TIN(IV) OR TIN(II)?

Objectives of this experiment: to design and implement an experimental procedure, using information that would typically be available in the literature. The technique of mass spectroscopy is introduced in the analysis of the product.

The trend in group IV is to favour the divalent state over that of tetravalency as one progresses down the group. Thus, lead is usually divalent whilst carbon is tetravalent (carbon monoxide being a complicated exception). Tin lies in the grey area of this trend and depending on the attached ligands, may take either oxidation state.

In this experiment, elemental tin is oxidised by iodine to form orange tin iodide. You will be expected to devise the preparative procedure using the accompanying notes.
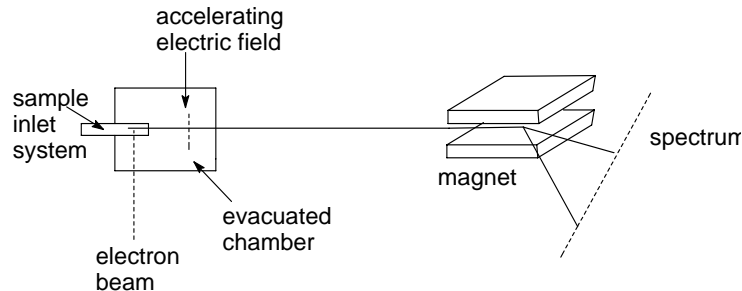

Figure 1: The principle of a mass spectrometer

One method of characterising a compound is to subject it to a mass spectroscopy experiment. A sample is vaporised into an evacuated chamber where it is bombarded with electrons. This bombardment knocks out a further electron to form a positive ion. Further bombardment may also cause fragmentation of that ion into smaller positive ions. These positive ions are accelerated, by means of an electric field, down a channel. The resulting beam of positive ions then passes through a magnetic field, which induces curvature in the trajectory perpendicular to the axis of the field. However, not only does the size of the charge dictate how much that beam is bent, but also the mass of the ions must be considered. Thus, heavier ions will not deviate from their original path as much as lighter ions. Consequently, elements with, say, two naturally abundant isotopes, will produce a series of double peaks. Scanning over the spread-out beam with a detector allows a graph of intensity against m/e (m = mass, e = charge) to be drawn.
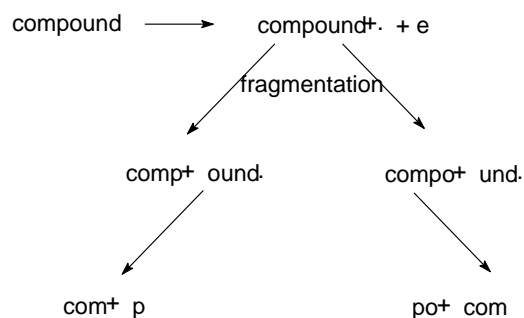
Among the possible ions observed will be compound$^+$, comp$^+$, compo$^+$, com$^+$ and po$^+$.

Another form of excitation used in this department is the technique of chemical ionisation. Methane gas is used as the target for the electron bombardment. The positive ion subsequently interacts with the sample to produce more positive ions characteristic of the sample. However, the parent ion now appears as M+1, with a much smaller pattern repeated at M+29 and even more diminished at M+41, instead of M as seen in the electron impact spectrum. This effect does not carry through with the fragment ions, so the heaviest ion can be identified as a parent or very stable fragment ion. Thus we have a method for molecular weight determination.

Reflux under an inert atmosphere:

Many reactions will take a period of time to finish. Sometimes, this period can be shortened by raising the temperature of the reagents. This in turn raises the average kinetic energy of the individual molecules, allowing them to collide with each other resulting in a more effective outcome.

