HIGH-FREQUENCY APPARATUS FOR PHYSICOCHEMICAL INVESTIGATION AND ITS USES

V. A. Zarinskii and I. R. Mandel'berg

(The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the USSR)

With the high-frequency apparatus developed by us, it is possible to determine concentrations in aqueous and nonaqueous binary solutions, to perform titrations, and to carry out other physicochemical investigations. In developing this apparatus we started from the requirements of an industrial control instrument. The instrument had to be portable, suitable for use in laboratories and under plant conditions, adaptable for remote control, and to remain sufficiently reproducible and precise for measurements over a wide range of concentrations.

The apparatus (Fig. 1) comprised a generator of high-frequency current at 5 Mc, a stabilized rectifier, a differential detector with a microammeter as indicator, and two resonant circuits for measurement and compensation.

The high-frequency generator was assembled according to a three-point scheme, with a grounded grid and parallel feeds. The resonant circuit L_3C_5 of the generator had a tapping a_1, connecting it to the cathode of the tube T_6, and acting as a reverse coupling. To step up the cathode potential and the stability of the generator, a grid leak R_3C_3 was included in the grid circuit of tube T_6. The anode of the generator was fed from the rectifier through the separating choke L_2, and the screen grid through the damping resistance R_2 and the condenser C_2, maintaining it at a constant potential. The generator circuit was weakly coupled with the coil L_6, connected to a low-power incandescent lamp T_3, through which high-frequency oscillations were induced. The generator T_6 was fed by the power transformer Tr, whose secondary winding was connected to the anodes of the kenotron T_1, thus producing the requisite 225 v direct current to feed the anode circuit of the generator. The voltage was freed from pulsations by the choke L_1 and the condenser C_1. The rectified voltage was stabilized by the resistance R_1 and the gas stabilizers T_4 and T_5, and this ensured stable working of the apparatus. The functioning of the power transformer was shown by the signal lamp T_2, included in the output to the filament of the tubes T_6 and T_7. The tapping a_1 was also used to supply high-frequency current through the condensers C_6 and C_7 to the operating and compensating circuits L_4C_{10} and L_5C_{11}, connected to the anodes of the double diode T_7, which acted as a differential detector. In order to preserve the high quality of the circuits, the capacity of the condensers C_6 and C_7 was made very small (5 $\mu\mu$f), and, in addition, the coupling of the generator and the differential detector with the circuits was not direct, but, through the leads a_2 and a_3, from 30% of the total number of turns of the coils L_4 and L_5. The effect of the high-frequency voltages on the anodes of the double diode T_7 was to produce a constant voltage across the resistances R_4 and R_5, positive with respect to the position of zero potential, which, according to the position of the three-way switch P, produced a different deflection of the microammeter. Thus, in the first position of the switch, the microammeter reading was proportional to the voltage in the compensating circuit, in the third position, to the voltage in the operating circuit, and in the second position, to the voltage difference in the two circuits. The sensitivity of the microammeter was adjusted by the resistances R_6 and R_7. The cell (feeder) D, which contained the solution under investigation, was connected by a high-frequency cable, provided with two connectors K_1 and K_2 and a condenser C_{12}, to the upper potential point of the operating circuit L_4C_{10}. The cell, shown in Fig. 1, had three casings, of which the middle one was operational, while the other two were screens at zero potential. The cell was also enclosed in a metallic screen which shielded the circuit from the experimenter's hand, from surrounding objects, and from high-frequency electromagnetic fields.

By connecting the resonant circuit L_4C_{10} in parallel with the high-frequency cable, shunting of the solution under investigation by parasitic capacities was prevented, since these were automatically included in the capacity of the resonant circuit. This makes it possible to connect the cell with the apparatus through a long cable, i.e., to make use of remote control. The resistance of the circuit L_4C_{10} at resonance amounted, in practice, to 50-100 kohm ; this made it possible to use the apparatus for solutions of electrolytes so dilute that their conductivity is similar to that of distilled water.

Depending on the adjustment of the condensers C_{10} and C_{11}, it was possible to use the apparatus for two qualitatively different ranges of operation, and to investigate both aqueous solutions of electrolytes and nonaqueous media, such as mixtures of polar and nonpolar liquids.

Variant A. Q-Metric Procedure

To obtain calibration curves for measuring the concentrations of different samples of solutions, or in the case of continuous flow, the cell was filled with a solution of known minimum concentration. Then the three-way switch P was set, first in the first position (see Fig. 1) and then in the third, and in each case the corresponding condenser C_{11} or C_{10} was adjusted to give the maximum deflection of the microammeter needle, i.e., to resonance in the circuits L_5C_{11} and L_4C_{10}. Then the switch P was set to the second position, and, by rotating the condenser C_{11}, the microammeter needle was adjusted to the desired initial reading; this corresponded to the initial point of the calibration curve. The remaining points on the curve were obtained by filling the cell with solutions of successively increasing concentration. The curve could subsequently be used for determining the concentration of unknown solutions placed in the cell. In titrations, the equivalent point was found, as usual, by extrapolating the right and left-hand branches of the curves relating microammeter reading and the number of milliliters of reagent used [1, 2].

