-]/[HA]$ is calculated at the pH at which the indicator color transition could be observed, pH 5.2:

$$pH = pKa\ analyte + \log\frac{[A^-]}{[HA]}; 5.2 = 2.87 + \log\frac{[A^-]}{[HA]} \rightarrow \frac{[A^-]}{[HA]} = 214$$

Titration reaction	HA	+	**OH^-**	➔	**A^-**	+	**H_2O**
Relative initial amounts	25		V		-		-
Relative final amounts	25-V		-		V		-

To get $\frac{[A^-]}{[HA]} = 214$, it is required that V/(25-V) = 214 and V = 24.88 ml and the bromothymol violet indicator error is only 25.0-24.88 = 0.1 ml, ~0.5%. This is valid for 1:1 reactions.

Appendix 3. Selected problems with answers

A. Acid-base indicators

Select acid-base indicators for the titration of 50.00 ml of hydrochloric acid, HCl, 0.0100 M, with 0.200 M NaOH.

ANSWER. The inflection of the titration endpoint goes from pH 4,573 to 9,422 (An Excel file with the calculation is available in the Electronic Supplementary Material). Using the procedure followed in Example 1, it is found that only indicators 7 to 10 from the table below are adequate.

Some acid-base indicators

#	Common name	Transition Interval	pKa*
1	Thymol blue	1.2–2.8	1.65
2	Thymol blue	8.0–9.6	8.96
3	Methyl yellow	2.9–4.0	
4	Methyl orange	3.1–4.4	3.46
5	Bromocresol green	3.8–5.4	4.66
6	Methyl red	4.2–6.3	5.00
7	Bromothymol violet	5.2–6.8	6.12
8	Bromothymol blue	6.2–7.6	7.10
9	Phenol red	6.8–8.4	7.81
10	Cresol violet	7.6–9.2	
11	Phenolphthalein	8.3–10.0	
12	Thymolphthalein	9.3–10.5	
13	Alizarin yellow	10–12	

* At ionic strength of 0.1 and the reaction $HIn^+ + H_2O \leftrightarrow H_3O^+ + In$. Modified from Skoog *et al.*[5]

B. Metal ion indicators

Determine if 0.0100 M solutions of the metal ions Ba^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, and Ca^{2+} can be titrated with 0.0200 M EDTA using Eriochrome black T as the indicator using the procedure from Example 2.

ANSWER: To calculate the concentration of metal $[M^{n+}]$ remaining at the indicator transition, the following equation is used, as in Example 2:

$$[M^{n+}] = 10 \text{ x } \frac{[H_3O^+]}{(K_{a,Hin})(K_{f\,Min})}$$

Indicator	**Metal ion**	**$K_{f,MIn}$**	**Metal ion-EDTA conditional formation constant $K_{f,MY}$ ¥**	**$[M^{n+}]$ at the indicator transition**	**Is the titration possible?**
Eriochrome black T, pKa_3 11.6	Ba^{2+}	$10^{3.0}$	$2.28x10^{7}$	0.398	No; 0.398>0.0100
	Cd^{2+}	$10^{12.74}$	$9.49x10^{15}$	$7.24x10^{-11}$	Yes
	Pb^{2+}	$10^{13.19}$	$3.00x10^{17}$	$2.57x10^{-11}$	Yes
	Mg^{2+}	$10^{7.0}$	$1.85x10^{8}$	$3.98x10^{-5}$	No; $K_{f,MY} \cong K_{f,MIn}$
	Ca^{2+}	$10^{5.4}$	$1.34x10^{10}$	0.00158	No; early transition

¥ at pH 10. pKa data is from Harris and Lucy[6] and K_{fMIn} data from Hulanicki *et al.*[23] An Excel file with the calculations is available as Electronic supplementary information.

C. Redox indicators

Find the appropriate indicators from Table S2 for the titration of 50 mL of Fe^{2+} 0.0500 M with Ce^{4+} 0.100 M (Figure 1).

ANSWER: The inflection of the titration endpoint goes from 0.909 to 1.56 V. Using the procedure followed in Example 3, indicators 8 to 11 are adequate. An Excel file with the calculations is available in the Electronic Supplementary Material.

Table S1. Analytical chemistry textbooks that include explanations, problems, or examples on the general procedure of indicator selection for acid-base, metal ion, or redox titrations. Some of these books have solution manuals that may contain additional information.

		Reference							
TITRATIONS	**Topic**	**Harris [6]**	**Skoog [5,b]**	**Vogel [9]**	**Christian [18]**	**Harvey [2]**	**Fifield [17]**	**Patnaik [24]**	**Kenkel [25]**
ACID-BASE	Theory	✓	✓	✓	✓	✓	✓	X	X
	Examples	✓	X	X	X	X	X	X	X
	Problems	✓	X	X	X	✓	X	X	✓
METAL ION	Theory	✓	✓	✓	~	✓	X	X	X
	Examples	X	✓	X	X	X	X	✓	X
	Problems	X	X	X	X	✓	X	X	X
REDOX	Theory	✓	✓	✓	X	✓	✓	✓	X
	Examples	X	X	X	X	X	X	X	X
	Problems	[a]	X [b]	X	X	✓	X	X	X

Theory: explanations on how to select indicators for a given titration. Examples: solved questions. Problems: unresolved questions even though the answers are in the appendices. ~ partially. [a] Incomplete. [b] only the answer is given.

Table S2. Redox indicators. Modified from Harris (2020)[6].

#	Indicator	E^0
1	Phenosafranine	0.28
2	Indigo tetrasulfonate	0.36
3	Methylene blue	0.53
4	Diphenylamine	0.75
5	Ethoxy-2,4-diaminoazobenzene	0.76
6	Diphenylamine sulfonic acid	0.85
7	Diphenylbenzidine sulfonic acid	0.87
8	Tris(bipyridine)iron	1.12
9	Tris(1,10-phenanthroline) iron (ferroin)	1.15
10	Tris(5-nitro-1,10-phenanthroline)iron	1.25
11	Tris(2,2.-bipyridine)ruthenium	1.29