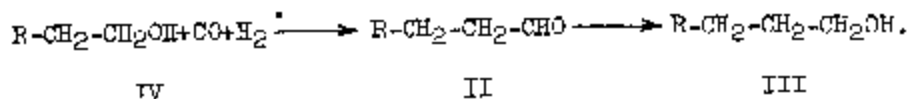


It has been found that, under the conditions (200-300 atmospheres, 160°-200° C.) of the OXO reaction, if an alcohol is used as a starting compound in place of the usual olefin, the final product consists of the homologous alcohol; that is, the alcohol containing one more carbon atom than the starting alcohol. The homologation reaction can be written:



The most obvious explanation of the homologation reaction consists in the assumption that the alcohol (IV) first loses water to give (I), which then proceeds to react according to the usual OXO reaction to give compound (III). This may be the explanation in certain cases, but evidence exists that the homologation does not proceed via an olefin intermediate. Instead, it is thought that the synthesis may occur via a hypothetical ionic intermediate which would explain the known formation of acids and esters. This scheme postulates that the reaction is homogeneous and catalyzed by the acid, cobalt hydrocarbonyl.

The homologation reaction has tremendous commercial significance. The conversion of one alcohol to the homologous alcohol is usually a tedious and arduous synthetic process. The reaction has important implications for the mechanism of the Fischer-Tropsch process as well. It is known that the OXO reaction occurs to a limited extent under certain conditions of operation of the Fischer-Tropsch process. If conditions (catalyst, temperature) can be found such that the alcohol homologation reaction is sufficiently rapid at pressures of not more than about 70 atmospheres, it may well replace the Fischer-Tropsch synthesis as a source of liquid fuels. The C₃ to C₁₀ alcohols could be converted to olefinic hydrocarbons by passage over haukite at about 300° C., and the C₁₀+ cracked and recycled. The advantages of such a process would be: (1) The synthesis gas need not be purified because the OXO reaction is not greatly retarded by sulfur compounds, and (2) the OXO reaction is a homogeneous catalytic reaction, and preparation of special contact catalysts would not be necessary.

Iron Catalysts and the Fischer-Tropsch Synthesis

Nitrided Catalysts

The deposition of carbon in Fischer-Tropsch catalysts is deleterious to their activity and durability. This is especially serious in the hot-gas-recycle and the fluidized-iron processes. The carbon is formed by the reaction: 2CO=CO₂+C. For some time, physical chemists in the synthetic liquid fuels research and development laboratories have considered it probable that the carbon-forming reaction proceeds in several steps, one of which is the formation and decomposition of iron carbides. In accord with this view, carbon formation should be eliminated or at least its rate greatly reduced by substituting, for the iron carbide, materials such as iron boride or iron nitride whose lattice structure is similar to that of the carbide.

The nitrides of iron cannot be formed by the action of molecular nitrogen, but they can be formed by the action of ammonia on iron, the nitride formed depending upon the temperature, time, space velocity of ammonia, and the ammonia:hydrogen ratio. Accordingly, fused-iron synthetic-ammonia-type catalysts were reduced in hydrogen at 450°-550° C. and nitrided at 350°-385° C. These nitrides of iron are interstitial compounds similar to the carbides of iron, normally formed when iron catalysts are used in the Fischer-Tropsch synthesis.

Literature data and preliminary experiments in which the nitrated catalysts were compared with reduced, carbided, or used catalysts under a variety of conditions show that the presence of nitrides of iron in Fischer-Tropsch catalysts increases their activity in a manner similar to carbides. The activity of the nitrated catalyst decreases with decreasing pressure; however, the catalyst is still moderately active, even at atmospheric pressure. A study of the distribution of liquid and solid products from nitrated catalysts shows that a much greater fraction is in the distillation range of $<185^{\circ}\text{C}$. than is found in the product from reduced catalysts. Analysis of the product shows that the fraction distilling to 185°C . contains 70-80 percent alcohol. When operated in the temperature range 200° - 245°C . and at 7-20 atmospheres, the nitrated catalysts produce very little high-boiling product. At higher temperatures, the nitrogen is rapidly removed by hydrogenation, and the beneficial effects of the nitrating (that is, the absence of carbon deposition and little or no formation of iron oxides) are lost. Nitrated catalysts, unlike the corresponding, reduced catalysts, are physically stable in carbon-monoxide-rich gas. As the production of gaseous hydrocarbons decreases with decreasing $\text{H}_2:\text{CO}$ ratio of the synthesis gas, this offers a method of decreasing the yield of light hydrocarbons formed by nitrated catalysts.

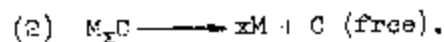
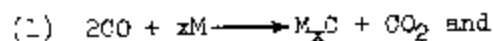
Carbided Catalysts

Studies of the carbides of iron were continued. The mode of transition from Fe_2C -Hagg to cementite, Fe_3C , was studied by following the course of the magnetic curves between the Curie points of the carbides (see figs. 35-37). The transition was found to be discontinuous, which means that precipitation starts with the formation of nuclei of the new crystal habit, followed by their growth at the expense of the existing structure.

The change in the composition of a fused-iron catalyst was studied during its use in the medium-pressure Fischer-Tropsch synthesis. X-ray diffraction and thermomagnetic analyses showed that Hagg carbide (Fe_2C) was formed very rapidly during the beginning of the experiment; a maximum amount had been formed sometime during the first 3 days of operation, after which it decreased linearly with time. No carbides other than Fe_2C -Hagg were identified. Similar examination of used iron catalysts after catalyst-testing studies showed that, of the three known ferromagnetic iron carbides, the hexagonal close-packed Fe_2C is rarely formed with fused catalysts under the usual synthesis conditions and that cementite, Fe_3C , does not appear to be formed during the synthesis except by overheating and simultaneous decomposition of the other forms of carbide.

