

KEEPING UP THE STANDARDS



A group experiment in Chemical Analysis
Royal Society of Chemistry Analytical Division
North East Region
Schools' Analyst Competition 2008

Analytical Chemistry is all about solving problems. The context could be pharmaceutical analysis such as the experiment that you are doing today, industrial analysis ensuring that an industrial process works efficiently and that the products are of the correct composition, clinical analysis analysing patient samples or environmental monitoring. In all these, analysts have to design experiments, carry them out and interpret the data.

Today's exercise is designed to give you a taste the type of work that an Analytical Chemist has to do. We hope that you find it interesting and challenging and perhaps consider Analytical Chemistry as a career.

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 questions complete the exercise.

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.

It is part of the RSC Schools' Analyst Competition being carried out in several centres and so we have to operate under the constraints of the competition and keep to time but primarily we hope that you enjoy doing the exercise.

Please read and understand the instructions before commencing and note that 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 laboratory coats and safety spectacles at all times.

Do NOT eat or drink in the laboratory.

Always use the pipette fillers provided, and handle glassware carefully to avoid breakage and cuts.

Keep long hair under control.

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.

Planning

To be successful you will need to plan how each member of the group will use their time. Our estimate of the time required for the experiments is

Experimental	2.0 - 2.5 h each
Calculation	0.5 - 1.0 h each

Decide how you will organise the work within your group; then write out a plan in the form of a flow chart (this is a simple diagram showing the key steps to be taken, in a series of boxes linked by arrows to show the sequence of events). Each box should explain, in brief, the action to be taken at that point. Individual responsibilities should be indicated for each step. The flow chart will be handed in with the results, so do it neatly.

Record the results neatly on the sheets provided, plot your graphs (remember to include titles), perform the calculations then, as a group, draw conclusions from your data. Finally, as a group, answer the questions in the spaces provided.

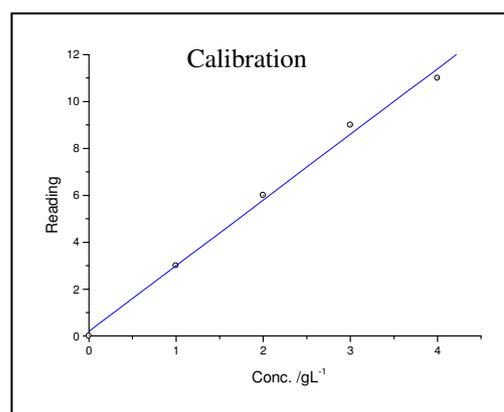
When you have finished hand in your flow sheet, the result sheets and your graph to the organiser.

Experimental work and treatment of results**Dilution**

When making up dilutions, always do so accurately by using a pipette and by making up to a fixed volume in a standardised flask. For example, if you start with a 200 gL^{-1} solution and wish to make up a 10 gL^{-1} solution, you need a 20 fold dilution so you could pipette 5.0 cm^3 of the standard into a 100 cm^3 volumetric flask and then dilute to the mark.

Calibration

Draw the points onto clearly labelled graphs. The method here should give a straight line and unless the points are clearly better fitted with a curve, you should estimate by eye the best fit straight line which will be one which minimises the distances from the line to the points rather than the one which passes through the most points.

**Assessment**

For the purpose of the competition, you will be assessed on your analytical results, your presentation of the results and your deductions. The questions at the end are tie-break and will be considered if there are a number of equally good teams.

TRADING STANDARDS.

Trading standards are there to protect the public from unfair practices, such as overcharging and shoddy or unsafe workmanship. They also ensure that the goods you buy are what they claim to be, so that for instance you do not pay a lot of money for "designer" clothes that turn out to be fake. Product safety is another important area; for example, children's nightwear and household furnishings should be properly fireproof, and children's toys should not contain parts which can cause injury. Trading Standards Officers help to enforce the laws in these areas, and to do this they often have to have samples analysed in a laboratory to determine whether they comply with the law or not.

