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Special Review

APPLICATIONS OF THERMAL ANALYSIS

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This review paper outlines some current developments in thermal analysis. The current status of standard methods, in particular those issued by the American Society for Testing and Materials (ASTM), using thermal analysis techniques are discussed. In the second place a simple method for the determination of the oxidative stability of polyethylene by DTA is reviewed. Finally the paper surveys some of the more recent work being carried out in fossil fuels and fuel oils.

In the life cycle of any analytical technique there are a number of identifiable phases. Some of these phases take a long time to develop whilst others are very rapid. Thermal analysis has been no exception to this and there are three phases to comment on:

Early phase: In this phase all instrumentation is home built and is used for specific studies, almost invariably emerging from an academic background, at different times and in different places. Thus it was that as late as 1958 Smothers and Chiang's book on Differential Thermal Analysis [1] was largely a compendium of individually developed equipment in use in different laboratories.

Developing phase: There are two trends here to comment upon. The first is the extending of the range of applications, even if certain academics comment adversely. For example in the preface of C. Duval's book he writes, "If certain innovations . . . point to the things to come, to us it will seem entirely useless . . . to trace out certain curves point by point – and all this merely to dehydrate some preserves or ham? Alas, why must this preface end on a mournful note?" [2] Along with a widening of the application fields for thermal analysis comes the commercialisation of the instrumentation. At the same time there is a strong emphasis on the technique itself rather than on what it can accomplish. Thus at the 1st International Conference on Thermal Analysis the instrumental section was a considerable proportion of the volume [3].

Current phase: In this phase the technique is used for a widening range of specific applications which may call for modifying of the standard equipment. As some of these specific applications are outside the research and development area there is a parallel simplifying of commercial equipment making it easier to use. In today's world this includes the easy addition of data processing facilities.

This paper outlines the current developments as far as issued standards in the thermal analysis field are concerned, as exemplified by those issued by the American Society for Testing and Materials (ASTM). In the second place it outlines a simple method for the determination of the oxidative stability of polyethylene by differential thermal analysis (DTA). Finally the paper surveys some of the more recent work being carried out on fossil fuels and fuel oils.

Standard test methods

Table 1 lists the current ASTM standards [4] in which one or more thermoanalytical methods are specified. The first three standards originated from work by two of the standing committees of the International Confederation for Thermal Analysis (ICTA), namely, its Committees on Standardization (E 472 and E 474) and on Nomenclature (E 473). This work has contributed to better communication between thermal analysts in encouraging full reporting of work done so that people could follow what was being done and the use of standard terminology helped to add to the universality of communicating. In addition the regular International Conferences organised by ICTA have been most valuable in helping achieve the same

Table 1

Standard No.	Title
ANSI/ASTM E 472-79	Standard Practice for Reporting Thermoanalytical Data
ASTM E 473-80	Standard Definitions of Terms relating to Thermal Analysis
ASTM E 474-73	Standard Method for Calibration of Temperature Scale for Differential Thermal Analysis
ANSI/ASTM E 537-76	Standard Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis
ASTM D 3417-75	Standard Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis
ASTM D 3418-75	Standard Test Method for Transition Temperatures of Polymers by Thermal Analysis
ANSI/ASTM E 698-79	Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials
ANSI/ASTM D 3159-78a	Standard Specification for Modified ETFE-Fluoroplastic Moulding and Extrusion Materials
ANSI/ASTM E 14-63(75)	Standard Recommended Practice for Thermal Analysis of Metals and Alloys
ASTM D 3386-75	Standard Test Method for Coefficient of Linear Thermal Expansion of Electrical Insulating Materials
ANSI/ASTM D 2236-70	Standard Test Method for Dynamic Mechanical Properties of Plastics by Means of a Torsional Pendulum
ANSI/ASTM E 659-78	Standard Test Method for Auto Ignition Temperature of Liquid Chemicals

goals. The third standard (E 474) incorporates the results of the long, extensive and continuing work of the Standardization Committee. The programme of work resulted in the issue of a number of standard materials now jointly issued through the International Confederation for Thermal Analysis and the National Bureau of Standards in the U.S. The materials are used for DTA temperature calibration purposes and apart from the two metals indium and tin, each material exhibits a $solid_1 \rightleftharpoons solid_2$ transition that is well-defined and highly reproducible. They have been characterised also by thermal techniques, are chemically stable and substantially inert. The published certified values are the means of values obtained by 34 different laboratories.

