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Polymer Analysis by Thermofractography

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This survey informs on possible applications of thermofractography for polymer analysis. Its place within the known polymer analytical procedures is established and a detailed description of the apparatus required and the procedures are given. The essential characteristics of the new method are introduced in practical analytical examples and the predominant advantages underlined. Identifications of natural polymers, such as lignins, tannins, cellulose and proteins are described as well as those of plastics, such as phenol resins, epoxy resins and hardeners, polycondensates and vinyl polymers, also of plastic additives such as PVC plasticisers. In most cases, an identification scheme is given.

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I Introduction

Plastics based on organic polymers have found use in almost all branches of technology and construction as a result of their superior material properties. The desire to have available a suitable "material to measure" for every conceivable purpose has left its mark on their development. Natural and, predominantly nowadays, synthetic polymers, fulfil this requirement virtually ideally. Their physical properties result from a number of closely related and mutually influential attributes of the material and the preparation. The character of a macromolecular system is determined primarily by the chemical nature of the polymerisable monomer on which it is based. The synthetic route influences the external state and the uniformity of the polymer material. Macromolecules with sufficiently uniformly defined structure are obtained only when the relevant reaction parameters are strictly controlled; this is accomplished in nature through specific catalysts and in chemical technology through heeding the information about the process. The macromolecular properties of polymers depend also on modifying additives. These include mainly the secondary components of plastics, built into the polymer skeleton through copolymerisation or polyaddition, for example so-called hardeners of epoxide resins or copolymers of PVC with other polyolefines, also termed internal plasticisers. Numerous additives of low molecular weight, such as plasticisers, stabilisers, antistatic agents, play similar parts in determining the external nature of high molecular weight natural and synthetic products. Finally, the form of polymer raw materials is affected also by added fillers and pigments and by some processing aids.

The combined effect of all these factors on the structure of the polymer accounts for the multiplicity and wide variation in the external form and desired properties of organic polymers. In order to be able to form an opinion about the real structure, one must therefore acquire as much physical and chemical structural information as possible with the help of a comprehensive analytical scheme[1)].

These data are fitted together like in a mosaic to yield an image of the constituents and of the macromolecular structure based on these polymer even though this picture is never complete and is always capable of extension. However, this touches on only one set of questions concerning polymer analysis, although of central importance. Polymer analysis assumes economic significance in connection with the problem of industrial synthesis and production of semi- and fully synthetic plastics. Of special interest in this service branch of technological chemistry is information about the molecular and macromolecular structure of the products concerned, perhaps the formulation of patent requirements. Further, constant testing of the quality and uniformity, within set limits of tolerance, of macromolecular products of synthesis is indispensable. This analytical monitoring of production batches through tests of identity is aimed primarily at excluding possible undesirable side reactions. More comprehensive analytical problems concern the polymer composition; intermediate synthesis stages leading to the wrong products; and residual monomers in the end product. Knowledge of the impurities, additives and auxiliaries is also of considerable interest. Finally, identification of the structural units of the polymers enables conclusions to be drawn about the origin and purity of the raw materials employed.

Another analytical domain is the testing of competing products. The questions of detail here demand, however, an analytical outlay which increases linearly to exponentially with the profundity of information and accuracy demanded. Much the same applies to the answers to analytical problems of forensic chemistry, where, because of their uniquity, polymers are often an object of investigation[2)].

In recent times the increasing health awareness of the public has given polymers analysis an established place in toxicological examination of packing material for medicaments and foodstuffs[3,4)]. This brief outline of the aims and fields of application of polymer analysis gives a clear idea of the extensive and tricky tasks and questions of this analytical sphere. The fundamentals and informative value of the analytical techniques hitherto known and used for this are discussed in the next chapter. Their pros and cons are examined critically. This then leads to *thermofractography*, the sole procedure at present for fast thermal analysis of high polymers using *gradient degradation* coupled with thin-layer chromatography.

II Methods of Polymer Analysis

II.1 Preliminary Remark

Polymers can rarely be identified using the known methods for chemical determination of compounds of low molecular weight. This is due to fundamentally different structure of macromolecular substances and the resulting special physical and chemical properties[1)]. As a rule, polymers are scarcely or only slightly soluble in the usual solvents; they can be vapourised generally only under decomposition; their molecular weights are by definition not uniform. The chromatographic and spectroscopic procedures which have shown their value when applied to compounds of low molecular weight furnish therefore results of only limited value.

