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UNIVERSITY OF LOUISVILLE

CONSTRUCTION AND APPLICATION OF
" A VACUUM TUBE POTENTIOMETER

A Thesis

Submitted to the Faculty

Of the Graduate School

In Partial Fulfilment of the

Requirements for the Degree of

Master of Science in Chemical Engineering

Department of Chemical Engineering

By

R. Palmer Benedict
"

1935

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wishes to express his deep appreciation
of the kind assistance and encouragment
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Dr. R. C. Ernst

TABLE OF CONTENTS

List of Illustrations	2
List of Tables	3
List of Curves	4
Introduction	5
Historical	8
Theoretical	12
Experimental	25
I Construction and Operation	26
II Application to Acid-Base Titrations	35
III Application to Lead Chromate Pigments	49
Conclusions	55
Bibliography	57

LIST OF ILLUSTRATIONS

Vacuum Tube Potentiometer

28

LIST OF TABLES

I	Titration of an Acid with a Base	39
II	Titration of an Acid with a Base	41
III	Titration of an Acid with a Base	43
IV	Titration of an Acid with a Base	45
V	Lead Chromate Colors	53
VI	Lead Chromate Colors	53

LIST OF CURVES

I	Titration of an Acid with a Base	46
II	Titration of an Acid with a Base	46
III	Titration of an Acid with a Base	46
IV	Titration of an Acid with a Base	46

INTRODUCTION

In a previous investigation of a vacuum tube potentiometer designed for application to potentiometric methods, the instrument constructed¹⁷ was found to lack sufficient sensitivity and diversity of application.

The present investigation was undertaken to redesign the instrument to overcome the difficulties experienced with the previous instrument. It is further planned to apply the instrument to industrial operation.

The application of the instrument to potentiometric titrations using the quinhydrone and glass electrodes, and to conductometric titrations will be undertaken. An attempt will be made to apply the instrument with the glass electrode to determine the pH of lead and chromate solutions as related to the resulting color of lead chromate pigments.

The apparatus is essentially a vacuum tube potentiometer so constructed that it will indicate the presence of a very small potential difference, and at the same time draw practically no current. It is to be constructed from commercial radio parts that can be easily obtained. It is to be operated from 110 volts AC.

The purpose of the investigation is to demonstrate that through the application of vacuum tubes, an instrument of general electrochemical utility can be built at low cost that will replace expensive galvanometers of high resistance, and that will reduce the errors due to audible measurements.

HISTORICAL

The application of vacuum tubes to the measurement of electrochemical potentials is not new. The first published circuit was developed by Goode¹ in 1922. Goode applied the vacuum tube to the quinhydrone electrode. He placed the cell in the grid circuit of the tube and calibrated a galvanometer in the plate circuit of the tube to read the potential. This circuit was operated entirely from batteries. Great care was necessary to make sure that all the potentials on the tube were the same whenever the instrument was used, in order that the calibration would be valid.

Calhane and Cushing² in 1923 constructed an instrument similar to that of Goode, except that they applied a grid bias to the tube, whereas Goode did not. The only advantage of their instrument over that of Goode is that the grid current of the tube is of a lower order. The same care in setting up the instrument is necessary.

Partridge³ constructed an instrument similar to the direct coupled system of Clark⁴. This circuit was published in 1929. The Clark circuit was first published and patented about 1915. The difference between the circuit of Partridge and the circuit of Clark is that Partridge

used a tetrode and a triode, where Clark used two triodes. This system used batteries for a source of power and used a method of measurement similar to the method used in the instrument constructed in this investigation. The Partridge circuit is unstable, showing a tendency for the plate current of the last tube to increase with time of operation. Otherwise, it represented the best that could be obtained with the tubes available at the time.

Rosebury⁴ built an instrument similar to that of Goode except he used a commercial tetrode instead of a triode. The circuit is no doubt accurate, but it is very complicated and requires more apparatus than the standard glass electrode potentiometer, and it is no more accurate.

Goode⁵ also built a direct reading pH meter using three tubes known as UV199. He included an elaborate method for restandardization. The circuit was the same as that of Clark. It was a practical instrument, but it is now out of date, because the tubes have been replaced by superior tubes.

In 1930 Major Loftin and Captain White⁶ of the Signal Corps developed a direct coupled amplifier. While this amplifier was developed as

an audio frequency amplifier, it can be slightly modified and used as a direct current amplifier.

