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Absolute Determination of the Electrochemical Equivalent and the Atomic Weight of Zinc II. Final Determination

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A new, successful approach to the determination of atomic weights of suitable elements has been demonstrated in this research. An absolute constant-current coulometric method was employed for the determination of the electrochemical equivalent and the atomic weight of zinc. The effects of possible sources of systematic error were investigated and appropriate corrections applied. The newly determined values of the two constants are 0.3387958 mg C^{-1} and 65.3771 respectively. The uncertainty in the atomic weight of zinc was reduced by more than an order of magnitude. The publication of partial data resulted in the revision of the value of the atomic weight of zinc by the International Union of Pure and Applied Chemistry.

Key words: Atomic weight; coulometry; electrochemical equivalent; zinc atomic weight.

1. Introduction

The nature of the problem of determining the electrochemical equivalent and the atomic weight of zinc and the general outline of the approach taken to achieve the objective have been reported in Part I of this publication [1].[1] The present paper includes the final measurements performed under what were considered to be optimum conditions as well as the conclusions drawn from these results.

In brief the research entailed accurate determination of the electrochemical equivalent of zinc by oxidizing zinc from the Zn^0 to the Zn^{++} state and measuring the electrical charge associated with a given mass change of the zinc amalgam anode. The number of moles of zinc dissolved was computed from the magnitudes of the electrolysis current and the time, employing Faraday's law. Partial results of such an approach have already been published [16].

Perhaps the most significant part of any determination of a constant of nature is in assessing the inaccuracy of the determined value. In the case of ordinary analytical determinations of major constitutents the accuracy of the analysis at a 0.1 percent level can be proven rather readily through the use of chemical standards. Clearly, for the determination of a physical constant no such standard exists. As a result one must resort to some other means of testing the accuracy. One method of testing the accuracy of the determined physical constant is to vary the experimental parameters over a wide range, preferably more than one order of magnitude, and determine whether or not this variation of parameters has any effect on the determined value. In the case of the determination of the electrochemical equivalent of Zn the following parameters were varied and their effects were investigated: the absolute value of the current, the mass of dissolved zinc, the charge passed through the coulometer, the area of the electrode, the current density, the electrolysis time, the origin of the material, the purity of the material, the nature of the pretreatment of the

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[1] Figures in brackets indicate the literature references at the end of this paper.

material (such as vacuum fusion or fusion in air). Variation of additional parameters, such as experiment sequence, arose naturally out of unavoidable lapses of time between sequential operations.

1.1. Materials

To evaluate the magnitude of the effects of the material source, its purity and treatment on the electrochemical equivalent of zinc, determined by the anodic dissolution of zinc metal from the saturated zinc amalgam, a number of materials from different sources were used. The following identifies each material by its code as used in the data table and, on the basis of the available data, gives as complete a description of each as possible.

High purity zinc (*code 4*). This is a high purity standard research material which is issued by the National Bureau of Standards as SRM 682. The material was prepared from a special lot of high-grade electrolytic zinc, purified by vacuum distillation, zone-refining and degasification.

The overall assessment of impurities (NBS certificate) indicates that this material is 99.9999 percent Zn. This clearly does not apply to the surface of the material, since the exposure of Zn to air leads immediately to oxide formation. This aspect will be discussed below.

In preparation of the electrodes the material was cut on a mill using a tungsten carbide tool.

Intermediate purity zinc (*code 6*). The National Bureau of Standards issues this material as SRM 683. This material was prepared from a high grade electrolytic zinc in a manner similar to that for high purity zinc (code 4).

The certificate of analysis of this material is available from the National Bureau of Standards. The sum of all other elements which were detected is less than 30 ppm. On the basis of impurity analyses the purity of this material is 99.997 percent Zn. The handling of the material and electrode preparation were the same as for material code 4.

Intermediate purity zinc (*code 105*). This is essentially the same material as material code 6 except that it is in pellet form (SRM 728). It was fused in Vycor[2] tubes into rod shaped electrodes. Fusion was conducted in vacuo. Estimated starting purity of the material on the basis of impurity analyses is 99.997 percent.

Intermediate purity zinc (*code 205*). With the exception of fusion, which was conducted in air, this material is the same as code 105 material.

Melting point standard zinc (*code 3*). This material was produced by the New Jersey Zinc Company, Palmerton, Pennsylvania and issued by the National Bureau of Standards as SRM 43g. It is in the form of rods which were cut directly into appropriate size segments for electrode fabrication.

Melting point standard zinc (*code 107*). This is one of the first zinc samples issued by NBS. The date of issue of this material is unspecified. The certificate is signed by the late NBS Director S. W. Stratton, which would date it back to 1923 or before. It was vacuum fused prior to electrode fabrication.

Commercial zinc (*code 2*). On the basis of impurity data for this material (Fisher Scientific Certified ACS grade zinc lot No. 781161) it is estimated to be 99.99 percent pure. The reported impurity content includes 0.003 percent Fe and 0.005 percent Pb. The rod-shaped material was cut and fabricated directly into electrodes.

Commercial zinc (*code 102*). This is the same material as described under code 2 but melted under vacuum for degassing and then used in electrode fabrication.

Commercial zinc (*code 1*). This material is sold by Baker and Adamson in the shape of cylindrical rods. The assay indicated by the distributor is 99.9 percent. The material contains less than 0.01 percent Fe and less than 0.01 percent Pb. It was also used in its original form for fabrication of electrodes.

Commercial zinc (*code 101*). This is the same material as described under code 1 but degassed under vacuum, similarly to material 102.

Zincs from other worldwide sources. A word of caution seems appropriate here. The origin of manufactured zinc does not necessarily prove that local zinc ores were exclusively used in each case. However, sampling from several worldwide sources is definitely shown. Materials coded 109, 110, and 111 are commercial grade zincs produced in Peru, Yugoslavia, and Italy respectively. They were also vacuum fused. Material 108 was obtained from the Electrolytic Zinc Company of Australasia Ltd. The manufacturer's evaluation of its purity is 99.995 percent. It was also vacuum fused.

Chemicals. All the reagents used were of the highest commercially obtainable purity. The mercury used in all experiments was a triple distilled material produced by the Bethlehem Apparatus Company, Inc. On the basis of the weighable residue test it contains impurities at the 1 part in 10 million (0.00001 percent by weight) level.

1.2. Procedure

The fabricated and amalgamated electrodes were washed in 0.1 M NH_4Cl, hot distilled water, air dried and weighed on a 20-g capacity Mettler microbalance. As the anode was readied for the experiment, the coulometer was filled with 25 wt percent $NH_4Cl + 3$ molal $ZnCl_2$ and deaerated by purging with water pumped nitrogen. Purging was performed by lowering the polyethylene tube, mounted in the cell top, into the electrolyte and permitting nitrogen to flow through it.

