INSTRUMENTAL ORGANIC ELEMENTAL ANALYSIS

Edited by

R. BELCHER

THE ANALYSIS OF ORGANIC MATERIALS

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FOREWORD

Throughout the history of elemental organic analysis it has been possible to discern definite stages in its progress; during some periods, different developments have run on parallel courses.[1,2]

The first stage probably lasted for over 100 years; major changes were not forthcoming until about the beginning of the present century. Although the basic Liebig method was to continue in use until well after the second World War, the first outstanding changes were due to Dennstedt; [1,2] his methods, though not widely used, continued well into the 1930's.

In the 1920's the methods of ter Meulen were developed but, like those of Dennstedt, they were not used as widely as they deserved. Nevertheless, they have been used continuously for the determination of nitrogen, halogens, and sulphur in special cases; more recently, they have been recommended for use in conjunction with the coulometric determination. The micro methods of Pregl were somewhat later than the Dennstedt methods and overlapping with the ter Meulen methods. From the micro methods, semi-micro methods were developed, much to Pregl's disgust as indicated by the remarks in some of the earlier editions of his book. These semi-micro methods were developed by investigators such as Dubsky, Bobranski and Sucharda, Roger and MacKay and others. As it turns out, the semi-micro methods are now rarely used, but at that time, despite Pregl's tirades, there were very good grounds for their development. They did not need the specialized skill of the micro-method, an ordinary balance could be used and, very often, the standard instruments of conventional quantitative analysis, e.g. macro-burettes, were suitable. Before the great developments in instrumental analysis which changed the teaching of practical chemistry extensively, the semi-micro methods were far preferable for student teaching purposes. Especially important was the fact that the (comparatively) expensive micro-balance and micro-equipment were not essential, as universities and colleges had to work on a shoestring until well after the end of the Second World War.

In the 1945–1960 period, the "empty-tube" method was used extensively in Britain; and on the Continent of Europe active catalytic fillings, such as cobaltocobaltic oxide, and activated manganese dioxide plus silver, were favoured.

The stage with which we are now concerned is that of the automated

analysers, which first began to appear in the early 1960's. This stage will obviously continue, with minor changes, into the foreseeable future.

It is, however, pertinent to mention that the idea of minimising the amount of manual labour required is not new. As early as 1905, Pregl introduced a moveable burner incorporating a clockwork motor for combustion analysis. For some years before the Second World War, partly-automated equipment was available; amongst these may be mentioned the methods of Reihlen and Weinbrenner and Bobranski and Sucharda. Automated combustion had become widespread throughout war-time Germany, as evidenced by the information in the B.I.O.S. reports;[3] notable contributors had been Zimmermann, Unterzaucher and Fischer. Furnaces operated by synchronized motors became commonplace in Britain after the War; (they were, however, only of use in slow combustion processes).

The main feature of the new automated methods, at least initially, was the elimination of the weighing procedure. Very fast combustion methods of various kinds had been developed long before, but, despite the introduction of various devices to accelerate weighing, this operation remained the main hindrance to reducing the time of operation further. The high sensitivity of the new instrumental forms of final measurement enabled a considerable reduction to be made in sample size; the more rapid combustion now possible is due to the small amount of sample taken and not to any great improvement in combustion efficiency.

The two systems chosen for inclusion in this Monograph are those of Perkin–Elmer and Carlo Erba, for these are the two most widely used. The former, by suitable modification, can also be used for the determination of oxygen and sulphur and the latter also for the determination of oxygen.

The determination of carbon in waters has become of great importance; several analyzers based on different principles have been developed commercially. It was considered that a general account of the available equipment would be of value in this Monograph. One feature which should interest older analysts is the system in which the combustion product, carbon dioxide, is converted to methane for measurement; in former times the aim was always to convert methane to carbon dioxide.

Undoubtedly, the simultaneous determination of nitrogen is one of the major advantages of the automatic methods. Nevertheless, the situation where only the nitrogen content is required often arises and nitrogen may be only a minor constituent, in which case the automatic method may not provide the accuracy required. The best of the newer systems, that of Merz, can be applied to the analysis of virtually any type of organic material and to any range of nitrogen. A short account of this method has therefore been included.

Finally, the great developments in coulometric analysis have led to the wide application of this technique in elemental analysis; all the common

organic elements (other than carbon and hydrogen) can be determined. Again, the great sensitivity of detection allows very small samples to be taken and this, in turn, decreases the time required for decomposition.

