Revisiting Millikan's Oil-Drop Experiment

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Most freshman chemistry courses and texts describe the classic experiments that led to the development of atomic theory. Among the experiments that are usually covered is Millikan's oil-drop experiment. The usual discussion explains that the oil droplets must pick up a fixed whole number of electrons as they are sprayed into a chamber. Every drop observed will have a charge that is a whole number times the charge of one electron. The chamber has plates at the top and bottom that can be charged with a voltage from a battery. The charged drops are attracted vertically by the positive plate at the top and simultaneously attracted to the bottom of the cell by the force of gravity.

Knowledge of the density of the oil, the viscosity of air, and a measurement of the time for a droplet to fall between two reference points when no voltage is applied is sufficient to determine the mass of the droplet and the gravitational force pulling it downward. If the voltage on the plates is suddenly turned on, an individual droplet can be timed as it rises between the same two reference points. These data are sufficient to determine the total charge on the droplet. By using nonvolatile gas-engine oil, it is possible to measure the charge on the same droplet over long periods of time as it picked up varying numbers of charges. In fact, Millikan *(1)* observed one single droplet for about four and one-half hours! This is why the oil-drop experiment succeeded when the same experiment with other fluids failed to give accurate results.

Usually, texts explain that the elementary charge is the common value that can be divided out of (factored from) each of the measured charges. This is certainly true. However, imagine trying to actually determine the common factor in the numbers: 60.85, 41.28, 69.52, 58.66, 52.14, 110.82, and 23.90. The common factor, 2.173, is not obvious. Now imagine trying to find a common factor in perhaps a hundred such numbers. Millikan did not "factor" the charges but, in fact, he determined the smallest difference observed between the measured charges and used that to determine the elementary charge of the "ions" picked up by the oil droplets.

The primary article by R. A. Millikan published in 1911*(1)* also never mentioned an electron! He spoke of the droplets picking up ions, both positive and negative. In fact, in his earlier report on single drops *(2)* the water and alcohol droplets all possessed positive charges. He did assume that the positive and negative charges would be exactly the same and that no "fractional" charges existed. Hendricks, Lackner, and Shaw made very careful measurements on 5,974,941 silicon oil drops searching for $(1/3)e$ and $(2/3)e$ (fractional) charges on quarks and concluded that the incidence must be less than one per 2.14×10^{20} nucleons *(3).* Several others *(4–6)* have addressed misunderstandings and discrepancies concerning the details of the Millikan's oil-drop experiment and textbook descriptions of the work.

Millikan's 1911 article is not only a classic. It is filled with image-provoking language. For example, consider the following fragment "…and supported by evidence from many sources that all electrical charges, however produced, are exact multiples of one definite, elementary, electrical charge, or in other words, that an electrical charge instead of being spread uniformly over the charged surface has a definite granular structure, consisting, in fact, of an exact number of specks, or atoms of electricity, all precisely alike, peppered over the surface of the charged body." This article is filled with many other examples of equally precise and colorful language *(4).* The article also clearly reviews all prior work and explains why Millikan's work is more accurate than the prior works, including a prior measurement by Millikan himself *(2).*

Millikan obtained accurate results because he changed from the use of water, alcohol, and other volatile liquids used in earlier works to nonvolatile oil, glycerin, and mercury. The works of other authors measured an average property of "swarms" of droplets and this work was able to make measurements on a single droplet over several hours without significant evaporation. However, the experiment was not simply determining the voltage needed to freeze the motion of a droplet and equating the electrostatic force upward to the gravitational force downward as explained in some texts. The data in this article (ref *1*, Table I) were obtained by Millikan while watching a single drop as it moved upward and downward under the influence of the electric and gravitational fields in the observation range of the telescope. He observed the droplet as it picked up or lost charges during four and a half hours of observation. The charge on the droplet was actually determined by measuring the rate of movement (upward or downward) when the forces were unequal. The data from this single droplet were considered by Millikan to be the most accurate but the article contains 10 other tables with 61 other measurements on droplets containing from 1 to 124 electrons with the uncorrected fundamental charge estimates ranging from 5.033×10^{-10} esu to 5.490×10^{-10} esu (where esu is electrostatic unit). When Millikan made the Stokes' law correction all these droplets led to essentially the same value for the fundamental charge.