Prior to delivery into the coulometer the electrolyte was stored in a scrubbing tower over saturated zinc amalgam. Nitrogen, presaturated with water vapor by passage through the solution of the same composition

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[2] A commercial product and company names are identified in this paper, in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that such a product is necessarily the best available for the purpose.

as the electrolyte, was continuously flowing through the stock electrolyte solution, stored in the tower. Thus, even before delivery into the coulometer the electrolyte was deaerated. The storage of the electrolyte over the saturated zinc amalgam was chosen to remove any impurities which are more easily reducible than zinc.[3]

After the Zn(Hg) anode had been weighed accurately it was suspended in the coulometer on the platinum support wire. The wire, in turn, was connected to the anode lead of the coulometric circuit. The upper surface of the suspended electrode, where epoxy resin was used to seal the suspension lead, was always above the solution-atmosphere interface. The area of the electrode cited in the data tables is that part of the apparent geometric area of the anode which was submerged into the electrolyte. Following the placement of the electrode into the coulometer the cell top was replaced, the polyethylene tube carrying the nitrogen pulled up so that the nitrogen could flow over the solution and the coulometer-timer switch thrown into the "on" position. After the expiration of the desired time interval the coulometer switch was turned off, the electrode removed, washed and dried and reweighed by the substitution method, using calibrated standard weights. The mass difference was always compensated by the standard weights within 10 mg. Differences smaller than 10 mg were observed on the optical scale of the balance. On the basis of the densities of air, Zn, and the materials from which the standard weights are fabricated (1–20 g stainless steel; 50–500 mg Ta; 1–20 mg Al) corrections were applied to the observed weight loss of the anode, converting it to the mass in vacuum. The amount of charge passed through the coulometer was computed from the values of the time interval of electrolysis (measured with an accuracy of 10 μs or 0.0001 percent whichever is greater) and the magnitude of the current, based on the values of the standard resistor employed and the emf of the saturated Weston cell.

2. Measurements

Nine sets of measurements were performed; the data for all nine sets, arranged according to the ordinal number of the experiment and the set number, are given in table 1. The data assembled in this table includes only the measurments on degassed materials. Column 4 of table 1 gives only an approximate current value and column 5 an approximate electrolysis time for correlation purposes. Accurately measured values of these parameters for each experiment were used in the computation of the charge, shown in column 7 of the same table. The electrode area (column 6) is an estimate of the apparent geometric area of the anode, immersed in the electrolyte during the electrolysis. The mass change of Zn(Hg) anodes (mass in vacuum) is presented in column 8.

The experiments with unprocessed material (no vacuum fusion) and material fused in air were intentionally incorporated and performed within the same experimental scheme as the experiments with degassed materials to make them equivalent, as much as possible. The data from these experiments, with materials containing dissolved gases, however, were extracted along with their ordinal numbers, compiled into a separate table (table 2) and processed as a separate entity, for reasons which will be discussed later.

Out of 150 final experiments, four (experiment numbers 58, 63, 99, 104) differed so far from the mean value that they were excluded from the data treatment as outliers according to Grubbs [2]. The choice of experiments was such as to shed some light on the possible errors which could be encountered. First of all, experiments designated as Set 8 (experiment numbers 139–150) were conducted to investigate the effect of material origin on the electrochemical equivalent of zinc. Secondly, six different levels of electrolysis current were used (including zero current as one level) covering six orders of magnitude from 0 to 1.0 A, although for the final calculation of the electrochemical equivalent, only three current levels are used in essence, viz., 0.1, 0.5, and 1.0 A. The electrolysis times required to improve precision of data at lower current levels are obviously prohibitive, and consequently only a few data points were obtained in this region. Thirdly, the electrolysis time ranged from 0 to 79000 s, again covering a range of six orders of magnitude. The electrode area was varied from 0.5 to 10 cm^2. The charge, passed through the cell, ranged from 0 to 29500 C. The mass of dissolved zinc ranged from a few micrograms to 10 g—a six orders of magnitude range. Material purity ranged from 99.9999 to 99.9 percent Zn. Finally, degassed materials, unprocessed materials, and air-fused materials were incorporated into the experimental scheme.

3. Treatment of Data

The simplest way of treating the electrochemical equivalent data is to assume a linear equation of the following form

$$W = kQ \tag{1}$$

where W is the mass difference in the electrode before and after electrolysis (mg) and Q is the charge passed through the coulometer (coulombs). Clearly the slope of such a plot, k, is the electrochemical equivalent in mg C^{-1}.

W and Q are measured experimental quantities which determine the value of k. The method of least squares was employed, using the OMNITAB FIT

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[3] It is quite clear that if Cu^{++}, for example, were present in the electrolyte it would spontaneously undergo the following reaction in the coulometer

$$\mathrm{Zn(Hg)} + \mathrm{Cu}^{++} \rightarrow \mathrm{Zn}^{++} + \mathrm{Cu\,(Hg)}$$

thus causing an error in the mass of Zn(Hg) anode equal to

$$\text{wt percent Cu} \times \frac{\text{At wt Zn}}{\text{At wt Cu}}.$$

The removal of such impurities from the electrolyte prior to the delivery into the coulometer, by the sacrificial use of Zn (Hg), eliminates this source of error.

TABLE 1. *Final data on the determination of the electrochemical equivalent of zinc with degassed materials*

