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Acid-Base Titrations in Nonaqueous Solvents

A Research Paper
Presented to
Alex R. Nisbet
Ouachita University

In Partial Fulfillment
of the Requirements for
Honors Special Studies

by
Gary Rice
May 1968

The acid-base titration is one of the simpler methods available to the analytical chemist. Many organic compounds exhibit acidic or basic properties. The majority of analytical work has always been done in water, which is a very convenient solvent, being readily available, nontoxic, inexpensive, and the most general solvent known. However, water is not a suitable solvent for titration of the weaker acids and bases.[1] Proper selection of solvent makes possible analytical determination of extremely weak acids and bases. Three solvent properties are important in determining the acid-base behavior of a solute.

The first property to be considered is the ability of the solvent to donate or accept protons. The true strength of any acid HA in the reaction $HA \rightleftharpoons p^+ + A$ is given by the equation $K_{HA} = \frac{a_{p^+} a_A}{a_{HA}}$, and is independent of the solvent. However, since bare protons cannot exist in solution, the reaction is a proton transfer described by the equations $HA + B \rightleftharpoons A + HB$ and $K = \frac{a_{HB} a_A}{a_{HA} a_B}$. This constant is a measure of the strength of the acid HA relative to a reference acid HB, which is usually a protonated solvent molecule.[2]

Solvents may be divided into four groups according to their proton donor and acceptor properties. Acidic solvents, such as acetic acid, readily donate protons but have little tendency to accept them. Basic solvents, such as liquid ammonia and pyridine, accept protons but are very weak donors. Amphiprotic solvents donate and accept protons about equally. Water is in this class, as are methanol and ethanol. Aprotic solvents do not readily participate in proton-exchange reactions. This last group is mainly hydrocarbons and substituted hydrocarbons.[3]

A given solvent may have either a leveling or an enhancing effect on solute acids and bases, depending upon the solvent acidic and basic properties. In water, hydrochloric acid and perchloric acid are much stronger proton donors than the hydronium ion, and therefore are leveled to it's strength. In glacial acetic acid, perchloric acid is a much stronger acid than hydrochloric acid, as hydrochloric acid is a weak acid relative to the protonated solvent molecule. Glacial acetic acid is said to be a differentiating solvent for these two acids.[4]

The second important solvent property relates to the autoprotolysis constant, K_s. Autoprotolysis is a proton-exchange reaction in which one solvent molecule acts as an acid and another acts as a base. The extent of the reaction depends on the solvents' acid strength, its base strength, and its dielectric constant. If K_s for a given solvent is relatively large, as for formic acid, its leveling influence on solute acids and bases renders it relatively useless as a solvent medium.[5]

The third property is the dielectric constant, which is defined by ϵ in the equation $F = \frac{Q_1 Q_2}{\epsilon r^2}$. Thus, a high dielectric constant results in a small force. In the reaction $A + S \rightleftharpoons B + SH^+$, the conjugate acid-base pair A and B differ by a proton and one unit of charge. If A is neutral and B a monovalent anion, the reaction also involves a separation of charges and will be favored by a solvent of high dielectric constant, in which the work of charge separation is small.[6]

Several things must be considered when selecting a solvent for a particular titration. Many organic acids and bases cannot be titrated in water due to their slight solubility and weak acidic or basic strength. The solvent chosen for titration of a weak base should be acidic, or at least non-basic; conversely, it should be basic, or non-acidic, for titration of a weak acid. As far as possible, the solvent should also be easily available, inexpensive, able to dissolve the titrated substance and titrant, and it should not enter into side reactions with any of the species present.[7]

Figure 1 shows two titrations of pyridine, a weak organic base, using perchloric acid as the titrant. The aqueous titration (A) is unsatisfactory because of the uncertainty of the end point. Repeating the titration in glacial acetic acid (B), a clearly defined end point is achieved. Glacial acetic acid, unlike water, is not sufficiently basic to compete with pyridine for hydrogen ions.