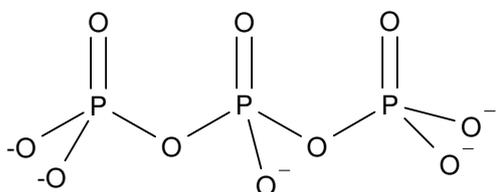
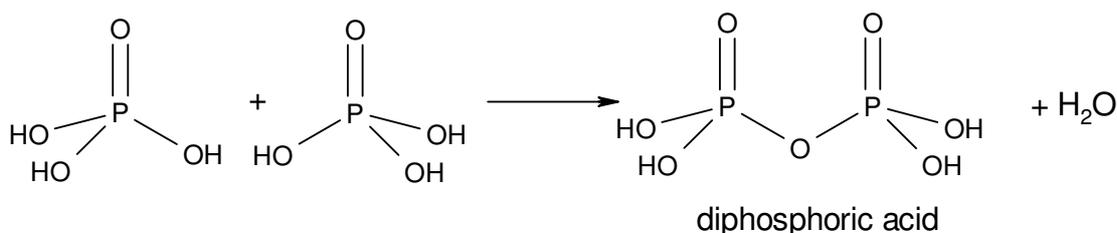
In this exercise you will take the part of a team in a Trading Standards laboratory. You have three cases to investigate:

- A local butcher, Burke & Hare's Specialty Meats Ltd, is suspected of using excessive quantities of polyphosphate to increase the weight of their chickens.
- Customers of the Yeti & Penguin Public House have complained that their landlady, Mrs Ima Fiddler, has been watering down their vodka.
- A consignment of brightly coloured plastic dolls, imported from China by the Weng-Chiang Wholesale Toy Emporium, is suspected of having dangerous levels of lead in the paint.

Your task is to determine whether any of these businesses have broken the law. Your team has three samples to analyse, and you will need to divide the work up among yourselves so that you can complete it in the time available. You will analyse for phosphate using visible spectroscopy, lead using atomic absorption spectroscopy and alcohol by density measurement.

Determination of Phosphate in Chicken - Background Information.**Phosphate in meat products**

You will be familiar with phosphoric acid, H_3PO_4 , and the phosphate ion, PO_4^{3-} , but perhaps not with polyphosphates. These can be regarded as forming by elimination of water between 2 or more phosphoric acid molecules:



The triphosphate anion, $\text{P}_3\text{O}_{10}^{5-}$

Polyphosphates are legitimately added to chicken and other meats. They help to protect the flavour, prevent discolouration and increase water retention, thus preventing the meat from drying out and improving its appearance. However this last property can be abused; excessive addition of polyphosphates can result in a large amount of water being retained. What looks like a plump juicy chicken may in fact have a large water content, and as it is priced according to its weight, the customer can end up paying for water rather than meat. Thus the amount of polyphosphate which may be added is limited by law.

The legal limit is defined by assuming that all the phosphorus is present as P_2O_5 ; the permitted level is 0.3% P_2O_5 by weight. This corresponds to 0.13% phosphorus or **0.40% PO_4^{3-}** .

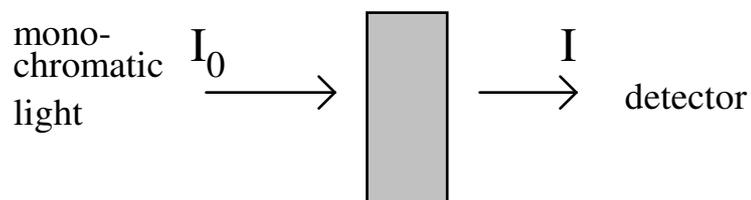
UV / visible spectrophotometry

Light itself 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:

$$A = \epsilon bc$$

where A = absorbance, ϵ = molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$),

c = concentration (mol L^{-1}) and b = optical pathlength (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 through the origin.

This is the basic equation of spectrophotometry. The spectrophotometer (or colorimeter) can only measure the intensity of light, however, so we need an additional relationship linking absorbance to I and I_0 . This is $A = \log (I_0/I)$.

1. Determination of Phosphate in Chicken.

Materials & Equipment

Stock phosphate solution $4.00 \times 10^{-3} \text{ mol L}^{-1}$.

Stock Nitric Acid solution, 1.0 mol L^{-1} .

Colour Reagent solution	Chicken Extract solution
6 x 100 mL volumetric flasks	5, 10 & 25 mL pipettes
4 x 50 mL beakers	Spectrophotometer & cuvettes
Pasteur pipette	graph paper

Prepare four standard solutions of phosphate in the concentration range $2-8 \times 10^{-4} \text{ mol L}^{-1}$ by pipetting appropriate volumes of the stock phosphate solution into 4 100-mL volumetric flasks. Also pipette 10 mL of 1.0 mol L^{-1} nitric acid into each flask. Prepare a blank in a fifth flask by adding the 10 mL of nitric acid but no phosphate. Into a sixth flask pipette 25 mL of the chicken extract; you do not need to add nitric acid to this flask as the extract already contains sufficient acid.