There are three sets, each of five materials with some overlaps:

SRM 758 KNO_3, In (metal), Sn (metal), $KClO_4$, Ag_2SO_4 – to cover the temperature range of 128–430°C

SRM 759 $KClO_4$, Ag_2SO_4, SiO_2, K_2SO_4, K_2CrO_4 – for the range 299 to 665°C

SRM 760 SiO_2, K_2SO_4, K_2CrO_4, $BaCO_3$, $SrCO_3$ – for the range 573 to 925°C

Each of the remaining standards as indicated by the title covers a wide range of materials. Three of the standards, namely E 537, E 698 and E 659, were the work of Committee E 27 which is concerned with the Hazard Potential of Materials. Thus E 537 is concerned with assessing the thermal stability of chemicals by DTA. Its use is recommended as an early test for previously uncharacterised chemical substances or mixtures. The test examines two criteria – the detection of an enthalpic change and the determination of the approximate temperature of that change. E 698 recommends the evaluation of the kinetic parameters by either DTA or DSC and the values are then used to predict a reaction half-life. Standards D 3417, 3418, 3159 and 2236 were the work of Committee D-20 on Plastics and each of these is concerned with the properties of plastics. Standard D 3417 and 3418 state that the tests (either DTA or DSC) are to be used both for specification acceptance and for research, whilst standard 3159 is basically a quality control test for three types of fluoroplastics used for moulding or extrusion purposes. The three types of material are:

(i) low flow rate for applications involving unusual environmental conditions;

(ii) medium flow rate for *general purpose* moulding and extrusion;

(iii) high flow rate for small diameter wire coating and thin section moulding.

Standard E-14 is an old standard in which DTA is one of the recommended methods for determining the phase changes of metals and alloys. The standard was the work of Committee E-37 on Thermal Measurements, which, incidentally was also responsible for the first three standards E 472-4. Finally, Committee D-9 on Electrical Insulating Materials published standard D 3386 in which the use of a thermal mechanical analyser with an amplification factor of at least X 1000 to study the materials in question is recommended.

Aside from the initial three standards, six of the remainder recommend either a DTA or a DSC techniques, one uses TMA whilst the remaining two use less well-known techniques. It seems probable that activity in this area of standards is likely to intensify in the coming years and a number of recommending and regulatory bodies will be involved. This brief survey has been concerned solely with those standards published by ASTM.

The oxidative stability of polyethylene [5]

The use of the DTA technique at constant temperature to measure the oxidative stability of polyethylene and other polyolefines as an alternative to the oxygen adsorption method is well established. The test is of particular interest to the cable industry where polyolefine-based rubber formulations are used as cable covers, either to compare the oxidative stability of finished products, or to test the oxidative stability of raw rubber mix to establish that sufficient anti-oxidant is present to prevent polymer degradation during processing. The test has also been used to measure the oxidative stability of oils used in the food industry.

In the work reported in reference [5] all the measurements were carried out using a Stanton Redcroft 671B low temperature differential thermal analyser. It was shown that the equipment could readily be used for the experiments and that it fulfilled three essential requirements:

(1) It must be possible to maintain the DTA cell within 1° of the required temperature for at least the duration of the test. Figure 1 shows the isothermal temperature record of the equipment over a prolonged period, namely 16 hours.

(2) The temperature of the sample must be measured accurately. Equipment in which the temperature measuring thermocouple is in direct contact with the sample is essential. This is the case with the instrument mentioned.

(3) The temperature of the sample must be displayed with high resolution using a high precision voltage source to back off say 7.5 or 8.0 mV (at 200°V the output of a chromel-alumel thermocouple is 8.137 mV with respect to an ice junction). The residual signal may then be displayed at 1 mV full scale deflection and one small chart division is thus equal to 0.25°. The relationship between thermocouple output and temperature is checked using the NBS-ICTA standard indium (Fig. 2).

