Extended Essay

-Chemistry-

Investigation of the magnitudal influence of pH and time on the iron enhancing ability of a typical cast iron skillet

Word count: ca 3500

MAY 2004

ABSTRACT

Iron is important in the diet of humans, as it is an essential component of hundreds of proteins and enzymes. Despite this, iron deficiency is the most common nutritional deficiency worldwide.

For this reason, I found it particularly worthy to investigate iron in a way that is closely linked to our diet. Because cast iron skillets are considered to add iron to food, I decide to investigate by what magnitude different pH and time would affect the iron enhancing ability of a typical one. The precise research question is:

"What is the magnitudal influence of pH and time on the iron enhancing ability of a typical cast iron skillet?"

Tap water was used as a medium for determining the iron enhancement due to boiling in the skillet. The quantitative analysis of the trace amounts of iron in the water was done by visible spectrophotometry, based on the formation of the red-orange iron(II) orthophenanthroline complex. The iron enhancing ability was found by boiling water samples of different pH for different periods of time in the skillet and measuring the corresponding absorbances. The mass of the iron enhancement was then found by consulting a calibration curve.

The iron enhancing ability of the cast iron skillet used in the investigation varied from 1.68-67.55 mg L^{-1}, when cooking periods were from 5-20 minutes in length and the pH of the medium was from 2-5. From the results, it was concluded that a decrease in pH by one unit or a doubling of the cooking time, roughly doubled the iron enhancement found from the skillet. Thus, the magnitudal influence of pH and time on the iron enhancing ability of a typical cast iron skillet was found to be a doubling.

TABLE OF CONTENT

1. Introduction

Iron is a key element in the metabolism of almost all living organisms [1]. In humans, iron is an important component of hundreds of proteins and enzymes [1]. The majority of the iron found in our body, about two thirds, is contained in the protein haemoglobin, which is the primary part of our red blood cells [1]. The vital role of haemoglobin lies in the ability of transporting oxygen to the rest of the body. As iron is essential in the formation of both proteins and enzymes, it is thus required for a number of vital functions such as growth, reproduction, healing and maintenance of immune system.

Knowing the importance of iron in the diet of humans, I was surprised to find iron deficiency to be the most common nutritional deficiency worldwide [2]. For this reason I found it particularly worthy to investigate iron in a way which is closely linked to our diet. There are many ways of increasing one's daily dietary intake of iron, for example one can eat food high in iron or take additional iron pills. Another way is by using suitable cooking skillets. It is rather well known to people that cast iron skillets can add iron to food, but is it known in what magnitudes?

I had initially planned to investigate how the iron content of different food would be affected by using cast iron skillets when cooking them. However, I found it hard to proceed with the task, as my intention was to establish a general idea of the iron enhancing effect of cast iron skillets. I soon realised that the iron enhancing effect would mainly be influenced by the period of time a food item is cooked in the skillet and the pH of the item itself, rather than the type of food. I therefore decided to investigate how these two key variables if altered, would affect the iron enhancing ability of a typical cast iron skillet by using tap water as the medium. My research question was consequently narrowed to:

"What is the magnitudal influence of pH and time on the iron enhancing ability of a typical cast iron skillet?

By my research I was hoping to make people more aware of the dietary iron found from cast iron skillets, which in my opinion, is a very often neglected and underestimated source of iron. Since the iron will be found only as a trace element in water, a sensitive method is needed to determine the iron content as accurately as possible. An appropriate method would therefore be using that of a spectrophotometrical method with high accuracy. The principle for this type of method is relating in this case the concentration of an iron solution, to its light absorbance at a given wavelength.

For the investigation, a spectrophotometer was employed to measure the amount of light that each iron solution absorbed. This kind of instrument operates by passing a beam of light through a particular sample and measuring the intensity of light reaching a detector. If the sample to be tested is coloured, then it will absorb light of a complementary colour within the visible spectrum. This allows a quantitative determination of the concentration of the particular lightabsorbing species.

The first step in my research will be to collect enough data to prepare a calibration curve. The calibration curve will then be used for determining the concentration of iron in any sample by measuring its absorbance. In my experiments I decided to use a very sensitive spectrophotometrical method which relies on the formation of the orange-red iron(II) orthophenanthroline complex [4].

