5.7 Candidate Individual Investigation Report 0409

Iron in audio tapes

Chemistry Coursework.

The aim of my coursework is to discover how much iron is in an audiocassette tape. To make sure that I work out an accurate amount, I will have to use several types of chemical analysis, as certain methods of analysis may be more accurate and reliable than others. From these different methods, I may be able to gain an accurate figure of the amount of iron in tape.

The Purpose of Iron in Tape.

Iron is used in tape, as it is a magnetic metal.

" In the most common method of sound recording, the magnetic method, transformed sound waves may be amplified and made to magnetize a metal oxide coated plastic recording tape so that magnetization varies with the frequency and intensity of sound. Sound recording involves some form of mechanical movement of the recording medium at a constant speed past the point of recording so that the sound recording may later be reproduced as a replica of the original sound. " (Feldman L. 1999)

Sound waves are converted into electrical impulses during recording, which are transferred to the tape by an electromagnetic record head. The playback head converts the magnetic fields back to electrical impulses, which in turn can be converted back to sound waves.

Bucket Chemistry

I wrote to "Maxell" to gain some information about the materials involved in the tapes they manufactured. Although they could not tell me about the magnetic coating, as it is a secret recipe, I did learn that the 'tape' itself is polyester film. From my work in 'Designer Polymers' I know that polyesters can be broken down into dicarboxylic and diol monomers.

1) Ethane-1,2-diol + Benzene-1,4-dicarboxylic acid → Polyester + water

As the creation of polyester (see equation 1) is caused through a condensation reaction, the opposite of this is a hydrolysis.

"The reverse of esterification corresponds to the breakdown of an ester by water. In other words, it is a hydrolysis.... A catalyst is effective for both directions of a reversible reaction, so sulphuric acid (or any other acid) will do.... another way of hydrolysing an ester is to add an alkali, such as sodium hydroxide solution.... the hydrolysis does not produce a carboxylic acid, but a carboxylate salt." (Burton G., Holman J., Lazonby J., Pilling G., Waddington D., 1994, Pg 319)

I thought that if the polyester broke down, its magnetic coating would be placed into solution. I therefore decided to reflux the tape to try and disintegrate the tape. In my preliminary test, I refluxed two pieces of tape, one in NaOH, and the other in HCl. The tape in NaOH became "bitty" when refluxed and the coating on the tape appeared to remain intact. The tape in HCl remained in tact, but the coating, which was brown,

came off into solution. The solution was amber, I suspected it was iron chloride, and could easily be decanted from the polyester.

The equipment I used to reflux this tape was a round-bottomed flask, heated by an electrical heater, as this gives a more even and consistent heat to the flask and hence the solution within it. As reactants that require reflux react at a temperature higher than their boiling points, a condenser was placed on top of the flask, so that the reactants would not evaporate. I added some anti-bumping granules, because they make sure the solution does not boil violently by spreading the heat through the solution evenly.

The solutions of iron chloride in the chemical cupboard were a similar colour to the solution produced from the reflux. I decided to test the solution to firstly check it was iron chloride and secondly see which oxidation states of iron were present. Potassium hexacyanofferrate detects iron (II) ions by turning blue (see equation 2). When added to my solution it turned green, suggesting iron (II) was not present in solution. Ammonium thiocyanate detects iron (III) by turning red (see equation 3). This occurred with my solution, suggesting iron (III) was the only oxidation state of iron present in solution.

Test	Result	Conclusion
Potassium hexacyanoferrate	Green	Fe^{2+} not present
Ammonium thiocyanate	Red	Fe^{3+} present

2) $Fe(H_2O)_6^{3+}{}_{(aq)} + SCN^-{}_{(aq)} \rightarrow [Fe(SCN)(H_2O)_5]^{2+}{}_{(aq)} + H_2O_{(l)}$ (Blood red)
(Ramsdan E., 1985, Pg 470)

3) $4\,Fe^{2+}{}_{(aq)} + 3[Fe(CN)_6]^{3-}{}_{(aq)} + H_2O_{(l)} \rightarrow Fe_4[Fe(CN)_6]_{3\,(aq)} + xH_2O_{(l)}$ (Prussian blue).

I had therefore made iron (III) chloride, $FeCl_3$. The iron oxide originally in the tape must have been iron (III) oxide, Fe_2O_3. This seems likely, as

"Studio recording tapes generally employ gamma ferric oxide (Fe_2O_3) as the main magnetic material." (Borwick J., 1994, Pg 246)

The reaction occurring in the reflux was:

4) $Fe_2O_{3\,(s)} + 6HCl_{(aq)} \rightarrow 2FeCl_{3\,(aq)} + 3H_2O_{(l)}$

Therefore, through serendipity, I had discovered a way of getting the magnetic material from tape into solution (see equation 4), without hydrolysing the polymer. This also saved me from having to worry about the dicarboxylic monomers reacting in the experiments I will perform. I was puzzled as to why the polyester did not hydrolyse under reflux. My only guess is that it is high tensile polyester, which has been strengthened for the purpose of vigorous sound recording. If it is very high tensile it may resist hydrolysis at the relatively low temperatures and concentrations achievable in the school laboratory.

When refluxing the tape for the experiment I used 1 metre of tape. Originally I used about 0.1 dm^3 of 2 mol dm^{-3} HCl, and made the solution up to 0.25 dm^3 in a volumetric flask, but the solution was too weak to gain a reading on the colorimeter, so instead I used 0.08 dm^3 HCl and used the flask rinsings and distilled water to make the solution up to 0.1 dm^3 in a volumetric flask. This ensured that I had a standard solution of iron chloride, which would allow easy calculation later in the experiment, when I performed titration. The volumetric flask is a very accurate way of making up a standard solution, as it has a low percentage error.
Percentage error = (error / reading) x 100
$(1 \times 10^{-3} / 0.1) \times 100 = 0.01\%$
This means I can accurately scale up any readings I get from titration, to say how much iron was in the metre of tape.

