Investigation of accuracy of measurements of flame photometer by measuring Na^+ ions in water samples

Session: May 2011

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IB subject of essay: Chemistry

Research Question: How accurate can a flame photometer measure the Na^+ ion concentration in some samples of water?

Supervisor's name: Okan Güzel

Word Count: 3852

Abstract

Flame photometry is a method that is used to determine the concentration of ions in an aqueous solution. In daily life, this machine is mostly used in biochemistry, to determine various concentrations of ions in aqueous solution. However this method is not precise as other methods in analytical chemistry. In this study, the aim was to find out how effectively does flame photometer measures the concentration of ions in aqueous solutions. An experiment was carried out by using Na^+ ions. Concentrations ranging from 1 to 25 ppm (mg/L) were used because below and upper levels does not give precise results. For the beginning of the experiment, standard solutions with known sodium ion concentration were prepared for the flame photometer. So a calibration curve was drawn showing the relationship between the concentration and emission in flame photometer. In this experiment, concentrations between 10 ppm to 25 ppm broke the linearity of the calibration curve, so standard solutions between 1 to 10 ppm were prepared. The calibration curve was linear at this time so water samples can be analysed. Some water samples were analysed. The results were mixed. Some results were close to the original value. However some results were really distant from their actual values. This shows the inaccuracy of the flame photometer. To conclude, this experiment showed that flame photometer is not a reliable method to measure concentration of ions in aqueous solutions.

Word count: 233

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BACKGROUND INFORMATION

Spectrophotometry is a common method used in analytical chemistry to measure the concentration of an ion in a solution. "It is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength."[1] There are mainly three methods to calculate the concentrations of an ion in the solutions:

1. Atomic Emission Spectrophotometry (Flame Photometry)
2. Atomic Absorption Spectrophotometry
3. Inductively Coupled Plasma Atomic Emission Spectrophotometry

Atomic absorption spectrophotometry is a way that works inversely as flame photometry. It is mostly used to measure the concentrations of metals like Al, Fe, Pb, Cu, Zn. In this spectrophotometry, the solutions are atomized in a flame. Second part of this, comes from the fact that metal atoms absorb UV lights. So they were given UV radiation from a bulb. The metals absorb these light waves. The remaining light will give an absorption by which the concentration can be determined.

Inductively coupled plasma atomic emission spectrometry is another method for determining the concentration of metals. It has a similar method with flame photometry but different materials. The principle comes from the fact that excited atoms emit radiation. However, to atomize the atoms, plasma formed from argon is used. As the plasma has a high energy, the atoms emit radiation. By using this emitted radiation, the concentration of metals ions can be determined. It is more effective method when compared to the flame photometer.

Flame photometry is the origin of analytical chemistry in determining the ion concentration of aqueous solutions. It has the very inaccurate results then any of the newly formed methods of spectrophotometry so it is important to see how accurate it functions.

In this study, an experiment will be carried out with flame photometer to determine how reliable it is. In this experiment known molarities of sodium 1+ ions will be measured using flame photometry and the original values will be compared with the experimental results to see how does the photometer functions.

Flame Photometry

Flame photometry is a method of measuring the concentration of ions of an aqueous solution. It consists of 4 fundamental parts. They are

1. The Atomizer

[1] http://en.wikipedia.org/wiki/Spectrophotometry

2. The Burner
3. The Optical System
4. Photosensitive Detectors[2]

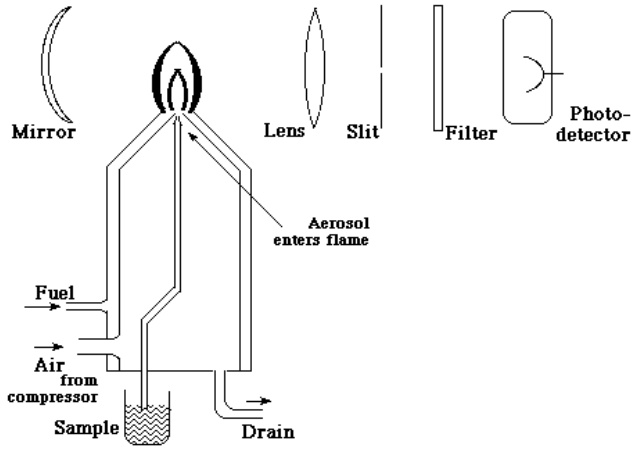


Figure 1: A schematic figure of a flame photometer.

