NERAD Regional Heat

SCHOOLS' ANALYST COMPETITION

2017

Dial 999 for Emergency!

INSTRUCTION BOOKLET

ROYAL SOCIETY OF CHEMISTRY | ANALYTICAL DIVISION NORTH EAST REGION

Welcome to the regional heat of the Schools' Analyst competition! We hope that you will all enjoy participating in this practical competition and, who knows, a few of you may become analysts later on in your careers.

Analytical Science is all about problem solving, whether it be forensic work, or keeping industrial processes running when they hit snags, or in the more intellectual sense of working out exactly what experiments are necessary to perform an analysis in the laboratory. You, therefore, are going to tackle a problem today.

You should already have enough background knowledge (but feel free to ask a demonstrator if there is anything that you do not understand), but you will need to show common sense and good organisational skills.

First you will have to decide how to tackle your problem, so that you can distribute the workload among your team of three so that each of you is always busy. Then you will need to carry out the experiments, perform the calculations and make some decisions based on the data obtained. A few tie break questions complete the exercise.

Please read and understand the instructions before commencing.

THERE IS A STRICT TIME LIMIT OF THREE HOURS FOR THE EXERCISE.

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Health and Safety

This is a practical exercise, so normal rules for safety in the laboratory apply.

Wear fully fastened laboratory coats and safety spectacles at all times.

Do NOT eat or drink in the laboratory.

Always use the pipette fillers provided, following the demonstration of how to attach it safely and handle glassware carefully to avoid breakage and cuts.

Keep long hair tied back and under control by tucking it inside your lab coat.

IF IN DOUBT ABOUT ANYTHING THEN ASK A DEMONSTRATOR.

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THE ORGANISERS THANK YOU FOR PARTICIPATING AND WISH YOU ALL THE BEST FOR YOUR FUTURE.

The experiments described in this booklet have been devised by Jeremy Hopwood, Ibrahim George, Natasha Reed and Margaret Scott of the University of Huddersfield

Thanks also to Beth Cutting [Southmoor Academy] and Aminah Shafiq [Bedlingtonshire Community High School] Nuffield Research Students 2016 who trialled the final experiments for the Regional Heats.

Dial 999 for Emergency!

The scenario

Alan Rutland works at the Smith aluminium foundry. On Tuesday evening, whilst on the late shift, he was opening one of the foundry venting valves when the valve jammed. On opening the valve some hot vapours containing aluminium dust escaped, Alan managed to avoid being hit by the gas but he did breathe in some of the vapours. He continued to work but developed a headache. A friend of his gave him some unlabelled tablets saying that he thought they were aspirin and Alan left the factory floor for a tea break. (As a small child Alan was found to be allergic to paracetamol.)

Working in the foundry is thirsty work and Alan was known for drinking many cups of tea in a day. Normally Alan would have used the kettle but someone had taken the electric cable and so he decided to use hot water from the copper boiler normally used for washing hands. The tea did not taste very nice but Alan drank it nevertheless and he took the tablets.

He returned to the factory floor but after 20 minutes complained to his friend of stomach cramps and dizziness. Both symptoms became worse and an hour later Alan was sick and then had diarrhoea. The pain became considerably worse, so one of the managers called for an ambulance to take Alan to hospital. By now he was on his back and in considerable pain.

The task

The doctors at the hospital need to know what has caused Alan to become ill. After finding out the above information given in the scenario you decide that there are three possible causes; copper poisoning, aluminium poisoning or an allergic reaction to paracetamol.

Case notes for the three different chemicals show that Alan would have the symptoms described above if any of the following occurred:

- The level of dissolved copper in the water from the boiler was between 1 – 10 mg/L
- The level of aluminium in his blood plasma is above 200 μg/L
- The pills were paracetamol and not aspirin.

The concentration of copper in the water from the boiler will be analysed by atomic absorption spectroscopy (A.A.S), the concentration of aluminium will be analysed by visible spectroscopy using catechol violet and the presence of aspirin will be checked by an acid base titration. If your competition venue does not have access to A.A.S. You will do an alternative experiment using chromatography to identify unknown metal ions.

Planning

To be successful you will need to plan how each member of the group will use their time.