In the test procedure adopted the following experimental conditions were used:

Sample weight	4.5–6.0 mg
Amplifier sensitivity	20 μV f.s.d.
Recorder sensitivity – DTA	20 mV f.s.d.
– Temperature	1 mV f.s.d.
Gas flow rates	100 ml min^{-1}
Crucibles	Aluminium
Reference	Empty aluminium crucible

The test sample was placed on the DTA at 200°±1° and held in nitrogen for 5±0.1 minutes. The gas was then changed to oxygen, and the oxidation allowed to proceed

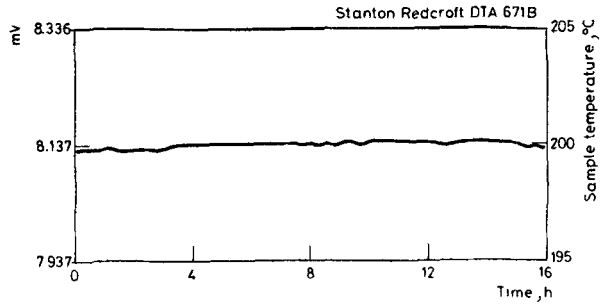

Fig. 1 Isothermal temperature record over 16 hours of low temperature differential thermal analysis

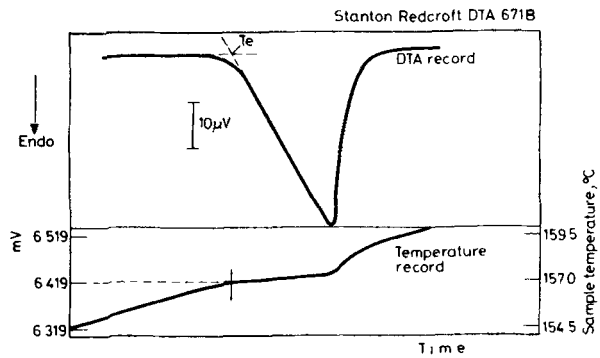

Fig. 2 Temperature calibration with indium. Heating rate 1 deg min^{-1}, sample weight 3 mg

until the DTA response drove the DTA pen off scale. A typical result is shown in Fig. 3 which shows how the oxidation induction time (OIT) could be evaluated.

The programme studied variables such as the effect of sample thickness, temperature and sample ageing. Figure 4 shows the variation of OIT with temperature for a polyethylene material. For this particular material a change in temperature of 1° causes a change in induction period of 1.9 minutes. This fact underlines the need for true isothermal conditions to be established within a very narrow temperature interval and for accurate temperature calibration to be carried out, especially if inter-laboratory comparisons are attempted.

The application of thermal analysis to fuels

Applications of thermal analysis to fossil fuels go back to the early days of the technique but there has been a renewed interest in recent years, particularly with the facilities offered by modern thermal analysis equipment. Instrumentation used in the

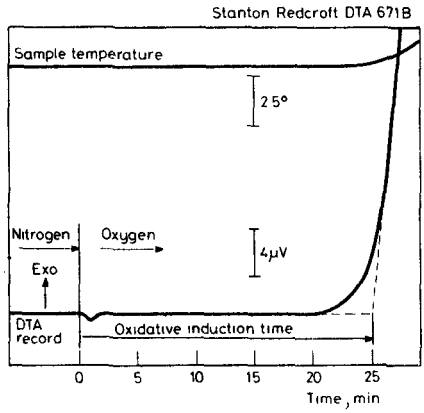

Fig. 3 Measurement of oxidative induction time (OIT)

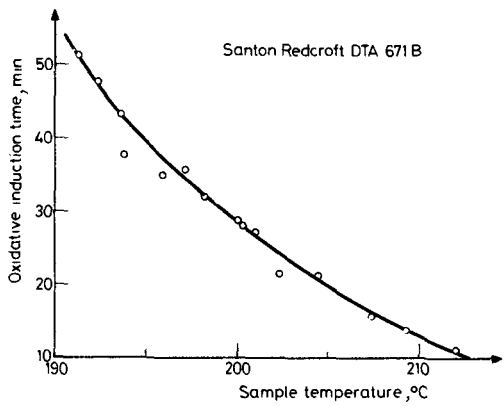

Fig. 4 Variation of OIT with temperature for a polyethylene material

applications discussed below has been fully described elsewhere [6, 7] but a brief mention here is appropriate. For work on the characterisation of fuel oils and fossil fuels the Stanton Redcroft simultaneous thermal analyser, the STA 781, has been used. Its advantages are (a) that it simultaneously measures TG–DTG–DTA and (b) that it is designed to give extremely close atmosphere control, in that the sample and reference head is suspended in a micro environmental ceramic cup with a series of ceramic discs and spacers sitting on the lid (Fig. 5). Gas atmosphere control is attained by passing gas up the support stem. Further advantages of this system lie in its ready connection to data processing facilities and to a gas analyser system such as a mass spectrometer. Other work reported in this section has been carried out

