

The relationship between the voltage during a process of anodizing and the thickness of the anodized layer

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March 7, 2019

Rationale

Regarding chemistry overall, I am most interested in industrial chemistry. Due to my affinity for physics and engineering, I am naturally drawn to everything regarding engineering, including industrial chemistry. As I was thinking about a topic for my Chemistry Internal Assessment, I oversaw my room-mate's *FiiO E10K* ("E10K"). The *FiiO E10K* is a device covered in anodized aluminum. I thought about how I never actually learned how anodized aluminum is made, and therefore I decided to conduct my research in the field of anodizing.

1 Introduction

In contact with atmospheric contents, aluminum surface becomes quickly coated with a layer of aluminum oxide with a thickness of up to $1 - 2\mu\text{m}$. Because of the low thickness of the aluminum oxide, high porosity and low mechanical strength, this oxide layer does not protect the aluminum in any significant amount (Ardelean, Marius and Lascău, S and Ardelean, Erika and Josan, Ana).

However, a sufficiently thick superficial oxide layer does prove to be both protective and aesthetically pleasing. Through the process of anodic oxidation, a thicker, around 20 to $50\mu\text{m}$, oxide film can be achieved. These artificial films are more mechanically stable, heat-resistant, porous, stable to water vapor and other corrosive agents, compared to their natural counterparts (Ardelean, Marius and Lascău, S and Ardelean, Erika and Josan, Ana). This process of artificial induction of the oxide layer is referred to as the process of *hard anodizing* (Sheasby, P. G.; Pinner, R.).

The process of anodizing has two main purposes - increasing the resistance to corrosion as well as decoration. The resistance to corrosion stems from the fact that the oxide layer cannot corrode. Anodized aluminum can be dyed making the oxide film decorative as well as protective.



Figure 1: An example of an anodized aluminum sheet (KI)



Figure 2: An example of colorful anodized aluminum parts (Fischer)

1.1 The anodizing process

The process of forming aluminum oxide film is a redox reaction which occurs in an electrochemical cell as shown in figure 3.

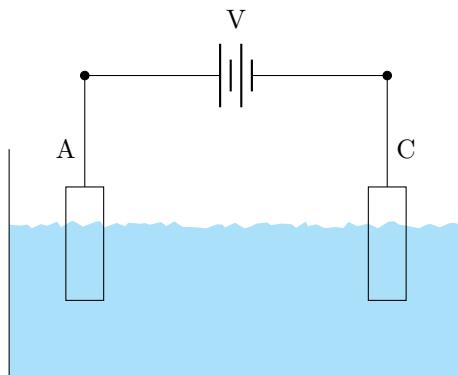
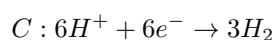
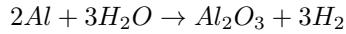


Figure 3: The anodizing electrochemical cell

Aluminum is used as the anode A as it will oxidize. The cathode C is a chemically inert electrode such as carbon or lead. The electrolyte can be chosen at will, however for a thick coating of aluminum oxide a strong acid proves to be more effective. When voltage V is applied an electrolysis reaction occurs. The following two reactions happen at the cathode C and the anode A :



The resulting anodizing reaction is:



1.2 The growth mechanism

The oxide film comes in two forms - a barrier type film and a porous type film (Ono), as shown in figure 4. The barrier type film is the one naturally most occurring while the porous type film is the one which is usually formed by anodizing. The barrier type film is a homogeneous sheet of Al_2O_3 , while the porous type film has small holes in which molecules fit. These small holes can be filled with dye molecules making the object colorful¹.

