ANALYTICAL TECHNIQUES

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ELEMENTAL MICRO ANALYSIS

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Elemental organic analysis is that area of chemistry that is concerned with the quantitative determination of the elements in organic compounds. The micro analyst utilizes samples weighing less than 5 milligrams.

Elemental organic analysis plays a central role in support of organic chemical research. It provides the data necessary to determine the structure of a new compound. The Air Force is engaged in the study of compounds which have potential applications in the formulation of polymers and synthetic lubricants. The products generated by these studies seldom exceed 100 milligrams and without the techniques of microchemistry these programs would not be feasible. Micro techniques have the additional advantage of being more rapid than corresponding macro procedures and are used even when large samples are available.

Micro analysis had its inception 50 years ago. The invention of the micro balance, at that time, enabled Pregl to develop the techniques for which he won the Nobel Prize. Many of his methods are still in current use. Figure 1 shows the Ainsworth micro-balance, which can weigh a 20 gram load with a precision of .002 milligrams.

In general, an analysis consists of the destruction of the molecule, followed by the separation and measurement of the elements. There are approximately 1,000,000 known organic compounds with great differences in composition, structure, and properties. Since the analytical approach must be predicated on composition and properties, a wide variety of techniques are required. It must be emphasized that no single procedure is universally applicable for a given element on all compounds. Methods must often be custom-made to do a given job.

A description of some representative techniques are given below. Figure 2 illustrates a carbon-hydrogen analyzer. A weighed sample is heated in a platinum boat in a regulated atmosphere of oxygen. The combustion products are swept through a combustion tube which contains reagents for insuring completeness of oxidation and removal of extraneous elements. The water and carbon dioxide are selectively absorbed and determined from the gain in weight of the absorption tubes.

The effectiveness of many different reagents have been studied and there is no general agreement regarding the best method for packing combustion tubes. A rapid combustion method has been developed in which the compound is oxidized in a rapid oxygen stream in an empty combustion tube (1). This method has not gained favor in this country but seems to be in extensive use overseas.

Figure 3 shows a Dumas nitrogen apparatus. The sample is oxidized by copper oxide and the liberated nitrogen is swept into a graduated vessel by a stream of carbon dioxide. The carbon dioxide is absorbed in a strong alkali solution and the volume of nitrogen is measured. (An automatic apparatus is on the market which is claimed to be capable of performing an analysis in less than ten minutes.)

Figure 4 illustrates a Shoniger flask. It is a simple device in which a weighed sample, held in a platinum basket, is combusted in an atmosphere of oxygen. It has proved effective

for the decomposition of a great variety of compounds and is rapidly replacing the use of sealed glass and metal bombs. This technique, on a micro scale, was introduced in 1955 and is used in the determination of halogens, sulfur, and phosphorus (2). Additional adaptations and refinements of this technique are appearing regularly in the literature. For comprehensive treatment of organic micro analysis the reader is referred to references 3, 4 and 5.

The synthesis of new compounds requires the concomitant development of analytical methods. The analysis is often more difficult than the preparation of the compound. Many compounds that are being studied by the Air Force pose challenging problems since they are frequently designed for a high degree of thermal and chemical stability and incorporate the use of unconventional elements in unusual combinations. Micro chemists often dream of an instrument which will provide a rapid and accurate analysis for all elements simultaneously, with a minimum of manipulation.

In recent years a new dimension has been added to analytical chemistry which offers a promise for the fulfillment of this dream. Various radiation sources have been applied successfully in the area of elemental analysis. The use of X-rays, beta-rays and neutrons appear most promising (6).

X-ray methods are analogous to other electromagnetic radiation methods such as infra-red, visible, and ultra-violet. The X-ray absorption method relates the concentration of elements to the amount of absorbed radiation at specific wave lengths. Radio-active isotopes are sometimes used as the X-ray source. For example, several laboratories are using iron-55 for the determination of sulphur, chlorine, and bromide in organic compounds.

X-ray fluorescence methods measure the amount of X-rays emitted after excitation. Figure 5 is a schematic of the operating principle behind this method. The sample is excited by an X-ray beam. The resultant fluorescent radiation is collimated and its wave lengths are separated by a crystal which acts as a diffraction grating. The analyzing crystal is slowly rotated and the intensity of the X-ray spectrum is measured with a Geiger counter. This method is being used for the determination of iron in hemoglobin, sulphur in oil, and lead in gasoline.

Since the lighter elements do not emit or absorb X-rays in the regions normally used, other radiation must be employed. Beta-ray and neutrons have been used in the determination of hydrogen. Beta-rays are most strongly absorbed by the light elements particularly hydrogen. Under controlled conditions, hydrogen concentration can be determined by means of Beta-ray absorption. Commercial equipment is available which uses strontium-60 for its Beta-ray source. Neutron activation analysis can be used for selected elements in organic materials and neutron moderation or slowing-down can be used as a measure of hydrogen concentration (see figure 6).