Making up Solutions

The dilution equation will be invaluable in helping you determine volumes to be used when making diluted standards.

$$C_1 \times V_1 = C_2 \times V_2$$

Where: -
C_1 is the concentration of the initial solution
V_1 is the volume of the initial solution
C_2 is the concentration of the new solution
V_2 is the volume of the new solution

Example:
You are provided with a stock solution of copper ions which has 500 mg/L.
You are required to make up 100 mL of a 25 mg/L solution.
How much of the initial solution should you use?

Since $C_1 \times V_1 = C_2 \times V_2$

$V_1 = C_2 \times V_2 \ / \ C_1$
$V_1 = 25 \times 100 / 500$
$V_1 = 5$ mL

So you would carefully measure out 5 mL stock solution and dilute to 100 mL in a volumetric flask using distilled/deionised water. Take care that the bottom of the meniscus is on the calibration line. Invert stoppered flask at least 7 times to ensure thorough mixing.

Experiment 1. Determination of Copper by atomic absorption spectroscopy

In this experiment you determine the concentration of copper by atomising the solution in a flame and measuring the absorption of light at 324.8 nm. You calibrate the atomic absorption spectrometer with standards of known concentration and then run your test solution.

Health and safety

All copper salts are accumulatively poisonous so make sure spills are mopped up immediately. GLP and PPE will be sufficient for this experiment.

Equipment & Reagents

250 mL volumetric flask
100 mL beaker
Plastic funnel
Glass rod
Pasteur pipettes X 2
25 mL bulb pipette
20 mL bulb pipette
5 x 100 mL volumetric flasks
25 mL graduated pipette
Wash bottle containing distilled/deionised water
Pipette filler
Atomic absorption spectrometer
1000 mg/L copper ion stock solution
Test solution (water from the boiler)

Procedure

1.1 From the 1000 mg/L copper ion stock solution make an interim solution of 100 mg/L. Prepare this by carrying out a 10-fold dilution by pipetting 25 mL stock solution into a 250 mL volumetric flask and making up to the mark with distilled or deionised water.

1.2 From this interim solution prepare a stock solution of 20 mg/L by pipetting 20 mL interim solution into a 100 mL volumetric flask and making up to the mark with distilled or deionised water.

1.3 From this stock solution, prepare in 100 mL volumetric flasks four working calibration standards in the range 1 – 4 mg/L. (See dilution equation page 4.)

1.4 Take the four concentration standards, the test solution and a blank (deionised water) to the atomic absorption spectrometer.

ASK A MEMBER OF STAFF TO SHOW YOU THE ATOMIC ABSORPTION SPECTROMETER AND THEN FOLLOW THE INSTRUCTIONS PROVIDED.

1.2 Flush the spectrometer thoroughly by aspiration of deionised water for 5 minutes before starting the analyses.

1.3 Zero the instrument with deionised water.

1.4 Run each calibration standard and record the results.

1.5 Run the test solution and record the result. Check that the result is within the calibration range. If it is not, then either your sample needs diluting or your calculation is wrong.

Results

Concentration:	0 mg/L	1 mg/L	2 mg/L	3 mg/L	4 mg/L	Test
Absorption:						

Draw a calibration graph with concentration as the x-axis and absorbance reading as the y-axis. The relationship should be linear so draw the best fit straight line. Use the fitted line to convert the absorption reading of the test solution to a concentration. Correct for any dilution of the test solution that you may have made. Show any calculations you have used in the experiment.

Concentration of copper in test solution (from graph): _____ mg/L

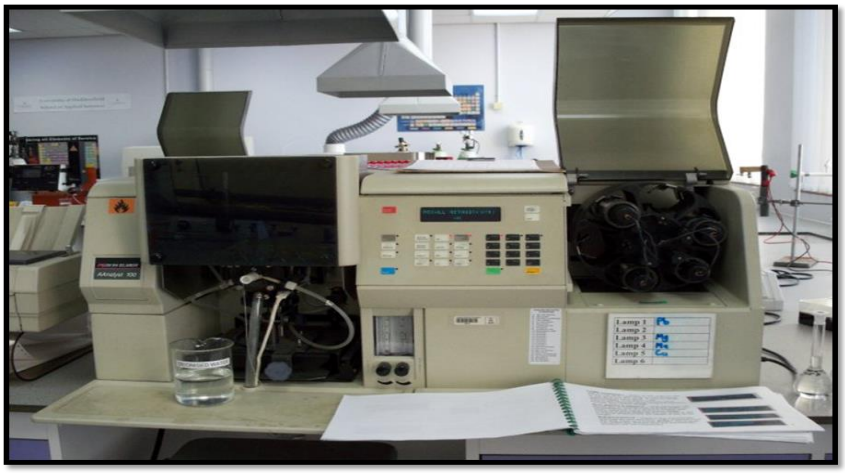
Conclusion:

Chemical background*

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements.
Atomic absorption is so sensitive that it can measure down to parts per billion of a gram ($\mu g.dm^{-3}$) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level. Atoms of different elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element.