Pipette 25 mL of colour reagent into each flask, then dilute to the mark with distilled water. Allow the solutions to stand for 10-15 minutes; during this time ask for a demonstration of the spectrophotometer.

Measure the absorbance of each solution at a wavelength of 430 nm. Plot a calibration graph of absorbance (on the y-axis) against concentration of phosphate (on the x-axis), and read off the concentration of phosphate in the diluted extract. Given that 100 mL of extract came from 5.0274 g chicken, calculate the percentage of phosphate in the chicken sample.

Determination of Alcohol in Vodka - Background Information.

Vodka gets its name from the word *voda*, which means “water” in Polish and Russian. The drink has been known in some form in Russia since the 9th century AD, and in Poland since the 11th century. Following the Bolshevik revolution in Russia in 1917 the vodka distilleries were taken over by the state. Several vodka makers emigrated to the west, including one named Smirnoff who set up a distillery in Paris in 1934. The popularity of vodka in the West has grown since then. The first British vodkas were produced in the 1960s, and nowadays Britain exports some high quality vodka to Russia¹.

To a chemist, however, the most famous name in the history of vodka is not Smirnoff, but Dmitri Ivanovich Mendeleev² – the creator of the Periodic Table. Mendeleev obtained his Doctorate in 1865 for a dissertation entitled “On the Combinations of Water with Alcohol”. In 1893, Tsar Alexander III appointed him as Director of the Russian Bureau of Weights and Measures³, where one of his first tasks was to come up with a legal standard for the alcohol content of vodka. The figure Mendeleev arrived at - 38% alcohol by volume – was rounded up to 40% for tax purposes⁴.

Nowadays, for a drink to be sold as vodka in the European Union, it must be made from alcohol “of agricultural origin” – usually wheat, rye, potatoes, molasses or rice – and must contain a **minimum of 37.5% alcohol by volume**¹. Some vodkas have alcohol contents as high as 50%.

(The alcohol analysis in real life would be done "on the spot" using a portable device called a hydrometer. The method you will be using is likely to be very similar to the experiments performed by Mendeleev himself.)

- 1 <http://www.ginvodka.org/history>
- 2 A Fish, Poster Presentation, University of Teesside 2006
- 3 http://en.wikipedia.org/wiki/Dmitri_Mendeleev
- 4 <http://en.wikipedia.org/wiki/Vodka>

2. Determination of Alcohol in Vodka**Materials & Equipment**

Ethanol	Vodka sample
5 mL pipette	5 x 50 mL volumetric flasks
25 mL burette	Pasteur pipette
6 x 50 mL beakers	12 sample vials with caps
Analytical Balance	Glass marker pen
Graph paper	Funnel for burette filling

Prepare five standard solutions of alcohol in the range 30-50% by adding appropriate volumes of ethanol from a burette into each of 5 volumetric flasks, and diluting to the mark with water. Label these solutions A, B, C, D, E.

Ask for a demonstration of how to use the analytical balance. Number each of your sample vials and weigh them (with caps on) to 4 decimal places. (*NB* Most analytical balances are accurate to ± 0.0003 g, so don't worry if the figure in the 4th decimal place fluctuates slightly.)

Pipette 5 mL of each of your standard alcohol solutions into 5 separate vials. Pipette 5 mL of the vodka sample into a sixth vial. Close the caps on each vial as soon as you have transferred the solutions, to prevent evaporation of alcohol. If time permits, prepare a second set of vials to provide you with duplicate measurements.

Weigh each of the vials in turn and calculate the density of the alcohol solutions. Plot a calibration graph of density (on the y-axis) against % alcohol (on the x-axis). From your graph, read off the alcohol percentage of the vodka sample.

Determination of Lead in Paint – Background Information.

As a relatively unreactive metal, lead has been known and worked since ancient times. Its chemical symbol, Pb, comes from the Latin name *plumbum*, indicating that the metal was known to the Romans. The modern word *plumber* arises from one of its major uses – as pipes to carry water. Lead compounds have also been used as pigments and cosmetics; lead carbonate, PbCO_3 , was used to whiten the complexion from the 16th century, with Queen Elizabeth I of England perhaps the most famous user. Other pigments include “red lead”, Pb_3O_4 , and the yellow lead chromate PbCrO_4 .