This brief discussion of radiation analysis is by no means comprehensive. It is intended to indicate a rapidly growing area which may displace many classical methods in the near future.

REFERENCES

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3. Pregl, Fritz, and Grant, Julius, Quantitative Organic Microanalysis.

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Figure 1.

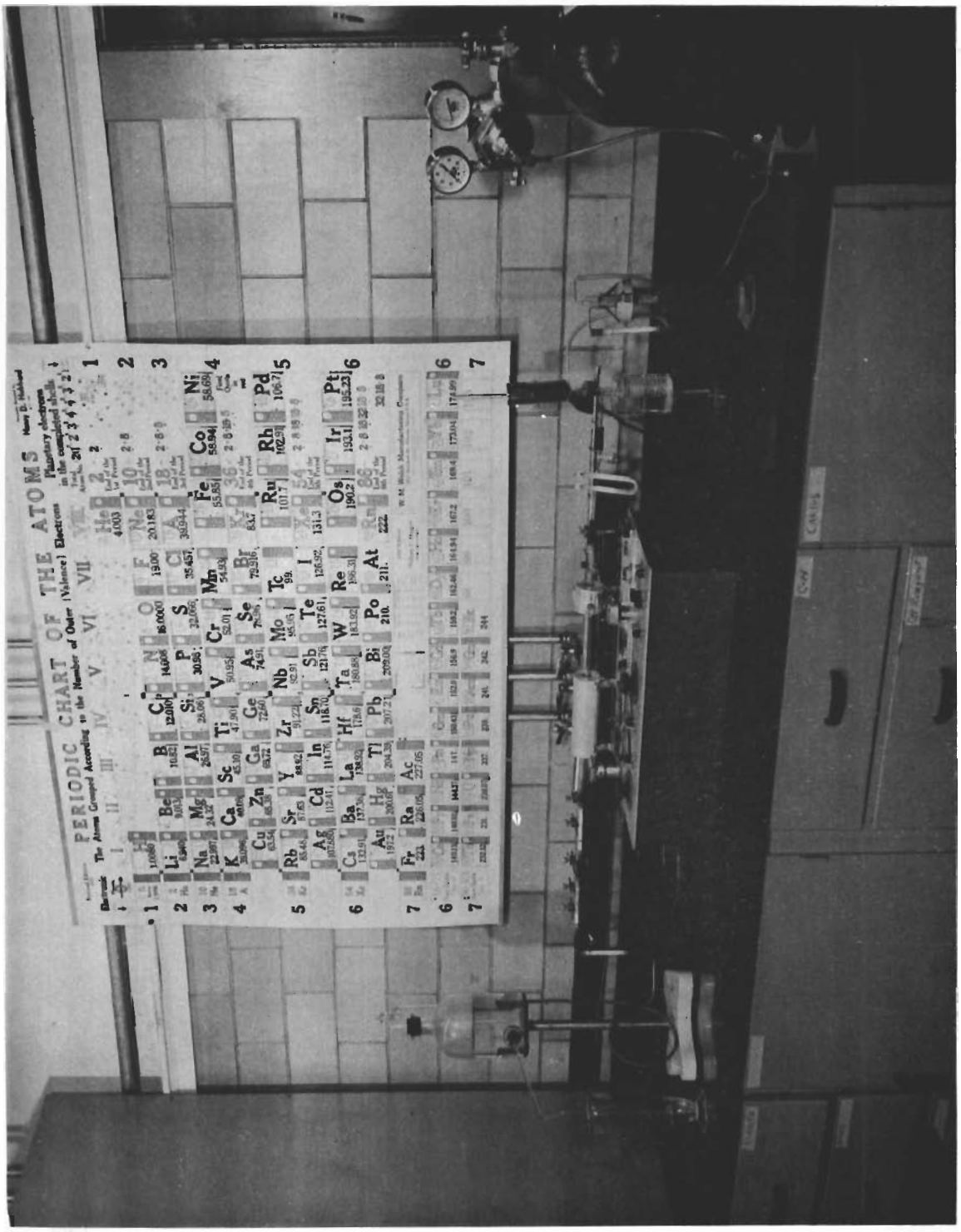

Figure 2.

Figure 3.