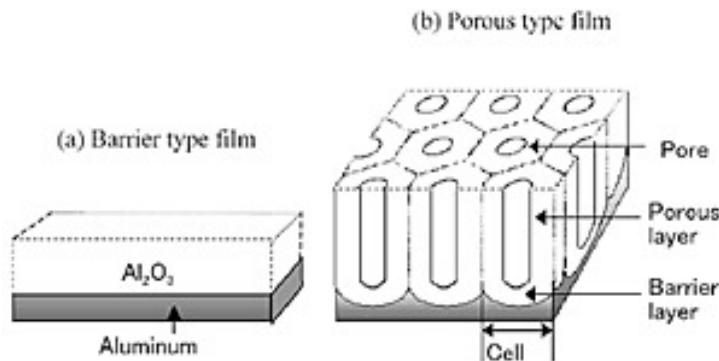


Figure 4: The two types of Al_2O_3 oxide film (Ono)

The formation of the oxide layer is as follows. At a constant power generated by a voltage generator, the relationships between the anodizing time and the voltage and current density are given in figure 5. The separate stages are represented in the figure. From stage I to II the barrier type film is formed. As the anodizing process continues, the voltage will increase. Between stages II and III, as the film grows, grooves will become etched in it. Between stage III and IV, pores will start forming.

1.3 Impact of voltage

The voltage applied during the anodizing process heavily impacts the thickness of anodized layer. Since the thickness of the anodized layer heavily impacts the *Vickers hardness*² of the overall aluminum, it is important to be able to predict the thickness of the film with respect to the voltage applied for a constant time.

Therefore, the research question of this paper is: *What is the relationship between the voltage applied during the process of aluminum anodizing and the thickness of the anodized film?*

¹It is interesting to note that anodized aluminum parts never come in the color white because of the fact that white dye (leuco dye) molecules are larger than the pores and therefore cannot fit inside the pores.

²A measure of a material's resistance to plastic deformation - irreversible changes to its shape

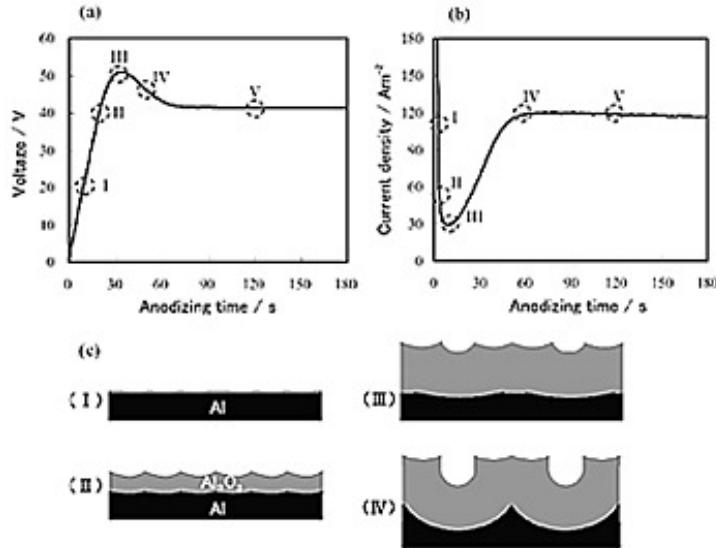


Figure 5: The formation of the porous oxide film (Ono)

It was hypothesized that the relationship between the voltage and the thickness of the anodized film to be logarithmically dependent - as the voltage increases, more of the film will form. However, as more of the film forms the electrical resistance will increase, decreasing the rate of anodizing.

1.4 Significance

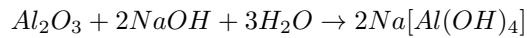
Research in this field could prove useful in consumer products. Anodized aluminum products are very common and products with a maximal hardness would be most resistant to scratching and other day-to-day material deformations. Moreover, since the thickness of the oxidized film impacts how resistant aluminum is to corrosion, research in the field could prove useful to both the automotive and the aeronautical industries as it would enable better prediction of the behavior of the industries' products.

2 Method

2.1 Anodizing

2.1.1 Cleaning

Before the actual anodizing reaction, it is necessary to clean the aluminum bars that are to be anodized. First they are cleaned using a detergent to remove any oils that may be present. After that, they are settled in a solution of $NaOH$ for about 3 minutes. The reaction that occurs is:



This reaction cleans off the already existing oxide film.