II.2 Analytical Procedures Preserving the Polymer Structure

II.2.1 Spectroscopic Procedures

As expected, IR-spectroscopy[1,5–10)], as a direct method, relatively simple to operate and non-destructive of sample, was long prominent in the development of a systematic scheme of polymer analysis for recognising characteristic structural elements of macromolecules. Nevertheless it became evident in the course of its application to nearly all problems of polymer analysis[5,7,9)] that copolymers and also the various additives, impurities and auxiliaries of polymers could be identified only incompletely, especially when present in low concentration. The characteristic IR-bands of the various absorbing polymer segments are often superimposed on one another and on those of additives in the same wave length region; or the band intensities are too weak to permit an unambiguous assignment. Widespread application of UV-[1,5,10)]

and NMR-spectroscopy[1, 5, 7, 10] are subject to similar difficulties. Both methods possess a certain significance in the qualitative and quantitative determination of aromatic and conjugated unsaturated structures; and in ascertaining the crystallinity, tacticity, conformation, sequence length and degree of branching of elastomers. But for the polymer systems used in practice – mostly fairly complex mixtures – they provide information often of little value. High polymers cannot be submitted directly (if at all) to mass spectrometry, the most modern and sensitive spectroscopic identification procedure. As a result of their spatial structure and very high average molecular weights they are not vaporisable.

II.2.2 Separation Procedures for Fractionating Polymers

Along with the application of spectroscopic methods for direct identification of macromolecules suitable techniques have been developed for separation of oligomer fractions, components of polymerisates and additives to plastics. Fractionation on the basis of solubility differences[1, 11] were those principally considered (fractional precipitation, extraction, gradient elution, counter-current distribution, ultra-filtration, dialysis, permeation, diffusion, sedimentation)[1]. Classical column chromatography (CC) steadily lost its importance in this sphere[1] and has been replaced largely today by high performance liquid chromatography (HPLC)[12–14]. Several effective separation procedures are available nowadays for separating macromolecules on the basis of their molecular size and molecular weight distribution. These differ markedly from one another in their outlay of apparatus. So-called gel permeation chromatography (GPC)[1] enables, for example, the relative molecular masses of various oligomer fractions to be determined; it can thus be applied to check the chemical homogeneity of polymers. High-voltage electrophoresis is still valuable, especially in polypeptide chemistry, for separating and purifying proteins according to their chemical nature and molecule size. Recently, both these established separation techniques have been supplemented to advantage by two further developments of thin-layer chromatography (TLC), a method really for separation of lipophilic substances of low molecular weight[15]. For example, according to experience so far reported, the newly introduced "Phase separation- or precipitation-TLC"[13] is highly suitable for characterising synthetic polymers according to their content of oligomer, homogeneity and degree of branching. Thin-layer electrophoresis prevails as a separation method in the domain of natural, mostly biogenic polymers[15].

II.2.3 Simple Physical and Chemical Test Procedures

The separation techniques mentioned above can be rationally employed only when suitable preliminary tests have established at least roughly the nature of the polymer and, in favourable cases, even the class of polymer. Such tests, especially important in large scale industrial chemical practice, include simple qualitative chemical tests for particular heteroelements and functional groups[1–6, 10, 11, 17–26]. A certain number of physical data, mainly of interest for quality and production control, can also yield criteria for identification of an unknown polymer[1–6, 10–11, 17–26]. These

include tests of mechanical and rheological properties, such as hardness, density, solubility, softening- and/or melting regions, viscosity, rigidity, ductility and dimensional stability. Other standard methods serve for acquiring optical (refractive index, colour, transmittancy), electrical (dielectric constant, specific resistance) and thermal (specific heat, coefficient of expansion, thermal conductivity and, last but not least, behaviour during thermal degradation) data. Their analytical usefulness is derived from comparison with tabulated standard values within definite limits.

During application of all the foregoing analytical techniques, the original polymer structure remains more or less unchanged. In the more physical methods of investigation the properties and activities of macromolecules can then be no more than summed values because the chemical factors influencing the individual structural elements of polymers, responsible for the macroscopic physical parameters, are externally additive. Consequently, conclusions about their presence and form, based on the data thus obtained, are possible only with reservation.