Free-Carbon Deposition. - One of the worst features of Fischer-Tropsch catalysts is their tendency to form relatively inert free carbon during the synthesis. This carbon plugs up the reaction vessel in fixed-bed converters; in fluidized-bed converters, it exerts a disintegrating effect on the catalyst particles, converting them into a fine dust which cannot be retained in the converter. In addition, it is thought that carbon deposition exerts a specific poisoning action on the Fischer-Tropsch reaction.

Carbon may very probably be formed by way of carbide, as follows:



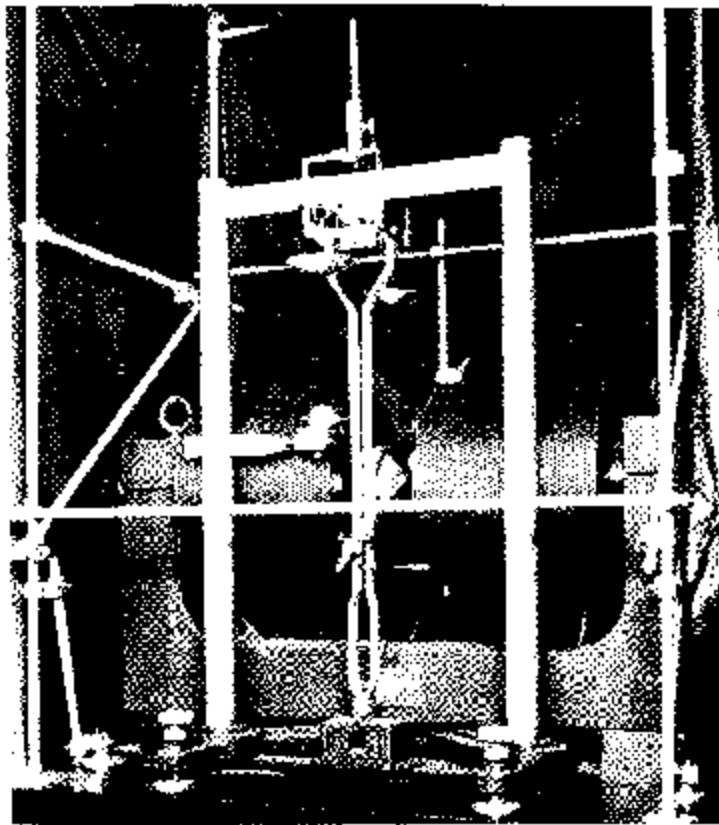


Figure 35. - Magnetic balance.

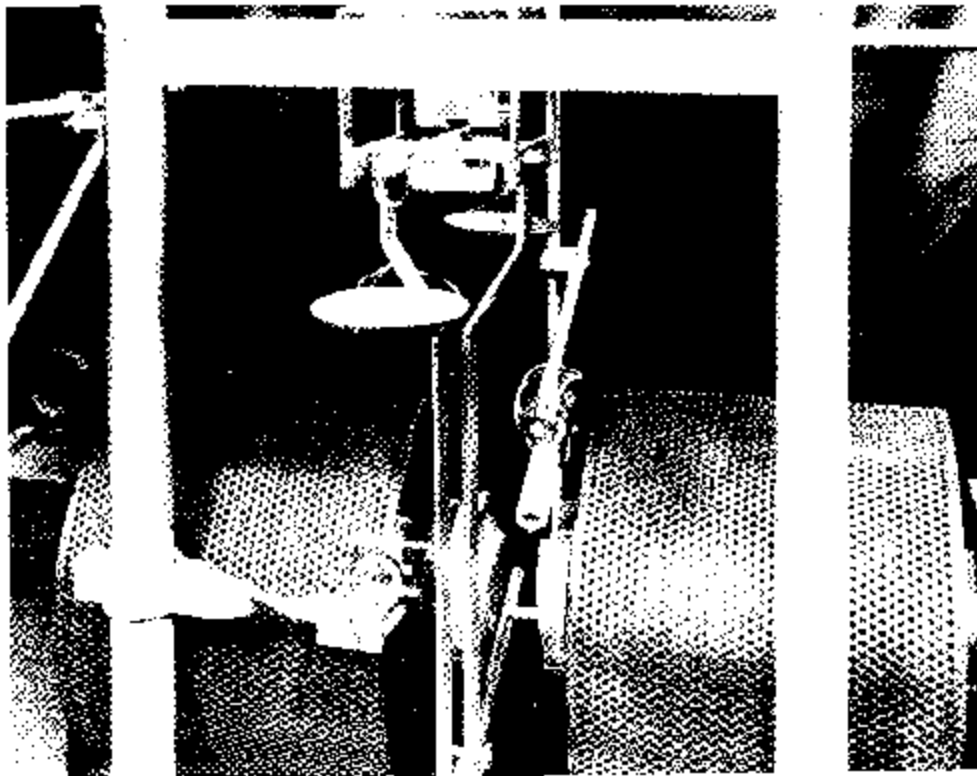


Figure 36. - Magnetic balance.