1. The Atomizer

Atomizer is the part when then the ions of atoms meet with the flame. Firstly, in the flame, the solvent of the solution is evaporated. The metal ions get into a gaseous phase. As the atoms gain energy because of the heat and the reducing fuel, the atoms become reduced as well. "These molecules are then dissociated by the heat of the flame into free atoms; some of these atoms recombine reversibly with other components of the flame, such as OH, and still others lose an electron and become ionized." The electron on the outer shell moves to a higher energy shell. Still, there are too much energy so the produced energy from the fuel will be taken up by the atoms. As modern theory of atom implies, when atoms get energy, they release it in the form of photon. An example chemical reaction for atomization and reduction is given below:

$$K^+_{(aq)} \longrightarrow K^+_{(g)}$$

$$K^+_{(g)} + e^- \longrightarrow K_{(g)}$$

To summarise, the atomizer is the part in which the atoms meet with the flame and start to emit light.[3]

[2] Atomic Spectroscopy Author: James Robinson
[3] Atomic Spectroscopy Author: James Robinson

2. The Burner

The flame that atomizer needs, is obtained by the burner. Gases like butane, propane reacted with air are the most suitable gases that is needed to heat the atomizer. They give an approximate heat of 2000K. The burner has an air entrance which enables the reaction of fuel with air or oxygen. Specific gases give good flame and heat whereas some gases give lesser heat. If a gas that gives cooler flame is used then the atoms couldn't get excited. So, ion concentration of aqueous solutions cannot be determined effectively. A gas that gives a hotter flame can also be a problem as the energy can break some parts of the photometer and it will be much harder to cool it down. Another problem might be that atoms can get excited too much that they form 2+ ions instead of 1+ ions, releasing more radiation. A list for the specific gases and the temperature of these gases are given in the table below.

Table 1: The specific gases that is used to give flame and the temperatures of that flame [4]

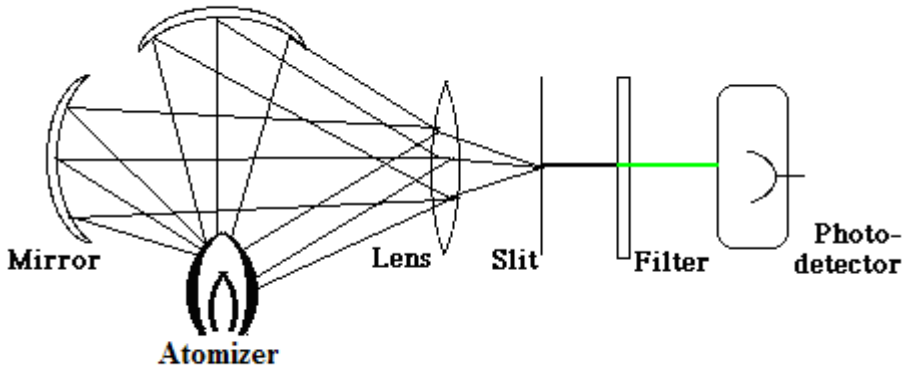
Fuel-oxidant mixture	Temperature (ºC)
Coal gas-air	1840
Propane-air	1925
Butane-air	1930
Acetylene-air	2050
Hydrogen-air	2115
Hydrogen-oxygen	2690
Acetylene-oxygen	3110
Hydrogen-perchloryl fluoride	3300
Hydrogen-fluorine	4000
Cyanogen-oxygen	4850

A good flame giving gas must be used in a flame photometer to determine the ion concentration of aqueous solution.

3. The Optical System

[4] http://www.chem.usu.edu/~sbialkow/Classes/361/flame.html

An optical system is required to focus the light emitted from the atoms to the photodetector of the photometer. The optical system consists of convex mirror, lens and filter. The convex mirror is in the part where the atomizer is. It surrounds the atomizer, so that the light emitted from the atoms are focused to the lens. If there is not a mirror then concentration cannot be determined because most of the light would be dispersed in the system and a little amount of light would reach the photodetectors, but that amount would be too small to measure it. Lens is the second part of this system. The convex lens' job is to focus the light on a point which is called slit. It collects the light emitted directly from the atoms and the reflections from the mirror. After the light passes from the slit, it goes to the filter. Filter as the name implies, filters the light at a specific wavelength that is required. It doesn't let the wavelengths different from the filter's wavelength pass to the photodetectors. For accurate results, there should be a perfect optical system.



[5]

Figure 2: Distribution of light rays through the optical system.

4. Photodetector

Photodetector is the final destination of the emitted light. These photodetectors have photomultipliers. When the light comes, they produce an electrical signal. The photomultipliers produce electrical signals directly proportional to the intensity of light. From this light intensity, the ion concentration of aqueous solutions can be determined.

Method of the Experiment

Research Question: How accurate can a flame photometer measure the Na^+ ion concentration in some samples of water?

