The Application of High Frequency Oscillations to Chemical Analysis.

Thomas Shepherd Burkhalter

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THE APPLICATION OF HIGH FREQUENCY OSCILLATIONS
TO CHEMICAL ANALYSIS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Thomas Shepherd Burkhalter
B.A., University of Oklahoma, 1947
M.S., University of Oklahoma, 1948
June, 1950
MANUSCRIPT THESES

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the advice and assistance of Dr. Philip W. West who directed this research.

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The financial assistance of the Esso Standard Oil Company is acknowledged.
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A paper
A High Frequency Oscillator Utilizing the Heterodyne
Principle to Measure Frequency Changes Induced by
Diverse Chemical Systems,
West, Philip W., Burkhalter, T. S., and Broussard, Leo
Anal. Chem. 22 469 (1950)

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ABSTRACT

An electronic instrument suitable for use as a chemical analyzer has been designed and constructed. The analyzer consists essentially of two high frequency oscillators (one a "reference" and the other a "working" oscillator) and a system for measuring the frequency difference between the two. Chemical analysis with the use of this instrument is based upon the principle that the frequency of an oscillator changes with a change in composition of the core material of the tank circuit coil. In this instrument, of the heterodyne type, the tank circuit coil form is hollow and the core material is changed by placing the chemical system under investigation within the hollow coil form. The magnitude of the frequency change caused by insertion of the chemical system is a function of the composition of the chemical system. Stability of operation has been checked.

The analyzer is adaptable to most types of conductometric titrations and is not subject to the objections associated with electrodes in contact with solution. Acid-base or precipitation titrations can be made readily. By use of a previously prepared calibration chart direct concentration measurements can be made on many organic binary systems. The frequency changes caused by a number of organic compounds have been measured and are listed.
CHAPTER I

REVIEW OF THE LITERATURE
suitable explanations of this dependency were not available during the early
part of the period. The essential work of the period was done on both the
background and potential of the applied fields was known, but

The dependence of compound solutions of electrolytes

The compoundation of compound solutions of electrolytes were advanced and necessary,

During the period the now accepted theories of the compoundation and

The compoundation for this work these principles of

The work described in this dissertation consists essentially of

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fall into one of four general classes; (1) the standing wave method, (2) the bridge method, (3) the resonance method, and (4) the heterodyne beat method.

The standing wave method of measuring dielectric constants was introduced by Drude (10, 11). Standing Hertzian waves were set up in two parallel wires, the wave lengths being inversely proportional to the square root of the dielectric constant of the medium between the wires. Excitation to produce the waves was obtained by means of two semicircles of copper wire, immersed in oil and connected to a Tesla transformer. Around the semicircles was a loop of wire connected to the two parallel wires in which the waves were set up by induction. Wave length measurements were made by determining the distance between two points at which a Geissler tube glowed most strongly. An initial nodal point was established by grounding an arbitrarily chosen point along the wire. Maximum high frequency potential points were thereby set up at distances from the initial nodal point equal to odd multiples of one quarter wave length. A Geissler tube glows most strongly when held directly above a maximum high frequency potential point. Working at frequencies between ten and three hundred megacycles, Drude measured the dielectric constants of a number of liquids and detected the dielectric dispersion of water. Coolidge (7) improved the precision of measurement by a modification of the method of determining the distance between nodal points. As late as 1921 Holborn (17) used a modification of this method to determine the dielectric constant of water.

W. Nernst (27) is generally considered the pioneer in the use of the alternating current bridge method of making conductance measurements, having
reported such measurements as early as 1895. The working principle of the bridge is so well known that no description is needed here; even today, the conductance bridge is standard equipment in every physics or physical chemistry laboratory. The development of this instrument has been chiefly along the lines of increasing precision by means of more sensitive null indicating devices, the elimination or fixation of stray wiring capacities and field affects, and the compensation for conductance of liquids when making dielectric measurements. In 1904 Nernst and Lersch (23), making conductance measurements at 1.5 megacycles, reported the use of a specially designed galvanometer to improve the sensitivity of null point detection. King and Patrick (21), after developing an amplifier to be used in the null indicator circuit of a bridge operating at one thousand cycles made a critical examination of the relative merits of the standing wave and the bridge methods of measurement. They reported that, due to the broad indication of nodal points, the precision of the standing wave method was inferior to that of the bridge at low frequencies; but inherent errors in the bridge made this type of measurement impractical at frequencies much above one megacycle.