For example, with copper, a lamp containing copper emits light from excited copper atoms that produce the right mix of wavelengths to be absorbed by any copper atoms from the sample. In AAS, the sample is atomised – ie converted into ground state free atoms in the vapour state in a furnace (using a flame) – and a beam of electromagnetic radiation emitted from excited copper atoms is passed through the vaporised sample. Some of the radiation is absorbed by the copper atoms in the sample. The greater the number of atoms there are in the vapour, the more radiation is absorbed. The amount of light absorbed is proportional to the number of copper atoms. A calibration curve is constructed by running several samples of known copper concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the copper concentration in the unknown sample. Consequently, an atomic absorption spectrometer needs the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed.

*Extract taken from www.rsc.org/education/teachers/learnnet/pdf/LearnNet/rsc/AA_txt.pdf



Alternative Experiment 1 to be used if no A.A.S. equipment is available at competition venue.

Detection of the presence of metal ions in the water from the boiler sample by chromatography.

Introduction

In this experiment, chromatographic paper will be used to determine the presence of copper ions in a sample of boiler water. A solvent is used to move the ions along the paper; the relative solubility of the cations in the solvent versus the relative adsorptivity of the cations for the paper results in their separation on the paper. A developing solution is used to intensify the position of the metal cation band on the paper.

In this experiment, chromatographic paper (similar to filter paper), a paper that consists of polar cellulose molecules, is a stationary phase. The mobile phase consists of one or more of the transition metal cations, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, dissolved in an acetone-hydrochloric acid eluent.
Each transition metal has its own unique adsorptive affinity for the polar, cellulose chromatographic paper; some are more strongly adsorbed than others. Also, each ion has its own solubility in the eluting solution. As a result of these two factors, some transition metal ions move further along the chromatographic paper than others to form bands at some distance from the origin, therefore indicating that the ions are separating.
For a given eluting solution, stationary phase, temperature, and so on, each ion is characterized by its own Rf (ratio of fronts) factor:

$$R_f,\ \text{ion} = \frac{\text{distance from origin to final position of ion}}{\text{distance from origin to solvent front}} = \frac{D_{\text{ion}}}{D_{\text{solvent}}}$$

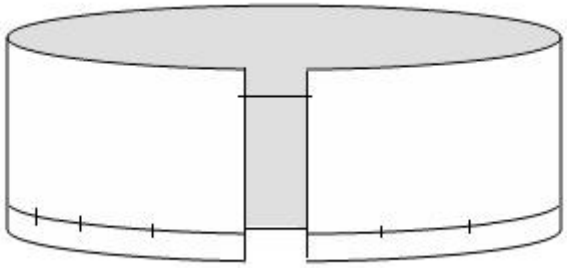
Procedure.

Safety comments:
All metal solutions are so dilute and used in such small quantities as to present minimal risk.
The elution solvent and ammonia developing solution however do pose a risk and so disposable gloves should be worn.

Equipment and Reagents:
600 mL beaker (chromatography tank)
Large watch glass (lid)
Chromatography paper
Capillary tube spotters
Pencil
ruler
stapler
Vials containing salt solutions
Elution solvent 9:1 mix acetone:6M HCl
Developing tank (in fume hood) 1 L beaker with lid containing small beaker with ammonia solution

1.1 Obtain one piece of chromatographic paper. Handle paper only along its top 20cm edge and place on a clean piece of paper (not directly on the lab bench). Draw a **pencil** line 2 cm from the bottom long edge of the paper. Starting 3 cm from the 10 cm edge and along the 2 cm line, make six x's with even separation leaving approximately 3 cm at the other end. Use a pencil to label each X below the 2 cm line for the five cations being investigated and boiler sample.

