DETERMINATION OF SMALL QUANTITIES OF VOLATILE ORGANIC ACIDS IN SULPHURIC-ACID SOLUTIONS

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ABSTRACT

A procedure is described for separating small quantities of volatile organic acids from the electrolyte of lead storage cells and from wood separator extracts containing 30 to 40 per cent of sulphuric acid. A subsequent procedure for separating acetic from formic acid in the distillates is also described. A modified differential potentiometric method for titrating acid solutions of the order of a few thousandths normal was found to be reliable in estimating the acidities of the distillates. Some phenolphthalein titrations of the distillates are compared with electrometric titrations.

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I. INTRODUCTION

In a study of the corrosive effect of various organic substances on the plates of lead storage cells, it was found that under certain conditions small quantities of acetic acid in the electrolyte definitely corroded the positive plates. In this connection, as well as in a study of the adequacy of treatment of wood separators, the necessity arose for determining the percentage of acetic acid in solutions containing 30 to 40 per cent of sulphuric acid.

For most purposes the volatile organic acid content of the electrolyte in a cell, which has been cycled, may be considered to be acetic. It is, however, to be expected that a considerable percentage of the volatile acids formed by partial hydrolysis of wood separators in sulphuric-acid solutions is formic acid. Because of the pronounced corrosive effect of acetic acid on the positive plates, it was desirable to distinguish between the percentage of acetic acid and the other volatile organic acids in the sulphuric-acid extracts of the separators.

Schorger [1] has studied the hydrolysis of wood by sulphuric acid and his procedure for distilling the volatile acids from a 1.5 per cent sulphuric-acid solution is given by Hawley and Wise. The percentage of acetic acid in a newly assembled cell may, however, be as small as a few hundredths of 1 per cent and dilution of the electrolyte to 1.5 per cent of sulphuric acid previous to distilling would in turn reduce the concentration of acetic acid to a very low value. Since the volatile organic acid content of sulphuric-acid solutions of separator extracts decreases with the adequacy with which the separator has been treated, it is likewise desirable to avoid dilution before distilling the volatile acids.

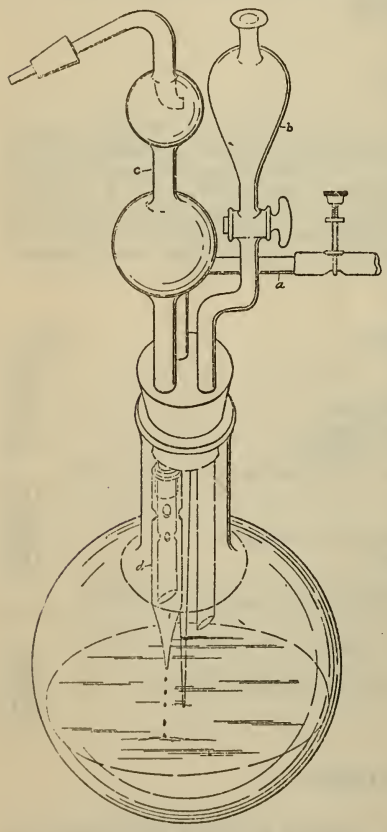

FIGURE 1.—*Distillation flask with fittings*

The object of this investigation was to establish a suitable procedure for determining small amounts of volatile organic acids in battery electrolytes, or in sulphuric-acid solutions of extracts of treated separators. This was accomplished by converting the sulphuric acid in part into sodium sulphate, and the remainder into the acid sulphate, with concentrated sodium hydroxide and distilling to dryness, thereby avoiding unnecessary dilution of the volatile acids. A known portion of the distillate, containing the volatile acids, was then titrated for total acidity. Another portion of the distillate was then treated with potassium permanganate and sodium carbonate to remove reducing organic acids, and, after again distilling, the second distillate was titrated for acetic acid.

The titrations were made with barium hydroxide solutions, using a differential potentiometric method. For the purpose of comparison, some titrations were made with phenolphthalein.