In 1934 Benedict¹⁷ built an instrument using a modified Loftin-White circuit. The instrument was of simple construction and produced fair results, but it was not entirely satisfactory as it was not very sensitive and flexible.

THEORETICAL

Within the last two years there have been developed vacuum tubes that lend themselves very well to the construction of a vacuum tube voltmeter of very high resistance and sensitivity. The necessity of a high resistance in a voltmeter is apparent when one considers the resistance of the source of potential used in electrochemical measurements.

In order to more clearly understand how a vacuum tube may be made to perform the operations of a galvanometer, it will be necessary to discuss at length the theory of operation of a vacuum tube.

It is a well known fact that when a body is heated to incandescence it will emit electrons. This property is made use of in vacuum tubes. The filament of the tube is heated and it emits electrons. Due to the property of these electrons, if a positively charged plate is placed in close proximity to the filament, the electrons will be attracted to this plate. The result is a flow of electrons, and hence a flow of current. But if this plate were made negative with respect to the filament, no current would flow, because the electrons would be re-

elled from the plate. If an alternating current were impressed across the system, current would flow only during the half of the cycle in which the plate was positive. This is the action of the rectifier tube that is used to convert alternating current into direct current. (The output of the rectifier must be smoothed by the use of adequate filters.)

If another plate that is porous to electrons is introduced between the first plate and the filament, it will receive its share of electrons emitted by the filament. This second plate is actually a coil or loosely woven screen of wire placed between the filament and the plate, and it is called a grid. If no charge is placed on the grid, it has no effect upon the action of the tube. But if the grid is made positive with respect to the filament, it will attract electrons. The grid however, is not solid, so only part of the electrons will strike it. The electrons that do not strike the grid are accelerated and eventually strike the plate. Since all the electrons that were emitted by the filament did not reach the plate when the grid was free, because they did not have enough velocity to get there; when the grid is made positive, more current will flow in the plate circuit, because the electrons have been accele-

rated and now more of them reach the plate.

If on the other hand the grid had been made negative with respect to the filament, then the electrons would have been repelled by the grid (none would strike the grid if it were made sufficiently negative), and fewer electrons would have reached the plate. Consequently when the grid is negative, less plate current will flow. If an alternating current is impressed upon the grid, the plate current of the tube will have the same wave form (if the amplitude is not too great) that the grid voltage has, except that instead of being of the zero axis, it will be entirely on the positive side of the zero current axis. The plate current of an ordinary vacuum tube is never negative.

The foregoing discussion of the action of the grid has been qualitative; its quantitative action, however, depends upon the actual construction of the tube. If the grid is widely spaced and placed closer to the filament than to the plate, the change in plate current will be much greater for a given change in grid voltage than if the grid were closer to the plate than to the filament. The ratio of the change in grid voltage to a change in plate voltage that will produce the same change in plate current, for a small

changes, is called the amplification factor of the tube, or it is sometimes called the μ of the tube. It would seem that the μ of a tube could be increased without limit by making the grid with smaller openings and moving the plate farther away. It would be well to mention the fact that a tube must not draw grid current, which it will do if the grid is positive, because when the grid draws current, it will be useless for the purpose for which it is to be used as will be shown later. The μ of the tube cannot be increased without limit, because as soon as the plate is moved away from the filament, the plate current will decrease. This is due to the fact that the electrons will not be moving fast enough to reach the plate. Since the grid is larger and must be negative, the plate current will suffer a further decrease. Therefore, as the μ increases, the plate current will decrease until it is infinitesimal. This low plate current brings in another factor--the plate resistance, which is the plate voltage divided by the plate current. It is a well known fact the the load on the generator must be equal in resistance to the generator in order to have the most efficient use of the power supplied. If the plate current approaches zero, the plate

resistance will approach infinity, and consequently the load resistance must approach infinity. It has been demonstrated mathematically that in order to utilize 50% of the μ of the tube, the load resistance must equal the plate resistance. This means that very high voltage drops will occur in the load. Assuming that the load resistance could be made equal to the plate resistance, the current would be so small that the gain could not be used. It might be argued that the plate voltage might be raised to increase the plate current by increasing the velocity of the electrons. This gives rise to another difficulty. The filament gives off only so many electrons, those that do not reach the plate float around in the space between the filament and the plate and saturate it. This saturation effect blocks any further electrons from reaching the plate and increasing the plate current.

