THE USE OF PARTIAL DIFFERENTIALS FOR THE ESTIMATION OF ERRORS IN VOLUMETRIC ANALYSIS*

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This work was undertaken to determine what accuracy might be obtained in carefully conducted volumetric analysis. It is desirable to have such data in view of the immense popularity which volumetric schemes enjoy.

DEVELOPMENT OF FORMULAE

First let us develop partial differential expressions for probable error in volumetric analysis.[1] We shall derive these from the usual forms of the equations used for the calculations of volumetric results.

The following symbols shall have the meanings assigned:

S = Sample weight in grams.
ml = Volume of standard solution in milliliters.
e = Milliequivalent weight of substance sought or primary standard weighed.
N = Normality of standard solution.

If a sample of S (in grams) of a standard substance, whose milliequivalent weight is e, reacts stoichiometrically with a volume ml (in milliliters) of a solution, we may say that the normality, N, of the solution is given by:

$$N = \frac{S}{ml \times e} \qquad (I)$$

We may then write (e is a constant):

$$dN = \frac{1}{ml \times e}\partial S - \frac{S}{(ml)^2 \times e}\partial\,(ml) \qquad (II)$$

Now let us divide II by I to obtain expression III:

$$\frac{dN}{N} = \frac{\partial S}{S} - \frac{\partial (ml)}{ml} \qquad (III)$$

If a weighed quantity, S, of a sample of milliequivalent weight, e, should require ml milliliters of a standard solution of normality, N, for stoichiometric reaction, we may calculate percentage purity by formula IV:

$$\% = \frac{ml \times N \times e \times 100}{S} \qquad (IV)$$

By the scheme described above we can obtain expression V:

$$d\% = \frac{N \times e \times 100}{S}\partial\,(ml) + \frac{ml \times e \times 100}{S}\partial N - \frac{ml \times N \times e \times 100}{S^2}\partial S \qquad (V)$$

Combining expressions V and IV we derive VI:

$$\frac{d\%}{\%} = \frac{\partial (ml)}{ml} + \frac{\partial N}{N} - \frac{\partial S}{S} \qquad (VI)$$

If two solutions, one of volume, ml and normality, N, and the other of volume, ml′, and normality, N′, react stoichiometically, we may write expression VII:

$$N \times ml = N' \times ml' \qquad (VII)$$

From this we may write expression VIII:

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$$dN = \frac{ml'}{ml}\partial N' + \frac{N'}{ml}\partial(ml') - \frac{N(ml')}{(ml)^2}\partial(ml) \qquad \text{(VIII)}$$

Dividing VIII by VII we obtain IX:

$$\frac{dN}{N} = \frac{\partial N'}{N'} + \frac{\partial(ml')}{ml'} - \frac{\partial(ml)}{ml} \qquad \text{(IX)}$$

It is necessary to give some consideration to the evaluation of the separate terms in equations III, VI, and IX. The term $\frac{\partial S}{S}$ is estimated from a knowledge of the sensitivity of the balance upon which the samples are weighed. The term $\frac{\partial(ml)}{ml}$ is estimated by careful weight calibrations of the burettes used. The pipets were standardized by the United States Bureau of Standards, and their error could be obtained directly from the certificate provided. In the case of equation IX, $\frac{\partial N'}{N'}$ is required. This is evaluated from previous calculations with equation III.

APPLICATION TO EXPERIMENTAL DATA

Table 1 contains data on the standardization of perchlorato-cerate solutions with samples of sodium oxalate. The over-all reaction is:

$$2\,H_2Ce(ClO_4)_6 + Na_2C_2O_4 = 2\,CO_2 + 2Ce(ClO_4)_3 + 6\,NaClO_4$$

A sample of about 0.25 gram of pure dry sodium oxalate is accurately weighed on a balance of known sensitivity and dissolved in about 100 milliliters of 2N perchloric acid. This solution is then titrated (in the cold) with the unknown solution of perchloratocerate from a previously calibrated burette with the ferrous complex of 5-nitro-(1,10)-phenanthroline as the indicator. Samples 4 through 7 were taken from publication 2 listed in References with the knowledge and permission of the author.

Examples 1, 2, 3, and 4 in Table 2 concern the quantitative oxidation of sucrose by a perchlorato-cerate solution in 4N perchloric acid.[2] The over-all reaction is:

$$C_{12}H_{22}O_{11} + 26\,H_2Ce(ClO_4)_6 + 12H_2O = 11\,H_2CO_2 + CO_2 + 26Ce(ClO_4)_3 + 78\,HClO_4.$$

Examples 5, 6 and 7 in Table 2 represent data obtained for the titration of a weighed sample of purified ceric ammonium nitrate titrated with sodium oxalate in 2N perchloric acid.

Table 3 contains data on the standardization of a perchlorato-cerate solution with a standard solution of sodium oxalate and the reverse of this standardization.

It will be noted that in each table values of maximum, minimum, and average values for the terms evaluated are given. These are obtained by summing the individual terms to get the largest and the smallest summation and finally averaging these two values. This average calculated error is usually quite close to the observed variations in the analyses as inspection of the tabulated data will show.

