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A 120 megacycle self-contained high-frequency titrimeter

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A 120 MEGACYCLE
SELF-CONTAINED HIGH-FREQUENCY TITRIMETER

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FORWARD

The analytical chemist is ever eager to improve and
expedite present analytical methods. In the past ten years
considerable interest has been elicited in the field of high
frequency oscillators and their application to analytical
chemistry. One of the main reasons for this interest is the
uniqueness of the apparatus. No direct contact is made
between the measuring instrument and the solution. Credit
for this interest must be given primarily to Jensen and
Parrack of Texas A & M University. Their article in 1946
described a simple tuned plate-tuned grid electronic
oscillator, operating in the high frequency range. A
solution was exposed to the electromagnetic field of the
plate coil. During the titration the electrical character-
istics of the solution changed. These changes were reflected
in measurements of the electrical constants of the oscillator.
Upon analysis the constants clearly showed the end point and
yet no physical contact had been made with the solution.
Since the instrument of Jensen and Parrack many modifica-
tions have appeared and even entirely new instruments.

However they still keep the one common feature: no contact with the solution. In addition to titrations, the instrument has been used to advantage in many other fields of analytical chemistry. After ten years it has clearly established itself as a valuable tool rather than just a laboratory curiosity.

The object of this present research was to build an original instrument and test its effectiveness in as many fields as possible.

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A DESCRIPTION OF THE INSTRUMENT

This is a heterodyne type of instrument. There are
two separate oscillators mechanically shielded from each
other and electrically isolated by the two identical buffer
stages. The working oscillator has its frequency determin-
ed by the solution that is placed in the special container.
The reference oscillator, however, is controlled by two con-
densers in parallel. This gives it a large tuning range and
enables the operator to find the frequency of the working
oscillator with rapidity and ease. As the two oscillators
approach the same frequency a heterodyne or beat frequency
will be heard. When the oscillators are tuned to exactly
the same frequency a zero-beat or null is heard. The buf-
fers are R-C circuits designed to isolate the oscillators
from each other. The mixer, detector and audio stages are
standard design. The earphones could have been replaced by
an additional audio stage and a loud-speaker, but it was
considered a luxury and not necessary.

Construction of this unit is relatively simple. The
most important consideration is the frequency stability.
Ideally the chassis should have been constructed from cadmium
plated steel. Aluminum was chosen instead because of the
ease of construction. The idea of this instrument is not
original. Actually this a combination of two separate and
original instruments. But a literature search reveals this

is the first time any one has ever combined both in this
fashion. West, Burkhalter, and Broussard (1950) built a
similiar instrument using a Clapp type oscillator in the low
frequency range. Johnson and Timnick (1956) built a single
120 megacycle oscillator and followed the reactions with a
Sargent Model XXI Polarograph to measure the grid current,
or observed the frequency shift with a BC-221 frequency
meter. The present instrument replaces the Clapp oscillators
with the 120 megacycle half-wave oscillators. The result is
a stable, easily operated instrument. The success of this
instrument depends on several factors. Both oscillators
have a common plate and filament supply. Any shift in
frequency because of power supply fluctuation will there-
fore cause a similiar shift in both oscillators. Since we
are measuring the difference between the oscillators at all
times, even though a shift takes place, the difference or
beat frequency remains a constant. The use of a miniature
955 tube and RG8/U flexible coaxial cable make a very simple
and stable arrangement at this high frequency. The RG8/U
cables are supported by a wooden frame for mechanical
stability.

The titration vessel is similiar to the one used by
Johnson and Timnick. It is attached to the chassis by three
banana plugs. The plastic solution container is held firmly
in place by plastic rings and is mechanically stable. This

is important since any movement of the container causes the frequency to shift. Although the plastic cup is firmly held it is easily slipped out for cleaning after each experiment. The container has a total capacity of 200 ml. It is a plastic bottle 2 inches in diameter and 6 inches long. The two oscillator electrodes are silver plated strips of metal about 3/4" x 2" and are curved slightly to fit around the plastic cup. Above the electrodes is a 1/2" piece of aluminum with a 2 1/6" hole drilled in it to act as a ground ring. This ground ring is a very important part of the apparatus. If liquid is slowly added to the empty cup the frequency shifts and can be followed with the variable reference oscillator. With the ground ring in place the shift takes place only up to about 80 ml. After this the frequency remains a constant. By starting every experiment with a minimum of 100 ml. of liquid in the vessel, any change that takes place is due to a shift in the solution composition and not just a result of physical capacitance.

As was previously stated, the reference oscillator has two tuning condensers in parallel. The black knob on the side of the reference oscillator controls the large condenser that is used to find the heterodyne. The small condenser is controlled from the front of the instrument by a National precision dial with a 1000:1 ratio. After the heterodyne is located by the large condenser the reaction is

then followed by moving the small condenser until a zero-beat is heard, and taking readings from the National dial.

The power supply is of conventional design. The only requirement is that it be constructed of quality components that are slightly over-rated for cool, efficient operation. The power supply shown in the accompanying photographs is much more complicated than is necessary. It is an experimental model that was already on hand and was used to save time and money.

Anyone with previous experience in electronics should have no difficulty in duplicating this instrument. Placement of parts is not critical. In the oscillator, leads should be kept short and mechanically stable. Number 12 tinned copper wire was used in both oscillators to increase mechanical stability. The 955 oscillator tube sockets are ceramic to minimize loss at the high frequency and are mounted on rubber grommets to reduce mechanical vibration. The length of the RG8/U coaxial cable is 90 cm. for a frequency of 120 mc. Shorter lengths were tried in an effort to raise the frequency, but the resulting instrument showed signs of instability and it was necessary to return to the 90 cm. length. The length of RG8/U on the reference oscillator is several cm. shorter than this however. The additional capacitancy of the parallel condensers compensates for this and keeps the tuning range

within 120 mc. The working oscillator is enclosed in a
2x3x6 inch box underneath the chassis. Connections to the
titration cell are made through the rear of the chassis by
three large, silver-plated banana plugs. The reference
oscillator is in a 5x5x6 inch box on top of the chassis.
The National dial is mounted on the front panel and is con-
nected to the smallest of the two frequency determining
condensers. On the side of the box is a knob directly con-
nected to the large frequency determining condenser.

Both oscillators have their plate voltage stabilized
by a voltage regulating tube (OA2). The output of both
oscillators is coupled through very small ceramic condensers
and coaxial cables to the grids of the buffer stages (6SK7).
Each of these tubes is a low gain R-C coupled stage designed
to isolate the oscillators from each other and prevent pull-
ing as the oscillators approach the same frequency. The
output of both buffers feeds into a 6L7 mixer. Here the two
frequencies heterodyne or beat together. There will be an
addition signal and a difference signal. Only the differ-
ence signal will be in the audio range and is passed on to
the detector (6H6) for rectification. This small audio
signal is then amplified through two 6SJ7 type pentode
amplifiers, and the final output is fed into a pair of
earphones. Each 6SJ7 grid is controlled by a seperate gain
control. The first control is on top of the chassis and is
adjusted by a screwdriver. This is adjusted for optimum per-

formance without overdriving the tube. The second control
is on the front panel and is adjusted as needed.

EXPERIMENTAL PROCEDURE

In all experiments, the following procedure was used. The power supply was turned on at least 45 minutes before a run was to be made. This eliminated drift and stablized the instrument. The plastic container was pushed into the cell holder and the holder was checked to be sure it was firmly attached to the chassis. The solution to be analyzed was then added to the cup (100 ml. is the minimum allowed at the beginning). The stirring rod was attached to the stirrer and adjusted no deeper than chassis level in the cup. The filled buret was then brought into place and the tip put into the cup. The stirrer motor was turned on and speed kept slow. The National dial was adjusted to about 120 and the large knob on the side turned until a signal was heard. The earphones incidently were not worn. They were left open on the talbe and the volume control adjusted to about two-thirds of full volume. The signal was easily heard under these conditions. After the signal was detected by adjusting the knob on the side of the instrument, then the National dial on the front panel was adjusted until a zero-beat resulted. A known quantity of liquid was added from the buret to the solution in the cup and again the National dial was adjusted until a zero-beat was heard. This procedure was followed until the end-point appeared passed. The data sheet now contained two columns: one indicated the volume of liquid added and the other the dial reading for

each successive addition of liquid. The data were then plotted on standard graph paper as dial reading (change in frequency) versus volume of liquid added. An interpretation of these curves will be given later. The procedure for the binary mixtures were a little different. It was not possible to remove the cup during an experiment because the frequency would be shifted slightly. All the solutions for the experiment were prepared and just 100 ml. of each was taken. The first solution was placed in the cup and the dial adjusted to about 230. As before the coarse adjustment was made by the knob on the side and adjustment to zero-beat and the whole procedure of emptying and filling was repeated. A check was made by making the last solution for the experiment the same composition as the first. If the dial reading was not the same as the original setting then the whole experiment was discarded. Agreement in almost all cases was excellent.