Exp. No.	Set No.	Material code	Current A	Electrolysis time, s	Electrode area, cm^2	Charge C	Mass of dissolved Zn, g
16	0	4	0.5	1160	1.5	590.382	0.200030
17	0	4	.5	2320	1.5	1180.743	.400023
18	0	105	.5	5800	4	2951.781	1.000048
20	0	101	.5	5800	7	2951.830	1.000196
21	0	101	0.5	5800	5	2951.800	1.000213
22	0	101	.5	290	5	147.615	0.050067
28	0	105	.5	116	5	59.066	.020087
30	0	4	.5	116	0.5	59.082	.019969
32	0	105	0.5	580	5	295.179	0.099982
36	1	4	.5	580	2	295.200	.100087
37	1	4	.5	580	1	295.195	.100098
38	1	4	.5	580	2	295.134	.100045
39	1	4	0.5	1160	2	590.303	0.200089
40	1	4	.5	58	2	29.564	.010059
41	1	4	.5	5800	2	2951.845	1.000064
42	1	4	.5	6	2	2.952	0.000942
43	1	6	0.5	5800	2	2951.845	1.000193
44	1	9	.5	29	2	14.784	0.005030
45	1	4	.5	2900	2	1475.913	.500031
46	1	4	.5	12	2	5.898	.001922
47	1	6	0.5	4060	2	2066.302	0.700096
48	1	4	.5	11600	2	5903.599	2.000038
49	1	4	.5	1450	2	738.010	0.250126
50	1	6	.5	290	2	147.564	.050010
51	1	4	0.5	29	2	14.790	0.005041
52	1	4	.5	29	2	14.830	.005026
53	2	4	1.0	10	2	10.308	.003523
54	2	4	1.0	2900	2	2951.791	1.000068
55	2	6	1.0	7250	2	7379.408	2.500127
56	2	4	1.0	290	2	295.143	0.099934
57	2	4	1.0	290	2	296.109	.100347
59	2	6	1.0	3	2	3.054	.001095
62	3	6	1.0	11600	4	11806.958	4.000194
64	3	4	1.0	2900	2	2951.767	0.999974
65	3	102	1.0	2900	4	2951.798	1.000076
66	3	102	1.0	5800	7	5903.484	1.999961
67	3	102	1.0	10150	7	10331.044	3.500364
68	3	107	1.0	5800	7	5903.474	2.000184
69	3	107	1.0	14500	7	14758.654	5.000353
70	3	107	1.0	30	3	30.539	0.010552
71	3	101	1.0	5800	7	5903.570	2.000219
72	3	4	1.0	30	2	30.513	0.010325
73	3	107	1.0	31	3	31.403	.010688
74	3	107	1.0	30	5	30.352	0.010301
75	3	4	1.0	30	2	30.759	.010296
76	3	101	1.0	17400	8	17710.343	6.000210
77	3	4	1.0	290	2	295.162	0.100018
78	3	107	1.0	290	5	295.213	0.100054
79	3	101	1.0	1450	8	1475.930	.500107
80	3	4	1.0	145	2	147.586	.050021
81	4	101	0.1	5800	5	590.324	.200049
82	4	107	0.1	5800	7	590.331	0.200039
83	4	4	.1	2900	1.5	295.162	.099965
84	4	101	.1	*1800	5	0.050	.000078
85	4	107	.1	58000	7	5900.507	1.998978

TABLE 1. *Final data on the determination of the electrochemical equivalent of zinc with degassed materials*—Continued

Exp. No.	Set No.	Material code	Current A	Electrolysis time, s	Electrode area, cm^2	Charge C	Mass of dissolved Zn, g
86	4	4	0.1	5800	1	592.898	0.200861
87	4	101	.1	18700	5	1903.308	.644818
88	4	4	.1	100	1	10.201	.003482
89	4	6	.1	35000	5	3541.969	1.200063
90	4	101	0.1	*3600	5	1.017	0.000393
91	4	4	.1	*4500	1	1.026	.000293
92	4	101	.1	*16900	5	1.022	.000387
93	4	4	.1	*69300	1	1.023	.000373
94	4	4	0.1	*3600	1	1.013	0.000315
95	4	101	.1	*6300	5	1.026	.000353
96	4	101	.1	*52200	5	1.023	.000432
97	4	4	.1	*1800	5	1.022	.000411
98	5	101	0.0	7200	6	0.0	0.000036
100	5	4	.0	1800	2	.0	.000028
101	5	107	.0	3900	6	.0	.000015
102	5	101	.0	1800	6	.0	.000016
103	5	4	0.0	19800	9	0.0	0.000118
105	5	107	.0	2700	6	.0	.000135
106	5	101	.0	5700	6	.0	.000153
107	5	4	.0	12000	9	.0	.000089
108	5	4	0.0	2700	9	0.0	0.000054
109	5	4	.0	45900	1	.0	.000092
110	5	4	.0	1800	7	.0	.000044
111	5	2	.0	4800	1	.0	.000027
112	5	4	0.0	4500	10	0.0	0.000079
113	5	4	.0	19500	10	.0	.000113
114	5	4	.0	12600	10	.0	.000067
115	5	4	.0	18000	2	.0	.000173
116	5	4	0.0	54000	9	0.0	0.000062
117	5	4	.0	79200	9	.0	.000157
118	5	4	.0	0	5	.0	.000038
119	5	4	.0	0	5	.0	.000107
120	5	4	0.0	0	2	0.0	0.000019
121	5	4	.0	0	2	.0	.000004
122	5	101	.0	0	7	.0	.000102
123	5	101	.0	0	7	.0	.000079
124	5	6	0.0	0	5	0.0	0.000058
125	5	2	.0	0	4	.0	.000017
126	6	4	.01	1000	9	10.1775	.003551
127	6	4	.01	1000	2	10.1776	.003558
128	6	107	0.01	5000	6	50.8878	0.017314
129	6	101	.01	*4500	5	40.7102	.013873
130	6	4	.01	6500	2	66.1539	.022518
131	6	4	.01	43764	9	445.4066	.150919
132	6	107	0.01	1650	5	16.7932	0.005742
133	6	107	.01	4500	8	45.7987	.015604
134	6	107	.01	13500	5	137.3959	.046566
135	7	101	.0001	8430	8	0.8430	.000271
136	7	4	0.0001	19500	2	1.9449	0.000700
137	7	101	.0001	14000	10	1.4000	.000555
138	7	4	.0001	60100	10	6.0100	.002269
139	8	4	.5	11600	10	5903.631	2.000151
140	8	4	0.5	23200	10	11807.189	4.000181
141	8	4	.5	29000	10	14758.990	5.000361
142	8	108	.5	53200	10	27075.126	9.173009
143	8	108	.5	11600	10	5903.587	2.000192

TABLE 1. *Final data on the determination of the electrochemical equivalent of zinc with degassed materials*—Continued

Exp. No.	Set No.	Material code	Current A	Electrolysis time, s	Electrode area, cm^2	Charge C	Mass of dissolved Zn, g
144	8	109	0.5	11600	8	5903.596	2.000202
145	8	109	.5	11600	8	5903.590	2.000132
146	8	110	.5	11600	8	5903.631	2.000135
147	8	110	.5	11600	8	5903.595	2.000092
148	8	111	0.5	11600	6	5903.615	2.000178
149	8	111	.5	11600	6	5903.658	2.000189
150	8	4	.5	58000	10	29517.796	10.000693

*In these experiments electrolysis time is the total time elapsed between the immersion of the electrode into electrolyte and its removal from the coulometer ($t=t^{1}+t^{11}$). Part of this elapsed time (t^{1}) was under condition $i=0$, while the remainder of time $\left(\frac{Q}{i}=t^{11}\right)$ under the condition when $i>0$. This latter current is indicated in column 4. These values were not included in the least squares fitting of the individual sets of data.