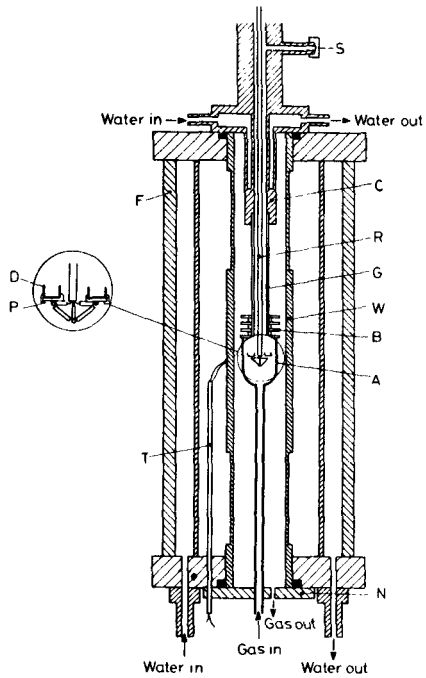

Fig. 5 Arrangement showing micro environment cup in simultaneous thermal analyser

on the Stanton Redcroft thermobalance, Model TG 761, or a modified TG 750. The TG 761 has the following features in that it allows a very fast heating rate, the maximum in standard form being 100 deg min^{-1}, although with very little alteration 1000 deg min^{-1} can be achieved. Secondly isothermal temperatures can be rapidly established and are precisely maintained. Thirdly there is extremely good atmosphere control, almost instantaneous change over the sample can be introduced by the use of the glass side arm branch as shown in Fig. 6. Lastly there is extremely rapid cooling in that cooling from 1000° to 100° is accomplished in less than four minutes. Percentage weight changes can be read directly from the recorded results since there are, in normal use, no weight corrections to be made.

Study of the particulates and hydrocarbons in diesel engine exhausts

Cuthbertson, Stinton and Wheeler [8] have developed and reported on a TG method for separating the components of diesel engine particulates to enable a total diesel hydrocarbon analysis for those hydrocarbons trapped on the particulate filter, and heated flame ionisation detection for those passing through the filter. The results have been compared to the total hydrocarbon analysis as used in the U.S. Federal Test Procedure and show a small gain in hydrocarbon recovery and an increase in overall information for the new instrumental arrangement.

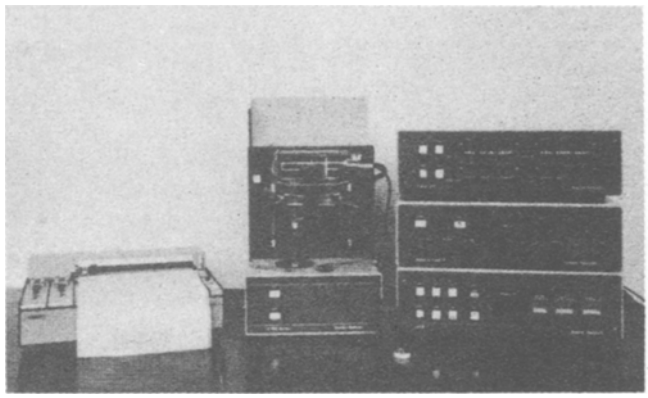

Fig. 6 Thermal analysis instrumentation for classification of fuels

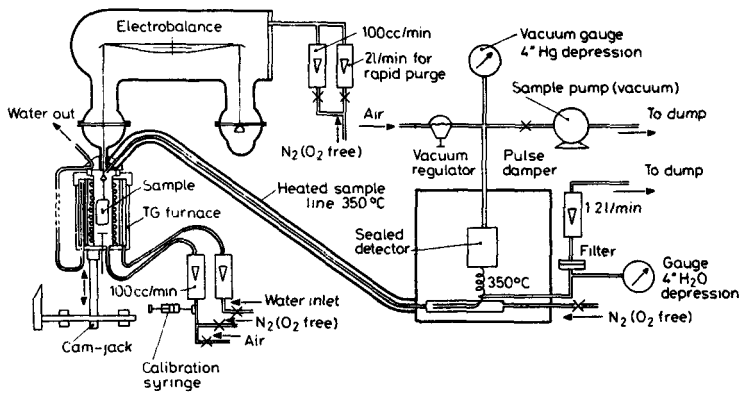

Fig. 7 Diagram of modified thermobalance interfaced with a flame ionisation detector (see ref. 8). Reprinted with permission © 1979 Society of Automative Engineers, Inc.