REFERENCES

1. If one is unfamiliar with this use of the partial differential expression, a standard textbook on calculus should be consulted. The following is recommended:

   Granville, Smith, and Longley, Elements of the Differential and Integral Calculus: Ginn and Company, New York, 1943. Revised Ed.
2. SMITH, G. F., Cerate Oxidimetry: G. Frederick Smith Chemical Co., Columbus, Ohio, 1942.

TABLE 1.—STANDARDIZATION OF CERATE

	Standard $Na_2C_2O_4$ Wt. in grams	∂s	$\frac{\partial s}{s}$	Titrating solution Vol. in milliliters	$\partial(ml)$	$\frac{\partial(ml)}{ml}$	N
1.	0.2500	±0.0003	±0.0012	36.90	±0.04	±0.0011	0.1012
2.	0.2517	”	±0.0012	37.15	”	±0.0010	0.1011
3.	0.2503	”	±0.0012	34.81	”	±0.0011	0.1010
4.	0.1132	”	±0.0026	34.81	±0.06	±0.0017	0.04856
5.	0.1092	”	±0.0027	33.63	”	±0.0017	0.04849
6.	0.0883	”	±0.0034	27.16	”	±0.0022	0.04855
7.	0.0958	”	±0.0031	26.46	”	±0.0023	0.04856

TABLE 2.—EXPERIMENTAL DATA INTER-

	Wt. of sample g.	∂s	$\frac{\partial s}{s}$	Titrating solution Vol. in milliliters	$\partial(ml)$	$\frac{\partial(ml)}{(ml)}$	N
1.	0.01250	±0.0003	±0.024	8.90	±0.06	±0.0067	0.1051
2.	”	”	”	”	”	”	”
3.	0.03371	”	±0.0089	24.50	”	±0.0025	”
4.	”	”	”	24.44	”	”	”
5.	2.5000	”	±0.00012	44.19	±0.04	±0.00091	0.1031
6.	”	”	”	44.16	”	”	”
7.	”	”	”	44.18	”	”	”

TABLE 3.—EXPERIMENTAL DATA INTER-

	ml′	$\partial(ml')$	$\frac{\partial(ml')}{ml'}$	ml	$\partial(ml)$	$\frac{\partial(ml)}{ml}$	N′	$\frac{\partial N'}{N'}$
1.	23.01	±0.02	0.00087	25.00	±0.002	±0.00008	0.1051	0.002
2.	23.02	”	”	”	”	”	”	”
3.	23.01	”	”	”	”	”	”	”
4.	47.02	”	0.00042	50.00	”	±0.00004	0.1012	0.001
5.	”	”	”	”	”	”	”	”
6.	47.03	”	”	”	”	”	”	”

SOLUTIONS WITH PRIMARY STANDARD $Na_2C_2O_4$

Max.	$\frac{dN}{N}$ Min.	Av.	Max.	dN Min.	Av.
±2.3x10^{-3}	±0.1x10^{-3}	±1.2x10^{-3}	±2.3x10^{-4}	±0.1x10^{-4}	±1.2x10^{-4}
±2.2 "	±0.2 "	±1.2 "	±2.2 "	±0.2 "	±1.2 "
±2.3 "	±0.1 "	±1.2 "	±2.3 "	±0.1 "	±1.2 "
±4.3x10^{-3}	±0.9 "	±2.6 "	±2.1x10^{-4}	±0.44x10^{-5}	±1.3 "
±4.4 "	±1.0 "	±2.7 "	±2.1 "	±0.48 "	±1.3 "
±6.6 "	±1.2 "	±3.9 "	±3.2 "	±0.58 "	±1.9 "
±6.4 "	±0.8 "	±3.6 "	±3.1 "	±0.39 "	±1.7 "

PRETED BY MEANS OF EQUATION VI

$\frac{\partial N}{N}$	% (Approx.)	Max.	$\frac{d\%}{\%}$ Min.	Av.	Max.	d% Min.	Av.
±0.0020	98.48	±0.022	±0.012	0.017	±2.2	±1.2	±1.7
"	98.49	"	"	"	"	"	"
"	100.28	±0.013	±0.0044	±0.008	±1.3	±0.4	±0.8
"	100.52	"	"	"	"	"	"
±0.00052	99.92	±1.5x10^{-3}	±0.27x10^{-3}	±0.9x10^{-3}	±0.15	±0.027	±0.09
"	99.88	"	"	"	"	"	"
"	99.91	"	"	"	"	"	"

PRETED BY MEANS OF EQUATION IX

N	Max.	$\frac{dN}{N}$ Min.	Av.	Max.	dN Min.	Av.
0.09673	±0.0022	±0.0018	±0.002	±2.1x10^{-4}	±1.7x10^{-4}	±1.9x10^{-4}
0.09678	"	"	"	"	"	"
0.09673	"	"	"	"	"	"
0.09517	±0.0014	±0.0005	±0.0009	±1.3x10^{-4}	±0.4x10^{-4}	±0.8x10^{-4}
"	"	"	"	"	"	"
0.09518	"	"	"	"	"	"