2.1.2 Anodizing reaction

The anodizing process can be done as follows. In a 250ml beaker, dilute sulfuric acid is carefully poured. The positive side of a lab bench power supply is connected to an aluminum rod. The negative side of the power supply is connected to a graphite cathode. These are both submerged in the sulfuric acid. The voltage is applied and the electrolysis process starts. The process is conducted for a fixed time after which the aluminum rod is pulled out of the solution.

2.1.3 Tempering

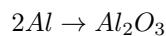
After the process of anodizing, the aluminum rod is put in boiling water for around 15 minutes and then cooled off to room temperature, which allows the newly formed film to temper itself.

2.2 Thickness of the film

Measuring the thickness of the oxide film is nearly impossible with conventional methods of using a caliper and micrometer. Calipers are not precise enough to measure the thickness of the film layer, and a micrometer is too precise to use multiple times accurately. As such, it is necessary to develop a different method which will enable the measurement of the layer.

In this paper, a different method is proposed. Instead of directly measuring the thickness of the anodized layer, it is proposed to measure the change in mass before the anodizing process and after it. With a sufficiently precise scale, it is, in theory, possible to accurately estimate the thickness of the film.

The method for estimating the thickness of the anodized layer is as follows. First, the mass of the un-anodized aluminum m_0 is measured. This is to be done immediately before the process of the anodizing reaction. After the reaction and the tempering, the mass of the anodized aluminum m_1 is measured. Since the process under which aluminum undergoes is



and since it is reasonable to assume that all of the Al_2O_3 will reside on the walls of the Al , it can be inferred that:

$$m_1 = m_0 + m(O)$$

$$m_1 = m(Al_2O_3) + m_0 - m(Al)$$

The mass of the aluminum can be calculated as follows. Since the mass of oxygen is known ($m(O) = m_1 - m_0$), the number of moles of oxygen is also calculable:

$$n(O) = \frac{m(O)}{M(O)}$$

Since there are 3 oxygen atoms in every molecule of Al_2O_3 , it follows that:

$$\begin{aligned} n(Al_2O_3) &= \frac{1}{3}n(O) \\ &= \frac{1}{3} \cdot \frac{m(O)}{M(O)} \end{aligned}$$

and then:

$$\begin{aligned} m(Al_2O_3) &= n(Al_2O_3) \cdot M(Al_2O_3) \\ &= \frac{1}{3} \cdot \frac{m(O)}{M(O)} \cdot M(Al_2O_3) \end{aligned}$$

The volume of Al_2O_3 is then:

$$\begin{aligned} V(Al_2O_3) &= \frac{m(Al_2O_3)}{\rho(Al_2O_3)} \\ &= \frac{1}{3} \cdot \frac{m(O)}{M(O)} \cdot M(Al_2O_3) \cdot \frac{1}{\rho(Al_2O_3)} \end{aligned}$$

2.2.1 Thickness calculation

Finally, to calculate the thickness of the anodized layer, the following method is employed. Let us first assume that the oxide film is uniform. Consider the modeled Al bar given in figure 6. The Al bar is given in black, and the oxide film is given in blue. Let us denote the dimensions of the Al bar as: a , b and c . The thickness (the distance from the edge of the aluminum to the edge of the oxide film) is t .



Figure 6: A model of the anodized Al bar

If the assumption is made that the oxide film grows around the aluminum bar during anodizing, then

the volume can be expressed as:

$$(a+t)(b+t)(c+t) = V_{Al_2O_3} + V_{Al}$$

$$abc + t^3 + (a+b+c) \cdot t^2 + (ab+ac+bc) \cdot t = V_{Al_2O_3} + V_{Al}$$

$$t^3 + (a+b+c) \cdot t^2 + (ab+ac+bc) \cdot t = V_{Al_2O_3}$$

$$t^3 + (a+b+c) \cdot t^2 + (ab+ac+bc) \cdot t - V_{Al_2O_3} = 0$$

The solutions for the cubic equation can be computationally achieved.