II. DISTILLATION OF VOLATILE ORGANIC ACIDS

Fifty-milliliter samples of sulphuric-acid solution (1.250 specific gravity) containing known quantities of acetic and formic acids, were used in the distillations for the purpose of checking the method. A solution of approximately 20 per cent sodium hydroxide, equivalent to the sulphuric acid in 35 ml of the sample, was added to the

[1] Hawley and Wise, The Chemistry of Wood, p. 132; 1926.

sample in a wide-mouthed, round-bottomed, 1,000 ml flask, containing a few pieces of porous plate. The flask was then provided with a rubber stopper containing: A glass tube, *a*, drawn out to a capillary, closed with a rubber tube and pinchcock, and extending to the bottom of the flask; a dropping funnel, *b;* a distilling column, *c*; and a tube, *d*, covering the lower end of the column. The flask, with its fittings, is shown diagrammatically in Figure 1.

The tube, *d*, the lower end of which is drawn to a capillary, is attached to the column by a rubber washer, fitting against the large rubber stopper. The staggered arrangement of the holes in the tube and in the distilling column aids in preventing mechanical carrying of spray into the condenser. A portion of the condensate collects in the capillary end of tube, *d*, and prevents vapor or spray from entering directly into the distilling column. A supply of ice water served to cool the 22-inch condenser, as well as a receiving flask, which was connected to an aspirator and a manometer. The rate of distillation was controlled by regulating the aspirator and adjusting the pinchcock. The temperature of a water bath surrounding the flask was maintained at 65° to 75° C., except at the end of the distillation, when it was raised to 80° to 85° C. After distilling to dryness, the temperature was lowered to about 70° C. and a few milliliters of water was added to the distilling flask by means of the separatory funnel, after which the temperature was again raised to about 85° C. and the distillation again carried to dryness. This procedure was followed twice at the end of each distillation so that the last traces of organic acids would be carried over. The distillate was transferred to and diluted in a volumetric flask and a known volume titrated for total acidity.

III. ELIMINATION OF FORMIC ACID IN THE DISTILLATES

Following the procedure of Jones [2] for oxidizing formic acid with potassium permanganate, 50 or 100 ml portions of the distillates containing both formic and acetic acid were added, in the distilling flask to 15 ml of molar sodium carbonate solution and an excess of approximately 0.1 *N* potassium-permanganate solution. The distilling apparatus was again assembled and the solution heated under atmospheric pressure for approximately 20 minutes at 80° to 90° C. Ten milliliters of sulphuric acid (1.250 specific gravity) together with a solution of sodium sulphate equivalent to 20 ml of sulphuric acid (1.250 specific gravity), was then added through the dropping funnel to the solution in the flask. The solution was then distilled, as described above, and a known portion of the distillate titrated for acetic acid. From the acidities of the first and second distillates and the dilution factors the percentage of each acid in the original sample can be calculated.

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[2] Am. Chem. J., 17, p. 539; 1895.

IV. DIFFERENTIAL TITRATION OF DILUTE ACID SOLUTIONS

The acidities of the distillates were determined with modifications of differential potentiometric methods described by Clarke and Wooten [3] and MacInnes and Dole.[4] A diagrammatic sketch of the cell vessel used in the present experiments and differing in some respects from that used by the above authors is shown in Figure 2.

The vessel was provided with a rubber stopper, through which projected a bubbling tube, *a*; a 25 ml burette, *b*; a shielding tube, *c*, containing the retarded electrode, *d*; and the electrode, *e*, projecting through the glass tube, *f*. The electrodes consisted of bright platinum wires sealed into glass tubes, containing a few drops of mercury for making contact with the leads to the potentiometer. The electrode tubes were held in place by means of small corks which were sealed into the flared openings of the tubes, *c* and *f*, with paraffin. The lower end of the shielding tube was drawn to such size as to retard diffusion, yet sufficiently large to give satisfactory galvanometer sensitivity. To the upper end of the shielding tube was attached a side arm for introducing hydrogen. Through a 3-way stopcock, *g*, hydrogen could be passed through the tube, *a*, or through the shielding tube, *c*, thereby making it possible to stir the main portion of the solution, while titrating, or to flush out the shielding tube when desired. A side tube attached to the upper end of the tube, *f*, provided a means of escape for the hydrogen. The hydrogen was passed through a heated quartz tube containing palladium-ized asbestos and in turn through a tower of soda lime. By momentarily opening the stopcock, *h*, after flushing out the shielding tube, sufficient solution rises in the shielding tube to cover the retarded electrode. A suitable potentiometer with a lamp and scale galvanometer served for measuring the potential differences. The barium hydroxide solutions used in the titrations were protected from carbon dioxide and were made by diluting saturated barium hydroxide solutions to approximately the strength desired with carbon dioxide free distilled water.