The problem was the small volume of solution produced and the amount of experiments to be conducted. I wasn't sure if I'd have enough solution to complete all the experiments, especially if something went wrong.

Colorimetry

I need several methods of analysis to ensure the accuracy of my results. As iron is a transition metal it forms highly coloured compounds such as the yellow iron chloride. Therefore I feel it is a logical step to perform colorimetric analysis on my sample.

The Chemistry and Principles of Colorimetry

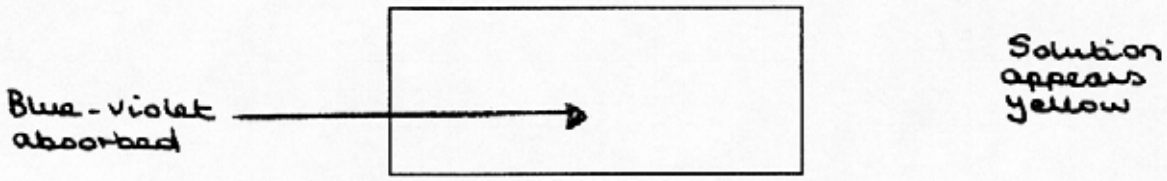
"A colorimeter is a simple type of visible spectrophotometer. Colorimetry is used to measure the intensity of absorption of coloured compounds over a narrow range of frequencies: it provides a useful way of finding the concentration of a coloured compound." (Burton G., Holman J., Lazonby J., Pilling G., Waddington D., 1994, Pg 158)

A filter must be chosen for the colorimeter appropriate to the sample being tested. For example, if a sample appears red to the eye, the sample is absorbing the complimentary frequency of light, blue-green. The blue-green filter is selected. The colorimeter is "zeroed" against a clear sample. The sample to be tested can then be entered. The colorimeter can tell you how much blue-green light has been absorbed. The stronger the concentration of solution, the more absorption will occur.
By using a number of known concentrations and their colorimeter readings, a calibration graph can be drawn. The reading for the unknown sample can be drawn in on the graph to obtain a concentration for the sample.

Complimentary colours.

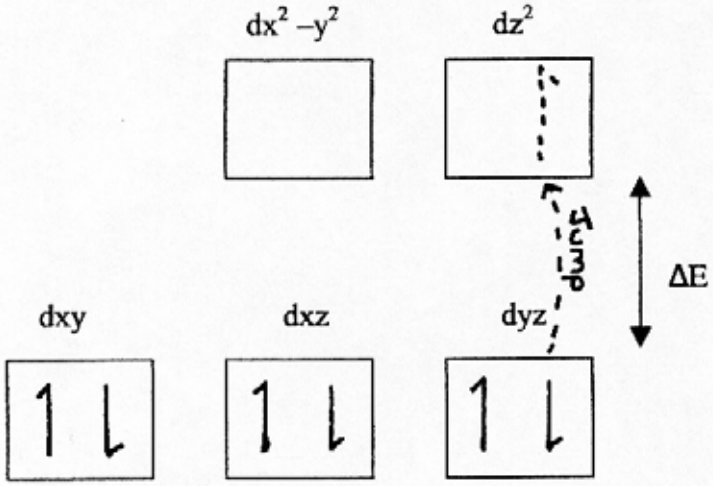
Red	Compliments	Blue-green
Orange	Compliments	Blue
Yellow	Compliments	Blue-violet
Yellow-green	Compliments	Violet

Colours of transparent objects.



(Burton G., Holman J., Lazonby J., Pilling G., Waddington D., 1994, Pg 155)

Iron is a transition metal and therefore forms coloured compounds. This is because they have partially filled d orbitals in their electron shells. The d shell is made up of five orbitals; dxy, dxz, dyz, dx^2-y^2 and dz^2. The latter two of these are orbits around axes. The ligands approach the transition metal along these axes. These two orbitals are then pushed to a higher energy level due to interactions with the ligands. As the d shell is incomplete, electrons can 'jump' between the energy levels created. The energy required to do this can correspond to visible light. The 'removal' of this frequency of light makes the compound appear to be the complimentary colour to that which it absorbs.



As colorimetry hasn't got a fixed unit to measure absorption, the first thing I needed to do was to create a calibration graph, so that I'd be able to deduce the amount of iron chloride present in the sample. From a 3 M solution I originally decided to make up 2 M, 1.5 M, 1 M, 0.5 M, 0.25 M and 0.1 M solutions. I achieved this through the usage of measuring pipettes, which I felt were a good way to accurately measure out small volumes of solution. I felt that these solutions would give a good range of results with which to draw a calibration curve.

Amount = concentration x volume

Have 3 mol dm^{-3} $FeCl_3$. If take 0.005 dm^3 of this, I have:

3 x 0.005 = 0.015 mol $FeCl_3$ present.

To make a 1.5 mol dm^{-3} solution, I need 0.015 / 1.5 = 0.01 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.005 dm^3 H_2O.

To make a 2 mol dm^{-3} solution, I need 0.015 / 2 = 0.0075 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.0025 dm^3 H_2O.

To make a 1 mol dm^{-3} solution, I need 0.015 / 1 = 0.015 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.01 dm^3 H_2O.

To make a 0.5 mol dm^{-3} solution, I need 0.015 / 0.5 = 0.03 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.025 dm^3 H_2O.

To make a 0.25 mol dm^{-3} solution, I need 0.015 / 0.25 = 0.06 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.055 dm^3 H_2O.

To make a 0.1 mol dm^{-3} solution, I need 0.015 / 0.1 = 0.15 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.145 dm^3 H_2O. (Or 0.001 dm^3 $FeCl_3$ and 0.029 dm^3 H_2O.)