[5] http://www.chem.usu.edu/~sbialkow/Classes/361/flame.html

As mentioned before, flame photometer is a device that is used to measure the concentration of metal ions in aqueous solutions. In order to measure the concentrations, a calibration curve must be drown with known concentrations of metal ions, because flame photometer doesn't accurately show what the concentration of the metal ion is in the solution. When a solution is put into flame photometer, it gives an emission, for instance 5.6. This 5.6 doesn't mean that the concentration of metal ion in that solution is 5.6 ppm. It is only a reading. The actual concentration of solution might be 2 ppm or 10 ppm or another. In order to prevent this, standard solutions with known molarities should be prepared and find out which concentration corresponds to the emission in the flame photometer.

"The intensity of the light emitted could be described by the Scheibe-Lomakin equation:

$I = k \times c^{n}$

where:

I = the emitted light intensity

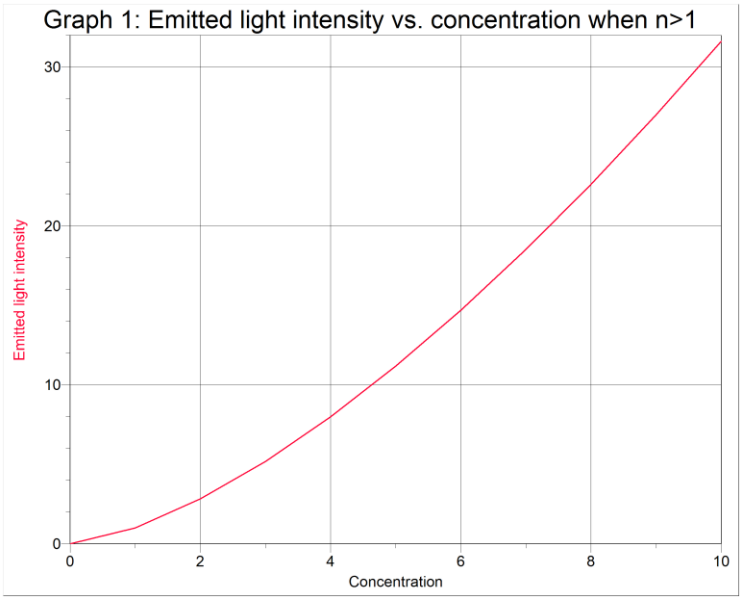
c = the concentration of the element

k = constant of proportionality

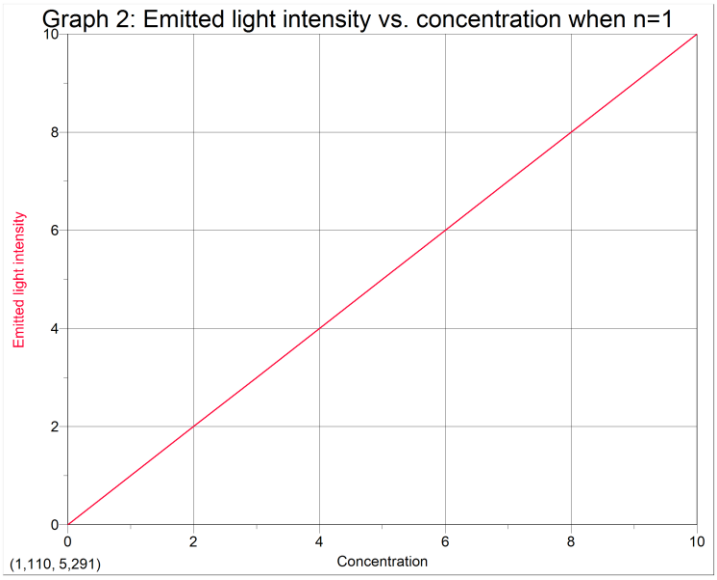
n ~1 (at the linear part of the calibration curve), therefore the intensity of emitted light is directly proportional to the concentration of the sample." [6]

If n>1 then the graph will look like a curve.

If n<1 then the graph would like the inverse of the other graph.