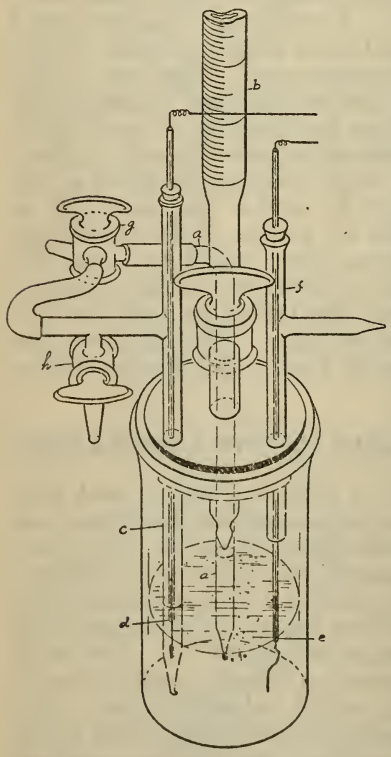

FIGURE 2.—*Cell vessel for differential potentiometric titrations*

The solution to be titrated was introduced into the vessel, together with a known quantity of potassium-chloride solution and a little

[3] J. Phys. Chem., **33**, p. 1468; 1929.

[4] J. Am. Chem. Soc., **51**, p. 1119; 1929.

quinhydrone. The vessel was then fitted with the rubber stopper and arranged as shown in the sketch. Hydrogen was then allowed to bubble through the solution with frequent flushing of the shielding tube, until satisfactory equilibrium was obtained as indicated by the constancy of the potential differences. The departure of the initial potential difference from zero seemed to increase somewhat with the rate at which hydrogen passed through the solution and the proximity of the hydrogen bubbles to the electrode. The sign of the potential difference indicates a slight catalytic reduction of the quinhydrone in the presence of hydrogen and platinum. No difficulty was experienced, however, in obtaining constant readings and, although the potential difference at the start of a titration was often as much as 15 mv, the increase in potential for additions of the same quantity of base was uniform for titrations involving the same acid and base solutions. When the titration was approximately 1 ml from the end point, as indicated by the potential changes, the shielding tube was again flushed and a new "zero" reading was noted. Potential readings were then noted for smaller increments of base. In this respect the method of titrating differed from that of the above authors [5] whose arrangement made no provision for stirring the main portion of the solution without flushing the shielding tube, making it necessary to obtain a new zero reading after each addition of base or to depend upon diffusion to establish equilibrium. The arrangement used in the present experiments permits continuous stirring and titrating of the main portion of the solution without necessitating a new zero reading until close to the end point.

V. TITRATION OF DILUTE SOLUTIONS OF KNOWN ACIDITIES

1. PREPARATION OF DILUTE SOLUTIONS OF HYDROCHLORIC, ACETIC, AND FORMIC ACIDS

Before distilling any of the samples, it was desirable to know the precision with which the results of the electrometric titrations could be used in judging the success with which the distillations had been carried out. For this purpose solutions of known acidities, of the order of a few thousandths normal, were titrated. These solutions were prepared by diluting more concentrated solutions of hydrochloric, acetic, and formic acids, the normalities of which were found to be: Hydrochloric, 0.5117; acetic, 0.2979; and a second solution, 0.4957; and formic, 0.2047. The solution of hydrochloric acid was standardized by the silver-chloride method and against potassium acid phthalate. A portion of the hydrochloric acid solution, diluted to approximately 0.1 N, was then titrated with a solution of barium hydroxide, which in turn was used to titrate solutions of acetic and formic acids made by diluting portions of the original acids to approximately 0.1 N. Phenolphthalein was used as the indicator in these titrations.