II.3 Analytical Procedures Involving Change of the Polymer Structure

Very useful hints about the analytical identity of polymer structures can be obtained from their changes and for those of physical reference values as a result of chemical reactions. For this, there is a number of methods, mainly physical, for degradating the primary polymer structure[27]. The desired analytical standard is attained, however, only by the thermal and hydrolytic degradation procedures when one looks at it from a practical and economic point of view. The thermal procedures in particular have proved to be especially suitable for depolymerisation of compounds of high molecular weight to defined fragments of low molecular weight. Moreover it is usually possible to combine them with suitable chemical or physical techniques of identification. Classical hydrolytic methods, especially for breakdown of condensation and addition polymers, have maintained their role in the analysis of polymers.

II.3.1 Differential Thermoanalytical Procedures

The techniques which are termed differential thermoanalytical methods[28–39] (thermogravimetry, TGA; differential thermal analysis, DTA; differential scanning calorimetry, DSC; thermaloptical analysis, TOA; and dilatometry) combine in principle thermal degradation with a physical detector system; this enables one to follow the changes in substance-specific values brought about by the supply of thermal energy. They have the advantage of permitting the behaviour of polymers during degradation to be followed quantitatively in a temperature gradient. Their shortcoming, the same as with the simpler physical test procedures, is that individual polymer segments, components or additives cannot be recognised. On the contrary, these techniques record no more than overall losses of mass, volume changes and alterations in optical properties resulting from elimination of secondary products, mostly of low molecular weight and gaseous.

II.3.2 Thermal Degradation in Combination with Chemical Separation and Identification Techniques

In order to characterise the individual products derived from thermal degradation of polymers, suitable separation and detection systems were sought, if possible directly coupled with the degradation unit. It is a fact that the type and number of possible thermolysis products is characteristic for the polymer composition and permits conclusions to be made about the structure of the polymer. A decisive breakthrough in the domain of chemical polymer analysis was accomplished by the development of thermoanalytical degradation procedures in indirect and direct combination with physico-chemical separation and detection methods.

II.3.2.1 Combination of Pyrolysis and IR-spectroscopy

IR-spectroscopy was employed at first for identifying the pyrolysis products of polymers[5,8,40–44]; considerable difficulties in interpretation were encountered, however, where no prior separation of the products was carried out.

II.3.2.2 Pyrolysis-GC and Pyrolysis-MS and Coupling of Both Procedures

The methods of pyrolysis-gaschromatography (PGC)[43–74] and of pyrolysis-mass-spectrometry (PMS)[75–82], both based on isothermal degradation, have proved to be highly efficient. They are distinguished by high sensitivity and outstanding reproducibility. They provide the possibility of compiling tables of "finger print" pyrograms for every class of polymer[5]. The combination of both procedures, pyrolysis-GC-MS, in the so-called "on-line" technique[56,61,62,81], furnishes even more informative analytical results. This analytical system while admittedly demanding a considerable outlay of apparatus, enables degradation, separation and identification to be carried out smoothly in a single working stage. Further, these pyrolysis procedures can be used for quantitative analysis of the polymer composition. However, despite these virtues, they have only limited value in the routine analysis of polymers.

II.3.2.3 Limits of Polymer Analysis by Pyrolysis-GC and -MS

1) Restriction to isothermal conditions.
2) Thermal breakdown processes cannot be followed.
3) No distinction of the polymer additives, residual monomers and thermolytically produced degradation products, all of which arise in differing temperature regions.
4) Polymer components cannot be pre-fractionated chemically during the thermal degradation.
5) Large demand of time and sample (> 10 mg).
6) Considerable requirement of money and personnel for equipping and manning the analytical system.

II.3.3 Thermal Degradation of Polymers in Combination with TLC

There has hence been no lack of attempts to introduce into polymer analysis simpler, faster and less costly separation and detection procedures for the products of thermolysis of polymers, if possible directly coupled with the thermolysis unit. Thin layer chromatography (TLC) was a first candidate here[15]. It is superior to more complex apparatus as far as ease of operation, economy and duration of analysis are concerned; and its sample requirement, efficiency of separation and reproducibility of analytical data are at least as favourable. In addition, many detectors, specific for groups and for individual substances[15,84] are already available in TLC; and several samples can be analysed and compared alongside one another[15,85]. These advantages stimulated the study also by TLC of the products of pyrolysis of polymers[1,5,6,25,86–93].