2.2.2 A more accurate model

Note that the aforementioned model is not perfect as it does not consider the fact that aluminum on the bar depletes becoming Al_2O_3 . Refer to figure 7 for a microscopic view of a model which does consider this. The following notation is used: t is the thickness of the oxide film, d is the equivalent thickness to the oxygen molecules that oxidized, l is the equivalent thickness of aluminum that oxidized and a is the width of the bar. This method is not employed due to its difficulty.

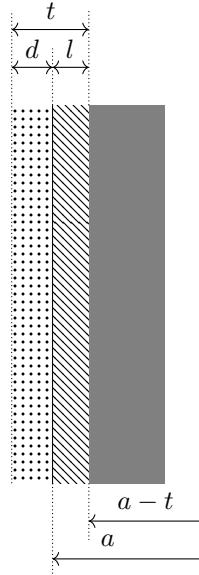


Figure 7: A microscopic view of the anodized Al bar

The method mentioned in section 2.2.1 allows only for calculating d and does not take into account that l also plays a role in t . In mathematical terms, section 2.2.1 assumes that $t = d$. However, it is impossible, with the methods described previously, to calculate the thickness of the anodized layer with the assumption that $t = d + l$.

2.3 Hazards and safety precautions

Sulfuric acid Sulfuric acid is highly corrosive and cause severe skin and eye damage. It is also highly damaging to the environment. It must be used with appropriate eye and skin protection, as well as have a neutralizer readily available in case of spillage. It is to be disposed according to the institution's regulations for disposing acid.

Sodium hydroxide A solution of $NaOH$ is severely damaging to skin and eyes. As with sulfuric acid, proper eye and skin protection must be worn. It is to be disposed among bases.

2.4 Experiment

Before the experiment solutions of sulfuric acid and sodium hydroxide were created, from a solution $2M$ sulfuric acid and powdered $NaOH$, respectively.

The experiment was done as described in section 2.1, with minor differences that are here given. The cleaning was done as described. Next, using a Vernier caliper the dimensions of the bar were measured, and after that the bar was weighed thrice. The anodizing process was done as described, however, instead of a graphite cathode, a cut open pencil was used, as shown in figure 8c. Moreover, due to the alligator clip used being made of iron, the aluminum bar was not completely dipped in the electrolyte solution, but was held inside it such that the alligator clip did not touch the solution. The bar was tempered. After that, it was weighed three times again. This was repeated for all bars of aluminum. All safety precautions given in section 2.3 were followed. Refer to figure 8 for images.

3 Data

3.1 Raw data

3.1.1 Solutions

Sulfuric acid The volume of $2M$ sulfuric acid was:

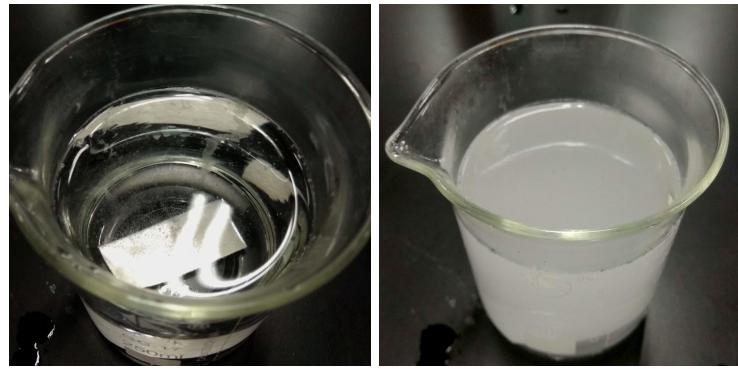
$$V(H_2SO_4)_{H_2SO_4(aq)} = (125 \pm 0.5)\text{ml}$$

The volume of water was:

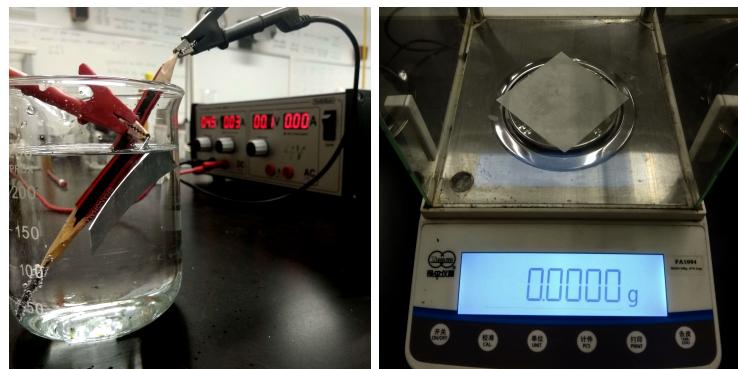
$$V(H_2O)_{H_2SO_4(aq)} = (125 \pm 0.5)\text{ml}$$

Sodium hydroxide The volume of water in the sodium hydroxide solution was:

$$V(H_2O)_{NaOH(aq)} = (250 \pm 0.5)\text{ml}$$



(a) Aluminum just dipped in a solution of $NaOH$ (b) Aluminum reacting in a solution of $NaOH$



(c) The anodizing of aluminum (d) The scale used

Figure 8: The experiment procedure

The mass was:

$$m(NaOH)_{NaOH(aq)} = (10.3535 \pm 0.0001)g$$

3.1.2 Experiment

The experiment was conducted at a constant, controlled:

$$t = 20^{\circ}C$$

The time of anodizing was:

$$t = 5\text{min}$$

The raw data is given in table 2, in the appendix.

Qualitatively, it was observed for bar 5 that successful anodizing occurred as, after tempering, it showed a noticeable chromatic change. This change is exemplified in figure 9. Note how the aluminum did not change its color at the edge where it was held by the clip and not dipped in the solution, at the bottom right corner.



Figure 9: A visible change in the color of the aluminum

$V(\pm 0.1)[V]$	5	8.5	12	15.5	18.5
$\Delta \bar{m}[\cdot 10^{-3}g]$	69.5	4.3	-7.4	10.5	1.4
$\sigma(\bar{m})[\cdot 10^{-3}g]$	122.1	8.8	8.4	11.0	6.1

Table 1: The relationship between the voltage and the change in mass

3.2 Data processing

3.2.1 Solutions

Sulfuric acid The concentration of sulfuric acid was calculated to be:

$$[H_2SO_4] = (49.041 \pm 0.398)M$$

Sodium hydroxide The concentration of sodium hydroxide was calculated to be:

$$[NaOH] = (1.04 \pm 0.00)M$$

3.2.2 Experiment

The data was processed and is given in table 3. σ denotes the standard deviation and μ denotes the propagated uncertainty.

A relationship was established between the voltage and the change in mass from before and after the anodizing and is given in table 1.

The lines of best fit was calculated using a *python (Python)* and *numpy (Numpy)* script. The three lines were calculated by taking the mean, maximum and minimum values into consideration. Refer to the script given in the appendix for more information. A graph is plotted and given in figure 10, as well

as the lines of best fit. The lines of fit are:

$$\Delta m(V)_{red} = 8.727 \cdot 10^{-5}V^3 - 3.425 \cdot 10^{-3}V^2 + 4.353 \cdot 10^{-2}V - 1.854 \cdot 10^{-1}$$

$$\Delta m(V)_{green} = -1.641 \cdot 10^{-4}V^3 + 6.684 \cdot 10^{-3}V^2 - 8.666 \cdot 10^{-2}V + 3.567 \cdot 10^{-1}$$

$$\Delta m(V)_{blue} = -4.155 \cdot 10^{-4}V^3 + 1.755 \cdot 10^{-2}V^2 - 2.376 \cdot 10^{-1}V + 1.036$$

It is obvious that the best line of fit is the green one.