Concentration req. / mol dm^{-3}	Volume 3M $FeCl_3$ /dm^3	Volume H_2O dm^3
3.00 Mol	0.0050	0.0000
2.00 Mol	0.0050	0.0025
1.50 Mol	0.0050	0.0050
1.00 Mol	0.0050	0.0100
0.50 Mol	0.0050	0.0250
0.25 Mol	0.0050	0.0550
0.10 Mol	0.0050	0.1450

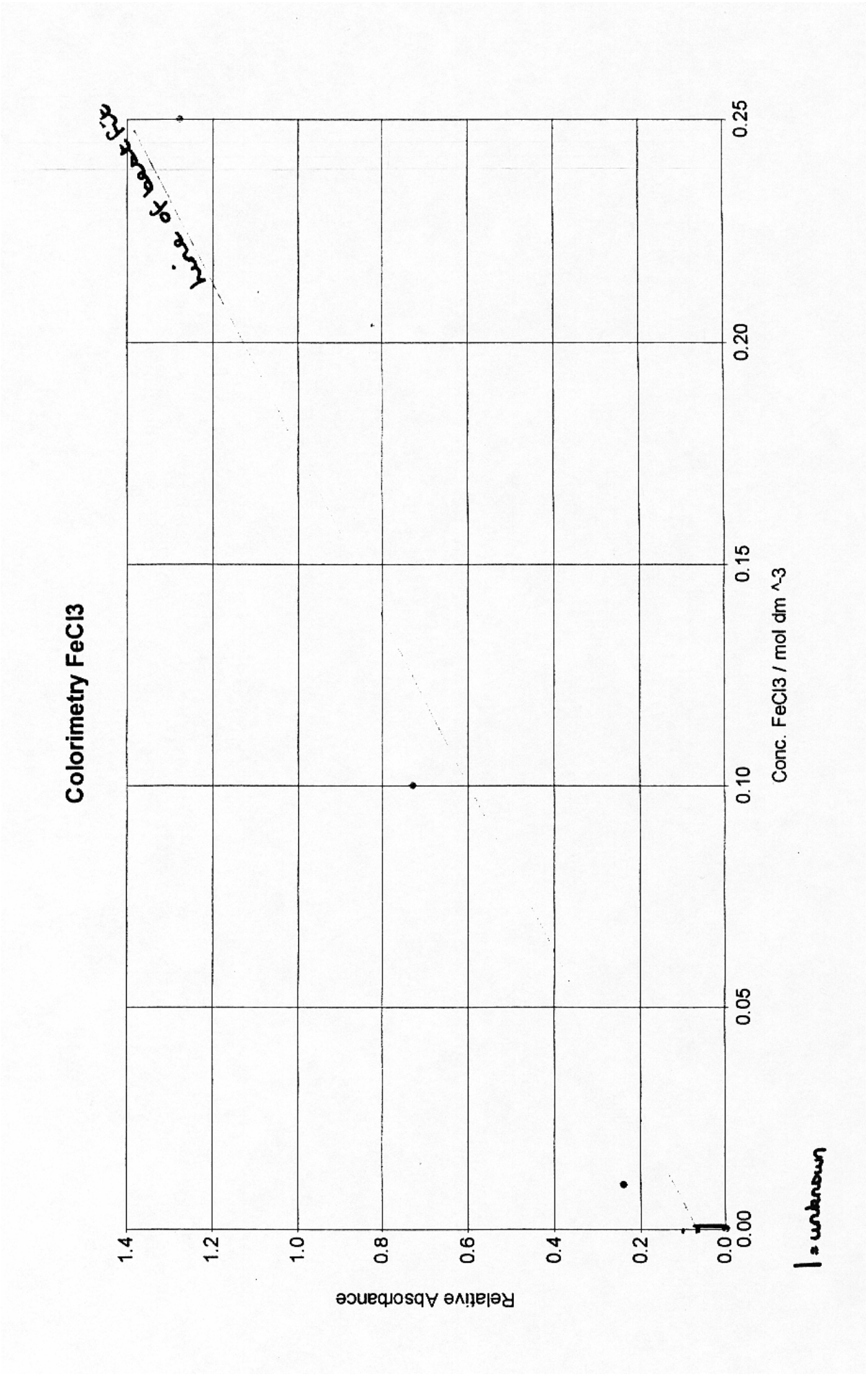
To make up these solutions, I used measuring pipettes, because they easily measure out small volumes of solution, but are far more accurate than a measuring cylinder. This is because for a volume of 0.01 dm^3, the error of the pipette is just 2.5 x 10^{-5}, compared to the larger error of 5 x 10^{-5}, which the measuring cylinder produces.
These solutions having been made up, I then needed to work out which filter to use in the colorimeter. As my solution was a kind of amber colour, I was unsure as to whether I would need to use the blue filter or the blue-violet filter. To work this out, I tested which one gave the larger absorption reading on my unknown sample. (N.B. I used distilled water to "zero" the colorimeter.) The blue filter gave a reading of 0, and the blue-violet a reading of 0.07. I therefore opted for the blue-violet filter, which allows light of wavelength 440 nm to pass through, as this would give me the best readings.

Putting The Colorimetry Into Practice.

I tested my samples in the colorimeter, beginning with the strongest. I noticed that everything above 0.5 mol dm^{-3} solution gave a default reading, "1A." The solutions were too strong for the colorimeter to take a reading. Here is a table of results.