[6] http://www.chem.usu.edu/~sbialkow/Classes/361/flame.html

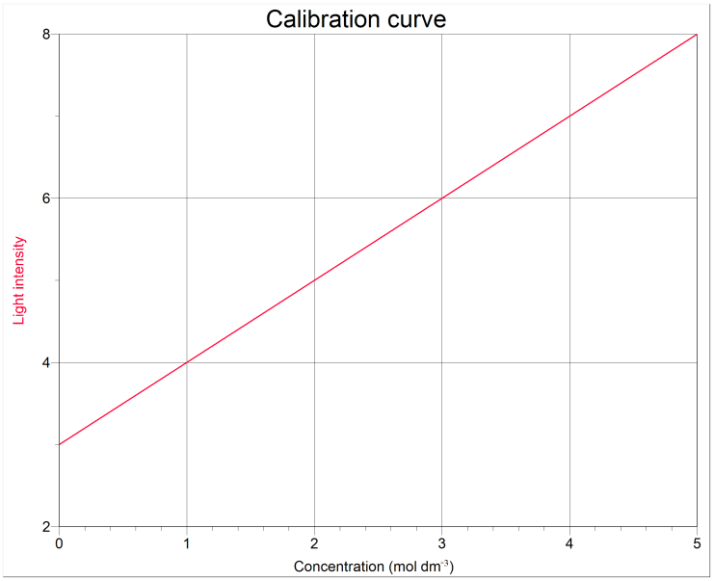


Another fact in the flame photometry is that higher concentration of ions doesn't give good results. The higher the concentration, the graph of concentration vs. light intensity will look like a curve. For linear results low molarities should be used. The reason for this fact is that all atoms in the atomiser cannot get enough energy from flame and without sufficient energy, the atoms cannot get excited, so no proper results could be obtained. If low molarities are used then there won't be enough light intensity. Without sufficient light intensity, exact concentration of ions cannot be determined. An optimum level is between 1 ppm to 20 ppm. For the experiment, concentrations would change between these two limits. Concentrations of Na^+ ion with 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm will be used. Any dilution will be done by using deionised water, since water may also contain some sodium ions.

A gas that gives a flame that is sufficient enough to excite atoms should be chosen. Gases like propane and butane reacting with air gives a temperature of 2000K in the flame. This is the optimum level for a metal like sodium as they can ionise quickly and easily.

The standardization of the flame photometer will be done by using an empty sample, called blank solution which contains deionised water. Then, the calibration curve will be drown with known concentrations of Na^+ ion of 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm.

As the solutions are put into the flame photometer, solutions will be taken up by the aspirator and then sprayed on the flame. A fuel is used to give a flame. That fuel will be propane reacted with air. When the atoms are excited, they will emit light. From the intensity of light emitted, Na^+ ion concentration in the solutions will be determined.



Graph 4: An estimated calibration curve

After measuring the intensity of light emitted, an estimated curve will be drown. By using this curve, any concentration of sodium ions can be determined within a limit, which is from 0 to 25 ppm. From this point concentrations of sodium ions can be measured using the instrument. For the accuracy, the results measured with the flame photometer will be compared with the actual results in these waters.

Independent variable: The concentration of sodium ion in water

Dependent variable: Emission in flame photometry

Controlled variables:

- Type of flame photometer used. Same flame photometer will be used.
- Sodium concentration of water used to make solutions to draw a calibration curve. In order to control this, deionised water will be used.
- Standardization. With the blank solutions, standardization will be made.
- The gas that will be used to react will always be propane. Propane will be burned with air, so that each trial will have same temperature of flame and same energy.

DATA COLLECTION and PROCESSING

1. Preparation of a solution with Na+ concentration of 1000 ppm

In order to prepare the solutions with different concentration of Na^+ ion, a standard solution with a 1000 ppm Na+ ion concentration was prepared by dissolving Na_2CO_3 in deionised water. Firstly, it is required to find out how much sodium carbonate is required to have 0.1 gram sodium.

Atomic mass of sodium: 22.99 g/mole

Atomic mass of carbon: 12.01 g/mole

Atomic mass of oxygen: 15.99 g/mole

Formula of sodium carbonate: Na_2CO_3

Molar mass of sodium carbonate: 22.99 * 2 + 12.01 + 15.99 * 3 = 105.96 g/mole

Mass of sodium carbonate required to have 0.1 gram of sodium: 105.96 / (22.99 * 2 * 10) = 0.23g

Mass of sodium carbonate used in experiment: 0.23 g ± 0.01

There is 100 mg of sodium.

ppm = mg of solute / L of solution

1 mg/L = 1 ppm

1g/L = 1000 ppm

0.1g/ 0.1L = 1000 ppm

0.1 L = 100 ml = Volume needed to form 1000 ppm solution.

Firstly, add some deionised water and dissolve sodium carbonate in it. Wait until the dissolving completes. Then fill the solution up to 100 ml.

Error Propagation

Uncertainty for sodium in sodium carbonate is calculated by using percentage error calculation. Firstly uncertainty is converted to a percentage by using the formula:

$(\Delta x / x) * 100$

In which Δx is the uncertainty of x

Percentage error of mass of sodium carbonate is 4.3%.