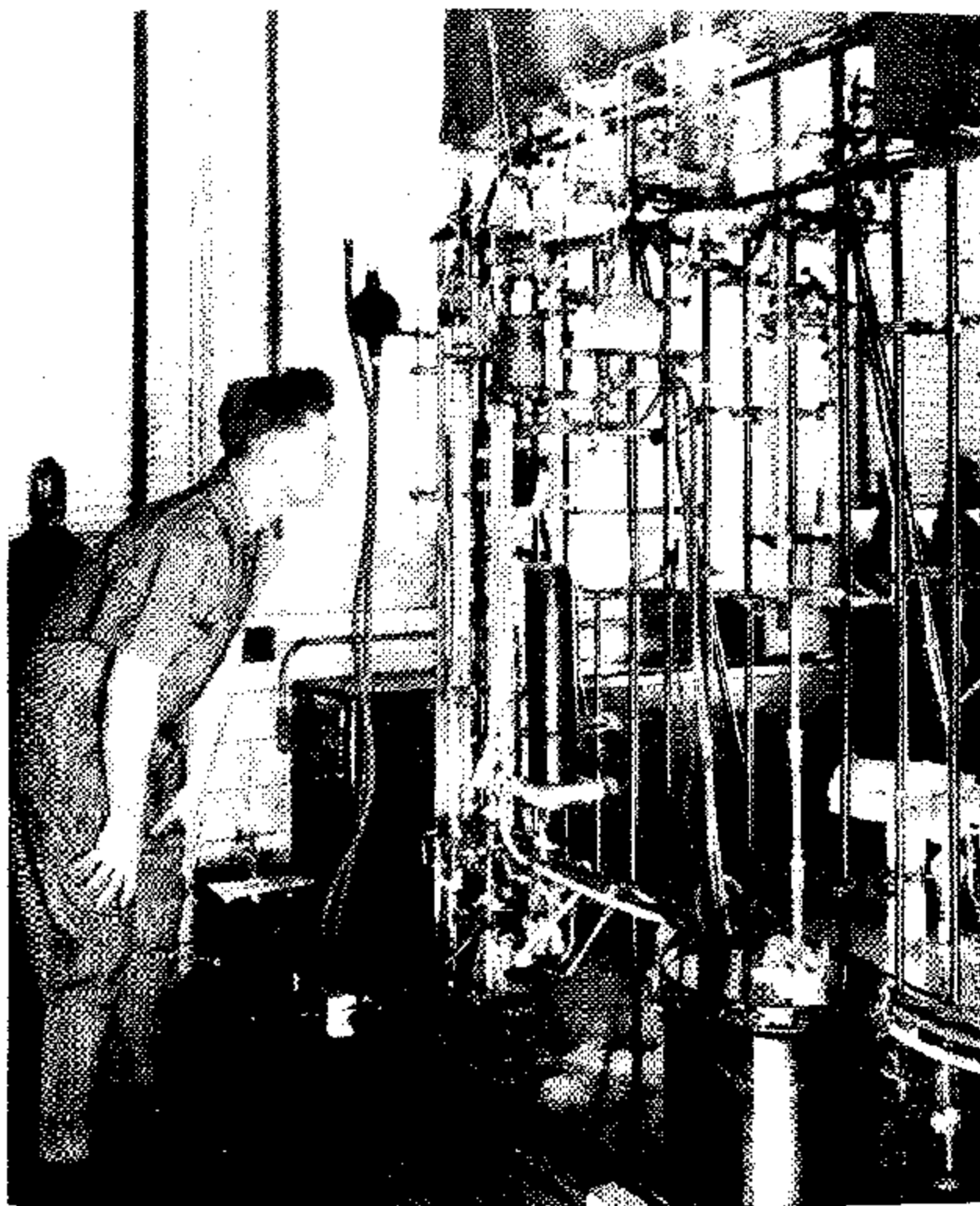


Figure 37. - Apparatus for studies of hydrocarbon-synthesis mechanism.

This theory is supported by the fact that only those metals which form metastable carbides are known to form free carbon from carbon monoxide. Reaction (2) is simply thermal decomposition of the carbide involved.

As a subject for a study to determine the nature of this decomposition reaction, nickel carbide was chosen, because (1) it could be prepared in a well-crystallized and pure form, (2) its crystal structure is well-known, and (3) it is, like carburized cobalt catalyst, nonferromagnetic. Therefore, the thermal stability of the carbide could be studied magnetically by the same method used previously for Co_3C , and the appearance of ferromagnetism could be ascribed to the formation of ferromagnetic nickel metal, a measure of the process of decomposition. Results of the study showed that the apparent energy of activation for the decomposition of nickel carbide is of the same order of magnitude as that found for the decomposition of a carburized cobalt catalyst. The decomposition of nickel carbide, however, was found to be preceded by an induction period which decreased with increasing temperature. This induction period indicates that the reaction requires the presence of nuclei which are difficult to form at a relatively rapid rate. Inhibiting the formation of these nuclei by various additives would, theoretically, delay the thermal decomposition.

Hydrogenation. - Comparative rates of carburizing and of hydrogenation of carbide on cobalt catalysts have been previously determined to get some information on the mechanism of the synthesis, although the possibility has been recognized that these rates, under synthesis conditions, may be much different from the observed rates in pure gases. Thus, fully or partly carburized cobalt catalysts are very rapidly hydrogenated with pure hydrogen and retain the carbide at comparable temperatures under 2:1 synthesis gas. Synthesis experiments were therefore carried out on partly carburized cobalt catalysts, using synthesis gas with an $\text{H}_2:\text{CO}$ ratio of 3:1 to 50:1. The results indicated that the hydrogenation of carbide is strongly inhibited by even small partial pressures of carbon monoxide and that the total reaction rate increases with decreasing partial pressure of carbon monoxide.

Surface Area, Porosity, and Synthesis-Rate Studies

Determination of surface area and mercury and helium densities of fused-iron catalyst showed that, during reduction, the external volume of the catalyst particle remains the same and pores are developed by removing oxygen from the interior of the grain. The average pore diameter remains very nearly constant throughout the reduction and is of the same order of magnitude as that found in reduced cobalt catalysts. The surface area varies almost linearly with extent of reduction. At 90- to 100-percent reduction, however, it appears that some sintering occurs, because the surface area does not increase as much as the pore volume.