Simply raising the temperature of the reaction mixture might cause the solvent to evaporate (even if the boiling point has not been reached) which in turn might cause a fire or the decomposition of the remaining solids. A water-cooled condenser is attached to the top of the flask so that solvent vapour will condense and drip back into the reaction mixture. This, then allows the boiling point of the solvent (which is easily controllable) to be chosen as the temperature of the reaction. This is known as a reflux.
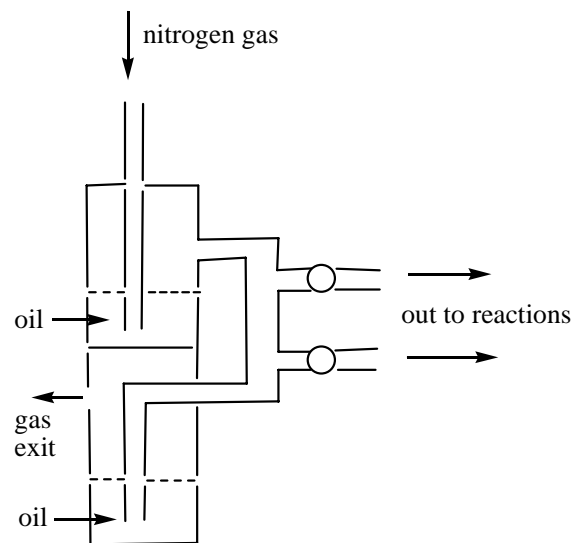

Figure 2: An oil-bubbler used for monitoring the use of nitrogen as an inert atmosphere.

If the reaction is air-sensitive, then it is usual to conduct the whole process under an inert atmosphere. The usual choice is nitrogen gas - which is supplied to each fumehood from a cylinder at the front of the room. The nitrogen is taken from the outlet, through a bubbler system and then connected to the cold side of the condenser. This prevents hot solvent from entering the nitrogen lines.

Experiment 5a Pre-lab assignment:
Use the following notes to plan the preparative procedure.

1. The reaction to examine is that between tin and iodine. The product will be tin iodide. Tin has two common oxidation states, II and IV. What are molecular formulae of the likely options? What are their molecular weights?

    Precautions:
    Glacial acetic acid & acetic anhydride: combustible & corrosive; lachrymator; harmful by inhalation, ingestion & skin contact.
    Iodine: may cause burns on contact with the solid.

2. Each student will be given 0.5 g tin foil.

3. Within your group, decide who will add (a) 1.0 equivalent of iodine, (b) 1.5 equivalents, (c) 2.0 equivalents & (d) 2.5 equivalents. Calculate the weight of iodine that this represents.

4. The reaction is exothermic, but needs some thermal energy to activate it.

5. Refluxing for at least 1 h after the initial reaction will ensure completion. Draw the apparatus for a reflux.

6. The product of the reaction between tin and iodine is very sensitive to decomposition in the presence of even trace amounts of moisture.

7. Acetic anhydride will soak up traces of moisture according to the following equation:
    $(CH_3CO)_2O + H_2O \rightarrow 2\ CH_3COOH$

8. An appropriate solvent for this reaction is acetic acid. It is best used in this case as a mixture of acetic acid (50%) and acetic anhydride (50%). A suitable volume is 50 mL.

9. Glacial acetic acid and acetic anhydride are known lachrymators. What does this mean?

10. Atmospheric moisture can be sufficiently abundant to ruin this reaction. Nitrogen gas supplied in cylinders contains less moisture.

11. The product of the reaction precipitates from the ice-cold reaction mixture.

12. Iodine readily dissolves in hexanes. The product of the reaction does not dissolve well in cold hexanes.

13. The vacuum line can be used for drying the solid. Instruction on its use will be provided by the TA.

14. All discarded liquids must be placed in the appropriate waste container. Glassware must be left in an appropriate state for use by the following class.

Determine the yield in grams and %, and compare this with the results of your group, particularly noting the observations of the reaction done with differing stoichiometries. Attempt to draw some conclusions about the stoichiometry of the reaction. Hand in the material that you have prepared.

Tabulating the mass spec data:
The naturally abundant isotopes of tin, with their percentage abundance (see the CRC Handbook in the Chemistry Library) are:

^{112}Sn	1.0%	^{116}Sn	14.7%	^{119}Sn	8.6%	^{124}Sn	5.6%
^{114}Sn	0.7%	^{117}Sn	7.7%	^{120}Sn	32.4%		
^{115}Sn	0.4%	^{118}Sn	24.3%	^{122}Sn	4.6%.		

Study the mass spectrum supplied at the end of this procedure.
1. Tabulate the relative heights within the parent group. Explain why the peaks appear as they do, given that the natural abundances of the isotopes are as described above. To help with your explanation, draw a stick-plot of the relative % abundance vs isotope number of tin.