When a circuit consisting of an inductance, a capacitance, and a resistance in series is excited at its natural frequency as determined by the values of the components of the circuit, a condition known as resonance is said to exist. The value of the current flowing through such a circuit is at a maximum under the condition of resonance. This phenomenon forms the basis for the resonance method of measuring dielectric constants. If in such a circuit the capacitive branch is formed by two condensers in
parallel and if the dielectric between the plates of one of these condensers is changed, the value of that condenser will be changed and the circuit cannot remain in a state of resonance. However, the circuit can be restored to a state of resonance by varying the value of the second condenser in such a manner as to compensate for the change in value of the first condenser; return to resonance is indicated by maximum deflection of a galvanometer registering the current through the circuit. The amount of capacity required to compensate exactly for the change in value of the first condenser is a function of the dielectric constant of the material between the plates of the first condenser. In actual practice the first condenser is usually a condenser type cell in which air is used as the dielectric during the original establishment of the condition of resonance. The air is then displaced by the liquid under investigation and resonance restored by tuning the second condenser, which is an accurately calibrated precision variable condenser. Tank (55) was among the early users of this method. Theodortschick (56), Walden, Uhlich, Werner (57), and Falckenberg (12) also carried out investigations in which this method was used. Lattey (22) published a critical review of the various modifications of the three general classes of methods. The principle objection to the method of resonance was the inability to determine the point of resonance precisely. A plot of frequency versus current showed a very sharp maximum at the point of resonance, provided the Q of the circuit was sufficiently high. However, when the molar conductance of the liquid under investigation was appreciable, it was impossible to maintain a high Q and the maximum current point was rather broad.
This inability to make precise measurements led to the development of the heterodyne beat method of determining dielectric constants.

The heterodyne beat method calls for two independent sources of oscillations, a stage for beating the two, and a means of determining the difference or beat frequency. In the determination of dielectric constants by this method, the frequency of one source of oscillations is held constant while the frequency of the other is varied by utilizing a condenser type cell as one of the frequency controlling elements. The circuits are tuned to a predetermined frequency difference (which may or may not be zero) with air between the plates of the condenser cell. When the air is displaced by the liquid under investigation, the frequency of oscillation of one source changes and consequently the frequency difference changes. The original oscillation frequency and the frequency difference may be restored by tuning a second precisely calibrated variable condenser in the same circuit until exact compensation has been made for the change in capacity of the condenser cell. The precision of this method depends in part upon the reproducibility of the beat note, since the beat note itself is the sensible indicator. Hyslop and Carman (18) were among the earliest of workers in this field. These investigators chose five hundred and twelve cycles as the predetermined value of the beat note and tuned to this beat by auditory comparison with a tuning fork. Fritts (14) used essentially the same instrumentation except that a photographic record of the beat was obtained. One side of a razor blade wedge slit was fastened to a tuning fork and the other to the diaphragm of a telephone actuated by the beat note. The slit was illuminated and the image allowed to fall upon light sensitive paper.
Jackson (19) was among the first to employ vacuum tubes as part of the oscillating circuit. The circuit was of the "tickler feed-back" type and tuned to a zero beat condition. Zahn (42, 43) employed the "tickler feed-back" arrangement to measure the electric moment of some gaseous molecules. The measurements were made at a frequency of one megacycle and the beat note was fixed by further mixing the beat with the signal from a one thousand cycle tuning fork. A significant contribution of the Zahn apparatus was the unique condenser arrangement which placed the cell condenser in series with a large fixed condenser which in turn was connected in parallel with a large precision variable tuning condenser. By this arrangement small changes in value of the capacity of the cell necessitated very large changes in the tuning condenser.

$$\Delta C = -\left[ \frac{c^2}{(K+K'+C)\Delta K + (K+K')^2} \right] \Delta K$$

In the above equation $c$ represents the capacity of the condenser cell, $K'$ is the capacity of the large fixed condenser, and $K$ is the value of the variable condenser. Williams and Krohna (39) simplified the heterodyne beat method somewhat by using the fixed frequency oscillating circuit as a dual purpose oscillator-mixer stage; however, this arrangement proved unsatisfactory because it permitted excess coupling between the two sources of oscillation and they could no longer be described as independent.

