Determination of sodium in potato chips

I ran this experiment to determine the amount of sodium in potato chips using flame atomic emission spectroscopy. My data and observations are given below; calculations are mainly on the spreadsheet. Report to follow.

1. Hazards table

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>irritant</td>
</tr>
<tr>
<td>Acetylene</td>
<td>flammable gas</td>
</tr>
<tr>
<td>Compressed medical air</td>
<td>keep away from heat, contents under pressure, danger of explosion</td>
</tr>
</tbody>
</table>

Ref for all data [www.wikipedia.com](http://www.wikipedia.com)

2. Calculations prior to the prep work (see also previously submitted plan)

Want a stock solution of sodium that contains 100 mg/L; will make 100 ml of stock solution in total.

In 0.100 L of a 100 mg/L solution there are 10 mg sodium, so weigh out 0.0100g sodium chloride.

To make standard solutions dilute stock solution to 1, 2, 3, 4 and 5 ppm

Using \(c_1v_1 = c_2v_2\) use 1 (2,3,4,5) ml of the stock solution in 100 ml to make standards.

Prepare a spike solution of 2.5 mg/L, using 2.5 mL stock in 100 mL.

After talking to the TA, decided to prepare a second set of standards.

To make standard solutions, dilute stock to 500, 700, 900, 1100, and 1500 ppm.

Sample: label claims that there is 700mg sodium in 40g chips, so if we take a 0.1g sample of chips there will be \(700/40 = 17.5\) mg/L when dissolved in 100 mL.

Method spike: dilute 2.5 ml stock in a 100ml flask to give 2.5 mg/L. Since this is a method spike, use the same preparation steps as the chip samples.

Sample spike: 0.05 chips would contain about 0.875 mg sodium, while 100 mg/L of the stock solution contains 0.1 mg/ml, so 10ml would contain 1 mg sodium, comparable to the amount in 0.05g chips.

So take 0.05g chips, add 10ml stock and proceed. Final concentration will be \(1.875\) mg/L then 10x dilution = \(1.875\) mg/L
3. **Preparation of samples**

Need 1 stock solution, 5 standards, 2 spikes, 1 blank, 3 samples.

Weigh out 0.010g NaCl. Actual mass was 0.0106g.

Make standards

Weight out 3 0.1g chip samples in separate flasks; weights were 0.1003g, 0.106g, 0.1011g.

Add 20mL water to each sample and homogenise – samples turned cloudy

Transfer to 100ml flasks and make up to mark – still cloudy

Transfer some to centrifuge tubes and centrifuge (use equal volumes in centrifuge so that this is balanced) - still cloudy

Syringe filter into a Nalgene bottle, dilute samples and sample spike by 10x.

Repeat for method spike and method blank; comment much easier for these – no solid observed

4. **Instrument readings using GLP order**

Abbreviated instructions taken from manual: turn on instrument, fill liquid trap, turn on gases, check regulator pressures, select wavelength, light flame, zero with deionized water, run solutions using glp order

<table>
<thead>
<tr>
<th>Blank</th>
<th>zeroed</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mg standard</td>
<td>0.517</td>
</tr>
<tr>
<td>1 mg standard</td>
<td>0.099</td>
</tr>
<tr>
<td>2 mg standard</td>
<td>0.199</td>
</tr>
<tr>
<td>3 mg standard</td>
<td>0.373</td>
</tr>
<tr>
<td>4 mg standard</td>
<td>0.0410</td>
</tr>
<tr>
<td>Blank</td>
<td>0.002</td>
</tr>
<tr>
<td>Sample 1</td>
<td>0.190</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.195</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0.221</td>
</tr>
<tr>
<td>Sample spike</td>
<td>0.199</td>
</tr>
<tr>
<td>Method spike</td>
<td>0.226</td>
</tr>
<tr>
<td>QC</td>
<td>0.351</td>
</tr>
<tr>
<td>5 mg standard</td>
<td>0.512</td>
</tr>
</tbody>
</table>