1.2 Note any colours of the aqueous metal ions in the "colours with water" column. Using the capillary tubes provide in the solutions "spot" the chromatographic paper with the five known solutions and the boiler sample. The microdrop should be no more than 5 mm in diameter. Place 3-4 drops of each solution at the corresponding X to increase amount of metal ion at the "spot" on the chromatographic paper. Air dry the paper between and after applications.



1.3 Form the chromatographic paper into a cylinder and, near the top, attach the ends with a staple; do not allow the two ends of paper to touch. Be sure the spots are dry.

1.4 Place the cylinder into the beaker with a developing solution (which is acetone: 6M HCl 9:1 mixture). The entire "bottom" of the cylindrical chromatographic paper must sit on the bottom of the beaker. Do not allow the paper to touch wall. Make certain that the eluent is below 2 cm line. Place watch glass on top of the beaker and wait until the solvent front has moved to within 3 cm of the top of chromatographic paper. Do not disturb the beaker once the paper has been placed inside. Note the colours of any spots in the "colour with Cl^{-}" column.

1.5 Remove paper from the beaker and quickly mark (with a pencil) the solvent front. Allow the chromatogram to air dry.

1.6 To enhance the appearance and locations of the bands, move chromatogram to the fume hood. Position the paper in the ammonia chamber and cover the 2L beaker with a watch glass. ***Caution: Do not inhale the ammonia fumes!*** *Use* ***gloves*** *when placing paper in the ammonia chamber.*

After the deeper colors of the bands are evident note them in the "colour with NH_3" column, remove the chromatogram and circle any new transition metal ion bands that have appeared.

1.7 Measure the distance travelled by the solvent front and by the ions for each band. Calculate R_f values for each transition metal ion and tabulate them in the following table.

Results:

Metal ion	Colour/s with water ligands	Colour/s with Cl^- ligands	Colour/s with NH_3 ligands	Distance travelled by ion (mm)	Distance travelled by solvent (mm)	Rf
Ni^{2+}						
Fe^{3+}						
Co^{2+}						
Cu^{2+}						
Mn^{2+}						
Boiler water (record any colours obtained separately)						

Conclusion:

Experiment 2. Determination of aluminium by reacting with catechol violet

Al^{3+} forms a coloured complex with catechol violet $C_{19}H_{14}O_7S$, which can absorb light of wavelength 585 nm. The absorbance measured will be directly proportional to the concentration. In this experiment a calibration graph is constructed using standards and then the concentration of the test solution determined.

1000 μg/L = 1 mg/L = 0.001 g/L

Health and safety

Care should be taken when using the concentrated HCl (5N). The Hexamine solution is an irritant. **Gloves must be worn.** The aluminium solutions and the catechol violet solution are not considered to be very harmful.

Equipment & Reagents

Visible spectrophotometer
1 cm path-length plastic cell
6 x 50 mL volumetric flasks
20 mL graduated pipette
10 mL bulb pipette x 2
25 mL bulb pipette
20 mL bulb pipette
Pipette filler
2 x 2 mL graduated pipette
100 mL volumetric flask
Pasteur Pipettes x 8

Al^{3+} standard solution (10 mg/L)
5 M HCl solution
Catechol violet solution
Hexamine buffer solution
Deionised water in wash bottle
50 ml beaker
Marker pen or labels
Stop clock
Test solution (blood plasma from Alan)

Procedure

Read parts 2.1 to 2.5 first and then decide your best plan of action.

2.1 Using the 10 mg/L Al^{3+} stock solution, prepare a 1 mg/L Al^{3+} stock solution in a 100ml volumetric flask. (See dilution equation on page 4.)

2.2 Using the 1 mg/L Al^{3+} stock solution, prepare four standard solutions of Al^{3+} of concentration 100, 200, 300 and 400 μg/L. These standards will be made up in 50ml volumetric flasks and will contain hydrochloric acid, catechol violet and hexamine buffer as well as deionised water.

2.3 To make the standards, pipette the appropriate amount of 1 mg/L Al^{3+} stock solution into the 50 ml volumetric flasks. The following must be done in the order stated, with mixing in between the addition of each reagent. To each flask add 10 mL of deionised water, 1.0 mL of 5 M hydrochloric acid, 2.0 mL of catechol violet solution and 20 mL of hexamine buffer solution. Mix well and make up to the mark with deionised water. Mix again and then leave to react for 15 minutes.