Concentration required /mol dm^{-3}	Relative Absorbance
Unknown	0.07
3.00	"1"

2 .00	"1"
1.50	"1"
1.00	"1"
0.50	"1"
0.25	1.28
0.10	0.73
As my unknown solution was a lot weaker than 0.1 mol dm^{-3}. I made a 0.01 mol dm^{-3} solution by adding 0.09 dm^3 H_2O to 0.01 dm^3 of the 0.1 mol dm^{-3} solution.	
0.01	0.24



I was not particularly happy with these results. My unknown would not fit onto my calibration graph very well. I only obtained three readings, which is not enough to be sure of an accurate calibration graph. Also I believed the 0.01 Mol solution to give an anomalous result, as the reading seems far too large. The solution should have one-tenth the amount of iron chloride particles as the 0.1 Mol solution and therefore I would logically expect a reading of about one tenth. Instead it is a third. I feel this was caused by inaccuracies occurring in the dilution of the stronger concentrations of iron chloride, due to repeated use of the pipette, increasing the mathematical chance of error.

This is because every time the full pipette is used, the error is 0.01 +/- 2.5 x 10^{-5}. The more times the pipette is used the greater the error created. This meant that the weaker solutions where the pipette was used more, were more likely to have bigger errors.

Therefore I decided to concentrate more on solutions below 0.5 mol dm^{-3}, as it appeared that my solution was weaker than this. I decided to make up 0.5M, 0.4M, 0.3M, 0.2M, 0.1M, 0.05M and 0.01M solutions. I felt that these would again give a good calibration graph, and hopefully my unknown would fit onto this curve.

Amount = Concentration x Volume

To make a 0.5 mol dm^{-3} solution, I need 0.015 / 0.5 = 0.030 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.025 dm^3 H_2O.

To make a 0.4 mol dm^3 solution, I need 0.015 / 0.4 = 0.0375 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.0325 dm^3 H_2O.

To make a 0.3 mol dm^{-3} solution, I need 0.015 / 0.3 = 0.050 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.045 dm^3 H_2O.

To make a 0.2 mol dm^{-3} solution, I need 0.015 / 0.2 = 0.075 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.07 dm^3 H_2O.

To make a 0.1 mol dm^{-3} solution, I need 0.015 / 0.1 = 0.150 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.145 dm^3 H_2O.

To make a 0.05 mol dm^{-3} solution, I need 0.015 / 0.05 = 0.300 dm^3 of solution, therefore 0.005 dm^3 $FeCl_3$ and 0.295 dm^3 H_2O.

To make a 0.01 mol dm^{-3} solution, I need 0.015 / 0.01 = 1.5 dm^3 of solution, therefore 0.005 dm^3 FeCl3 and 1.495 dm^3 H_2O.

N.B. As it required a lot of water and therefore repeated usage of pipettes to make the 0.2 and 0.1 mol dm^{-3} solutions, I divided both amounts by five to reduce error as, as proved above, increased usage of pipette leads to increased chance of error, and therefore inaccuracies occurring. The 0.05 and 0.01 mol dm^{-3} would have still required too much repeated usage of the pipettes, even when the ratio was reduced, so these were made as dilutions from the 0.1 mol dm^{-3} solution. (Ratio 1 $FeCl_3$: 9 H_2O for 0.01 mol dm^{-3} and 2 $FeCl_3$: 8 H_2O for 0.02 mol dm^{-3}.)

Concentration required / dm^{-3}	Volume 3M $FeCl_3$/ dm^3	Volume H_2O / dm^3
0.50	0.005	0.0250
0.40	0.005	0.0325
0.30	0.005	0.0450
0.20	0.005	0.0700
0.10	0.005	0.1450
0.05	0.005	0.2950
0.01	0.005	1.4950

The readings I got from these solutions are as follows:

Concentration / dm^{-3}	Relative absorption
0.50	"1"
0.40	1.89
0.30	1.51
0.20	1.10
0.10	0.68
0.05	0.56
0.01	0.10

Although my unknown still doesn't fit between any of these results, it is very close to the 0.01 result. Inaccuracies may still have come from the dilution of a strong solution to a weak solution, as repeated dilution leads to greater chance of inaccuracy occurring, as explained above.

Conc. FeCl3 vs colorimeter
Relative Absorbance
Concentration FeCl3 mol /dm-3
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0.1
0.2
0.3
0.4
I = Unknown

Analysis and evaluation of colorimetry.

The graph shown shows me that the stronger the concentration of iron chloride, the stronger the absorption of blue-violet light. The line of best fit is a straight line as expected and passes through the origin, as no iron chloride molecules, means there isn't any absorption. Through drawing on my unknown's absorption, I can see that my sample probably has a concentration of just under 0.01 mol dm^{-3}.

In the iron chloride there were just under (volume x concentration = amount)

$0.1 \times 0.01 = 0.001$ moles of iron chloride.

Iron (III) chloride = $FeCl_3$, meaning that for every one mol iron, there are three moles chlorine.

This shows there were just under 0.001 moles of iron in the tape.

From the graph I can also see that the 0.05 mol dm^{-3} sample has quite a high reading, as it seems slightly out of line with the other points. I feel that the weaker the concentration I was making up, the greater the error likely to occur. This is due to the measuring pipettes having to be used more than once, increasing the mathematical chance for error.

I would like to increase the amount of readings taken around 0.01 mol dm^{-3} to get a better idea of what the concentration of the unknown sample is. The problem of this however, is the weak concentrations required and the problem of being able to accurately measure out large volumes of water to dilute 3 mol dm^{-3} iron chloride.

More Colorimetry

As the unknown's reading was near 0.01 mol dm^{-3}, I decided to make up a solution of iron (III) chloride that was a lot weaker than the 3 mol dm^{-3} that I had previously been diluting down. I made 0.1 dm^3 of 0.1 mol dm^{-3}. I hoped this would increase the accuracy of my results, as it should reduce the errors caused by repeated use of the pipettes. This is because I would have to use the pipette once, and the volumetric once leading to smaller errors, e.g.