The National dial is a precision dial that can be read to three places directly and the fourth place estimated. In the judgement of the writer it can be estimated to ± 0.05. When the dial is exactly adjusted to a zero-beat the dial can be moved about ± 0.05 without affecting the signal. This represents a precision of 0.2% for the average titrational 10 dial units.

Over all this apparatus is stable, but care must be taken not to move or jar the equipment once an experiment is

under way. Care should also be taken in stirring the
solution. If it were stirred too rapidly, a cone of air
would be drawn into the cup and greatly affect the readings.

THEORETICAL CONSIDERATIONS FOR HIGH FREQUENCY OSCILLATORS

Instruments are divided into two classes, depending on their mode of coupling the sample to the instrumental circuit. If the sample is exposed to the electrostatic field of the condenser, it is said to be capacitively coupled; if it is placed in the plate coil, then inductively coupled. Either method of coupling depends on the dielectric constant, specific conductance, or both (depending on the specific circuitry). The indication from such a change is dependent to a greater or lesser extent upon the electronic circuitry. The capacitive effect can be predicted with a high degree of accuracy from theoretical considerations, but the inductive effect is very complex and cannot be predicted with accuracy. While the inductive effect has been studied in great detail for specific instruments most of the theoretical work has concerned the capacitive type. In the actual instruments measurement of grid current, plate current, frequency shift, capacity change, etc. are all used as an indication of the changes that are taking place in the solution. In addition to the methods utilizing the direct effects of the solution on tuned circuits and oscillators, additional methods for high frequency titration have been described. Hall and Gibson (1951) used a twin-T impedance-measuring circuit to study changes in solutions.

A review of circuits in use in high frequency instruments would most likely include one of the following basic oscillators.

<u>Clapp oscillator</u>-(Fig 12) characterized by its extreme stability, and excellent choice for this type of instrument. The circuit owes its stability to relatively large capacitances in parallel with the tube capacitances. Variation of the latter due to vibration of thermal expansion have only a slight effect on the frequency. No investigator has been successful with this circuit above 30 megacycles, however.

<u>Hartley oscillator</u>-(Fig. 15) one of the simplest self-excited oscillators. Its distinguishing feature is the tapped coil that is used to obtain the feedback necessary for oscillation.

Colpitts oscillator-(Fig. 13) obtains the feedback necessary to support oscillation by dividing the tuned circuit into two parts. This division is accomplished by means of a capacitative voltage divider made up of C_1 and C_2 in series shunted across the coil L. It will be noticed that the principle involved is the same as that used in the Hartley circuit except that it is the capacity which is tapped instead of the coil.

<u>Tuned plate-tuned grid oscillator</u>-(Fig. 16) proper tuning requires two controls unless a gang condenser is used. Its principle advantage is the great flexibility of tuning.

Because both plate and grid circuits can be tuned, optimum feedback and frequency conditions can be obtained, with resultant gain in output stability.

Crystal oscillator-(Fig. 14) the circuit is fundamentally a tuned plate-tuned grid oscillator, except that a crystal is used as the grid tuned circuit. Positive feedback is provided by the grid to plate capacity of the tube. The crystal oscillator is sueful because of its simplicity, the fact that the components necessary are not as critical as those found in more elaborate types of crystal oscillators.

The tuned plate-tuned grid oscillator of figure (16) has two tuned circuits which must be adjusted to resonate at approximately the same frequency for oscillation to take place. In order to use this device to follow a titration, the cell is placed in the plate circuit and then the plate and grid condensers are resonated to bring the circuit into oscillation. As the titration proceeds the resonance of the plate circuit will change. The amplitude of radio-frequency oscillation will be reduced and there will be corresponding changes in the plate and grid currents and voltages. Such a device can be made very sensitive and many investigators have done excellent work with them. One of the disadvantages, however, is that the adjustment may be critical and it may be difficult to achieve sufficient range and stability for some work. The crystal oscillator of figure (14) is similar to the tuned plate-tuned grid oscillator, except that a

quartz crystal between metal plates replaces the tuned grid circuit. It has two advantages over the other oscillator circuits. It may be readjusted to the same resonant frequency as the loading is changed, and as the value of C is decreased, the point at which oscillation starts is abrupt and can be reproduced very exactly. If a cell were placed in parallel with the tuned plate circuit, C would have to be readjusted to compensate for any changes that took place in the solution. As C is varied so will the grid bias voltage change. A graph of maximum grid bias voltage versus C then would be a good indication of the changes taking place in the solution. The Colpitts circuit of figure (13) has only a single tuned circuit for both plate and grid circuits of the tube. Hence, capacitive changes across the terminals of the inductance coil of this circuit will shift the frequency, but will not cause the plate circuit to detune with respect to the grid circuit. If two such identical oscillators were used and only one loaded with a solution, the other could be used as a reference oscillator and beat against the other for detection of any frequency shift. This is the principal that is used in the writer's instrument. In instruments that have been described at low frequency, this change in frequency is very slight, usually only a few hundred cycles for a given increment of titrant. The usual method of detecting a change as small as this is first to tune the two oscillators to a beat frequency

of say 5000 cycles per second, using a frequency meter or
audio oscillator and oscilloscope as a standard. After the
increment of titrant is added to the cell the beat frequency
shifts to a new value and the new frequency is then deter-
mined, using either of the latter instruments. When the
present instrument was constructed, it was hoped that a
larger change that would be more easily measured could be
obtained. To do this the frequency was raised to 120
megacycles, where a small capacitance change would cause a
considerable shift in frequency. In addition the cell
geometry was made relatively large. The cell geometry can
not have too much capacitance at this frequency or the load-
ing will be excessive. Next the reference oscillator was
fitted with a very tiny condenser coupled to a National
precision dial of high mechanical ratio. As the change
occurs in the cell, it shifts the frequency. This change
is then followed with the reference oscillator, by using
an audible beat. The instrument is self contained and no
auxillary pieces of apparatus are needed. In addition to
the above reasons for selecting an instrument frequency of
120 megacycles, there is the question of solution concentra-
tion. Most titrations use a practical concentration of .1M.
The earliest experimenters soon found that they were serious-
ly restricted in many reactions by using very low concentra-
tions to obtain the necessary sensitivity. The change of
frequency of an oscillator due to the change in dielectric

constant of an electrolytic solution is a function of con-
centration at a particular frequency. A response can be
obtained only in that concentration region where the
dielectric constant of the solution (and oscillator
frequency) change with concentration. The data of Forman
and Crisp (1946) allow a prediction of the concentration of
maximum sensitivity for various electrolytes. These authors
have given a simple empirical relation between the concen-
tration of a solution and the frequency at which the
adsorption of energy is a maximum: $lc=k$, where l is the wave
length in centimeters, c is the normality, and k is a con-
stant, characteristic of the electrolyte employed. With the
use of this formula it can be shown that the optimum
frequency for use with concentrations of about .2 M would be
approximately 360 megacycles. However, building a stable
oscillator at this frequency has some serious stability
problems. Blaedel and Malmstadt (1950:3) have constructed
such an instrument and the authors claim that it works well.
At 100 megacycles the optimum concentration is about .05 M.
However, results with the writer's instrument at 120
megacycles using .1 M solutions have been very encouraging.
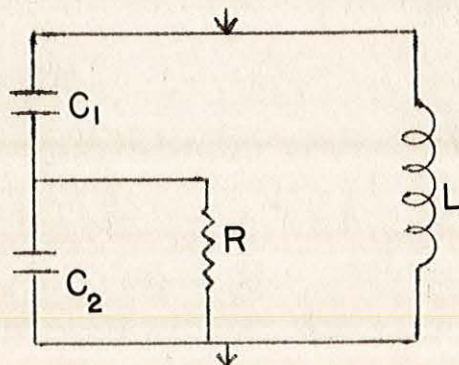
This is the equivalent circuit of a capacitively coupled high-frequency oscillator (Blaedel, Halmstadt, Petitjean and Anderson 1952). C_1 represents the capacity of the solution which remains fairly constant. R is the resistance of the solution, inversely proportional to the conductivity and varies greatly as the solution changes from dilute to concentrated, but C_2 is independent of the electrolyte concentration over a wide frequency range. L represents the inductance of the network. In the author's instrument an S-shaped curve is obtained if the concentration of any electrolyte is plotted versus the change in frequency. As was pointed out earlier, the concentration and sensitivity depend on the frequency. To explain this S-shaped curve it must be realized that when the impedance of R is compared to that of C_2, the latter is almost shorted out, and the frequency approaches $1/2\pi\sqrt{1/LC_1}$ in concentrated solutions.

In the case of dilute solutions, the impedance of R is large compared to that of C_2 and the frequency approaches $1/2\pi\sqrt{(C_1+C_2)/LC_1C_2}$. In between these two extremes you have varying intermediate situations.

CHEMICAL ANALYSIS WITH THE HIGH FREQUENCY OSCILLATOR

This section will be divided into several groups. Because of the uniqueness of the instrument, analysis with the high frequency oscillator has been extended to many fields.