Notably Braun and co-workers have developed a useful aid for polymer analysis, involving relatively crude pyrolysis in a test tube and subsequent manual transfer of the pyrolysate to TLC; they give a scheme for separation of plastics based on this[25,26,89–92].

II.3.4 Hydrolytic Degradation Procedures in Combination with TLC

Classical alkaline and/or acid hydrolysis is often employed for defined break-down of hydrolysable polymers (condensation and addition polymers). The fission of the macromolecules then usually reverses the reaction of formation. Moreover, preliminary chemical separation of the hydrolysis products into basic, acidic and neutral parts is facilitated in the basic or acidic medium. Hydrolytic degradation of such polymers is thus combined with a chemical pre-fractionation of the components of hydrolysis. Almost only TLC has been used for separation and detection of the hydrolysis products[94–102]. Only occasionally has GC found use for this[101,103]. Disadvantages are, however, the extremely long time of hydrolysis (sometimes > 18 h) and the relatively large sample (1–2 g). More recently, the hydrolytic breakdown of condensation polymers has been extended and accelerated by introducing the old established method of alkali fusion, then followed by GC-identification of the hydrolysis products[104]. Problems arise, however, of the "point application" and of interference by larger amounts of water during the chromatography.

II.3.5 Coupled Procedure Thermolysis-TLC

II.3.5.1 TAS-Procedure

The TAS-procedure, developed originally for rapid extraction of the drug content of natural plant material, was an important move towards a thermolysis-TLC-coupling[105–108]. During the initial testing stage of the new coupling procedure, the possibility of characterising polymers through TLC of their products of thermal degradation was pointed out[108]. Even before this, it had been shown that an experimental arrangement, essentially that of the TAS-procedure, with direct combination of pyrolysis unit and TLC-separating system, was suitable for polymer analysis[109].

II.3.5.2 Thermofractography

The further development of the TAS-apparatus led then to thermofractography (TFG)[110]. The decisive new feature is the temperature-programmed degradation of polymers using a pre-selectable linear increase of temperature, accompanied by a simultaneous movement of the thin layer which is synchronised with the temperature rise. Apart from the more physical breakdown procedures of differential thermal analysis, thermofractography offers for the first time an analytical technique for continuous degradation of macromolecular substances in a temperature gradient and coupled directly with TLC[111]. The individual chemical characterisation of polymer fragments through their "thermofractogram" provides a qualitative and semi-quantitative identification of natural and synthetic polymers. The procedure is by no means limited to thermal degradation. The construction and instrumental side of the TFG-apparatus (TASOMAT) can be sufficiently modified so as, for example, to be able to carryout even the alkali fusion in it as a hydrolytic procedure for condensation polymers.

Both coupled techniques are described below and the various procedural variants are discussed. The equipments expressly designed for these purposes are presented. In the main part of this survey, the application and performance of TFG in the analysis of natural and synthetic polymers are then shown. Also below is a compilation of the most important methods for qualitative polymer analysis (see Scheme 1).

III Presentation of the Method

III.1 TAS-Procedure and Thermofractography

The TAS-procedure was described in 1967–68 as a simple thermal micro-separation and application procedure coupled directly with thin-layer chromatography[105–108]. Substances which are volatile at higher temperature are hereby separated from involatile material and brought directly on to a thin-layer chromatographic start point. For this, a few mg of sample are introduced into a special glass cartridge, one end of which is drawn out into a capillary; the other end of this so-called TAS-cartridge is closed with a silicone membrane. The cartridge is pushed into the TAS-oven maintained at a definite temperature. Within 1–2 min the volatile substances leave the capillary exit as a fine stream of vapour and condense as a start point on the thin-layer plate held directly opposite the exit (Fig. 1).