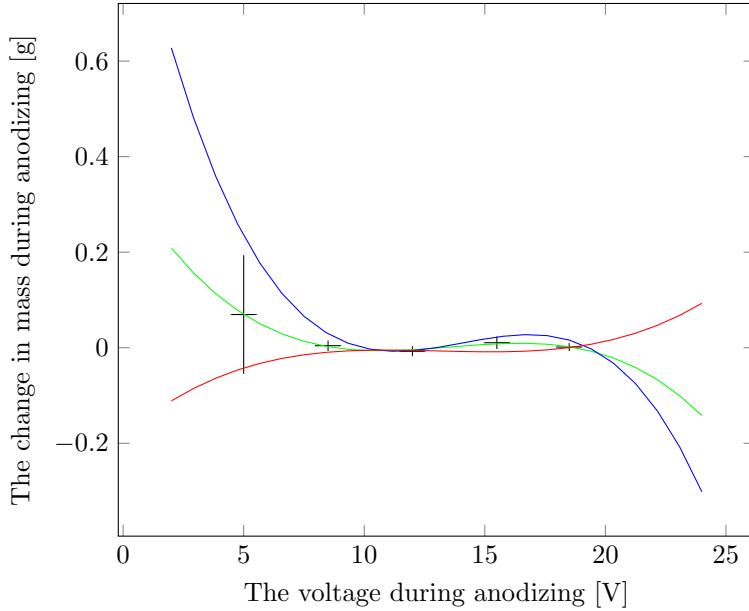


Figure 10: The relationship between the voltage and the change in mass

4 Analysis

The cubic relation indicates that it is impossible to accurately gauge the thickness of the oxide layer, due to issues presented in section 2.2.2.

The relationship also indicates that at one point the process of anodizing stops adding mass (attributed by the extra addition of oxygen), and rather starts decreasing the mass of the aluminum. The point at which this effect comes to be, for a constant time and temperature of anodizing, is given by the solutions to the given equation:

$$\begin{aligned}\Delta m'(V) &= 0 \\ -4.923 \cdot 10^{-4}V^2 + 13.368 \cdot 10^{-3}V - 8.666 \cdot 10^{-2} &= 0\end{aligned}$$

These solutions are:

$$V_1 = 16.460\text{V}$$

$$V_2 = 10.965\text{V}$$

At 5min as the time of anodizing, from $V = 0\text{V}$ to $V = 10.965\text{V}$, it can be assumed that the film produced is of the barrier type. From $V = 10.965\text{V}$ to $V = 16.460\text{V}$, it is likely that the pores start forming. From $V = 16.460\text{V}$ onward, it is most likely that the pores become deeper, decreasing the resistance, and therefore increasing the rate of anodizing.

5 Evaluation

The obvious issue with the data presented is that the uncertainties are quite high. The uncertainty of bar 1 is exceptionally high and to a great extent skews the data. This outlying uncertainty is most likely due to a systematic error. The most likely error is due to the measurement conducted after the anodizing of bar 2 as it shows an exceptional deviation from the rest. This systematic error is probably that after the anodizing and the tempering of the bar it was improperly dried and, therefore, during the weighing process, more mass was present. As such, it is possible that the data presented is somewhat invalid.

However, on the other hand, the remaining data has relatively low uncertainties and can be considered sufficiently precise. It is far more likely that the

6 Conclusion

The data does not prove the original hypothesis as the fit function is a cubic one:

$$\Delta m(V)_{green} = -1.641 \cdot 10^{-4}V^3 + 6.684 \cdot 10^{-3}V^2 - 8.666 \cdot 10^{-2}V + 3.567 \cdot 10^{-1}$$

However, this research indicates that the anodizing process does have 4 separate stages. This reaffirms the research done by Ono.

Overall, this research did not give exact quantitative trends due to the low precision, however it did show the general qualitative trend of the anodizing process, with its four distinct stages.

Works Cited

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Appendices

Fitting code

```
import numpy as np

V = np.array([5, 8.5, 12, 15.5, 18.5])
V_unc = np.array([0.5, 0.5, 0.5, 0.5, 0.5])

m = np.array([0.0695, 0.0043, -0.0074, 0.0105, 0.0014])
m_unc = np.array([0.1221, 0.0088, 0.0084, 0.011, 0.0061])

V_max = np.add(V, V_unc)
m_max = np.add(m, m_unc)

V_min = np.subtract(V, V_unc)
m_min = np.subtract(m, m_unc)

print(np.poly1d(np.polyfit(V, m, 3)))
print(np.poly1d(np.polyfit(V_max, m_max, 3)))
print(np.poly1d(np.polyfit(V_min, m_min, 3)))
```

