SAFANIYA BITUMEN - VERIFICATION OF CHEMICAL PROPERTIES

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AN IMPORTANT NOTE FOR THE READER

The material contained in this report is the output of research and should not be construed in any way as policy adopted by Transit New Zealand but may form the basis of future policy.

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EXECUTIVE SUMMARY

During the 1990/91 sealing season numerous unexplained chipseal stripping failures occurred on New Zealand roads. Many of the examples had been reported where normal sealing practices had been used but stripping has occurred, sometimes only weeks after construction.

In the absence of any other obvious common factor, a change in the properties of the Safaniya bitumen used was considered a possible reason for the failures. The physical properties of all roading bitumen used in New Zealand are monitored regularly by Transit New Zealand, and no change outside specification limits in physical properties such as viscosity and penetration had been detected. Unfortunately a laboratory test procedure which is able to detect the adhesion properties of bitumen in real chipseals does not exist.

However, tests which provide a **relative** adhesion value that can be determined in a very simplified and closely controlled laboratory environment are available. In the present work one such laboratory test (based on the Vialit test) was used to compare the relative adhesion of bitumens from 1986 (before the stripping problem was reported) and 1991 productions. No significant differences in adhesion were observed.

Although the bitumen's physical properties were consistent, it was considered possible that changes in the chemical composition of the bitumen had occurred and were affecting adhesion. Thus a range of chemical analytical techniques were used to compare the gross chemical composition of a bitumen produced in 1986 to the three bitumens produced during 1991.

Elemental analysis, asphaltene content, differential scanning calorimetry, infrared spectroscopy and proton nuclear magnetic resonance spectroscopy all failed to detect the presence of significant differences between the 1986 and 1991 bitumens. Using these techniques did, however, allow easy differentiation between the Safaniya bitumens and others (used as controls) that were produced (at Marsden Point) either by butane precipitation or from a Venezuelan crude.

Thermogravimetric (TG) analysis in air did detect differences between the 1986 and 1991 Safaniya samples and, as a consequence, the study was expanded to analyse eight Safaniya 180/200 penetration bitumens produced between 1984 and 1992. Differences were also detected between these extra materials, but no trend or pattern relative to the date of production was observed.

The conclusion is that the differences revealed by thermogravimetric analysis are simply batch to batch variation, and analogous to the expected batch to batch variation in physical properties.

Although no significant difference in the composition of the 1986 and 1991 bitumens is obvious from the results presented here, only a very small sample of the total bitumen production over that period has been studied.

In addition, the binder actually used in the field is almost always modified with adhesion agents, fluxes and cutters, and the effects of these additives have not been considered here.

It is important to remember also that bitumen-aggregate adhesion is a property determined not only by the properties of the bitumen, but also by the mineralogical characteristics (and physical state) of the aggregate. All are significant factors in determining bonding efficiency.

ABSTRACT

One 1986 and three 1991 180/200 penetration grade Safaniya bitumens (from Saudi Arabia) produced by the Marsden Point Refinery were analysed by a range of procedures to detect any significant differences in chemical composition. Changes in chemical composition may have helped explain the unusually high incidence of chipseal stripping failures that occurred over the 1990/91 sealing period.

Elemental analysis, asphaltene content, differential scanning calorimetry, infrared spectroscopy and proton nuclear magnetic resonance spectroscopy all failed to detect the presence of significant differences between the 1986 and 1991 bitumens. Using these techniques did, however, allow easy differentiation between the Safaniya bitumens and others (used as controls), produced either by butane precipitation (at Marsden Point) or from a Venezuelan crude.

Thermogravimetric (TG) analysis in air did detect differences between the 1986 and 1991 Safaniya samples and, as a consequence, the study was expanded to analyse eight Safaniya 180/200 penetration bitumens produced between 1984 to 1992. Differences were also detected between these extra materials, but no trend or pattern relative to the date of production was observed.

The conclusion is that the differences revealed by thermogravimetric analysis are simply batch to batch variation and analogous to the expected batch to batch variation in physical properties.

A simple laboratory adhesion test was also used to compare the relative adhesion of 1986 and 1991 bitumen productions. No significant differences in adhesion were observed.

1. INTRODUCTION

During the road sealing seasons of 1990-91 and 1991-92 numerous comments had been made by field personnel that the properties of the bitumen used in New Zealand have changed. Specifically these comments centre on the perceived very slow development of bond between sealing chip and the bitumen.

Many cases have been reported where normal sealing practices have been used, but stripping has resulted only weeks after construction. These reports have been received from throughout New Zealand and do not appear to be associated with any particular area. The perceived change in bitumen performance has been noted by contractors, consultants and local authority staff.

In New Zealand bitumen is manufactured at only one source, Marsden Point. There it is produced in accordance with the requirements of TNZ M/1 Specification (1986). The quality monitoring programme funded by Transit New Zealand has not shown any changes in the properties specified over the last five years.

The adhesive properties of bitumen are not directly specified in the TNZ M/1 Specification. Although differences in adhesive properties are known to exist between bitumens, no recognised tests are available to directly measure this property for chipseal applications. Such tests that are available (e.g. the Vialit test) produce **relative** adhesion data in a controlled laboratory environment and results from these tests cannot be directly related to the adhesion behaviour of a real chipseal. Although research into adhesion has been performed, it is a very complex process, dependent on both physical and chemical aggregate properties, on road construction practices, and environmental factors of temperature and moisture.

In the research reported on here, a range of chemical analysis techniques has been used to compare the gross chemical composition of a Safaniya (Saudi Arabia) bitumen produced in 1986 to that of three Safaniya bitumens produced during 1991. As a control, and to demonstrate the sensitivity of the techniques used, one Venezuelan (Boscan) and one butane-precipitated bitumen were studied. In addition, a simple physical adhesion test was carried out to detect any major difference (ignoring problems of repeatability and relevance to road conditions) in relative adhesion properties between the 1986 and 1991 productions. At present, no accepted simple relationship is known between chemical composition and bitumen/aggregate adhesion, although gross differences in composition suggest that the problems being presently experienced may be caused by a change in the adhesive properties of the bitumen.

The analyses reported here are relatively rapid and inexpensive to perform yet provide considerable information on the chemical composition of the binders. A limitation of this work is that the failure to detect any differences does **not** necessarily prove that there are no differences in adhesive properties. The main objective of this work was simply to identify the chemical differences (if any) between the bitumens, and little attempt has been made to interpret the results in more depth.

2. BITUMENS USED

The composition, date of production and physical properties of the bitumens studied are given in Table 1. All bitumens were produced by the Marsden Point Refinery and conformed to the TNZ M/1 Specification (1989) for 180/200 grade bitumens, with the exception of bitumen 343 which had a slightly higher penetration. Bitumen 343 was part of a trial production run and has not been used for sealing work.

Table 1. Physical properties(1) and constitution of the studied bitumens.

Bitumen	Crude Composition	Blend(2) Composition	Density at 25°C	Penetration at 25°C 100 g, 5 s (dmm)	Durability(3)	Softening Point (°C)	Viscosity at 70°C (mm^{2}s^{-1})	Viscosity at 135°C (mm^{2}s^{-1})	Flash Point (°C)	Date of Manufacture
537	Safaniya 100%	100% SR	1.020	186	14	38.8	22000	254	>250	April 1986
52	Safaniya 100%	100% SR	-	188	n.d.	41.2	18600	242	302	February 1991
225	Safaniya 100%	100% SR	-	181	n.d.	39.5	18400	236	314	May 1991
478	Safaniya 100%	100% SR	-	184	n.d.	42.0	20500	244	302	November 1991
501*	Boscan 100%	100% SR	1.024	183	3	40.5	29700	256	>250	December 1985
343*	Arab Light 4% Murban 87% Oman 9%	58% SR 42% B	1.014	204	20	38.1	12100	184	338	October 1989

(1) Measured according to ASTM D3279 (1992) standard methods
(2) Composition by mass: SR ≡ straight run vacuum distilled, B ≡ butane-precipitated residue
(3) Measured according to AS 2341.13 (1986)

n.d. = not determined
* Venuzuelan
** Butane-precipitated

3. ELEMENTAL ANALYSES

Carbon, hydrogen, nitrogen, sulphur and oxygen (by difference) contents were determined by the Microanalytical Facility at Otago University. The ash contents of the bitumens (as determined by thermogravimetry) were less than 0.1% w/w and were ignored in the calculations.

Results of the elemental analyses are presented in Table 2. The 95% confidence limits quoted are based on the pooled standard deviation*.

There is no noticeable difference between any of the bitumens studied, with the exception of sample 343 which has a smaller atomic H/C ratio, indicative of a more aromatic material. None of the bitumens contain significant amounts of oxygen.

Table 2. Elemental analyses of the bitumens.

Bitumen (No. of Replicates)	**Mean % Weight(1)**					**H/C Atomic Ratio (±0.02)**	**(N+S+O)/H Atomic Ratio (±0.004)**
	Carbon ±0.1(1)	**Hydrogen ±0.1**	**Nitrogen ±0.1**	**Sulphur ±0.1**	**Oxygen**		
537 (6)	83.7	10.8	0.5	5.5	-	1.53	0.019
52 (4)	83.6	10.8	0.5	5.9	-	1.54	0.020
225 (4)	83.6	10.7	0.5	5.9	-	1.53	0.021
478 (4)	83.6	10.5	0.6	6.1	-	1.50	0.022
501 (6)	83.0	10.4	0.9	5.6	0.3	1.50	0.019
343 (2)	86.2	10.6	0.3	3.5	-	1.46	0.022

(1) 95% confidence limits based on the pooled standard deviation

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$$* \quad Sp = \sqrt{\left[\frac{\sum_{i=1}^{i=p} (n_i - 1)\, S_i^2}{\left[\sum_{i=1}^{i=p} n_i\right] - p}\right]}$$

where n_i = number of replicate determinations for the ith bitumen
s^2_i = variance of the replicate data for the ith bitumen
p = number of different bitumens

4. MOLECULAR WEIGHT DETERMINATION

Molecular weights were determined by vapour pressure osmometry in chloroform at 37°C. It is known that the association of polar species in solution can lead to anomalously high molecular weights (for example, in the case of asphaltene solutions) (Moschopedis et al. 1976). To minimise errors caused by this effect, molecular weights were measured at three concentrations (~0.5, ~1.0, ~1.5 % w/v), plotted, and extrapolated to zero concentration, to obtain the values presented in Table 3. To determine the precision of the procedure, replicate determinations were made. The 95% confidence limits quoted are based on the pooled standard deviation of the combined data.

Examination of the results shows that the three 1991 bitumens have somewhat higher molecular weights than the 1986 material. However, even the 1991 bitumens show considerable scatter in the results, and drawing conclusions from these results alone would be premature.

Table 3. Molecular weights of the bitumens by vapour pressure osmometry.

Bitumen	Molecular Weight			Mean (±50)*
537	743	630	557	643
52	886	860		873
225	685	805		745
478	880	892		886
501	745	870	776	797

* 95% confidence limit based on the pooled standard deviation

5. INFRARED SPECTRA (IR)

Infrared spectra were determined on a Bio-rad FTS-7 fourier transform infrared spectrophotometer. Spectra were recorded using thin films on single potassium bromide disks and as 4.0% solutions in tetrachloroethane using a 1.0 mm potassium bromide cell. Two hundred scans at 2 cm^{-1} resolution were collected to produce the final spectrum.

Spectra of the bitumens studied are presented in Figures 1 to 4. The methyl and methylene C-H stretching region (2800-3000 cm^{-1}) is shown separately (Figure 1) because, relative to the rest of the spectrum, absorption in this part is very strong and the bitumens show no spectral features in the 3000-4000 cm^{-1} and 1800-2800 cm^{-1} regions.