Similar studies with precipitated-iron catalysts suggest an explanation for the greater activity of precipitated catalysts as compared to fused catalysts. The surface of the precipitated catalysts may be more accessible to the reacting gases as a result of the presence of pores with diameters about three times as large as those found in fused catalysts. The enhanced activity of reduced cemented catalysts may be similarly explained.

Effect of Chloride Ion

Early in the development of the Fischer-Tropsch catalysts, it was found that active catalysts could not be prepared from ferric chloride, although a precipitated catalyst prepared from a mixture of ferrous, ferric, and cupric chlorides according to the procedure of Fischer exhibited satisfactory activity. Tests made with

several preparations in which the constituents of this catalyst were varied showed that the ferrous iron was the significant constituent. Chemical analysis showed that the chloride content of the inactive ferric iron catalysts was at least 20 times greater than that of the active ferrous-ferric preparations. On the basis of this information and additional data obtained by X-ray diffraction analysis (fig. 38), the following explanation of the deactivating effect of chloride is proposed.

1. In the presence of chloride and ferric iron alone, β - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ was produced which retained chloride in the catalyst structure. During synthesis, chloride present on active centers deactivated the catalyst.
2. In the presence of chloride and ferrous and ferric iron (at least 35 percent Fe^{+2}) or ferrous iron alone, the formation of β - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ was inhibited. Instead, magnetite (Fe_3O_4) or ferrous hydroxide ($\text{Fe}(\text{OH})_2$) or a mixture of both was formed; from this crystal structure chloride was easily removed by washing.

Analysis of the Products from the Hydrogenation of Carbon Monoxide

A detailed characterization is being made of the Fischer-Tropsch products obtained from iron catalysts. The determination of the oxygenated compounds in Fischer-Tropsch products by infrared spectrometry (see fig. 39) has been facilitated by the derivation of absorption coefficients for the functional groups of alcohols, ketones, aldehydes, esters, and acids in mixtures with hydrocarbons. This has minimized the previous requirements that pure calibration compounds be available. Thus, the limitations imposed by differences in molecular weight and density have been reduced, and calibrations based on the simpler C_{10} oxygenated compounds now can be used to analyze oxygenated compounds in the C_{10} and higher ranges. Analysis of synthetic blends of alcohols, acetic acid, acetone, and water by means of the mass spectrometer suggest that such analyses of water solutions from the Fischer-Tropsch process may be accurately done for the principal oxygenated components. Development of a self-filling micropipet method of introducing samples into the mass spectrometer greatly facilitated analysis of the oxygenated compounds in the absence of water.

In connection with evaluation of the distillation column operating at reduced pressures, the use of a test mixture of a hydrocarbon with hydrogen atoms of mass 1 and the same hydrocarbon containing some deuterium atoms (hydrogen atoms of mass 2) is highly desirable. Accordingly, a method of analysis for deuterated hydrocarbon was developed which is superior to the analytical methods previously used.

Special distillation and gas-collecting equipment (see figs. 40-42) was installed to give, in five fractions, rough molecular-weight-range characterizations of Fischer-Tropsch liquid and solid products. Work with the mass spectrometer, which is used for most of the gas analyses, has resulted in improvements in equipment design and operating technique. A method is being developed for the quantitative analysis of $-\text{CH}_3$ and $-\text{CH}_2-$ groups in mixtures of aliphatic hydrocarbons; this method may be applied to the determination of aromatic CP and naphthenes. Analysis for $-\text{CH}-$ and $-\dot{\text{C}}-$, which would be necessary for a complete evaluation of chain-branching in high-boiling Fischer-Tropsch products, is not practicable, however. Combination of functional-group analysis with determinations of $-\text{CH}_3$, $-\text{CH}_2-$, and aromatic CH should provide much useful information. Assembly of the small mass spectrometer (fig. 43) for analyses up to mass 44, the purpose of which is to decrease the analytical load on the larger instrument, is about 90 percent complete.

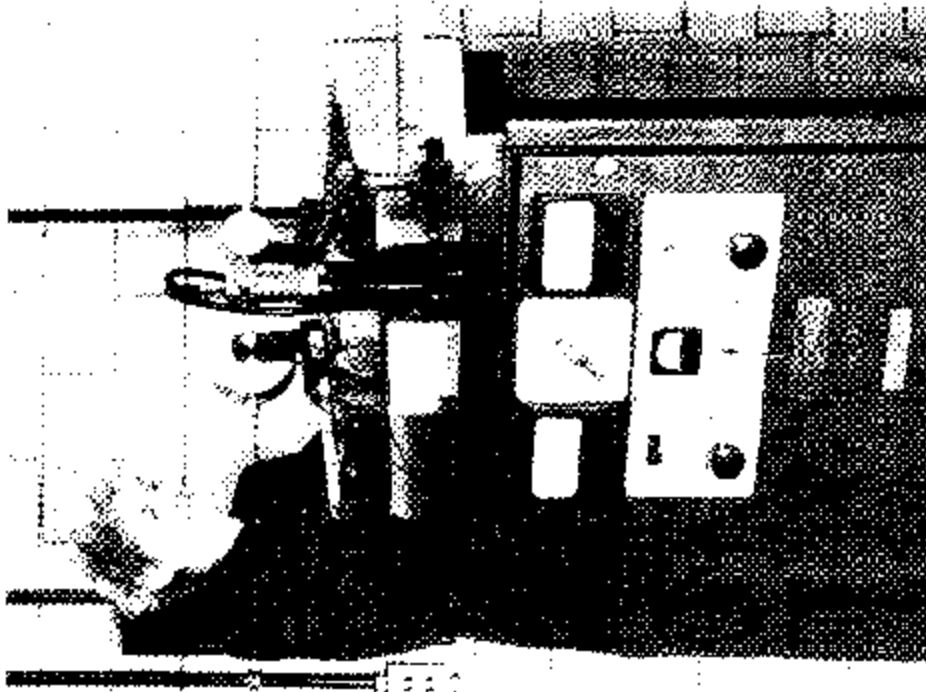


Figure 38. - X-ray diffraction equipment.