By adding another element to the tube some of the bad effects of removing the plate from close proximity of the filament can be partially overcome. This fourth element is called the screen grid, and it is a screen surrounding the plate. The effect of it is to speed up the electrons that get past the first or control grid, so that they reach the plate

and cause an increase in plate current. As this screen grid is positively charged, it receives some of the electrons, but the increase in the number of electrons reaching the plate is greater than the number absorbed by the screen grid. This tube still has a rather high plate resistance, but is very much lower than that for a three element tube of the same μ . If there some way of increasing the plate voltage without causing secondary emission, the plate resistance of the tube could be further reduced. This can be done quite simply by the introduction of a fifth element, which is another grid between the screen grid and the plate, called the supressor grid. The grid is normally connected to the filament and serves to trap any secondarily emitted electrons, thus keeping the space surrounding the plate free from electrons with no velocity, which tend to block the plate from the electrons emitted by the filament. This grid can be used fro other functions as well, but they have no bearing on this discussion and will be omitted.

There is another mathematical relation between the grid voltage and the plate current. It is the mutual conducatance or G_m of the tube. The change in plate current divided by the change in grid

voltage necessary to produce that change in plate current multiplied by 1,000,000 is the G_m and its units are micromhos. (A mho is a reciprocal ohm.) It can also be shown that the G_m is equal to the μ divided by the plate resistance in megohms.

In order to be of the slightest use in electrochemical measurements, the instrument must not draw current from the source of potential it is measuring, because the cells used in the measurements have a high internal resistance. If some current is drawn from them, the potential measured by the instrument would be the actual voltage of the cell minus the drop in the internal resistance of the cell. In conductance measurements with a Wheatstone bridge this consideration is not so important, but the higher the resistance of the indicating device, the sharper the balance. It may be of some interest to note that the input resistance of a vacuum tube is in the order of 10^{10} ohms.

This brings about the point of how to utilize the vacuum tube for voltage measurements. The cell whose voltage is to be measured can be connected in the grid circuit of the tube in series with a small battery arranged with a switch so that the battery could be connected either thru the cell or directly to the grid. The potential change in the

battery necessary to bring the plate current to the same value as when the cell was in the circuit is the potential of the cell. Or a curve of plate current vs. grid voltage could be plotted and the voltage of the cell determined from the curve. The second method is not very satisfactory, because the curve would change every time any part of the circuit changed. Since it is almost impossible to keep all the parts of a vacuum tube circuit constant for any length of time, frequent recalibration of the instrument would be necessary. With the first method, a change in the parts of the circuit would have very little effect upon the system, because these changes would be slow and the time consumed in making a reading is so short as to make the effect of the changing conditions nil. There is a drawback to the use of a single tube, however, it is that the change in plate current of the tube for a change in grid voltage of the order of the voltages used in electrochemical measurements for the necessary accuracy, is so small in comparison with the total plate current that it would be difficult to obtain an instrument that would show the change in plate current. This is true of either method.

When an attempt to use more than one tube is made there are several difficulties that must be overcome. It is very simple to make an amplifier

of one or more tubes that will amplify an alternating current as is testified by the amplifier of a radio set. But the problem is, in a manner of speaking, to amplify a direct current to such a point that it can be measured. It is easy to see that any system that depends upon transformers, or capacities to transfer the voltage from one tube to the next will not work. The only mechanism that will satisfactorily transfer a direct current voltage is a resistance. This means that the plate of one tube must be directly connected to the grid of the next tube. This is not so difficult as it seems. All that is necessary is that the change in grid voltage of the first tube amplified is applied to the grid of the second tube in such a manner that for one grid voltage on the first tube, the second tube will have one plate current; and that for some other grid voltage on the of the first tube, the plate current of the second tube has some other value. If the set up is such that the plate current of the second tube is a function, not necessarily linear, of the grid voltage of the first tube, and the first method of measurement is used, the problem is solved.

The foregoing condition can be fulfilled

if in the plate circuit of the first tube there is a resistor of suitable value so that most of the μ of the first tube is utilized, and the drop across this resistor applied to the grid of the second tube in series with a voltage of such a value as to leave only the proper grid bias on the second tube. From this it will be seen that the change in plate current of the second tube will be the product of change in grid voltage of the first tube, the G_m of the first tube, the load resistance, and the G_m of the second tube. An the whole set-up will function as one tube with the G_m that is the product of the G_m of the first tube, the load resistance and the G_m of the second tube. Thus two tubes are made to function as one and the requirement for a direct current amplifier is fulfilled.

