

## CHARACTERIZATION OF PETROLEUM PRODUCTS BY DSC ANALYSIS

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Some petroleum products, as paraffin waxes, microcrystalline waxes, lube oils, fuel oils, bitumens, were studied using DSC. DSC makes it possible to determine the wax content of various petroleum fractions, to study the effects of additives, to determine the glass transitions of bitumens; it is a useful technique both for research and for product analysis.

During the distillation process of crude oil, the most volatile components, gases and gasoline, are removed from the top of the column while other distilled products, usually kerosene and gas oil, are removed from the column as side-streams.

The bottom products can be used as fuel oils and if they are not too dense they can be mixed with lighter products, usually gas oil, to reduce the viscosity. The bottom products can also be fed into another vacuum column from which bitumen and lube oils are obtained.

Petroleum products are frequently tested to characterize them in terms of chemical composition, structure and physical properties. Such tests are often complex, lengthy to perform and above all, highly empiric.

During the tests energy changes in the samples frequently take place due to melting, crystallization, degradation, etc. This makes it possible to use analysis and methods based on Differential Scanning Calorimetry [1-7].

DSC gives information which, even if in certain cases cannot be considered completely accurate, is generally more reliable than the results of normal technological tests. Moreover, a great amount of data is collected simultaneously, which means that only one test is needed to acquire information usually obtained with many conventional tests.

The object of this paper is to show how DSC can be used to characterize some petroleum products.

The following products were analysed: paraffin waxes and petrolatum, lube oils, fuel oils, bitumens.

As more than one product was examined, for each one a number of indicative tests was carried out, bearing in mind the fact that more detailed tests could provide further results. From each test the most interesting and immediate data were collected, with a view to giving a fairly precise idea of the possibilities of DSC in the petroleum field.

## Experimental

The tests were carried out using a Perkin-Elmer Differential Scanning Calorimeter model DSC-1A, working in a dynamic nitrogen atmosphere. Runs were performed within a temperature range of  $-80$  and  $+80^{\circ}$ , using liquid nitrogen as coolant.

Sample weights ranged from about 6 to 40 mg according to the melting heat of the samples, while for the paraffin wax and for similar products small quantities were sufficient to give well defined results. In the case of the other products, such as the bitumens, it was necessary to use bigger quantities maintaining the instrument at a higher sensitivity setting.

The experimental results are reported separately according to the group to which the product belongs.

### *Paraffin wax and petrolatum*

Solid waxy hydrocarbons are present in many types of crude oil. When an oil is distilled, some of this wax comes over mainly with the lubricating oil distillate and some is left behind in the residue. Wax must be removed from the lubricating oil otherwise the oil will tend to solidify on cooling.

Table 1  
Characteristics of analysed waxes

	Oil content, % ASTM D 721	Aromatics, % (1)	Saturated, % (1)	C atoms range (2)	Melting point, $^{\circ}$ C, ASTM D 127
Paraffin wax ( <i>p</i> )	3.6	0.2	99.8	18/35	49
Microcrystalline wax ( <i>m</i> )	22.5	5.2	94.8	—	60

(1) Silicagel chromatography, 100–200 mesh, *n*-heptane eluent.

2) Gas chromatography, F 8M, 5% SE-52.

Table 2  
Melting heats of a paraffin wax containing different percentages of oil

Name	Paraffin wax content, %	Oil content, %	Weight, mg	Melting $\Delta H$ , cal/g
<i>p</i>	96.4	3.6	6.0	30.5
<i>p</i> <sub>1</sub>	85.4	14.6	19.9	26.6
<i>p</i> <sub>2</sub>	63.1	36.9	35.6	18.9
<i>p</i> <sub>3</sub>	46.4	53.6	22.0	13.8
<i>p</i> <sub>4</sub>	20.8	72.2	20.9	6.9

Two classes of wax are generally recognized, the distillate waxes which are crystallized to a high degree are known as paraffin waxes and the residual waxes, in which the crystals are microscopic in size, are known as microcrystalline waxes. Petrolatum consists of microcrystalline waxes associated with oil.