The measurements were far more complex than the description we see in textbooks. The droplets were moving through the air in the chamber. The temperature had to be carefully controlled and the opening had to be closed so that there would be no turbulence in the air surrounding the drop. The voltage had to be controlled carefully and accurately known. Likewise the movement of the droplet between the reference points had to be carefully timed. The movement of the droplet was slowed because of the viscosity of the air, and the mass was corrected for the buoyancy of the air as well. The equations are complex and the simple Stokes' law

Table 1. Millikan's Data[a] Analyzed by Microsoft Excel

1	2	3	4	5	6	7	8	9
Observation	Total Charge/ (10^{10} esu)	Sorted/ (10^{10} esu)	Differences/ (10^{10} esu)	Single Charge/ (10^{10} esu)	Number of Charges	Rounded Whole Number of Charges	Difference Squared	Variance about Regression[b]
1	34.47	83.22	4.88	4.88	17.03985	17	0.0015879	0.01184
2	39.45	78.34	9.69	4.84	16.04064	16	0.0016513	
3	44.42	68.65	0.00	4.85	14.05654	14	0.0031973	
4	49.41	68.65	0.00	4.97	14.05654	14	0.0031973	
5	39.45	68.65	4.97	4.56	14.05654	14	0.0031973	
6	59.12	63.68	0.00	5.20	13.0389	13	0.0015135	
7	44.42	63.68	4.56	4.51	13.0389	13	0.0015135	
8	49.41	59.12	0.00	4.99	12.10521	12	0.0110699	
9	53.92	59.12	0.00	4.97	12.10521	12	0.0110699	
10	49.41	59.12	0.00	4.91	12.10521	12	0.0110699	
11	44.42	59.12	5.20	4.85	12.10521	12	0.0110699	
12	59.12	53.92	0.00	5.02	11.04048	11	0.0016385	
13	53.92	53.92	0.00	4.94	11.04048	11	0.0016385	
14	68.65	53.92	4.51	–	11.04048	11	0.0016385	
15	83.22	49.41	0.00	4.884	10.11703	10	0.0136952	
16	78.34	49.41	0.00	–	10.11703	10	0.0136952	
17	68.65	49.41	4.99	–	10.11703	10	0.0136952	
18	63.68	44.42	0.00	–	9.095291	9	0.0090803	
19	59.12	44.42	0.00	–	9.095291	9	0.0090803	
20	63.68	44.42	4.97	–	9.095291	9	0.0090803	
21	59.12	39.45	0.00	–	8.07765	8	0.0060295	
22	68.65	39.45	0.07	–	8.07765	8	0.0060295	
23	53.92	39.38	4.91	–	8.063317	8	0.004009	
24	24.60	34.47	0.00	–	7.057962	7	0.0033596	
25	34.47	34.47	0.00	–	7.057962	7	0.0033596	
26	39.38	34.47	4.85	–	7.057962	7	0.0033596	
27	34.47	29.62	0.00	–	6.064892	6	0.004211	
28	29.62	29.62	0.00	–	6.064892	6	0.004211	
29	24.60	29.62	5.02	–	6.064892	6	0.004211	
30	24.60	24.60	0.00	–	5.037014	5	0.00137	
31	24.60	24.60	0.00	–	5.037014	5	0.00137	
32	19.66	24.60	0.00	–	5.037014	5	0.00137	
33	29.62	24.60	0.00	–	5.037014	5	0.00137	
34	24.60	24.60	0.00	–	5.037014	5	0.00137	
35	19.66	24.60	4.94	–	5.037014	5	0.00137	
36	29.62	19.66	0.00	–	4.025516	4	0.0006511	
37	24.60	19.66	–	–	4.025516	4	0.0006511	

[a]Millikan data from ref *1*, Table I, pp 356–358.

[b]The variance about regression is calculated similar to the standard deviation except the deviations are from the regression line instead of deviations from the mean.

approximation for the viscosity used by other authors was found to be invalid. Millikan determined the exact relationship for the deviation from Stokes' law and applied this correction to his data. This was an easily understood experiment but certainly not a simple one.

