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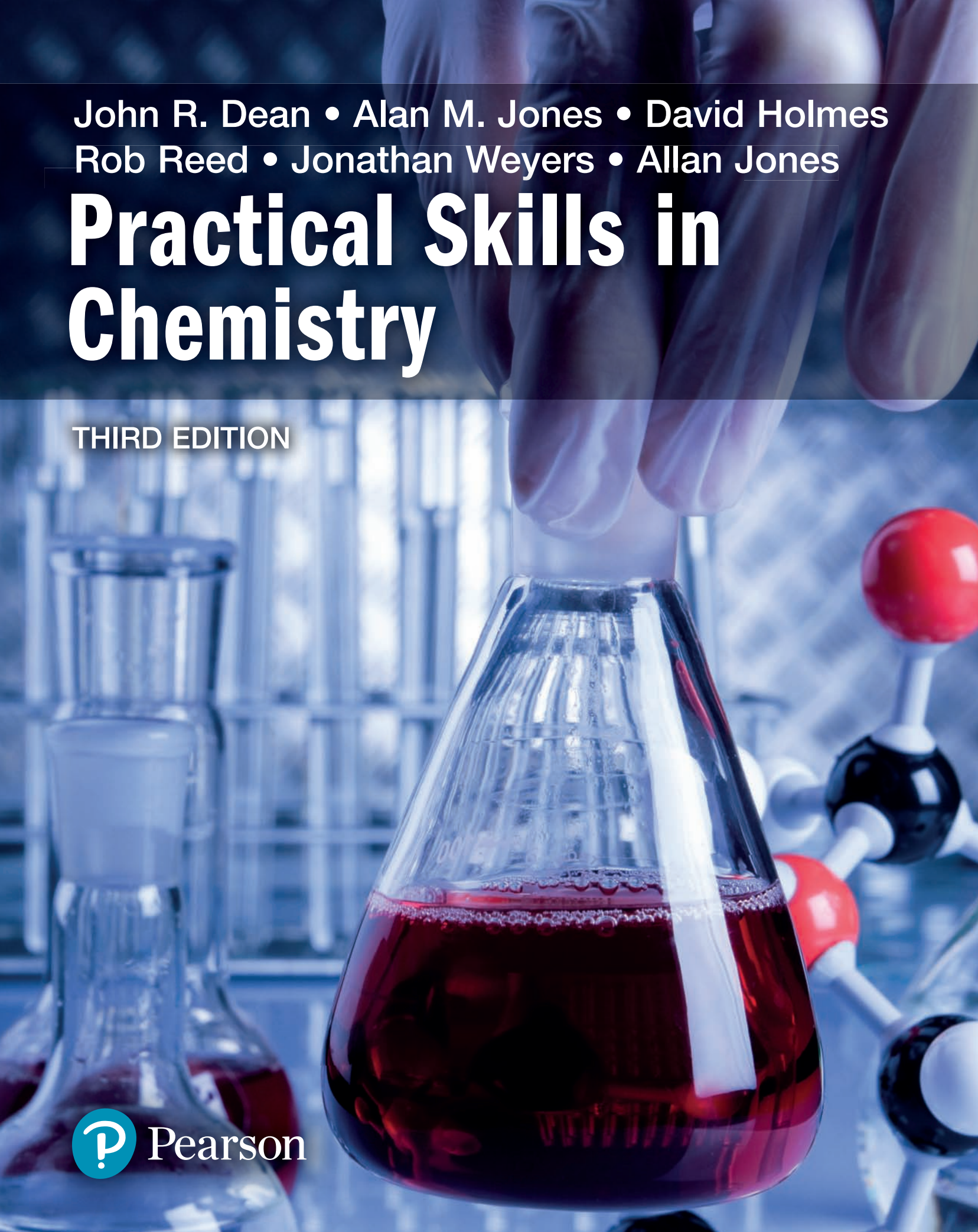
Practical Skills in Chemistry

THIRD EDITION



Pearson

Practical Skills in Chemistry

21 Qualitative techniques for inorganic analysis

Qualitative techniques are used to identify cations and anions in aqueous solution by simple reactions, mostly involving the production of a precipitate, evolution of gas or a visual colour change. It is important to make observations accurately and to interpret them in a step-wise manner.