Fig. 1 shows the DSC curves of paraffin wax containing various amounts of oil, and of a petrolatum (see Tables 1 and 2).

The paraffin wax shows a characteristic curve with two endotherms, one sharper due to the melting transition and one due to a solid-solid crystalline

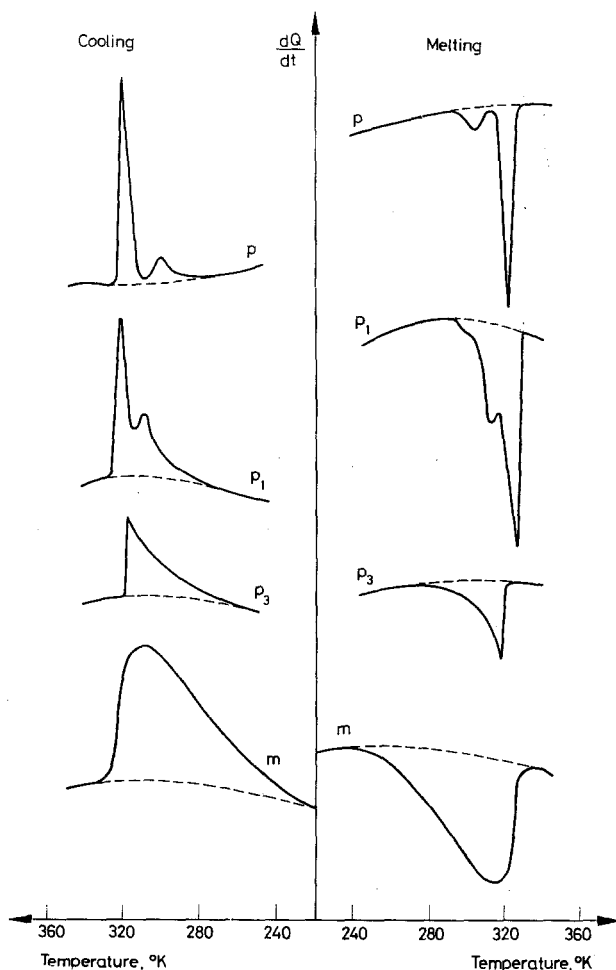


Fig. 1. DSC curves of hydrocarbon waxes (heating rate  $8^\circ/\text{min.}$ ). *p*: paraffin wax, 6.0 mg; sensitivity 8 mcal/sec (for full-scale deflection); *p*<sub>1</sub>: paraffin wax containing 14.6% oil, 19.9 mg; sensitivity 8 mcal/sec; *p*<sub>3</sub>: paraffin wax containing 53.6% oil, 22.0 mg; sensitivity 8 mcal/sec; *m*: microcrystalline wax, 17.5 mg; sensitivity 4 mcal/sec

transition from orthorhombic to hexagonal form [8–9]. This transition is usually characteristic of paraffin waxes.

Curves  $p_1$  and  $p_3$  in Fig. 1 show paraffin  $p$  in two different states of purity. We can see that with the increase in the oil percentage the effect of the solid–solid transition tends to merge with the melting endotherm. The overall global effect, though remaining sharp, decreases with the increase in oil content. This suggests a way to determine the quantity of oil contained in paraffin wax which is much quicker, more practical and accurate than those conventionally used (ISO 160; ASTM D 721; IP 158). Table 2 shows  $\Delta H$  calculated from the melting heats of