= (0.23 g ± 4.34%) * (45.98 / 105.96) = 0.1 ± 4.3%

= 0.100 ± 0.004

The flask has an uncertainty value of 0.1 ml. This uncertainty can be neglected because it changes the error for 0.001%. The uncertainty of the solution is again found by percentage error calculation given by the formula at the calculation of masses:

(100 mg ± 4) / (0.1 L)

(100 mg ± 4%) / (0.1 L)

(1000 ppm ± 4%)

1000 ppm ± 40

Picture 2: Preparing the solutions

2. For preparation of 100 ppm standard solution:

As both solutions will have same amount of moles then the equation below can be used.

$[A] \times V_a = [B] \times V_b$

in which [A] and [B] are concentrations and V_b and V_a are the volumes. In order to prepare 100 ml of 100 ppm solution:

1000 ppm x V = 100 ppm x 100 ml

V = 10 ml

10 ml of 1000 ppm solution is required to prepare that solution. 10 ml is diluted with 90 ml of deionised water. So a solution of 100 ppm can be obtained. From this solution, 100 ml solutions of 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm will be prepared. By doing the same measurements, the volume required from 100 ppm solution to make solutions of 100 ml of other solutions can be determined.

The uncertainty is again found by using percentage error method.

(1000 ppm ± 40) . (10 ml ± 0.1) / (100 ml ± 0.1)

(1000 ppm ± 4%) . (10 ml ± 1%) / (100 ml ± 0.1%)

(10000 ppm * ml ± 5%) / (100 ml ± 0.1%)

(10000 ppm * ml ± 5%) / (100 ml ± 0.1%)

100 ppm ± 5.1%

100 ppm ± 5.1

Other solutions with Na^+ ion concentrations, which are 5 ppm, 10 ppm, 15 ppm, 20 ppm and 25 ppm are prepared by dilution of the 100 ppm solution. A table is set to show volumes of deionised water and 100 ppm solution used. Uncertainties are also added in the table, calculated with percentage error method done in previous calculations.

Table 3: Volume of deionised water and 100 ppm solution used and the solutions uncertainties

Concentration of Na^+ (ppm)	Volume of deionised water (ml) (±0.1)	Volume of 100 ppm solution used (ml) (±5.1)	Uncertainties
5	95	5	0.32
10	90	10	0.62
15	85	15	0.89
20	80	20	1.16
25	75	25	1.43

Picture 3: The solutions of 25, 20, 15, 10, 5 ppm from left to right

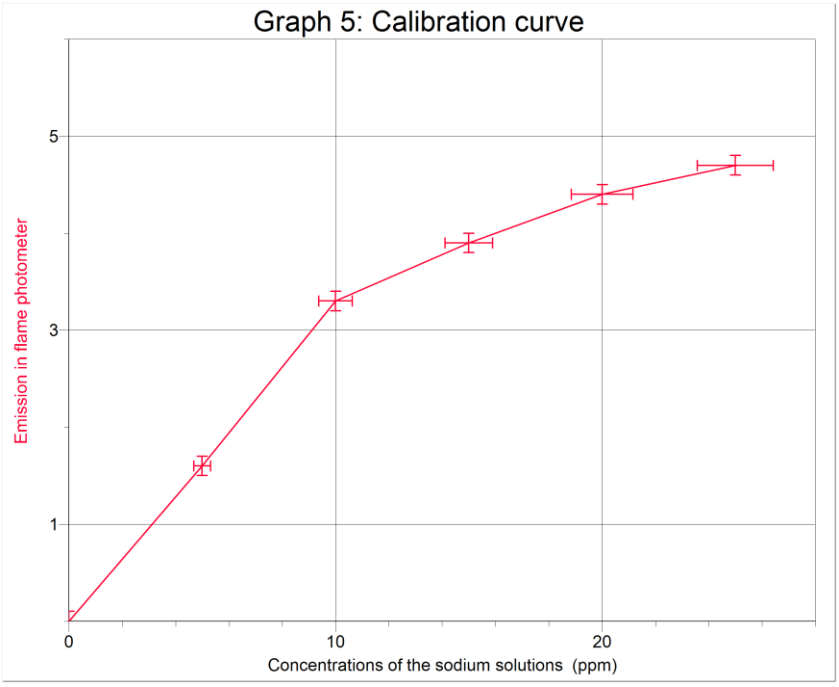
As the solutions are ready, the test with flame photometer can be made. Firstly standardization is made with deionised water. With deionised water the flame photometer showed also a value but standardization is made with the flame photometer and the blank solution. The blank solution consists

of only deionised water. With the blank solution, the flame photometer is standardized with showing the value zero for blank solution. The flame photometer is now ready for the experiment. The solutions are put into the flame photometer and the data is collected. As predicted, the sodium gives an orange colour when it is put into the flame photometer.