Binary Solutions

One of the simplest applications of this instrument is an analysis of a binary system. Since the response is primarily due to dielectric changes in the solution, a study of binary systems involving widely different dielectric constants should be interesting. The writer chose water and absolute ethyl alcohol, water and acetone, water and dioxane, water and acetic acid, water and propionic acid, and benzene and nitrobenzene. In every case there was a very significant change in frequency (instrumental response) as the concentration of the binary mixture varied. The graphs of these results are shown in figure (8-10). It will be observed that although the graphs are not straight lines, the curves are very uniform. Below is a table of dielectric constants of the liquids involved.

Dielectric Constants at 20°C.

Acetic Acid 6

Acetone 21

Benzene 2.3

Dioxane 2.2

Ethyl Alcohol 26

Nitro Benzene 36

Propionic Acid. 3

Water 80

Only miscible binary systems were investigated. Distilled water was used and the organic chemicals were technical grade. Purification was not necessary since only an indication of instrumental response was sought. If the dielectric constants in the table are compared with the order of the curves in the graph in figure (9), a direct relationship will be observed to exist. As would be expected the largest difference in dielectric constant causes the greatest change in frequency. Although the response is not linear, the results are very reproducable and could be very easily adapted to measure the purity of solvents, the amount of moisture present, etc. The writer is very enthusiastic over the analytical possibilities in this area, because the instrumental response was the greatest of any of the fields of analysis tried. It should be pointed out now that the response obtained by varying the concentration of electrolytes does not follow a particularly uniform pattern. The reason is that the change is usually not due to a change in dielectric constant, but is rather an effective capacity change introduced into the circuit by the shunting effect of the conductance on the circuit. The curves of acetic acid and propionic acid are easily distinguishable by the small

humps at low concentration. These are undoubtedly due to
the weak ionization constants of these acids and are a com-
bination of the dielectric constant and the conductance.
The literature lists some interesting studies of high
frequency methods in the field of binary analysis. West,
Robichaux and Burkhalter (1951) analized a static ternary
system of water, benzene and methylethyl ketone. Their
method involved the removal of water in the system with a
drying agent that remained in the cell for the second
measurement and did not affect the reading. West, Senise
and Burkhalter (1952) describe a number of alcohol-water
systems including some partially-miscible ones and includ-
ing several polyhydric alcohols. Hall, Gibson, Critchfield,
Phillips and Siebert (1954) used a General Radio twin-T
impedance measuring circuit to study binary liquid systems
and a mathematical analysis is made of the results. The
system dioxane-water-potassium chloride is studied
particularly. One practical industrial application was
demonstrated by Thomas, Faegin and Wilson (1951) of the
Humble Oil and Refining Co., Baytown, Texas. They rely on
the measurement of dielectric constant to monitor a stream
of toluene or xylene to determine its purity. They used a
high frequency oscillator in connection with a capacity type
cell, located in a sampling bypass tube from the main
stream. An automatic recorder keeps an accurate record of
the per cent of toluene or xylene in the run. Jensen, Kelly

and Burton (1954) describe a method for the determination of
moisture in solids. Although sodium chloride and ammonium
nitrate were employed in their investigation the method
should work for other compounds too. Takahashi, Kimoto and
Yamada (1951) describe a procedure for analysis of binary
mixtures in several mixtures in several organic solvents.
Nitrobenzene-aniline and other similar organic compounds
were studied including the effect of moisture and impurities
on the accuracy of the analysis. Weaver, Whitnack and Gantz
(1956) of the U.S. Naval Test Station, China Lake, California,
used a Sargent Model V Oscillometer to determine the mois-
ture content of hydrazine and 1,1-dime thylhydrazine. They
found that the 1,1-dime thylhydrazine-water system could be
determined accurately, but the water-hydrazine system could
not.

Titrations - The field of primary interest in high frequency
methods of analysis is an end point indicator in titrations.
The idea of performing a titration and eliminating any
direct contact with the solution is very appealing and has
no doubt spurred many investigators into constructing an
instrument and trying it. Moreover many titrations lack a
suitable end point indicator for one reason or another and
the high frequency method could be the answer. In general
the response of the high frequency apparatus is basically
similar to a conductometric titration except there are no

electrodes involved. The shape of the curve obtained
depends on many factors and will depend on such things as:
which electronic variable is being measured by the instru-
ment, weak or strong electrolyte, frequency, temperature,
etc. But regardless of the general shape, an abrupt change
in the curve represents an abrupt change of dielectric
constant or conductance (or both), and is an indication of
and end point. It is possible to secure sensitivities
comparable to most conventional methods and in some cases
even exceed them. The high frequency method has now been
extended to non-aqueous titrations and the results have
been very gratifying.

The first experiment performed with the author's
instrument was with NaOH and HCl figure (1). It will be
seen that the slope drops and rises evenly. The end point
is sharply defined. The ionic reaction is:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$
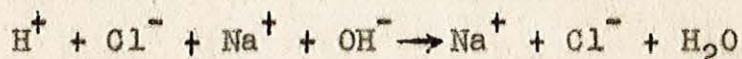
Per mole of NaOH added, the effect is to replace one mole
of H^+ with one of Na^+ before the equivalence point; whereas
after the equivalence point, the effect is to add one mole
of Na^+ and one mole of OH^-. The dielectric constant depends
on the ion mobilities and their concentration. We are re-
placing the more mobile H^+ with the slower Na^+, hence the
curve drops. At the equivalence point we now start to add
an excess of the more mobile OH^- and the curve begins to
rise once more.

In figure (2) is given the titration curve for NaOH and HAc ($HC_2H_3O_2$). The ionic reaction is:

$$HAc + Na^+ + OH^- = Na^+ + Ac^- + H_2O$$

The previous discussion concerning the HCl and NaOH also applies here, but the curves are not identical. The HAc is only slightly ionized, and there are few actual H^+ ions present in the solution. Per mole of NaOH added, we are then replacing 1 mole of HAc with one mole of Na^+ and one mole of Ac^- until the equivalence point is reached. After this we are just adding one mole of Na^+ and one mole of OH^-. Because there is only a slight difference in ion mobility between the Ac^- and HAc the curve rises slowly. After equivalence the faster OH^- causes the curve to rise rapidly and it resembles figure (1) from this point on.

Figure (3) is the titration curve for oxalic acid and NaOH. The ionic reactions are:

$$H^+ + HC_2O_4^- + Na^+ + OH^- \rightarrow HC_2O_4^- + Na^+ + H_2O$$
$$HC_2O_4^- + Na^+ + OH^- \rightarrow Na^+ + C_2O_4^= + H_2O$$
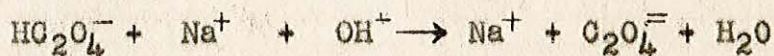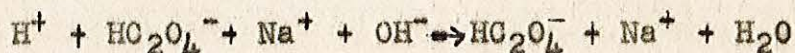
This curve shows two end-points and this is expected since oxalic acid is dibasic. The first end-point is, of course, one-half the calculated or second observed end-point. This is analogous to the situation observed in conductometric titrations. This curve resembles both of the two previous curves. Before the first equivalence point, the faster moving H^+ is being replaced with slower moving Na^+ and the curve drops. After equivalence the slightly ionized $HC_2O_4^-$

is replaced with faster Na^+ and the curve rises slowly.
After the second equivalence point the faster OH^- begins to
add and the curve rises rapidly.

Figure (4) represents the titration curve of H_3PO_4
and NaOH. In the writer's opinion, this was not successful.
The instrument apparently fails if the ionization constant
is too weak. A conductometric titration figure (5) was also
run on the same acid in an effort to interpret the results.
In any event it is very difficult to analyze. All end
points were checked using phenolphthalein as the indicator.

A titration of Cl^- and $AgNO_3$ was attempted. The
ionic reaction is:

$$Ag^+ + Cl^- + Na^+ + NO_3^- = AgCl + Na^+ + NO_3^-$$
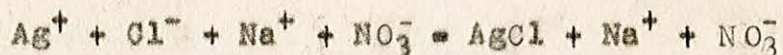
Before the equivalence point the effect is to replace one
mole of Cl^- with one mole of NO_3^- and afterward with one
mole of Ag^+ and one mole NO_3^-. From previous experiments it
seems that the change should be large enough to be clearly
defined and experimentally it is practical. The presence of
the precipitate undoubtedly contributes to the general lack
of uniformity of the curve until the end point is reached.
The end point was checked using a chromate indicator. Other
types of titrations were attempted with this instrument,
but the results were not too encouraging. Several oxidation-
reduction reactions were tried, with concentrations from
0.01-1.0 M. In every case the degree of response from this
instrument was not sufficient for analytical purposes.