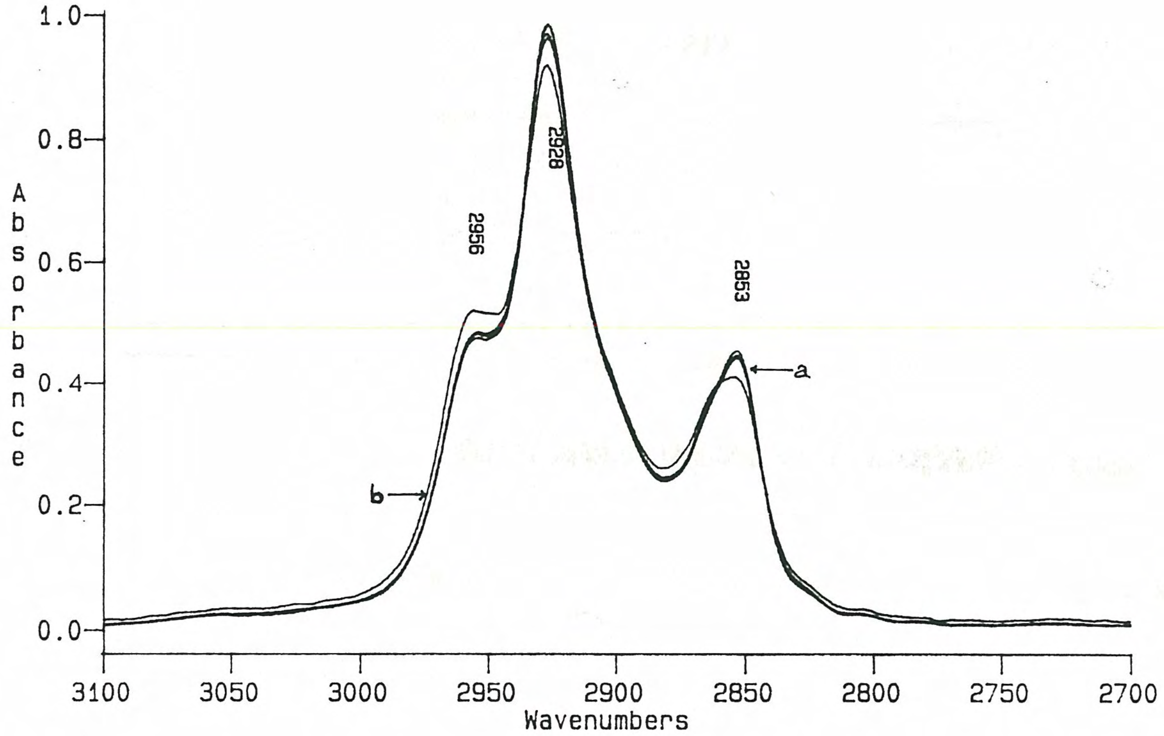


Figure 1. Infrared spectra (Aliphatic stretching region):
(a) 537, 52, 225, 478, (b) 501

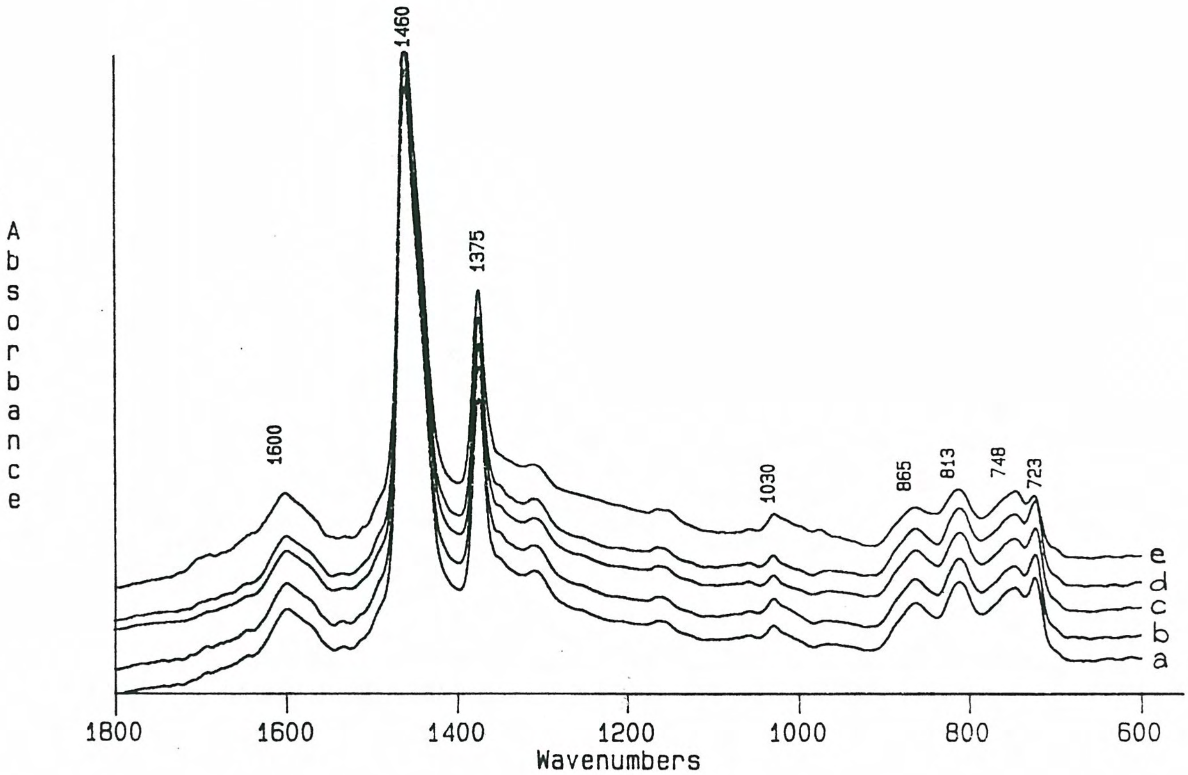


Figure 2. Infrared spectra: (a) 537, (b) 52, (c) 225, (d) 478, (e) 501

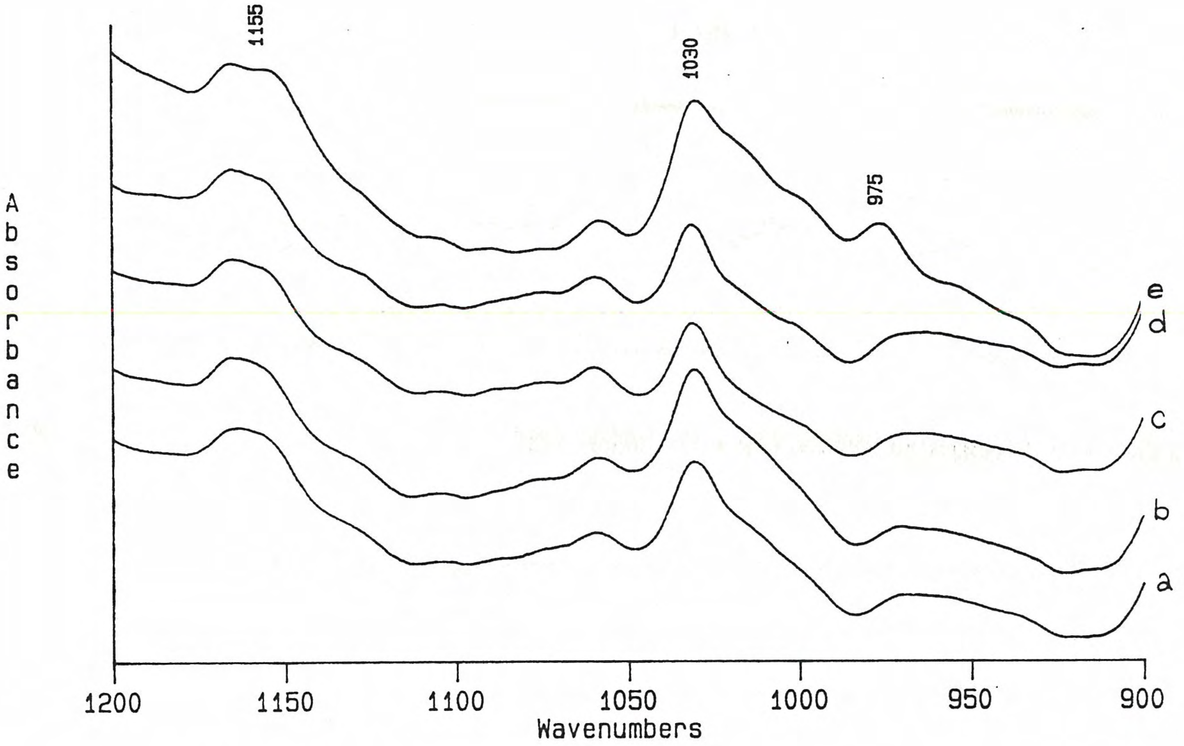


Figure 3. Infrared spectra (Sulphoxide region):
(a) 537, (b) 52, (c) 225, (d) 478, (e) 501

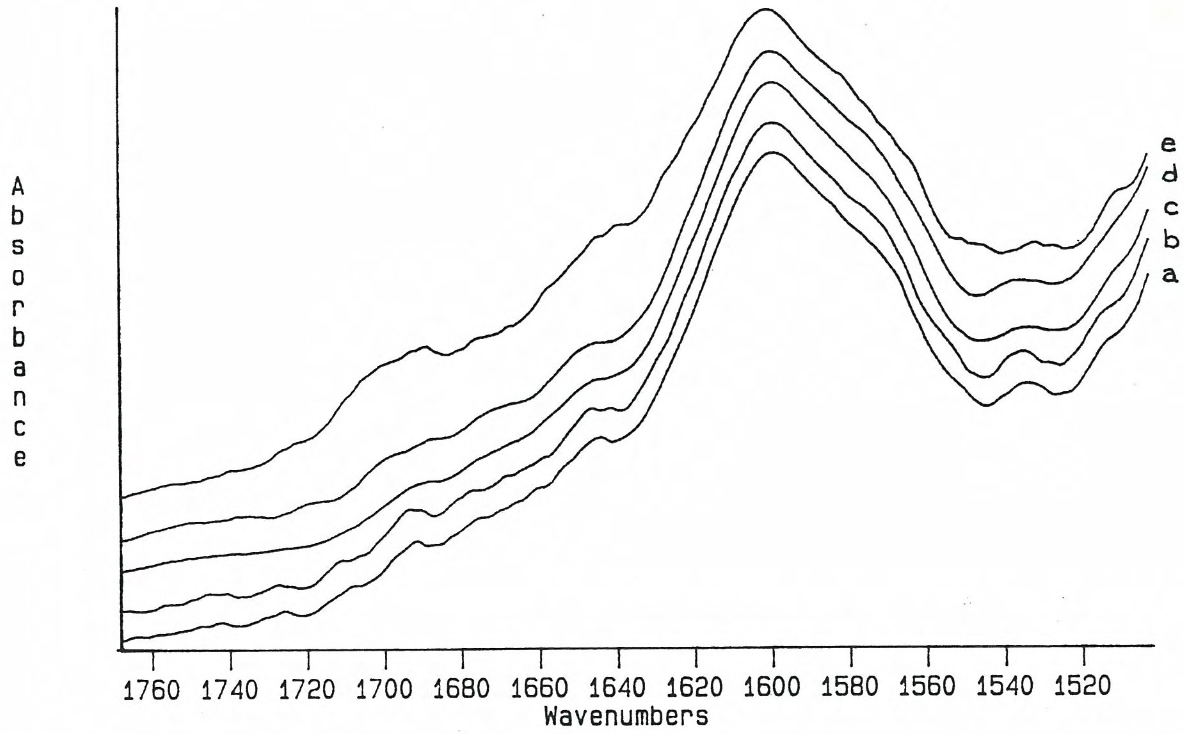


Figure 4. Infrared spectra (Carbonyl region):
(a) 537, (b) 52, (c) 225, (d) 478, (e) 501

The strong absorptions in Figure 2 at 1460 and 1375 cm^{-1} are related to the deformation of CH_3 and CH_2/CH_3 groups respectively. The broad absorption near 1600 cm^{-1} is largely attributable to skeletal vibrations of aromatic species. The series of peaks between 700-900 cm^{-1} are also attributable to these groups. The exception is the 723 cm^{-1} band which is indicative of the presence of paraffinic chains with four or more carbons. The absence of any strong carbonyl absorption in the 1700 cm^{-1} region and the small sulphoxide peak at 1030 cm^{-1} suggest that none of the bitumens have been oxidised significantly.

The sulphoxide and carbonyl regions can be more clearly seen in Figures 3 and 4. The degree of absorption in these regions is a good indication of the extent of binder oxidation. Species formed during oxidation such as carboxylic acids are thought to be important in the mechanism of bitumen/aggregate disbonding (Plancher et al. 1977).

Overall the spectra for the Safaniya bitumens are virtually identical to one another. The Venezuelan bitumen (sample 501), used as a control, can however be clearly distinguished, in particular in the 2800-3000 cm^{-1} region and at 975 and 1160 cm^{-1}.

6. ASPHALTENE CONTENT

Asphaltenes (n-heptane) were determined according to ASTM D3279 (1992), except grade 4 porosity sintered glass crucibles replaced asbestos fibre filter mats, and the dispersions were allowed to stand for 17-20 hours after reflux. The latter modification allows a more complete precipitation of the asphaltenes (Speight et al. 1984).

Results are given in Table 4. The 95% confidence limits given are based on the pooled standard deviation of the duplicates. The asphaltene contents do not suggest any difference between the four Safaniya bitumens.

Table 4. Asphaltene content of the bitumens.

Bitumen	**Asphaltenes % w/w**		**Mean (±0.2)***
537	13.16	12.81	13.0
52	13.15	13.16	13.2
225	13.46	13.17	13.3
478	13.40	13.61	13.5
501	16.36	16.67	16.5

* 95% confidence limit based on the pooled standard deviation

7. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC analyses were carried out in April 1992 at DSIR Chemistry using a Perkin-Elmer instrument. A 3-6 mg sample was sealed in an aluminium pan and heated to 80°C. The sample was precooled (10°C/min) to -80°C and then heated at 10°C/min to 80°C. An empty aluminium pan was used as the reference.

The thermograms obtained are presented in Figures 5 to 9. Figures 5a and 5b show replicate runs on bitumen 537. The variation in the general slope of the curve is an instrumental artefact, the important features in the thermograms being those relative to the curve itself and these appear quite reproducible.

The mid points of the transitions detected were determined in the manner shown in Figure 7, and are reported in Table 5. All the bitumens showed two transitions, with the exception of bitumen 478. The general shape of the curves is similar to those obtained by others (Noel and Corbett 1970, Huynh et al. 1978, Enustun et al. 1990) and, following these researchers, the lower temperature transition was attributed to the glass transition (Tg). Given the subtlety of the transition, as shown in the thermograms of the other bitumens, the failure to detect a Tg in bitumen 478 is probably simply related to a lack of sensitivity in the instrument.