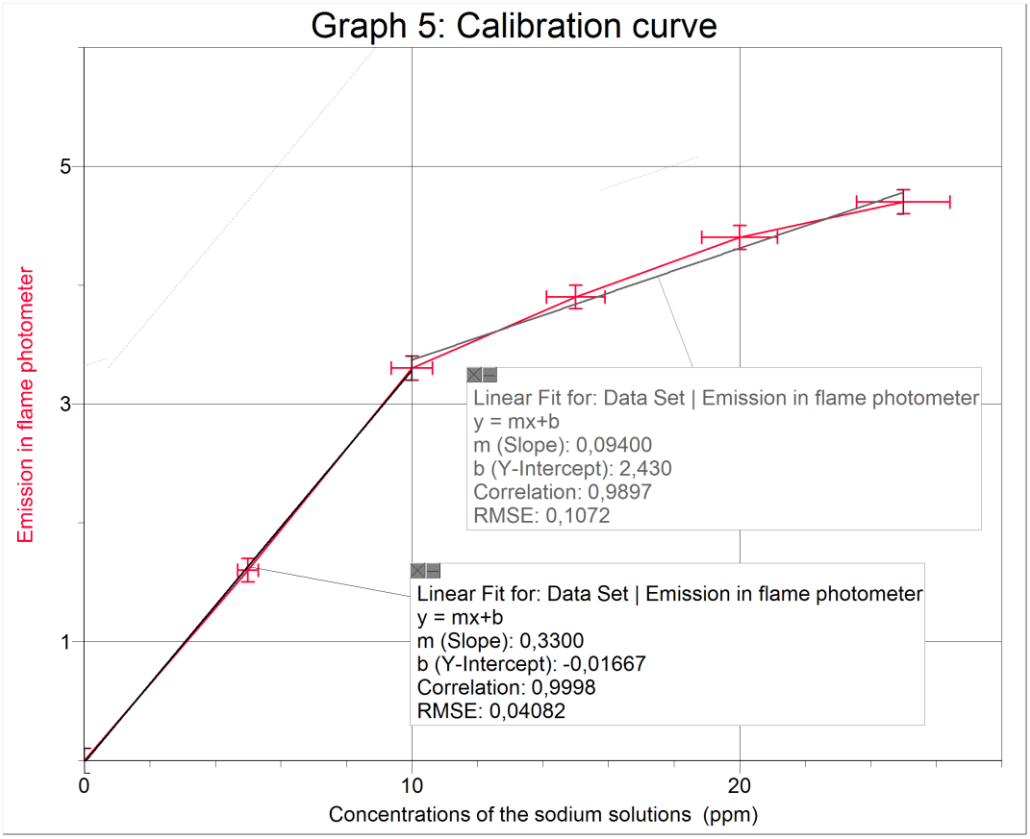
Picture 4: The flame photometer that is used in my experiment. From the colour of the flame (orange), it can be seen that sodium is being burned.

Table 4: Reading on the flame photometer for each sodium solution with the uncertainties

Na solution (ppm)	Uncertainty	Emission (± 0.1)
0	0	0
5	0.32	1.6
10	0.63	3.3
15	0.90	3.9
20	1.16	4.4
25	1.43	4.7



The calibration curve is not straight. It follows a parabola from the shape. It means too high concentration was used for the photometer to measure. The linearity is broken at the concentration of 10 ppm. So standard solutions under 10 ppm should be prepared.



Black line is the linear fit for the data between 0 to 10 ppm. Gray line indicates the linear fit for the rest of the data.

The graph implies that high molarities are used. These high molarities are after than 10 ppm so molarities lower than 10 ppm should be used. Solutions of 2, 3, 7 ppm would be enough with the existing 5 ppm and 10 ppm solutions. The same calculations are done when calculating 100 ppm solution. Error propagation is also done by percentage error done in calculation of 100 ppm solution.