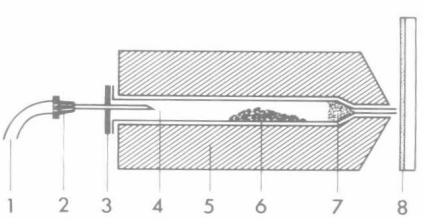
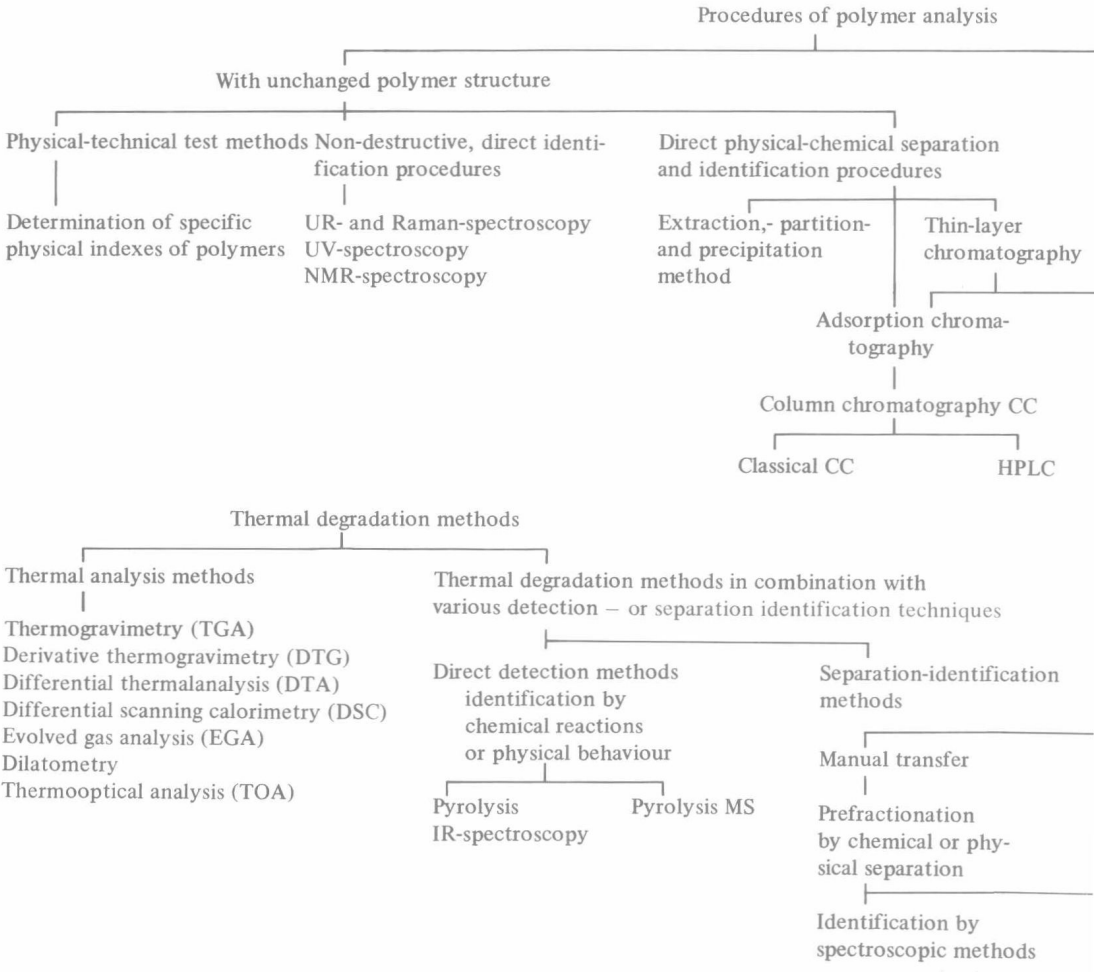
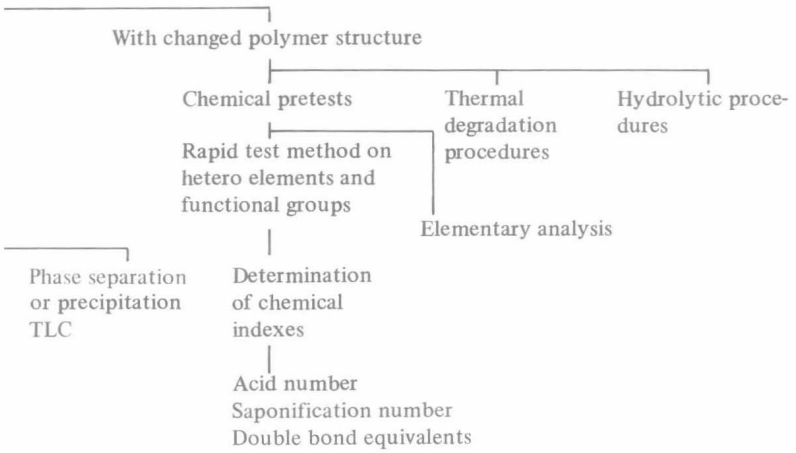
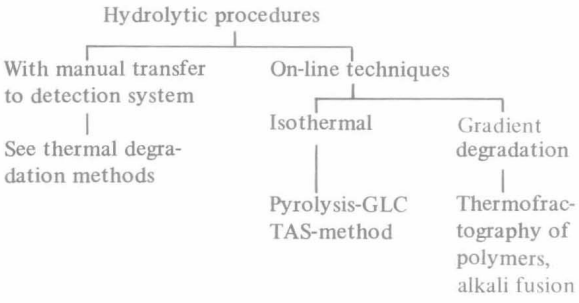