One other area was explored which holds the greatest
potential of any tried. Titrations in non-aqueous solvents
open many new fields in analytical chemistry and the detec-
tion of the end point is usually difficult. Color indica-
tors are not practical and electrodes for conductometric
methods are not always readily available. The high frequency
method then becomes the method of choice. One titration
figure (6) was run for aniline. This weak base was dissolv-
ed in glacial acetic acid and was titrated with perchloric
acid also dissolved in glacial acetic acid. The response
of the instrument was sufficient to indicate a sharp end
point. The writer wishes that more time were available to
explore this area more fully. Because of the interest in
applying the high frequency method to titrations, there are
numerous references in the literature. Dean and Cain (1955)
used dimethylformamide as a medium to titrate acids.
Lippincott and Timnick (1956) were able to titrate aniline
and 9- substituted anilines using glacial acetic acid as a
solvent. Masui (1955) studied the titration of dicarboxylic
acids and their salts in non-aqueous solvents such as
methanol-benzene and acetic acid-glycol. Weak organic acids
were titrated with sodium methylate in a benzene methanol
mixture by Ishidate and Masui (1953-2) and by Jensen and
Parrack (1946). Masii (1953) has also titrated organic
bases and amino acids in nonaqueous solution. It is report-
ed to be feasible for bases with dissociation constants on

the order of 10^{-10}. Hall (1952) discusses the practicality
of the high frequency method as an end point indicator.
Blaedel and Malmstadt (1952) devised a differential method
for determining end points and in some cases obtained great-
er accuracy than may be obtained from the primary curve.
Jensen, Watson and Vela (1951) used soap solution to titrate
the Calcium and magnesium in water as a measure of its
hardness. Goto and Hirayama (1952) used a 0.1 N oxime solu-
tion to titrate copper, zinc, aluminum and iron. Copper,
zinc, calcium and magnesium were titrated with ethylene-
diaminetetraacetic acid by Blaedel and Knight (1954).
Blaedel and Malmstadt (1951) used oxalic acid to determine
thorium and report that it is free to error from interfering
substances that caused trouble in the conventional gravi-
metric procedures. Anderson and Revinson (1950) describe
the titration of Beryllium with ammonium phosphate and
ammonium hydroxide or sodium hydroxide. Young (1955)
studied the non-aqueous titration of strong acids. Ishidate
and Masui (1953:1) describe the alkalimetry of alkaloids and
weak organic bases. Chloride determinations have been
studied by Blaedel and Malmstadt (1950:2:3). Jensen and
Parrack (1946), Anderson, Bettis and Revinson (1950) and
Young (1955). The titrating reagents used were mercuric
nitrate and silver nitrate. Sulfate precipitate determin-
ations are discussed by Bien (1954), Musha (1952), and
Milner (1952). Grant and Haendler (1956) developed a method

for the determination of fluoride by titration with thorium.
Tanaka and Nishigai (1952) evolved a micro-method of deter-
mining ammonia by titrating with sulfuric acid, and Kono
(1951-52) used a micro-Kjeldahl procedure. A similar
procedure is described by Kremen, Mathews and Borders (1949).

Complexes - Several attempts were made to determine the
feasibility of using this instrument for studying coordina-
tion numbers of complexes. Iron was titrated with potassium
thiocyanate, nickel with dimethylglyoxime and copper with
ammonium hydroxide. In all instances there was a change in
frequency. However, the graphs did not show any breaks that
would indicate that the method could be used for analytical
purposes. It must be remembered that the instrument can
only be successful when there is a significant change in
dielectric constant or conductance of a solution. Apparent-
ly there is not a sufficient difference between the metallic
ions and their complex ionic form. Ethylenediaminetetraace-
tic acid was used by Hara and West (1954-55) to successfully
determine calcium, nickel, copper, zinc, lead and manganese.
Also for uranium (1955) Hall, Gibson, Phillips and Wilkinson
(1955) describe their work with nickel and dimethylglyoxime.
Hara (1951) studied the complexes of copper, nickel, zinc,
iron, manganese and cadmium with pyridine, hexamethylene-
tetramine, ethylenediamine and bipyridyl. The complex of α
and β -naphthylamine, m- and p-diaminobenzene, picric acid

and titan yellow with cadmium, cobalt, iron, magnesium, calcium, barium, nickel, mercury, silver, lead, copper were also studied.

Reaction Rates - One other type of reaction was studied-reaction rates. Results were disappointing. Alkaline saponification of ethyl acetate was attempted at several concentrations, but no significant change of frequency occured. Ester formation was tried by mixing various proportions of glacial acetic acid and absolute ethyl alcohol and allowing it to stand for a maximum of three days. The mixtures were run by the binary solution method each day for three days and the results tabulated to see if any significant change had taken place. No change was discernable. The iodine clock reaction was also tried in several concentrations, but no change was observed. Jensen, Watson and Beckham (1951) were able to follow the saponification of ethyl acetate. Duke, Bever and Diehl (1949) followed the rate of precipitation of barium sulfate. Flom and Elving (1953) used the method for measuring the rate of alkaline hydrolysis of lower aliphatic esters and esters of chloro-acetic acid. A recording device permitted the investigation of half times of 10 seconds or less.
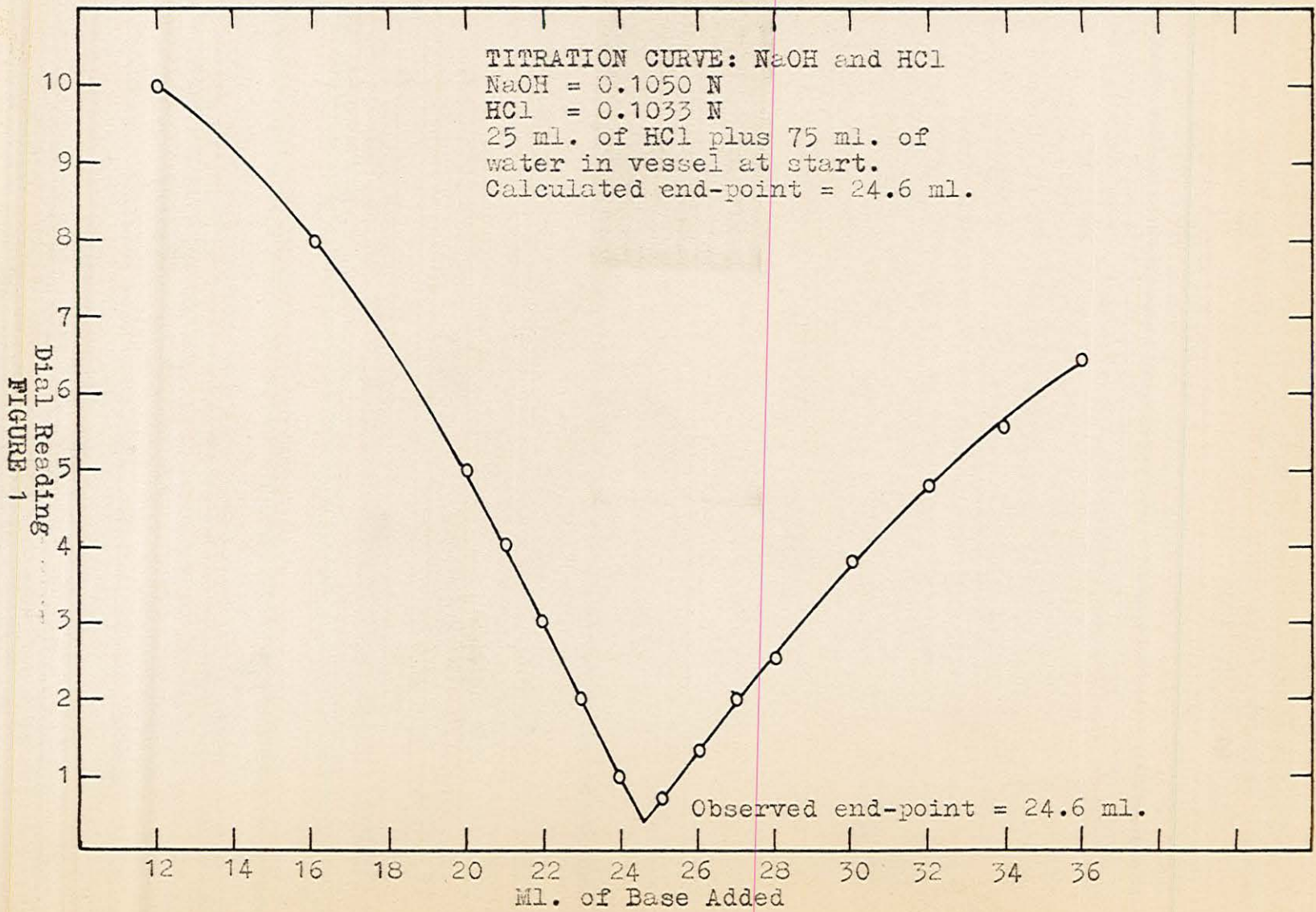
Chromatography - The literature lists one other very interesting application. This is the analysis of eluents in the chromatographic processes. Monaghan, Moseley, Burkhalter and

Nance (1952) mounted a pair of condenser plates at the bottom of a chromatographic column and determined the analysis of the successive elutions. Similar apparatus was used by Laskowski and Pulscher (1952) and Troiskii (1940). Honda (1952) used a coil from a portion of a high frequency oscillator to detect the location of metallic ion bands on a resin cation exchanger. Bauman and Blaedel (1956) followed the separation of carboxylic acids by using a capacity type of monitor on the effluent stream from a chromatographic column. Hashimoto and Mori (1952) adopted a capacity type device to determine the position of various substances on paper after chromatographic separation.