Williams and Weisberger (40) rectified this condition by returning to the use of a third separate mixer stage. In this modification two Hartley type circuits were employed. Stuart (34) obtained some measurements with a high
degree of precision by employing the Zahn condenser arrangement with both a phone and a galvanometer in the null circuit. Sanger and Steiger (32) studied the structure of the water molecule employing dielectric constant values obtained through use of the Stuart apparatus. McAlpine and Smyth (36) studied the polarization of hydrocarbon vapors using an instrument similar to Zahn's, but substituted two Hartley oscillators operating at five hundred kilocycles. De Bruyne (7) determined the dipole moment of deuterammonia with the same instrument. Lewis, Wiswall, and Smyth (23, 41) used a crystal controlled oscillator as the source of constant frequency oscillation, and placed the cell condenser in the frequency controlling circuit of a Hartley type oscillator. The beat note was matched with a one thousand cycle tuning fork.

As instrumentation developed and more attention was turned toward precision of measurement, it became evident that the oscillator frequency drift constituted a source of error. This objectionable feature could be eliminated from the so-called "constant frequency" source by using a crystal controlled oscillator; however, this method could not be applied to the oscillator containing the condenser cell as it of necessity must be of the variable frequency type. Consequently, investigators began to seek for methods of stabilizing the operation of variable frequency oscillators. Llwellyn (24) discussed the manner in which frequency of vacuum tube oscillators depend upon the operating voltages, derived a theory of dependence, and showed how it indicated a method of causing frequency to be independent of the voltage applied. A mathematical formula was derived for calculating values of inductance and capacitance in order to gain maximum frequency
stability, Stranathan (33) developed a "Portable Alternating Current Oper-
ated Heterodyne Beat Apparatus of Unusual Frequency Stability" employing one
variable frequency oscillator and one crystal controlled oscillator working
at one half megacycle. The variable frequency oscillator was of the electron
coupled type with a Hartley circuit; grid and plate condenser values were
calculated from the Llwellyn formula. Clapp (6) investigated the dependence
of frequency stability upon thermal and inter-electrode effects of the tube,
His studies revealed that maximum frequency stability necessitated a high
internal impedance generator loosely coupled to a low impedance high Q
circuit. Translated into physical reality, this meant a series resonant
tank circuit and a vacuum tube with a high value of plate resistance. Clapp
incorporated the series resonant circuit in a basic Colpitts design with
the voltage divider feed-back condensers parallel to the tube inter-electrode
capacitances. Gramer (15) in the QST laboratories studied the operating
characteristics of this oscillator and described it as an oscillator of
superior frequency stability, almost independent of tube thermal effect.
The Clapp design forms the basic circuit of the chemical analyzer described
in this dissertation.

The report in 1946 of Jensen and Parrack (20) of an electrodeless
conductometric titrimeter marked a turning point in the field of conductance
measurements as applied to analysis. Previously all conductometric work
had been done with electrodes in contact with the solution, thereby sub-
jecting the operation to all the objectionable features of electrodes, such
as chemical non-uniformity, non-homogeneous surface characteristics, concen-
tration polarization, and gas evolution. Further, conductance investiga-


at high frequencies had been almost entirely confined to attempts to con-
firm or disprove the inter-ionic theories of Debye, Huckel, and Onsager.
As early as 1923 Sand (31) believed that dilute solutions of strong electro-
lytes would show increased conductance at high radio frequencies. In 1926
Debye and Falkenhagen (9) as a result of calculations based upon the Debye-
Huckel theories, predicted quantitatively an increase in conductance of
electrolytes at high frequencies. Numerous investigators including Zick,
Zalm, Wein, Malseh, Gaertner, and Arnold (30, 44, 33, 25, 15, 2) tested
the validity of the Debye-Falkenhagen prediction by measuring the conduct-
ance of several electrolytes over a range of high frequencies. Although
experimental difficulties involving the control of stray fields at these
high frequencies prohibited close agreement between individual investigators,
still it was apparent from the results of these workers that qualitatively
at least the Debye-Falkenhagen prediction had been confirmed.