TABLE 2. *Final data on the determination of the electrochemical equivalent of zinc with materials not subjected to vacuum fusion*

Exp. No.	Set No.	Material code	Current A	Electrolysis time, s	Electrode area, cm^2	Charge C	Mass of dissolved Zn, g
1	−1	1	0.5	11600	4	5903.604	2.000357
2	−1	1	.5	11700	8	5954.507	2.017550
3	−1	1	.5	41500	8	21120.554	7.156331
4	−1	2	.5	5750	3	2926.352	0.991514
5	−1	2	1.0	5800	3	5903.488	2.000106
6	−1	2	1.0	11600	15	11806.968	4.000604
7	0	2	0.5	11600	10	5903.608	2.000179
8	0	1	.5	11600	4	5903.615	2.000363
9	0	1	0.5	17400	8	8855.445	3.000217
10	0	3	.5	40600	10	20662.469	7.001076
11	0	2	.5	11600	3	5903.629	2.000290
12	0	2	.5	5800	2	2951.827	1.000226
13	0	1	0.5	57990	21	29512.774	9.999688
14	0	3	.5	17400	16	8855.369	3.000898
15	0	3	.5	11600	3	5903.568	2.000192
19	0	2	.5	1160	2	590.405	0.200099
23	0	2	0.5	1160	2	590.369	0.200075
24	0	205	.5	5800	3	2951.754	1.000296
25	0	3	.5	1160	2	590.379	0.199828
26	0	2	.5	116	3	59.026	.019914
27	0	3	0.5	116	3	58.990	0.020001
29	0	205	.5	8700	3	4427.722	1.500478
31	0	2	.5	580	3	295.154	0.099989
33	0	3	.5	580	3	295.185	.100011
34	0	3	.5	17400	7	8855.384	3.000889
35	0	3	.5	15000	7	7379.436	2.500424
60	3	2	1.0	1450	1	1475.945	0.500156
61	3	1	1.0	2900	7	2951.747	1.000334

program [3] and NBS UNIVAC 1108 computer facility. It seemed reasonable, however, to fit the data to the equation of a more general form

$$W=k_1Q+k_2. \qquad (2)$$

If k_2 in eq (2) has a value different from zero, a process or processes other than the passage of the measured charge must be responsible for the mass change of the anode. It was known, from the preliminary studies discussed earlier [1], that two processes occur on the zinc surface immersed in the electrolyte: (1) zinc oxide formed on Zn(Hg) between the time that the electrode is cleaned and the time it is immersed into the coulometer (i.e., during drying and weighing period) dissolves; (2) zinc metal corrodes spontaneously. Therefore, having found a statistically significant intercept, k_2, in eq (2), it appeared desirable to reconsider the data treatment and introduce the necessary parameters into the equation to make it describe the behavior of this system as completely as possible in terms of these physically significant parameters rather than combining their average effect into a single empirical constant, k_2.

The primary parameter which determines the weight loss of the anode is, of course, the amount of charge, Q, passed through the coulometer. Thus k_1Q should be the first term in the new modified equation. The weight loss of anode due to the dissolution of ZnO will obviously be proportional to the surface area of the electrode, a, if one hypothesizes that the zinc amalgam surface is covered relatively uniformly with ZnO. Thus k_2a should be another term in the equation. In the spontaneous corrosion of Zn(Hg) both the area of the electrode, a, as well as the time of electrolysis, t, play an important role. Thus weight loss due to corrosion should be represented by a variable of these two coupled parameters.

A number of model equations were tested to establish the most accurate representation of the experimental data. Some representative test equations along with the computed fitting coefficients are shown in table 3.

TABLE 3. *Test equations for electrochemical oxidation of* Zn

(1) $W=k_1Q$	$k_1=0.33880104+0.00000131$
(2) $W=k_1Q+k_2a$	$k_1=0.33879579\pm0.00000129$ $k_2=0.0091\pm0.0012$
(3) $W=k_1Q+k_2a+k_3t$	$k_1=0.33879539\pm0.00000133$ $k_2=0.0084\pm0.0013$ $k_3=(4.67\pm4.02)\times10^{-10}$
(4) $W=k_1Q+k_2a+k_4(at)$	$k_1=0.33879540\pm0.00000137$ $k_2=0.0085\pm0.0014$ $k_4=(-4.62\pm5.50)\times10^{-11}$
(5) $W=k_1Q+k_2a+k_5J$	$k_1=0.33879586\pm0.00000129$ $k_2=0.0093\pm0.0012$ $k_5=-0.0165\pm0.0270$

W mass of Zn dissolved, mg (milligrams).
Q charge passed, C (coulombs).
a apparent surface area of Zn anode, cm^2.
t time of coulometric experiment, s.
J current density, A cm^{-2}.
k_1 electrochemical equivalent of zinc, mg C^{-1}.

The physical significance of k_1 and k_2 is as follows: k_1 is the electrochemical equivalent of zinc; k_2 represents the weight of ZnO formed on the surface of zinc amalgam exposed to air in the course of 1–2 h.

Fitting the data of table 1 to the two-parameter equation (2) gave the following values for the fitting coefficients:

$$k_1=0.33879579\pm1.29\times10^{-6}\ \mathrm{mg\ C^{-1}}$$
$$k_2=0.00914\pm1.21\times10^{-3}\ \mathrm{mg\ cm^{-2}}$$

The cited uncertainty is the standard deviation of the respective coefficients. The least-squares fit of table 1 data to a one-parameter test equation (1), neglecting k_2, yields a different value of the primary coefficient:

$$k_1=0.33880104\pm1.31\times10^{-6}\ \mathrm{mg\ C^{-1}}.$$

The inclusion of k_2 into the equation changes the value of k_1 by 0.0015 percent, thus affecting the atomic weight of zinc only by 0.00098.

4. Discussion of the Results

4.1. The Effects of Variables

A least-squares fit of the experimental data to a two-parameter equation does not necessarily constitute the accurate description of the coulometric behavior of the system. It must be shown that other variables in the system have no effect on this function. The most direct way to approach this problem is to examine the dependence of the residuals (W_i-W) on the value of each varied parameter. W_i is the observed change of mass of zinc anode and W is the mass change computed from the least-square fit.

If a given variable, V_j, affects the results, then the residuals (W_i-W) can be described as some function of that variable i.e.,

$$(W_i-W)=f(V_j). \tag{30}$$

Again using a linear relationship as the first approximation, subject to further refinement if warranted, one can write

$$(W_i-W)=k_j(V_j) \tag{31}$$

and fit the data to this equation by the method of least squares. If k_j does not reach statistical significance at the desired confidence level, the residuals and the original function itself may be taken as independent of that variable V_j. (See for example Mandel [4].)