A white precipitate occuring in the titration of pyridine in glacial acetic acid was identified as the salt pyridinium perchlorate. The precipitate was separated from the mother liquor by suction filtration and washed with glacial acetic acid, in which it was virtually insoluble. It was also insoluble in benzene, ethanol and ethyl ether, indicating that it was probably a polar or ionic compound. It was slightly soluble in hot ethanol and soluble in hot benzene. It was easily soluble in cold water. The water solution gave off an odor of pyridine which became much stronger upon addition of a base. Since the original precipitate was washed thoroughly, any pyridine present was in the precipitate. The water solution was treated with a large quantity (2-3 grams) of sodium nitrite to effect reduction. Addition of silver nitrate produced a white precipitate which was soluble in an ammoniacal solution and which discolored very slowly (dim light) on standing. Since silver salts of acetate, nitrate, and perchlorate are fairly soluble in water, this second precipitate was judged to be silver chloride, the chloride ion being produced by reduction of perchlorate ion.

Figure 2 shows three titrations of phenol. Phenol, a weak organic acid, must be titrated in a solvent of very low acidity. The aqueous titration (A), using potassium hydroxide as the titrant, has no discernible end point because of the high acidity of water relative to phenol, phenol being only slightly more acidic than water. Titration with potassium hydroxide in ethanol (B) gives a curve similar to that for aqueous titration because of the acidity of ethanol. In a comparison of ethanol and water as acids in isopropanol solution, ethanol was found to be 0.95 as acidic as water.[8] Titrating with sodium methoxide in benzene (C), the curve is greatly improved but still unsatisfactory. The lack of a clear end-point is presumed due to the very weak titrant solution, sodium methoxide being only slightly soluble in benzene. A more soluble base should be capable of producing a satisfactory end point.

In conclusion, it should be said that while much work remains to be done in the field of nonaqueous solvents in determining pK values of acids, bases, and indicators, and in developing a system similar to the pH scale of aqueous solutions, the use of nonaqueous solvents is quite promising, permitting the analytical chemist to carry out many determinations which would be impractical using other methods.

Footnotes

[1] Alexander I. Popov and Ronald T. Pflaum, *Introductory Analytical Chemistry* (Boston: D. C. Heath and Company, 1966), p. 68.

[2] *Ibid*, pp. 102-104.

[3] *Ibid.*, p. 105.

[4] H. A. Laitenen, *Chemical Analysis* (New York: McGraw-Hill Book Company, Inc., 1960), pp. 60-61.

[5] *Ibid*, pp. 62-64.

[6] *Ibid.*, pp. 64-65.

[7] Popov and Pflaum, pp. 105-106.

[8] Laitenen, p. 63.

Bibliography

Ayres, G.H. *Quantitative Chemical Analysis*. New York: Harper and Row, Publishers, 1958.

Casey, A.T. and Starke, K. "Acidimetric Titration of Metal Acetates in Glacial HAc," *Analytical Chemistry*, 31: ~~1876~~ 1060. 1959. show year

Kolling, O.W., and Smith, M.L. "Selected Triphenylmethane Dyes as Acid-Base Indicators in Glacial HAc," *Analytical Chemistry*, 31: 1876. 1959.

Laitinen, H.A. *Chemical Analysis*. New York: McGraw-Hill Book Company, Inc., 1960.

Paul, R.C., Vasisht, S.K., Malhotra, K.C., and Pahil, S.S. "Fluorosulfonic Acid as a Titrant in HAc," *Analytical Chemistry*, 34: 820. 1962.

Popov, A., and Pflaum, R. *Introductory Analytical Chemistry*. Boston: D.C. Heath and Company, 1966.

Sisler, H.H. *Chemistry in Nonaqueous Solvents*. New York: Reinhold Publishing Corporation, 1961.