The higher temperature transition is of uncertain origin. Noel and Corbett (1970) attribute it to the fusion of crystallised waxes in the bitumen, while Enustun et al. (1990) believe it may be a manifestation of a gel-sol transformation.

All the Safaniya bitumens gave similar values for Tg (~-25°C) and the higher temperature transition (~+7°C). The Venezuelan bitumen has a similar Tg, but a much higher value (24°C) for the higher temperature transition.

Table 5. Differential scanning calorimetry analyses of the bitumens.

Bitumen	**First (Glass) Transition* (°C)**	**Second Transition* (°C)**
537	-25	+8
52	-25	+7
225	-24	+7
478	-	+8
501	-25	+24

* Calculation procedure shown on Figure 6

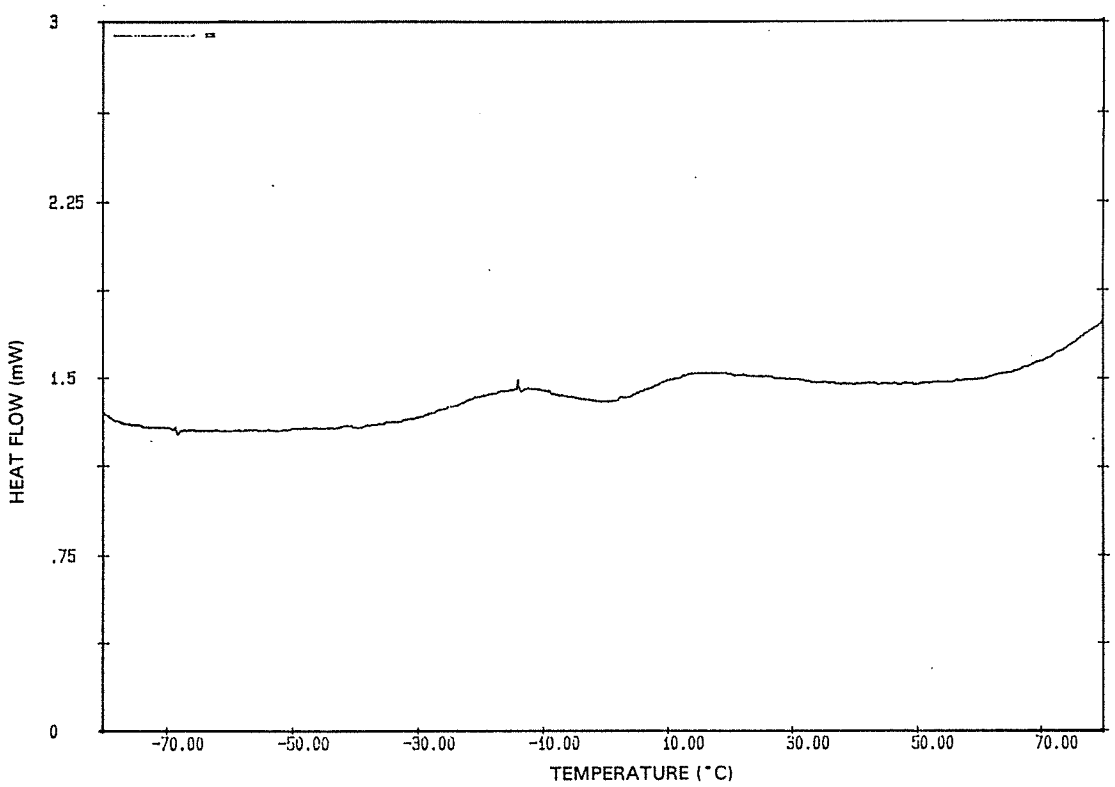


Figure 5a. DSC curve for bitumen 537

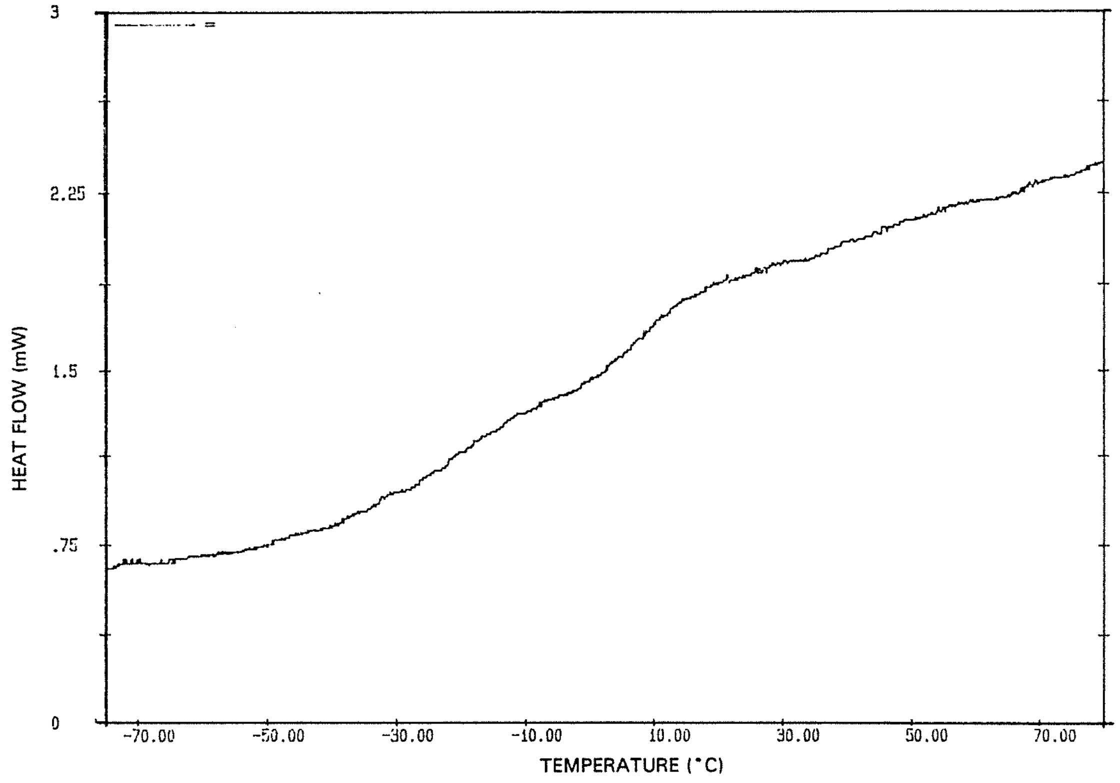


Figure 5b. DSC curve for bitumen 537 (replicate)

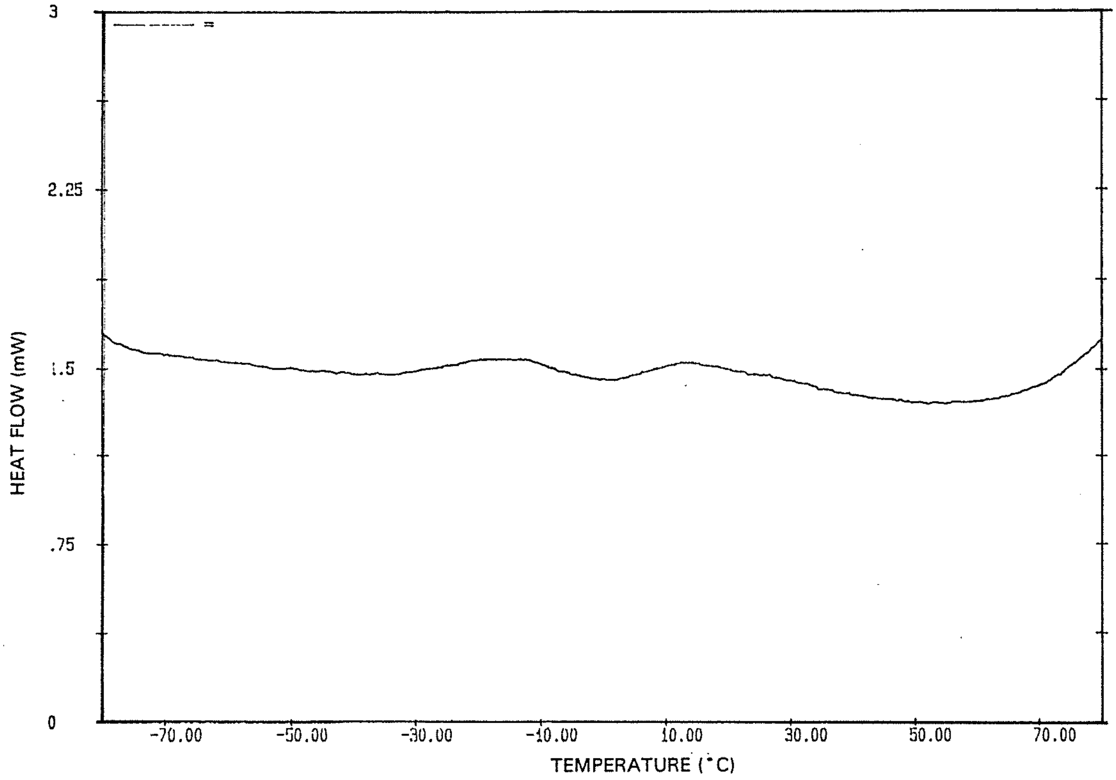


Figure 6. DSC curve for bitumen 52

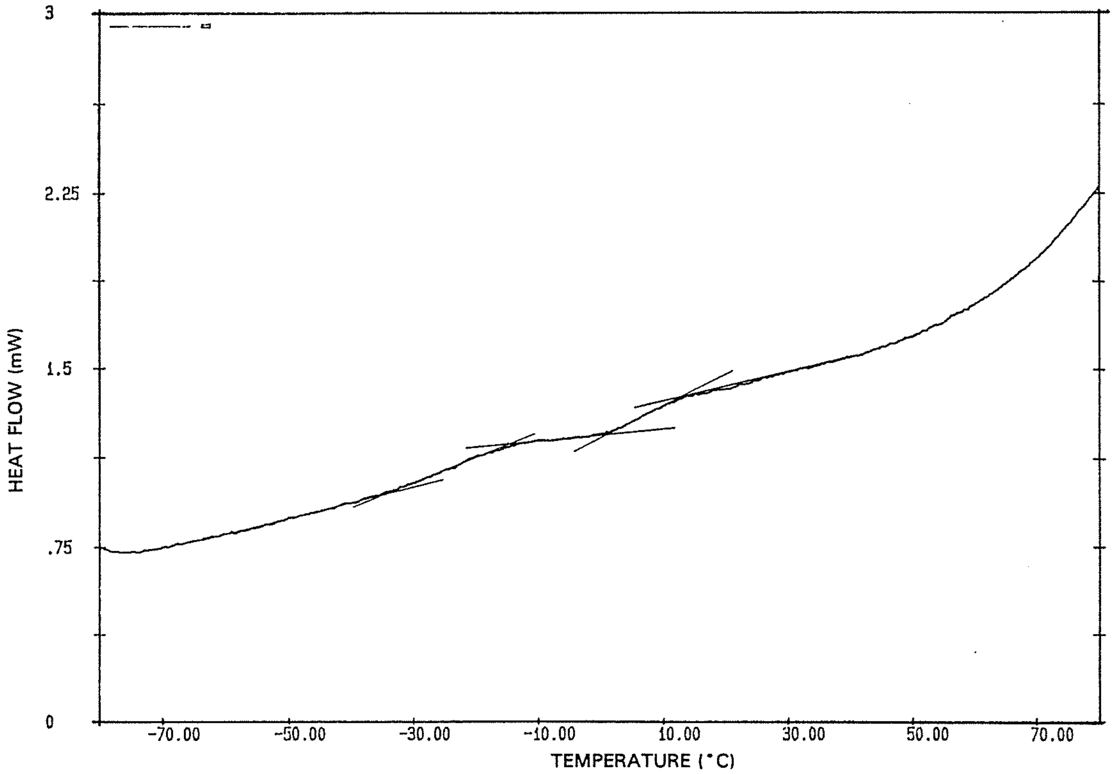


Figure 7. DSC curve for bitumen 225 showing procedure for the calculation of transition temperatures