SUMMARY

A heterodyne type high-frequency titrimeter, operating at 120 megacycles was constructed. The instrument is an original device, combining the best features of two previous instruments (West, Burkhalter and Broussard 1950 and Johnson and Timnick 1956), and incorporating several innovations of the author. It is self-contained and no auxilary equipment is necessary to operate the unit. The cell holder plugs into the chassis with three banana plugs and can easily be modified Colpitts type using a 90 cm. length of RG8/U coaxial cable as a half-wave resonator. After a suitable warm up time the instrument shows very good stability. The 120 megacycle frequency was chosen because it represents the upper limit of easily attained stability and still permits the use of 0.1 M solution concentrations. The instrument has capably shown its worth as an analytical tool by titrating weak and strong acids and bases in aqueous and non-aqueous solutions, as well as precipitation type reactions. In addition it is well suited for binary solution analysis. In the author's opinion the instrument is very easy to operate. This, together with its versatility and stability help make it a valuable analytical tool in the field of high-frequency titrimetry.

APPENDIX

TITRATION CURVE: NaOH and HCl
NaOH = 0.1050 N
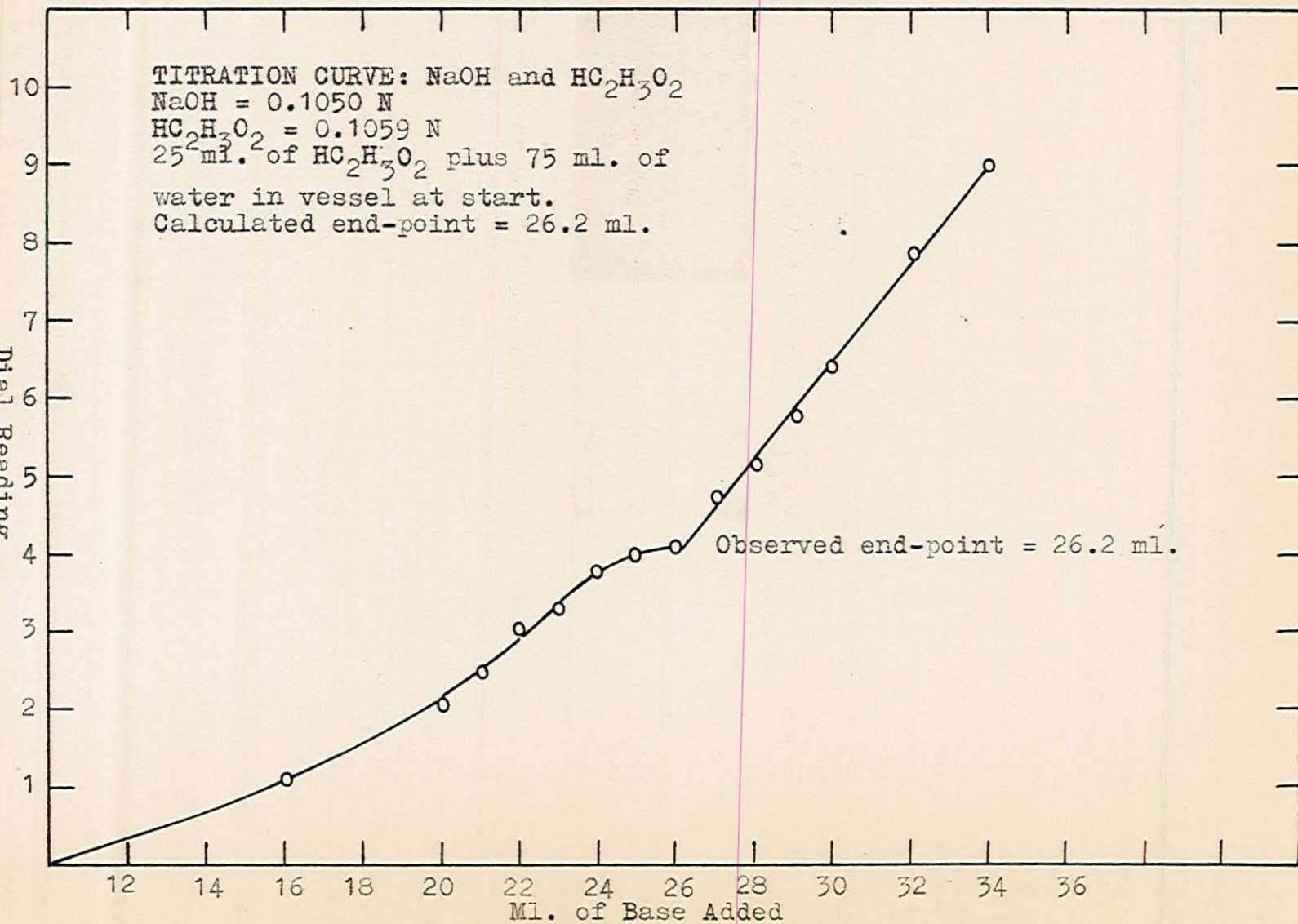HCl = 0.1033 N
25 ml. of HCl plus 75 ml. of
water in vessel at start.
Calculated end-point = 24.6 ml.

Observed end-point = 24.6 ml.

Dial Reading
FIGURE 1

Ml. of Base Added

30

TITRATION CURVE: NaOH and $HC_2H_3O_2$
NaOH = 0.1050 N
$HC_2H_3O_2$ = 0.1059 N
25 ml. of $HC_2H_3O_2$ plus 75 ml. of
water in vessel at start.
Calculated end-point = 26.2 ml.

Observed end-point = 26.2 ml.

Dial Reading

FIGURE 2

Ml. of Base Added

31

TITRATION CURVE: NaOH and $H_2C_2O_4$
NaOH $= 0.1015$ N
$H_2C_2O_4 = 0.1050$ N
25 ml. of oxalic acid plus 75 ml.
of water in vessel at start.
Calculated end-point = 24.2 ml.

Observed
end-point = 24.4 ml

First H⁺ end-point = 12.2 ml.

Dial Reading

FIGURE 3

Ml. of Base Added

TITRATION CURVE: NaOH and H_3PO_4 (High-Frequency Method)
NaOH = 0.1050 N
H_3PO_4 = 0.1070 N

25 ml. of phosphoric acid plus 75 ml. of
water in titration vessel at start.
Calculated end-point = 25.5 ml.

Observed end-point = 25.6 ml.

First H^+ = 12.3 ml.

Dial Reading

Ml. of Base Added

FIGURE 4

TITRATION CURVE: NaOH and H_3PO_4 (Potentiometric)
NaOH = 0.1050 N
H_3PO_4 = 0.1070 N
25 ml. of phosphoric acid plus 75 ml.
of water in titration vessel at start.
Calculated end point = 25.5 ml.

First H^+ = 12.6 ml.

Observed
end-point
= 25.8 ml.

pH

FIGURE 5

Ml. of NaOH Added

34

FIGURE 6

Titration Curve: Aniline and $HClO_4$
using glacial acetic acid as a solvent.
126 mg. of aniline found experimentally.
129 mg. of aniline was dissolved in
100 ml. of glacial acetic acid at start.
Aniline was stock purity and not redistilled.
$HClO_4$ = 0.2000 N

Dial Reading

Observed end-point = 6.8 ml.

Ml. of $HClO_4$ Added

TITRATION CURVE: NaCl and AgNO$_3$

NaCl = 0.1000 N
AgNO$_3$ = 0.0993 N

25 ml. of sodium chloride plus
75 ml. of water in vessel at start
Calculated end-point = 25.2 ml. (Volhard)

Observed end-
point = 25.2 ml.