Not all of the varied parameters are easily adaptable to the least squares data treatment. Material pretreatment (degassing) is one such parameter. It can be experimentally realized and verbally described, but the quantification of treatment cannot be performed very readily. One possible way of quantifying this parameter would have been to analyze the material for the total gas content after each treatment. The determination of gases in zinc is in itself a formidable problem and was not undertaken. It was decided to resort to the cause (treatment) and the observable effect approach. Similarly, the origin of material (e.g., Australia, Peru, etc.) cannot be readily quantified, and therefore one is again forced to resort to the statistical testing of observable differences between different unquantifiable groups of data for significance.

4.2. Effect of Gases in Zn

One parameter, mentioned above, which can not be quantitatively incorporated into the linear equation describing the electrochemical behavior of Zn(Hg) is the effect of gases (oxygen) dissolved in the metal. It was therefore tested on three distinctly different groups of materials.

Two experiments (No. 24 and No. 29) performed with the air-fused material yielded the following values of the fitting coefficients:

$$k_1 = 0.3388235 \pm 3.2 \times 10^{-6} \text{ mg C}^{-1}$$

$$k_2 = 0.0107 \pm 1.5 \times 10^{-3} \text{ mg cm}^{-2}.$$

To make this solution feasible by the method of least squares the data of experiments 24 and 29 were combined with the "zero current" data, shown as set No. 5 in table 1.

Using the values of k_1 for materials subjected to different treatments the apparent values of the atomic weight of zinc were computed from Faraday's law and are shown in table 4.

It is quite clear from these data that the atmosphere in which molten zinc solidifies has a significant effect on the apparent electrochemical equivalent of zinc. The atomic weight of zinc computed on the basis of data for air-fused materials is about 0.02 percent higher than for vacuum fused materials.

TABLE 4. *Apparent atomic weight of zinc as a function of material treatment*

Material treatment	Apparent atomic weight
Air Fused Zn	65.3932
Unfused Zn	65.3823
Degassed Zn*	65.3771

* In addition to the vacuum fused commercial materials, this data includes the unfused high purity Zn (code 4) and the intermediate purity Zn (code 6). The latter two materials were deoxygenated by the manufacturer, as indicated in the corresponding certificates of analysis.

The commercial grade zincs without any *a priori* processing yield a 0.008 percent higher value of the electrochemical equivalent than the same materials subjected to vacuum fusion. This can be explained by the presence of gases, notably oxygen, in the commercial material which are removed under vacuum fusion conditions.

4.3. Effect of the Apparent Surface Area of the Electrode

It has been already shown that the apparent electrode surface area has a significant effect, resulting from the dissolution of ZnO formed on the surface of the amalgam during exposure to air. The magnitude of this effect is obtained by solving for the coefficient k_2 in eq (2). Three sets of data were used to obtain the three solution for k_2. The data of all coulometric measurements with degassed samples were used to obtain one solution. The data on unprocessed materials (table 2) were used to obtain the second solution. Finally the data of "zero current" set No. 5 (experiments 98–125) were used to obtain the third, independent soultion. The constants obtained in these three treatments are given in table 5 in the above described sequence. The mean value of the coefficient k_2 is 0.0102 ± 0.0040 mg cm^{-2}.

TABLE 5. *Three independent solutions for the coefficient* k_2

Solution No.	k_2, mg cm^{-2}	$\bar{s}$	Degrees of freedom
1	0.0079	0.0017	90
2	.0121	.0087	26
3	.0107	.0015	25
Mean.......	0.0102	0.0040	

4.4. Effect of Origin of Material

Another parameter which is not easily quantifiable in the sense of permitting the least-squares treatment of data is the geographic origin of the material. Here again the data can only be compared by testing the difference for significance. Experiment numbers 139 through 150 were performed as the final set of data [16]. Only the data of this set for high purity zinc (code 4) were used in the intercomparison. If all measurements on this material were used, the pooled standard deviation would have been overwhelmingly dependent on the high purity zinc data.

On the basis of data presented in table 6, there

TABLE 6. *Atomic weight of zinc determined by coulometry for materials of different origins* [16]

Experiment No.	Origin of material	Atomic weight of zinc
139	Canada	65.3759
140	Canada	65.3761
141	Canada	65.3782
142	Australia	65.3783
143	Australia	65.3778
144	Peru	65.3786
145	Peru	65.3764
146	Yugoslavia	65.3761
147	Yugoslavia	65.3751
148	Italy	65.3784
149	Italy	65.3783
150	Canada	65.3791
Mean....	....	65.3773_6

Pertinent Statistical Data.
Standard deviation of a single determination $s = 0.00134$.
Standard deviation of the mean $s/\sqrt{n} = 0.00039$.
Two sided 95 percent confidences interval for the mean based on 11 degrees of freedom $ts/\sqrt{n} = \pm 0.00086$.

appears to be no significant difference between the atomic weight values for materials of different origins even at the 10 percent level of significance. The published results of mass spectrometric investigations [5, 17] also indicate no significant differences in the isotopic composition of zinc.

4.5. Effect of Impurities

To investigate the effect of Zn purity on the coulometrically determined atomic weight the data obtained for material 4, high purity zinc (99.9999%), material 6, intermediate purity zinc (99.997%), material 109, Australian zinc (99.995%) and material 101, a commercial vacuum fused material (99.9%), were intercompared. (Table 7.)

TABLE 7. *Effect of purity of Zn on the determined atomic weight*

Material code	Purity, percent	Atomic weight of zinc
4	99.9999	65.3770
6	99.997	65.3774
109	99.995	65.3760
101	99.9	65.3768

Pooled standard deviation $s = 0.0013$.

A mere inspection of these data, clearly demonstrates that three orders of magnitude range of purity of the material has no significant effect on the determined atomic weight. This is not inconsistent with our understanding of the metallic impurity effect. The elements generally present as impurities in Zn are Pb, Cu, Fe, Ag, and Cd. Since Zn is more active than any of these elements, it would be expected that zinc would be oxidized preferentially and the impurities left in the amalgam.

4.6. Other Parameters

In addition to the three above-discussed parameters (gases in Zn, purity and origin), quantification of which for the purpose of the least-squares treatment was not possible, there were a number of variable parameters in the experiments which can be quantified and their effects can be easily tested. To perform the test for significance, the residuals (i.e., $W_i - W$), obtained for each experiment in the fit of table 1 data to eq (2) in table 3 were least-square fitted as a linear function of each of the variable parameters. The coefficients for each of these parameters, k, their respective standard deviations, $\bar{s}_k$, and $k/\bar{s}_k$ ratios are given in table 8.