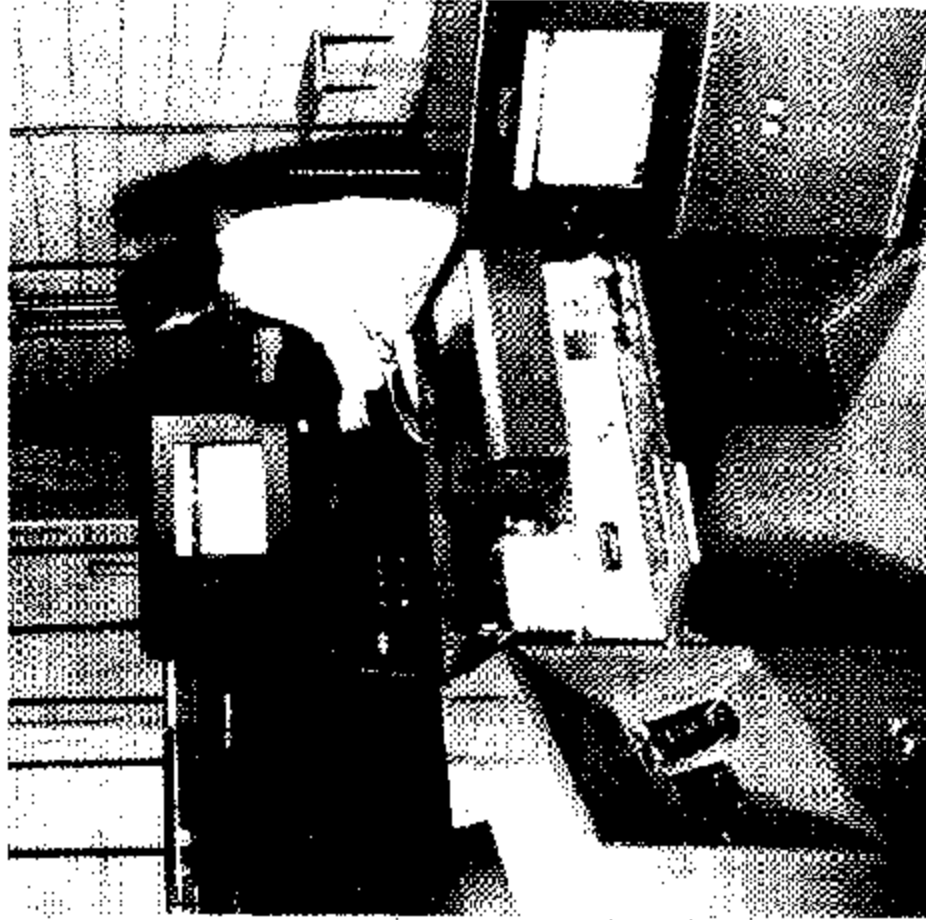


Figure 39. - Infrared (foreground) and ultraviolet (background) spectrophotometers.