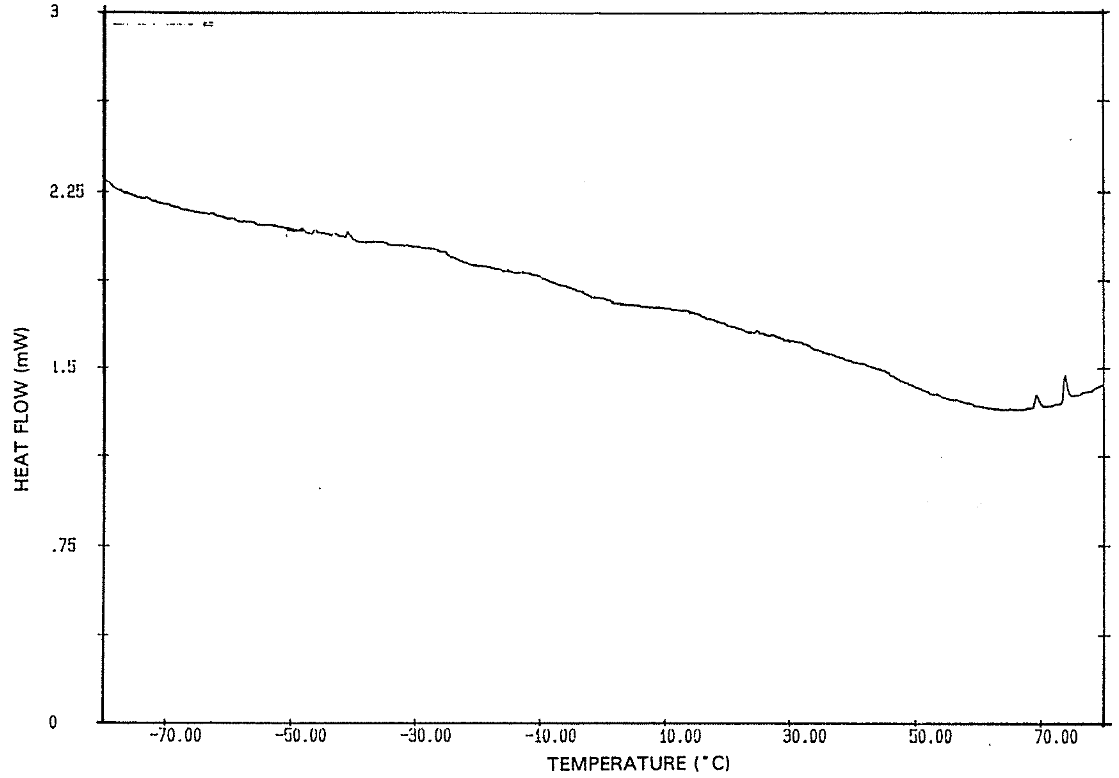


Figure 8. DSC curve for bitumen 478

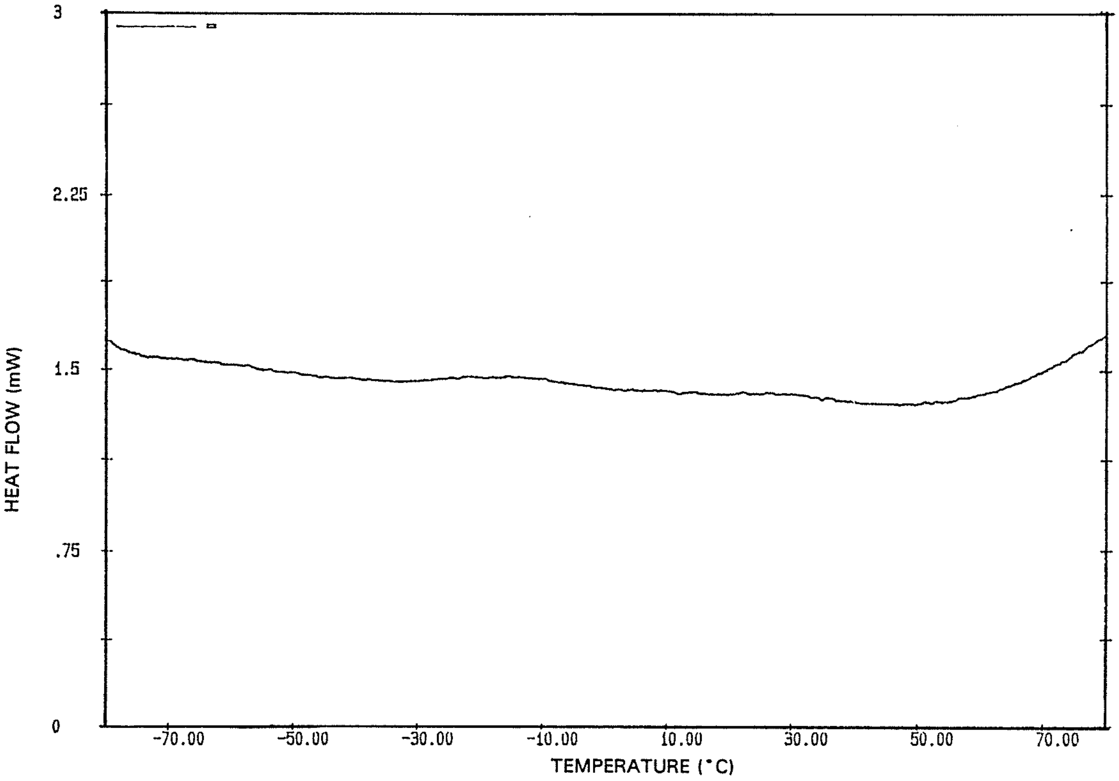


Figure 9. DSC curve for bitumen 501

8. PROTON NUCLEAR MAGNETIC RESONANCE (nmr) SPECTRA

Proton nmr spectra were recorded in April 1992 at DSIR Chemistry. Samples were run at room temperature as 10.0% solutions in $CDCl_3$ on a Bruker 250 MHz instrument using trimethyl-silane (TMS) as internal standard.

A number of replicate samples were run for each bitumen, and some existing data for similar bitumens were used to help establish confidence limits.

The spectra of the bitumens were qualitatively identical as can be seen from Figures 10 to 14. Following the literature (Dereppe et al. 1978, Dickinson 1980), the spectra were divided into regions according to the proton type contributing to the signal in that region. These assignments were as follows:

Chemical Shift Range (ppm from TMS)	Assignment (relative to anaromatic ring)
0.5-1.0	H_γ (γ or greater CH_3)
1.0-2.0	H_β (β CH_3, β or greater CH_2, β or greater CH)
2.0-4.5	H_α (α CH_3, α CH_2, α CH, $\alpha\alpha$ CH_2 possibly some CH_2 as in indane)
4.5-6.0	$H_{olefinic}$ (not observed in any of the bitumens studied)
6.2-9.3	H_a (aromatic ring protons, aromatic heterocycles)

Following the approximation usually made in the literature, the contribution from protons directly attached to heteroatoms (which would be very small) was ignored.

The results for hydrogen type are given in Table 6, expressed as a percentage of the total integral. The 95% confidence limits given are based on the pooled standard deviation of the data given in the table plus other results on similar bitumens.

The distribution of hydrogen types among the Safaniya bitumens is very similar and does not support the contention that the bitumens are different in any way. The technique does expose differences between the Safaniya and Venezuelan bitumens, as expected from examination of the aliphatic stretching region of the infrared spectra (Figure 1).

Table 6. Proton nmr analyses for the bitumens.

Bitumen (No. of Replicates)	**Hydrogen Type as % of Total Integrated Intensity (Mean of Replicate Determinations)**				**$H_a/H_\alpha + H_\beta + H_\gamma$ ±0.002**
	H_α ±0.1	**H_β ±0.3**	**H_γ ±0.3**	**H_a ±0.1**	
537 (12)	13.5	62.4	18.0	6.1	0.065
52 (2)	13.4	61.3	18.8	6.5	0.070
225 (2)	13.5	61.5	18.4	6.6	0.071
478 (2)	13.4	61.9	18.4	6.3	0.067
501 (6)	14.8	59.0	20.2	6.2	0.066