Figure 1

A: Titration of pyridine with $HClO_4$ in water

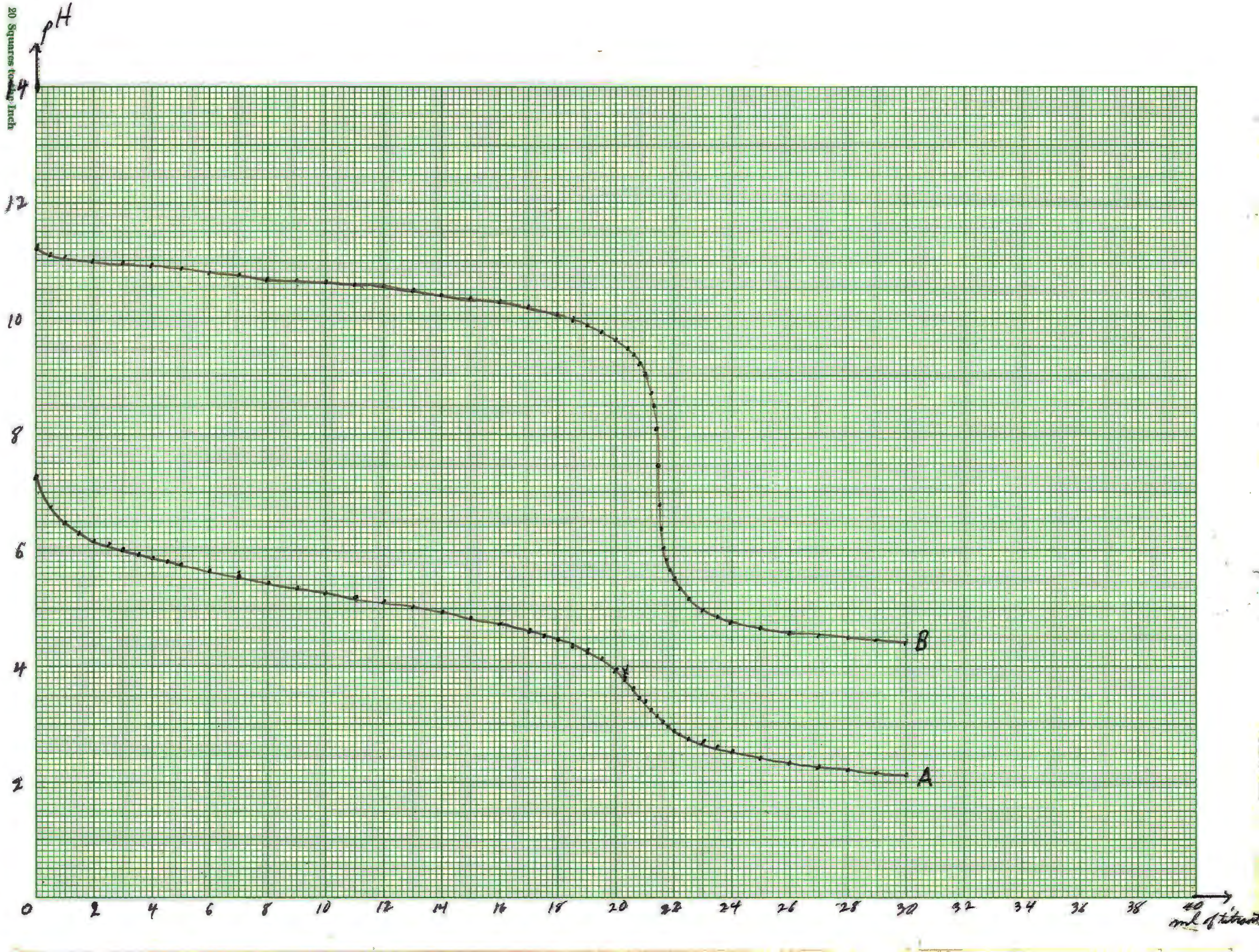
B: Titration of pyridine with $HClO_4$ in glacial acetic acid