The parent compound has a pair of nitrogen atoms located in such positions that each can form a covalent with the iron(II) ion [4]. 3 orthophenanthroline molecules combine with each iron ion to yield a complex with the structure shown below:

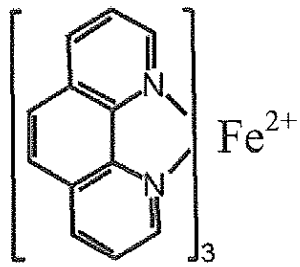

Figure 1.1: The structure of the iron(II) orthophenanthroline complex.

Orthophenanthroline is a weak base and in acidic solution the principal species is the phenanthrolium ion, Ph H^+ [3]. Thus, the complex formation reaction of orthophenanthroline with iron is best described by the equation:

$$Fe^{2+} + 3\ PhH^+ \leftrightarrow Fe(Ph)_3{}^{2+} + 3H^+$$

2. Method for finding the calibration curve for iron

To construct the calibration curve, several complex solutions of iron had to be prepared and their absorbance measured. The standard iron solution used for making complex solutions of iron of various concentrations, contained iron in the form of $FeS0_4.(NH_4)_2SO_4.6H_2O$. 0.702 g of the compound was poured into a 1000 ml volumetric flask, and dissolved in 50 ml of water which contained 1 ml of concentrated sulphuric acid. The flask was then diluted up to the mark with distilled water.

Because the iron in the orthophenanthroline complex undergoes reversible oxidation-reduction reactions, an excess of reducing agent is added to the solution in order to keep it in the divalent state [4]. A solution of 5g hydroquinine / 200 ml distilled water was therefore prepared. The pH of this solution was adjusted to 4.5 ± 0.1 by introducing sufficient amount of sodium citrate. Because the quantitative formation of the o-phenanthroline complex is observed in the pH region 2-9, and a pH of about 3.5 is ordinarily recommended to prevent precipitation of different iron salts, a sodium citrate and a citric acid solution was prepared by dissolving 125 respectively 5g of solid / 500 ml of distilled water. Finally, a solution of 0.3000g± 0.0001 o-phenanthroline / 100 ml distilled water was also prepared.

The complex solutions of iron were then made in the following way: 0.00, 0.05, 0.25, 0.50, 1.25, 2.50 and 5.00 ml of the standard iron solution was transferred into a beaker using a pipette. The pH was then brought to 3.5 ± 0.1 by adding sodium citrate solution and measuring the pH using a meter and magnetic stirrer. I noted the number of drops required to reach this pH and discarded the solution. I then measured a fresh 0.00, 0.05, 0.25, 0.50, 1.25, 2.50 and 5.00 ml aliquot of the standard solution and transferred it to a 100 ml volumetric flask, added 1 ml of the hydroquinine and 3 ml of the o-phenanthroline solution for every complex solution. The same quantity of sodium citrate solution as was needed for the preliminary titration was introduced and the

contents of the volumetric flask were mixed thoroughly. The mixtures were then allowed to stand for 5 minutes, so there would be enough time for the complex to form before measuring the absorbance. The absorbance of the prepared complex solutions was thereafter measured at 508 nm, after 15 minutes.

2.1 Calculation of the mass of iron in the complex solutions made

To construct the calibration curve, the concentration of iron needs to be related to the absorbance. It is therefore necessary to calculate the concentration that each complex solution above has.
The standard iron solution was made by dissolving 0.702 g of $FeS0_4.(NH_4)_2SO_4.6H_2O$ in 1000 ml of distilled water. Consequently there are n moles of $FeS0_4.(NH_4)_2SO_4.6H_2O$ in 1000 ml of distilled water.