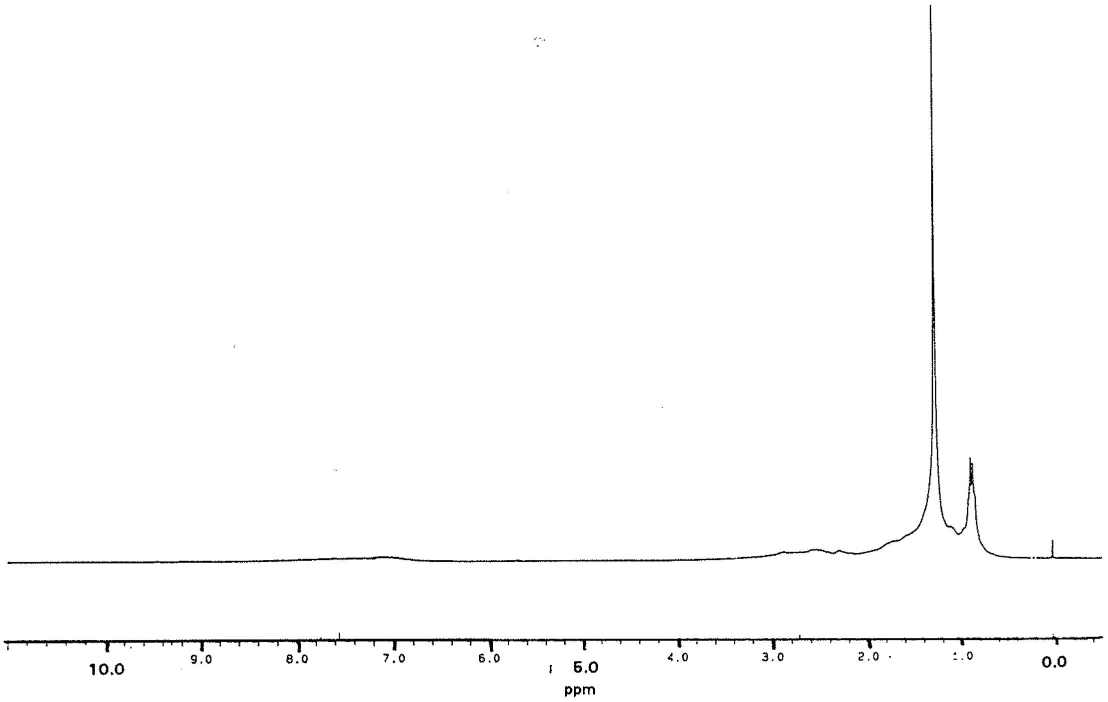


Figure 10. Proton nmr spectrum for bitumen 537

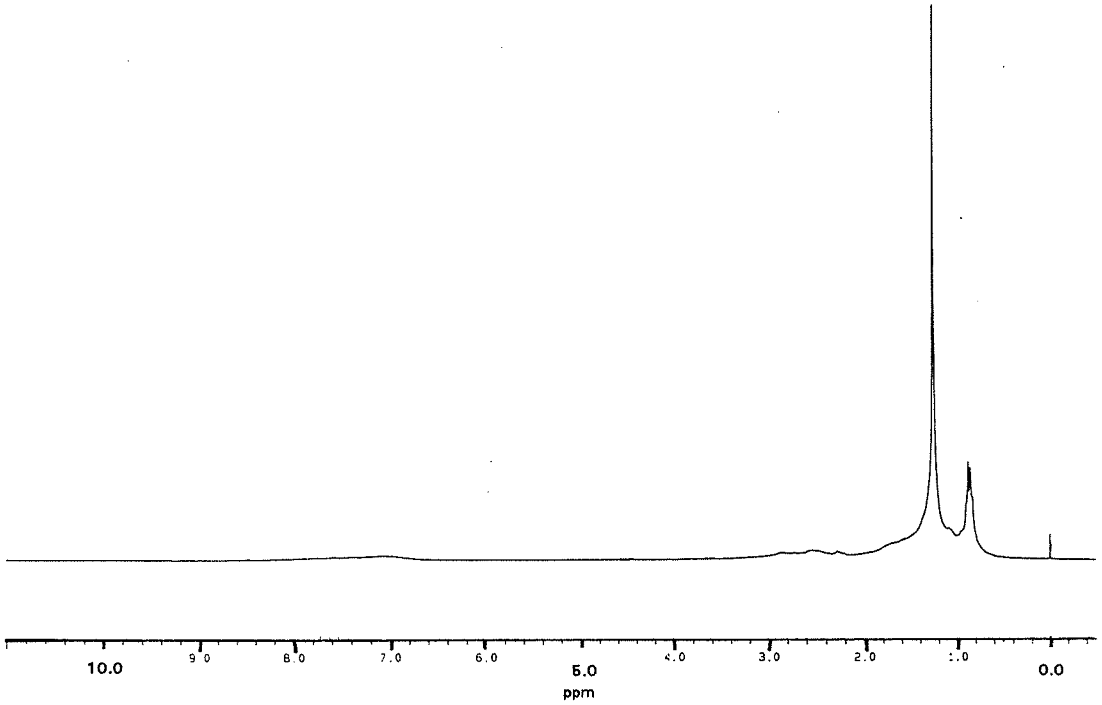


Figure 11. Proton nmr spectrum for bitumen 52

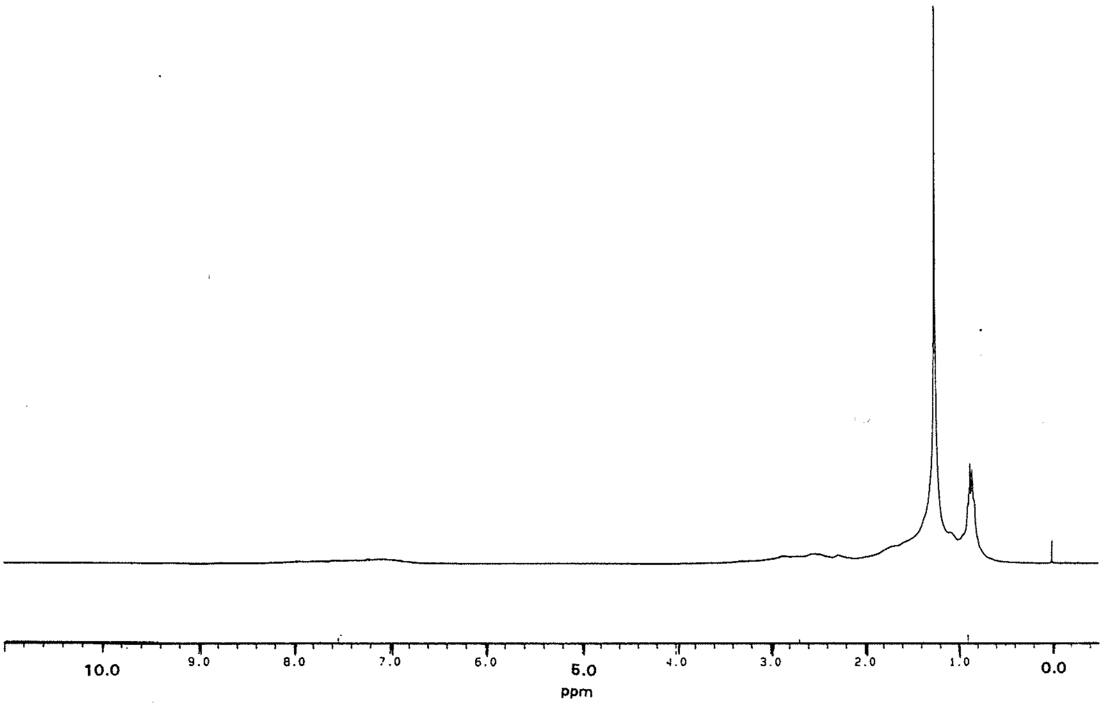


Figure 12. Proton nmr spectrum for bitumen 225

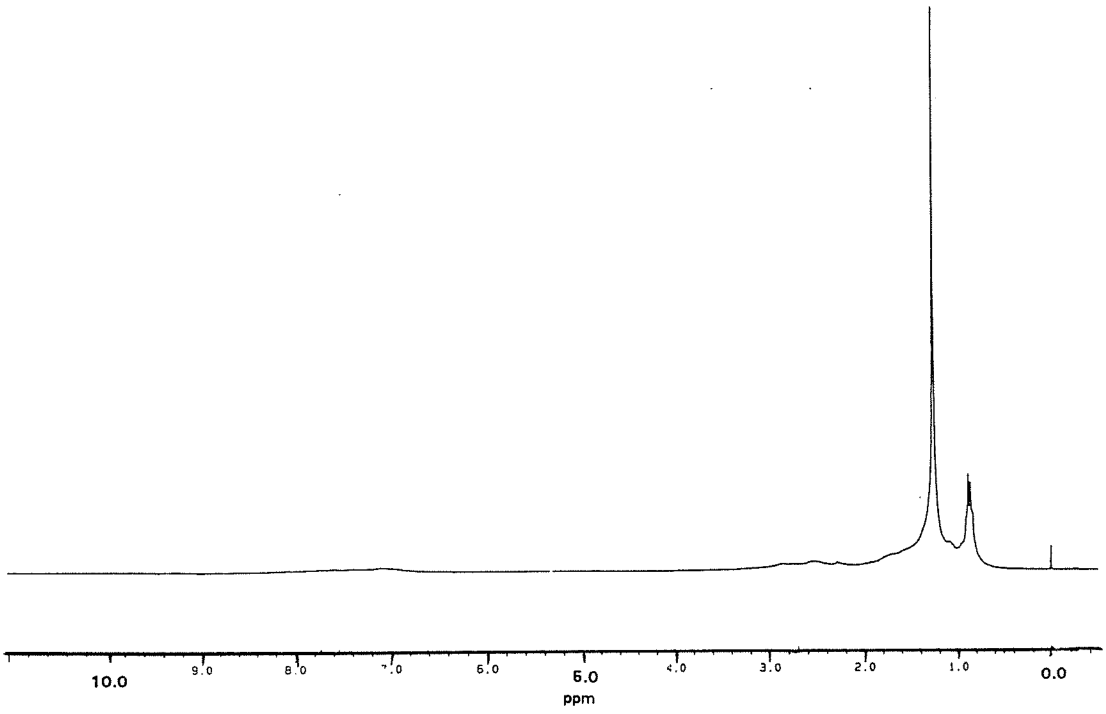


Figure 13. Proton nmr spectrum for bitumen 478

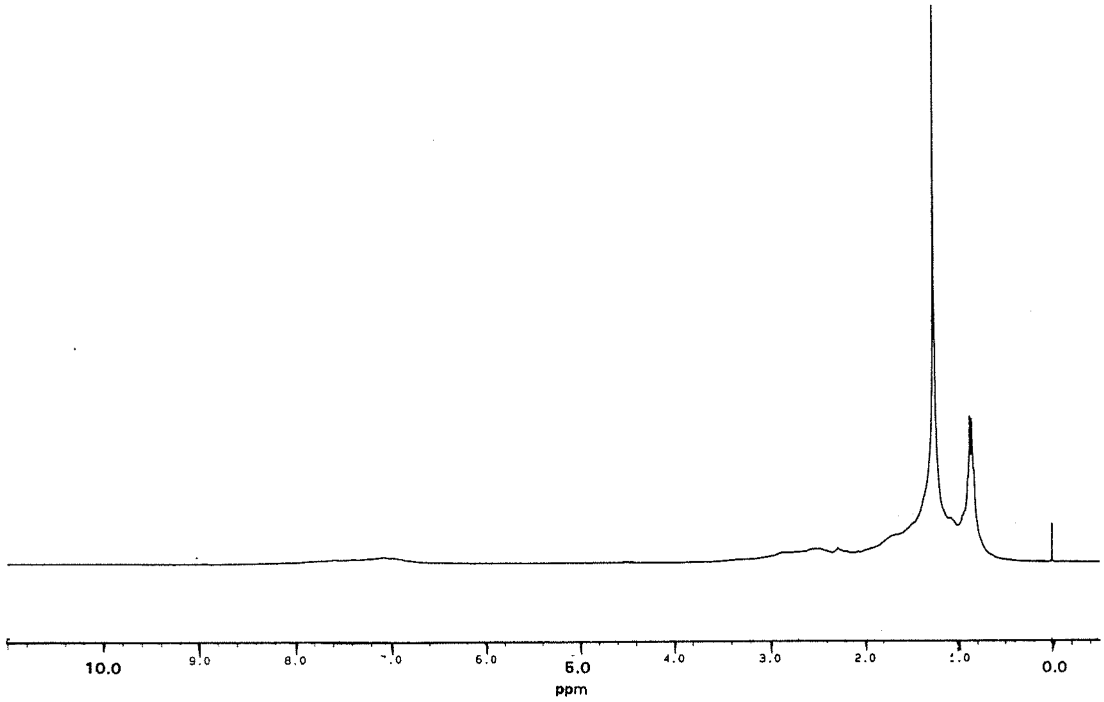


Figure 14. Proton nmr spectrum for bitumen 501

9. THERMOGRAVIMETRIC ANALYSES

Experiments were carried out on a Mettler TG50 thermobalance controlled by a Mettler TC10A processor. The raw data were transferred to a computer for analysis. Bitumen samples (10-11 mg) were heated at 5°C/min in an open platinum crucible (5 mm high, 5 mm id) in an air- or nitrogen-purge gas (200 cm^3 min^{-1}). Inorganic ash contents of the bitumens were negligible (<0.1% w/w), and were ignored in the subsequent data treatment.

Thermogravimetric curves for the bitumens under air and nitrogen atmospheres are presented in Figures 15 to 23. The first derivative of each curve is also shown (i.e. the rate of loss of weight with time) which makes visual comparison of the curves easier. Tables 7a and 7b list weight losses under air and nitrogen over the specified temperature intervals as a percentage of the total weight lost.

All experiments run under air show numerous non-reproducible sharp spikes and peaks that can occur at any point in the profile, although they usually appear between ~340-460°C. This noise is not an instrumental artefact and its origin has been discussed elsewhere (Herrington et al. 1992). Apart from this region, the curves for the Safaniya bitumens are qualitatively similar.

The Venezuelan bitumen can be easily distinguished by the temperature (~460°C) of the largest dtg (differential thermogravimetric) maxima, as it is always somewhat lower than that of the Safaniya materials (~510°C).

The thermogravimetric curves for the bitumens under nitrogen (Figures 20-23) are qualitatively very similar. Examination of the weight loss data extracted from these curves (Table 7b) also fails to show any difference between the bitumens. The weight loss data under air (Table 7a) do, however, show a clear difference between the 1986 and 1991 Safaniya bitumens in the 400-600°C region. Given that the analyses previously discussed showed no significant difference between the Safaniya bitumens, it was considered important to verify the weight loss results (in air) before drawing conclusions. To this end four other 180/200 Safaniya bitumens were selected for study.

Two of these (samples 204, 284) were recently produced (March and May 1992 respectively), another (606) was produced September 1990, and a fourth (448) was a November 1984 bitumen that had only recently been found. Thermogravimetric analyses under air, using the same conditions as for the first set of samples, were carried out on the extra bitumens and the results are presented in Table 7c. (Unfortunately the fourth bitumen was located too late to be included in the other analyses carried out as part of this study.)

All eight Safaniya bitumens show that the weight losses in the 400-600°C interval vary considerably, though without any obvious trend or pattern. Clearly the low result obtained for bitumen 537 is also somewhat anomalous. The lack of any trend relating to the date of production can be clearly seen in Table 8 by comparing mean weight losses in the 400-500°C and 500-600°C regions:

Table 8. Mean weight losses (%) of Safaniya bitumens between 400°C and 600°C.

Bitumen	448	537	606	52	225	478	204	284
Sample date	1984 (Nov)	1986 (Apr)	1990 (Sept)	1991 (Feb)	1991 (May)	1991 (Nov)	1992 (Mar)	1992 (May)
Temperature	Mean Weight Loss (%)							
400-500°C	47.6	52.8	49.9	47.3	47.8	48.0	49.8	45.7
500-600°C	25.0	16.0	20.2	21.8	22.6	21.1	20.7	25.1

Although there is variation in weight loss in the 400-600°C region between the bitumens, the results for replicate determinations on the same material are relatively consistent. This suggests that the differences are systematic and not just a random effect.

Table 7a. Thermogravimetric analyses of the bitumens in air.

Temperature (°C)	Weight Loss as Percentage of Total Weight Lost														
	Bitumen 537 (Safaniya)			Bitumen 52 (Safaniya)			Bitumen 225 (Safaniya)			Bitumen 478 (Safaniya)			Bitumen 501 (Venezuelan)		
	Run 1	Run 2	Mean	Run 1	Run 2	Mean	Run 1	Run 2	Mean	Run 1	Run 2	Mean	Run 1	Run 2	Mean
35-100	0	0	0	0	0.1	0.05	0	0	0	0	0	0	0	0.1	0.1
100-200	0.2	0.2	0.2	0.4	0.4	0.4	0.3	0.4	0.4	0.2	0.3	0.3	2.8	2.7	2.8
200-300	7.6	8.0	7.8 ±0.2	8.9	8.7	8.8 ±0.2	7.5	8.7	8.1 ±0.2	9.0	9.4	9.2 ±0.2	16.4	15.9	16.2 ±0.2
300-400	22.4	20.8	21.6 ±0.6	21.0	22.1	21.6 ±0.6	21.8	20.3	21.1 ±0.6	21.0	22.0	21.5 ±0.6	17.5	16.5	17.0 ±0.6
400-500	54.4	51.1	52.8 ±1.3	48.2	46.4	47.3 ±1.3	47.6	48.0	47.8 ±1.3	48.2	47.7	48.0 ±1.3	63.1	64.7	63.9 ±1.3
500-600	15.4	16.6	16.0 ±0.2	21.4	22.2	21.8 ±0.2	22.7	22.5	22.6 ±0.2	21.6	20.6	21.1 ±0.2	0.1	0	0.1
600-630	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 7b. Thermogravimetric analyses of the bitumens in nitrogen.

Temperature (°C)	Weight Loss as Percentage of Total Weight Lost				
	Bitumen 537	Bitumen 52	Bitumen 225	Bitumen 478	
35-100	0	0	0	0	0
100-200	0.4	0.4	0.4	0.4	0.4
200-300	9.0	9.5	9.2	9.7	9.9
300-400	34.8	35.0	34.4	35.5	35.8
400-500	31.9	32.9	33.1	32.2	31.3
500-600	5.2	4.5	5.1	4.5	4.8
600-700	10.7	10.7	10.6	10.8	11.2
700-800	5.4	5.1	5.2	4.9	4.9
800-900	2.3	1.9	0.1	1.9	1.5
900-930	0.4	0	0	0	0

Bitumen sample 501 - results not available.

Table 7c. Thermogravimetric analyses in air of the four additional Safaniya bitumens.