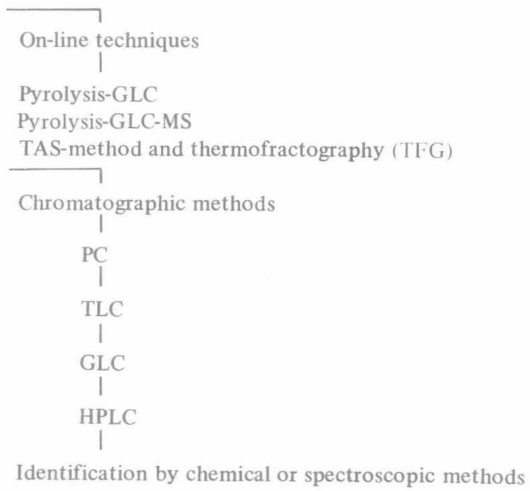
Fig. 1. TAS oven, longitudinal section: 1 carrier gas, 2 injection needle, 3 seal, 4 TAS glass cartridge, 5 heating block, 6 sample, 7 quartz wool, 8 TLC plate with layer



Scheme 1: Analytical methods in the field of polymers


With changed polymer structure
Chemical pretests
Thermal degradation procedures
Hydrolytic procedures
Rapid test method on hetero elements and functional groups
Elementary analysis
Phase separation or precipitation TLC
Determination of chemical indexes
Acid number
Saponification number
Double bond equivalents


Hydrolytic procedures
With manual transfer to detection system
See thermal degradation methods
On-line techniques
Isothermal
Gradient degradation
Pyrolysis-GLC
TAS-method
Thermofractography of polymers, alkali fusion


On-line techniques
Pyrolysis-GLC
Pyrolysis-GLC-MS
TAS-method and thermofractography (TFG)
Chromatographic methods
PC
TLC
GLC
HPLC
Identification by chemical or spectroscopic methods

The effectiveness of transport of the sample to the thin layer can vary. "Forced convection" gives the smallest yields. Appreciably better results are attained when a so-called propellant, that produces steam for example, is added. Best of all, however, is to carry out a carrier gas distillation by passing a current of inert gas at low speed over the sample, *i.e.*, through the TAS-cartridge. The TAS-procedure is isothermal and makes use of a stationary thin-layer. In the thermofractographic method, however, the sample is heated gradually from room temperature to a maximum temperature of 450 °C. At the same time, the thin layer is slowly moved forward, thereby yielding a band of condensed substances fractionated according to their volatility. This coupling of linear temperature increase of the sample with a fractionated capture of the volatile or pyrolysed substances is termed thermofractography (TFG)[110]. A special apparatus, called the TASOMAT, is used to carry out the procedure. It can be employed for the TAS-procedure, for preparative winning through band condensation under isothermal conditions, and also for the procedure, just described, of fractional collection of the substances which have been heated in the temperature gradient. The result of the described procedure after chromatography is termed a thermofractogram. The substances are separated along the abscissa of the thin layer according to their boiling or sublimation temperatures or thermolysis behaviour; and along the ordinate according to their chromatographic behaviour.