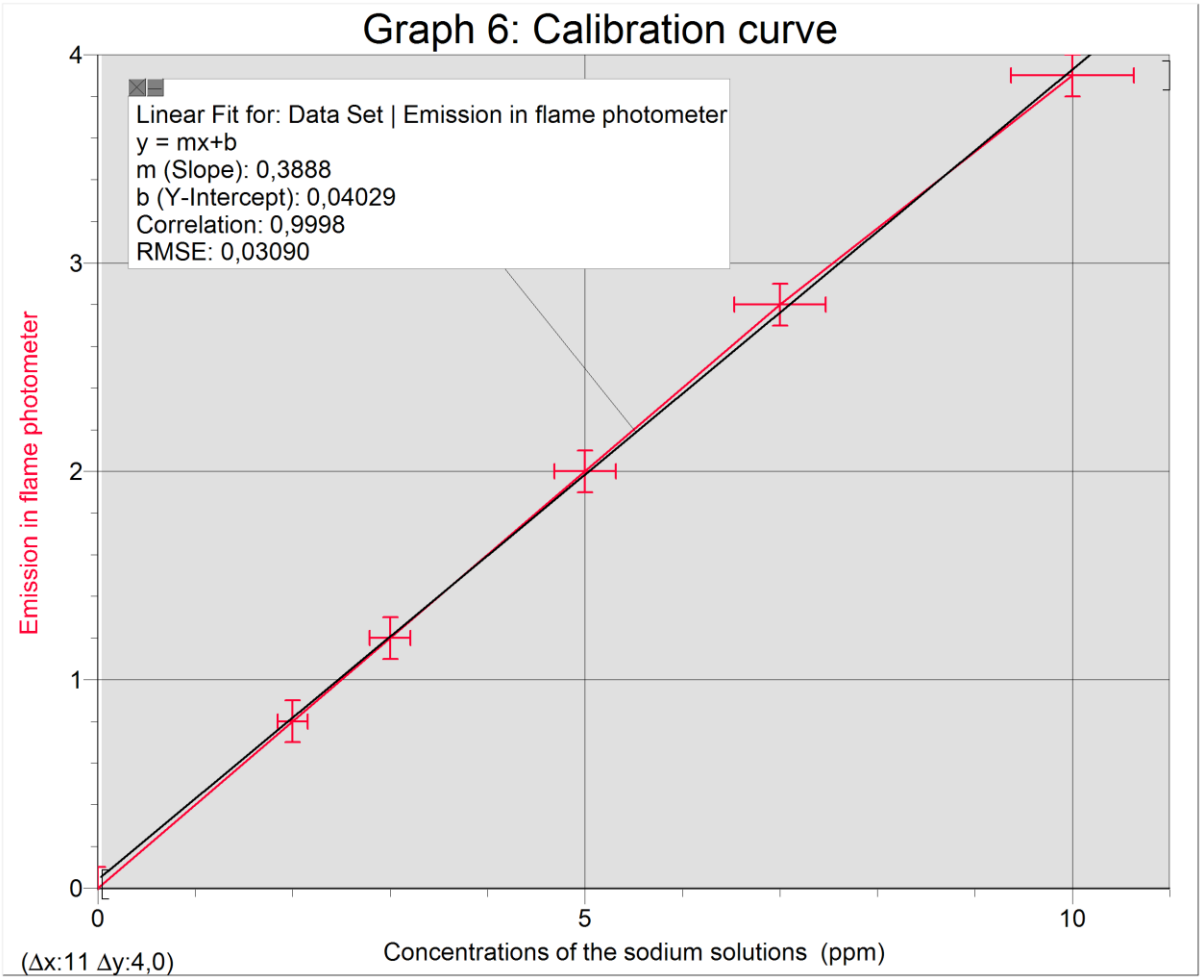
Table 5: Volume of deionised water and 100 ppm solution used and the solutions uncertainties

Concentration of Na^+ (ppm)	Volume of deionised water (ml) (±0.1)	Volume of 100 ppm solution used (ml) (±5.1)	Uncertainties
2	98	2	0.15
3	97	3	0.21
5	95	5	0.32
7	93	7	0.47
10	90	10	0.63

Now another calibration curve can be drown as the solutions are ready.

Table 4: Reading on the flame photometer for each sodium solution with the uncertainities

Na solution (ppm)	Uncertainty	Emission (± 0.1)
0	0	0
2	0.15	0.8
3	0.21	1.2
5	0.32	2.0
7	0.47	2.8
10	0.63	3.9



The graph is linearly fit. The equation shows y = 0,3888x + 0,04029 in which y is the emission in flame photometer and x is the concentrations of the solutions. The correlation is 0,9998 which shows that the graph is linear. Now the flame photometer is ready for a test with waters.

Table 5: Reading on the flame photometer with waters	
Waters	Emission (± 0.1)
Erikli water	0.6
Damla water	0.8
Tap water	6.5
Aquafina	0.8
Koru water	0.4

From the emissions by putting the values in the equations, the concentration of the waters were calculated.

- For Erikli Water:

0.6 = 0.3888x + 0.04029

0.6 – 0.04029 = 0.3888x

0.55971 = 0.3888x

x = 1.44

The result is near compared to the original value.