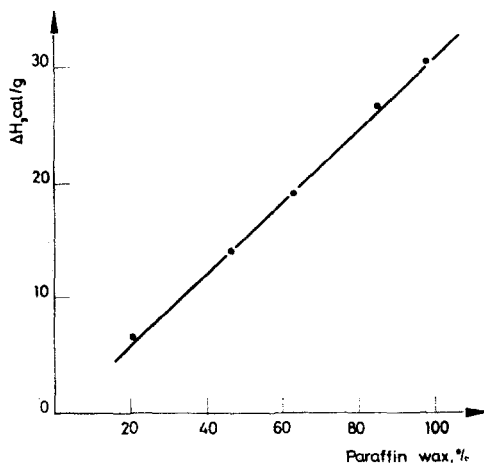


Fig. 2. Melting  $\Delta H$  plotted against paraffin wax content

the paraffin wax  $p$  at different grades of purity. With such  $\Delta H$  the curve in Fig. 2 was drawn enabling us to calculate the oil content in the paraffin. The methods of calculating  $\Delta H$  are described in an earlier paper [1]. Similar curves can naturally be drawn from the  $\Delta H$  of crystallization. While the melting curve of paraffin waxes shows relatively sharp endotherms, microcrystalline waxes show only broad endotherms and no transitions other than melting (Fig. 1, curve  $m$ ).

This reflects the difference in the molecular structure between paraffin waxes which are composed mainly of saturated normal paraffins in the approximate range  $C_{18}$ – $C_{40}$  and microcrystalline waxes which are composed of branched paraffins with a greater number of C atoms ( $C_{25}$ – $C_{65}$ ) and a greater molecular weight.

Similarly, as with paraffin waxes, it is also possible, using DSC, to measure the quantity of oil contained in a petrolatum [10].

Naturally, the melting and crystallization intervals of the waxes are measured at the same time much more accurately than with the conventional methods (ASTM D 938; D 127, D 87; IP 76, 133, 55).

*Lube oils*

Using DSC we examined four oils, two paraffin based ones and two aromatic types (Fig. 3).

Oil No. 1 was distilled under reduced pressure and 7 fractions were obtained to distinguish better the different groups of hydrocarbons present in the oil. Table 3 shows the principal characteristics of the oils examined and of the fractions found in oil No. 1 and also the melting  $\Delta H$  and the temperature at the beginning and end of melting.

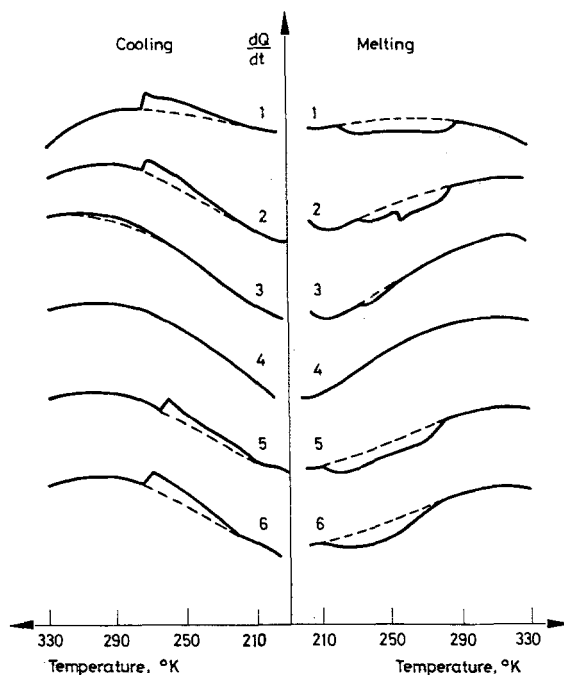


Fig. 3. DSC curves of mineral oils (heating-rate  $8^{\circ}/\text{min}$ ; sensitivity 2 mcal/sec). 1. Paraffin-base oil 31.2 mg; 2. paraffin-base oil, 27.6 mg; 3. naphthene-aromatic-base oil 26.7 mg; 4. naphthene-aromatic-base oil 26.7 mg; 5. new 20W-40 multigrade oil, 35.8 mg; 6. used multigrade oil, 28.1 mg