2. ESTIMATION OF END POINT

In Table 1 detail data are given for the titration of dilute solutions of hydrochloric, acetic, and formic acids, and also a portion of a distillate containing acetic and formic acids. ΔE denotes the change in

[5] See footnotes 3 and 4, p. 172.

potential between the electrodes when an increment of base ΔB is added to the solution. For the purpose of graphical interpolation the values of $B+\frac{\Delta B}{2}$ are given for the four curves in Figure 3. The agreement of the end points determined directly by noting the volume

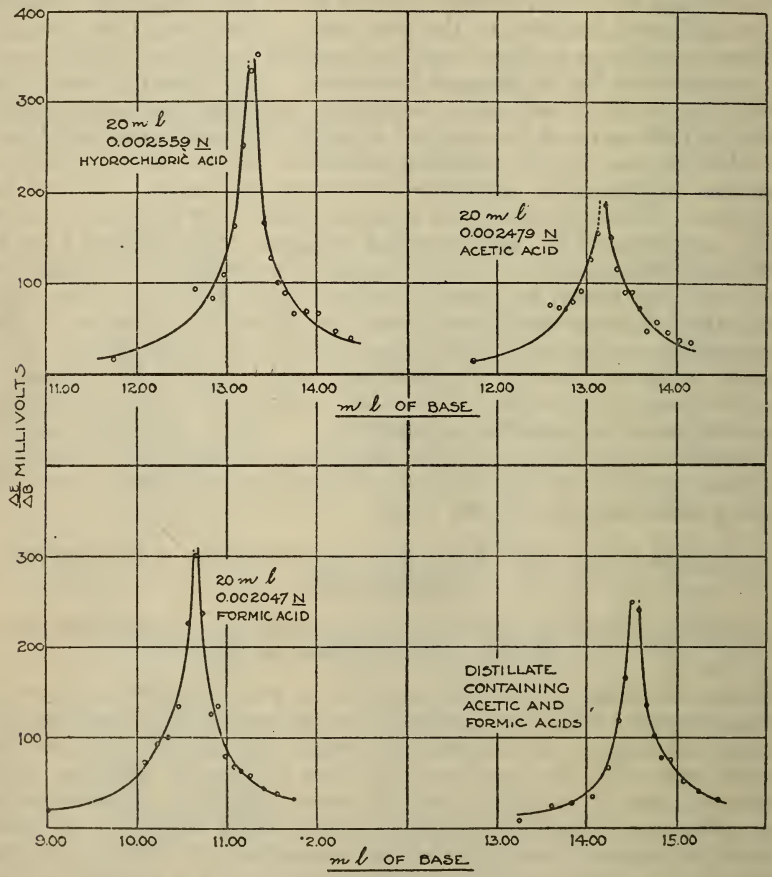

FIGURE 3.—*Differential potentiometric titration curves*

of base corresponding to a maximum value of $\frac{\Delta E}{\Delta B}$ and by graphical interpolation, indicates that for most purposes the shorter method is as satisfactory as the graphical method. In these titrations, the volume of the solution in the shielding tube was always less than 0.5 ml and the tube was flushed when the titration was within 1 ml of the end point on the acid side.