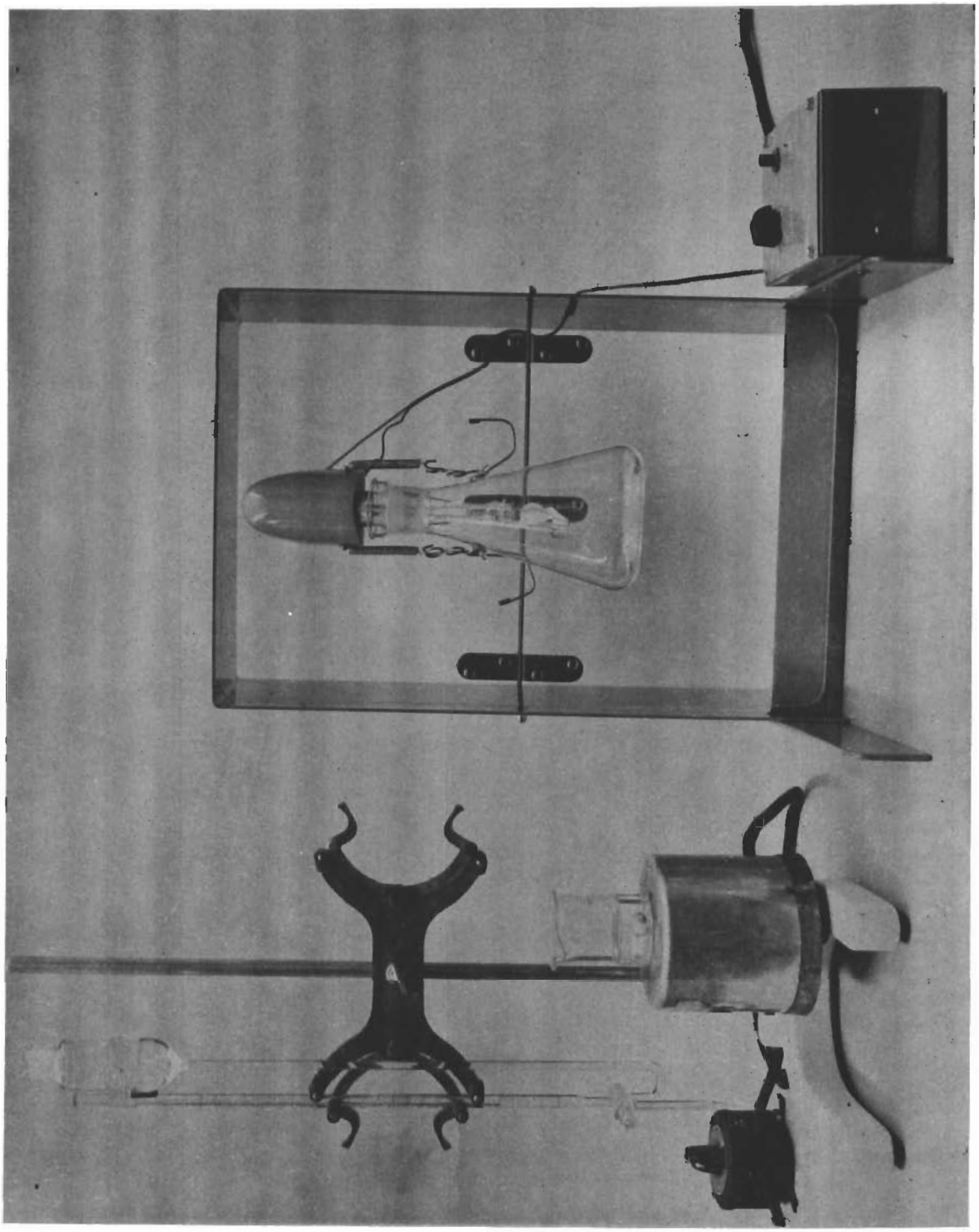

Figure 4.