2.4 Prepare a fifth standard of concentration zero μg/L Al^{3+} using the same method as in 2.3 but do not add any Al^{3+} stock solution.

2.5 Prepare your test sample using the blood plasma from Alan. Add 20 ml of the test sample to a 50 mL volumetric flask. Then add 1.0 mL of 5 M hydrochloric acid, 2.0 mL of catechol violet solution and 20 mL of hexamine buffer solution. Mix well and make up to the mark with deionised water.

ASK FOR A DEMONSTRATION OF THE USE OF THE SPECTROPHOTOMETER.

2.6 Set the spectrometer to 585nm.

2.7 Fill a U.V. cell with the zero concentration solution. Set the instrument zero.

2.8 Take absorbance readings for each of the standards in order of increasing concentration, starting with the zero standard.

2.9 Record the absorbance of the test solution.

Results

Concentration:	0 μg/L	100 μg/L	200 μg/L	300 μg/L	400 μg/L	Test
Absorbance:						

Draw a calibration graph with concentration as the x-axis and corrected absorbance reading as y-axis. Draw a best fit straight line or a smooth curve, whichever is more appropriate. Use the fitted line or curve to convert the absorbance reading of the unknown test solution to a concentration. Correct for any dilution of the test sample that you may have made. Show any calculations you have used in the experiment.

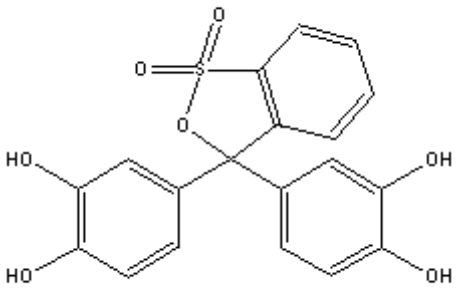
Concentration of aluminium (III) in test solution (from graph): _____ $\mu g\ L^{-1}$

Calculations:

Conclusion:

Chemical background

Catechol violet, also called pyrocatechol violet, forms a co-ordination complex with Al^{3+}. The aluminium ions co-ordinate with the OH groups releasing H+ ions.



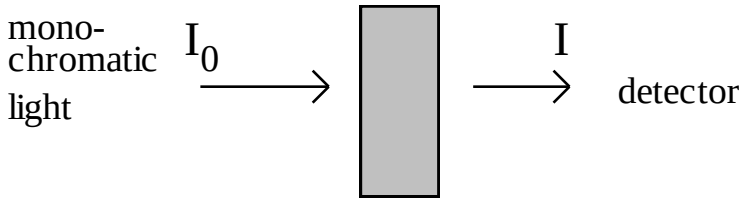
A good analytical reagent for a metal ion should form a very strong complex with the metal ion of interest but also be very specific, that is not react with any other metal ions in solution. Catechol is such a reagent, which is reasonably specific for Al^{3+} forming a blue complex. The colour can be used to determine the concentration of the aluminium (III) ions. See below for explanation of spectroscopy.

UV / visible spectrophotometry

Light can be split into the spectrum of colours that we see in a rainbow; different colours signify different wavelengths and, therefore, different energies. We call a beam of light of one colour monochromatic. Light will be absorbed by an atom, ion or molecule when the energy of one quantum of a particular wavelength of light matches the energy required to cause an electron in an outer orbital to jump to a higher energy level.

Each absorption band is caused by the transition between a given pair of energy levels; because the energy level differences vary with different electronic structures, absorption spectra can often be used to help identify the analyte atom, ion or molecule.

The technique of spectrophotometry relies on the absorption of light by the analyte; the intensity of a beam of light is measured in the absence then presence of analyte and the decrease in transmitted intensity is used to determine the analyte concentration.



The Beer-Lambert law expresses the relationship between absorption and concentration:

$$\mathbf{A = \varepsilon cd}$$

where A = absorbance, ε = molar absorptivity (L mol^{-1} cm^{-1}), c = concentration (mol L^{-1}) and d = optical path-length (the distance that light travels through the sample, in cm). If this relationship is valid, then a graph of absorbance against concentration for a solution will be a straight line, which passes though the origin.

Experiment 3. Titration of analgesic tablets with a base.