2. Tabulate the full spectrum. It is common to pick one identifying peak in each cluster and just report the data for that peak (considered to be representative of the others). To tabulate, report the relative height (y-axis) and m/e value (x-axis). In a third column, indicate which molecular fragment that each cluster of peaks represents.

Report:
The first part of the report must be written up in time for the start of the next lab class. Bring a copy of this electronic file (or your laptop) to the second week <u>and</u> email a copy to yourself as a back-up. A laptop will be available for your use to complete the report. The results from the second part of the experiment (5b) will be added during the lab next time. The whole report will be due at the end of the next class.

This report does not require an abstract or introduction. It does require balanced equations, though. You are also required to write the procedure in detail (see below). You are not required to write a discussion, but you must include a brief conclusion that comments on the mass spectra and your observations, along with the calculations and results from the titrations.

Write the procedure in paragraph form as though it is an entry in your lab notebook. It must be a record of exactly what you did, *not what you planned to do.* Don't forget to include the equations, observations and calculations. A well-written report will allow the reader to reproduce your experiment exactly (including any mistakes!).

The tabulation and analysis of the mass spectrum will be an important section in this report, and should be completed before starting exp 5b.

Experiment 5b:
Pre-lab assignment

1.   How much potassium iodate must be used to make 250 mL 0.01800 M KIO_3 solution?
2.   Will hexane float or sink in water? Explain your answer.
3.   During the titration, a violet coloration is seen in the organic layer. What causes this?
4.   Which product did you make last week based on the mass spectrum?
5.   Write one balanced equation for the overall reaction of $IO_3^- \rightarrow ICl_2^-$ using the equations given in the procedure.
6.   Calculate the volume of IO_3^- (assume 0.01800 M) needed for the titration as described in the procedure, for your product.
7.   Given the following three data sets of titration results, would you need to perform a fourth titration? Explain the reason for your answer.
      Trial 1: 0.1818g sample requiring 32.53 mL aqueous KIO_3.
      Trial 2: 0.1808g sample requiring 32.46 mL aqueous KIO_3.
      Trial 3: 0.1846g sample requiring 32.91 mL aqueous KIO_3.
8.   Draw a flowchart for the procedure you plan to follow.
9.   Prepare your data tables for the in-class write up.

Analysis of the product:
Prepare 250 mL 0.018 M potassium iodate solution.   Potassium iodate is a primary standard and thus a dried sample of known mass can be used to accurately prepare a solution of exact concentration.

Precautions:
Potassium iodate: oxidizing agent; irritant; risk of explosion on shock, friction or heating.
Hydrochloric acid: corrosive.

Weigh accurately three samples of about 0.18 g tin iodide on an analytical balance. Add these to each of three Erlenmeyer flasks. Add about 30 mL of concentrated hydrochloric acid and 15 mL of hexanes. Titrate with the standard solution of potassium iodate until the violet coloration in the hexane layer disappears on vigorous stirring (in order to facilitate that vigorous stirring, choose your Erlemneyer flask carefully).   Check the reproducibility of your data and perform further titrations if necessary.

The aqueous titration waste must be discarded into the special waste container provided.

During the initial action of the iodate, free iodine is increasingly produced in the liquid, to which it gives a brown colour. Towards the end of the reaction this iodine is removed again as it is oxidised to iodine monochloride, ICl, which as the anion ICl_2^-, gives the yellow colour to the final aqueous layer, and removes the purple colour from the hexane layer.

The equations describing these reactions are:-
$$IO_3^- + 5\ I^- + 6\ H^+ \text{-----}> 3\ I_2 + 3\ H_2O$$

$$IO_3^- + 2\ I_2 + 6\ H^+ + 10\ Cl^- \text{-----}> 5\ ICl_2^- + 3\ H_2O$$
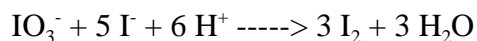
In the presence of acid and iodide ions, all the tin is liberated as free ions. Therefore, the only oxidation that need be considered is that of the iodide ion. The mass spectrum should indicate

whether the product is likely to be tin(II) iodide or tin(IV) iodide. Use this conclusion in calculating the percentage purity of your product from the analytical data. How do the titration results compare with those reported by other members of your team? What factors might influence these results?