These methods of elemental organic analysis based on instrumentation have been well-established for more than a decade. As far as it is known, no monograph has dealt exclusively with these methods. It was felt that such a monograph would be useful to the increasing number of laboratories using such apparatus. I was fortunate in obtaining the services of analytical chemists as contributing authors who have had first-hand experience with such systems for a large number of years. It is hoped that this monograph will be of benefit to all analysts who need to apply these methods.

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CONTENTS

1. THE PERKIN–ELMER MODEL 240 ELEMENTAL ANALYZER: CARBON, HYDROGEN AND NITROGEN

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I. INTRODUCTION

During the early 1960s, details were published[1] of a new approach to organic elemental microanalysis. Professor W. Simon and co-workers of the Swiss Federal Institute of Technology in Zürich showed that it was possible to automate some existing procedures of microanalysis, in particular carbon and hydrogen, and as a result many of the drawbacks of the classical methods could be eliminated.

On the basis of Professor Simon's original work, the Perkin–Elmer Corporation of Norwalk, Connecticut, U.S.A., developed in 1963 an instrument for the automatic determination of carbon, hydrogen and nitrogen, in which the classical techniques of Pregl for carbon and hydrogen, and Dumas for nitrogen, were combined. Many of the manual sequences of the classical methods, such as the use of bunsen burners, weighing of absorption tubes, etc., were rendered out of date and replaced by automatic combustion and modern electronic detection of the gaseous products. The combustion system of the instrument differs partly from the classical methods, for its sample combustion takes place under static conditions in a constant amount of oxygen, consequently the blank values are not affected on prolonged combustion of refractory compounds. Further application of modern techniques resulted in an automatically controlled and versatile instrument, which provided excellent reproducibility of the conditions, while variability of these conditions was incorporated to suit the type of compound to be analyzed.

The Model 240 elemental analyzer (Fig. 1) was introduced commercially in 1965[2] and during the following years of continued research by the Company, only small changes, such as updating of electronic components, were made to the instrument itself. One of the developments was a conversion of the instrument to allow direct determination of oxygen[3] and later also sulphur;[4] these conversions will be discussed in a separate chapter.

Attention was given to further automating the various stages of operation from weighing of the sample to the final reporting of results. Most advances
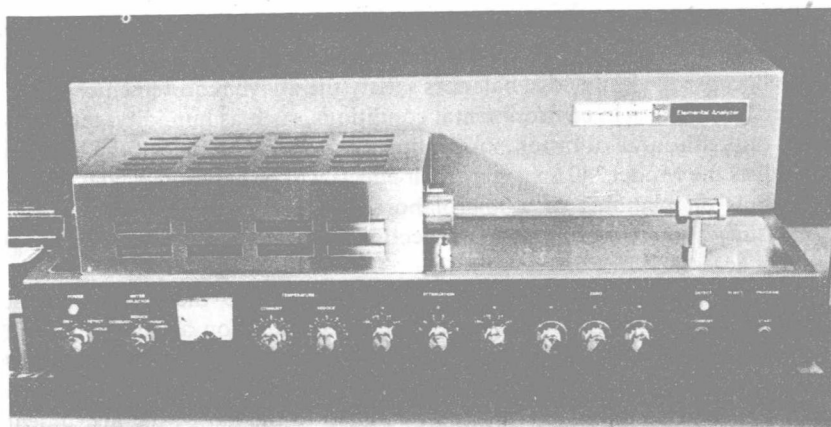
FIG. 1. Model 240 Elemental Analyzer.

in automation were made in those areas where reproducible operation from one analysis to another could be applied without the need for operator involvement. Recently[5] an automated sample introduction system, capable of handling up to 60 samples, was introduced and its combination with a programmable calculator rendered the system almost fully automatic.

The stage of sample preparation, however, is dependent on the type of compound to be analyzed. Compounds, which are for example a liquid, air-sensitive, or boron derivatives, require special treatment in the preparation. Automation of the sample preparation stage may be feasible when relatively simple and stable compounds, which require little more than accurate weighing, are to be analyzed continuously.

As in most microanalytical laboratories a variety of compounds are handled, most stages, except the sample preparation, can at present be made automatic by means of accessories to the Model 240 elemental analyzer.

Although the instrument is at present predominantly used for routine analysis in organic chemistry, the wide variety of compounds analyzed show that its field of application is very wide.

Weighing is an important part of an accurate analysis and as sophisticated automatic instrumentation cannot be justified without an accurate balance, some mention will be made of suitable balances.

The Model 240 microanalyzer takes generally 13 minutes for the completion of one analysis, consequently a balance capable of weighing milligram

levels of sample to an accuracy of 0.1% within a few minutes is essential for the continuous operation of the instrument. Several modern electrobalances as well as precise knife-edge balances satisfy the above requirements.