This set up can be applied to another method that is a variation of the first method of balancing. Instead of one battery in the grid circuit there are two arranged with potentiometers so that the voltages can be varied. One of the voltages is made equal to the proper operating bias, and the other is varied until its voltage is exactly equal and opposite to the cell voltage. This point can be determined by connecting the positive terminal

of the bias battery to the filament and arranging the other terminal so that it can be connected to the grid directly or thru the bucking battery and the cell to the grid. The bucking battery voltage is equal to the voltage of the cell when the plate current of the second tube shows no change when the negative terminal of the biasing battery is connected in either position.

When the set up is used for conductance measurements the bucking battery is omitted, but the switching arrangement is retained. It is connected so that the grid is connected to the biasing battery either thru the galvanometer terminals of the Wheatstone bridge or direct. The bridge is balanced when there is no change in plate current of the second tube when the grid is changed from one connection to the other. The potential source of the bridge may be any that is available. If the bridge is one that has non-inductive resistances, and practically no internal capacity, almost any frequency within reason may be used. If the bridge is not of the highest quality, it will probably be necessary to use a very low frequency source, because the coupling thru the inductance and capacity in the bridge

will not allow a sharp balance point to be obtained. With a high quality bridge it is possible to use a vacuum tube oscillator, and it is suggested that a circuit with more inductance than capacity and with a battery bias be used to suppress harmonics. It is not necessary to use audible frequencies with a good bridge. If a loud speaker is connected in the plate circuit of the second tube thru the proper type coupling unit, an audible as well as visible indication of the balance is obtained. If a radio frequency oscillator is used it will be necessary to shield all parts of the circuit, as the amplifier by its very nature is a very sensitive receiver and can pick up signals from the oscillator as well as it can from the bridge. A high frequency is desirable in conductance measurements in order to eliminate polarization. If audible balance is desired at radio frequencies, the bias battery of the oscillator may be replaced by a grid leak and condenser of such a value as to make it self-modulating.

The amplifier must be well shielded, because it is very sensitive to any sort of electrical disturbance.

EXPERIMENTAL

- I CONSTRUCTION AND OPERATION
- II APPLICATION TO ACID-BASE TITRATIONS
 - a QUINHYDRONE TITRATIONS
 - b GLASS ELECTRODE TITRATIONS
 - c CONDUCTANCE TITRATIONS
- III APPLICATION TO LEAD CHROMATE PIGMENTS

I CONSTRUCTION AND OPERATION

The instrument is shown diagrammatically in Figure 1. The operation for a visual balance is as follows:

The cell potential is introduced across the input terminals and applied to the grid of the 58 tube. In addition to the cell potential there is a potential on the grid of the 58 tube for the purpose of keeping the grid negative at all times. This potential is supplied by the battery B_2 and the resistor R_3 . The potential of the cell is opposed by means of the potential obtained from the battery B_1 and the resistors R_1 and R_2 . This opposing potential may be measured by means of a millivoltmeter or any other means that are desirable. If the opposing potential of the battery is the same as the potential of the cell, there will be no change in the grid potential of the 58 tube when the switch S_1 is moved from one position to the other. If the cell potential is not balanced out, there will be a change in the grid potential of the 58 tube, and hence a change in its plate current. This change in plate current will cause a change in the drop across the resistor R_4 which in turn will cause a change in the grid potential of the 2A3 tube and hence a change in the plate current of the 2A3 tube.

COMPONENTS OF FIGURE 1

R₁ 100 ohm potentiometer
R₂ 20 ohm potentiometer
R₃, R₆ 200 ohm potentiometers
R₄ 2,000 ohm potentiometer
R₅ 50,000 ohm potentiometer
R₈, R₇ 10,000 ohm potentiometers
R₉, R₁₆, R₁₇ 500,000 ohm fixed resistors
R₁₀ 5,000 ohm fixed resistor
R₁₁, R₁₈ 25,000 ohm fixed resistors
R₁₂ 100,000 fixed resistor
R₁₄, R₁₅ 50,000 ohm fixed resistors
R₁₉ 40 ohm rheostat
S₁ SPDT push-button switch
S₂ DPDT switch
S₃, S₄, S₅, S₆, S₇, S₈, S₁₀, S₁₁ SPST switches
S₉ SPDT switch
J₁, J₂, J₃, J₄, J₅, J₆, J₇ closed circuit jacks
J₈ open circuit jack
C 8 mfd electrolytic condensers
L 20 henry chokes
V 0-400 millivoltmeter
M₁ 0-L milliammeter
M₂ 0-15-150 milliammeter
T₁, T₂ Power transformer: 700 volt CT.
2.5 volt ct., 5 volt ct., 5 volt secondaries
115 volt primary