Figure 2

A: Titration of phenol with KOH in water

B: Titration of phenol with KOH in ethanol

C: Titration of plenol with CH_3ONa in benzene


20 Squares to the Inch
pH
14
12
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4
6
8
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12
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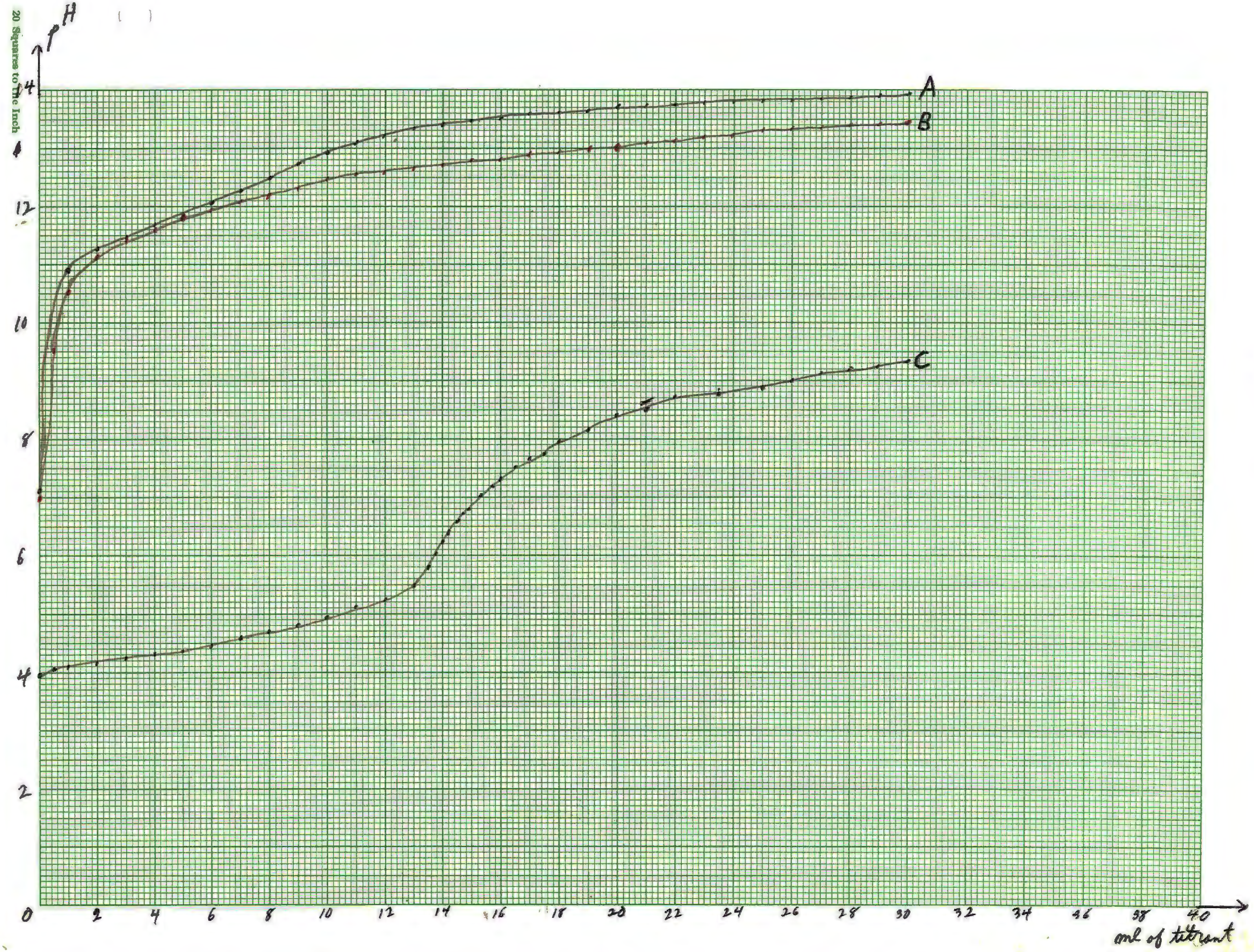
16
18
20
22
24
26
28
30
32
34
36
38
40
ml of titra
A
B