In this experiment you undertake three titrations, one with paracetamol, one with aspirin and one with the unknown. The titrations will be followed using a pH meter and the data will be used to plot 3 graphs. The unknown will be identified by comparing the shapes of the curves.

Health and safety

Both paracetamol and aspirin are harmful if taken orally in large amounts. If you are allergic to aspirin or paracetamol, then you should let a member of staff know as touching either of these may bring about an allergic reaction.

Equipment & Reagents

Pestle and mortar
100 mL x 3 volumetric flasks
100 mL beaker
25 mL bulb pipette
50 mL burette
Clamp stand and clamp
Plastic funnel

Paracetamol tablet
Aspirin tablet
Unknown analgesic tablet
70 % ethanol solution
0.1 M potassium hydroxide solution
pH meter and electrode
magnetic stirrer bar/flea
stirrer (hot plate)

Procedure

3.1 Crush one of the tablets in a pestle and mortar then add 20 mL of 70 % ethanol. Stir the mixture gently until most of the tablet has dissolved (some of the filler will remain un-dissolved). Transfer the soluble mixture to a 100 mL volumetric flask and fill to the mark with distilled/deionised water. Repeat the procedure for the other 2 tablets.

3.2 Pipette 25 mL of one of these tablet extraction solutions into a 100 mL beaker.

3.3 Add a magnetic stirrer bar/flea to the 100 mL beaker and place the beaker on the stirrer (hot plate).

3.4 Place the pH electrode into the beaker. The pH meter has already been calibrated but check that the electrode is giving the correct reading by placing the electrode first into a pH 7.00 buffer. Then rinse with water and place in a pH 4.00 buffer. If either reading is out, please ask the demonstrator to re zero your device or follow the written instructions if they are provided.

3.5 Titrate against 0.1 M potassium hydroxide using a 50 mL burette and following the reaction with a pH meter. Allow the flea to gently stir the solution throughout the titration, recording a 0 mL KOH pH reading.

3.6 Add the KOH from the burette in 0.5 mL amounts and record the pH in the table provided. Continue the titration until 15 ml of KOH has been added in total, recording a zero KOH reading as well.

3.7 Repeat the procedure with the other two analgesics.

Results:

Accurately record the pH and the volume of KOH used in the tables provided. Then draw three titration curves, one for each tablet. By comparing the curves decide which is in the unknown tablet. Describe how you compared the three pH curves and hence show how you reached your decision.

Name of tablet: Aspirin

Volume of 0.1M KOH added, cm^3	pH
0.0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	
7.5	
8.0	
8.5	
9.0	
9.5	
10.0	
10.5	
11.0	
11.5	
12.0	
12.5	
13.0	
13.5	
14.0	
14.5	
15.0	

Name of tablet: Paracetamol

Volume of 0.1M KOH added, cm^3	pH
0.0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	
7.5	
8.0	
8.5	
9.0	
9.5	
10.0	
10.5	
11.0	
11.5	
12.0	
12.5	
13.0	
13.5	
14.0	
14.5	
15.0	

Name of tablet: Unknown

Volume of 0.1M KOH added, cm^3	pH
0.0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	
7.5	
8.0	
8.5	
9.0	
9.5	
10.0	
10.5	
11.0	
11.5	
12.0	
12.5	
13.0	
13.5	
14.0	
14.5	
15.0	

Name of tablet*:

Volume of 0.1M KOH added, cm^3	pH
0.0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	
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9.5	
10.0	
10.5	
11.0	
11.5	
12.0	
12.5	
13.0	
13.5	
14.0	
14.5	
15.0	

*****spare table

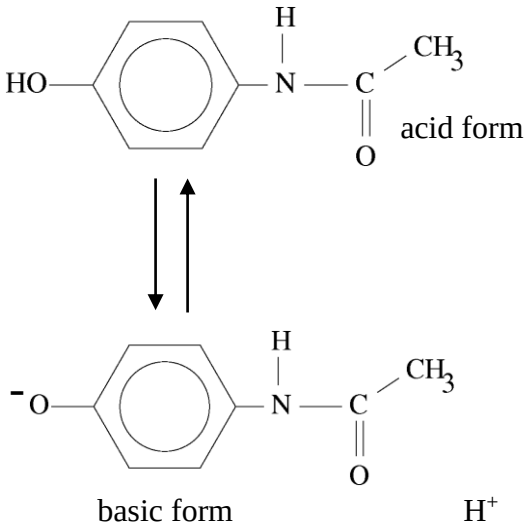
Conclusion:

Chemical background

Paracetamol.