The plate current of the 58 tube is about 0.8 milliamperes and the value of the resistor R_p is about 500,000 ohms, this makes the drop about 400 volts. This drop leaves the grid of the 2A3 tube about 300 volts above the ground potential, but the cathode of the 2A3 tube is approximately 350 volts above the ground, which leaves the proper operating bias of 50 volts negative on the grid of the 2A3 tube. The drop in the resistor R_p is adjusted so that the 2A3 tube is drawing the proper plate current, 50 milliamperes, by varying the screen grid potential of the 58 tube by means of the resistor R_s .

When using the apparatus for visual indication of balance, the switch S_3 is closed and the switch S_4 is opened. This stabilizes the operation of the apparatus by keeping the cathode of the 2A3 tube approximately 350 volts above the ground. In the plate circuit of the 2A3 tube are the output terminals O_1 combined with the switch S_5 to make provision for connecting a loud-speaker or an additional milliammeter in the output circuit. The switch S_5 provides means of switching the device connected to the output O_1 in or out of the circuit. The resistor R_b in conjunction with the battery B_2 of the rectifier provides a means of bucking the

current thru the milliammeter M_2 , the output O_2 , and the jack J_2 , in such a manner that the net current thru all of them is approximately zero. This is done so that the 0-1 milliammeter may be plugged into the jack J_2 to increase the sensitivity of the instrument.

The resistors R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , and R_{15} are multipliers for the milliammeter to make it read the voltages of the various parts of the circuit. At the jack J_1 is read the bias supplied by the battery B_2 and the resistor R_2 ; at jack J_2 , the bias supplied by the resistor R_4 ; at jack J_3 , the bucking bias supplied by the drop in the resistors R_7 and R_{15} ; and jack J_4 , the voltage of the screen grid of the 58 tube; at jack J_5 , the potential of the cathode of the 2A3 tube; at the jack J_6 , the plate potential of the 2A3 tube; at the jack J_7 , the plate potential of the 2A3 tube; and at the jack J_8 , the milliammeter is used as an indicating meter to show a change in the plate current of the 2A3 tube for very accurate work.

When the device is used for audible measurements, the switch S_4 is closed and the switch S_2 is opened. Then the system is practically the same as the Loftin-White circuit, which has been fully discussed in the literature.

The potentials for the plates and the filaments of the vacuum tubes are obtained from the transformers T_1 and T_2 . The alternating current is rectified by the type 80 full-wave rectifiers and filtered by the chokes L and the condensers C .

For visual indication of balance the switches S_1 , S_2 , S_3 , and S_{11} are closed and the switch S_4 is opened. Then the AC current is turned on by the means of the switch S_{10} . The cell is connected to the input terminals and a millivoltmeter to its proper terminals. The resistors R_7 and R_8 are adjusted so that there is no drop across them. The bias of the 58 tube is adjusted to -3 volts by means of the resistor R_9 , then the screen grid voltage of the 58 tube is adjusted so that the plate current of the 2A3 tube is 50 milliamperes by means of the resistor R_6 . Then the switch S_5 is closed and the resistor R_5 is adjusted so that the milliammeter reads almost zero. Then the plug is inserted in the jack J_6 and the resistor R_{10} is placed in the position of minimum resistance, then the switch S_7 is opened. The resistance of R_{10} is increased and at the same time the resistor R_6 is adjusted so that the 0-1 milliammeter stays on scale. Then the switch S_1 (This switch is of the push-button

type, wired so that in the normal position the grid of the 58 tube is connected to the bias battery.) is depressed and the resistors R_1 and R_2 (R_1 is for coarse and R_2 is for fine adjustment) adjusted so that the reading of the milliammeter in the jack J_6 is the same as when the switch S_1 is released. The potential of the cell is then equal and opposite to the voltage read on the millivoltmeter. The switch S_2 will reverse the potential of the bucking battery.