- For Damla Water:

0.8 = 0.3888x + 0.04029

0.8 – 0.04029 = 0.3888x

0.75971 = 0.3888x

x = 1.95

The result is near compared to the original value.

- For tap water:

6.5 = 0.3888x + 0.04029

6.5 – 0.04029 = 0.3888x

6.45971 = 0.3888x

x = 16.61

This cannot be compared with original solutions but as it is too much it should be greater than this value.

- For Aquafina Water:

0.8 = 0.3888x + 0.04029

0.8 – 0.04029 = 0.3888x

0.75971 = 0.3888x

x = 1.95

The result is not near compared to the value there is a 3 ppm difference with the original solution.

- For Koru Water:

0.4 = 0.3888x + 0.04029

0.4 – 0.04029 = 0.3888x

0.35971 = 0.3888x

x = 0.93

The result is not near compared to the value there is a 2 ppm difference with the original solution.

Table 6: Percentage errors of water concentrations detected in photometer			
Waters	Calculated concentration (±0.1)	Actual Concentration (ppm)	Percentage error (%)
Erikli	1.44	1.4	2.8
Damla	1.95	2.0	2.5
Aquafina	1.95	5.0	61
Koru	0.93	3.2	71

CONCLUSION and EVALUATION

Flame photometer is an instrument of analytical chemistry that measures the concentration of alkali metals in a solution. However this method cannot be reliable process to measure the concentrations of the solutions. Other methods of analytical chemistry are much more reliable compared to the flame photometry. Flame photometry is a cheap method to determine the concentration. There are some reasons why it is unreliable.

Firstly, flame photometer cannot be used to measure the high ion concentrations. It is because of the flame that is used. The flame is not hot enough to provide enough energy to excite high amounts of atoms so the emission is reduced down. In the study, concentrations like 20 ppm were very high and broke the linearity of the emission. These values show that flame photometer cannot be a precise instrument if high concentrations of ions are used.

Secondly, a calibration curve should be drawn to measure the concentration of metal ions, so standard solutions must be made to draw the calibration curve. Although this process spends time it is better and faster than other chemical analysis.

Thirdly, the flame photometry is not a precise method to measure the concentration. Some of the results that are found are very close to the exact value like Erikli water with 2.8% percentage error. There is always a little inaccuracy. Nevertheless, in some of the water samples, flame photometer didn't give an emission even close to the actual values. Koru water is a strong evidence for this fact with percentage error of 71%.

In addition to these facts, flame photometer couldn't be able to detect ion concentration for a specific atom if there are other ions present in the medium. Other ions would also take up the energy of the flame so there would be less energy for that specific ion to excite. Without excitation there would be lesser concentration reading in flame photometer. For this study, the aim was to measure sodium ion concentration in water. However, there were other ions like Mg, Fe, Ca etc. present in the water. These ions would also get the energy of the flame, leaving sodium with less energy.

Apart from the bad sides, it is a fundamental instrument in analytical chemistry. It can measure very small concentrations of ions sometimes not precisely. Development of other analytic chemistry instruments, started with the development of flame photometry. Atomic absorption spectroscopy is one of the examples which use a different technique than flame photometer. It gives of

light to metal atoms. Then it measures how much of the light is absorbed by the metal and determines the concentration of that metal. Inductively coupled plasma uses the technique of flame photometry, but it uses plasma instead of flame. Plasma gives better energy to the atoms, thus making it more efficient than the flame photometer. There are other methods of atomic spectroscopy methods but flame photometry is the essential part for all of the atomic spectroscopy.

One of the limitations is the concentration limit. Neither too low, nor too high concentrations of metal ions can be measured wit the instrument. In this study, concentrations between 2 ppm to 10 ppm gave favourable results. Although this limit could broaden a bit, it is still a limiting factor to measure too low concentrations as well as too high concentrations of metal ions.

Moreover, the flame photometer can only measure the concentrations of ions which has 1+ oxidation state. This limits the investigation for the alkali metals like K, Na and Li. Measurement of concentration of ions which has 2+ or more oxidation state cannot be measured by this method.

Another study can be carried out using atomic absorption spectrometry or inductively coupled plasma to ensure whether these techniques are better than flame photometer. These may be better than flame photometry and may give better results. These machines are highly sensible and can provide more energy for the atoms. The ions can be formed easily, thus having a more efficient measurement.

Further investigations can be handled out with making the instrument to reach equilibrium where concentrations of metal ions can be measured effectively. In order to do this, rechecks, blanks and controls should be properly studied to make flame photometer an effective machine.

Word Count: 3854

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