Paracetamol is a very weak acid. The R-OH, hydroxyl group is able to dissociate into $R\text{-}O^-$ and H^+ ions. The un-dissociated paracetamol is called the acid form and the dissociated paracetamol is called the basic form.

During a titration with KOH the acid form is converted to the basic form. At pH 9.5 the two forms are present in equal amounts i.e. there is a 50:50 mixture of the two. Above pH 9.5 the basic form predominates and below pH 9.5 the acid form predominates Paracetamol is said to have a pKa value of 9.5.



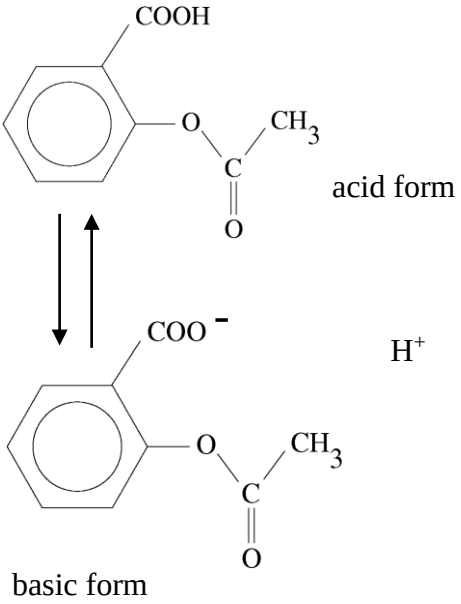
Aspirin

Aspirin is a weak acid similar in acidity to ethanoic acid. The R-COOH, carboxyl group is able to dissociate into $R\text{-}COO^-$ and H^+ ions. The un-dissociated aspirin is called the acid form and the dissociated aspirin is called the basic form.

During a titration with KOH the acid form is converted to the basic form. At pH 3.5 the two forms are present in equal amounts i.e. there is a 50:50 mixture of the two. Above pH 3.5 the basic form predominates and below pH 3.5 the acid form predominates Aspirin is said to have a pKa value of 3.5.

For information only:
The pKa value for aspirin can be easily determined from a pH titration curve. To find the pKa of aspirin first find the volume at the equivalence point. Then divide this value by 2 (the half equivalence volume). Then record the pH at this half volume. The pH value at this point corresponds to the pKa value.

(pKa for paracetamol can be found in a similar way to that for aspirin but it is more difficult as the equivalence point is less obvious)



Pooled Results and conclusion.

Enter your results here.

Copper concentration (or the metal ions present) in the boiler water

Aluminium (III) concentration

Analgesic tablet identified

Your conclusion about these results.

*(Comment on what you deduce from **each** of the results.)*

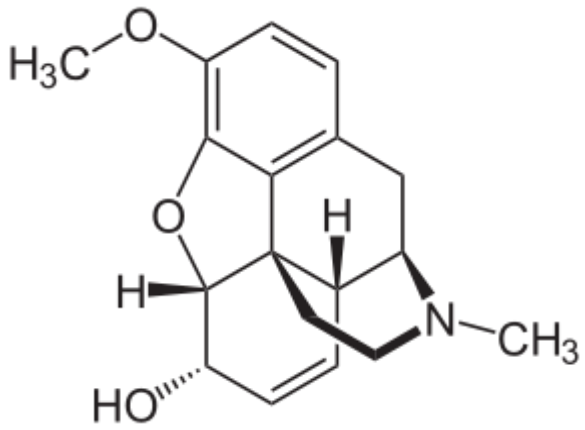
Tie Break Questions

1 Suggest pros and cons for copper and plastic water pipes in the home.

2 Over time a white residue develops in an aluminium pan. Suggest what this could be and give a possible chemical equation for this reaction.

3 Aspirin is used for pain relief but what other medical conditions can it be used to treat?

4 Codeine has the molecular structure shown below:



Describe one chemical test that you could use to distinguish codeine from paracetamol and aspirin.

5 The solubility of aspirin and paracetamol can be increased by adding a base, explain why this is the case.