Turn off instrument with TA supervising
**COMMENTS AND QUESTIONS**

**Notes:**

1. There is a danger that, when the students do this exercise, they may focus on single, very specific errors in the write-up, rather than noting the general principles of good experimental and reporting technique. For example, noting that the samples were not numbered, they may see this as if it were a potentially common problem they much watch out for. In reality of course, the key message is that they need to follow good record keeping principles; neglecting to number samples is a serious error, but no more significant in itself than several other types of blunder. Stress that the message here is that care and thought needs to be used when doing the experiment and write-up; it’s not the individual errors in this exercise that are important, it’s the overall message.

2. Feel free to discuss with your section whatever topics seem to be most valuable. You might wish to go through these forms as they stand, or pick and choose topics, for example how to use statistical tests, or how to assess accuracy, or even how to conduct an experiment so as to get the most reliable results. Remember that you’ll lose 1/3 of the class to prep work part-way through the session, and those students that make this change should not miss out on anything critical.

1. **Preprep calculations**

   Find an error in the preprep calculations

   A) "In 0.100 L of a 100 mg/L solution there are 10 mg sodium, so weigh out 0.0100g sodium chloride." 0.01g NaCl does not contain 0.01g sodium.

   B) She decided to prepare a second set of standards, but gives no indication of why she did this, or what made her choose the quoted concentration range. There’s no justification for her choice of concentration range for either set of standards, even though those ranges may be sensible. She might have chosen the second set of standards because she thought the samples were more concentrated than her initial standards, so would lie outside the calibration curve. Or she might have noted that there are several different wavelengths that could be used to analyse for sodium, so decided to run two determinations, one using the high sensitivity 589nm line, and one using a second line of lower sensitivity (requiring stronger solutions). Or she might just have been trying to impress the TA.

   C) All solutions in the second set of standards are stronger than the stock solution she used for the first set, so she must have prepared a second stock, but didn’t tell us about it.

2. **Flowchart and observations**

   Criticise the flowchart and observations. You should be able to spot several problems.

   A) She writes that she wants to prepare five standards, but earlier it was ten.
B) The weights of the three samples are not quoted to the same number of decimal places.

C) "Weigh out 0.100g NaCl. Actual mass was 0.0106g". The fact that the weight is not exactly 0.01g is not a problem in itself. What is a problem is that it's not clear whether this new weight was used in the subsequent calculations, or the 0.01g.

D) The weights of the solids are given (but one to only 3 dp) but the flasks into which these samples are measured are not numbered; which is which?

3. Instrument readings

What criticisms do you have of the section of instrument readings?

A) Insufficient figures/readings in some places

B) No data recorded for the second set of standards, even though they are on a spreadsheet; were they written on a sheet of loose paper?

C) Readings have been taken for the spiked sample, but there's no record of which sample was spiked; perhaps these readings were just for the spike solution itself? If this is just the reading of the spike solution, what is the purpose of the spike?

D) The student failed to take a final blank reading at the end of the experiment to check for instrument drift.

E) A Method blank and a standard blank were used, but there's no indication of how these were prepared. Nor are they identified on the observations or spreadsheet; only "blank" is shown. Details on preparation of the two blanks in the lab notebook are vague. The reader cannot make assumptions about experimental procedure; that’s why detailed notebook entries are important.

F) No instrument data! Gas pressures, current through the lamp, etc should be recorded.

4. The second set of standards

What problems might arise in preparing the second set of standards?

A) If the stock solution that was used for the first standards is faulty, then all the standards will be faulty, not just the first set. It would thus be better to prepare the second set using a fresh stock solution. The difference in the concentrations of the two sets of standards suggests that there were two stock solutions, but quite possibly one was prepared from the other, which would still lead to problems if the stronger stock solution is faulty.

5. The spreadsheets

Comment on the entry at the top left of the spreadsheet.
A) Why is trichloromethane being used as the solvent in flame AA? Would this dissolve sodium ions? This must be a mistake.