Variant B. Reactance Procedure

As distinct from procedure A, in the first and third positions of the switch P the condensers C_{11} and C_{10} were adjusted to 1/2 to 2/3 of the maximum resonance deflection of the galvanometer needle. Since the resistance of the resonant circuit L_4C_{10} then had a reactive component, the apparatus was sensitive to a comparatively small change (of the order of a percent) in the dielectric constant of liquid dielectric under investigation. Consequently, with a change in the composition of the solution in the cell, there was a change in the voltage on the circuit L_4C_{10} and also of the differential current through the microammeter, when the switch P was in the middle (second) position. This made it possible to construct a calibration curve for a definite range of concentration of the substance to be analyzed in a nonaqueous medium, and hence to use the value of the dielectric constant as a means of control.

We considered the conditions for the maximum sensitivity of the high-frequency apparatus and established the optimum relations between the parameters of the apparatus and the cell.

The maximum sensitivity Δi was given by

$$\Delta i = \frac{15\ \mu a}{1\%\ \rho}\ .$$

Here Δi is the change in microammeter reading for a 1% change in the specific electrical conductivity ρ.*

The apparatus was sensitive to a change in conductivity for the condition $R_s/X_w \geq 3$.

Here R_s is the maximum value of the reactive component of the resistance of the solution in the cell; $X_w = \frac{1}{\omega C_w} = \frac{1}{2\pi f C_w}$ (f is the frequency in cycles, 5 Mc for the given apparatus, and C_w is the electrical

* This value was obtained by calculation from the minimum total resistance in the microammeter circuit $R_q = R_6 + R_7 + R_8 = 15$ kohms. The range of the microammeter scale was taken as 0 to 300 μa; the anode potential of the generator was taken as 200-250 v).

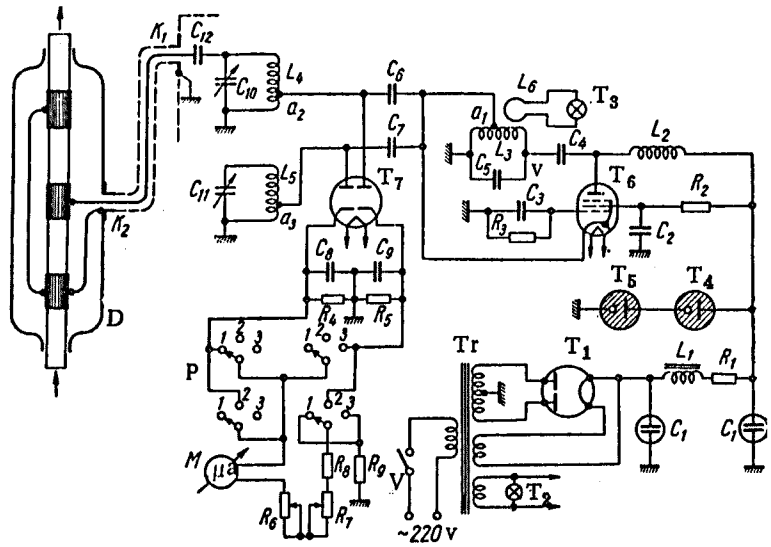

Fig. 1. Diagram of high-frequency apparatus for industrial chemical control.

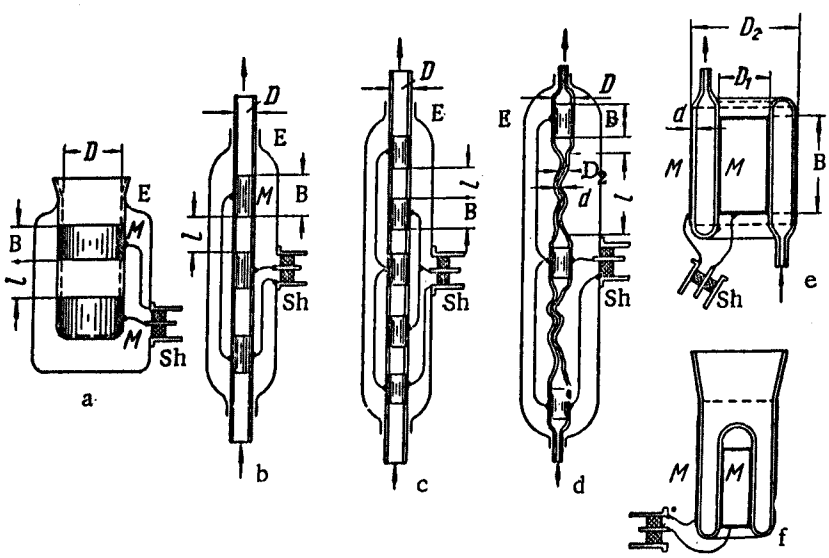

Fig. 2. Basic types of capacity cells (feeders) for controlling flowing liquids and for titrations.

capacity of the cell wall between the outer metal coating and the solution.