Temperature (°C)	Weight Loss as Percentage of Total Weight Lost													
	Bitumen 448 - November 1984				Bitumen 606 - September 1990				Bitumen 204 - March 1992			Bitumen 284 - May 1992		
	Run 1	Run 2	Run 3	Mean	Run 1	Run 2	Run 3	Mean	Run 1	Run 2	Mean	Run 1	Run 2	Mean
35-100	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.1
100-200	0.2	0.3	0.3	0.3	0.5	0.4	0.5	0.5	0.3	0.2	0.2	0.3	0.3	0.3
200-300	6.1	5.8	5.8	5.9 ±0.2	8.4	7.8	8.5	8.2 ±0.2	7.9	8.0	8.0 ±0.2	7.6	7.5	7.6 ±0.2
300-400	20.2	20.8	21.2	20.7 ±0.6	21.0	21.1	20.6	20.9 ±0.6	21.2	21.5	21.4 ±0.6	20.9	21.5	21.2 ±0.6
400-500	49.2	47.0	47.6	48.0 ±1.3	45.3	46.8	29.9	47.3 ±1.3	48.5	51.0	49.8 ±1.3	46.1	45.2	45.7 ±1.3
500-600	24.1	26.0	25.0	25.0 ±0.2	24.8	23.7	20.2	22.9 ±0.2	22.1	19.2	20.7 ±0.2	24.9	25.3	25.1 ±0.2
600-630	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1

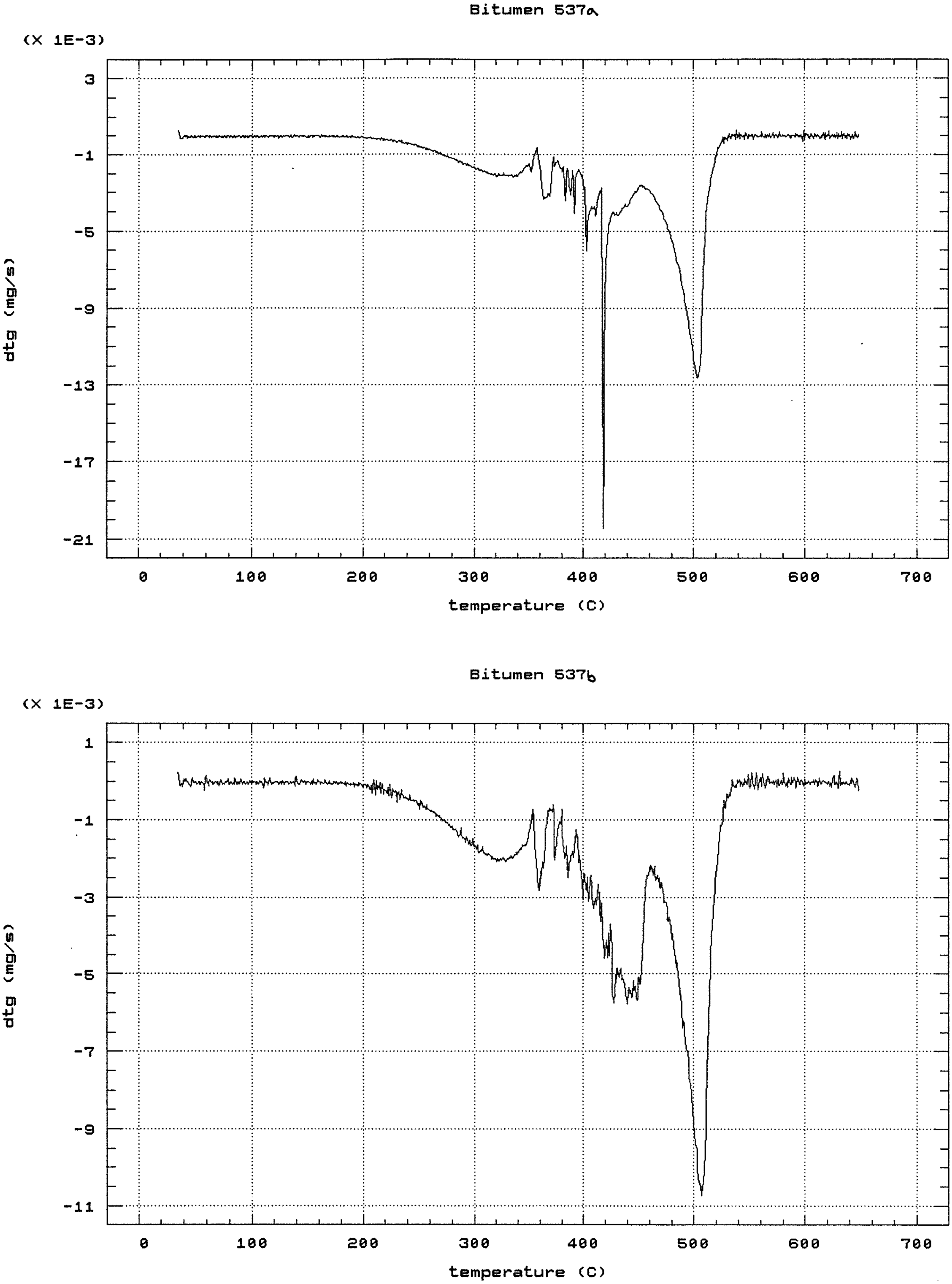
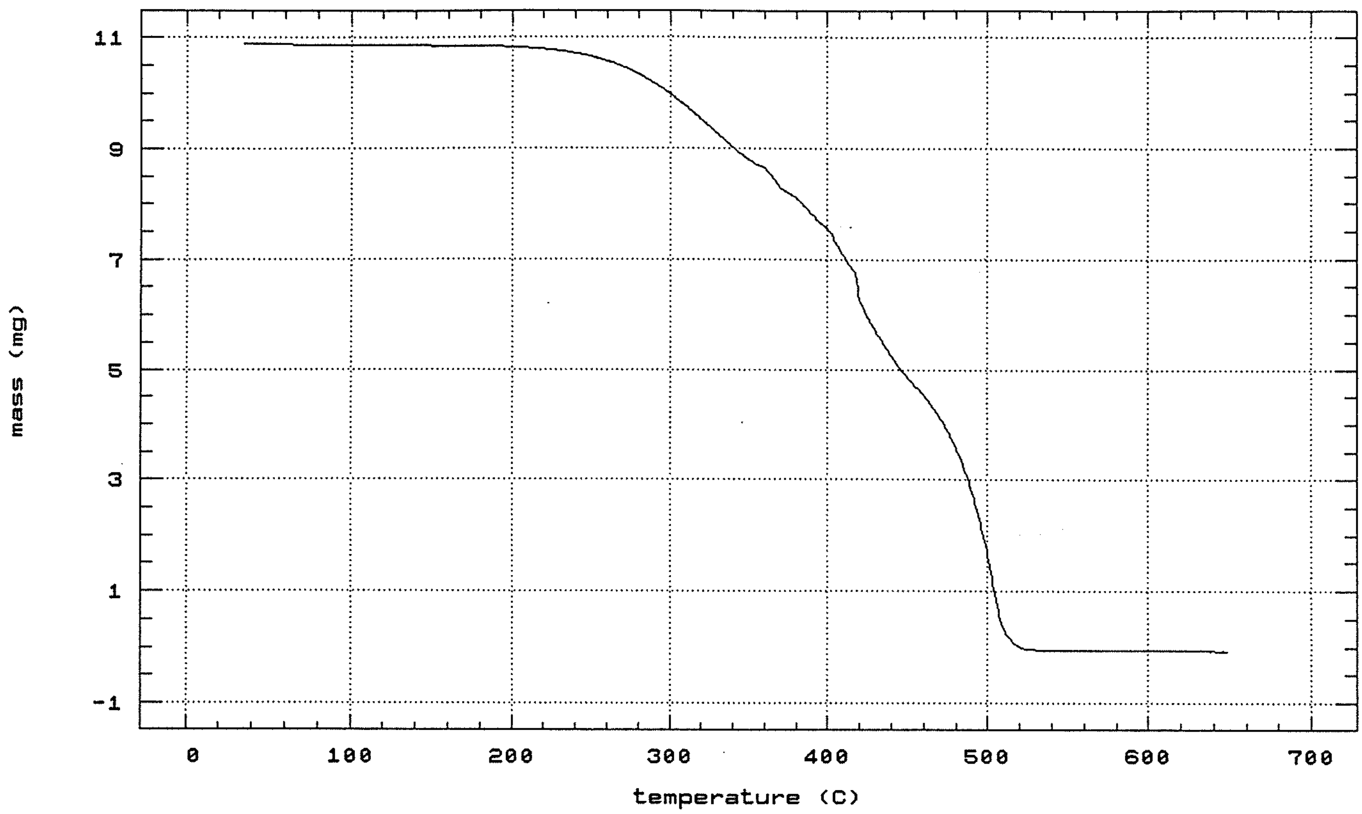
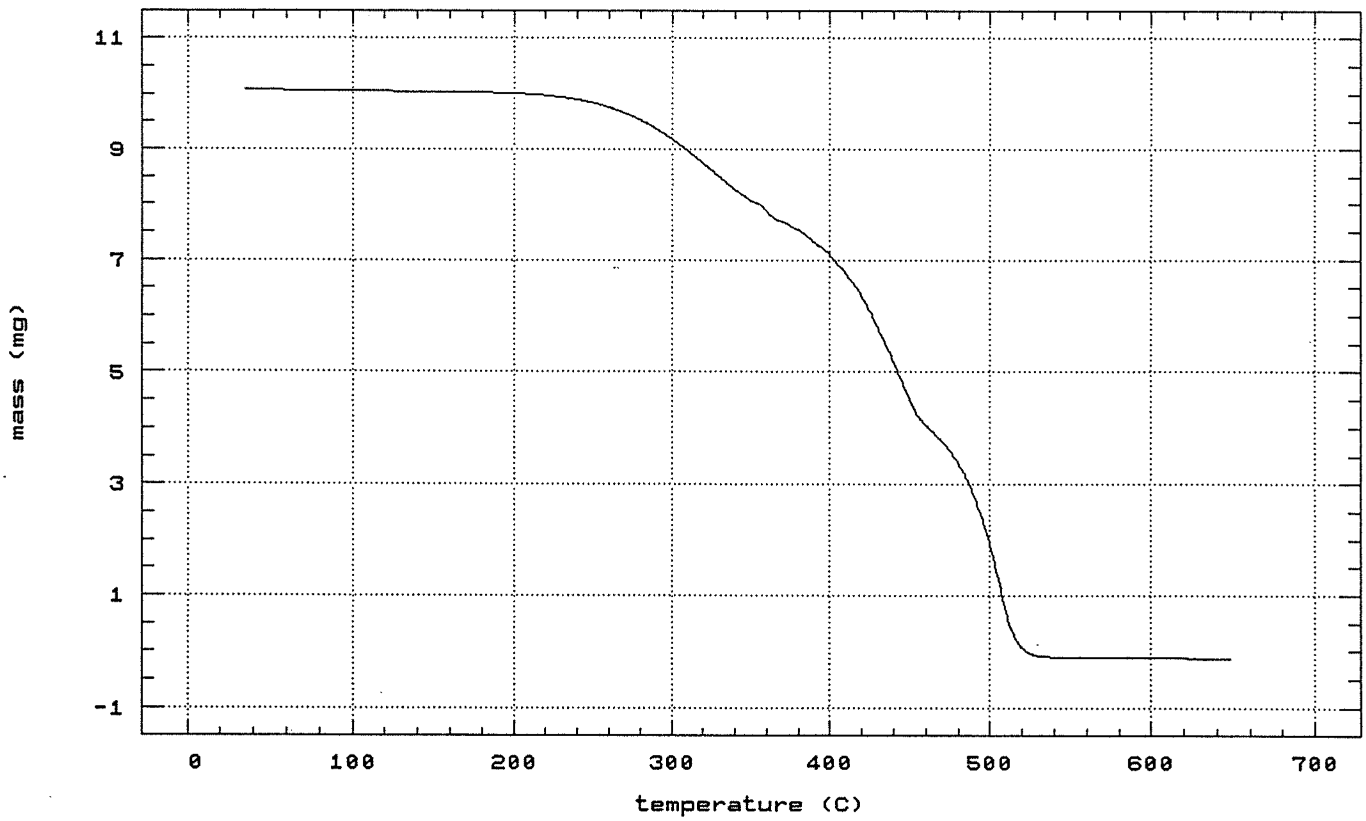


Figure 15. Thermogravimetric curves (air atmosphere), bitumen 537
First derivative of mass curves (two replicates)