Clearly there is no evidence that any of these tested parameters have an effect on the electrochemical equivalent, or the atomic weight of zinc. This conclusion can be made on the basis of the last column in the ratio of coefficient of each fitted parameter to the standard deviation of that coefficient. The test for significance indicates that there exists no dependence between the residuals of the final fit and the tested parameters.

TABLE 8. *Effect of variable parameters*

Variable	Coefficient k	Standard deviation of k, $\bar{s}_k$	$k/\bar{s}_k$
Charge, Q	-5.39×10^{-10}	16.60×10^{-10}	-0.32
Time, t	1.65×10^{-10}	7.33×10^{-10}	0.23
Current, i	2.34×10^{-5}	2.83×10^{-5}	0.83
Current density, J	-5.31×10^{-5}	5.4×10^{-5}	-0.98
at product	-1.38×10^{-11}	10.42×10^{-11}	-0.13

5. Summary of Findings

1. In the preliminary studies [1] it was found that the zinc amalgam electrodes are more stable than the unamalgamated electrodes. Zinc amalgam electrodes show no perceptible fall-off of material in the course of electrolysis.

2. The presence of oxygen (air) in the electrolyte has a significant effect on the rate of spontaneous corrosion of zinc. This in turn affects the experimentally determined electrochemical equivalent and the atomic weight of zinc. For this reason air was removed from the electrolyte by purging with nitrogen. A nitrogen atmosphere was maintained in the coulometer in all final determinations of the electrochemical equivalent of zinc.

3. On the basis of current density-potential studies it was established that even at current densities as high as several amperes per square centimeter the oxidation of zinc proceeds at 100.000 percent current efficiency. This was verified further by the coulometric experiments conducted at current densities ranging from 10^{-5} to 1.0 A cm^{-2}, which show no relation between the current density and the measured electrochemical equivalent of zinc.

4. Commercial grade zincs without any prior processing yield a higher measured electrochemical equivalent (on the order of 0.008%) than the same materials subjected to vacuum fusion. This is explained by the presence of oxygen in the commercial material which is removed under vacuum fusion. Air-fused zinc samples yielded an even higher value than the unprocessed Zn (0.02 %).

5. The geographic origin of material has no apparent effect on the measured electrochemical equivalent of zinc.

6. The presence of metal impurities does not have any significant effect on the measured electrochemical equivalent and the atomic weight of zinc.

7. Other investigated parameters which have no apparent effects as shown by the residual analysis of the least-squares fit include: current in the 10^{-4} to 1.0 A range; electrolysis time, up to 7×10^4s; amount of charge passed through the cell, up to 3×10^4C; mass of dissolved Zn, up to 10 g.

8. Only the electrode area, a, is the parameter which must be included in the final equation for the electrochemical equivalent of Zn. The effect of electrode

area arises from the disolution of ZnO formed on the surface of Zn(Hg) during the handling of the electrode in air.

The final least-squares fit, therefore, includes all data in table 1 since all samples of Zn used in these experiments were deoxygenated and the correction for the surface ZnO was applied by using the electrode area as one of the parameters in the equation.

9. The resulting equation is:

$$W = 0.338{,}795{,}79\ (\pm 0.000{,}001{,}29)\ Q + 0.009{,}1\ (\pm 0.001{,}2)\, a$$

where W is the mass of zinc dissolved (in milligrams), Q is the charge (in coulombs) and a is the electrode area (in cm^2). Subsequent fit of the residuals as a function of a and Q shows no significant correlation. Therefore the assumption that the first order equation, with respect to these two variables, is appropriate and is accepted by us as valid. The uncertainty figures for the coefficients in the above equation represent the deviations of the means based on 116 degrees of freedom.

10. As a final check on the imprecision measure calculated from the least-squares fit of all the data in table 1, we could compute the electrochemical equivalent for each of the six sets (0, 1, 2, 3, 4, 8) and take the average of these six values. The spread among these values would include variabilities due to sets, if any, and allow a more conservative estimate of the uncertainty of the value determined. The low current values, set numbers 6 and 7, were not included in this calculations because of their inherent imprecision. The results are given in table 11. The unweighted average is 0.33879491, agreeing very well with the least value for all the data points, but the standard error of the average (.00000435) is larger by a factor of four. It was decided that the final value of the electrochemical equivalent should be the value using all the data (to allow for better estimation of the effect of areas of electrodes). Its uncertainty, however, should be estimated in the conservative way, i.e., a 95 percent confidence interval for the mean using the standard error calculated from the six sets with five degree of freedom, or:

$$0.33879579\ (\pm 0.00001120).$$

Thus for Zn the determined molar mass is equal to:

$$\text{Molar mass of Zn} = 0.338{,}795{,}79\ \mathrm{mg\ C^{-1}} \times 96{,}484.56\ \mathrm{C\ mol^{-1}}(e) \times 2\ \mathrm{mol}\ (e)/\mathrm{mol\ (Zn)} \times 10^{-3}\mathrm{g\ mg^{-1}}$$

$$= 65.37707 \pm 0.00216\ \mathrm{g/mol\ (Zn)}$$

where the uncertainty is the 95 percent confidence interval.

There is a distinction between the molar mass and atomic weight. The latter is a dimensionless quantity numerically equivalent to molar mass. Thus the mean value of the atomic weight of Zn based on 118 final coulometric measurements under the optimum condition is 65.3771 ± 0.0022.

The two-sided 95 percent confidence interval for the mean, ±0.0022, reflects adequately the uncertainty in this value due to the random sources of error. The accuracy of the result, however, depends not only on the random error of measurement, but also on the biases which could exist in the various stages of the measurement process and in the constants which are employed in the calculation of the results. An assessment of the magnitude of these sources of error must be made and incorporated into the uncertainty statement.

5.1. Assessment of Errors

In addition to the random error of measurement some systematic errors can be encountered which are not revealed in the statistical treatment of data.

The uncertainty in each standard weight can be as large as 3 μg. The average weight of zinc dissolved in the final coulometric experiments is 1 g. Thus this source can contribute as much as 0.0003 percent error.

Electrical current measurements can be biased systematically (due to uncertainty in the standard resistor, saturated Weston cell and comparator error) by 0.0004 percent.

The timer was never found to have an error as great as 0.0001 percent. For the purpose of estimation of error it is assumed that it can be off by as much as 0.0001 percent.