The range of operation of the cell lay within the limits 0.1 ρ_{av} to 10 ρ_{av}, where

$$\rho_{av} = R_s \frac{q}{l_{av}};$$

q is the internal cross section of the cell in cm^2 and l_{av} is the average path length of the current in the solution.

The apparatus was mounted on a welded iron chassis of dimensions 33.4 × 20.6 × 25.6 cm, with a sloping control panel, on which were the knobs for the condensers C_{10} and C_{11}, the handle of the switch P, the sensitivity regulators R_6 and R_7, the microammeter M, the signal lamps T_2 and T_3 and the tumbler switch V.

A horizontal panel in the chassis carried the transformer Tr, the tubes T_1, T_4, T_5, T_6 and T_7, the choke L_1 and the coils L_4 and L_5. The coil L_3, the fixed condensers, and the resistors were supported under this panel. The

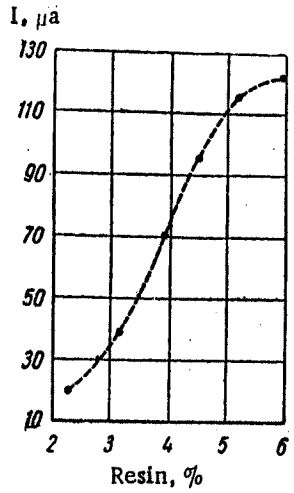

Fig. 3. Calibration curve for the determination of the concentration of melamine-formaldehyde resin in a 0.75% solution of hydrochloric acid.

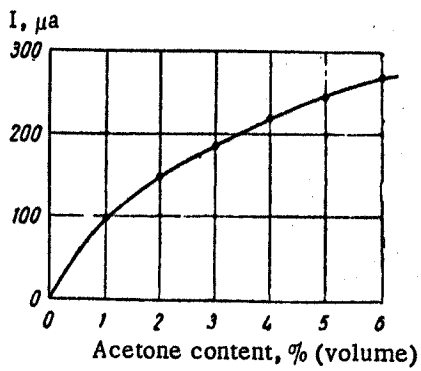

Fig. 4. Calibration curve for mixtures of CCl_4 and acetone.

Values of the Cell Parameters and of the Capacity C_W for Different Types of Cells
(The symbols l, D, D_1, D_2, d and B are explained in Fig. 2)

Cell type	l_{av}	q	C_W
a	l	$\frac{\pi D^2}{4}$	$\frac{\varepsilon DB}{8d}$
b	l	$\frac{\pi D^2}{2}$	$\frac{\varepsilon DB}{8d}$
c	l	πD^2	$\frac{\varepsilon D_1 B}{4d}$
d	l	$\frac{\pi D_2^2}{2}$	$\frac{\varepsilon D_1 B}{4d}$
e, f	$\frac{D_2 - D_1}{2}$	$\frac{\pi B(D_1 + D_2)}{2}$	$\frac{\varepsilon B(D_1 + D_2)}{16d}$

high-frequency connector K_1 was in the back of the chassis.

The quality of the verniers, used to refine the adjustment of the condensers C_{10} and C_{11}, was important. Well-made verniers ensured fine control and ease of manipulation of the apparatus.

Figure 2 shows the different types of cells used for measuring the concentrations of solutions and for titrations. The specific electrical conductivities of solutions, which could be investigated in these cells, varied over a range corresponding, for example, to a change in the concentration of hydrochloric acid from 1 to 10^{-6} N. Titrations could be carried out with all types of cells a to f; with cells b to e the solution was drawn into the cell by a rubber bulb after each addition of titrant.

Cells a and f could be used for high-frequency titration in aqueous and nonaqueous media, and for determining the components of binary mixtures of liquid dielectrics with different dielectric permeabilities, of mixtures of polar and nonpolar organic solvents, etc. Cells b, c, d and e could be used for determining the compositions of flowing binary solutions. The walls of the cells had to be as thin as possible (0.3-0.6 mm), so that their capacitative conductivity was large enough.

The coatings M were best prepared by applying a layer of copper or silver to the surface of the vessel, but, in the case of cells for temporary purposes, the use of BF glue to stick on a thin coating of tin foil, aluminum, or copper is also recommended; in the latter case it is easy to solder on connections to the generator and to ground (for the screen). The outer screens E (see Fig. 2) were made of tin plate; they supported the high-frequency coaxial plug connectors Sh. To eliminate the "volume effect," i.e., the change in reading with a change in the volume of solution in the cell, the outside of the plug was connected to the outer screen, whose electric field did not extend within the cell.