The experimental set up is shown in diagrammatic form in Fig. 7. The key to success is the total exclusion of air and the thermobalance furnace was modified to ensure this. The technique is to filter the exhaust fumes into a suitable filter medium, for routine work an inert filter Whatman type GF/A was used. The filter paper and the deposits were then transferred to the thermobalance and the run carried out in an atmosphere of nitrogen up to a temperature around 700–750°. After a period of isotherming at that temperature oxygen was introduced for an exothermic oxidation. A typical curve is shown in Fig. 8. The workers reported on some results of four engine and car development programmes on a routine basis.

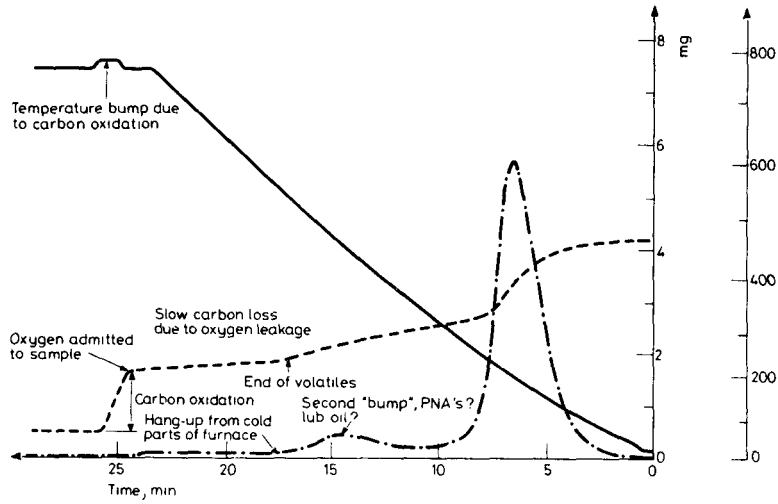

Fig. 8 TG interfaced with an HFID-weight loss and hydrocarbon curves for a soot sample (see ref. 8). Reprinted with permission © 1979 Society of Automative Engineers, Inc.
——— Temperature, — — — Weight, —·—·— FID trace

Characterisation of fuel oils and fossil fuels

Thermal analysis techniques have been applied to three areas of characterisation in some detail: (a) burning profile test, (b) evaporation profile test, and (c) proximate analysis.

The burning profile test is a test of the measure of the combustibility of the coal or fuel oils. A sample of finely divided coal or fuel oil is heated at a standard heating rate in a stream of air in the thermobalance and the DTG or derivative curve is plotted. The evaporation profile or volatile release test is similar except that the stream of air is replaced by a stream of oxygen-free nitrogen. Both tests give rise to curves showing a maximum. The temperatures at which these maxima occur vary with the coal or oil examined and relate to the rank of oil or type of fuel oil and are a measure of the ease of burning (the burning profile test) and of the pyrolysis mechanism (the evaporating profile test). The results for a heavy diesel oil are reproduced in Fig. 9. The evaporation profile shows a single maxima but with some indication of splitting and the tailing which occurs from 265° to 350° would indicate a spread of molecular weights. The burning profile peak has two maxima, one at 265° and the other at 305°. Peak one corresponds to the evaporation peak maximum whilst the second peak can be attributed to the oxidation of the non-evaporated heavier fractions.

Cummings [10] concludes that these techniques provide an excellent means of distinguishing between samples of different oils and identifies three areas of application. The first and main area would seem to be the comparison and identification of samples. Thus two oils of similar viscosity could be compounded of completely dif-

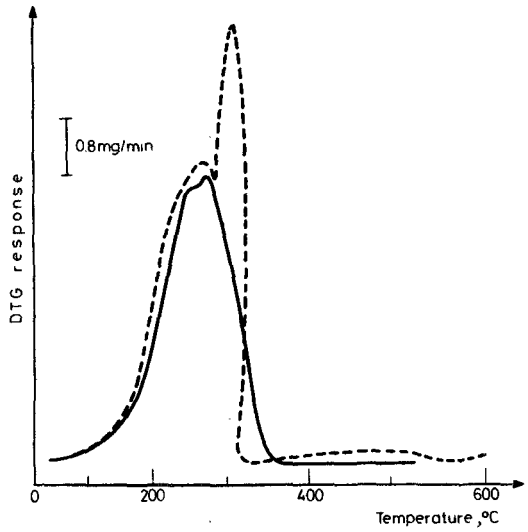

Fig. 9 Evaporation and burning profiles of heavy diesel oil (visc. 5.8 $mm^2 5^{-1}$ at 38°C). Reprinted with permission © 1981 from the Journal of the Institute of Fuels
——— Evaporation, — — — Burning