TABLE 1.—*Experimental results for titration of dilute solutions*

20 ml 0.002559 *N* hydrochloric acid				
Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.10				
3.00	2.90	1.45	17	6
6.00	3.00	4.50	15	5
9.00	3.00	7.50	21	7
11.00	2.00	10.00	19	10
	1.54	11.77	26	17
	New "zero" observed			
12.54	.26	12.67	24	92
12.80	.12	12.86	10	83
12.92	.13	12.99	14	108
13.05	.08	13.09	13	162
13.13	.08	13.17	20	250
13.21	.09	13.26	30	333
13.30	.08	13.34	28	350
13.38	.09	13.43	15	167
13.47	.07	13.51	9	128
13.54	.08	13.58	8	100
13.62	.09	13.67	8	89
13.71	.12	13.77	8	67
13.83	.13	13.90	9	69
13.96	.15	14.04	10	67
14.11	.19	14.21	9	47
14.30	.20	14.40	8	40
14.50				

20 ml 0.002479 *N* acetic acid				
Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.35				
3.00	2.65	1.33	30	11
6.00	3.00	4.50	23	8
9.00	3.00	7.50	22	7
11.00	2.00	10.00	15	8
	1.53	11.77	18	12
	New "zero" observed			
12.53	.15	12.61	11	73
12.68	.07	12.72	5	71
12.75	.07	12.79	5	71
12.82	.09	12.87	7	78
12.91	.09	12.96	8	89
13.00	.08	13.04	10	125
13.08	.09	13.13	14	155
13.17	.07	13.21	13	186
13.24	.08	13.28	12	150
13.32	.08	13.36	9	112
13.40	.08	13.44	7	88
13.48	.08	13.57	7	88
13.56	.07	13.60	5	71
13.63	.09	13.68	4	45
13.72	.13	13.79	7	54
13.85	.12	13.91	5	42
13.97	.12	14.03	4	33
14.09	.16	14.17	5	31
14.25				

20 ml 0.002047 *N* formic acid				
Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.19				
4.00	3.81	1.91	29	8
8.00	4.00	6.00	36	9
10.00	2.00	9.00	36	18
	.17	10.09	12	71
	New "zero" observed			
10.17	.11	10.23	10	91
10.28	.13	10.35	13	100
10.41	.12	10.47	16	133
10.53	.08	10.57	18	225
10.61	.09	10.66	27	300
10.70	.08	10.74	19	237
10.78	.09	10.83	11	122
10.87	.06	10.90	8	133
10.93	.09	10.98	7	78
11.02	.09	11.07	6	67
11.11	.08	11.15	5	62
11.19	.12	11.25	7	58
11.31	.17	11.40	7	41
11.48	.16	11.56	6	38
11.64	.20	11.74	6	30
11.84				

20 ml of distillate containing acetic and formic acids				
Burette readings	ΔB	$B+\frac{\Delta B}{2}$	ΔE	$\frac{\Delta E}{\Delta B}$
ml	*ml*	*ml*	*mv*	
[1] 0.20				
3.00	2.80	1.40	29	10
[2] 6.00	3.00	4.50	29	10
9.00	3.00	7.50	23	8
11.00	2.00	10.00	16	8
13.00	2.00	12.00	20	10
	.50	13.25	3	6
	New "zero" observed			
13.50	.24	13.62	5	21
13.74	.20	13.84	5	25
13.94	.22	14.05	7	32
14.16	.16	14.24	10	63
14.32	.07	14.36	8	114
14.39	.08	14.43	13	162
14.47	.08	14.51	20	250
14.55	.07	14.59	17	242
14.62	.09	14.67	12	133
14.71	.08	14.75	8	100
14.79	.08	14.83	6	75
14.87	.11	14.93	8	73
14.98	.16	15.06	8	50
15.14	.21	15.25	8	38
15.35	.24	15.47	7	29
15.59				

[1] Initial readings.
[2] Calculated amount of base equivalent to formic acid=4.20 ml.

26284°—30——12

The error arising from failure to bring the portion of solution in the shielding tube completely to the end point must be less than $\frac{0.5 \text{ ml}}{\text{ml acid} + \text{ml base}}$ 1 ml, and in these titrations is less than 0.02 ml. Clarke and Wooten [6] have formulated an equation for calculating the end point, but the symmetry of these titration curves seems to justify the estimation of the end point by graphical interpolation. It is also of interest to note that no marked irregularities are seen in the values of $\frac{\Delta E}{\Delta B}$ close to the end point on the alkaline side. It is suggested that the short time required for completing the titration after passing through the end point and the slight excess of base required, when added in small increments, to give a sufficient number of potential readings for plotting the curve on the alkaline side of the end point, explains in part the absence of irregularities in the observations, which might be expected to arise from the behavior of quinhydrone in more alkaline solutions. It is also of interest to note that in the data for the titration of the distillate containing formic and acetic acids no maximum occurs when the amount of base calculated to be equivalent to the formic acid content of the solution is added.