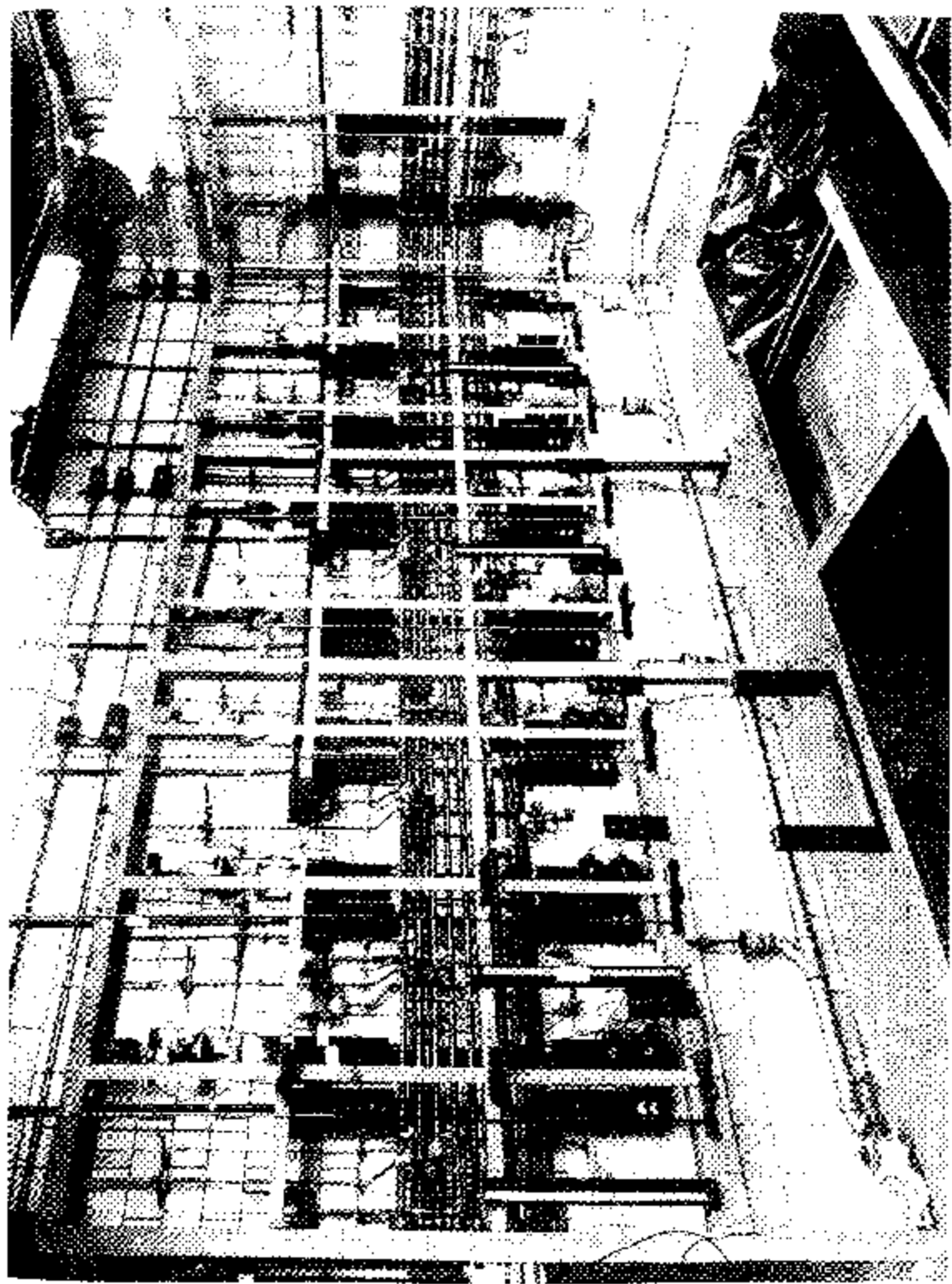


Figure 40. - Distillation laboratory - controls and supplementary equipment.

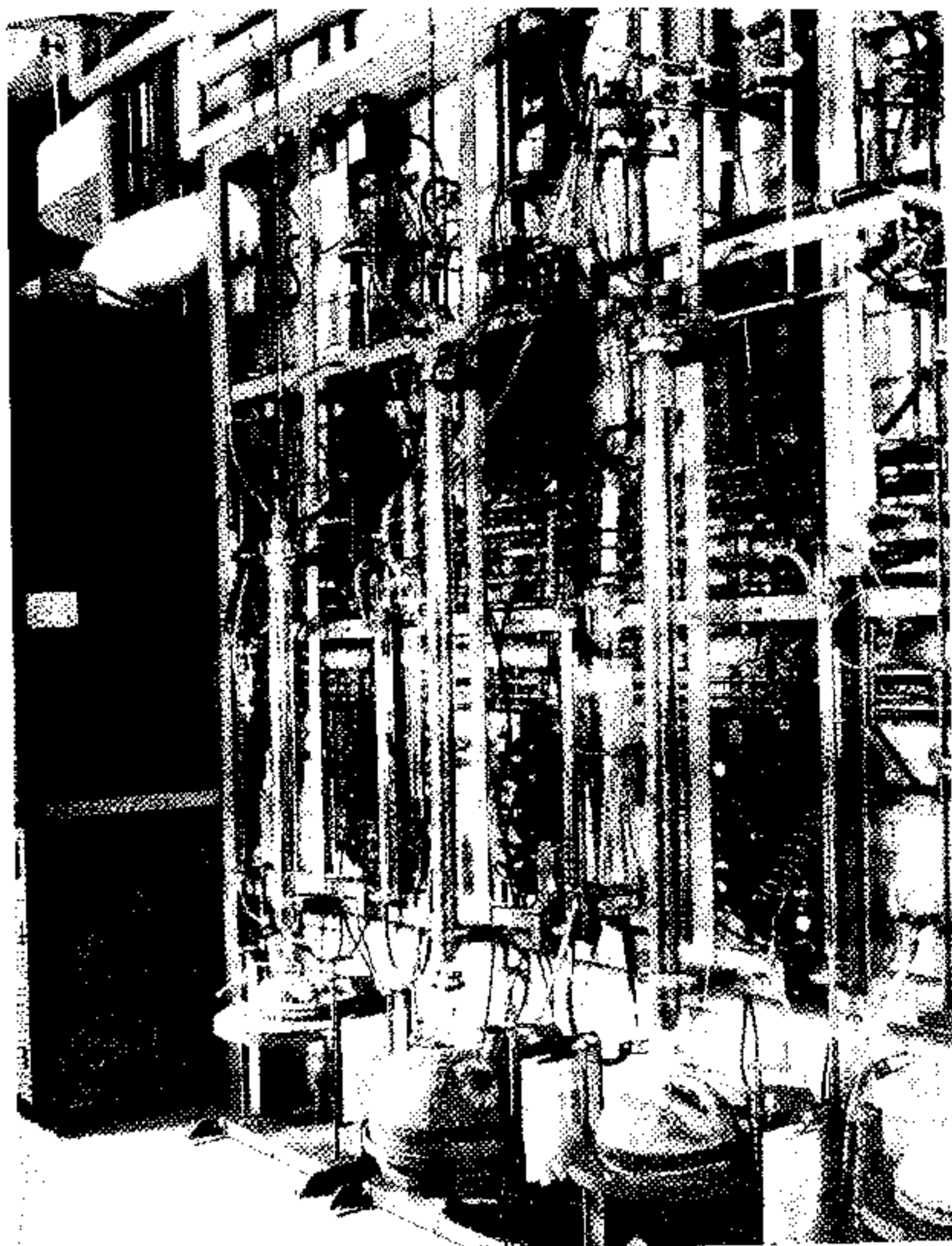


Figure 41. - Distillation Laboratory - column assemblies.