The following basic equipment is required to carry out qualitative analysis:

- Test tubes – in which the reactions are performed. (p. 65)
- Sealing film or plastic stoppers – for the protection of the contents of test tubes from contamination and for safe storage. (p. 67)
- Test tube rack – this allows test tubes to be stored upright when not in use.
- Test tube holder – this allows individual test tubes to be heated safely. (p. 177)
- A glass rod – this has several functions including the stirring, transfer of solutions, and the break-up of precipitates.
- Watch-glasses these have several functions including the covering of beakers to prevent contamination and as a receptacle for solutions.
- A wash bottle containing distilled water.
- Spatula – for transferring small quantities of solids.
- Pasteur pipettes – for transferring liquids. (p. 63)
- Micro-Bunsen burner – for heating solutions to boiling and for evaporating solutions. (p. 172)
- Evaporation crucible – this is used as a container for solutions when complete evaporation of liquid is required, leaving a solid product.
- Crucible tongs – for removing the crucible from the heat source.
- Centrifuge – for separating precipitates from solution.
- Heated water bath. (p. 173)

Wash bottle – always keep a wash bottle of distilled water handy.

Spatula – never place the spatula in the test solution, it may lead to false-positive tests for iron and chromium.

Reagents

At the start of your experimental work always check that the appropriate reagents are readily available (a list of commonly used reagents is given in Table 21.1). Note that it is essential to use distilled water in all qualitative analysis. Tap water contains ions such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, SO_4^{2-} and Cl^- and its use could lead to 'false-positive' results.

Table 21.1 Typical reagents for qualitative analysis

2 M NH_4OH	Conc. HCl
2 M NaOH	0.1 M HNO_3
2 M $AgNO_3$	2 M HNO_3
2 M CH_3COOH	Conc. HNO_3
2 M $BaCl_2$	2 M H_2SO_4
0.1 M HCl	Conc. H_2SO_4
2 M HCl	

Testing for anions and cations

Specific literature containing tests for the determination of anions and cations can be found on p. 182. In general, however, the following tips are useful when carrying out qualitative analysis:

- Always work tidily to prevent cross-contamination of samples.
- Ensure that all glassware has been cleaned thoroughly in detergent and then rinsed twice with distilled water. Invert the test tubes to drain; never dry the inner surface with towelling or tissue.

Qualitative tests for cations and anions

An unknown solution was tested as follows:

Test	Observation	Conclusion
2 drops of dilute HCl, boil, then add 1 drop $BaCl_2$ solution	White precipitate	Sulphate (SO_4^{2-}) present

Test performed on unknown solution

Report of the observations made

Conclusion drawn from the observation

Fig. 21.1 Recording your observations in qualitative analysis.

A clear solution is transparent – a 'colourless' solution has no colour.

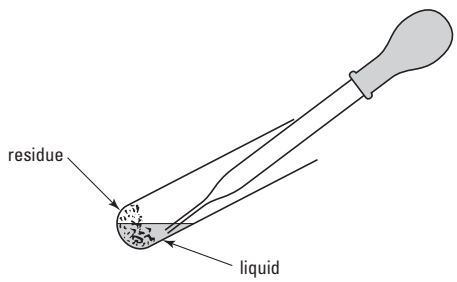


Fig. 21.2 Separation of liquid from a residue using a pipette.

- Label test tubes at the start – it may prove difficult to remember what you have done later on.
- Always test solutions with a known composition before you attempt to analyse solutions with an unknown content. This allows you to gain the necessary experience in solution manipulation, observation skills and the interpretation of results.
- The colour of solutions and/or precipitates has to be interpreted from written or oral information. Interpretation of colour can be subjective, so you will need to gain sufficient experience using solutions of known content to establish how a particular colour appears to you.
- Establish a protocol for recording of observations after carrying out different tests (Fig. 21.1).
- Reagents should be added from Pasteur pipettes held with the tip just above the mouth of the test tube. Never put Pasteur pipettes inside test tubes as this can lead to contamination of the reagents.
- Effective mixing of the test solution and added reagents is essential. This can be achieved by holding the test tube between the thumb and index finger of one hand and 'flicking' the tube with the index finger of your other hand. Alternatively, solutions can be mixed by bubbling air from a Pasteur pipette held at the bottom of the test tube.
- Evolved gas can be drawn up into a Pasteur pipette and then bubbled through a test solution, e.g. CO_2 can be drawn into a Pasteur pipette and then 'blown' out through lime water [$Ca(OH)_2$ solution] giving a milky-white solution.
- Solutions can be tested for pH using litmus paper. Never place litmus paper directly into the test solution. Instead, dip a glass rod into the solution, remove, touch the wet glass rod onto the litmus paper and note the colour. Acidic solutions change blue litmus paper to red; alkaline solutions change red litmus paper to blue. Alternatively, universal indicator paper can be used. In this case, the orange paper turns 'reddish' with acidic solutions and 'bluish' with alkaline solutions. By comparing any change in colour with a chart (supplied with the universal indicator paper), the pH of the solution can be estimated.