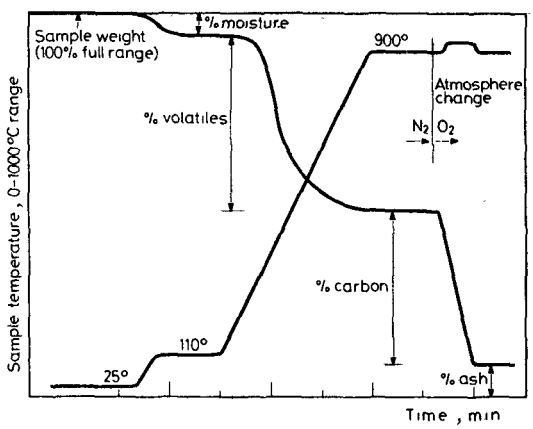

Fig. 10 TG curve proximate analysis curve for a coal. Reprinted from M. Ottaway, *Fuel*, **61** (1982) 713–716 by permission of the publishers, Butterworth & Co. (Publishers) Ltd. ©

ferent compositions of light and heavy components which would be clearly distinguished by these tests. The second application is a method of measuring the ignitability of oils where an assessment of the ease of combustion might be based on the temperature at which the two tests diverge. A final area of application is an extension of the first in that the tests could be used to identify sources of oil pollution. Thus samples of polluting oils could be compared with samples taken from suspect vessels.

Proximate analysis

Proximate analysis is the term used for the standard method for the measurement of parameters for classifying and characterising coals, (i) the moisture content, (ii) volatile matter, (iii) fixed carbon, and (iv) the ash content [11, 12]. A number of workers have reported TG methods as a feasible and rapid alternative [13, 14]. The test method developed in our laboratories [14] takes less than ten minutes to perform.

The TG conditions require that the sample is prepared in the manner laid down in the standard method BS 1016 Part 3, and some 10 mg is weighed into the thermobalance in which a flow of oxygen free nitrogen is established. The four stages of the experiment are as follows (Fig. 10).

1. Water determination: Heat to 110° at 250 deg/min, hold for 1 minute. The weight loss is due to water loss.

2. Volatile matter determination: Heat to 900° at 250 deg/min, hold for 1 minute. The weight loss is due to loss of all volatile matter.

3. Carbon determination: Holding the temperature at 900° the gas atmosphere is changed from nitrogen to oxygen. The carbon is oxidised and the weight loss is due to a fixed carbon.

4. Ash: The residual weight corresponds to the ash content of the coal or coke. The results reported show both good reproducibility and good equivalence with the standard test method.

Conclusion

The examples set out in the paper were chosen as representative of the type of specific problem encountered in the third phase of the development of a technique. It is one in which both the instrument manufacturer and the scientist or engineer with the problem must co-operate fully but which offers a great deal of satisfaction.

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Zusammenfassung – Dieses Referat umreisst einige zeitgemässe Entwicklungen der Thermoanalyse. Es wird der derzeitige Stand der Standardmethoden besprochen, besonders derjenigen, die durch die American Society for Testing + Materials (ASTM) veröffentlicht wurden, und die ein thermoanalytisches Verfahren verwenden. In zweiter Reihe wird eine einfache Methode zur Bestimmung der oxydation Stabilität des Polyäthylens mittels DTA bekanntgemacht. Zum Schluss übersieht die Arbeit einige neuere Arbeiten, die an festen Heizmaterialien und Heizölen durchgeführt wurden.

Резюме – В обозрении представлены общие наброски некоторых текущих разработок в термическом анализе. Используя методы термического анализа, обсуждено состояние в настоящее время стандартных методов, в особенности, выдаваемых ASTM. Во второй части представлено обозрение простого метода определения методом ДТА устойчивости полиэтилена к окислению. В заключительной части рассмотрены некоторые из недавних работ, выполненных с ископаемым топливом и топливными маслами.