6. The calibration curves

Do you have any comments about the calibration curves?

A) There are problems with both calibrations. In the first calibration, one point is well off what is otherwise a good straight line. The student may not know what the problem with this point is, but it is clearly wrong, and should be discarded (statistical tests exist that would allow one to identify and discard this point, but these tests are not within the course).

B) There are a couple of problems with the second calibration: first, a smooth curve or a straight line through the points would both give a non-zero intercept; second, the line is clearly curved so Beer’s law does not apply very well. The non-zero intercept indicates a systematic error. The intercept would in fact mean that a solution containing a finite amount of sodium would give rise to a zero absorption; this suggests that the blank contains some sodium, or that the water used to prepare all the solutions had some sodium in it. The second problem is the curvature; this curvature suggests that Beer’s law is starting to fail. There are several possible explanations for this, but the most probable one is that the concentration range is too high, so a significant proportion of the total incident light is being absorbed (Beer’s law only works when the fraction of incident light that is absorbed is small.)

How should the student deal with the calibration curves?

A) The first curve is much better. Discard the errant point and use the resulting straight line. If the second curve has to be used, because all the samples available have a high sodium content and so lie well beyond the range of the first set of standards, a curve should be drawn by hand through the data points, since the fit this gives is more likely to be scientifically reasonable than the curve calculated by a spreadsheet program.

7. Accuracy and precision

(i) Comment on the accuracy and precision of the student’s preparation of samples

A) The sample of sodium chloride that the student intends to weigh (10 mg) is very small, which could lead to a significant error in weighing and transferring. Instead she should weigh out a larger sample, to reduce the percentage error, and use this to make a first stock solution, then prepare a second stock by dilution.

(ii) Check that the average reading for sample 1 as given on the spreadsheet is correct.

A) It is

(iii) As shown on the spreadsheet, the sample signals have been corrected; by what?
A) By subtraction of the average blank signal; this is the method blank, not the standard blank. The standard blank should be used to correct the standards. Unfortunately, the student's observations do not explain which blank was used.

(iv) What is %RSD?
A) Defined in manual {uncertainty/average value} x 100%

(v) Locate the %RSD for the overall method as well as for the instrument. What do the values tell us about the analysis?
A) Instrumental %RSD, which is shown on the spreadsheet, is the %RSD for a sample, the QC, etc. The values vary from one sample to the next, but each is a measure of instrumental precision.

The overall method precision is the precision of the three samples, which was 8.8%, so the instrument precision is better than that of the overall method. We would expect this, since the overall precision combines instrumental precision, preparation precision, and sampling precision. Potato chips are fairly heterogeneous, as well as variations during sample preparation there is likely to be sampling variation.

How should you discuss accuracy and precision? Assess the accuracy and precision of all available data, both the values that you have directly measured (e.g., weights, volumes of dilutions, etc) and instrumental precision, as indicated by scatter of replicate readings. Be quantitative. Apply ANOVA if appropriate. Don't just pluck figures out of the air – justify figures wherever possible.

8. Statistical tests to compare the two sets of results

(i) How does one compare two separately-determined values of a parameter to determine whether they are, within experiment error, the same?
A) This process is described in the manual on pages 14 and 15. When an experimental value is being compared with a known value (e.g., the measured concentration of the QC is being compared with the known concentration), the t-test is used. When two experimentally-measured values are being compared, we first calculate the variances, then use the table for the F-test.

B) If there's time, and the students show an interest, you can consider the follow two scenarios:

a) A QC has a -16% error, but passes the t-test. What is the likely reason? What does a passed t-test like this tell you about the results?