The Faraday, which is used for final computation of the atomic weight, has 0.27 C $\mathrm{mol}^{-1}(e)$ uncertainty [6]. This corresponds to 0.00028 percent.

It would appear highly unlikely for all of these errors to be of the same sign. In fact a root-mean-square (rms) estimate of the possible combined effect would be appropriate and realistic. The overall rms estimate of the possible systematic error is 0.0006 percent (or 0.00040 in the atomic weight of Zn). Thus, the total error in the atomic weight of zinc, consisting of the sum of the random error contribution and possible systematic error estimate is 0.0026.

The new, accurate value of the atomic weight of zinc presented here is:

$$65.3771 \pm 0.0026.$$

5.2. Comparison With Previous Work

Only one earlier published research paper, that of Gladstone and Hibbert [7], describes work that is directly comparable with the research reported here. They also used Zn(Hg) anodes, made from sheet zinc. Three important features set apart the experiments of Gladstone and Hibbert from those conducted in this research: (1) commercial zinc, not subjected to degassing, was used by Gladstone and Hibbert while both types of materials were used here; (2) the charge consumed in the electrochemical reaction was measured by Gladstone and Hibbert by means of a silver deposition voltameter (coulometer) while the absolute current and time measurements were employed in this work; (3) the experiments reported in [7] were conducted without the exclusion of air while an inert atmosphere (N_2) was maintained in the coulometer used in this research.

It is desirable to analyze these differences and establish what effects they would produce in the final measured value of the atomic weight.

The first of these differences, the effect of gases in commercial zinc, was investigated directly. The difference between the atomic weight for the untreated material and the vacuum fused material is 0.00521 (or 0.00976%), the untreated material being the one which yields the higher value.

Secondly, the use of a Ag deposition coulometer invariably entails some occlusion errors. This aspect of the cathodic silver coulometer was treated in some detail by Hamer [8]. Hamer arrives at a value of 0.0102 ± 0.0014 weight percent as the mean error of the Ag deposition coulometers. Consequently, an error of this magnitude is probably incorporated into the results reported in [7] and propagated into the value for the atomic weight of Zn computed by Gladstone and Hibbert.

Finally, the presence of air in the electrolyte has a pronounced effect on the rate of spontaneous corrosion of zinc amalgam. This error again was no doubt affecting the work reported in reference [7] while it was minimized in the final experiments reported in this research by the use of deaerated electrolyte and the maintenance of an inert atmosphere in the coulometer. The average current density employed in the experiments of Gladstone and Hibbert [7] was $94\ \mathrm{mA \cdot cm^{-2}}$. From the studies of corrosion of Zn(Hg) in air saturated electrolyte, conducted here, the corrosion current density is found to be $J_{\mathrm{corr}} = 1.37 \times 10^{-3}\ \mathrm{mA \cdot cm^{-2}}$. Thus the error from this source is on the order of 0.0015 percent. This estimate, however, may involve a somewhat questionable extrapolation. Gladstone and Hibbert used $ZnSO_4$ electrolyte while $NH_4Cl + ZnCl_2$ were used here.

Since reference [7] gives no data on the surface area of the anodes it is not possible to make any corrections for ZnO, formed on the surface during drying of electrodes, which dissolves when the electrodes are immersed in the electrolyte. Moreover, in reference [7], electrodes were washed in alcohol and then dried at 40 °C, which probably accelerates the rate of oxidation of Zn(Hg).

The mean value of the Ag/Zn weight ratio reported in reference [7] is 3.298 ± 0.001. Using 107.93 as the atomic weight of silver Gladstone and Hibbert computed the atomic weight of Zn as 65.44. Using the presently accepted value for the atomic weight of silver, 107.868, the above value becomes 65.414. To this value the sum of all the above discussed corrections must also be applied. The total correction is -0.0197 percent. Thus the value of the atomic weight of zinc based on the data of Gladstone and Hibbert, corrected for known possible sources of error, is 65.40 ± 0.02. A copper coulometer, operated in series with a Zn and Ag coulometer, gave a Zn/Cu weight ratio of 1.0322, yielding 65.58 as the atomic weight of zinc. As pointed out by the authors themselves, the combining weight ratio 1.0322 is too high, thus this value contributes little to the the information on the atomic weight of zinc. The only inference which can be made is that the Cu coulometer gives an error of about $+0.3$ percent in the charge integration.

The above computed value of the atomic weight of Zn 65.40, based on the Ag/Zn ratio, is not in very good agreement with our final value (65.3771). The difference is on the order of 0.033 percent. It must be remembered, however, that no information is given regarding the material used in the work reported in reference [7]. If one supposes that the zinc was fused in air to form sheets which were then fabricated into the electrodes then the Zn atomic weight value obtained should be corrected for the effect of oxygen in the metal by a much greater amount than estimated above. Using the data of this research this additional correction is 0.011. Thus the Gladstone and Hibbert's value becomes 65.39 ± 0.02. Now the values are consistent within the experimental uncertainty.

Most of the results on the atomic weight determinations prior to 1910–1915 have been collected, analyzed and evaluated critically by Clarke [9, 10]. Since at the time Clarke did his reevaluation many of the atomic weights were not known accurately, and since the atomic weight scale has changed from the chemical atomic weight scale (based on oxygen = 16 exactly) to the unified C^{12} scale,[4] the values obtained by Clarke must be recalculated for the purpose of meaningful comparison.

It is rather fortunate that in science certain measured quantities remain truly invariant. Such constants are usually dimensionless ratios. The combining weight ratios are in this select group of constants. Even if the standard weights used in the measurements are inaccurate, as long as the same weights are used in the determination of the ratio, and the comparison method itself is flawless, the ratio is accurate.

Usually this latter condition, the flawlessness of the method, is the one which is difficult to realize.

Clarke arrived at the following group of combining weight ratios and his assessment of the uncertainties:

(1) $ZnO:Zn = 100:80.349 \pm 0.00065$
(2) $ZnSO_4:ZnO = 100:50.413 \pm 0.0020$
(3) $H_2O:Zn = 100:366.319 \pm 0.088$
(4) $2CO_2:ZnO = 100:93.169 \pm 0.012$
(5) $H:Zn = 100:6507.9 \pm 0.0036$
(6) $4Ag:K_2ZnCl_4 = 100:66.111 \pm 0.0023$
(7) $2Ag:ZnBr_2 = 100:104.38 \pm 0.0007$
(8) $2AgBr:ZnBr_2 = 100:59.962 \pm 0.0004$
(9) $Au:Zn = 197.2:65.436 \pm 0.0087$

The data used for the intercomparison must be judiciously selected. It is quite clear that all of the

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[4] One mole of substance is now defined to contain as many entities (atoms, molecules, electrons, etc.) as there are atoms in exactly 12 g of C^{12} isotope.

combining weight ratio data, given above, are not equivalent in reliability. Ratios (3), (4) and (5) should be ignored because the gasometric methods can be hardly considered accurate in view of the fact that real gases do not obey the ideal gas law, and, in general, volume measurements on real gases are susceptible to many errors. Ratio (6) can also be discarded because K_2ZnCl_4 is a compound of questionable stoichiometry. The calculated atomic weights of Zn based on the remaining 5 combining weight ratios are given in table 9. The agreement of the mean of these 5 ratios 65.384 ± 0.016, and the value found in this research is well within the assigned uncertainty bounds.