Using the formula, $\frac{m}{M} = n$, where m is the mass of $FeS0_4.(NH_4)_2SO_4.6H_2O$ in g and M is the molar mass of $FeS0_4.(NH_4)_2SO_4.6H_2O$ in g mol^{-1} gives:

$$\frac{0.702g}{392.19gmol^{-1}} = n_{FeSO_4.(NH_4)_2SO_4.6H_2O} = 1.79\times10^{-3}\,\text{mol}$$

Taking flask # 1 as an example, the amount of iron in 0.05 ml of standard iron solution can be found using the relationship n = V×c, where V is the volume of standard solution used in dm^3 and c is the concentration of iron in the standard solution.
Substitution gives: $n_{FeSO_4.(NH_4)_2SO_4.6H_2O} = 5\times10^{-5}\,dm^3 \times 1.79\times10^{-3}\,\text{mol}\,dm^{-3} = 8.95\times10^{-8}\,\text{mol}$

The mass of iron is then found by converting the amount of substance into mass using the formula m = Mn, where $n_{Fe} = 8.95\times10^{-8}$ mol and $M_{Fe} = 55.85$ g mol^{-1}
$\therefore\ m_{Fe} = 8.95\times10^{-8}\,\text{mol} \times 55.85\,\text{g mol}^{-1} = 5.00\times10^{-6}\,\text{g}$

The quantity of iron in 0.05 ml of standard solution being so small is better converted into mg of iron for convenience. The concentration of iron in flask # 1 is $\therefore$ found to be 5×10^{-3} mg.
The concentrations of the remaining flasks of complex solution (containing 0.25, 0.50, 1.25, 2.50 and 5.00 ml of the standard iron solution) were found in the same way and are presented in a table below.

2.2 Data Collection

Table 1: The table below shows the volume of standard solution used per dm^3 of complex solution, the concentration of each complex solution and corresponding absorbance measured after 5, 10 and 15 minutes respectively.

Flask #	Volume of standard solution used (ml)	Concentration of iron ($mg\ dm^{-3}$)	Absorbance after ±0.5 (s)		
			300	600	900
1	0.05	0.005	0.022	0.018	0.017
2	0.25	0.025	0.052	0.051	0.050
3	0.50	0.050	0.098	0.096	0.097
4	1.25	0.125	0.223	0.222	0.222
5	2.50	0.250	0.504	0.505	0.503
6	5.00	0.500	0.975	0.977	0.976