Experimental

The charges of the oil drop for the 37 measurements in Table I of Millikan's work *(1)* are shown in the second column of Table 1. The charges are sorted into descending order in column 3. Column 4 shows the differences between adjacent rows and represents the charge difference between two experiments. Note that the difference between row 2 and row 3 after sorting (9.69 second row of column 4) clearly represents two charges. These two charges are recorded as 4.84 and 4.85 in column 5. The same difference (about 5×10^{-10} esu) is found to appear frequently. Column 5 contains all the unique differences with duplications and zeros removed. The average of the unique charges (4.884) is the final entry (row 15) in column 5. This is a first estimate of the elementary charge (charge of the electron.) Column 6 represents the calculated number of elementary charges using the average value at the end of column 5. Column 7 rounds the number of electrons on the drop to the nearest whole number. Column 8 is the square of the difference between the number of charges calculated and the rounded integer (column 6 and column 7). The single entry in column 9 is the variance about regression between the calculated number of charges and the rounded integers. Comparing the individual values in column 8 to the variance about regression in column 9 could justify throwing out outliers in the data set. All the values in Millikan's data are valid.

The best value for the elementary charge is obtained by plotting (Figure 1) the charge observed on the oil drops (column 3, y axis) against the number of charges (column 7, x axis). The slope of the best-fit linear regression line is the measured value of the elementary charge. The average value (last value in column 5) resulted in a variance about regression of 0.01184. When Millikan's value, 4.917, is entered as the average in column 5, the variance about regression is 0.005632. Entering the 4.9147 value from the linear regression line leads to a variance about regression of 0.005429. The regression-line value improves the variance about regression only slightly from Millikan's value. All three values predict the same integers for the number of electrons on each of the drops.

The best value using modern spreadsheet analysis and linear regression was 4.915×10^{-10} esu. This compares to 4.917×10^{-10} esu determined by Millikan using the raw data in Table I of ref *1*. It should be noted that Millikan corrected these data by about 0.5% for the viscosity and buoyancy of air. His final value was 4.891×10^{-10} esu. Two years later, Millikan *(7)* repeated the experiment with a better apparatus and other refinements and obtained $4.774 \pm 0.009 \times 10^{-10}$ esu for the elementary charge and $6.062 \pm 0.012 \times 10^{23}$ for Avogadro's number. The accepted value for the elementary charge is 4.80298×10^{-10} esu, an error of only 1.47% for work completed in 1910! His 1913 value was in error by only 0.6%. As expected, Millikan's linear regression by hand and published in 1911 was almost identical to the value determined by linear regression analysis using Microsoft Excel. The value of $R^2 = 0.9999$ indicates almost no deviation from linearity and validates the assumption of a single elementary charge present in varying numbers on all the oil drops.

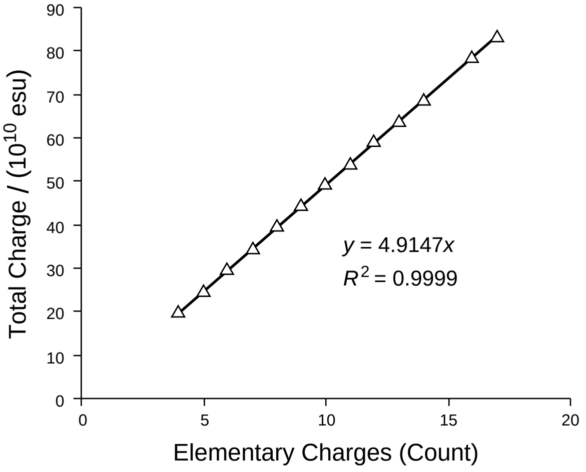

Figure 1. Excel plot of Millikan's data in Table 1.

Conclusion

Millikan's article not only represents a classic experiment, it is filled with colorful descriptions that show the state of understanding of fundamental physical principles of the era. The data were not only good for 1911 but also stand the test of time. His careful analysis of the data by hand is confirmed with a modern computer using Microsoft Excel. This exercise could be used as a laboratory experiment or classroom demonstration in physical chemistry to illustrate the use of spreadsheet analysis while reviewing a classical work in the development of atomic theory.