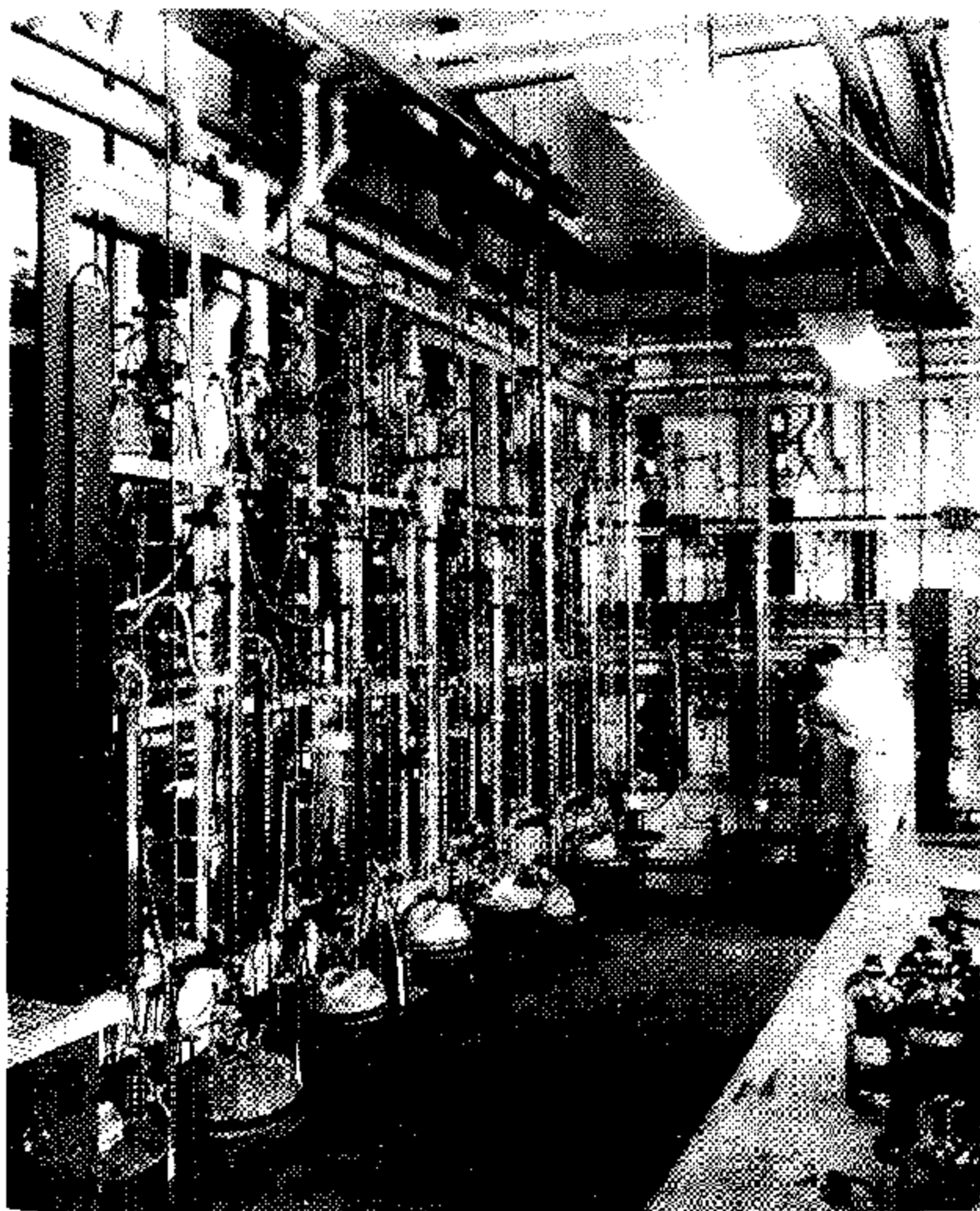


Figure 42. - Distillation laboratory - column assemblies.