2.3 Data Analysis

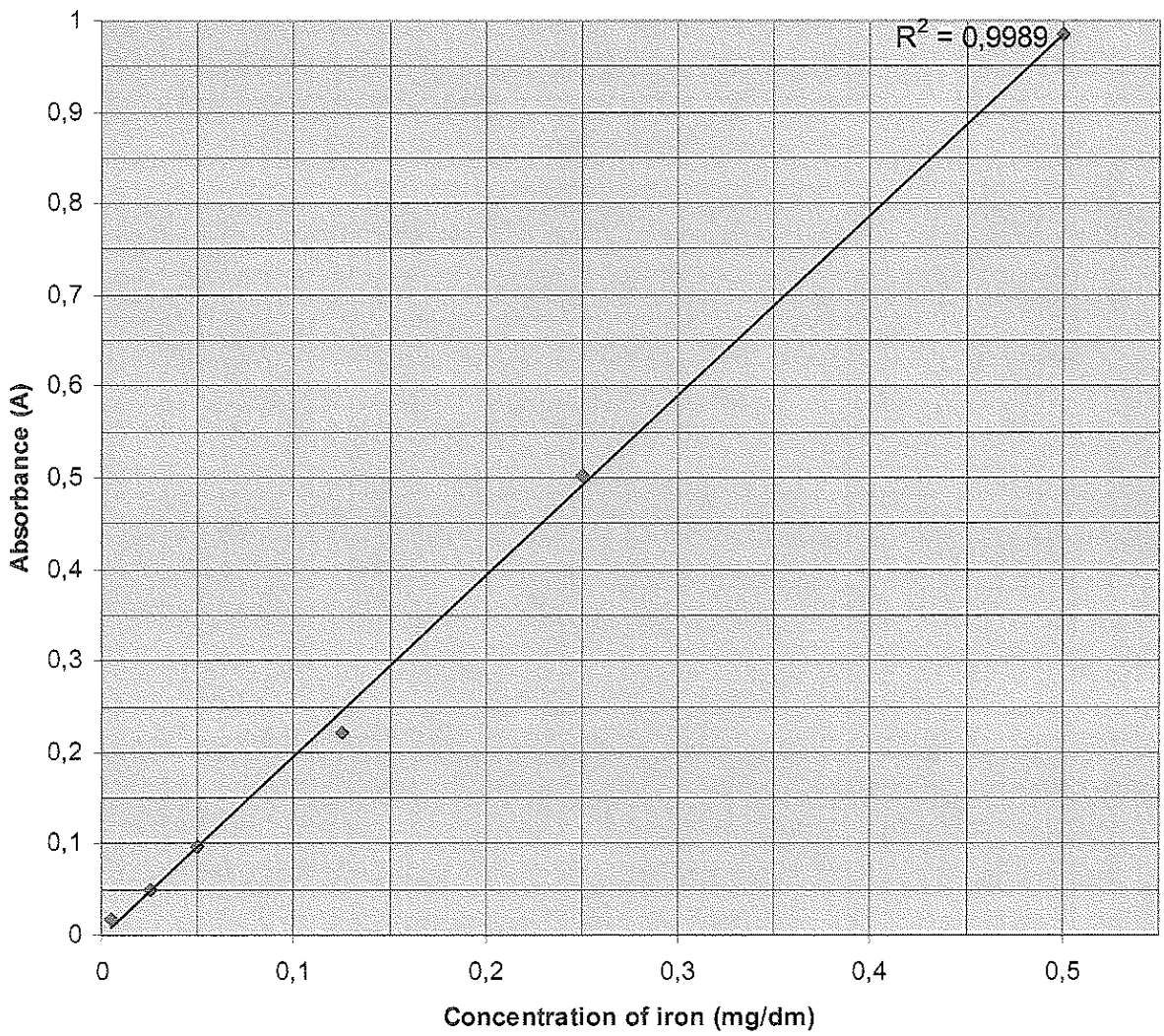

Figure 1.2: The calibration curve for iron drawn from the above data.

To be able to make an exact measurement of the light absorbed by a particular iron complex solution, the instrument was first calibrated using a blank solution containing all reagents except iron. This means that all the absorbance values recorded are in respect to this blank.
The complexes displayed relatively stable absorbance values after only five minutes. This is probably because of the properties of the organic chelating agent of o-phenanthroline which once having formed a complex with iron stays stable for long periods of time [4].

The chosen wavelength setting at 508 nm for the absorbance measurements is where the maximum change in absorbance occurs for an iron solution of any concentration. This allows obedience to Beer's Law: $A = \varepsilon lc$, where A is the absorbance of the solution, ε is the molar extinction coefficient, l is the distance the light passes through the solution and c is the concentration of the solution [4]. Because the same cuvette has been used in the measurements, the measurements have been made at the same wavelength setting and the same complex is formed when measuring the absorbed light, l *and* ε must be constant. This gives rise to a new constant and implies that a graph of absorbance (A) against concentration (c) is a linear graph passing through origin [5]. From the R^2 value of the calibration curve, it can be seen that the relationship between the absorbance and concentration agrees well with the linear regression. This means that the drawn calibration curve is of good accuracy and has a good adherence to Beer's Law.

3. Method devised for finding the magnitudal influence of pH and time on the iron enhancing ability of a typical cast iron skillet

To find out how the two key variables, pH and time, affect the iron enhancing ability of a cast iron skillet, a simple method was devised. For the investigation, the local tap water of Borås, Sweden and my own cast iron skillet of the brand Everex® were used. The pH of the water was altered using lemon juice on can, because this unlike freshly squeezed juice requires no filtration. The method devised was divided into three parts: The first part was to prepare water solutions of four different pH, the second to boil each water solution for various periods of time and the third was to complex the boiled samples and measure their absorbance.

(I) Four different 1000 ml beakers were filled with tap water up to the mark. The pH of each beaker was then adjusted to 2.0, 3.0, 4.0 and 5.0 $\pm$ 0.1 respectively by transferring lemon juice drop wise using a Pasteur pipette and a meter. 100 ml of each solution was saved for measuring the absorbance later.

(II) Having four water solutions ready, each one was poured into 3 different 300 ml beakers. Once each of the solutions was divided into 3 equal parts, each part was boiled for 5, 10 and 20 minutes respectively. Using a stopwatch, the timing began as the temperature of the water reached 100.00 $\pm$ 0.01 degrees centigrade. The temperature was measured by using an electronic thermometer. The boiled samples were then collected into marked beakers.