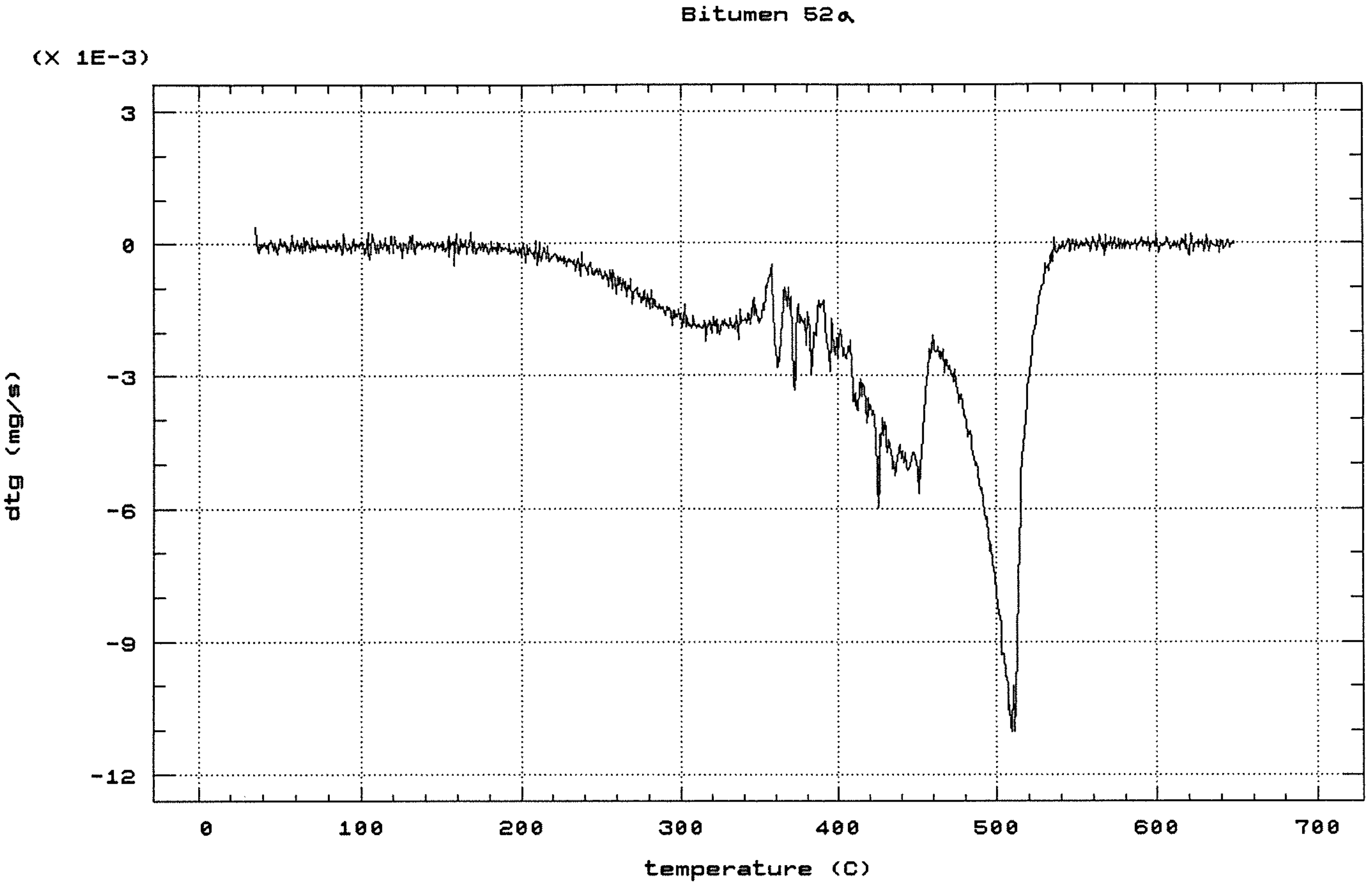


Bitumen 537a



Bitumen 537b

Figure 15. Thermogravimetric curves (air atmosphere), bitumen 537
Mass curve (two replicates)



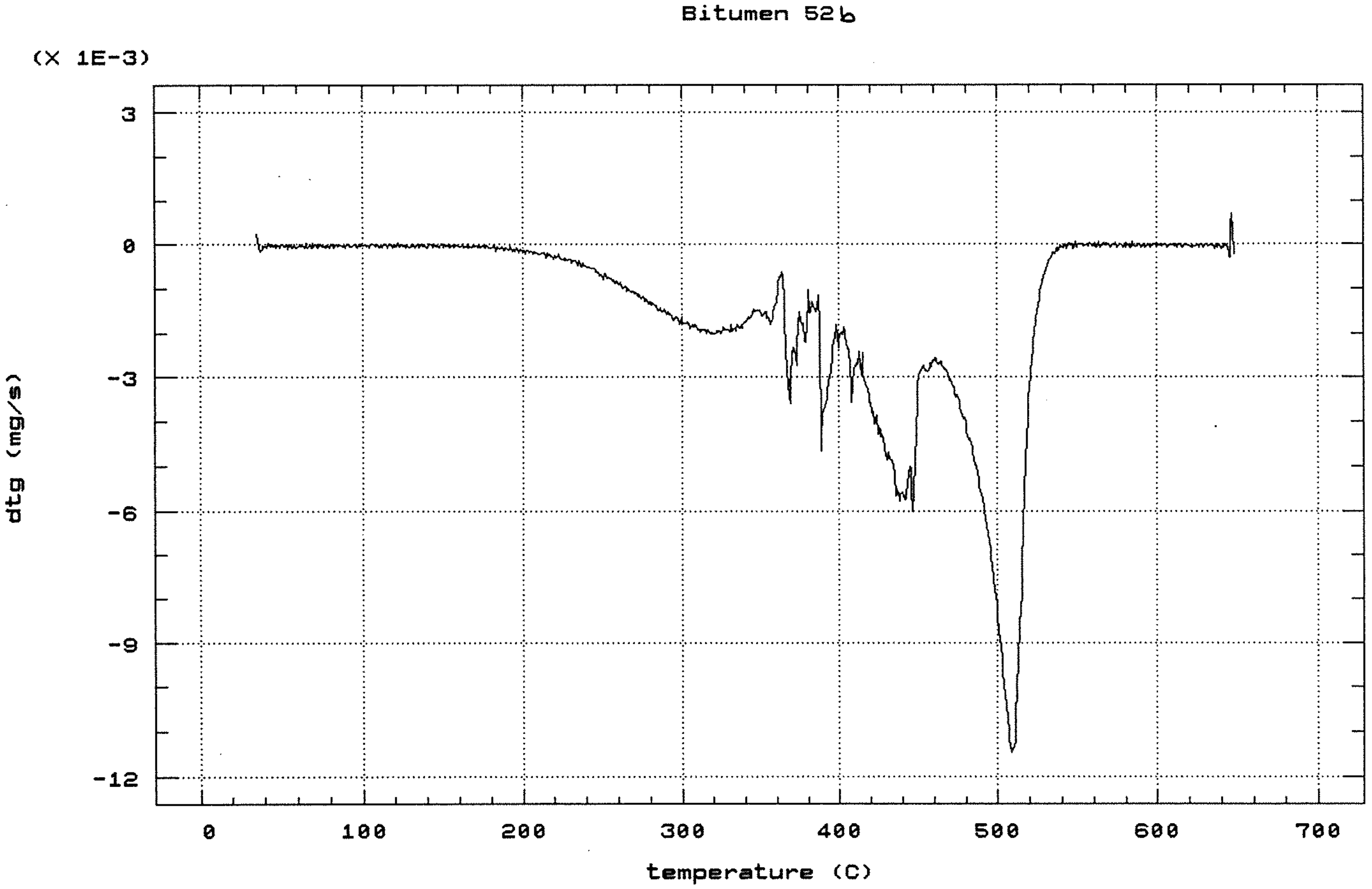
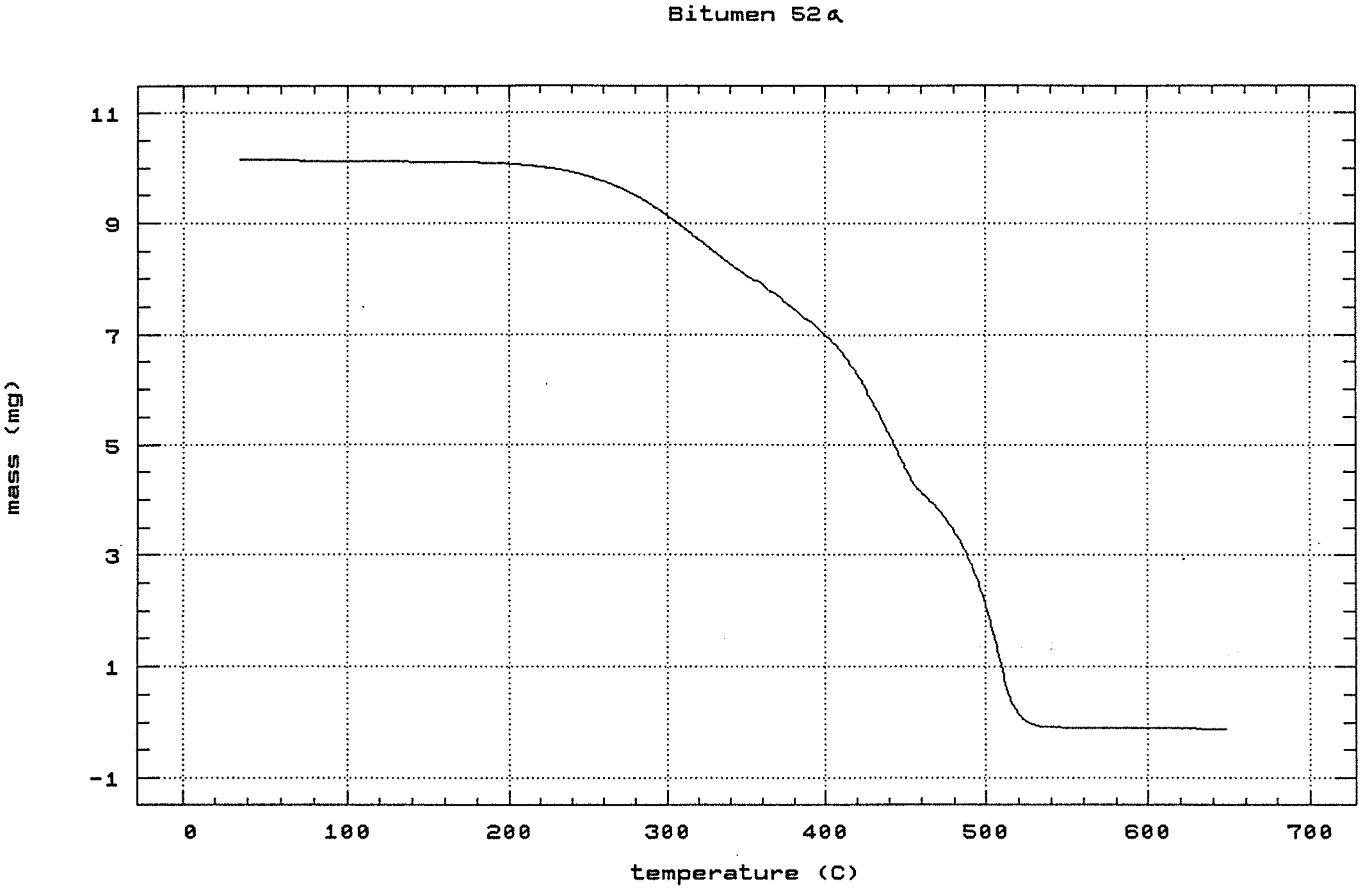


Figure 16. Thermogravimetric curves (air atmosphere), bitumen 52
First derivative of mass curves (two replicates)