The purpose of this question is to get the student away from the idea that a passed t-test necessarily indicates accuracy. The t-test is about statistical difference. A failed t-test is considered evidence of systematic error.
With a large %error, the only way to pass the t-test is with a very large standard deviation (note the presence of s in the denominator in the expression for $t_{calc}$). This occurs if the uncertainty is so large that a number could be far from the experimental value and still within the huge confidence interval. Therefore the results for this experiment should not be considered reliable; unless the precision is improved the results are valueless. Such a conclusion should still be discussed in a report. It is not sufficient to state that the results were bad, without going through the appropriate calculations and discussion.

b) A QC has a 0.4% error but fails the t-test. Why might this occur? In this scenario, is the analysis accurate?

In this case the standard deviation is probably extremely small so it even excludes points that could be very close to it. The analysis is accurate and precise. However, the t-test indicates the presence of a small amount of systematic error, which cannot be ignored.

The point, again, is that t-test results need to be considered in light of all other results (% errors, %RSDs). They should never be dismissed because of these other factors, but the discussion of t-test results is not necessarily simple (for example, concluding that because the t-test was passed, the results must be accurate), and care should be taken in the discussion of these points.

How should you use statistical tests? The main relevant tests are the t-test and the F-test. If you have a QC, or other sample whose concentration is known accurately, compare this to the measured data using the t-test and discuss the cause of any significant difference. Be quantitative as far as possible, especially if the QC and the measured reading are found to be different; what is the cause of the difference? If you have two independent readings for the same sample, or readings of two samples which you would expect to give comparable results, use the F-test to determine whether, within experimental error, the readings are the same.

9. Use of multistandards

You will use multistandards in the GC experiment. A multistandard is a standard solution that contains at least two analytes. As described in the instructions to the experiment, there is more than one way in which we might prepare multistandards. The simplest ways are:

(i) Make up a single stock solution containing all the required analytes at some suitable concentration; prepare all standards by direct dilution of this stock.

(ii) Make up each standard individually, using a different ratio of analytes in each one.

What are the advantages and disadvantages of using these two types of multistandards?

A) Discussed briefly in the manual.
How should you discuss multistandards? If you run an experiment with a single set of multistandards and a QC is available, compare experimental results with the QC to check whether the analyte concentrations measured for the QC are mainly high or low, indicating a possible fault in preparation of the stock solutions. If you have more than one set of multistandards, prepared in different ways, use both sets of standards to calculate two independent values for the concentrations of each analyte in the unknown. Compare the calculated concentrations of each analyte using each calibration curve and, if possible, determine which calibration curve gives the more reliable results. Use statistical tests if these will help.

10. Method validation
(i) What is the difference between a method blank and a standard blank?

(ii) The method blank is subtracted from the instrument signal of samples, spikes, and QC. A concentration for the blank is never calculated. Is this correct?
A) Yes, the method blank should be used in this way. Since one signal is subtracted directly from another, there's no need to calculate a concentration. But it shouldn't be used to correct the QC signal as it is not something you prepared.

(iii) What is a spike? What is its purpose?

(iv) The method blank is used to correct the signals for the samples, spikes, and QC only. Is this correct for this specific experiment?
A) The QC has not been treated in the same way as all the other solutions, including the method blank, so it's not appropriate to correct this with the method blank, though this is correct for the remaining solutions.

(i) Calculate a % recovery for the method spike.

A) The method spike recovery is 84.8%. (Use the calibration curve to calculate what signal a solution of concentration 2.5 ppm should give, then find the ratio between this and the actual signal. The figure of 84.8% uses the calibration curve constructed using all points.)

B) Discuss the implications. It would appear that there is loss of analyte during the method. However, point out that this conclusion would be justified only if the % recovery is off by more than the magnitude of the overall %RSD.

How should you discuss method validation? If you were expected to use spikes in the experiment, calculate spike recoveries from your instrumental data. Determine whether the spike recovery is 100% within experimental error and discuss any factors that might give rise to a statistically
significant difference. Identify all steps in the procedure which could affect the amount of analyte eventually measured (i.e., those steps that could potentially introduce error) and estimate the likely magnitude of each error. Compare your estimate of the overall error with your spike recovery and provide appropriate comment. Compare the measured and actual concentrations of the QC sample and comment on the results.