Certain changes in environmental conditions, such as humidity, temperature, draughts, and vibration, may influence the performance of the balance as well as the Model 240 analyzer; their effects will be mentioned later (p 48).

Details on planning of a microlaboratory have been published,[6] but some suggestion will be made in connection with the siting of the Model 240 and its accessories.

In order to avoid spillage on transfer of the sample, the balance is best positioned to the right of the instrument, preferably on an anti-vibration bench, and a small working area between the balance and the instrument is useful for preparation of the sample before its introduction into the Model 240. The data handling device is best situated to the left of the instrument within easy viewing distance of the operator in case attenuation is required. A calculator should be at hand for immediate calculation of the results.

These chapters on the Model 240 are mainly aimed at providing basic information to students and present or future users of the instrument. In order to promote the understanding of basic functions of the instrument, some detailed information will be included, but it is not intended to cover in detail aspects which are readily available in the Perkin–Elmer manual.[7]

II. PRINCIPLES OF AUTOMATION AND CHEMICAL REACTIONS

A divison has been made here between the basic stages and the automatic sequences of the Model 240, in order to assist in the understanding of its operation.

The basic stages cover briefly all stages of the analysis, while in the automated sequences the stages are explained in more detail in connection with the automated operation of the instrument.

The chemical reactions of combustion, reduction, and absorption are discussed separately.

A. Basic stages of operation

The operating functions in connection with the Model 240 can be divided into five main stages, as shown in Fig. 2.

1. Sample preparation

This stage is dependent on the particular methods of sample preparation

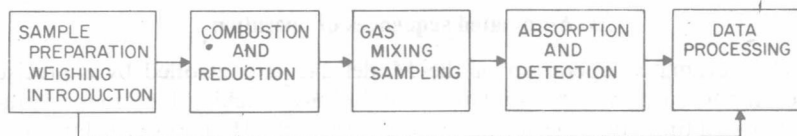| SAMPLE PREPARATION WEIGHING INTRODUCTION | COMBUSTION AND REDUCTION | GAS MIXING SAMPLING | ABSORPTION AND DETECTION | DATA PROCESSING |

FIG. 2. Operating stages of the Model 240.

employed, such as drying, special weighing techniques (encapsulation, etc.), and addition of oxidants, but basically the accurately weighed sample is transferred to a sample carrier for convenient introduction into the instrument.

2. *Combustion and reduction*

The instrument is prepared for sample combustion by introducing pure oxygen into the combustion tube. The combustion furnace is held at a temperature of approximately 950°C. After oxidation of the sample, interfering compounds are removed and the products H_2O, CO_2, and oxides of nitrogen are transferred to the reduction stage by means of helium. The oxides of nitrogen are reduced to elemental nitrogen and residual oxygen is removed. The final combustion products of H_2O, CO_2 and N_2 are transferred by means of helium to the mixing stage.

3. *Gas mixing and sampling*

The four gaseous components are homogenized in a constant volume, temperature and pressure and then passed through a sampling volume before part of this mixture is used for detection.

4. *Absorption and detection*

The gaseous mixture from the sampling volume is transferred to the detectors where chemical absorbers remove sequentially H_2O and CO_2. A detection system measures conductivity changes before and after absorption and the differential signal for each gas is recorded.

5. *Data processing*

The signals from the detectors are normally displayed on an analog strip chart recorder, but other more sophisticated data-handling devices such as printers and computers can be used. The recorded data are then processed to give the percentages of carbon, hydrogen and nitrogen. Information from a balance can also be fed in at this stage, when computing devices are employed.

This completes the analysis and the instrument automatically returns to a standby condition awaiting the introduction of a further sample.

B. Automated sequences of operation

The automated operation of the Model 240 is controlled by a precise programmer unit which completes a total of 64 switching functions at predetermined times during a 13-minute analysis cycle. High purity helium and oxygen are used for purging and oxidation respectively, while the pressure is controlled via stainless steel diaphragm regulators which have a very low rate of diffusion. Highly reproducible inlet pressure control is essential, particularly in connection with the helium supply, if the desired analytical precision is to be achieved. In order to avoid slight changes in pressure and volume within certain critical parts, such as mixing and sampling volumes, pressure switches, and detectors, these parts are enclosed in an oven which is maintained at $75° \pm 0.05°C$.

Gas flow rates and directions are controlled by capillary restrictor tubes and solenoid valves. The schematic diagram of Fig. 3 will be used to describe the operating sequence together with the gas flow directions at each stage of the operation.

