

A RAPID PROCEDURE FOR THE DuCLAUX ANALYSIS OF DILUTE MIXTURES OF FORMIC AND ACETIC ACIDS

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Introduction

Several methods (1, 2, 3, 4) which require considerable time in their operation have been devised for the analysis of mixtures of formic and acetic acids. It was decided to develop a more rapid modification of the DuClaux (5) method for the determination of volatile acids in sulphuric

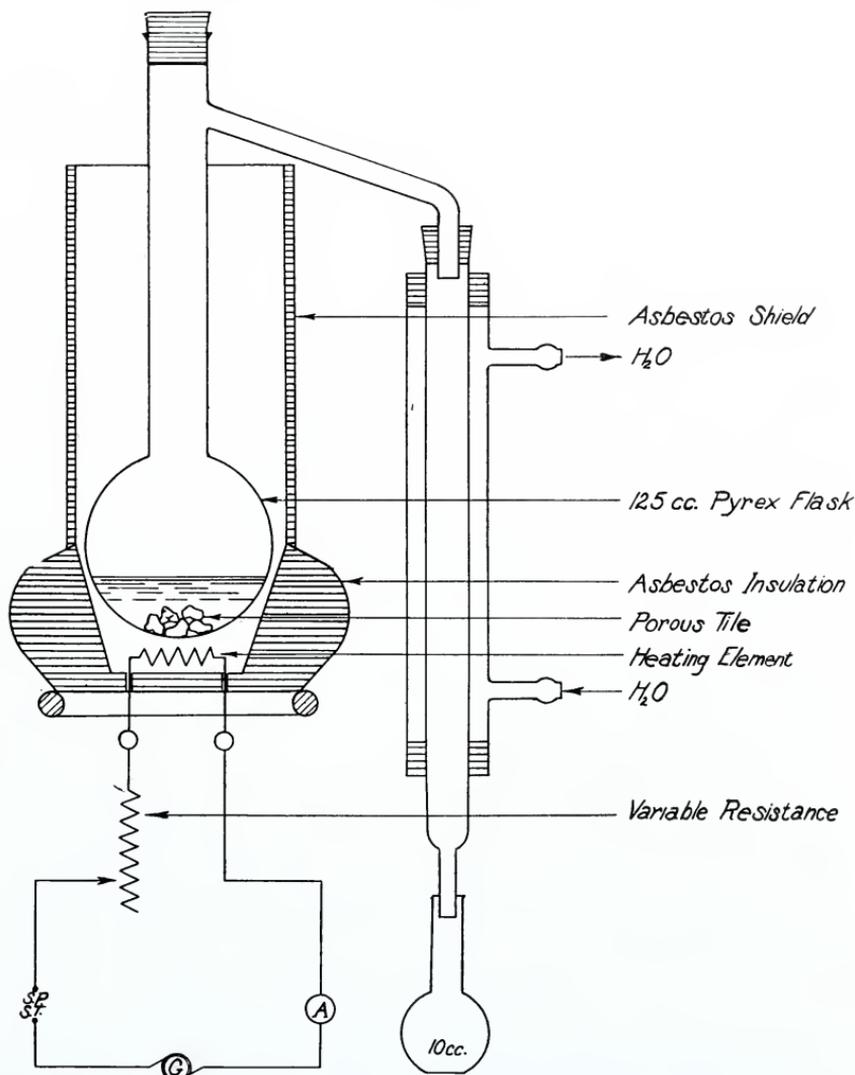


FIG. 1.

acid solutions resulting from the electrochemical oxidation of acetone. This procedure depends upon the regularity with which the two volatile acids distill, whether alone or in the presence of each other.

Experimental Procedure

Apparatus.—The flask for the acid distillation consisted of a 125 c.c. Pyrex distilling flask with the delivery tube bent to fit into the upper end of a twelve-inch vertical Liebig condenser. The lower end of the condenser was drawn out to fit well into a 10 c.c. volumetric flask, which served as a receiver of the distillate. Two such flasks were needed. The distilling flask was partially insulated by means of a cylindrical asbestos shield extending up to the delivery tube. See Figure 1.

The heating element consisted of twenty feet of B. and S. No. 22 Nichrome resistance wire made into five series coils well insulated with asbestos. A variable resistance of thirty feet of the same size Nichrome wire was placed in series with the heater element so that the rate of distillation could be controlled. The variable resistance was adjusted so that the rate of distillation was fairly rapid.

Procedure.—The solution to be analyzed was made up to 100 c.c. with carbon dioxide-free (6) 1.5 sulphuric acid. Ten cubic centimeters of this solution was diluted to 250 c.c., of which 5 c.c. was further diluted to 25 c.c. and used for the determination of formic and acetic acids. This solution was placed in the apparatus and distilled. The distillation was allowed to proceed until a 10 c.c. fraction had been collected and removed, and a second 10 c.c. fraction had been collected. Bumping was prevented by the addition of five small pieces of porous tile. The same pieces of tile were used throughout all subsequent determinations.

Each of the two 10 c.c. fractions was washed into a flask with carbon dioxide-free water and titrated¹ with 0.01*N* barium hydroxide solution (7), using phenol red (8), as the indicator. The titration values of each fraction were then corrected by a blank titration on the chemicals used, and the amounts of formic and acetic acids present in each fraction were calculated.