The Jensen titrimeter eliminates the electrodes in contact with
solution, and renders non-objectionable the effect of stray fields at high
frequencies. It is pertinent to point out that the Jensen apparatus was
designed not as a tool for investigation of physico-chemical phenomenon;
but rather as an analytical tool for following the change of some property
of a chemical system; this property is known to be concentration dependent
but, as yet, has not been sharply defined. The importance of the Jensen
titrimeter was immediately evident. Although the possible utility of con-
ventional conductometric titrimetry was recognized, acceptance of this
method as a routine analytical tool had not been widespread because of the
rather cumbersome apparatus and critical manipulation accompanying a conventional conductometric titration. The Jensen titrimer represented an instrument which required of the operator only the ability to read a buret and an ammeter. Both Blake and Arditti (4, 5, 1) have offered modifications of the Jensen titrimer. The Arditti instrument differs from that of Jensen only in that the grid current rather than the plate current of the oscillator is measured. In the Blake apparatus, the conductometric cell forms the core of a radio frequency coupling transformer; the rectified current in the secondary is measured as a function of concentration. Both of these methods utilize current as the sensible indicator; magnitude of the current is a function of loading of the circuit; loading, in turn, is a function of the concentration of the components of the system. The work presented by this author constitutes both a refinement of instrumentation and an expansion of the applications of the Jensen method.
CHAPTER II

A PAPER
High-Frequency Oscillator

Utilizing Heterodyne Principle to Measure Frequency Changes Induced by Diverse Chemical Systems

PHILIP W. WEST, T. S. BURKHALTER, AND LEO BROUSSARD
Louisiana State University, Baton Rouge, La.

A high frequency oscillator utilizing the heterodyne principle has been designed for use in measuring frequency changes induced by diverse chemical systems. The increased sensitivity obtained can be utilized to detect and measure concentration changes of a nature that would require long and tedious procedures by ordinary chemical methods.

HIGH-frequency oscillations have been used for almost 40 years to determine dielectric constants, which have served to indicate the course of reactions, to follow the progress of fractional distillations, to determine the composition of binary mixtures of certain isomers, and in some cases to determine the moisture content of solids (1, 2). However, the direct application of high-frequency oscillations to chemical analysis has received little attention until very recently.

In 1946 Jensen (4) reported a high-frequency oscillation titrator applicable to the performing of conductometric titrations without the use of standard-type electrodes. The conductometric cell is placed inside the field of the tank circuit coil of a high-frequency oscillator and the change in plate current of the oscillator tube is plotted against volume of the titrating reagent added to the cell. The reversal of the curve of plate current versus volume indicates the equivalence point of the titration. In 1947 Blake (2) reported the use of radio-frequency oscillations in making conductometric titrations. In the Blake apparatus the output of a radio-frequency oscillator is coupled inductively to a metering system where the radio-frequency current is rectified and the direct current is plotted against volume of titrating reagent. Reversal of the curve of current versus volume indicates the equivalence point.

The instrument designed by the present authors is based upon the principle that the frequency of an oscillator changes with a change of composition of the core material of the tank circuit coil. In this instrument, of the heterodyne type, the tank circuit coil form is hollow and the core material is changed by placing a small glass cell, filled with any desired chemical system, within the hollow coil form. The frequency change is plotted as a function of concentration. Because frequency changes as small as 10 in 4,000,000 cycles may be measured accurately, the increased sensitivity thus obtained can be utilized to detect and measure concentration changes that would require long and tedious procedures by ordinary chemical methods.

EXPERIMENTAL

The heterodyne analyzer consists essentially of two high-frequency oscillators (one a "reference" and the other a "working" oscillator), and a system for measuring the frequency difference between the two oscillators. The purpose of the reference oscillator is to make possible a means of measuring the frequency change of the working oscillator without measuring the actual frequency. By beating the output of the working oscillator with that of a reference oscillator, a difference (beat) frequency in the audio range may be obtained. A change in frequency of the working oscillator will thus cause a frequency change of equal magnitude in the beat frequency. This beat frequency change can be measured with a satisfactory degree of accuracy. The block diagram (Figure 1) illustrates the manner of operation of the analyzer.