The curves of the paraffin based oils all reveal a similar trend which shows the melting and crystallization intervals, while the naphthene-aromatic type oils do not apparently show phase changes. They only show variations in the slope of the curve due to the change in the heat capacity at different temperatures. With regard to the fractions obtained from paraffin oil No. 1 the extent of the crystallization and melting range decreases with the increase in average molecular weight of the components of each fraction. Moreover, with the increase of average molecular weight the temperature at the start of melting decreases. In the first

Table 3

Characteristics of the oils studied and of fractions obtained from oil No. 1

Oil No.	Type	Boiling range (20 mmHg), °C	Specific weight at 20 °C	Refractive index $n_D^{20}$	Melting $\Delta H$ , cal/g	Melting range, °C	
						initial	final
1	paraffinic	—	0.8882	1.4880	2.99	222	288
2	paraffinic	—	0.8959	1.4900	2.67	226	284
3	naphthene- aromatic	—	0.9169	1.5069	0.175	232	245
4	naphthene- aromatic	—	0.8853	1.4865	—	—	—
1	fraction I	230–275	0.8750	1.4790	5.82	208	288
	fraction II	275–281	0.8835	1.4830	4.85	211	288
	fraction III	281–292	0.8886	1.4865	4.50	217	288
	fraction IV	292–303	0.8912	1.4883	5.28	219	287
	fraction V	303–315	0.8922	1.4892	5.18	220	284
	fraction VI	315–327	0.8942	1.4900	2.84	226	290
	fraction VII	<327	0.9001	1.4955	2.39	234	287

fractions hydrocarbons with long chains are present, which give the oil a prevalently paraffinic character. With the increase in average molecular weight the quantity of naphthene hydrocarbons with shorter isoparaffin side chains increases.

This also applies to oils Nos 1 and 2 if they are considered as fractions of a single original crude oil. Oil No. 2 should therefore contain hydrocarbons with shorter and more branched chains than No. 1.

For the fractions of one oil the latent heat of melting decreases with the increase in average molecular weight. This is also true for oils of the same type with different average molecular weights (oils Nos 1 and 2). The decrease in melting heat indicates a suppressed paraffinic character and enhanced isoparaffin and naphthene character.

To determine  $\Delta H$ , the order with which the crystallization and melting operation is carried out is important. So for routine analysis it is necessary to put the samples through the same runs.

The results show that DSC can detect the wax crystallization process and simultaneously indicate the amount of wax in the oil, based on the area of the

Table 4

Characteristics of the multigrade oil, new and used

Test No.	Type	Specific weight at 20 °C	Refractive index $n_D^{20}$	Melting $\Delta H$ , cal/g	Melting range, °C	
					initial	final
5	20 W–40 new	0.8851	1.4820	3.48	212	278
6	20 W–40 used	0.8969	black	2.51	213	274

crystallization exotherm. The use of DSC has been proposed to determine the paraffin wax content of mineral oils [2]. Since DSC was found to determine the temperature for the onset of crystallization easily, a correlation with the ASTM cloud point method (D2500) has also been found [7].

Another interesting possibility is the relationship between DSC crystallization data and ASTM pour points (D97) [7]. In the case of cloud points the relationship appears to be general, whereas for pour points the relationship is **probably** limited to base stocks without pour depressants.

The DSC also makes it possible to study the characteristics of commercial lubricating oils, new and used.

Curves 5 and 6 in Fig. 3 refer to a multigrade oil before and after use (4000 km in a medium sized car). Table 4 shows the characteristics, the melting  $\Delta H$  and the melting ranges of the new and used oil.