In addition to Clarke's collection more recent data are also available on the determination of the atomic weight of Zn.

Baxter and Grose [11] determined $Zn:Br_2$ ratio by preparing pure $ZnBr_2$, depositing Zn from weighed samples of $ZnBr_2$ into a mercury cathode, then weighing the deposit. Their value of $Zn:Br_2 = 0.409063$. Using 79.904 for the atomic weight of Br the calculated atomic weight of Zn becomes 65.3715.

TABLE 9. *Atomic weight of zinc based on selected combining weight ratios*

Ratio No.	Atomic weight of Zn
1	65.418
2	65.392
7	65.377
8	65.376
9	65.359
Mean	65.384 ± 0.016

Baxter and Hodges [12] determined the ratio $Zn:Cl_2 = 0.92195$ by the same method as [11]. Using 35.453 for the atomic weight of Cl the calculated atomic weight of Zn is found to be 65.3718.

Hönigschmid and von Mack [13] also utilized $ZnCl_2$ in their determinations, but titrated Cl with Ag^+. Their $ZnCl_2/2AgCl$ ratio is 0.475424, yielding the value 65.3698 for the atomic weight of Zn.

Using the relative isotope abundance values, determined by Leland and Nier [14] and by Hess et al. [5], as well as Mattauch's [15] data on mass defects for the five Zn isotopes, the atomic weight of zinc can be readily computed.

The summary data of these most recent determinations of the atomic weight of Zn are given in table 10.

The mean value of the six independent determinations by previous investigators, reported in table 10, 65.3777, is in a remarkable agreement with 65.3771, the final value derived from this research.[5]

TABLE 10. *Most recent data on the atomic weight of zinc*

Method	Source (reference)	At. wt. of Zn
Zn/Br_2	[11]	65.3715
Zn/Cl_2	[12]	65.3718
$ZnCl_2/2AgCl$	[13]	65.3698
ZnI_2 Mass spectr.	[14]	65.3873
Do.	[5]	*65.3911
Do.	[5]	**65.3744
Mean		65.3777

* Electrolytic Zn.
** Zn produced by chemical reduction.

TABLE 11. *Analysis of data by sets*

Set No.	Number of measurements	Current, A	K_1, mg C^{-1}	Standard error of K_1
0	9	0.5	0.33880890	0.00001644
1	17	.5	.33878853	.00000957
2	6	1.0	.33879535	.00000675
3	18	1.0	.33879872	.00000510
4	8	0.1	.33877785	.00000997
8	12	.5	.33880008	.00000200

Mean	0.33879491 mg · C^{-1}
Standard error of the mean	0.00000435 mg · C^{-1}
95 percent confidence interval	± 0.00001120 mg · C^{-1}

6. Conclusion

Based on the publication of partial results of this research [16] the IUPAC Commission on Atomic Weights has published [18] a new value, 65.38 ± 0.01, for the atomic weight of Zn.

The new, more accurate value of the atomic weight of zinc, determined by an absolute coulometric method in this research is

$$65.3771 \pm 0.0026.$$

7. References

[1] Marinenko, G., and Foley, R. T., J. Res. Nat. Bur. Stand. (U.S.) **79A,** (Phys. and Chem.), No. 6, (1975).
[2] Grubbs, F. E., Technometrics **11,** 1 (1969).
[3] Hilsenrath, J., Ziegler, G. G., Massina, C. G., Walsh, P. J., and Herbold, R. J., OMNITAB–A Computer Program for Statistical and Numerical Analysis, Nat. Bur. Stand. (U.S.), HandB 101, 285 pages (Mar. 1966).
[4] Mandel, J., The Statistical Analysis of Experimental Data (Interscience Publishers, New York, 1964) pp. 185–192.
[5] Hess, D. C., Inghram, M. G., and Hayden, R. J., Phys. Rev. **74,** 1531 (1948).
[6] Cohen, E. R., and Taylor, B. N., J. Phys. Chem. Ref. Data **2,** No. 4, 741 (1973).
[7] Gladstone, J. H., and Hibbert, W., J. Chem. Soc. **55,** 443 (1889).
[8] Hamer, W. J., J. Res. Nat. Bur. Stand. (U.S.), **72A** (Phys. and Chem.), No. 4, 435–439 (July–Aug. 1968).
[9] Clarke, F. W., The Constants of Nature Part V. A Recalculation of the Atomic Weights, Third edition, Smithsonian Institution Publication, Washington, D.C., (1910), pp. 223–234.
[10] Clarke, F. W., The Constants of Nature Part V. A Recalculation of the Atomic Weights, Fourth revised and enlarged edition, Government Printing Office, Washington, D.C., 1920, pp. 179–187.

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[5] This suggests that unless a method has been proven to be accurate it is desirable to resort to as many different, judiciously selected, independent methods as possible. Nature will in turn cooperate by distributing errors randomly so that the mean value of these many, less accurate methods, will be a better approximation of the true value than any one particular determination.

[11] Baxter, G. P., and Grose, M. R., J. Am. Chem. Soc. **38,** 868 (1916).

[12] Baxter, G. P., and Hodges, J. H., J. Am. Chem. Soc. **43,** 1242 (1921).

[13] Hönigschmid, O., and von Mack, M., Z. anorg. and Allgem. Chem. **246,** 363 (1941).

[14] Leland, W. T., and Nier, A. O., Phys. Rev., **73,** 1206 (1948).

[15] Mattauch, J. H. E., Thiele, W., and Wapstra, A. H., Nucl. Phys., **67,** 1 (1965).

[16] Marinenko, G., and Foley, R. T., J. Res. Nat. Bur. Stand. (U.S.), **75A** (Phys. and Chem.), No. 6, 561–564 (Nov.–Dec. 1971).

[17] Rosman, K. J. R., Geochim. et Cosmochim. Acta, **36,** 801 (1972).

[18] IUPAC Commission on Atomic Weights, Pure and Applied Chemistry, **30,** 639 (1972).

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