Centrifugation of solutions

Centrifugation causes particulate material to accumulate at the bottom of the test tube. The procedure for centrifuging your sample is described in Box 21.1. The speed and time of the run will depend on the centrifuge available, but will typically be in the range 5000–10000 rpm for 5–10 min, respectively. Always allow the centrifuge to stop in its own time, as abruptly halting the centrifuge will disturb light precipitates. After centrifugation, hold the test tube at an angle so that it is easy to remove the liquid component (or centrifugate) with a Pasteur pipette (Fig. 21.2). You will find that it is difficult to remove all the centrifugate from the precipitate, and to maximise the transfer of centrifugate it is necessary to wash the precipitate. This is carried out as follows:

- Add a small quantity of distilled water to the precipitate.
- Use a glass rod to break up the precipitate and mix thoroughly.
- Recentrifuge the mixture.

Box 21.1 How to use a low-speed bench centrifuge

1. **Choose the appropriate test tube size,** with stoppers where necessary. Most low-speed machines have four-place or six-place rotors. Use the correct number of samples to fill the rotor assembly whenever possible.
2. **Fill the tubes to the appropriate level:** do not overfill, or the sample may spill during centrifugation.
3. **Ensure that the rotor is balanced during use.** To achieve this prepare identical test tubes and place these diametrically opposite each other in the rotor assembly. However, for low-speed work, where you are using small amounts of particulate matter in aqueous solution it is sufficient to counter-balance a sample with a second test tube filled with water.
4. **If you are using centrifuges with swing-out rotors,** check that each holder/bucket is correctly posi-tioned in its locating slots on the rotor and that it is able to swing freely. All buckets must be in position on a swing-out rotor: even if they do not contain sample tubes, buckets are an integral part of the rotor assembly.
5. **Load the sample test tubes into the centrifuge.** Make sure that the outside of the centrifuge tubes, the sample holders and sample chambers are dry: any liquid present will cause an imbalance during centrifugation (as well as potentially causing corrosive damage to the rotor). Balanced tubes must be placed opposite each other; use a simple code if necessary, to prevent errors.
6. **Bring the centrifuge up to operating speed** by gentle acceleration. Do not exceed the maximum speed for the rotor and tubes used. If the centrifuge vibrates at any time during use, switch it off and find the source of the problem.
7. **On completion of the run, allow** the rotor to stop spinning, release the lid, and remove all test tubes. If any sample has spilled, make sure you clean it up thoroughly.
8. **Finally,** close the lid (to prevent the entry of dust) and return all controls to zero.

SAFETY NOTE Take care when heating unknown solutions. As well as the risk of burns, some reactions can be violent.

SAFETY NOTE Never point a test tube towards yourself or, for that matter, towards anyone else while evaporation is being carried out.

SAFETY NOTE Never look down into a test tube (even with safety glasses on – there is still a risk of hot solution suddenly being ejected into your face). Always view coloured products through the wall of the test tube.

SAFETY NOTE Noxious fumes can be given off in some instances. Be careful not to breathe them in. Always work in a well-ventilated room or a fume cupboard.

- Transfer the liquid obtained to the original centrifugate and store this solution for further analysis.
- Repeat the washing process, but this time discard the centrifugate, and retain the precipitate for further tests.

Heating test tubes and other containers

It is often necessary to heat a solution in a test tube, either to cause precipitation or to dissolve a precipitate. You can carry out this heating effectively and safely by partially immersing the test tube containing the mixture in a simmering boiling-water bath (remember to use a test tube holder!).

It is possible to reduce the volume of the solution in the test tube, i.e. to pre-concentrate the sample, by evaporation. Two different methods can be employed.