In a laboratory exercise for physical chemistry, the students would be given Millikan's original raw data, a description of the apparatus, and the relevant equations (see Table 2). The students would use Microsoft Excel to analyze the data and determine the fundamental charge, e. Millikan's data from Tables IV to XII in ref *1* measure the fundamental charge for droplets of varying radii. Groups of students could be assigned different size drops and asked to calculate the value of e using Stokes' law and discover that this law fails for small droplets. They could then be asked to extrapolate to zero or infinite drop size to obtain a more accurate result and see whether they can get a value closer to the currently accepted value. They could also follow the procedure outlined in Table 2 to correct for Stokes' law deviations as was

Table 2. Equations and Analysis Used by Millikan *(1)*

Equation Number	Equation	Definition of Terms	Description
3	$v_1 = 2ga^2/9\mu(\sigma - \rho)$	v_1 = velocity of fall (gravity) g = acceleration of gravity a = radius of drop μ = coefficient of viscosity σ = density of drop ρ = density of medium	This equation was used to get an initial value for the radius of drops assuming Stokes' law.
4	$e_n = (4/3)\pi(9\mu/2)^{3/2}\{1/[g(\sigma - \rho)]\}^{1/2} \bullet [(v_1 + v_2)v_1^{1/2}]/E$	e_n = charge on droplet v_2 = velocity of rise (electric field) E = electric field strength	This equation was used to calculate the charges listed in Tables I–XII in Millikan's article without correcting for failure of Stokes' law as low drop radius.
8	$v_1 = [2ga^2(\sigma - \rho)]/\{9\mu[1 + A(\ell/a)]\}$	A = arbitrary constant ℓ = characteristic of the medium	This equation was used to calculate the radius of the drop once a value of $A\ell$ is determined from the plot of eq 9. This correct Stokes' law for small drops. If ℓ is taken as the mean free path in air, Millikan obtained $A = 0.817$.
9	$e^{2/3}[1 + A\ell(1/a)] = e_n^{2/3}$	e = absolute charge e_n = charge calculated from eq 4	This equation was used to determine $A\ell$ from the slope of the line obtained by plotting $e_n^{2/3}$(y axis) against $1/a$ (x axis). The values of a are initially determined from eq 3 for the plot. This equation also calculates the absolute charge once the radius of the drop is calculated using eq 8. This equation gave 4.901×10^{-10} esu for drops that did not follow Stokes' law (compare to 4.891×10^{-10} esu for drops that did follow Stokes' law).

done by Millikan. Alternately, the lab instructor could discuss the corrections to Stokes' law (surface slip and Basset's correction) that were used by Millikan. This experiment would be an excellent opportunity to discuss the differences between random and systematic errors as student groups compare their results. Such an experiment would combine an excellent review of an experiment of historical significance and the power of modern spreadsheet analysis. While the calculations are extremely tedious if done by hand, even the Stokes' law corrections would be easily accomplished using Excel or other spreadsheet programs.

Millikan's article is recommended reading for all who have an appreciation for the history of chemistry and physics and those fortunate enough to teach atomic theory to the next generations of students. This article truly is a timeless work.

[W]Supplemental Material

The Excel spreadsheet of the data is available in this issue of *JCE Online*.

Literature Cited

1. Millikan, R. A. *Phys. Rev.* **1911,** 32*,* 349–397.
2. Millikan, R. A. *Phys. Rev.* **1909,** 29*,* 560–561.
3. Hendricks, C. D.; Lackner, K. S.; Shaw, G. L. *Phys. Rev. D* **1996,** *53,* 6017–6032.
4. Castellion, M. E.; Bailar, J. C., Jr. *J. Chem. Educ*. **1982,** *11,* 970.
5. Harris, S. P. *J. Chem. Educ.* **1984,** 61*,* 89–90.
6. Brower, H. *J. Chem. Educ.* **1985,** 62*,* 455.
7. Millikan, R. A. *Phys. Rev.* **1913,** *2,* 109–143.