Pipette: Error = 0.01 +/- 0.000025 dm^3
Volumetric: Error = 0.1 +/- 0.0001 dm^3

As the errors would not fluctuate so greatly from solution to solution as is the case the pipette made solutions, these results were mathematically more likely to be accurate. Also these solutions have a smaller percentage error than the pipette made solutions, so are more likely to give accurate results.

Calculations:

Molar masses: Fe = 56g mol -1
Cl = 35.5g mol -1

Formula is $FeCl_3$ Therefore I need (56 + (35.5 x 3) = 162.5g iron chloride in 1dm^3 to make a 1 mol dm^{-3} solution.

Therefore I would need 16.25g in 1 dm^3 to make a 0.1 mol dm^{-3} solution. But as I only need 0.1 dm^3, I will use 1.625g in 0.1dm^3 distilled water.

So I made some solution up in a beaker with the magnetic stirrer, as iron chloride is quite chunky and hard to dissolve, and then rinsed the beaker into a 0.1dm^3 volumetric flask, and made the solution up to 0.1dm^3 with distilled water. However, the scales only took mass to two decimal places, so there is scope here for an error.
Possible error / reading x 100 = percentage error
(0.005 / 1.63) x 100 = 0.31 % (2.d.p.)

I used the 0.1 mol dm^{-3} solution to make up a 0.01 mol dm^{-3} solution, by putting 0.01 dm^3 of the 0.1 mol dm^{-3} solution into a 0.1 dm^3 volumetric and making it up to 0.1 dm^3 with distilled water. I made up a 0.05 mol dm^3 solution in a similar way. I tested the 0.01 and 0.1 and 0.05 mol dm^3 solutions in the colorimeter and found that as expected, the previous dilutions of these strengths had been inaccurate. This was because unlike the earlier solutions, these had been made up in volumetric flasks, which are more accurate than measuring pipettes.

The results were as follows:

Concentration /dm^{-3}	Relative Absorbance
0.10	0.43
0.05	0.23
0.01	0.04

These results showed me that my unknown was stronger than 0.01 mol dm^{-3} after all, so I made up a 0.02 mol dm^{-3} solution.

Concentration / dm^{-3}	Relative Absorbance
0.02	0.10

Analysis and Evaluation of Graph and Colorimetry.

The graph's x-axis scale is that 0.245 cm = 0.001 mol dm^{-3}.
The unknown is 2.45 + 1.45 cm along the axis, so 3.9 / 0.245 = 15.9184 (4d.p.).
15.9184 x 0.001 = 0.0159 mol dm^{-3} (4d.p.)
I can see that the unknown solution of iron chloride has a concentration of 0.016 mol dm^{-3}.
Amount = Concentration x Volume, and I had 0.1 dm^3 of iron chloride, so
0.1 x 0.016 = 0.0016 moles of iron chloride created from one metre of tape.
This suggests that there were 0.0016 moles of iron present in the tape.

The graph created is a straight line as expected, as the amount of iron chloride is directly proportional to the amount of light adsorbed. None of the points seem to be anomalous, created I think by the solutions being made up in volumetric flasks which have a reduced mathematical error compared to measuring pipettes. However, I would be slightly worried about the size of the percentage error created by the scales. The line of best fit runs through the origin, as no iron chloride would give a reading of zero.

Redox Titration

As iron can easily be oxidised and reduced between its oxidation states iron (II) and iron (III), I felt that a redox titration would be another good way of analysing the amount of iron in my unknown sample. Redox can be described as *"electron transfer"* (Burton G., Holman J., Lazonby J., Pilling G., Waddington D., 1994, Pg 207). Oxidation is the loss of electrons (equation 6), and reduction if the gain of electrons, (equation 5). By using a known concentration of an agent, the amount of iron in solution may be calculated, by knowing exactly how much agent was required to complete the reaction.

5) $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ (reduction)
6) $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ (oxidation)

As Fe^{3+} is in tape, I needed to find an oxidising agent to reduce the iron $^{3+}$ and I needed an indicator to show when this happened.

The following reaction (7) occurs between iron (III) and potassium iodide:

7) $2Fe^{3+}_{(aq)} + 2KI_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2\,(aq)} + 2K^+_{(aq)}$

The iodine liberated is an orange brown colour, which becomes colourless when titrated with sodium thiosulphate, (equation 8).

8) $I_{2\,(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

"When the brown colour of iodine fade as the end point approaches, a little starch is added. This gives an intense blue colour with even a trace of iodine. At the end-point the blue colour vanishes." (Ramsdan E. 1985, Pg 55)

This is because a starch iodine complex forms to give the blue colour, however, when all of the iodine has been reduced, this no longer forms, so the end point is shown when the colour disappears.
The amount of iodine liberated will therefore be proportional to the amount of iron present. This means that by titrating the iodine, I will be able to tell how much iron is present.

I then used my colorimetry results to try and roughly work out the strengths and volumes of solutions that I would require in my titration.

I know I roughly have a 0.01 mol dm^{-3} solution of iron chloride. This was a standard solution of 0.1 dm^3. Therefore I have 0.01 x 0.1 = 0.001 moles of $FeCl_3$ in solution. I do not have a lot of solution, I will have to perform titrations on 0.01 dm^3 of the unknown. This will give roughly 0.01 x 0.01 = 0.0001 moles of $FeCl_3$ reacting.

9) $2Fe^{3+}_{(aq)} + 2KI_{(aq)} \rightarrow 2\,Fe^{2+}_{(aq)} + I_{2\,(aq)} + 2K^{+}_{(aq)}$

Therefore for every 2 moles of Fe^{3+} present, 1 mole of iodine will be liberated (equation 9). Therefore, about 0.00005 moles of iodine should be liberated.

0.0001 moles of potassium iodide will be needed to react with the iron ions. I have a 1 mol dm^{-3} solution of this, so I need 0.0001 / 1 = 0.0001 dm^3 of this. However as it is essential that this be added in excess to ensure all the iron (III) is reduced to iron (II), I will add 0.0005 dm^3.