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a (± 0.01) [mm]	49.80	47.22	46.80	49.70	49.82	49.80	49.80	49.82	49.68	49.62	49.58	49.58	49.0	49.62	49.68
b (± 0.01) [mm]	20.30	20.30	20.30	20.40	20.38	20.10	20.28	20.20	20.30	20.34	20.28	20.18	20.30	20.20	20.22
c (± 0.01) [mm]	0.72	0.50	0.58	0.60	0.62	0.88	0.58	0.55	0.62	0.48	0.64	0.60	0.50	0.54	0.42
m_{b1} (± 0.0001) [g]	1.1555	1.1482	1.2061	1.1753	1.1432	1.1660	1.1679	1.1599	1.1478	1.1292	1.1624	1.1090	1.1065	0.9998	0.9758
m_{b2} (± 0.0001) [g]	1.1651	1.1462	1.2064	1.1752	1.1478	1.1671	1.1697	1.1614	1.1492	1.1639	1.1446	1.1107	1.1294	1.0014	0.9759
m_{b3} (± 0.0001) [g]	1.1720	1.1919	1.1987	1.1746	1.1505	1.1673	1.1695	1.1614	1.1559	1.1643	1.1034	1.1104	1.0921	0.9996	0.9759
V (± 0.1) [V]	5.0	5.0	5.0	8.5	8.5	8.5	12	12	12	15.5	15.5	15.5	18.5	18.5	18.5
m_{a1} (± 0.0001) [g]	1.1851	1.1767	1.1875	1.1734	1.1555	1.1644	1.1691	1.1582	1.1401	1.1623	1.1431	1.1098	1.0910	0.9771	0.9794
m_{a2} (± 0.0001) [g]	1.1636	1.1768	1.1888	1.1750	1.1736	1.1657	1.1843	1.1588	1.1478	1.1986	1.1450	1.1115	1.1106	1.0306	0.9800
m_{a3} (± 0.0001) [g]	1.1876	1.7610	1.1887	1.1762	1.1558	1.1659	1.1540	1.1161	1.1478	1.1640	1.1467	1.1117	1.1098	1.0111	0.9794

Table 2: The raw data

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$V(\pm 0.1)$ [V]			5		8.5			12			15.5			18.5	
\bar{m}_b [g]	1.1642	1.1621	1.2037	1.1472	1.1472	1.1668	1.1690	1.1609	1.1510	1.1525	1.1368	1.1100	1.1093	1.0003	0.9759
$\sigma(m_b)$ [g]	0.0083	0.0258	0.0044	0.0004	0.0037	0.0007	0.0010	0.0009	0.0043	0.0202	0.0303	0.0009	0.0188	0.0010	0.0001
\bar{m}_a [g]	1.1788	1.3715	1.1883	1.1749	1.1616	1.1653	1.1691	1.1444	1.1452	1.1750	1.1449	1.1110	1.1038	1.0063	0.9796
$\sigma(m_a)$ [g]	0.0132	0.3373	0.0007	0.0014	0.0104	0.0008	0.0152	0.0245	0.0044	0.0205	0.0018	0.0010	0.0111	0.0271	0.0003
$\Delta \bar{m}[\cdot 10^{-3}\text{g}]$	14.6	209.4	-15.4	-0.1	14.4	-1.5	0.1	-16.5	-5.8	22.5	8.1	1.0	-5.5	6.0	3.7
$\mu(\Delta \bar{m})[\cdot 10^{-3}\text{g}]$	21.5	36.31	5.1	1.8	14.1	1.5	16.2	25.4	8.7	40.7	32.1	1.9	29.9	28.1	0.4
$\Delta \bar{m}[\cdot 10^{-3}\text{g}]$			69.5		4.3			-7.4			10.5			1.4	
$\sigma(\Delta \bar{m})[\cdot 10^{-3}\text{g}]$			122.1		8.8			8.4			11.0			6.1	

Table 3: The processed data