3. EFFECT OF ADDING POTASSIUM CHLORIDE TO SOLUTIONS

It was pointed out above that potassium chloride was added to increase the conductivity of the solutions to be titrated electrometrically. A solution, containing 0.19 g potassium chloride per milliliter, was prepared for this purpose and, since 0.3 ml was found to give sufficient galvanometer sensitivity, this quantity was used in all titrations, except some for which the results are shown in Table 2. The values shown in this table for the amount of base required for titrating acetic-acid solutions, to which varying quantities of potassium chloride solution were added, indicate that the quantity of base required decreases slightly with increasing quantities of potassium chloride. The agreement, however, between the observed and calculated volumes of base, used in titration of dilute solutions of hydrochloric, acetic, and formic acids of known acidities, shown later in Table 3, indicates that any error due to the addition of 0.3 ml of the potassium-chloride solution is small. Furthermore, if the base is standardized with solutions of the acids found in the distillates, any error due to potassium chloride should be compensated.

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[6] See footnote 3, p. 172.

TABLE 2.—*Effect of varying quantities of potassium-chloride solution in titrations of acetic acid*

[Solution containing 0.19 g potassium chloride per milliliter]

Acetic acid		Amount of potassium chloride solution added	Base required for titration	
Amount	Normality		Approximate normality	Amount
ml		*ml*		*ml*
10	0.002383	0.3	0.002	11.91 11.98 11.84
				Mean 11.91
		3.0	.002	11.64 11.77 11.68 11.77
				Mean 11.72
20	.002479	.3	.004	12.83 12.82 12.87
				Mean 12.84
		1.5	.004	12.83 12.77
				Mean 12.80
		3.0	.004	12.66 12.79
				Mean 12.73

TABLE 3.—*Electrometric titrations*

[Comparison of observed and calculated volume ratios]

Acid			Base required for titration		Volume ratios			
Formula	Amount	Normality	Approximate normality	Amount	Acids	Observed	Calculated	Deviation observed from calculated
	ml			*ml*				*Per cent*
HCl	20	0.002559	0.004	13.23 *13.16				
				Mean 13.20				
CH_3COOH	20	.002479	--------	*12.83 12.82 12.87	CH_3COOH / HCl	0.973	0.969	0.41
				Mean 12.84				
HCOOH	20	.002047	--------	10.51 *10.47	CH_3COOH / HCOOH	1.224	1.211	1.06
				Mean 10.49				
					HCOOH / HCl	0.795	0.800	−0.63

* Titration data given in Table 1.

TABLE 3.—*Electrometric titrations*—Continued

[Comparison of observed and calculated volume ratios]

Acid			Base required for titration		Volume ratios			
Formula	Amount	Normality	Approximate normality	Amount	Acids	Observed	Calculated	Deviation observed from calculated
	ml			*ml*				*Per cent*
HCl	20	.003070	0.005	13.60				
CH_3COOH	20	.002979	--------	13.25 13.20 13.23	CH_3COOH / HCl	0.974	0.970	0.41
				Mean--13.23				
HCOOH	20	.002047	--------	9.18 9.07	CH_3COOH / HCOOH	1.449	1.455	−0.41
				Mean---9.13				
					HCOOH / HCl	0.671	0.667	0.60
HCl	10	.003070	.002	15.15 15.21				
				Mean--15.18				
CH_3COOH	10	.002383	--------	11.91 11.98 11.84	CH_3COOH / HCl	0.785	0.776	1.15
				Mean--11.91				
HCOOH	20	.002047	--------	20.45 20.38	CH_3COOH / HCOOH	1.166	1.165	0.09
				Mean--20.42				
					HCOOH / HCl	0.673	0.667	0.87

4. EXPERIMENAL RESULTS OF TITRATIONS

In Table 3 are given the volumes of base required for the electrometric titration of dilute solutions of hydrochloric, acetic, and formic acids. These solutions were prepared by diluting a known portion of the standard solutions in a volumetric flask. The ratios of the observed volumes of base required for these dilute solutions are compared in the table with the volume ratios calculated from the dilution factors and normalities of the standard acid solutions. Detail titration data are given in Table 1 for the values in Table 3 marked with an asterisk (*) and in the last column the percentage differences between the observed and calculated volume ratios are given.