The iodine is titrated with sodium thiosulphate (equation 10).

10) $2S_2O_3^{2-}{}_{(aq)} + I_{2\,(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^{-}{}_{(aq)}$

As 0.00005 moles of iodine are present, (0.00005 x 2) 0.0001 moles of sodium thiosulphate will need to be added in order to reduce the iodine to iodide ions.
As I have a 1 mol dm^{-3} solution of sodium thiosulphate this will take
Amount / concentration = volume
0.0001 / 1 = 0.0001 dm^3 to achieve.
This is far too small an amount to gain an accurate titration, and ideally the titration should be roughly the same in volume as the unknown. To achieve this I would need
Amount / volume = concentration
0.0001 / X = 0.01.
Therefore X= 0.0001 / 0.01 = 0.01 mol dm^{-3} of sodium thiosulphate.

Therefore I needed to make up 0.01 mol dm^{-3} solution of $Na_2S_2O_3$. I did this by taking 0.0025 dm^3 of 1 mol dm^{-3} $Na_2S_2O_3$, and making it up to 0.250 dm^3, in a volumetric flask.

In my titration, I used a burette, rinsed with sodium thiosulphate, in order to give accurate results. The burette has an accuracy of 0.05cm^3 i.e. 0.00005 dm^3.

Results and Analysis

The first three titres went like this:

Start	End	Titre cm^3	Titre dm^3	Comment
0.30	4.10	3.80	0.00380	Overshot end.
4.10	7.85	3.75	0.00375	
7.85	11.85	4.00	0.00400	

I noticed that the titre was less than half of that which I was expecting and then, all of the titrated samples returned to purple colour, showing that iodine was being released again! At first, I thought that maybe the iron was reacting with the starch in some way, but I couldn't find anything to suggest this may be the case. This suggested that the reaction was very slow, so I left a mixture of iron chloride and potassium iodide to react over the weekend.

The result of this titre was:

Start	End	Titre cm^3	Titre dm^3
16.10	27.10	11.00	0.011

This was more like the titre expected, even though it did change colour some time after titration had been completed. At this point I had to make up some new iron chloride mixture, as the old had run out. Although there would be slight differences in composition, they shouldn't be hugely different.
I made up four new mixes of iron chloride and potassium iodide and left them to react for two days. The results gained were as followed:

Start	End	Titre cm^3	Titre dm^3
16.90	23.90	7.00	0.00700
23.90	31.20	7.30	0.00730
31.20	37.20	6.00	0.00600
37.20	44.35	7.15	0.00715

Although two of the results were within 0.0015 dm^3 of one another, I was not happy about there accuracy as the strange colour changes were still occurring after titration and an extra day of reaction seemed to have the effect of adding 0.00400 dm^3 onto the titre. As this had happened with both reflux solutions, I feel the source of contamination must be in the tape. One possibility is chrome, which is often used in tapes.
"Chromates react with reducing agents in the same manner as potassium dichromates... in liberating iodine from potassium iodide solution." (Durrant, 1939, pg 625.)
(See equation 11). One such chromate is potassium chromate.

11) $2K_2CrO_{4\,(aq)} + 6KI_{\,(aq)} + 16\,HCl_{\,(aq)} \square\ 10KCl_{\,(aq)} + 2CrCl_{3\,(aq)} + 8H_2O_{\,(l)} + 3I_{2\,(aq)}$

This is how I think the potassium chromate formed:

$2Fe^{3+}_{\,(aq)} + 2KI_{\,(aq)} \rightarrow 2Fe^{2+}_{\,(aq)} + I_{2\,(aq)} + 2K^{+}_{\,(aq)}$

The potassium ions released could then react with chrome oxide (equation 12). I feel that the chrome oxide may have come from the metal oxide powder in the tape, and as *"chromium (VI) oxide is very soluble in water"* (Liptrot, 1971, Pg 361), this may have been put into solution when the tape was refluxed in aqueous acid.

12) $4K^+_{(aq)} + 4I^-_{(aq)} + 2CrO_{3(aq)} + O_{2(g)} \rightarrow 2K_2CrO_{4(aq)} + I_{2(aq)}$

The acidic conditions created by the HCl reflux could then cause the release of I_2, which would upset all of the redox equilibriums.
If this chromate was present, it would be 'disguised' in iron chloride, as they are both yellow solutions. I tried to test for the presence of this chromate by using hydrogen peroxide, which turns blue if the chromate is present. The only problem was that the chromate would be formed with the addition of the potassium iodide, (to supply the potassium for the potassium chromate) so the blue colour (CrO_5, see equation 13), if it was present at all was covered by the strong colour of the iodine released. I did notice that a grey precipitate formed when I added the hydrogen peroxide, but it could not be magnetised, so unfortunately wasn't iron. If it had been iron, I would have performed a gravimetric analysis on it. I have also discovered (Ramsdan E. 1985, Pg 450) that in acidic conditions (the solution was refluxed in HCl so is very acidic) K_2CrO_4 can react to form $K_2Cr_2O_7$, which is orange, so would also be disguised if present. This is an oxidising agent, so could reduce Fe^{3+} or I_2, and 'interfere' with the equilibrium of the iron reduction due to Le Chatilier's principle.

13) $Cr_2O_7^{2-}{}_{(aq)} + 2H^+_{(aq)} + 4H_2O_{2\,(aq)} \rightarrow 2CrO_{5\,(aq)} + 5H_2O_{(l)}$ (Brown, 1974, pg 336)

If this chromate, or a similar was present, the act of adding sodium thiosulphate from the burette would push the equilibrium of the above equation to the right, due to Le Chatilier's principle.

