Indicators

One of the most interesting and appealing topics in the whole of science is that of colour. While the fundamentals of colour are more usually covered in physics, once we get to the colours of materials – paints, dyes and the like, we are firmly in the realms of chemistry.

One group of coloured substances that is widely used from Early Years and Primary up to Advanced Higher and beyond is indicators, which have the benefit of being useful as well as aesthetically pleasing. This article sets out to give an overview of some of the more common types of indicators and their uses in chemistry.

Colours of red cabbage acid (l) to alkali (r).

Acid-base titrations

The most common type of chemical indicator is the acid-base indicator. These have a long history: the Spanish physician Arnaldus de Villa Nova began using litmus to study acids and bases in around 1300 and litmus, a dye extracted from certain species of lichen, has entered the language in general terms to refer to a diagnostic test.

Litmus in acid & alkali.

Litmus is an example of a 'natural' pH indicator and these are more common that might be imagined. Most learners are familiar with the impressive range of colours that can be generated from red cabbage.

However, there are many more natural compounds that change colour in different pH solutions. The largest group of these is the anthocyanins. These are all variations on the same basic structure (see Figure 1) with different groupings present.

These are the main compounds responsible for the colour of flowers - so many flower petals can be used as indicators. They are also widely found in fruits, particularly the darker ones such as brambles and elderberries.

Other plant materials that can be used as indicators are turmeric (cucurmin), tea (theoflavins), beetroot (betanin) and many more.

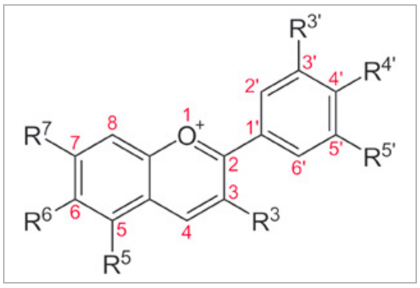
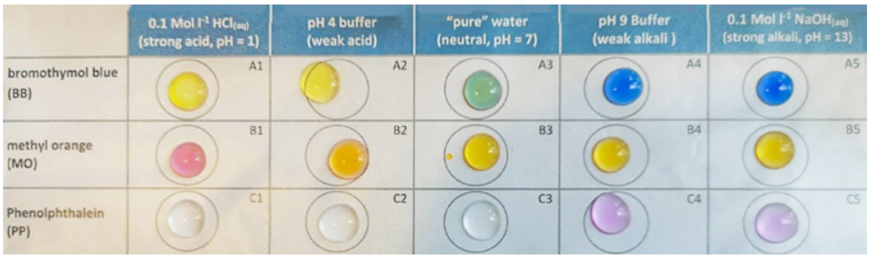


Figure 1 - Generic anthocyanin structure.



Colours of some common indicators.

Commercial pH indicators

The pH indicators we use in the laboratory are not extracted from plants though. They are synthesized in a range of ways. Quite a lot of them are types of azo-dyes, though not all.

There are dozens of different indicators and they vary in both their colour changes and the pH at which these take place. Some of the ones that are most commonly encountered in schools are:

- Methyl orange which changes from red in acid to yellow in neutral/ alkali at around pH 4.
- Bromothymol blue which changes from yellow in acid to blue in alkali at about pH 7.
- Phenolphthalein which changes from colourless in acid/neutral to bright pink at around pH 9.

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Choosing a pH indicator

Indicators are widely used in acid-base titrations to show the end-point of the reaction. Depending on the nature of the acid and base involved, the pH of the end-point will be different and so different indicators are used.

Looking at these two titration curves (see Figure 2), the one at the top has a mod-point of about pH 7 so Bromothymol blue would be a suitable choice, while the one below it has a mid-point of a lower pH, around pH 5 so methyl red would be a better choice.

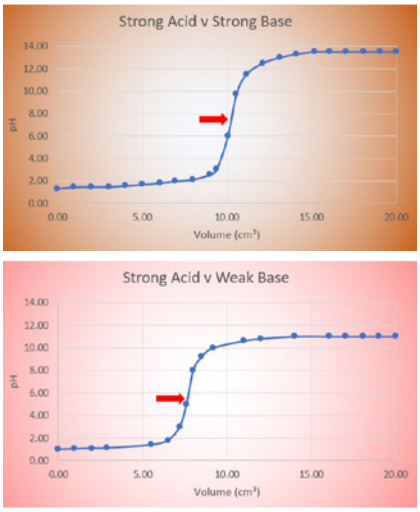

Figure 2 - Titration curves showing different mid-pointse.

How do pH indicators work?

pH indicators are weak acids. More than that, they have a different colour when protonated than when not. As a weak acid, the indicator will dissociate in solution as shown in this equation. (In = indicator molecule, HIn = protonated indicator)

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

This dissociation of the weak acid indicator causes the solution to change colour.

The key point here is that this equation describes an equilibrium and as such it is subject to Le Chatelier's principle. So, if you add acid, you increase the concentration of H_3O^+ (H^+) the equilibrium is shifted to the right and as you remove H_3O^+ it shifts to the left.