The table shows approximate values of l_{av}, q and C_W required in the construction of cells for use with solutions in the range of concentration given.

Cells of type b and c were used for very dilute aqueous solutions.

Using these cells, we developed, together with S. L. Lel'chuko and A. M. Shtifman, a method for the quantitative determination of traces of HCl (10^{-3} to 2×10^{-4}%) in silico-organic compounds, with a relative error of ±2%. For this purpose, 20 ml of silico-organic compound, 20 ml of toluene and 40 ml of distilled water were placed in a 200 ml separating funnel. After vigorous shaking, the mixture was allowed to separate into two layers, and the lower aqueous layer, containing the extracted acid, was run out of the funnel and placed in the cell, the microammeter reading was observed, and comparison with the

calibration curve gave the content of acid in the sample. The method received practical application in an enterprise of the Ministry of Chemical Industry.

With the aid of this high-frequency apparatus, it was possible, for instance, to control the content of melamine-formaldehyde resin in hydrochloric acid solutions, used for the sizing[1] of paper (Fig. 3).

An interesting application of the high-frequency apparatus was the determination of the concentration of hydrogen peroxide in aqueous solutions, tried out by L. M. Shtifman. The usual low-frequency conductometric method could not be used for this purpose, since hydrogen peroxide decomposed when the solutions were in contact with platinum or other metals.

The apparatus can be used as a dielectric meter for the analysis of binary mixtures of different organic liquids, using a calibration curve. There are three possible cases. If the components of the mixture have the same, or only slightly different, dielectric constants, then the resultant value for the mixture will not differ from the dielectric constant of either component. In this case, neither the high-frequency apparatus, nor other methods of measuring dielectric constant, can be used for precise analysis of the mixture.

The presence of a polar liquid in a nonpolar one, for instance, of nitrobenzene in benzene, of acetone in CCl_4, etc, raises the dielectric constant of the mixture, and makes it possible to construct a calibration curve for its analysis (Fig. 4).

On mixing two dielectrics showing ionic conductivity, or electrolytes with nonpolar solvents, the ionic conductivity is superimposed on the change in dielectric constant of the mixture. In this case, the microammeter reading is a function of the two characteristics of the solution, but it is still possible to construct a calibration curve for serial analyses of samples, or for controlling a flowing solution. A practical example of the analysis of nonaqueous media was the determination of the dry residue in SKB varnish[2] using a calibration curve; the determination took about a minute, and the error was not greater than ± 0.3%.

The determination of traces of hydrochloric acid in silico-organic liquids can be performed without recourse to aqueous extraction; the sample to be analyzed is dissolved in a definite volume of isobutyl alcohol;[3] this solution is placed in a cell of type f, and the microammeter reading is compared with a calibration curve.

In the case of aqueous solutions, the adjustment of the apparatus is carried out according to variant A, and cells of types a and f are used for titrations. Titrations in nonaqueous media can be performed according to variants A or B. Consider the requirements of the solvent; it must dissolve the reagents and the products of reaction; it must have a high enough dielectric permeability to prevent molecular association of the substance titrated; the product formed in the course of titration must have a considerable electrical conductivity [3, 4, 5]. For instance, in our experiments,[4] and in agreement with the literature [6], distinct equivalence points were obtained in the titration of paranitroaniline, using glacial acetic acid as a solvent both for this base and for the hydrochloric acid used as titrant.

LITERATURE CITED

[1] V. A. Zarinskii and D. I. Koshkin, J. Anal. Chem. 10, No. 2, 111-118 (1955).[5]

[2] V. A. Zarinskii and I. R. Mandel'berg, Zavodskaia Lab. 22, No. 3, 263 (1956).

[3] N. A. Izmailov, J. Anal. Chem. 4, No. 5, 267 (1949).

[4] A. I. Shatenshtein, "Theory of Acids and Bases," Chapter 14, Goskhimizdat (1949).[6]

[5] I. S. Fritz, Anal. chem. 26, 11, 1701 (1954).

[6] W. T. Lippinkott and A. Tinnick, Anal. chem. 28, 11, 1690 (1956).

[1] This work was done in cooperation with V. T. Ivanova and A. M. Afanas'eva (Scientific Research Institute of the Administration for Engraving State Banknotes and for Minting Coins and Medals).

[2] This work was done in cooperation with T. S. Sokolova (of the laboratory of the "Red Athlete" factory).

[3] This work was done in cooperation with S. V. Siavtsillo and L. M. Shtikhman.

[4] This work was done in cooperation with A. A. Nemodruk (of the laboratory of the "Red Athlete" factory).

[5] Original Russian pagination. See C. B. Translation.

[6] In Russian.