Dial Reading

Ml. of AgNO$_3$ Added

FIGURE 7

36

BINARY MIXTURE
Benzene and Nitrobenzene

FIGURE 8

BINARY MIXTURE

(1) Water and Dioxane

(2) Water and Acetone

(3) Water and Ethyl Alcohol

Dial Reading

FIGURE 9

Water   Wt. %

38

BINARY MIXTURE

(A) Water and Acetic Acid

(B) Water and Propionic Acid

Dial Reading
FIGURE 10

Water Wt. %

39

CLAPP OSCILLATOR

FIGURE 12
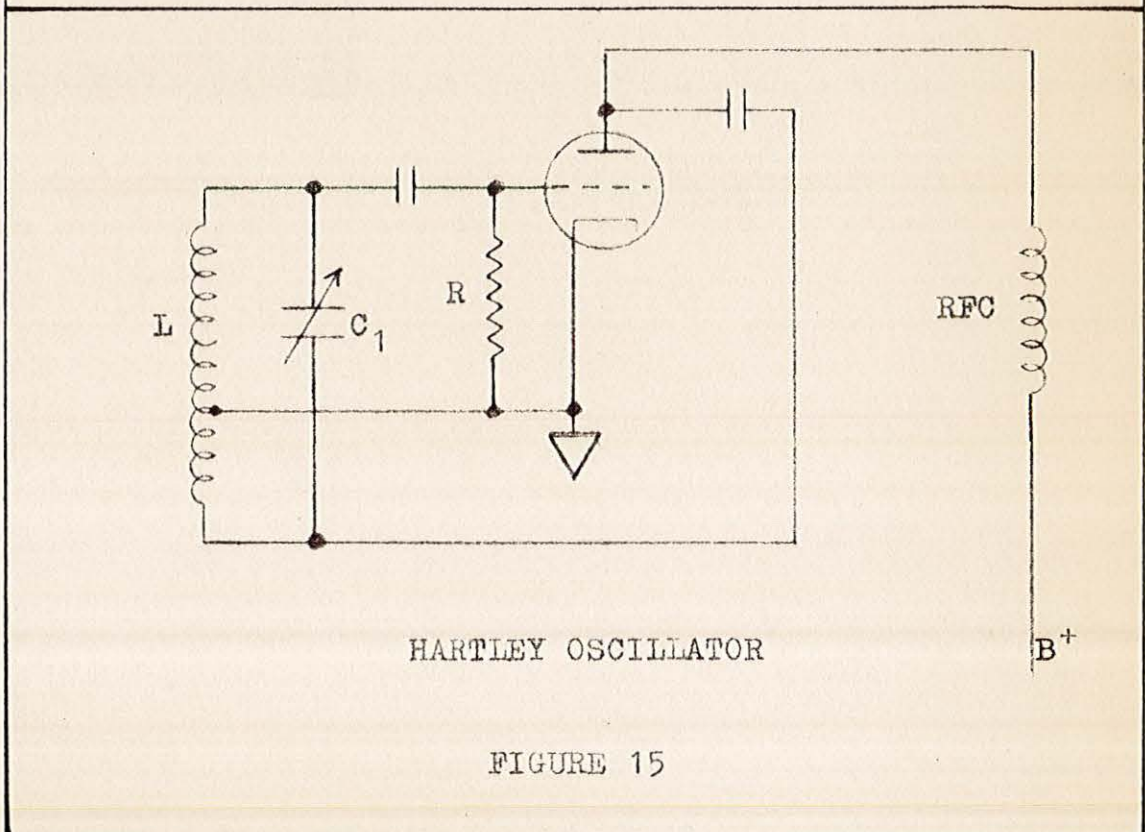
COLPITTS OSCILLATOR

FIGURE 13

41

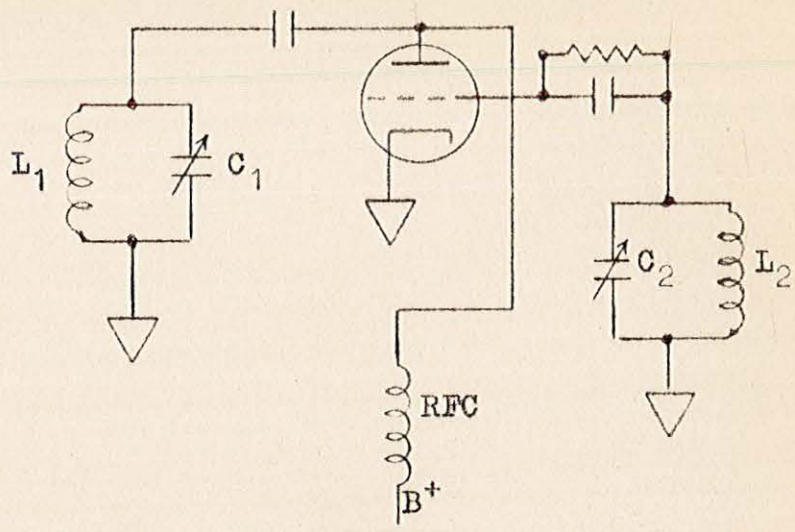CRYSTAL OSCILLATOR

FIGURE 14

HARTLEY OSCILLATOR

FIGURE 15

TUNED PLATE-TUNED GRID OSCILLATOR

FIGURE 16

STABILITY

Dial Reading

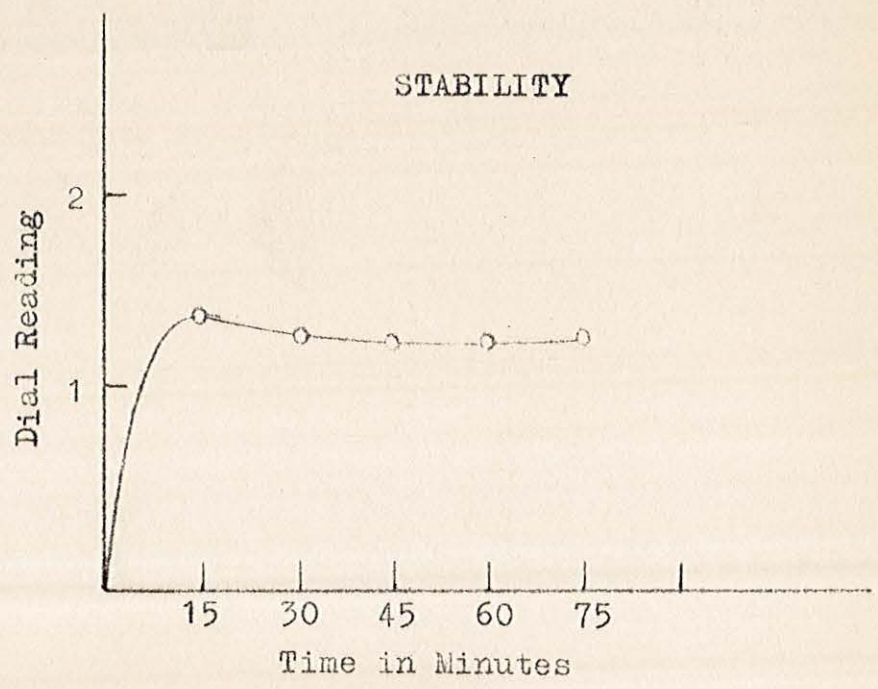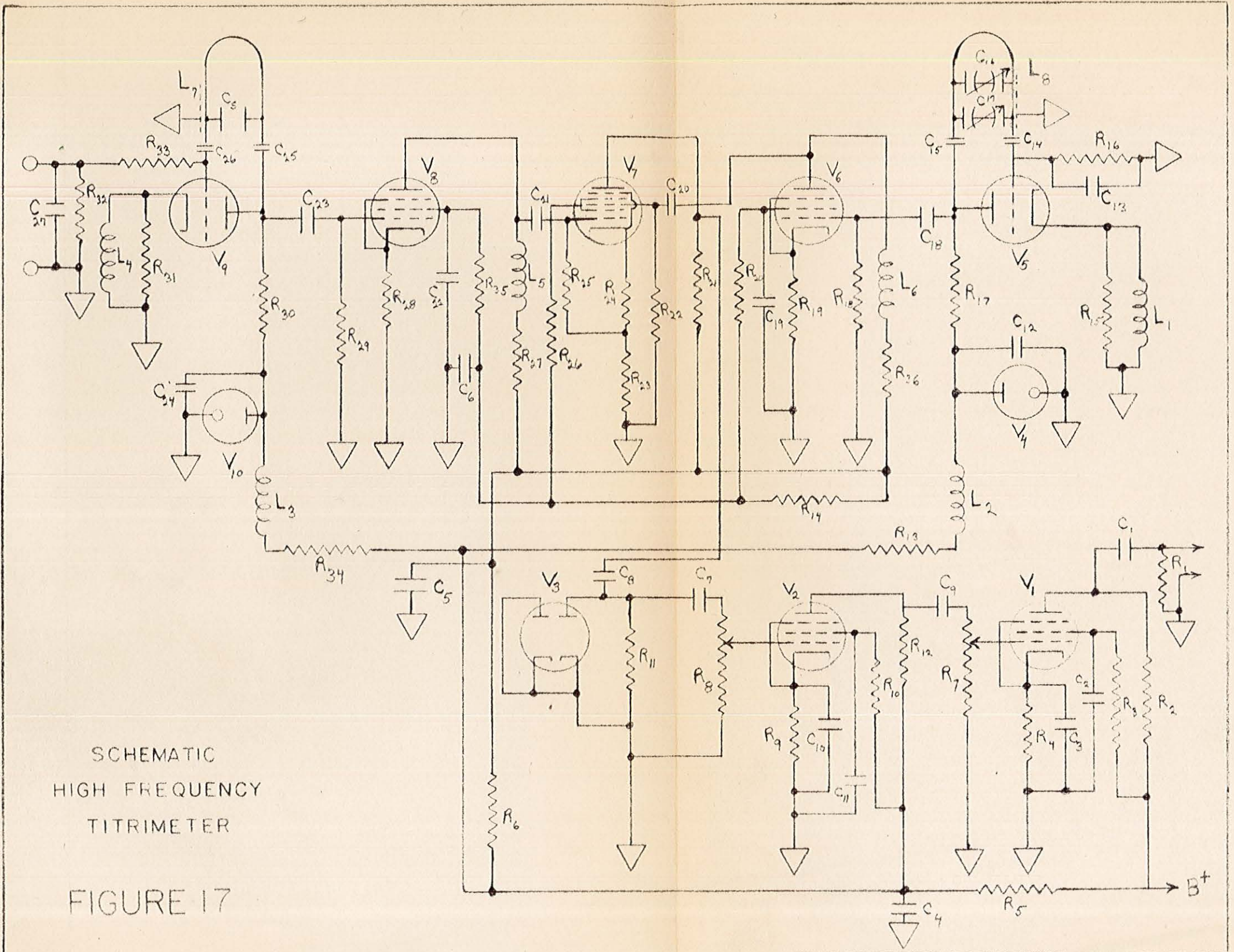Time in Minutes