"If a system is at equilibrium, and a change is made in any of the conditions, then the system responds to counteract the change as much as possible." (Burton G., Holman J., Lazonby J., Pilling G., Waddington D., 1994, Pg 166)

This would cause the release of some more iodine, and hence explain the return of colouration to the titrated mixture.

However, it may be possible that the chromate does not interfere until after the titration. If this were so, then taking 0.00715 dm^3 as the average of the three closest pieces of data, then the calculations would be as follows.

0.00715 dm^3 of 0.01 mol dm^{-3} $Na_2S_2O_3$ added from burette.
Moles = Volume x Concentration.
Moles $Na_2S_2O_3$ added = 0.00715 x 0.01 = 0.0000715 moles.

$2S_2O_3^{2-}{}_{(aq)} + I_{2\,(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$

This means there were 0.0000715 / 2 = 0.00003575 moles of I_2 present.

$2Fe^{3+}{}_{(aq)} + 2KI_{\,(aq)} \rightarrow 2\,Fe^{2+}{}_{(aq)} + I_{2\,(aq)} + 2K^+_{(aq)}$

This means there were 0.00003575 x 2 = 0.0000715 moles of iron chloride present, in 0.01 dm3.
So in the standard solution (0.1 dm^3), I had 0.0000715 x 10 = 0.000715 moles.
In 1 dm3, I would then have 0.000715 x 10 = 0.00715 moles.

This means the solution is (amount / volume = concentration)

$0.00715 / 1 = 0.00715$ mol dm^{-3}.

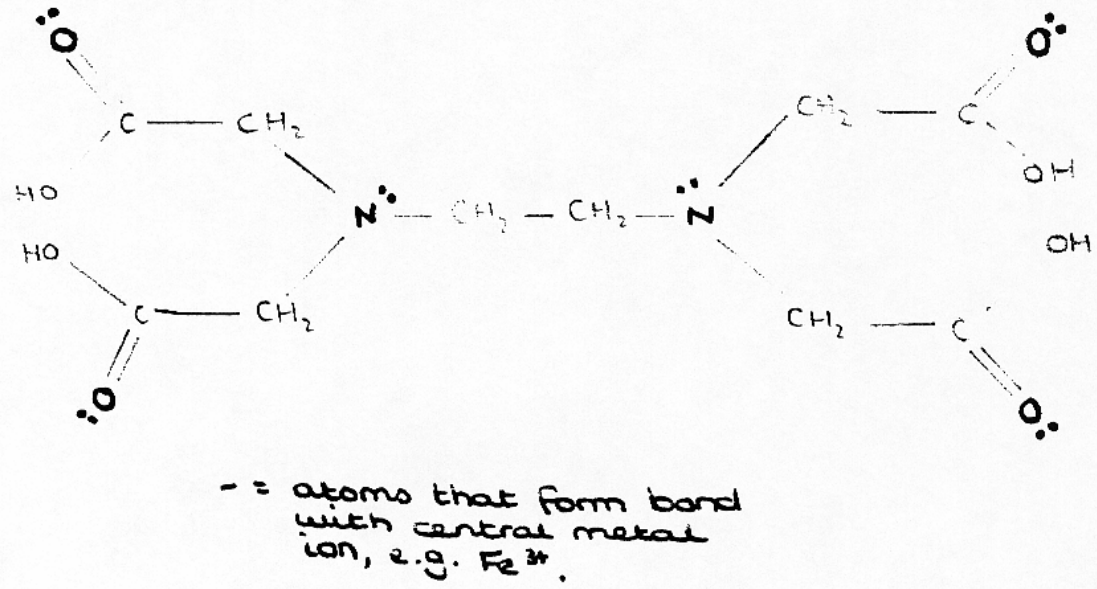
Evaluation of Redox Titration.

My third colorimetry, which I believe to be the most accurate, gave the solution to be 0.016 mol dm^{-3}. Therefore, this titration seems to be less than half of what it should be. I believe this to be due to the 'contamination' possibly caused by chrome or something else in the tape. It is possible that some error crept in through experimental error, such as the errors caused by the scales, pipettes and volumetric flask, but I do not think that this justifies the amount of error that appears to have occurred in this experiment.

Complexiimetric Titration

As iron is a transition metal, it can also be the central atom in a complex. Ligands cluster around the central atom. One ligand that is particularly effective is EDTA, ethylenediaminetetraacetic acid. This has six lone pairs, which means it wraps around the central metal atom of the complex. It is known as a chealating agent as it forms a ring like structure, which gives stability to the complex.
One mol of EDTA should therefore react with one mol of iron atoms.

Diagram of EDTA Molecule (Lewis and Berry, 2000, Pg 658)



The iron (III) EDTA complex has a very high K_f value. This is the constant of formation of the complex."1 x 10^{25}" (Tissue B., 2000). This high constant means that

EDTA should easily 'displace' the chloride ligands to form this stable complex with the ions. From looking at an old practical exam paper, (AQA, Summer 2000), which contained a magnesium EDTA titration, I could see that the reaction conditions for this experiment were pH 10 and 45°C, although this was with copper ions, not iron ions. Eriochrome black, made up in ethanol, was the indicator.
First, I had to make up the buffer solution, from 6.75g ammonia chloride in 0.057 dm^3 of 0.880 aqueous ammonia in the fume cupboard, which was then made up to 0.1dm^3 in a volumetric flask. I then made up the eriochrome black indicator, which needs to be fresh. This is made by dissolving 1g of eriochrome black, in 0.1 dm^3 of ethanol. This indicator changes from red to blue when the titration has finished. This is because in the presence of E.D.T.A. the indicator is blue, but for this to be the case, there must be one molecule of E.D.T.A. that is unreacted, and for this to be the case, all of the iron ions must have reacted. Meanwhile the water bath was heating up to 45°C. I did some preliminary tests on the buffer when added to iron chloride, using the pH probe, and I found that the buffer was 9.4. I needed to add about 0.01 dm^3 to 0.01 dm^3 of iron chloride to get a pH of 9.4. But the buffer was strongly alkali, and the OH ions reacted with the Fe^{3+} ions to form a foxy red precipitate, iron hydroxide.
I carried on and tried to titrate the mixture, but no reaction occurred. The iron hydroxide was insoluble and therefore no reaction took place. To be able to perform this titration, I would probably need to find a way of getting the iron into solution at about pH 10 and then titrating with EDTA, so the addition of a buffer would not cause iron hydroxide to form. I am not sure whether E.D.T.A. would react effectively at any other pH, as pH 10 is a preferred reaction condition.