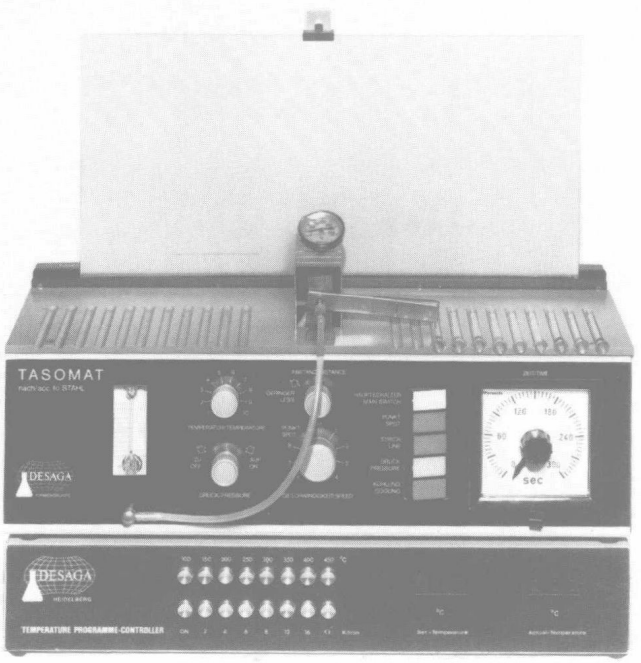


Fig. 2. Front view of the *Tasomat* (above) and control unit (below)

III.2 Apparatus

The TFG-apparatus is known under the name of TASOMAT (Fig. 2, above). The oven block (Fig. 1) has the same dimensions as the TAS oven block but is made from a steel alloy, of lower coefficient of thermal expansion than aluminium. This is important for maintaining constant the small gap between cartridge tip and collecting layer as the temperature rises.

Heating to the maximum temperature of 450 °C is accomplished by a heating cartridge built into the block. For temperature setting under isothermal conditions (TAS-procedure) the apparatus has a built-in thyristor stepless control device. However, in order to obtain a linear rise in temperature of the oven block and various rates of heating, a specially adapted control unit must be available (Fig. 2, below). The desired rate of heating and end-temperature can be selected with a press button device on the control apparatus. The actual and set temperature values of the oven block are given digitally. At the end of an experiment, the oven block can be cooled rapidly with a built-in ventilator. The gap between the tip of the TAS-cartridge and the thin layer can be rapidly regulated by turning a screw knob. The size of the gap is seen from the projected shadow of the cartridge tip on the thin-layer (Fig. 3).

The TAS-cartridge is made of Pyrex glass and of such length and thickness that it fits tightly in the partitions of the oven block. In contrast to the usual procedure, a sheath made of aluminium foil, open at both ends, is inserted into the TAS-car-

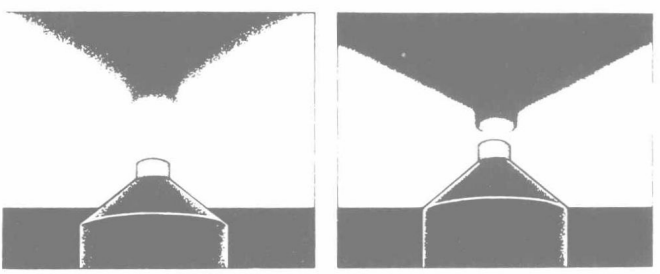


Fig. 3. Distance regulation by shadow projection of the oven tip on to the TLC plate. Left: distance too far, blurred projection; right: distance under 1 mm, exact projection on to the thin layer

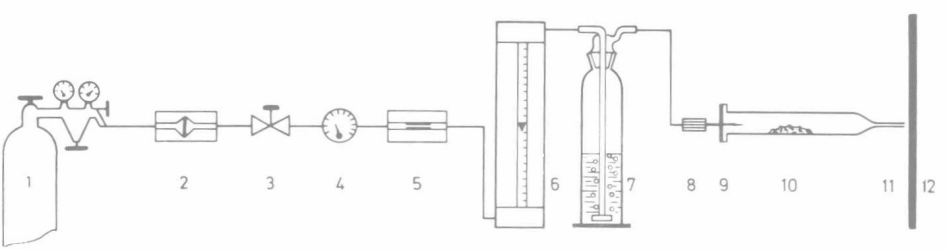


Fig. 4. Flow diagram, from the nitrogen cylinder (1) to the TLC plate (12): 2 filter, 3 fine adjustment valve, 4 manometer, 5 reducing capillary, 6 flow meter, 7 special purposes washing bottle for the saturation of gas, 8 injection needle, 9 seal, 10 TAS cartridge with sample, 11 capillary of the TAS cartridge