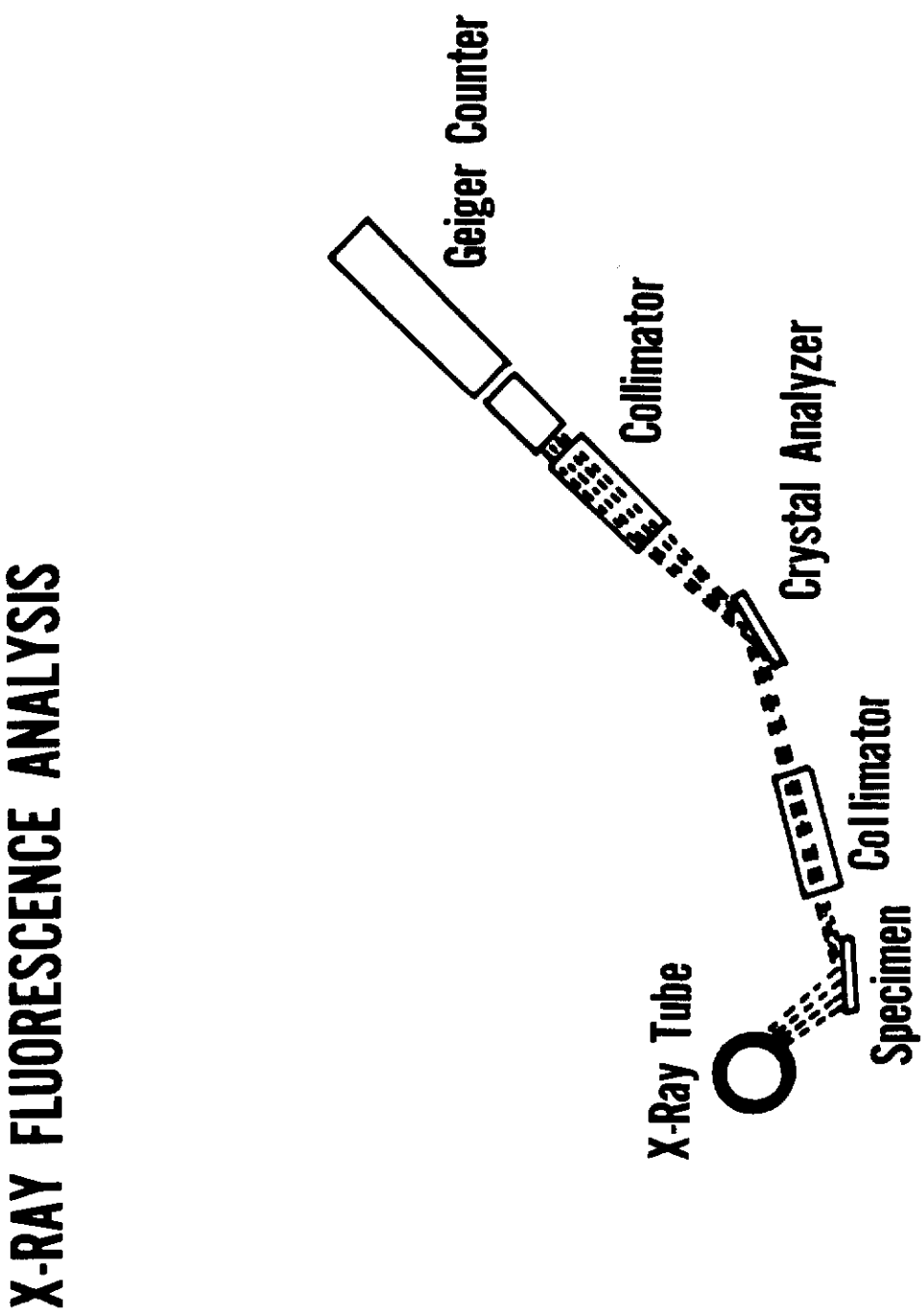

Figure 5.

NEUTRON MODERATION

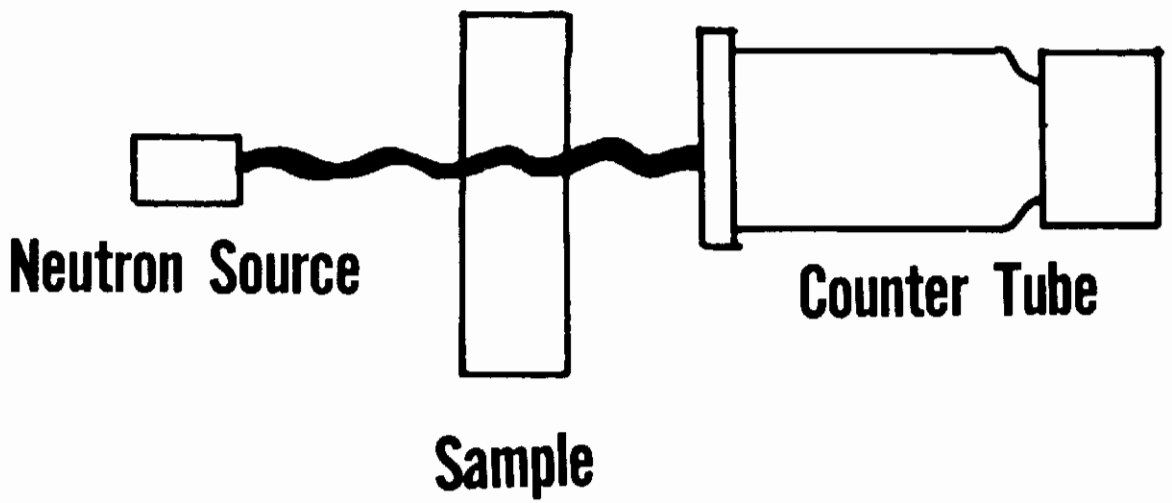

Figure 6.