Interchange of energy between the two oscillators through the mixer tube is prevented by the two buffer stages. The output of each oscillator is fed into its buffer stage and thence into the mixer tube. No amplification is gained in the buffer stage; rather, the buffer serves solely to isolate completely the sources of oscillation from each other, so that a change in frequency of the working oscillator cannot affect the reference oscillator. The output of the mixer stage, consisting of the two original frequencies, the sum, and the difference of the original frequencies, is conducted to the detector system where the beat frequency is isolated. The beat frequency is then amplified in the audio-amplifier stage and can be measured by any standard frequency-measuring device.

In this laboratory an accurately calibrated audio-oscillator (Hewlett-Packard 200-1) and an oscillograph (DuMont 208-B) were used. The output from the audio-amplifier stage was fed to the vertical plates of the oscillograph while the output of the audio-oscillator was fed to the horizontal plates. The frequency of the audio-oscillator was varied until the Lissajous pattern on the screen of the oscillograph indicated that the frequency of the audio-oscillator was equal to the beat frequency. The choice of an audio-oscillator-oscillograph combination for a frequency meter was purely expedient. A number of commercial direct reading audio-frequency meters could have served just as satisfactorily.

Figure 1. Block Diagram of Heterodyne Analyzer

The change in frequency of the working oscillator, caused by insertion of a chemical system into its field, is measured in the following manner:

Under normal stand-by conditions (no chemical system within the field of the working oscillator) the frequency meter indicates the difference (beat frequency, stand-by) between the frequencies of the working and reference oscillators. If a chemical system is then placed inside the tank coil of the working oscillator, the frequency of this oscillator will change while the frequency of the reference oscillator is unaffected. The frequency meter will then indicate the difference (beat frequency, loaded) between the frequencies of the reference oscillator and the working oscillator with a chemical system in its tank coil. The difference between the two meter readings (beat frequency, stand-by minus beat frequency, loaded) is equal to the change in frequency of the working oscillator.

One of the most important physical characteristics of the instrument is the frequency stability of the two oscillators. The

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1 Present address, Esso Laboratories, Esso Standard Oil Company, Baton Rouge, La.
The stability of the oscillators in the heterodyne analyzer is shown in Figures 3 and 4. Figure 3 shows the frequency drift from a cold start of each oscillator relative to that of a 4.3-megacycle crystal-controlled oscillator. The output of each oscillator independently was beat with the output of the previously warmed up crystal oscillator. The difference frequency was measured

two oscillators under stand-by conditions must be able to maintain a constant frequency difference. The circuit diagram for the oscillators (Figure 2) is the Clapp modification of a Colpitts-type oscillator and is especially well suited for work of this kind. A description of the individual parts is given in Table I. The oscillator circuit is described by Gramer (3), who investigated the stability of the oscillator in the QST laboratories, and reports that the circuit "results in an oscillator whose frequency is almost independent of plate voltage and tube thermal effects." The unusual stability is due to loose coupling between the oscillator tube and a high Q tuned circuit. The large capacity of C5 and C6 compared to C1, makes coupling between the tube and the tuned circuit very loose, so that the circuit Q can be kept very high; in addition, these large values "swamp" the grid to cathode and plate to cathode capacities to such an extent that the effect of any change in these capacities becomes negligible.

![Figure 2. Circuit Diagram of Heterodyne Analyzer](image)

![Figure 3. Frequency Drift of Each Oscillator](image)