VI. TITRATION OF DISTILLATES

1. TITRATION OF DISTILLATES FROM SULPHURIC ACID SOLUTIONS CONTAINING ACETIC AND FORMIC ACIDS

In Table 4 the observed volumes of base required for distillates from sulphuric-acid solutions containing known amounts of acetic and formic acids are compared with the calculated volumes. The

latter were calculated from the volumes of base required for titrating dilute solutions of each of these acids of known acidities. Except for the low value observed for experiment No. 3, the observed volume of base required agrees well with the calculated volume.

TABLE 4.—*Comparison of calculated and observed amounts of base required to titrate distillates from sulphuric acid solutions containing known amounts of formic and acetic acids*

Experiment No.	Calculated amount of base required			Observed amount of base required for titration		Deviation of observed from calculated value
	Acetic acid	Formic acid	Total	Approximate normality	Amount	
	ml	*ml*	*ml*		*ml*	*Per cent*
1	8.78	2.96	11.74	0.003	11.82	0.7
2	8.78	2.96	11.74		11.58	−1.0
3	4.41	6.05	10.46	.005	10.04	−4.0
4	6.62	2.27	8.89		8.78	−1.2
5	5.29	3.63	8.92		8.97	.6
6	6.62	9.07	15.69		15.75	.4
7	6.62	2.27	8.89		8.91	.0
8	6.43	5.52	11.68	.004	11.62	−.5
9	8.56	1.75	10.31		10.22	−.9
10	10.29	4.20	14.49		*14.33	−1.1
11	10.29	4.20	14.49		14.29	−1.4
Mean						−1.0

* Titration data given in Table 1.

2. TITRATION OF DISTILLATES CONTAINING ACETIC ACID AFTER REMOVAL OF FORMIC ACID

After titrating portions of the distillates containing both acetic and formic acids, experiments were carried out in which the formic acid in portions of the distillates was oxidized by potassium permanganate and, after a second distillation, portions of the second distillates were titrated for acetic acid.

In Table 5 the observed volumes of base required for portions of distillates free from formic acid and containing acetic acid are compared with the volumes of base equivalent to the calculated acetic acid content. Although the percentage differences between the calculated and observed values in this table are larger than in Table 4, the agreement is perhaps satisfactory considering that the quantity of acetic acid in the original samples was about 0.1 per cent, and that a second distillation is involved in obtaining these observed values. The larger quantity of base required than calculated suggests that either the formic acid was not completely oxidized or that traces of the solution in the distilling flask contaminated the distillate. The addition of barium chloride to portions of the distillates acidified with hydrochloric acid did not prove to be entirely satisfactory in testing for such small quantities of sulphate, which if carried over mechanically from the distilling flask as sodium acid sulphate would require an appreciable quantity of base.

TABLE 5.—*Calculated and observed amounts of base required to titrate distillates containing acetic acid after removal of formic acid by oxidation and a second distillation*

Experiment No.	Calculated amount of base required	Observed amount of base required for titration		Deviation of observed from calculated value
		Approximate normality	Amount	
	ml		*ml*	*Per cent*
1	8.78	0.003	9.05	3.1
2	8.78		8.80	.2
3	7.94	.005	8.20	3.3
4	7.94		8.95	12.6
5	12.65	.004	12.92	2.1
6	13.19		13.56	2.8
Mean				4.0