When the instrument is used for audible measurements the switches S_3 , S_8 , S_9 , and S_{11} are left open and S_4 and S_{10} are closed. Then the screen grid potential is adjusted until it is the same as before. Then the resistors R_4 and R_7 are adjusted so that when the plate current of the 2A3 tube is 50 milliamperes, the potential measured at the jack J_2 is 20 volts and the potential at the jack J_3 is 3 volts less. The instrument is now adjusted as a Loftin-White amplifier, and may be used for any purpose that may be desired. It will also function as a detector of a modulated wave.

When the instrument is used for a visual indicator for conductance measurements, it is adjusted in the same manner as for potentiometric measurements. However, the balancing is different.

The switch S_2 is opened and the Wheatstone bridge is adjusted so that there is no change in the deflection of the 0-1 milliammeter when the switch S_1 is depressed. This is the balance point.

II APPLICATION TO ACID-BASE TITRATIONS

- a QUINHYDRONE ELECTRODE TITRATION
- b GLASS ELECTRODE TITRATIONS
- c CONDUCTANCE TITRATIONS

The instrument has been applied to acid-base titrations using the quinhydrone electrode, the glass electrode, and conductance measurements.

The solutions used in the acid-base titrations were approximately N/10 HCl and N/10 NaOH. The HCl was made up to approximately N/10 and standardized with Na_2CO_3 using the quinhydrone electrode and the vacuum tube potentiometer. The NaOH solution was made up to approximately the same strength as the HCl and titrated roughly against the HCl. The double break that was found indicated that there was Na_2CO_3 present, so the calculated amount of $\text{Ba}(\text{OH})_2$ was added to get rid of the CO_2 . The solution was allowed to stand over night and was then filtered. Another rough titration showed that the CO_2 had been completely removed.

The following titrations are given as typical of those obtained with the methods used.

A titration of the acid with the base using the quinhydrone electrode and a standard potentiometer is given in Table I

A titration of the acid and the base is given in table II using the quinhydrone electrode and the vacuum tube potentiometer. In these titrations and the titrations with the glass electrode, a millivoltmeter was used to determine

the potential of the bucking battery after a balance was obtained. The millivoltmeter was in the circuit at all times so that the current drawn by it would not cause an error in the readings.

In Table III is a typical titration obtained with the glass electrode and the vacuum tube potentiometer.

In the conductance titrations, a Wheatstone bridge and a microphone hummer were used. The electrode used was a dipping electrode similar to those used to find the conductance of plating baths. A typical titration is given in Table IV.

Table I gives the titration of 25 cc. of .1290N HCl with .1302N NaOH using the quinhydrone electrode and the standard potentiometer.

TABLE I

TITRATION OF HCl WITH NaOH

cc. NaOH	EMF	dE/dc
0.0	-0.3888	_____
5.0	-0.3830	0.0012
10.0	-0.3785	0.0011
15.0	-0.3625	0.0032
20.0	-0.3445	0.0036
22.0	-0.3290	0.0077
23.0	-0.3160	0.0130
24.0	-0.2890	0.0270
24.2	-0.2780	0.0550
24.4	-0.2600	0.0800
24.6	-0.1900	0.3500
24.8	+0.0460	1.1800
25.0	+0.0990	0.2650
25.2	+0.1320	0.1650
25.4	+0.1600	0.1400
25.6	+0.1860	0.1300
25.8	+0.1970	0.0550
26.0	+0.2090	0.0600
27.0	+0.2240	0.0150
29.0	+0.2270	0.0015
34.0	+0.2295	0.0005

Table II gives the titration of 25 cc. of .1290N HCl with .1303N NaOH using the quinhydrone electrode and the vacuum tube potentiometer with a millivoltmeter.

TABLE II

TITRATION OF HCl with NaOH

cc. NaOH	EMF	dE/dc
0.0	-0.388	-----
5.0	-0.384	0.0008
10.0	-0.378	0.0012
15.0	-0.364	0.0028
20.0	-0.342	0.0044
22.0	-0.332	0.0050
23.0	-0.312	0.0200
24.0	-0.282	0.0300
24.2	-0.276	0.0300
24.4	-0.256	0.1000
24.6	-0.192	0.3200
24.8	+0.044	1.2300
25.0	+0.098	0.2700
25.2	+0.130	0.2100
25.4	+0.156	0.1300
25.6	+0.184	0.1400
25.8	+0.194	0.0550
26.0	+0.208	0.0700
27.0	+0.222	0.0140
29.0	+0.230	0.0040
34.0	+0.232	0.0004

Table III gives the titration of 25 cc. of .1290N HCl with .1302N NaOH using the glass electrode and the vacuum tube potentiometer with a millivoltmeter. In this titration the 25 cc. of acid was diluted with 50 cc. of H_2O in order to cover the glass electrode.