However adverse health effects arising from exposure to lead have also been documented from around the 2nd century BC. Nowadays, not only have lead water pipes been replaced by copper, but even lead-containing solder used to join copper pipes together is recognised as a potential health hazard.

Lead ingested into the body acts as an inhibitor of many enzymes; a particularly important one is ALA-dehydratase, which catalyses a key step in the synthesis of hemoglobin, the protein which transports oxygen around the body. Thus anemia is one symptom of lead poisoning. The compound on which this enzyme acts, δ -aminolevulinic acid or ALA, builds up in the body as it is not being converted. It is structurally similar to GABA (γ -aminobutyric acid), which is an important neurotransmitter. Excess ALA has adverse effects on the brain and central nervous system. This can be particularly serious in young children, where the brain is still developing. Many studies have shown a link between lead exposure in early childhood and learning difficulties in later life; this is one of the main reasons why lead additives are being phased out of petrol.

Given the propensity of babies and toddlers to stick their toys in their mouths, it is obviously not a good idea if the bright colours of such toys are the result of lead-containing pigments. The international recommended limit for lead in paint is currently 600 parts per million or 0.06%, though the legal limit in this country is still slightly higher at **0.1% (1000 ppm)**. Most toys nowadays are manufactured in China, and although the Western parent companies specify the type of paint to be used, cheaper alternatives are sometimes employed which can contain extremely high proportions of lead. In late summer 2007 one well-known toy company had to recall products on three separate occasions after it was found that the Chinese-manufactured items had lead levels up to 200 times the permissible maximum.

Atomic Absorption Spectroscopy

The technique of Atomic Absorption is similar to UV/visible spectrophotometry in that the light absorbed by a sample can be related to the concentration of the absorbing species. The energy of the absorbed light is used to promote an electron from a lower to a higher energy level. In atoms, unlike molecules, the energy levels are very "narrow", so the energy gaps between them (corresponding to the energy of the light which can be absorbed) are very precise. The wavelengths of light which can be absorbed in any one transition typically span a range of less than one nanometre (10^{-9} m), as opposed to 100 nm or more in molecules. (This is due to the absorption of energy by vibrating bonds in molecules – there are no bonds in single atoms).

Typical atomic spectrum:



Typical molecular spectrum:



In order to provide light at precisely the correct wavelength for an atom to absorb, the lamp in an atomic absorption spectrometer has a filament made from the element to be analysed. In this exercise, therefore, the instrument is set up with a lead lamp. As this lamp emits radiation arising from electronic transitions in lead atoms, only lead atoms in the sample can absorb the radiation – the energy level differences in other elements are very unlikely to match exactly those of lead. Atomic absorption is thus a very *selective* analytical technique – it can analyse for one individual element even though many others may be present in the same solution.

Concentration units in AA:

Atomic absorption is also a very *sensitive* technique – it can measure very low concentrations, at the level of parts per million (ppm) or even parts per billion (ppb). These units may refer to volume (1 ppb by volume is 1 mL in 1 billion mL) or mass (1 ppm by mass is 1 g in 1 million grams). In the special case of dilute aqueous solutions (as encountered in atomic absorption analysis), ppm is a particularly convenient unit. This is because the density of water is very close to 1 gram per cubic centimetre (= 1 g/mL); thus 1 litre (1 dm³ = 1000 cm³) of water has a mass of 1 kilogram. A concentration of 1 ppm (by mass) is 1 gram per million grams, or, dividing by 1000, 1 milligram per kilogram; since a kilogram of water has a volume of 1 litre, **1 ppm = 1 mg/L** for dilute aqueous solutions.

3. Determination of Lead in Paint.**Materials & Equipment**

Stock solution of lead, 80 ppm	Paint sample solution
Nitric Acid 1.0 mol L ⁻¹	3 x 50 mL beakers
7 x 100 mL volumetric flasks	2, 5 & 2x10 mL pipettes
Pasteur pipette	Graph paper

Prepare 4 standard solutions of lead in the range 1-8 ppm, by pipetting appropriate volumes of the 80 ppm stock solution into 4 separate 100 mL volumetric flasks. Pipette 10 mL of 1.0 mol L⁻¹ nitric acid into each flask, and prepare a blank containing the same amount of nitric acid but no lead.

Prepare two dilutions of the provided paint sample by pipetting 10 mL of the sample solution into a 100-mL volumetric flask and diluting to the mark. You do not need to add nitric acid to these as the sample solution already contains sufficient acid.