20 Squares to the Inch
pH
14
12
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0
2
4
6
8
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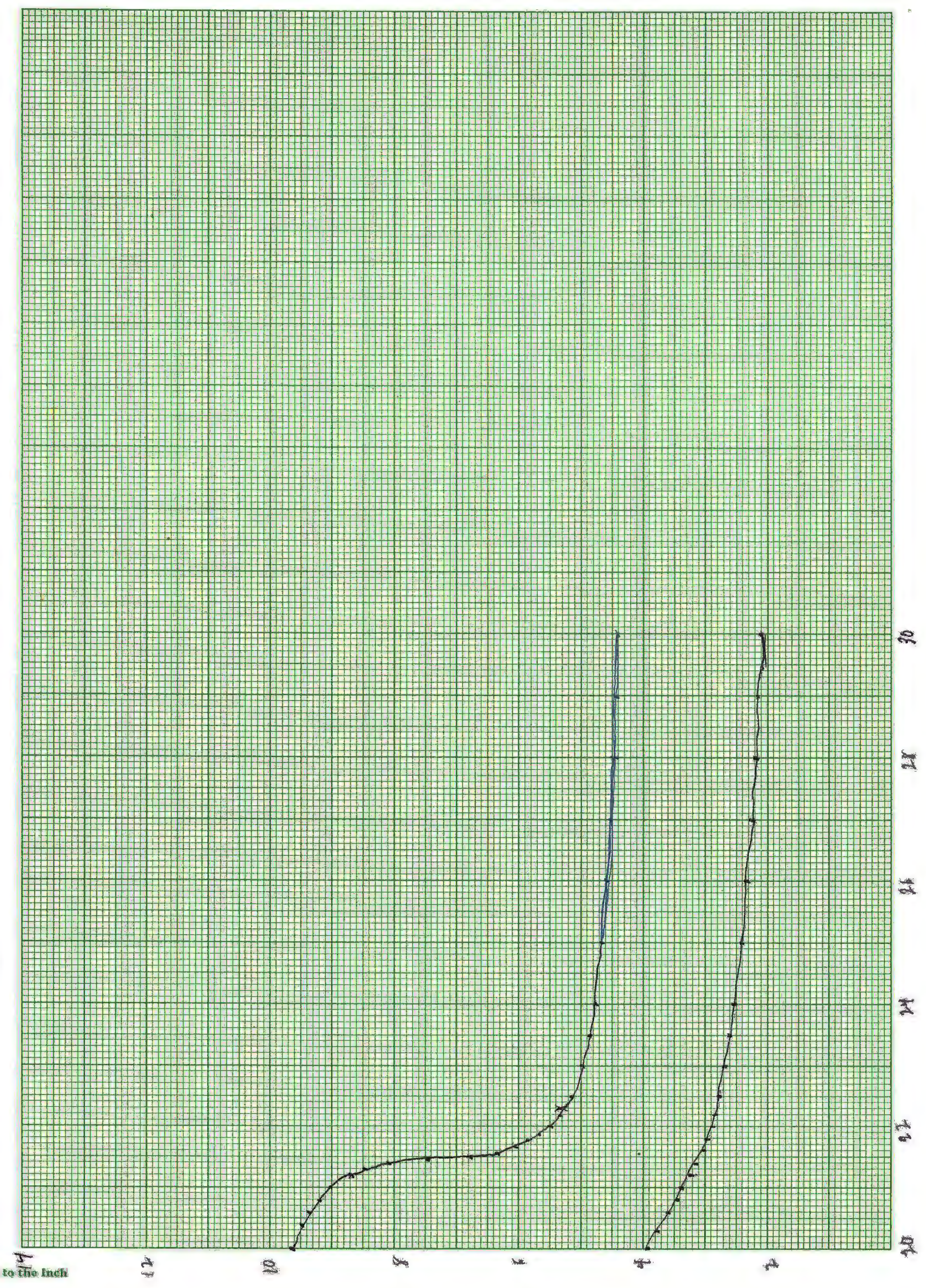
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
ml of titrant
A
B
C

Titration of pyridine with $HClO_4$ in water

ml of $HClO_4$	pH	ml (cont.)	pH (cont.)
0.0	7.24	18.0	4.44
0.5	6.72	18.5	4.35
1.0	6.48	19.0	4.25
1.5	6,30	19.5	4,11
2.0	6.16	20.0	3,91
2.5	6,09	20,3	3,79
3,0	6.00	20.6	3,60
3,5	5,91	20.8	3,46
4.0	5,84	21.0	3,37
4.5	5,78	21,2	3,23
5,0	5,72	21.4	3,12
6,0	5,61	21.6	3,02
7,0	5,51	21,8	2,96
8,0	5,43	22.0	2,88
9,0	5,36	22,2	2,81
10,0	5,28	22.5	2,74
11,0	5,20	23,0	2.68
12,0	5,11	23.5	2,60
13,0	5,02	24,0	2,51
14,0	4,92	25,0	2,40
15,0	4,81	26,0	2,32
16,0	4,72	27,0	2.25
17,0	4,60	28,0	2,20
17.5	4,51	29,0	2,16
		30,0	2,11