1. *Standby condition*

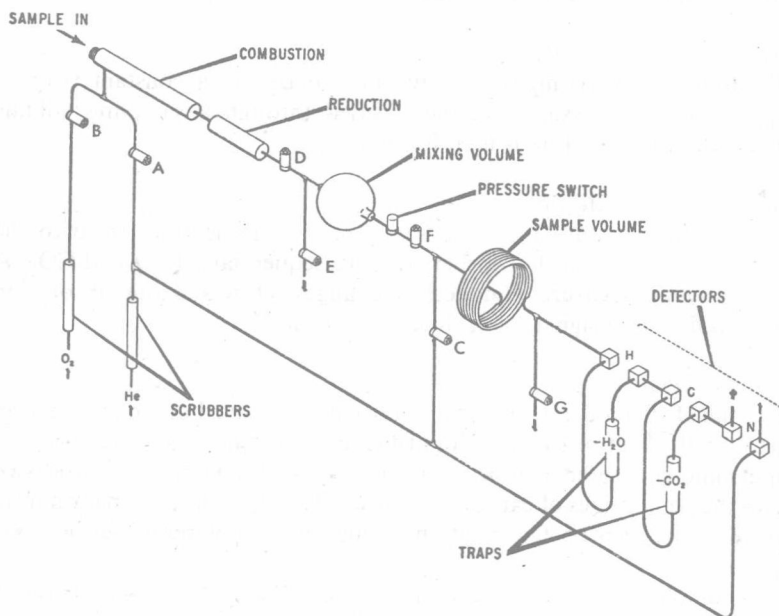The Model 240 is maintained in a standby condition awaiting the start of

FIG. 3. Schematic diagram of the instrument.

an analysis. Helium from which H_2O and CO_2 are removed by scrubbers continually purges the vessels of the instrument at a flow rate of approximately 30 ml/min. The route which is followed by helium through the instrument in standby condition is shown in Fig. 4. The combustion and reduction furnaces are maintained at their normal operating temperatures of 950°C and 670°C respectively.
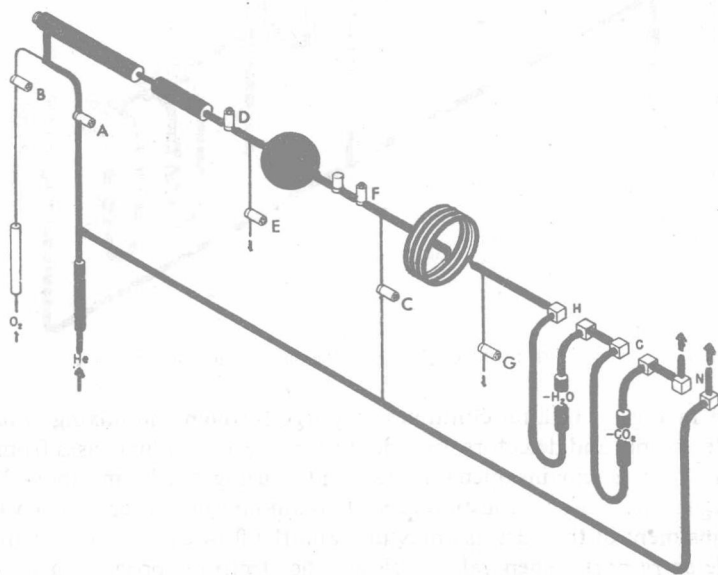

FIG. 4. Flow of helium in stand-by condition.

2. Sample introduction and purging sequences of gases

At the start of an analysis a weighed sample is introduced into the cold section of the combustion tube by means of a quartz sample carrier and the program is initiated by a push button on the front panel of the instrument. Initially all solenoid valves are opened (except the oxygen valve, valve B), which allows a purging sequence by helium through all the vessels of the instrument at various flow rates, as shown in Fig. 5. Air introduced with the sample, the carrier, and any remaining combustion gases from the previous analysis are removed from the system before the combustion of the new sample takes place.