1. Transfer the solution to a small evaporating dish. Place the evaporating dish on a wire gauze located on a tripod stand, and apply heat using a micro-Bunsen burner. Note that the volumes of solutions in qualitative analysis are often small, and excessive heating might result in hardening of any residue, making it unusable.
2. Alternatively, evaporate the solution directly in a test tube by gentle heating over a micro-Bunsen burner. Remember to use a test tube holder. Position the test tube at an angle with the tip of the Bunsen burner flame positioned at the upper surface of the liquid. Place a glass rod inside the test tube and rotate constantly. This acts to disperse bubbles of steam that are given off. Extreme caution is required with this method of evaporation, as the steam bubbles can cause the solution to 'bump' out of the test tube (see p. 87).

Beware – hot glass looks exactly like cold glass.

'Bumping' can result in hot (and maybe toxic) substances being ejected over a surprisingly large distance.

Flame tests

Simple flame tests can be carried out on solid samples. Place a little of the solid on a watch-glass and moisten with a drop of concentrated hydrochloric acid. The purpose of the hydrochloric acid is to produce metal chlorides which are volatile at the temperature of the Bunsen burner.

Pre-clean a platinum or nichrome wire by holding it in the hottest part of the Bunsen flame (just above the central blue cone) until there is no coloured flame from the wire. Cool, then dip the cleaned wire into the moistened solid sample. Place the wire at the edge of the Bunsen flame (Fig. 21.3) and record the colour of the flame from the sample (see Table 21.2).

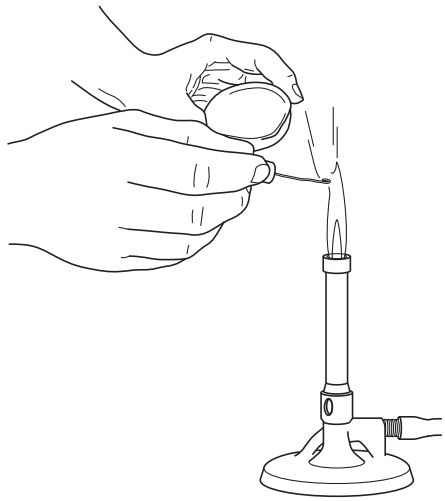


Fig. 21.3 Holding a nichrome wire in a flame test.

Table 21.2 Flame tests for cations

Cation	Flame colour
Barium	Apple-green
Calcium	Brick-red**
Copper	Green
Potassium	Lilac*
Sodium	Intense yellow
Strontium	Crimson**
Lead, arsenic, antimony and bismuth	Dull blue

*The colour is often obliterated by trace impurities of sodium present (sodium gives an intense yellow colour). You can overcome this by viewing the colour through cobalt-blue glass which allows the lilac coloration from potassium to be seen.
**Viewing through cobalt-blue glass also allows calcium and strontium to be distinguished. In this case, calcium is light green in colour while strontium appears purple.

Sources for further study

Dean, J.A. and Patnaik, P. (2004) *Dean's Analytical Chemistry Handbook*, 2nd edn. McGraw-Hill Co. Inc.

Hardcastle, W.A. (1998) *Qualitative Analysis. A guide to best practice.* Royal Society of Chemistry, Cambridge.

Kramer, B.K. and McCormick, J.M. (2013) *Inorganic Qualitative Analysis.* Available: http://www.chemlab.truman.edu/CHEM131Labs/QualAnalysis.asp Last accessed 05/01/16.

Lagowski, J.T. and Sorum, C.H. (2005), *Introduction to Semimicro Qualitative Analysis* 8th edn. Prentice Hall, Harlow, Essex.

Svehla, G. (1996) *Vogel's Qualitative Inorganic Analysis,* 7th edn. Longman, Harlow, Essex.

Svehla, G. (1989) *Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis,* 5th edn. Longman, Harlow, Essex.

Witten, KW., Davis R.E. Peck, M.L. and Stanley, G.G. (2006) *A Qualitative Analysis Supplement*, 8th edn. Thomson Brooks/Cole Publishing, Belmont, CA.

Study exercises

21.1 Why is it necessary to use distilled water in qualitative inorganic analysis?

21.2 Analysis of a solid gave the following analysis results:

(a) Treatment of the solid with dilute HCl gave off a gas, which when bubbled through a $Ca(OH)_2$ solution gave a fine white precipitate.

(b) A flame test gave a green flame.

Deduce possible identities for the solid compound.