FIGURE 11

SCHEMATIC
HIGH FREQUENCY
TITRIMETER

FIGURE 17
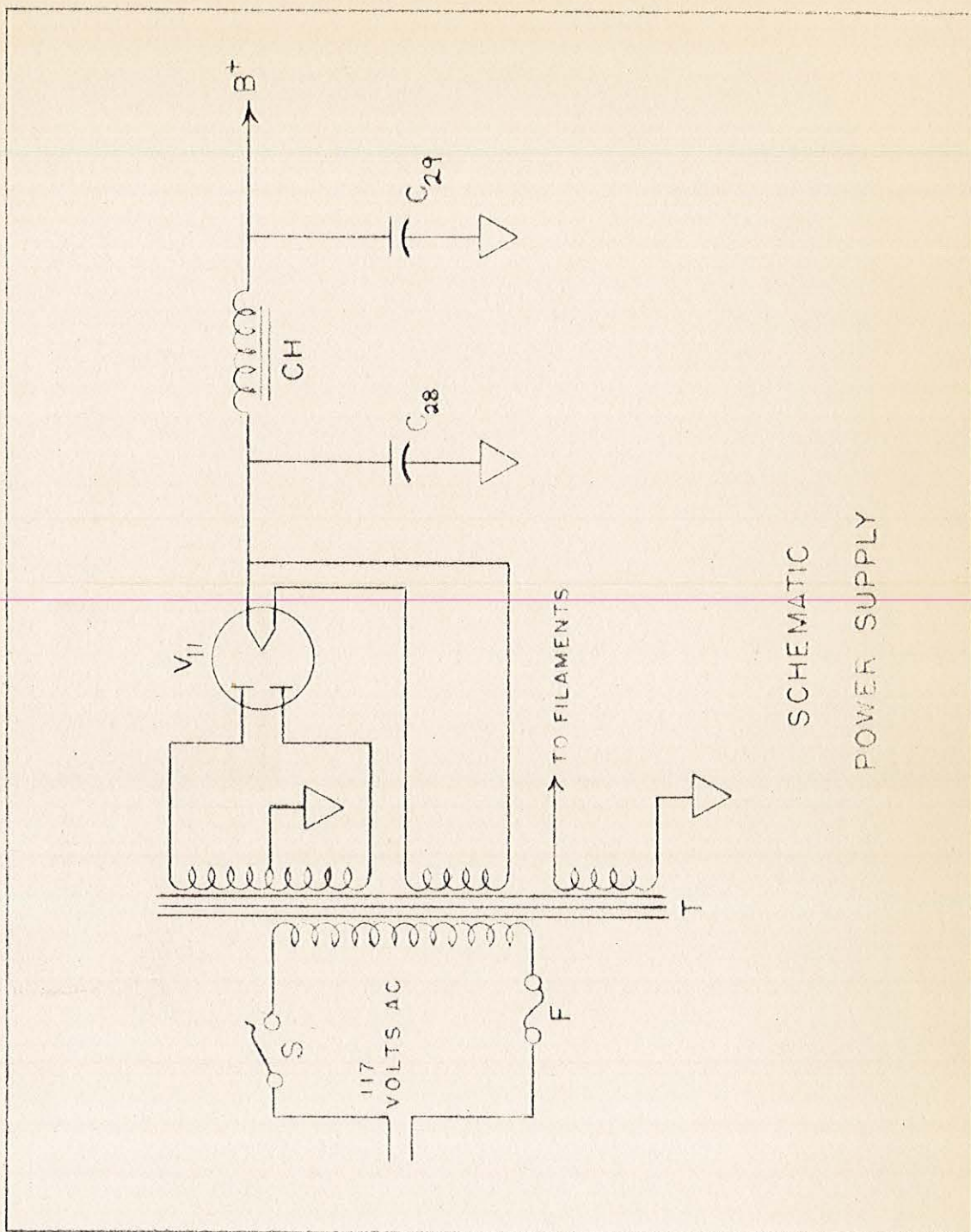
FIGURE 18

LIST OF PARTS FOR INSTRUMENT AND POWER SUPPLY

RESISTORS

Resistor No.	Value*	Resistor No.	Value*
1	4700	19	400
2	100K	20	250K
3	500K	21	600K
4	600	22	500K
5	2K-5W	23	680
6	2K-5W	24	330
7	500K	25	150K
8	500K	26	5600
9	600	27	250K
10	500K	28	400
11	500K	29	750K
12	100K	30	15K
13	5K-10W	31	100-2W
14	4700-2W	32	1K
15	100-2W	33	15K
16	15K	34	5K-10W
17	15K	35	250K
18	750K	36	250K

* All resistors are 1 watt unless specified.

LIST OF PARTS FOR INSTRUMENT AND POWER SUPPLY

CONDENSERS*

Condenser No.	Value, mfd.	Condenser No.	Value, mfd
1	0.1	16	50-50 mmf. (Split-stator)
2	0.1	17	1-3 mmf. (Butterfly)
3	25 @ 25v		
4	10 @ 450v	18	5 mmf.mica
5	10 @ 450v	19	0.01
6	10 @ 450v	20	0.002
7	0.1	21	0.002
8	500 mmf. mica	22	0.01
9	0.1	23	5 mmf.mica
10	25 @ 25v	24	100 mmf.mica
11	0.1	25	100 mmf.mica
12	100 mmf. mica	26	100 mmf.mica
13	100 mmf. mica	27	100 mmf.mica
14	100 mmf. mica	28	8 @ 450v
15	100 mmf. mica	29	8 @ 450v

* All condensers 600v except as noted.

LIST OF PARTS FOR INSTRUMENT AND POWER SUPPLY

TUBES

V_1	6SJ7	V_6	6SK7
V_2	6SJ5	V_7	6L7
V_3	6H6	V_8	6SK7
V_4	OA2	V_9	955
V_5	955	V_{10}	OA2
		V_{11}	5U4-G

COILS

Coil No.	Value mh.
1	10 Turns No. 22 wire wound around R_{15}
2	2.5
3	2.5
4	10 Turns No. 22 wire wound around R_{31}
5	2.5
6	2.5
7	90 cm. length of RG8/U coaxial cable
8	90 cm. length of RG8/U coaxial cable