TABLE III

TITRATION OF HCl WITH NaOH

cc. NaOH	EMF	dE/dC
0.0	-0.304	-----
5.0	-0.304	0.0000
10.0	-0.304	0.0000
15.0	-0.304	0.0000
20.0	-0.284	0.0040
22.0	-0.270	0.0070
23.0	-0.252	0.0180
24.0	-0.224	0.0280
24.2	-0.212	0.0600
24.4	-0.194	0.0800
24.6	-0.054	0.7000
24.8	+0.092	0.7300
25.0	+0.130	0.1900
25.2	+0.158	0.1400
25.4	+0.170	0.0600
25.6	+0.180	0.0500
25.8	+0.190	0.0500
26.0	+0.196	0.0300
27.0	+0.216	0.0200
29.0	+0.220	0.0020
34.0	+0.230	0.0020

Table IV gives the titration of 25 cc. of .1290N HCl with .1302N NaOH by the conductance method, using the vacuum tube set-up to indicate the balance point. In this titration the 25 cc. of acid was diluted with 50 cc. of H_2O in order to cover the dipping electrode.

TABLE IV

TITRATION OF HCl WITH NaOH

cc. NaOH	Resistance (Ohms)
0.0	12.9
5.0	20.0
10.0	24.0
15.0	32.0
20.0	45.0
22.0	54.0
23.0	59.0
24.0	65.0
24.2	65.8
24.4	67.5
24.6	68.0
24.8	67.0
25.0	66.7
25.2	66.5
25.4	65.8
25.6	65.0
25.8	64.5
26.0	63.7
27.0	60.4
29.0	55.0
34.0	40.0
40.0	36.0

TITRATION CURVES OF 25cc OF .1290N HCL

cc. .1302N NaOH

WITH .1302N NaOH

OH

By plotting EMF against cc. the curves 1, 2, and 3 are obtained. The end point of an acid-base titration is known to be at a pH of 7:0. This corresponds to an EMF of -0.044. Therefore, where the curve crosses the -0.044 ordinate is the end-point of the titration, and the number of cc. is determined by extrapolating to the abscissa. In the three potentiometric titrations the end-point found in the manner just described was found to be 24.72 cc. of NaOH.

By plotting resistance in ohms against cc. in conductometric titrations curve 4 is obtained. The end point of the reaction is at the peak of the curve. This was found to be 24.72 for the titration given in Table IV.

The greatest discrepancy between the vacuum tube potentiometer and the standard potentiometer is only four millivolts. This is not so great when it is considered that the millivoltmeter cannot be read closer than two millivolts. The curve of the glass electrode begins at a lower EMF(higher pH) than the other two curves, because of the dilution with 50 cc. of H_2O .

Using the millivoltmeter the accuracy of the system is high enough for all practical purposes. Two millivolts corresponds to three hundredths of a pH. For greater accuracy a pot-

entiometer could be used in place of the millivoltmeter. The standard potentiometer is calibrated to 0.05 millivolts, but the galvanometer ordinarily used with it does not permit a balance closer than one millivolt.

The conductance curve is not so smooth as it might be, but this is due to the fact that the bridge used contained a small amount of inductance and capacity which prevented a sharp null point from being obtained.

These results show that a simple vacuum tube potentiometer of moderate cost can replace the potentiometer and galvanometer now in use, and can be used as an aid in conductance measurements.

This instrument could be made portable for industrial application. It should be sufficiently accurate for most industrial purposes.

III APPLICATION TO LEAD CHROMATE PIGMENTS

In this part of the application an attempt was made to apply the instrument with the glass electrode to the control of the color of lead chromate pigments. Spanyer¹⁸ and others have shown that the color of the pigments to be a function of the pH of the striking solutions. In previous investigations the quinhydrone electrode was used to determine the pH of the solutions. This presented the difficulty that as soon as a pH greater than 7.0 was obtained in the solution after striking, the quinhydrone would discolor the pigment.