Future Work
Instead of using a soluble complex such as E.D.T.A., a ligand such as *"o – phenanthroline,"* (Brown, Pg 486) could be used to react with the iron (III) ions, and produce an insoluble complex. This insoluble complex could then be weighed gravimetrically, to determine the amount of iron present through using the fact that one mole of iron has a mass of 56g.

Iron in used tape.
I was interested to find out whether used tape contained the same amount of iron as blank tape. I suspected this would be the case, as I think that recording on to tape just causes a realignment of magnetic material, as opposed to a loss of material in any way.

To make sure that the test was fair I recorded on to the same type and batch of the blank tape I used earlier. I then refluxed it using the same method as above. As the only seemingly conclusive results from earlier came from colorimetry, I decided to employ this method on the refluxed solution.

The reading from the colorimeter was 0.06 A.

The unused tape read 0.07A.

This could suggest three things. 1. That a slight amount of iron is lost on recording.
2. There were experimental errors in the process, (e.g. the colorimeter only reads to two decimal places. These samples could be 0.01, to a miniscule amount apart, if they are on the 0.649 0.650 border.) 3. The amount of iron varies slightly from tape to tape.

I would have to conduct further experimentation in order to be able to say which of these is true.

Hazard Assessment

Chemical	Minimal	Irritant	Harmful	Corrosive	Toxic	Precautions
Iron (III) Chloride		If stronger than 0.75 M				Goggles
Hydrochloric Acid		If stronger than 2M				Goggles
Sodium Thiosulphate	Minimal					
Potassium Iodide	Minimal					
E.D.T.A	Minimal					
Hydrogen Peroxide		Irritant				Goggles
Sodium Hydroxide				If stronger than 0.5M		Goggles, gloves
Potassium Hexacyanoferrate	Minimal					
Ammonium thiocyanate			Harmful			Goggles
Ammonia Chloride			Harmful			Goggles, fume cupboard, gloves.
Ammonia				Corrosive	Toxic gas	Goggles, fume cupboard
Eriochrome Black	Minimal					

Table of Knowledge

Knowledge	Module	AS / A level
Polyester construction	Designer Polymers	A
Moles, masses, molecular masses	Elements of Life	AS
Moles, volumes, concentrations	Minerals to Elements	AS
Colorimetry	Steel Story	A
Complexes	Steel Story	A
Reflux	What's in a Medicine	AS
Redox	Minerals to elements	AS
Titration – Redox - Complexiметric	Elements of Life Steel Story	AS A
Le Chatilier and equilibrium.	The Atmosphere	AS

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5.8 Commentary on Individual Investigation Report 0409

Iron in audio tapes

Introduction

This is a high quality investigation into a topic that is often done badly. It is a good example of how experimental procedures can be modified in order to ensure reliable and accurate data. Often, candidates concentrate on the quantity of data collected at the expense of the quality of that data.

The structure of the report is unusual, preferring to provide a continuous narrative rather than splitting it up into four clear sections. This approach works well here, but many candidates are better helped by a clear separation of the skill areas so that they have a framework that links closely to the descriptors that they have to satisfy.

Planning

The theoretical background provided to support the plan is comprehensive and relevant. All expected equations and structures are included in a clear and chemically mature account. A full risk assessment is written in the form of a table and detailed references are included within the text as well as a bibliography at the end. This part of this section meets all of the requirements of the descriptors up to, and including, level P11b.

A coherent experimental plan is developed through the report. Beginning with some preliminary work, experimental procedures are developed and modified in the light of experience. The explanation of choices made as the investigation proceeds demonstrate a sound understanding of the chemistry involved.

Overall, the plan satisfies the requirements of all descriptors and a mark of 11 is appropriate.

Implementing

Both initial observations and subsequent measurements are reported with a clear sense of purpose. Data is recorded in appropriate detail and format and is accompanied by helpful comments.

All of the descriptors in the recording strand of implementing are satisfied, up to and including, level I11b.

Analysing

Calculations based on raw data are carefully carried out and clearly explained. Calibration curves are well drawn and labelled.

Deductions are made throughout the report which make excellent use of detailed, relevant underlying chemical knowledge and understanding. Conclusions drawn from the evidence demonstrate a good understanding of the chemistry involved and an ability to suggest explanations for unexpected outcomes.

The opportunity could have been taken to compare and contrast in more detail the effectiveness of different methods that are used, but the work in this section already satisfies the requirements of the descriptors up to, and including, level A11a and A11b so a mark of 11 is appropriate.

Evaluating

The limitations of experimental procedures are discussed in great detail. This discussion leads to modification of procedures within the investigation and to proposals for further work. This assessment is sound and justifies the need for changes in plan in order to increase the reliability and accuracy of evidence.

The uncertainties associated with specific measurements are also calculated. The assessment of the relative significance of all of the limitations and uncertainties and their likely effect on the final conclusions is less strong and does not quite meet the requirements of the descriptors at level E11b.

Overall, the evaluation throughout the report satisfies the descriptors at level E8 and most of the requirements at level E11. A mark of 10 for this section is therefore appropriate.