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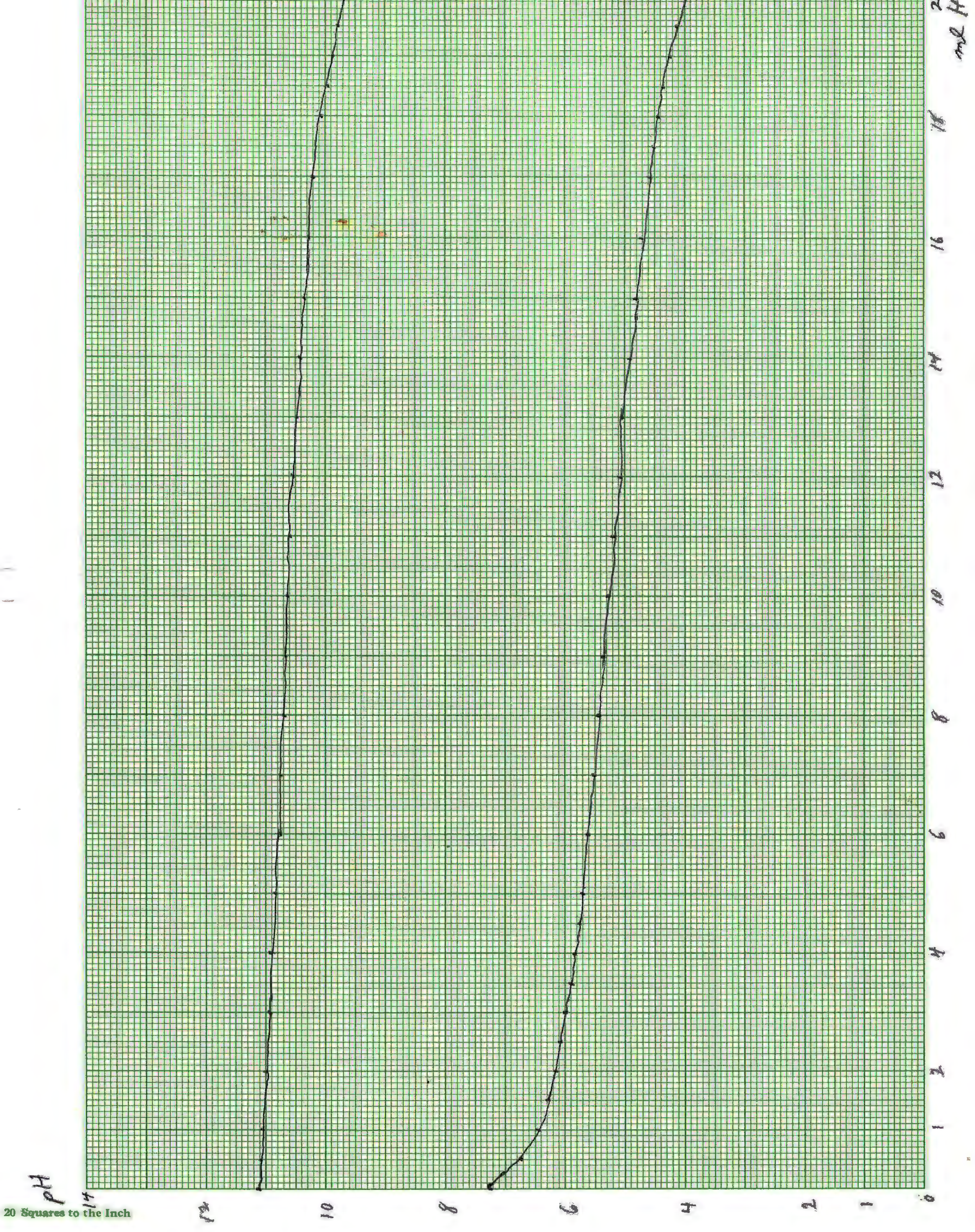
pH
14
12
10
8
6
4
2
1
0
ml H
1
2
4
6
8
10
12
14
16
18
2
20 Squares to the Inch