In determining the pH of these solutions before striking, the glass electrode and the quinhydrone electrodes were placed in the solution at the same time. It was found that the glass electrode was stable and gave the same reading for as long as fifteen minutes, but the quinhydrone electrode gave a reading of a pH smaller than the glass electrode and continued to drift towards a lower pH the longer it was in the solution. The same was true of the solutions after striking.

The solutions of $\text{Pb}(\text{NO}_3)_2$ and $\text{Na}_2\text{Cr}_2\text{O}_7$ were made up to 0.5N and enough of each taken to provide 15 gm. of the dried pigment. The pH of the solutions before striking was adjusted by the means of 5N HNO_3 and 5N NaOH using the glass electrode and the vacuum tube potentiometer. In all cases the $\text{Pb}(\text{NO}_3)_2$ solution was added to the $\text{Na}_2\text{Cr}_2\text{O}_7$ solution. The time of striking was approximately 30 seconds. After striking the pH of the solution was determined with the glass electrode. Then the pigment was washed three times by decantation and filtered through a Buechner funnel, and dried at 60°C .

The pH of the lead solution was found to be 5.2 and the chromate to be 2.5 in the .5N solutions.

Table V shows the result of changing the pH of the chromate solution. Samples 1, 2, 3, 4, 5, and 6 were all yellow when struck, but some hydrolized to orange on the first wash. Sample 7 was orange when struck. It was attempted to make the pH of sample 7 to be 11, but the highest pH that could be obtained was 10.2.

Table VI shows the result of changing the pH of the lead solution. Sample 14 was the only one that was orange when struck. It may be interesting

to note the the pH of sample 14 is less than that of sample 13, although sample 14 had 2.5 times as much base added to it as sample 13.

TABLE V

LEAD CHROMATE COLORS

Sample No.	Na ₂ Cr ₂ O ₇		Final	
	EMF	pH	EMF	pH
1	+0.160	5.0	-0.398	1.0
2	-0.100	6.0	-0.376	1.4
3	-0.040	7.0	-0.070	6.5
4	+0.018	8.0	-0.033	7.15
5	+0.077	9.0	+0.035	8.25
6.	+0.135	10.0	+0.066	8.7
7	+0.142	10.2	+0.142	10.2

The pH of the Pb(NO₃)₂ was 5.2 in all cases.

TABLE VI

LEAD CHROMATE COLORS

Sample No.	Pb(NO ₃) ₂		Final	
	EMF	pH	EMF	pH
8	-0.160	5.0	-0.123	5.7
9	-0.100	6.0	-0.338	2.0
10	-0.040	7.0	-0.156	5.1
11	+0.018	8.0	-0.140	5.4
12	+0.077	9.0	-0.125	5.6
13	+0.135	10.0	-0.094	6.05
14	+0.120	9.7	+0.120	9.7

The pH of the Na₂Cr₂O₇ was 2.5 in all cases.

Two more sample were made, 15 and 16, in which the pH of both solutions was made up to some definite value. In sample 15 both solutions were made up to a pH of 7.0 and treated in the same manner as the previous samples. The color after striking was orange, and the pH of the solution was 8.75. In sample 16, both solutions were made up to a pH of 6.0 and treated in the same manner as the previous samples. The color on striking was yellow and the pH of the solution was 5.7.

An attempt was made to use the polarizing microscope to obtain some clue as to the mechanism of the color change of the pigments as the acidity of the solution is decreased. The investigation with the microscope was of very little value, because the pigments seemed to be amorphous. It is possible the under a magnification of 5000 diameters that some crystal structure may be in evidence, but the highest power used, 1500 diameters, was not sufficient to resolve the crystal, if there were any present.

CONCLUSIONS

The apparatus described in this paper was found to be satisfactory in every respect. It is sensitive and flexible, and at the same time it is portable. The cost of the instrument built from standard radio parts is about one-fourth the cost of the standard potentiometer for the glass electrode. The instrument has the further advantage that it contains no standard cell to freeze or polatize, and no galvanometer with an easily broken suspension. It can be operated anywhere there is a 110 volt AC outlet.

The results of the acid-base titrations show that the instrument is sufficiently accurate to be used for almost any purpose.

The result of the application of the instrument with the glass electrode to the determination of the pH of lead and chromate solutions in the striking of lead chromate pigments show that it can be applied to operation industrially.

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