After having purged with helium for a period of $1\frac{3}{4}$ minutes, valve A closes which stops the helium flow to the combustion and reduction tubes, and valve B opens allowing pure oxygen to enter the combustion tube; this is
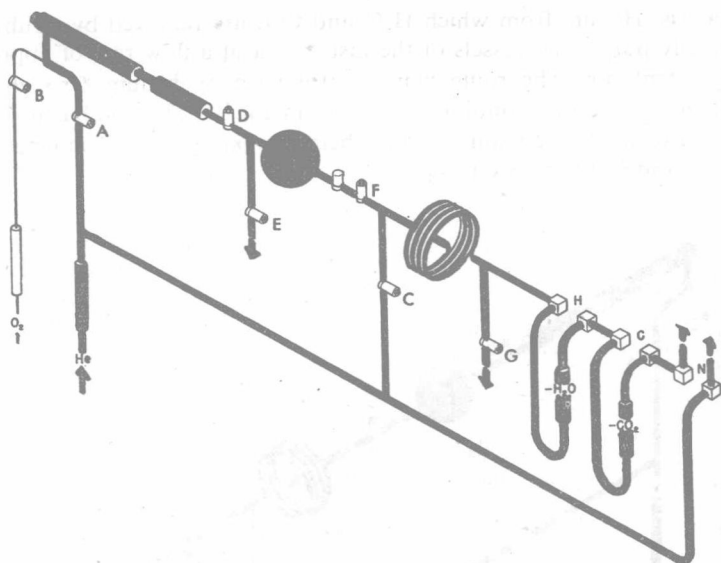
FIG. 5. Flow of helium in the purge condition.

shown in Fig. 6. Helium continues to purge through the mixing volume, sample volume and detectors, in order to remove all residual gases from the system. Valve B remains open for 30 seconds, during which time about 25 ml of oxygen enters the combustion tube. This amount of oxygen can be varied · by adjustment of the inlet gas pressure, and the flow can be checked at the sample entry port. When valve B closes, the electronic programmer stops, which is indicated by a light on the front panel informing the operator that the sample can be introduced into the combustion furnace.

3. Combustion and reduction sequences

The sample carrier is transferred to the combustion furnace by means of a simple hand-held magnet, which positions the sample in the hottest part of the furnace. This operation can be automated by means of a recent accessory to the Model 240 (p. 23).

As the combustion takes place under static conditions, valves D and E remain open for the first 30 seconds of the combustion time, which allows relief of pressure to atmosphere, in order to avoid damage due to sudden expansion of gases when highly reactive samples are analyzed. The remaining $1\frac{3}{4}$ minutes of combustion is sufficient to oxidize the majority of compounds, but the combustion time can be extended by holding the program cycle for any length of time.
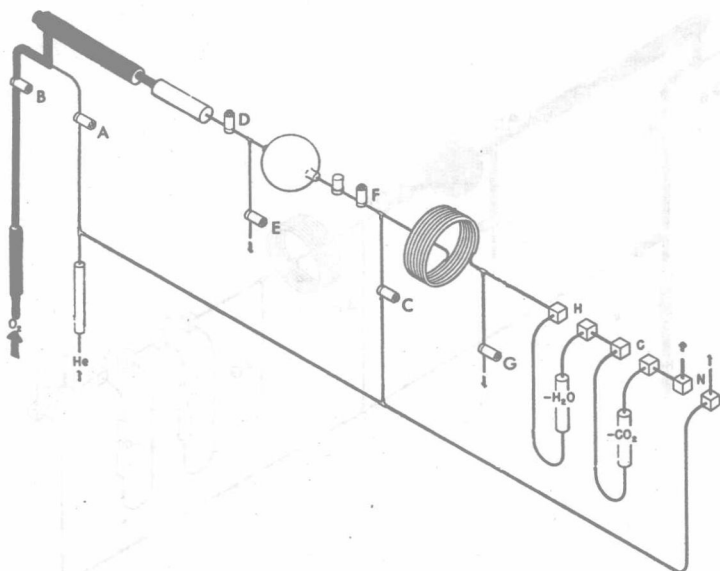
FIG. 6. Introduction of oxygen into the combustion tube.

The last seven inches of the combustion tube contain a series of chemicals, some of which assist in the oxidation and some absorb interfering combustion products (p. 26). At the end of the normal combustion period a flash heater, which is positioned just before the combustion furnace, is switched on and its temperature of approximately 1000°C quickly vaporizes any condensates. Then those oxidation products, which are not absorbed, are carried to the reduction tube by means of helium. The hot copper in the reduction tube removes any remaining oxygen and reduces the oxides of nitrogen to elemental nitrogen.

4. Homogenizing of the combustion products

During the final part of the oxidation–reduction stage valves E and F close, so that the remaining H_2O, CO_2, N_2 and helium flow into the mixing volume (Fig. 7). When the helium pressure reaches 1500 mm Hg, a sensitive pressure switch operates, which closes valve D and encloses the three combustion gases and helium in the mixing volume (Fig. 8). This condition is maintained for a period of $1\frac{1}{2}$ minutes in which time a homogeneous mixture of the four gases is formed.

At the same time signals from the three detector bridges are recorded for