Report:
This week's work will be written up in class and added to the report for experiment 5a. It is due by the end of the class - no late reports, please.

The electron impact mass spectrum of the pure product of tin + iodine:
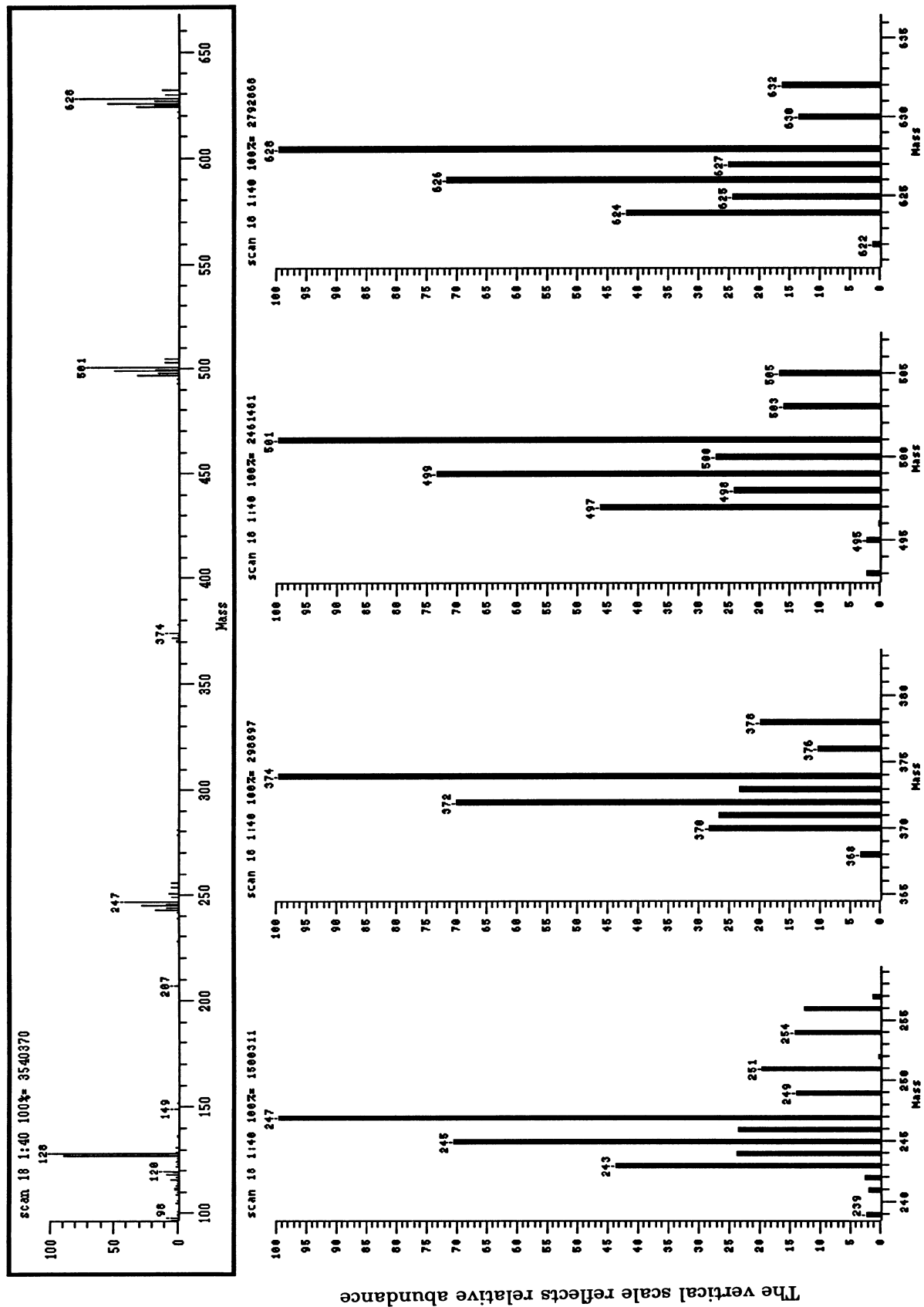
The vertical scale reflects relative abundance