(III) The procedure then followed to complex the water samples (including the samples that were not actually boiled), so as to develop colour in them, was the same as performed previously when preparing the calibration curve. Amounts ranging from 5-50 ml of sample were transferred into a 100 ml beaker and the pH was adjusted to about 3.5 using sodium citrate solution or citric acid solution where appropriate, and measuring the pH using a meter and magnetic stirrer. The quantity of acid or alkali required for the preliminary titration was noted and the contents of the beaker were discarded. I then transferred amounts of sample ranging from 5-50 ml of into a 100

ml volumetric flask, added 1 ml hydroquinine and 3 ml of o-phenanthroline solution. The noted quantity of acid/alkali solution was introduced and the flask was allowed to stand for 5 minutes before diluting up to the mark with distilled water. The absorbance was then measured at 508 nm after the intervals of 5, 10 and 15 minutes respectively.

3.1 Data Collection

Table 2a-2d: The tables below show the boiling period of the samples, the volume of sample used per dm^3 of complex solution, the pH of each sample and their respective absorbance values after 5, 10 and 15 minutes.

Table 2a

Sample #	Boiling period (s) ± 0.5	Volume of sample used (ml) ± 0.02	pH ± 0.1	Absorbance after ± 0.5 (s) 300	600	900
1	0	50.00	2.0	0.138	0.139	0.139
2	0	50.00	3.0	0.087	0.087	0.089
3	0	50.00	4.0	0.058	0.060	0.060
4	0	50.00	5.0	0.048	0.048	0.047

Table 2b

Sample #	Boiling period (s) ± 0.5	Volume of sample used (ml) ± 0.02	pH ± 0.1	Absorbance after ± 0.5 (s) 300	600	900
5	300	5.00	2.0	0.160	0.161	0.161
6	300	10.00	3.0	0.164	0.163	0.163
7	300	20.00	4.0	0.166	0.168	0.167
8	300	50.00	5.0	0.229	0.231	0.231

Table 2c

Sample #	Boiling period (s) ± 0.5	Volume of sample used (ml) ± 0.02	pH ± 0.1	Absorbance after ± 0.5 (s) 300	600	900
9	600	5.00	2.0	0.338	0.336	0.334
10	600	5.00	3.0	0.154	0.157	0.158
11	600	20.00	4.0	0.304	0.305	0.305
12	600	20.00	5.0	0.175	0.174	0.174

Table 2d

Sample #	Boiling period (s) ± 0.5	Volume of sample used (ml) ± 0.02	pH ± 0.1	Absorbance after ± 0.5 (s) 300	600	900
13	1200	5.00	2.0	0.672	0.674	0.674
14	1200	5.00	3.0	0.344	0.341	0.342
15	1200	10.00	4.0	0.324	0.326	0.327
16	1200	10.00	5.0	0.161	0.163	0.164

8. Data Analysis

From the derived absorbance values it is possible to determine the mass of iron in each of the boiled water samples from the calibration curve constructed before. It is also possible to determine how much the iron content of the water samples has increased upon boiling them in the cast iron skillet, by consultation of the same calibration curve.

Taking sample number 14 *(see table 2d)* as an example:

The iron content after 20 minutes of boiling was found to be 35.91 mg L^{-1} from the calibration curve. Subtracting this by the iron content before boiling which was 0.91 mg L^{-1}, gives an iron enhancement of 35 mg as:

Iron content after boiling/35.91 mg L^{-1} – Iron content before boiling/0.91 mg L^{-1} = Iron enhancement/ 35.00 mg L^{-1}

The remaining samples have been processed in the same way and the results are presented in the table below.

Table 3: Shows the pH of each sample and the corresponding iron enhancement after 5, 10 and 20 minutes of boiling in a cast iron skillet.

pH ± 0.1	Iron enhancement (mg L^{-1}) after		
	300 ± 0.5(s)	600 ± 0.5(s)	1200 ± 0.5(s)
2.0	16.43	32.65	67.55
3.0	8.33	16.24	35.00
4.0	4.24	7.81	16.75
5.0	1.88	3.97	7.94