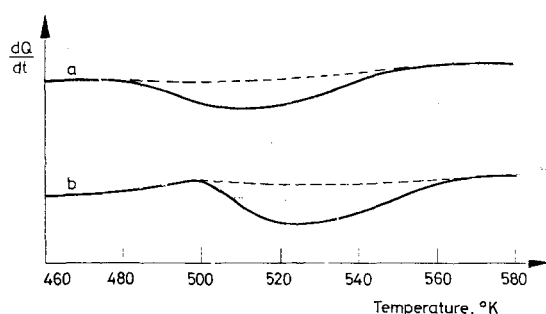


Fig. 4. Endotherms due to oxidative degradation of lube oil: *a*: oil without additives; *b*: oil containing 1% of an antioxidant additive

The curves show that this oil is of the paraffinic type and that the additives do not modify substantially the thermochemical behaviour. The used oil shows a crystallization range and a starting crystallization temperature lower than the new oil. This is due to partial cracking during its use.

By means of DSC it is also possible to study the oxidative degradation process of an oil. Fig. 4 shows the DSC curves of a lube oil without additives (curve *a*) and with 1% of an antioxidant additive (curve *b*). It is clear that the antioxidants increase the oxidative stability of the oil. This is indicated by the higher temperature at the onset of oil oxidation. It is thus possible to study the effectiveness of the various additives and decide on the quantity to be added to an oil to obtain the desired effects. Correlations were found between DSC data and the ASTM Rotary Bomb Test (D-2272) designed to determine the stability of lube oils [7].

### *Fuel oils*

The commercial products described as fuel oils usually are the residues of primary distillations of the crude oil or the residues of cracking, which are made more fluid according to the Customs and Trade Requirements, adding a fluidifying

Table 5  
 Characteristics of the fuel oils examined

	Test	Viscosity, °E	Boiling range, °C	Gas oil, %
Gas oil	G	1.0	180–360	100
Iraq residue	R	17.4	—	0
Fuel oil (from Iraq residue)	F	3.0	—	20

agent, usually a gas oil. In the field of fuel oils obviously DSC offers the same possibilities as with the lube oils. In the specific case of fluidified fuel oils it offers a further advantage. Fig. 5 shows the DSC curves of a gas oil, of a primary residue from an Iraq crude oil and of a fuel oil obtained by fluidifying the Iraq residue with a gas oil (see Table 5).

The gas oil reduces the effect of the paraffin. In practice it is possible for the same type of gas oil and residue to draw a curve plotting  $\Delta H$  of various residue–gas oil mixtures against gas oil content. In this way it is possible to arrive at gas oil content of a mixture of unknown composition.

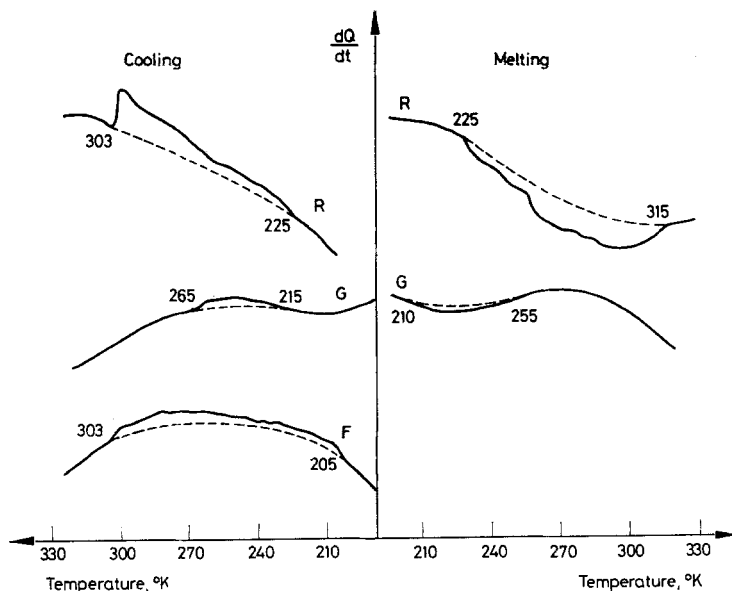


Fig. 5. DSC curves of fuel oils (heating rate  $8^{\circ}/\text{min.}$ ; sensitivity  $4 \text{ mcal/sec}$ ); R: primary residue from Iraq crude oil, 19.6 mg; G: fluidified gas oil, 14.6 mg; F: fuel oil obtained by fluidifying the Iraq residue with gas oil (20%), 13.6 mg