**Table I. Values of Component Parts of Analyzer**

<table>
<thead>
<tr>
<th>Condenser</th>
<th>Value, mfd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>150 mfd.</td>
</tr>
<tr>
<td>C2</td>
<td>0.001</td>
</tr>
<tr>
<td>C3</td>
<td>0.001</td>
</tr>
<tr>
<td>C4</td>
<td>0.001</td>
</tr>
<tr>
<td>C5</td>
<td>100 mfd.</td>
</tr>
<tr>
<td>C6</td>
<td>0.001</td>
</tr>
<tr>
<td>C7</td>
<td>0.001</td>
</tr>
<tr>
<td>C8</td>
<td>0.001</td>
</tr>
<tr>
<td>C9</td>
<td>0.001</td>
</tr>
<tr>
<td>C10</td>
<td>0.001</td>
</tr>
<tr>
<td>C11</td>
<td>0.001</td>
</tr>
<tr>
<td>C12</td>
<td>0.001</td>
</tr>
<tr>
<td>C13</td>
<td>0.001</td>
</tr>
<tr>
<td>C14</td>
<td>0.001</td>
</tr>
<tr>
<td>C15</td>
<td>0.001</td>
</tr>
<tr>
<td>C16</td>
<td>0.001</td>
</tr>
<tr>
<td>C17</td>
<td>0.001</td>
</tr>
<tr>
<td>C18</td>
<td>0.001</td>
</tr>
<tr>
<td>C19</td>
<td>0.001</td>
</tr>
<tr>
<td>C20</td>
<td>0.001</td>
</tr>
<tr>
<td>C21</td>
<td>0.001</td>
</tr>
<tr>
<td>C22</td>
<td>0.001</td>
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<table>
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<tr>
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<tr>
<td>L2</td>
</tr>
<tr>
<td>L3</td>
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<tr>
<td>L4</td>
</tr>
<tr>
<td>L5</td>
</tr>
<tr>
<td>L6</td>
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<tr>
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<th>Value, K.°</th>
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<tr>
<td>R1</td>
<td>100</td>
</tr>
<tr>
<td>R2</td>
<td>750</td>
</tr>
<tr>
<td>R3</td>
<td>400 ohms</td>
</tr>
<tr>
<td>R4</td>
<td>250</td>
</tr>
<tr>
<td>R5</td>
<td>5, 6</td>
</tr>
<tr>
<td>R6</td>
<td>150</td>
</tr>
<tr>
<td>R7</td>
<td>330 ohms</td>
</tr>
<tr>
<td>R8</td>
<td>880 ohms</td>
</tr>
<tr>
<td>R9</td>
<td>500</td>
</tr>
<tr>
<td>R10</td>
<td>600</td>
</tr>
<tr>
<td>R11</td>
<td>250</td>
</tr>
<tr>
<td>R12</td>
<td>250</td>
</tr>
<tr>
<td>R13</td>
<td>400 ohms</td>
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<tr>
<td>R14</td>
<td>750</td>
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<td>R16</td>
<td>360</td>
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<td>150</td>
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<tr>
<td>R18</td>
<td>1200 ohms</td>
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<td>R19</td>
<td>30</td>
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<tr>
<td>R20</td>
<td>50</td>
</tr>
<tr>
<td>R21</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Type</th>
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<tbody>
<tr>
<td>V1</td>
<td>6J5</td>
</tr>
<tr>
<td>V2</td>
<td>6K7</td>
</tr>
<tr>
<td>V3</td>
<td>6K7</td>
</tr>
<tr>
<td>V4</td>
<td>6J5</td>
</tr>
<tr>
<td>V5</td>
<td>6H5</td>
</tr>
<tr>
<td>V6</td>
<td>6J5</td>
</tr>
<tr>
<td>V7</td>
<td>84UG</td>
</tr>
<tr>
<td>V8</td>
<td>V-R 150</td>
</tr>
</tbody>
</table>

* 1000-ohm units.
every minute for 96 minutes. Because the crystal oscillator has negligible drift, the variation of the difference frequency is due to the drift of the oscillator. The two curves are almost parallel throughout their length and after 45 minutes show practically zero drift and a constant frequency difference. Figure 4 is a plot of time versus beat frequency, stand-by from a cold start. During the first 45 minutes the beat frequency gradually increases, then slopes off and becomes constant within 10 cycles. The frequency of each oscillator varies about 1 cycle per volt with fluctuations of line voltage, but the frequency difference is unaffected.

![Figure 4. Time vs. Beat Frequency](image)

The buffer, mixer, detector, and amplifier stages are all of standard design and may be modified in any way necessary to fit a particular need. The buffer is an R-C coupled 6L7 R-F amplifier. The mixer stage consists of a 6L7 tube with a split cathode resistor to maintain proper bias on each of the control grids. A diode-type detector circuit is employed utilizing a 6J6 tube. The audio-amplifier uses a 6J5 tube with the component values adjusted to give approximately a linear amplification factor of 14 over a frequency range of 500 to 5000 cycles.