MISCELLANEOUS

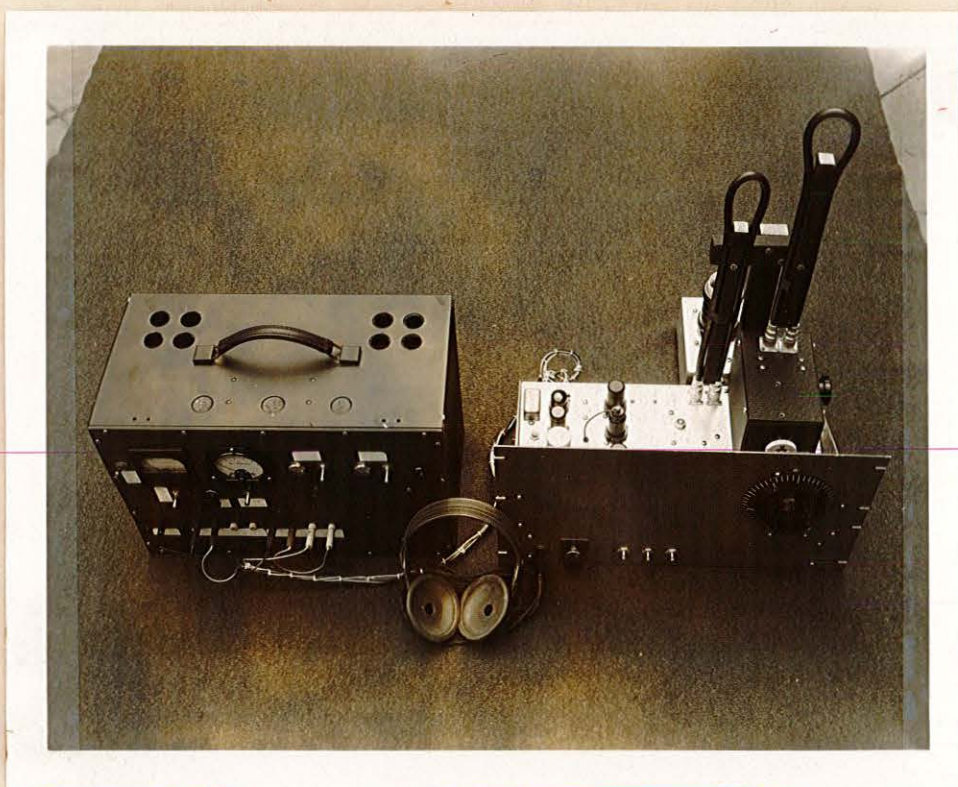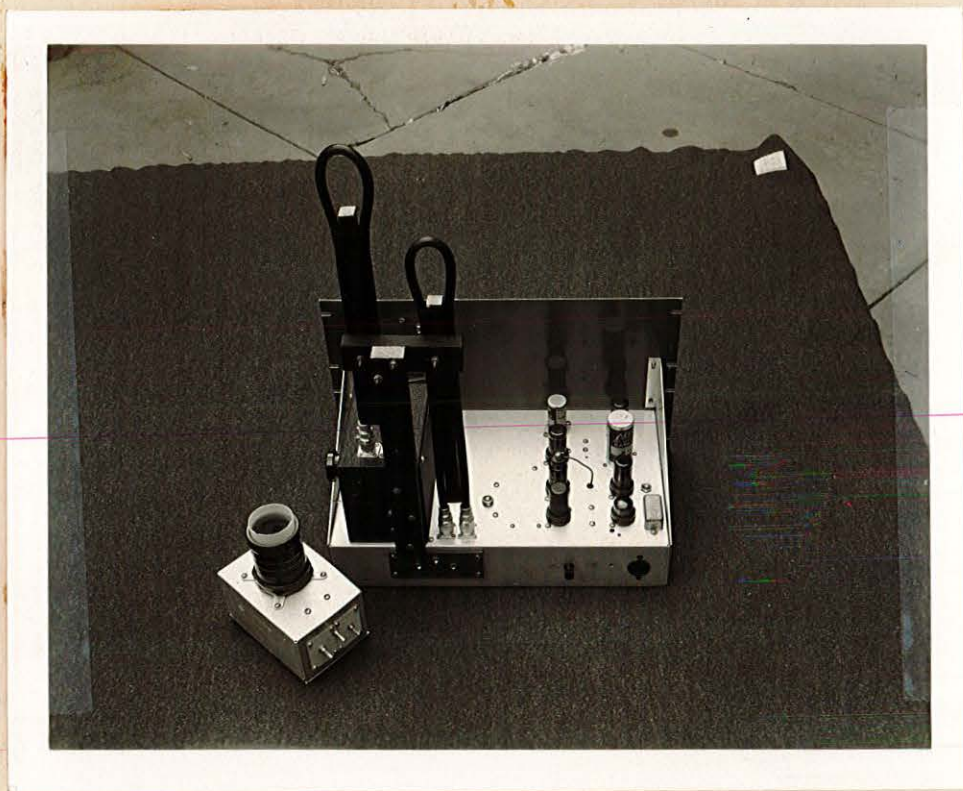|	
CH	Filter Choke - 10 henries.
S	S P S T
F	3A
T	350-0-350 100 m.a.
	5v - 3A
	6.3v - 4A

FIGURE 19

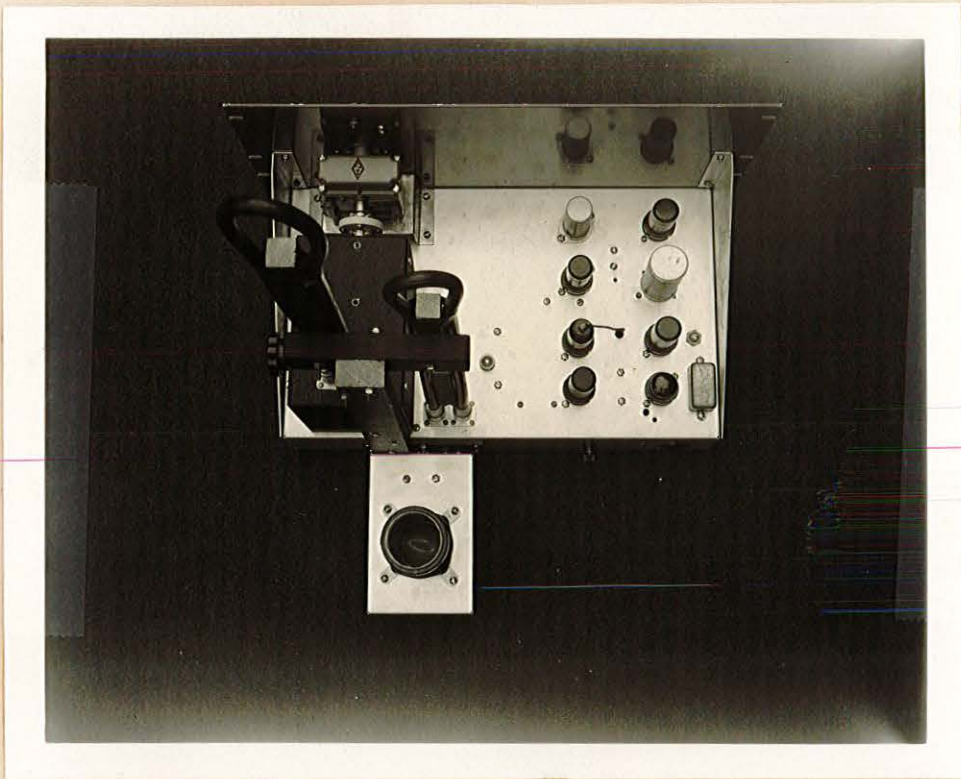Instrument and Power Supply

FIGURE 20

Instrument - Back view

FIGURE 21
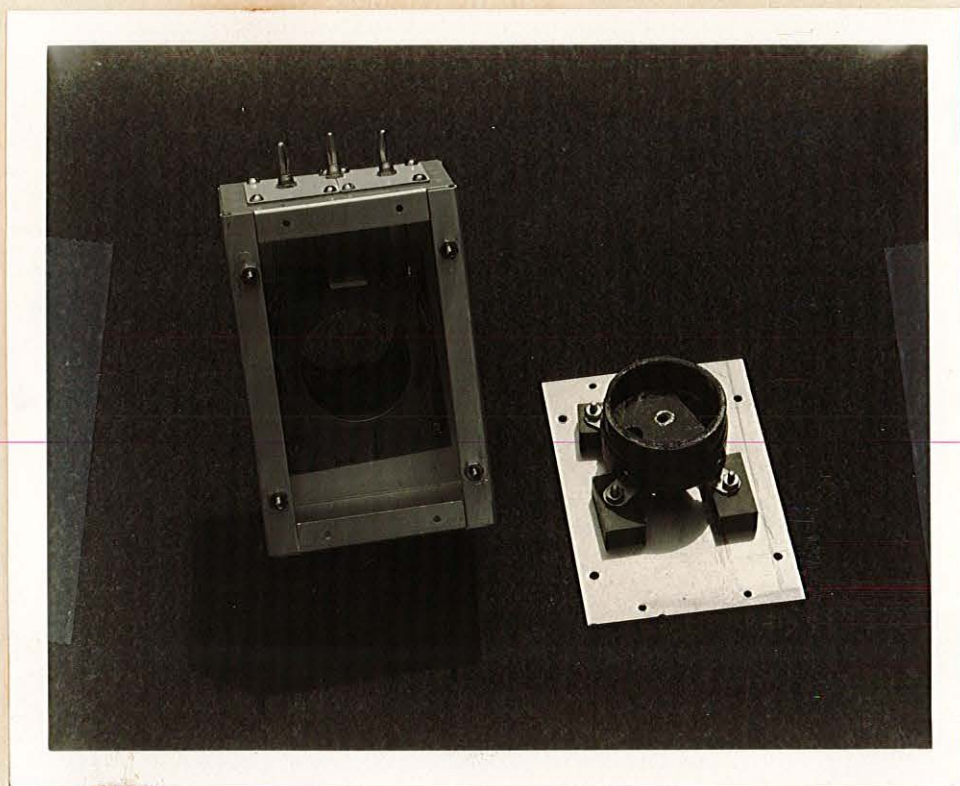
Instrument - Top view

FIGURE 22

Cell Holder - Bottom Removed

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