Ask for a demonstration of the atomic absorption spectrometer and run each of your solutions in turn, along with the paint sample solutions. Plot a calibration graph of absorbance (on the y-axis) against concentration of lead (on the x-axis) and read off the lead concentration in the analyte solution.

Given that the paint sample solution contained 0.0512 g of paint in 100 mL, calculate the proportion of lead in the paint.

***** *We hope you have all enjoyed the competition. This year we give thanks to the Dr Joe McGinnis and Technical and Academic staff at the University of Teesside for the development of the competition******

1. Determination of Phosphate in Chicken.

Flask No.	Volume of $4.00 \times 10^{-3} \text{ mol L}^{-1}$ phosphate added	Phosphate concentration / mol L^{-1}	Absorbance at 430 nm
1	0	$\frac{0}{100} \times 4.00 \times 10^{-3} =$	
2			
3			
4			
5			
6	25 mL chicken extract	Value read from graph =	

Calculation:

Concentration of phosphate in diluted chicken extract (from graph)

$$= \text{mol L}^{-1}$$

Concentration of phosphate in undiluted chicken extract

$$= \text{diluted concentration} \times 100/25 = \text{mol L}^{-1}$$

Amount of phosphate in 100 mL undiluted chicken extract (in moles)

$$= \text{concentration (mol L}^{-1}\text{)} \times \text{volume (Litres)} = \text{mol}$$

Mass of phosphate in chicken extract

$$= \text{Amount (mol)} \times \text{RMM (g mol}^{-1}\text{)} = \text{g}$$

(O = 16.00 g mol^{-1} , P = 30.97 g mol^{-1})

Percentage of phosphate in chicken sample:

$$=$$

Is Burke & Hare's Speciality Meats using illegal amounts of phosphate in its chickens?

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2. Determination of Alcohol in Vodka

Solution	Volume of ethanol added	% alcohol
A		
B		
C		
D		
E		

Vial No.	Weight empty	Weight + 5 mL alcohol solution	Mass of alcohol solution	Density of alcohol solution ($\rho = m/V$)	Identity of solution (A, B, C, D, E or Vodka)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					

Solution	% alcohol	Average density
A		
B		
C		
D		
E		
Vodka	Value read from graph =	

Is Mrs Ima Fiddler watering the vodka for the customers of the Yeti & Penguin?

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3. Determination of Lead in Paint

Flask No.	Volume of 80 ppm lead solution added	Lead concentration/ppm	Instrument reading
1	0	$\frac{0}{100} \times 80 =$	
2			
3			
4			
5			
6	Paint Sample A	Value read from graph =	
7	Paint Sample B	Value read from graph =	

Calculation:

Average concentration of lead in analysed solutions = ppm
= mg/L

Concentration of lead in original paint sample solution
= diluted concentration $\times 100/10$ = mg/L

Mass of lead in original paint sample solution
= concentration (mg/L) \times volume (**Litres**) = mg
= g

Percentage of lead in paint sample

=

Proportion of lead in paint sample in *parts per million*

=

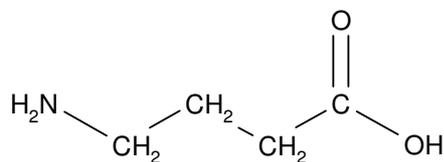
(**NB** 1% = 1 *part per hundred*. You know how to convert a fraction to a percentage, what do you have to do to convert the same fraction to ppm?)

Is the Weng-Chiang Toy Emporium selling dangerous dolls?

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Tie Break Questions:

- 1 Show by calculation that 0.3% P_2O_5 is equivalent to 0.4% PO_4^{3-} .
(Hint: Consider a 100g sample. 0.3% is equivalent to 0.3g in 100g. How many moles of P_2O_5 is this? If all the phosphorus was present as phosphate, what would the weight be?)
- 2 What other common household products contain large amounts of phosphate?
- 3 A solution of lead was found to have a concentration of 56 ppm. What is this in moles per litre? (Atomic weight of lead = 207.2 g mol^{-1} .)
- 4 The structure of GABA is shown below. What is its systematic name?



Summary sheet

<u>1. Determination of Phosphate in Chicken.</u>	% phosphate
<u>2. Determination of Alcohol in Vodka</u>	% alcohol
<u>3. Determination of Lead in Paint</u>	ppm lead in paint

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