*Bitumens*

Bitumens, usually known in the USA as "asphalts", are very complex mixtures of hydrocarbon types. They contain paraffin, naphthene and aromatic hydrocarbons largely in mixed hydrocarbon form. The mixed paraffin-naphthene and the paraffin-aromatic types appear to predominate although minor percentages of both linear paraffins and isoparaffins always seem to be present. These paraffins readily crystallize from solution when chilled, and can be separated to yield what is commonly referred to as wax.

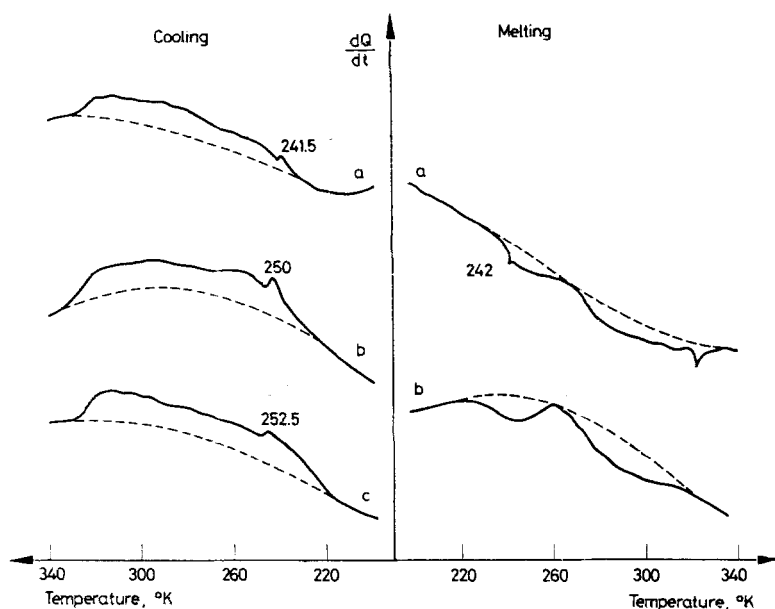


Fig. 6. DSC curves of a straight run bitumen and of two blown bitumens (heating rate  $8^{\circ}/\text{min}$ ; sensitivity 2 mcal/sec): a: straight run bitumen, 30.1 mg; b: blown bitumen (3 hrs), 40.0 mg; c: blown bitumen (5 hrs), 39.8 mg

It is generally considered that there is a connection between the paraffin wax content and the quality of a bitumen, though opinions on this differ [11].

Various methods have been proposed and discussed to determine the wax content of bitumens [11, 12]. Those usually used are complicated and not very accurate (DIN 1995-U 11; Norme CNR 1951, Fasc. 2).

A method based on DSC, similar to that applied to the oils, even if it presents limits due to the difficulties of drawing in the base lines to define the DSC areas, offers at least the same guarantees as the conventional methods. This method,

however, has the advantage of being much quicker and needs very small quantities of bitumen [3].

The mechanical properties of bitumen are currently assessed by a variety of empirical tests. All of these involve experimental uncertainties and considerable difficulties in interpretation [13]. It has been shown that a similarity exists between the visco-elastic behaviour of simple amorphous polymers and bitumen. As the glass transition temperature ( $T_g$ ) is a very important parameter of an amorphous polymer, it should also be useful in interpreting the properties of bitumens. This has been used as a basis to describe such systems mathematically [14]. There is also a connection between  $T_g$  and the brittle point of a given bitumen. The brittle point is measured by the Fraass test (IP 80/53) which is very difficult to carry out and is not easily repeatable.

The DSC provides the possibility of determining  $T_g$  more accurately and speedily. Fig. 6 shows the DSC curves of a straight run bitumen whose characteristics are shown in Table 6. The glass transition, which appears at 241.5°K, is evident mainly during the cooling runs and is characterized by a sharp shift in the base line.