![Figure 5. Acid-Base Titrination](image)

The layout and mechanical construction of a high-frequency oscillator of exceptional stability are at least partially an art. Stray wire capacity, chassis currents, radiation effect, etc., constitute individual problems with every set. The technician who has had no previous experience with high-frequency oscillators will meet with some difficulty in his first attempt. However, any radio amateur or veteran with radio-radar maintenance experience should have no difficulty in obtaining the required stability.

**APPLICATIONS OF THE ANALYZER**

The analyzer is adaptable to most types of conductometric titrations. Acid-base or precipitation titrations can be made readily. A common 50-ml. heat-resistant test tube (25 by 105 mm.) fits snugly into the coil form. The titrant is added from a microburet, the beat frequency change is measured after the addition of each increment, and a plot is made of volume versus beat frequency change. Figure 5 is a sample graph made by this method. Ten milliliters of 0.01000 N potassium hydroxide in the test tube were diluted to approximately 30 ml. and titrated with 0.1060 N hydrochloric acid.

### Table II. Beat Frequency Change Induced by Various Organic Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Beat Frequency Change, Cycles/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>660</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>681</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>697</td>
</tr>
<tr>
<td>Methanol</td>
<td>5560</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4763</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>4288</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>4117</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>3895</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>3906</td>
</tr>
<tr>
<td>sec-Butanol</td>
<td>3658</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>2998</td>
</tr>
<tr>
<td>n-Amyl alcohol</td>
<td>2031</td>
</tr>
<tr>
<td>tert-Amyl alcohol</td>
<td>2038</td>
</tr>
<tr>
<td>n-Octyl alcohol</td>
<td>2550</td>
</tr>
<tr>
<td>Acetone</td>
<td>4597</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>4103</td>
</tr>
<tr>
<td>Diethyl ketone</td>
<td>3922</td>
</tr>
<tr>
<td>Methyl n-amyl ketone</td>
<td>3002</td>
</tr>
<tr>
<td>Aetophenone</td>
<td>4014</td>
</tr>
<tr>
<td>Benzene</td>
<td>810</td>
</tr>
<tr>
<td>Toluene</td>
<td>830</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>1672</td>
</tr>
<tr>
<td>Aniline</td>
<td>2040</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>5720</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2999</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>1242</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>1094</td>
</tr>
<tr>
<td>Caproic acid</td>
<td>1005</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>2135</td>
</tr>
<tr>
<td>Methyl n-propionate</td>
<td>1890</td>
</tr>
<tr>
<td>Methyl n-butyrate</td>
<td>1887</td>
</tr>
</tbody>
</table>

By using a small volumetric flask (special design, 19-ml capacity) which fits entirely inside the coil form and a previously prepared calibration chart, direct concentration measurements can be made on many binary organic systems. The calibration curve of composition versus beat frequency change is nearly linear and for many systems is sufficiently steep so that accuracy of the order of 0.2 to 2.0% can be attained. A calibration chart of the aniline-nitrobenzene system shows that the curve is a straight line with a slope of 36 allowing an accuracy 0.3%.

The slope of the calibration curve is determined by the difference in the beat frequency change induced by the pure components. The greater the difference in the beat frequency change induced, the steeper the slope of the calibration curve and the greater the attainable accuracy. The beat frequency changes induced by a number of organic compounds have been measured and are listed in Table II. A difference of beat frequency change equal to 5000 cycles between any two compounds represents an attainable accuracy of 0.2%.

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**LITERATURE CITED**


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BEAT FREQUENCY CHANGE

NITROBENZENE, WT. %

FIGURE 6  CALIBRATION CHART OF ANILINE-NITROBENZENE SYSTEM
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Thomas Shepherd Burkhalter was born in Sayre, Oklahoma September 27, 1919. He received his elementary and secondary education in the public school system at Sayre, Oklahoma. He was graduated from the University of Oklahoma with the B.A. degree in 1947 and with the M.S. degree in 1948. While attending the University of Oklahoma he served as graduate assistant for one term and as instructor in chemistry for one summer session.

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Major Field: Chemistry

Title of Thesis: THE APPLICATION OF HIGH FREQUENCY OSCILLATION TO CHEMICAL ANALYSIS

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

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J.L.E. Ericsson

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Date of Examination:

May 10, 1950