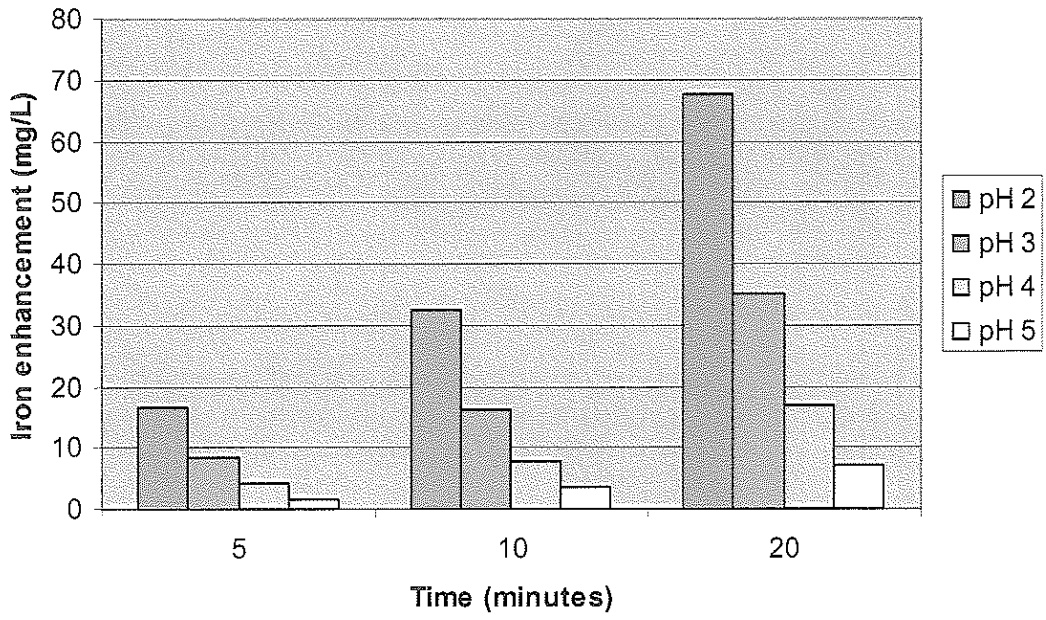

Figure 4: The graphical representation of the results obtained in table 3.

9. Evaluation

The results of the performed investigation showed visible trends reflecting the iron enhancing ability of a cast iron skillet. All samples showed an increase in iron enhancement as the pH analogously decreased. Also, as the cooking period was doubled, the iron enhancement increased as a result. The increase in iron enhancement was in both cases roughly a doubling.

From the results, it can also be seen that the sample that had the greatest difference in iron enhancement due to varying of pH relative to the other samples, was the sample of pH 5 *(see Table 3)*. For example, the difference in iron enhancement after 5 minutes of boiling was 97% between the sample of pH 2 and 3 and 125% between the sample of pH 4 and 5. In fact the range of the increase in iron enhancement, both due to a decrease in pH by one unit and a doubling of the cooking period, was between 84-115%. Although the sample of pH 5 deviated more than the other samples due to its pH, the increase in iron enhancement due to a doubling of the cooking period was similar to the results obtained for the other samples.

The exact reason for the deviation occurring is hard to know and gives rise to a new question emerging from the investigation. One possible explanation might be an error in the initial adjustment of the pH for this particular solution. Also, I noticed when boiling the samples that although a lid was used, some vapour was escaping. This can have altered the concentration of the water in the skillet slightly and hence influenced all the results. This could have been avoided by adopting a proper reflux-system.

The major source of errors in the spectrophotometrical procedure followed to analyse the quantities of iron, is most likely to emerge from the indeterminate error in the absorbance measurement [4]. Determination of absorbance requires evaluation of the power of the beam that has passed through a particular solution as well as its power after passage through the blank [4]. This, in order to find for example uncertainties in the wavelength setting or source fluctuations in the instrument [4]. The influence of these uncertainties are not always obvious and much the less their final impact on the results. Due to time limitations, evaluation of the spectrophotometer's accuracy was not possible and in addition this was not considered part of my investigation. Other possible sources of error could also arise from sample preparation, imperfections in the cuvette, pH adjustment of the complex solution, and the temperature of the complex solution [4].

These uncertainties are not likely to have caused great errors in the results. For example, the pH was carefully controlled throughout the investigation although this was not required for the method followed. The presence of interfering species is therefore negligible. The same cuvette was used in all absorbance measurements and no imperfections were detected. Although the temperature of the complex solution was not controlled, this could not have had any great influence on the formation of the iron(II)orthophenanthroline complex. This is because the equilibrium constant for this reaction is 2.5×10^6 at 25 degrees centigrade and the experiments were performed in a room temperature of about 20 degrees centigrade.