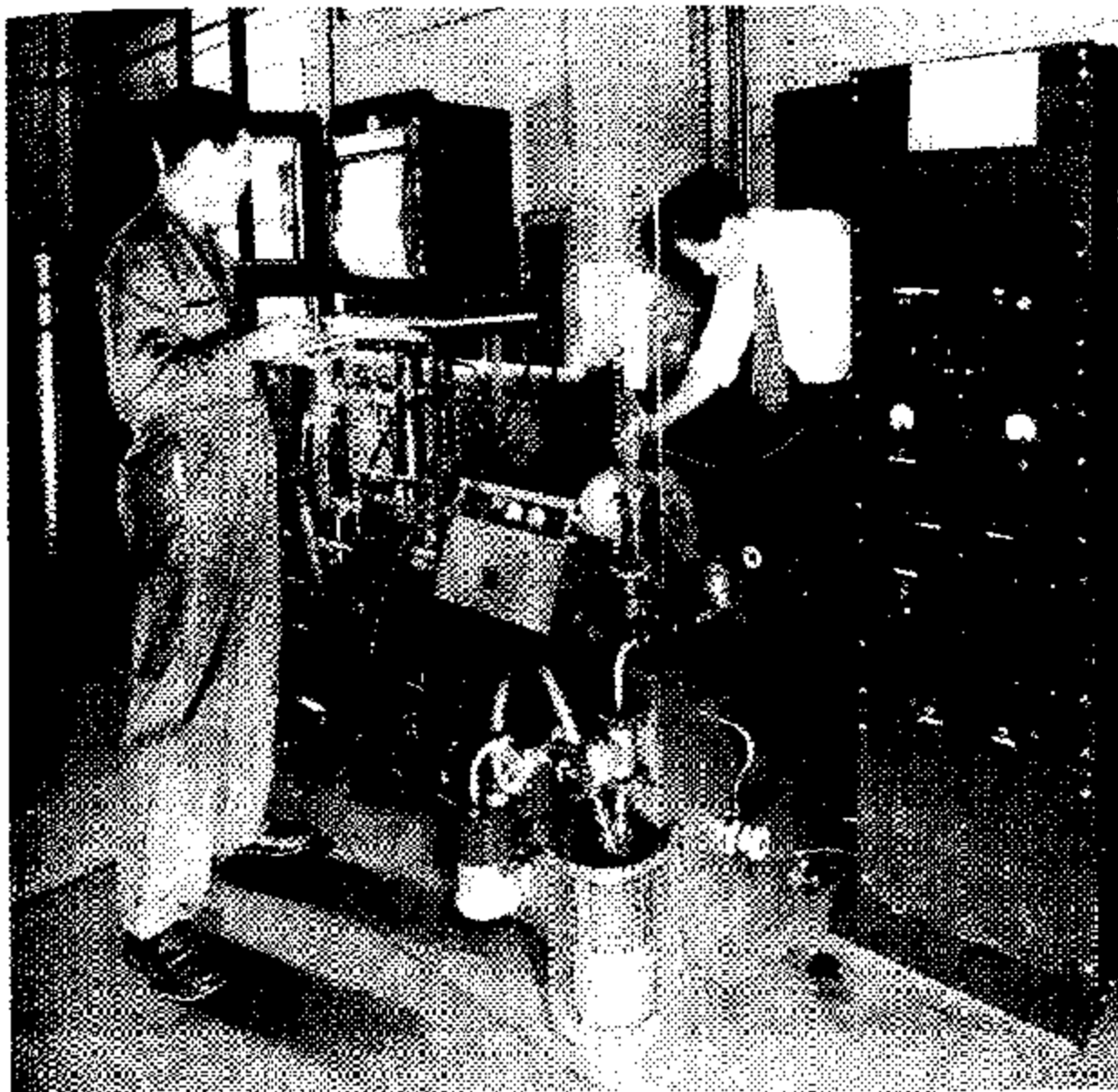


Figure 43. - Small mass spectrometer.

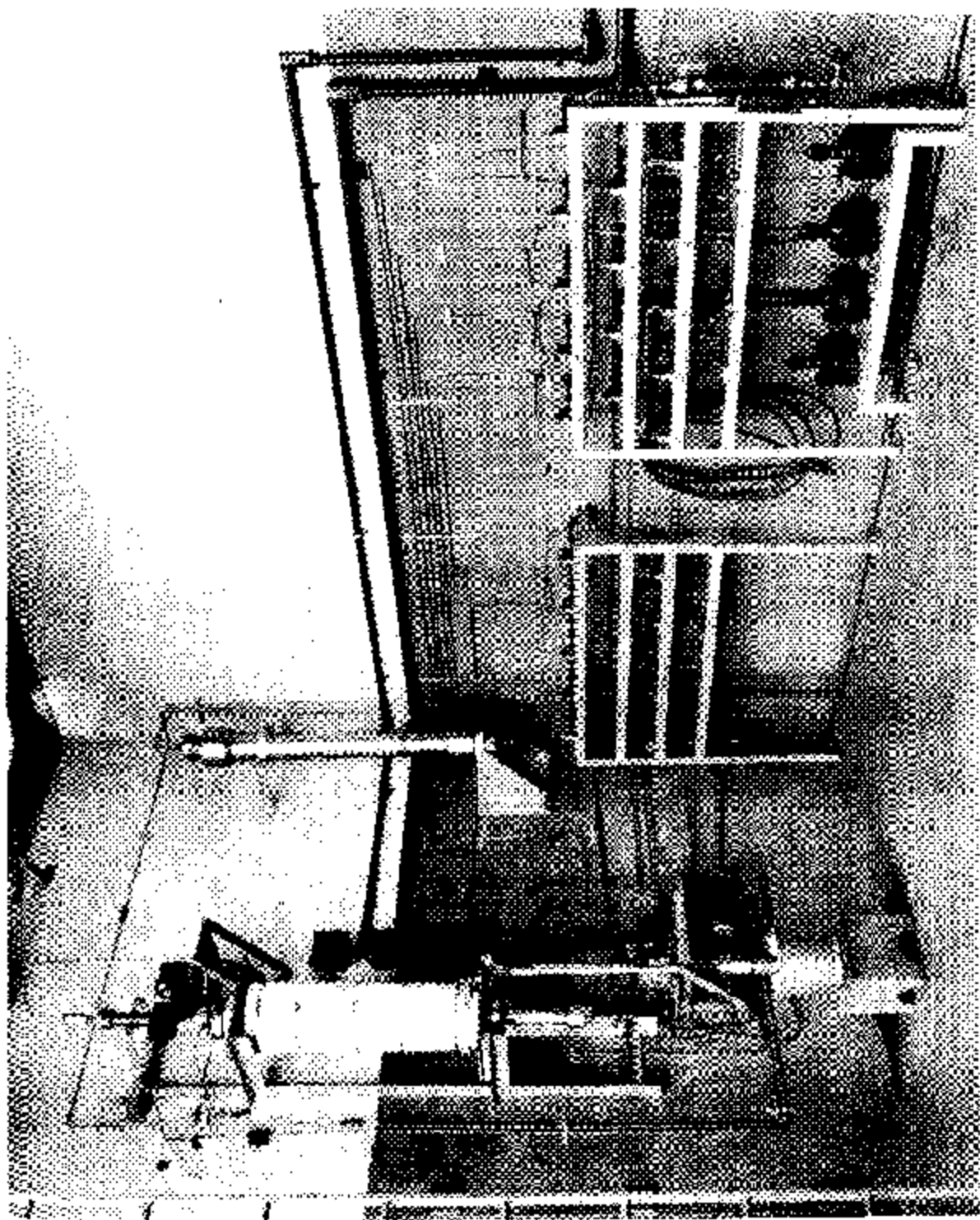


Figure 44. - Variable-contact-time unit for coal hydrogenation.