Standardization of Apparatus.—DuClaux showed that aqueous solutions of either formic or acetic acid distill in the presence of each other, exactly as if only one acid were present. The apparatus described above was standardized by the distillation, collection, and titration of the first and second 10 c.c. aliquots of separate sulphuric acid² solutions of formic and of acetic acid. From the data obtained and from the original concentrations, a *titration constant* for each acid was calculated. This was expressed in terms of cubic centimeters of 0.01*N* barium hydroxide per milligram of sample in each of the two 10 c.c. fractions. This permitted the calculation of the amount of formic and of acetic acids present in a mixed sample. From these data, presented in Table I, the following facts were obtained:

$$\begin{aligned} a &= 0.239 \text{ Ac} + 0.202 \text{ Fo} \\ b &= 0.294 \text{ Ac} + 0.295 \text{ Fo} \end{aligned}$$

¹The buret was graduated in intervals of 0.05 c.c.

²This was prepared to contain the same concentration of sulphuric acid as the solution to be analyzed.

Here *a* and *b* are the titration values of the first and second 10 c.c. fractions, respectively. *Ac* and *Fo* represent the quantities of acetic and formic acids, expressed as milligrams, present in the sample. If the two above equations are solved simultaneously for *Ac* and *Fo* the following equations are obtained:

$$Ac = \frac{1.46 a - b}{.55} \qquad Fo = \frac{a - 239 Ac}{.202}$$

By substituting the titration values obtained, the amount of formic and acetic acids present in a mixed sample may be determined.

TABLE I
Standardization of Apparatus

Sample in Milligrams	H ₂ SO ₄ Content in cc.	Observed Titration in cc. of 0.01N Ba(OH) ₂ Corrected for Blank		Titration Constant per mg. of Sample	
		1st Fraction	2nd Fraction	1st Fraction	2nd Fraction
ACETIC ACID					
5	5	1.195	1.470	0.239	0.294
10	5	2.388	2.950	0.239	0.295
15	5	3.590	4.400	0.239	0.293
20	5	4.745	5.980	0.239	0.294
Average				0.239	0.294
10	10	2.250	2.600	0.225	0.260
FORMIC ACID					
5	5	1.010	1.470	0.202	0.295
10	5	2.050	2.950	0.205	0.295
15	5	3.000	4.450	0.200	0.296
20	5	4.040	5.880	0.202	0.294
Average				0.202	0.295
10	10	1.900	2.700	0.190	0.270

¹10 c.c. of 1:4 H₂SO₄, diluted to 250 c.c.

Analysis of Known Solutions.—In Table II are shown the results of analyses of known samples of mixtures of formic and acetic acids, both in the absence and presence of acetone. The table shows the titration values of each fraction, also the amount of acetic and formic acids present in the sample and the amount of each found.

Discussion.—A change in the rate of distillation, the size of the distillation flask, and the concentration of the sulphuric acid in the liquid to be distilled introduce variations in the titration constants, making the values tabulated in this article hold only for the apparatus for which they were determined. Any substance in the liquid to be distilled which, upon distillation, decomposes to form volatile acids or carbon dioxide will cause an erroneous interpretation of the results.

Exactly the same amount of indicator solution must be added for each determination. To prevent small drops of the distillate from adhering to the sides of the condenser, the apparatus must be thoroughly cleaned before each determination.

TABLE II
Analysis of Known Solutions

Sample in Milligrams	<i>a</i> —1st Fraction cc. 0.01N Ba(OH) ₂	<i>b</i> —2nd Fraction cc. 0.01N Ba(OH) ₂	Found Acetic Milligrams	Found Formic Milligrams	Acetone Present Milligrams
5 Acetic 10 Formic	3.21	4.41	4.9	10.1	None
10 Acetic 10 Formic	4.41	5.89	9.8	10.0	None
10 Acetic 5 Formic	3.40	4.42	9.9	5.1	None
2 Acetic 5 Formic	1.49	2.08	2.0	4.9	None
15 Acetic 5 Formic	4.59	5.88	14.9	5.1	None
5 Acetic 15 Formic	4.23	5.89	5.1	14.9	None
5 Acetic 10 Formic	3.21	4.41	4.9	10.1	25
10 Acetic 10 Formic	4.42	5.89	9.9	10.0	25
10 Acetic 5 Formic	3.40	4.42	9.9	5.1	25

Volumes other than 25 c.c. of the liquid to be distilled were used with success except for the fact that larger volumes required more than the average time. The procedure, as outlined, permits a complete analysis in twenty minutes. An examination of the data in Table II shows a reasonable check between the amounts of acetic and formic acids present and the amounts found by analysis. This adaptation of the DuClaux method was successfully used for the analysis of anolytes obtained in the electrochemical oxidation of aqueous acetone-sulphuric acid solutions.

Literature Cited

1. Craig, 1931. Bur. of Stand. J. Res. 6:169-82.
2. Scott, 1925. Standard methods of chemical analysis, p. 1545, 4th ed.
3. Nelson and Beck, 1918. J. Am. Chem. Soc. 40:1001-05.
4. Held and Zeileis, 1913. Ber., 46:1171-77.
5. Blyth, 1888, 1909. Foods: Their composition and analysis. 3rd ed., pp. 487-496 and 6th ed., pp. 449-450.
6. Findlay, 1923. Practical physical chemistry. 4th ed., p. 144.
7. Ibid, p. 145.
8. Hall, 1930. Textbook of quantitative analysis. p. 42.