Different indicators have their equivalence points (the 'balance' point of the equilibrium) at different pH values so with change colour at different points.

Redox titrations

Another main type of indicator is one used for finding the end point of redox reactions. In this case the different coloured forms are the oxidised and reduced form of the substance. Again, like with pH indicators, these two forms are in equilibrium (Figure 3).

Figure 3 - Iodine (l) and starch-iodine complex (r).

In this case, the indicators change colour at a specific electrode potential rather than pH, although some are pH dependent as well. Many redox titration, however, especially those carried out in schools and colleges, do not use separate indicators. They rely on colour changes inherent in the reaction.

For instance, titrating a reducing agent with a solution of iodine (yellow/brown) to produce iodide (colourless). Starch is usually used as an indicator to assist in the visualisation of a clear end-point though this is not actually a redox indicator.

Another example is titrating with potassium manganate VII, using the inherent purple colour of the permanganate ion as the indicator.

Complexinetric titrations

The third class of indicators include the starch mentioned above. In this class, the end point of the titration is indicated by the formation or dissolution of a sudden complex. The most common type of titration uses EDTA (ethylenediaminetetraacetic acid) as a titrant to determine a variety of metal cations: calcium and magnesium concentrations in water is a common experiment.

The reaction depends on the relative stability of different complexes. The indicator is added to the solution. For calcium or magnesium, murexide is a common one (Figure 4). This forms a red complex. The solution is

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Figure 4 - Colour changes of murexide/magnesium complex (l) and uncomplexed murexide (r).

then titrated with EDTA. EDTA forms a more stable complex with the metal ions and so abstracts the metal leaving the non-complexed form of the indicator, which is blue.

$$MgIn^{-} + HY^{3-} \rightleftharpoons MgY^{2-} + HIn^{2-}$$
$$(Y = EDTA)$$

By varying the indicator and the pH at which the titration takes place, it is possible to vary the relative stability of the metal-indicator and metal-EDTA complexes.

Precipitation titrations

In this case, the titration involves the formation of a precipitate during the experiment. The titration is continued until the last of the precipitate is formed. At that point any excess titrant reacts with an indicator causing a colour change. The best-known example of this sort of titration is an argentometric titration, which is used to investigate the concentration of chloride (or other halides) by titration with silver nitrate (Figure 5). As the reaction proceeds, a precipitate of the silver halide is formed. Mohr's method uses potassium chromate as an indicator which forms red silver chromate at the end point. Farjan's method is similar but uses fluorescein dye that changes from yellow to pink at the endpoint.

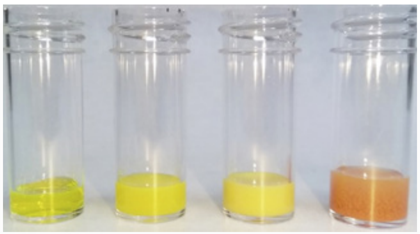

Figure 5 - Silver-chloride titration using fluorescein (Farjan's method).

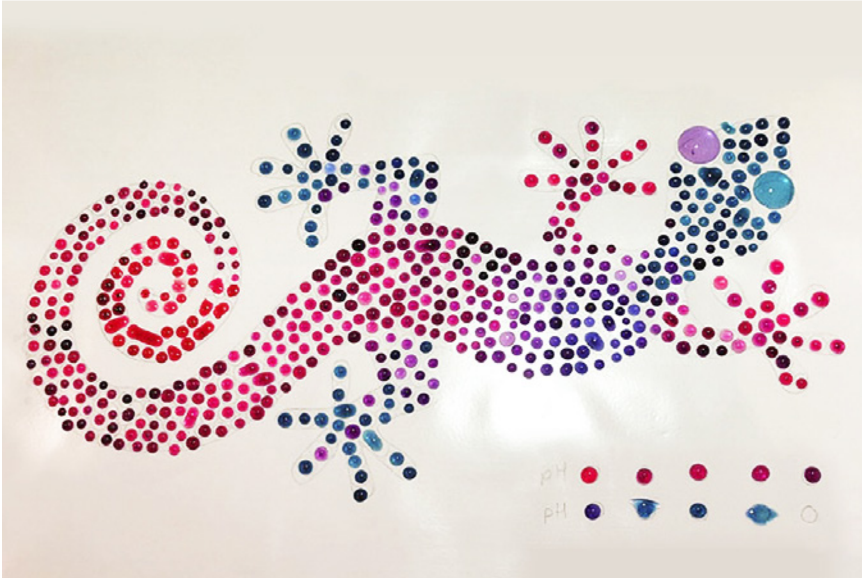

Figure 6 - PH Lizard made from drops of red cabbage indicator.

Indicators and Art

It is possible to use the lovely colours generated by indicators for artistic purposes – a sort of pH related painting by numbers. There are some lovely examples, including the one here, in an article by Isobel Everest in Chem 13 News from a few years ago (Figure 6).

In conclusion

We have barely scratched the surface of this topic and as you can see there is a plethora of indicators that can be chosen from for a wide variety of purposes. Details of many, can be found on the SSERC website and if you need details of ones we don't list, just get in touch. <<