Table 6  
Characteristics of the bitumens examined

Bitumen	Blowing time, hrs	Penetration, dow at 25 °C d, mm	Asphaltenes (n-pentane), %	$T_g$ , °K
Straight run (a)	0	186	22	241.5
Blown (b)	3	24	41	250.0
Blown (c)	5	15	45	252.5

In doubtful cases, to have more defined transitions even during heating runs, one can bring about a rapid heating after a slow cooling similar to that for the polymers [4, 7].

Curves *b* and *c* in Fig. 6 refer to two bitumens prepared by blowing air into straight run bitumen *a* at 250° (see Table 6). Blowing increases the hardness of bitumen; blown bitumens have a more rubber-like consistency and a better resistance to flow at high temperatures. These properties are required for many industrial applications: for coating steel pipes and cables; as adhesives; for covering terraces; as waterproof agents. The blowing process involves oxidation with air so that some of the hydrogen in the starting product is removed as water and the molecules from which the hydrogen atoms have been eliminated polymerize to form larger molecules.

From the curves it can be seen that the blowing process causes the  $T_g$  to occur at higher temperatures, as was foreseen. A method can therefore be suggested for controlling the blowing process of the bitumens based on DSC.

## Conclusions

From what has been said it is evident that in the petroleum field DSC is a useful technique both for research and for product analysis. For these products, in fact, the range of temperature explored using DSC is more than sufficient. The DSC makes it possible to

- determine the waxes in a crude oil and in various fractions such as oils and bitumens, in a much more practical and rapid way than with the conventional methods normally used;
- distinguish between the principal types of waxes and determine their purity;
- study the behaviour of oils and gas oils during oxidation;
- study the effects of various additives (antioxidants, pour point depressants, etc.) added to lubricating oils and fuel oils;
- check how much an oil has been used and check the quality of the regenerated oil;
- determine the glass transitions of the bitumens;
- control the oxidation process of bitumens (using  $T_g$  measurements).

It should be emphasized that though the operating of the equipment is not particularly difficult, the interpretation of the DSC curves requires trained personnel since an inexperienced person would find it difficult to judge the areas of the thermal effects and to distinguish the glass transitions. Routine control carried out on similar types of products is much easier and any person can become an expert in a short time. However, even the normal tests on petroleum products should always be entrusted to specialized personnel.

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RÉSUMÉ — On a étudié par calorimétrie différentielle compensée (DSC) quelques produits pétroliers tels que les paraffines, les paraffines microcristallines, les huiles lubrifiantes, le mazout et les bitumens. Cette technique permet de déterminer la teneur en paraffines des diverses fractions pétrolifères, d'étudier les effets des additifs et de déterminer la transition vitreuse des bitumes; c'est une technique utile aussi bien pour la recherche que pour les opérations de contrôle analytique.

ZUSAMMENFASSUNG — Einige Erdölprodukte, wie z.B. Paraffinwaxe, mikrokristalline Wachse, Schmieröle, Heizöle und Bitumina wurden mittels Differential Scanning Kalorimetrie studiert. Die Differential Scanning Kalorimetrie (DSC) ermöglicht die Bestimmung des Wachsgehaltes verschiedener Erdölfractionen, das Studium der Wirkung von Additiven, die Ermittlung des Glas-Überganges von Bitumina; sie ist eine nützliche Methode sowohl für die Forschungsarbeit als auch für die Analyse von Erzeugnissen.

Резюме. — Методом ДШЦ изучены некоторые продукты нефти, такие как парафиновые смолы, микрокристаллические смолы, машинные и топливные масла и битумы. Метод ДШЦ дает возможность определять содержание смолы в различных фракциях нефти, изучать эффекты добавок, определять переходы, обусловленные стеклованием битумов; эта методика рекомендуется как при проведении исследовательских работ, так и для анализа продуктов.