Concentration errors in most absorption methods are fairly low (1-2%) when absorbances measured lie in the range of 0.15 to 1.0 [4]. In my experiments some of the absorbances measured lie below the lower limit of 0.15 (*see Table 1 and 2a*). For these absorbances, relative concentration errors greater than 2% are inevitable. During the investigation I was aware of the importance of getting good and reliable absorbance measurements, but due to time limitations it was not possible to conduct repetitions of the experiment. By the time the experiment was finished, there was no longer any sample left. The absorbance measurements required a large

volume of sample because the concentration of iron in these was very low and I had to increase the volume of sample each time the absorbance reading was below 0.15, to get a more accurate reading. Repetitions on the final absorbance measurements (of which the absorbance values are recorded in table 2a-2d) were not conductible because of the large quantitative use of sample. Most errors in this investigation could simply have been avoided if more time would have been available and more replications were made.

If more time had been available, I would have analysed the factors that could have caused the deviation for the sample of pH 5 mentioned before, more closely. The extent to which the results obtained in this investigation rely on the particular cast iron skillet used, is not clear. It is generally thought that the newer a cast iron skillet is, then the greater is its iron enhancing ability [3]. Furthermore, the particular alloy of iron used for producing the skillet may also affect the amount of iron released from it. To extend the investigation, it would therefore be interesting and worthy to see how the age and brand of a cast iron skillet would affect its iron enhancing ability. The skillet I used was 3 years old, that is, neither old nor new. Hence the skillet used is more of a typical one in this aspect. Also, both the pH region (2-5) and the cooking periods (5-20 minutes) could be extended to see how this might affect the obtained results and thereby get a more complete understanding of the reliability of the results.

10. Conclusion

From the undertaken research it was found that a decrease in pH by one unit roughly doubled the iron enhancing ability of a typical cast iron skillet. In the same way a doubling of the cooking time, also roughly doubled the iron enhancement. Thus, the magnitudal influence of pH and time on the iron enhancing ability of a typical cast iron skillet was a doubling.

The iron enhancing ability of the cast iron skillet used in the investigation varied from 1.68-67.55 mg L^{-1}, when cooking periods were from 5-20 minutes in length and the pH of the medium was from 2-5.

The iron enhancement was at least 1.68 mg after a cooking period of only 5 minutes in the pH region 2-5. In the same way the iron enhancement was at least 3.97 and 7.94 mg after a cooking period of 10 and 20 minutes respectively. Based on these lowest values of the iron enhancement, which are to be found in the medium of pH 5, the results from this research give a clear indication of the effects of using cast iron skillets in our daily cooking of acidic food with high moisture content, such as soups and sauces. The results yielded from the research can well be compared to the RDA (Recommended Dietary Allowance) value found in the USA, which suggests approximately 10-15 mg of iron in the daily diet of adult men and females [2]. In most cases the cooking periods for various food exceed those used in this investigation and implies that an even higher iron enhancement could be expected when food is cooked in a cast iron skillet. For this reason, switching to using cast iron skillets would according to the obtained results be a good idea if one were looking for an effective way of increasing the daily dietary intake of iron.

11. Bibliography

1. The Linus Pauling Institute, Iron, Copyright 2001-2003 (Last updated:2003-03-27) [Visited 2003-05-07]. Available from World Wide Web:

http://www.lpi.oregonstate.edu/infocenter/minerals/iron/iron.html

2. MEDLINEplus Medical Encyclopaedia, Copyright 2002 A.D.A.M., Inc. [Visited 2003-08-02]. Available from World Wide Web:

http://www.nlm.nih.g...dlineplus/ency/article/002422.htm

3. Columbia University's Health Question & Answer Internet Service, Copyright 2003 (Last Updated: 2003-03-28) [Visited 2003-08-02] Available from World Wide Web:

http://www.goaskalice.columbia.edu/2378.html

4. Skoog Douglas A., West Donald M., *Fundamentals of analytical chemistry*, third edition, USA, 1976.

5. Green John, Damji Sadru, *Chemistry for use with International Baccalaureate Diploma Programme*, 2001 IBID Press, Victoria, Australia.