VII. COMPARISON OF PHENOLPHTHALEIN WITH ELECTROMETRIC TITRATIONS

In order that the procedure outlined for distilling the volatile acids from battery electrolytes and separator extracts may be followed by titrating the distillate, using phenolphthalein as an indicator, rather than following the procedure for the electrometric titration, it was of considerable interest to compare some titration values obtained electrometrically with those obtained with phenolphthalein. In Table 6 are given some values obtained for the titration of dilute solutions of acetic and hydrochloric acids, both electrometrically and using phenolphthalein. Since no precautions were taken to protect the acid solutions from carbon dioxide while being titrated with phenolphthalein, and since the equivalence point for the titration of these dilute solutions is perhaps on the acid side of the phenolphthalein range, it is to be expected that a larger quantity of base would be required for the titrations with phenolphthalein than for those carried out electrometrically. If, however, the differences are due partly to indicator error and partly to carbon dioxide, it is to be expected that at least a portion of the errors from these sources would be compensated if distillates of approximately the same acidities were titrated under the same conditions as in standardizing the base.

TABLE 6.—*Comparison of electrometric and phenolphthalein values for titrating dilute solutions of known acidities*

(Base approximately 0.0038 *N*)

Acid			Base required for titration	
Formula	Amount	Normality	Electrometric method	Indicator method
	ml		*ml*	*ml*
HCl	20	0.002559	13.23	13.52
			13.16	----------
CH_3COOH	20	0.002479	12.83	13.11
			12.82	13.12
			12.87	----------

TABLE 7.—*Comparison of calculated and observed volumes of base required for phenolphthalein and electrometric titrations of distillates*

Present in distillate	Indicator values			Difference	Electrometric values		
	Calculated	Difference	Observed		Calculated	Difference	Observed
	ml	*Per cent*	*ml*	*Per cent*	*ml*	*Per cent*	*ml*
Acetic and formic acids	12.01	−1.2	11.87	1.6	11.68	−0.5	11.62
	14.79	−2.9	14.36	−.9	14.49	−1.1	14.33
	14.79	−.7	14.68	1.3	14.49	−1.4	14.29
Acetic acid only	13.56	.5	13.63	2.5	13.19	2.8	13.56
Mean		±1.3		±1.6		±1.5	

Accordingly in Table 7 are given the calculated and observed volumes of base required for titrating distillates from sulphuric-acid solutions containing known amounts of acetic and formic acids. The volumes of base required are calculated from the volumes of base given in Table 6 for the electrometric titration of acetic-acid solutions of known acidities, as well as from those given in Table 6 for titrations with phenolphthalein. The percentage deviation of the observed volumes of base required for the phenolphthalein titrations from the calculated volumes are within the experimental error of the distillations shown in Table 5.

It was pointed out above that the volatile organic acid content of the electrolyte of a cell which has been cycled may be considered to be acetic acid. This is probably also true for electrolyte which has stood in contact with active material of the positive plates, for formic acid can be oxidized not only by a charging current, but also by lead peroxide. Experiments in this laboratory show, however, that acetic acid is not oxidized by the active material of the positive plates. For these reasons no serious error would arise in many cases, if with no further attempt to remove the formic acid, the acid of the first distillate from a sample of electrolyte taken from a cell were considered to be acetic.

VIII. SUMMARY

A procedure has been described for the estimation of small quantities (of the order of 0.1 per cent) of volatile organic acids in the electrolyte of lead storage cells and in 30 to 40 per cent sulphuric-acid solutions of wood separator extracts. The volatile acids are distilled after neutralizing about 70 per cent of the sulphuric acid, and portions of the distillates titrated for total acidity. After oxidation of the formic acid in another portion of the distillate, the acetic acid is redistilled and estimated separately.

A modification of a recently described differential potentiometric titration apparatus has been devised and was used in titrating acid solutions of the order of a few thousands normal. It was found to be reliable in estimating the volatile organic acids in the distillates from the sulphuric-acid solutions.

Phenolphthalein titrations were compared with the electrometric titrations of the distillates in order that information might be available regarding the reliability of titrations made with phenolphthalein in such dilute solutions.

IX. ACKNOWLEDGEMENT

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