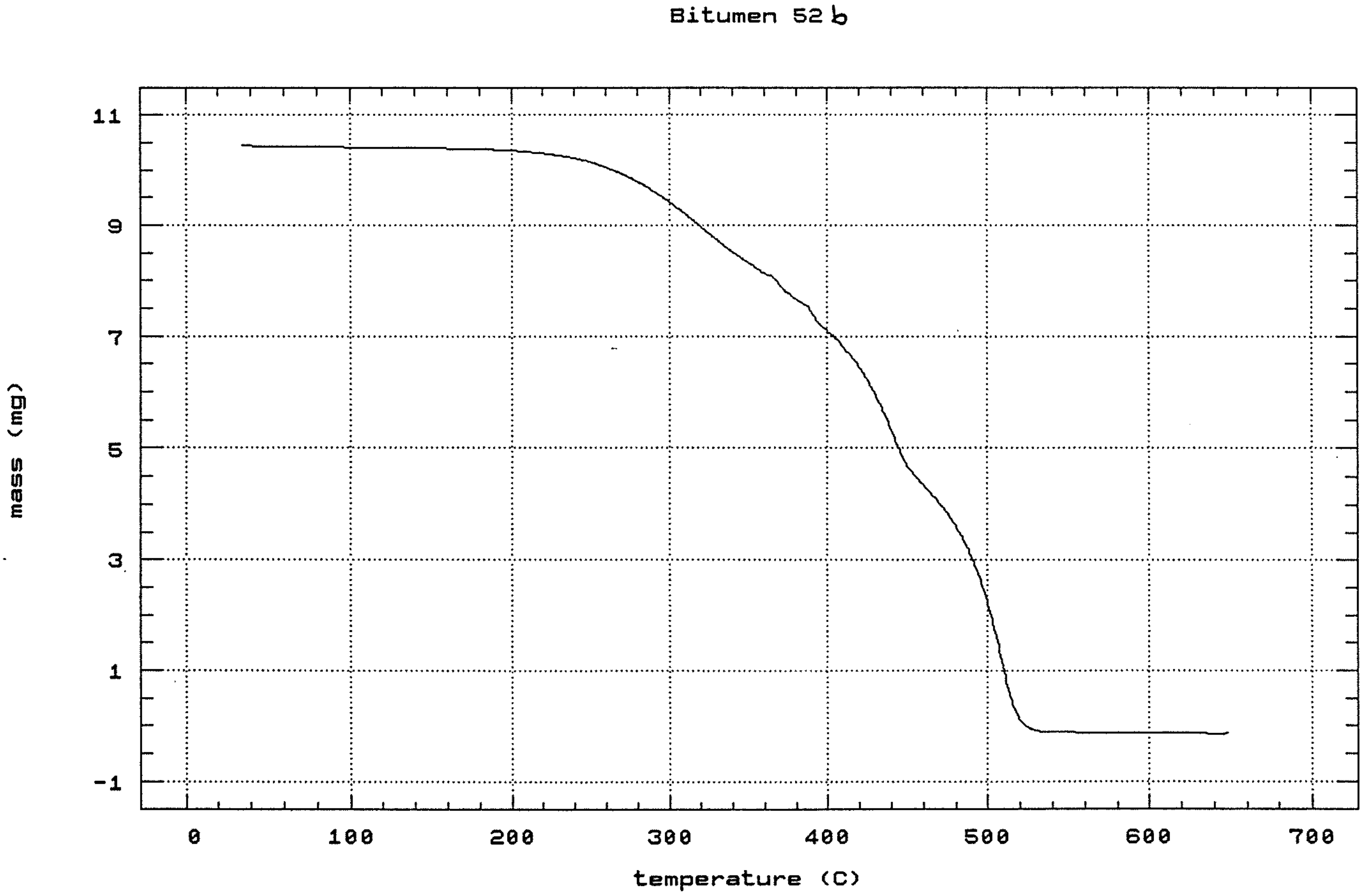
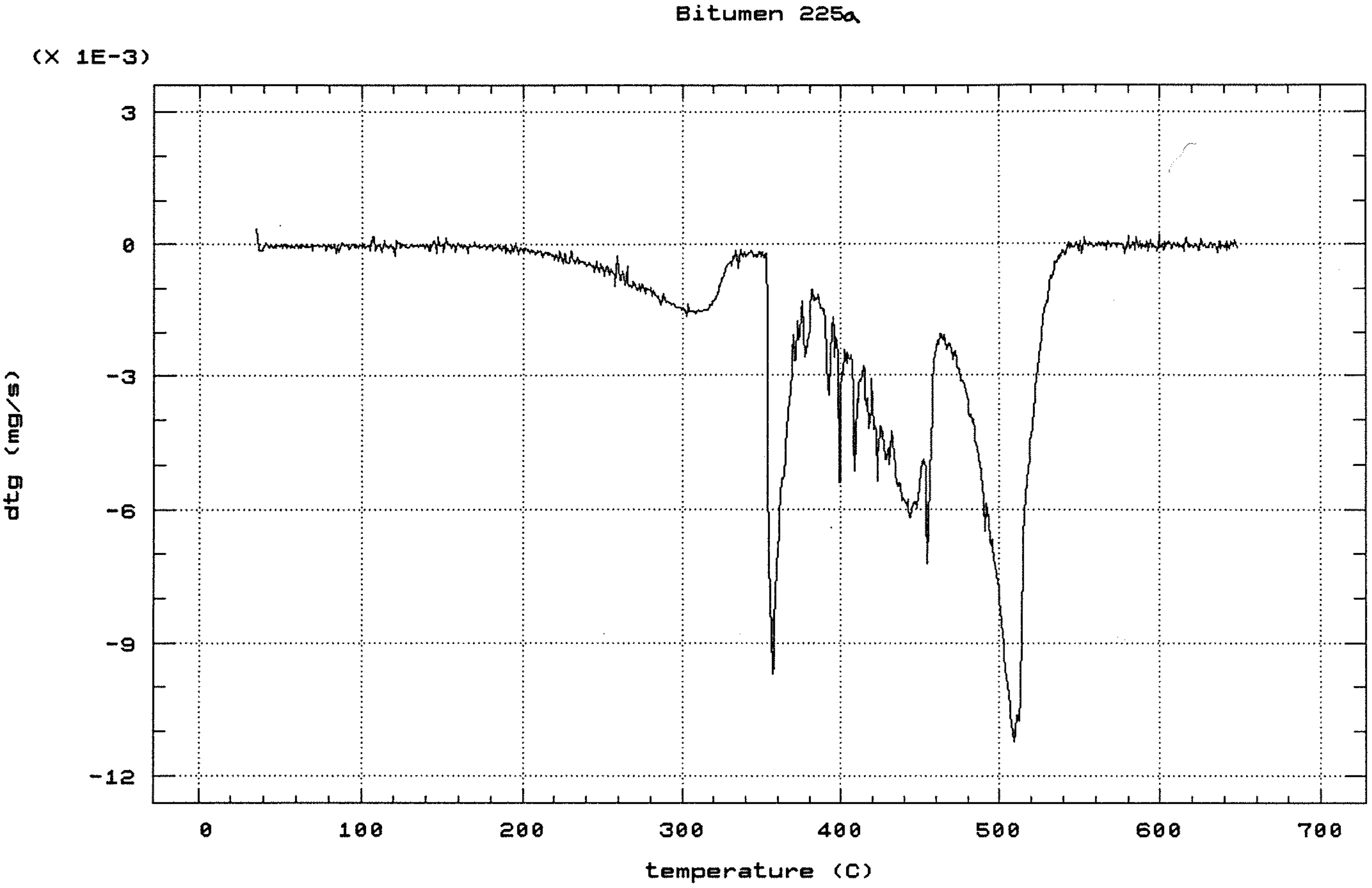


Figure 16. Thermogravimetric curves (air atmosphere), bitumen 52
Mass curve (two replicates)



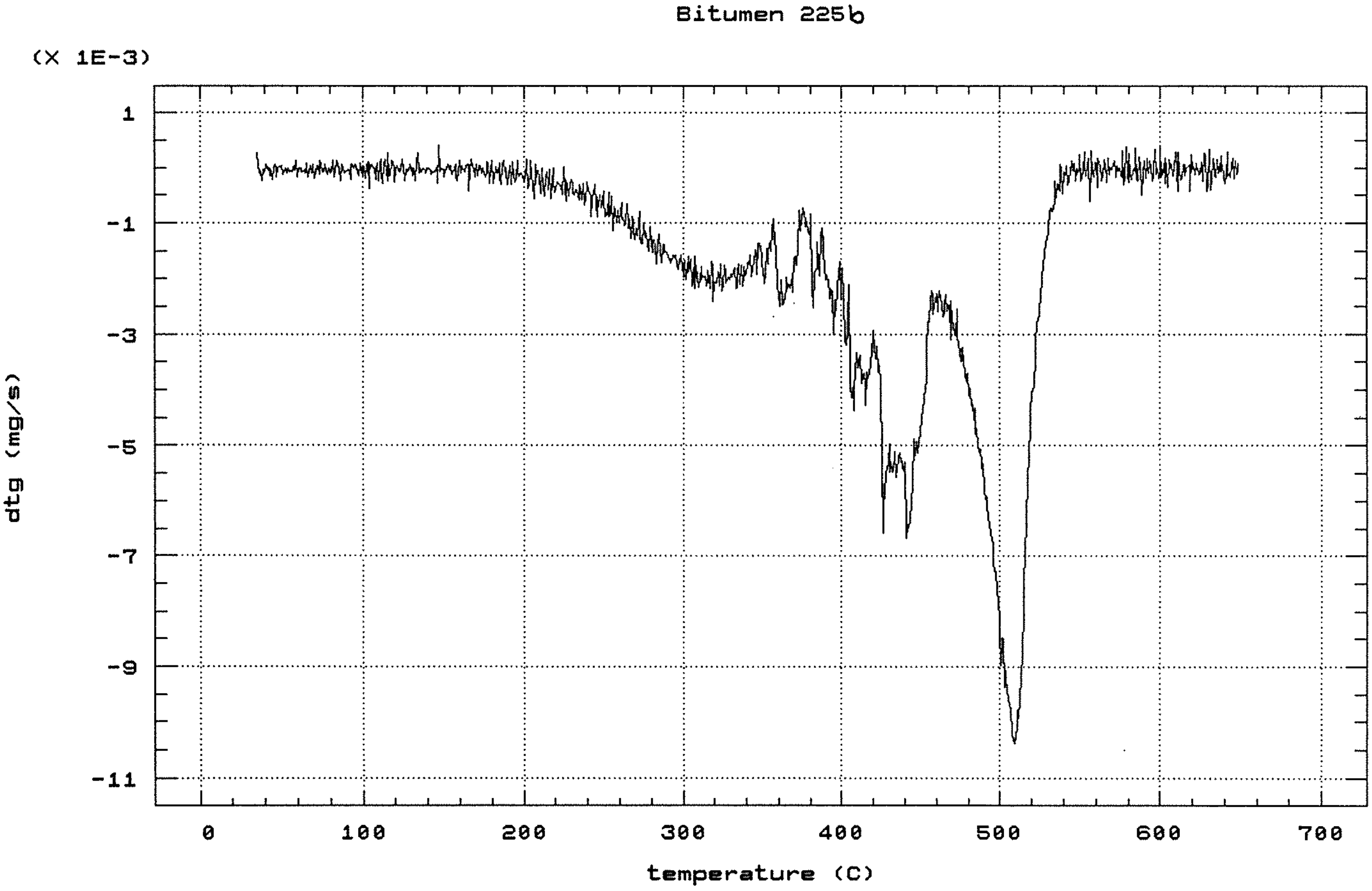
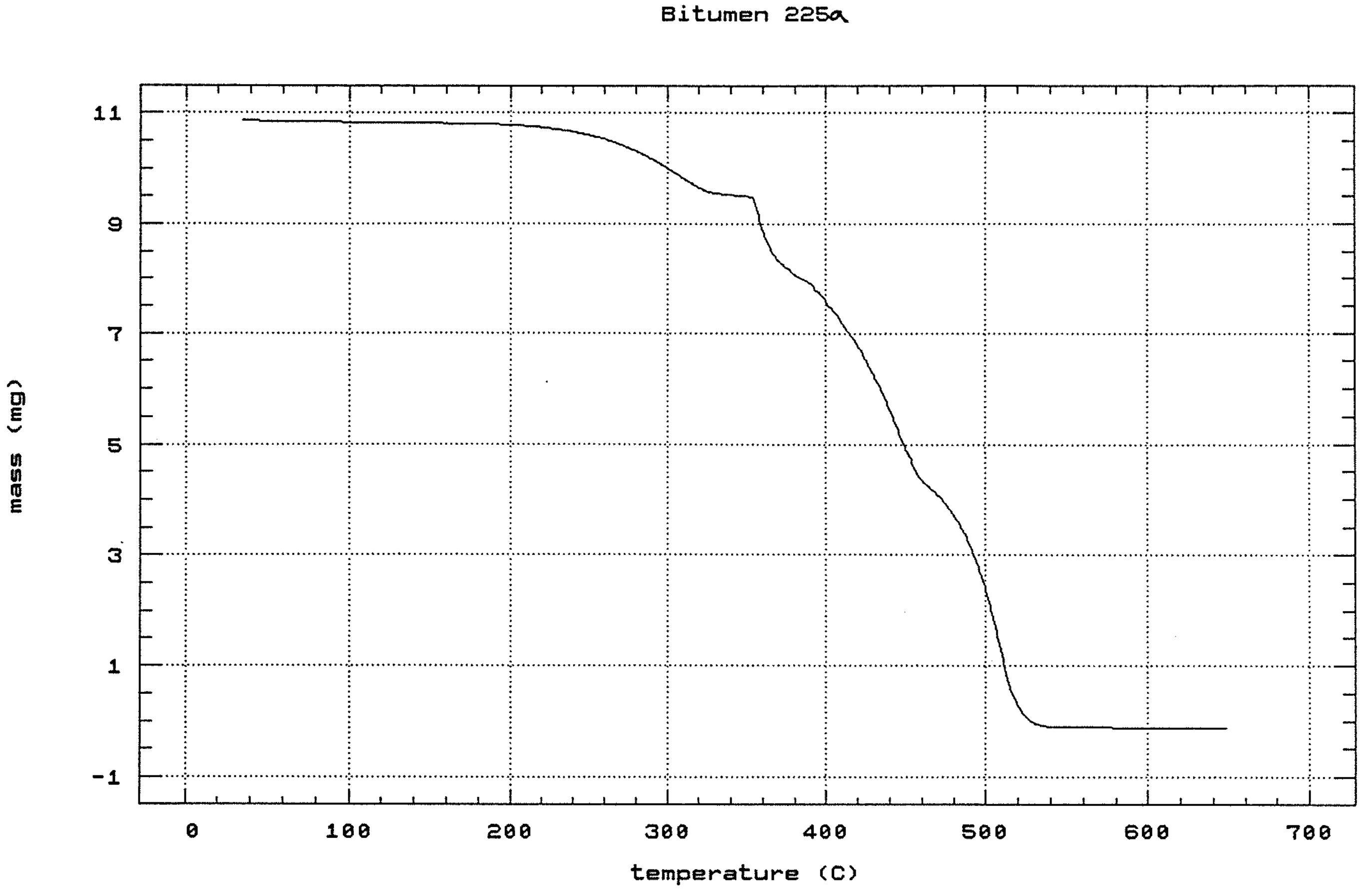


Figure 17. Thermogravimetric curves (air atmosphere), bitumen 225
First derivative of mass curves (two replicates)



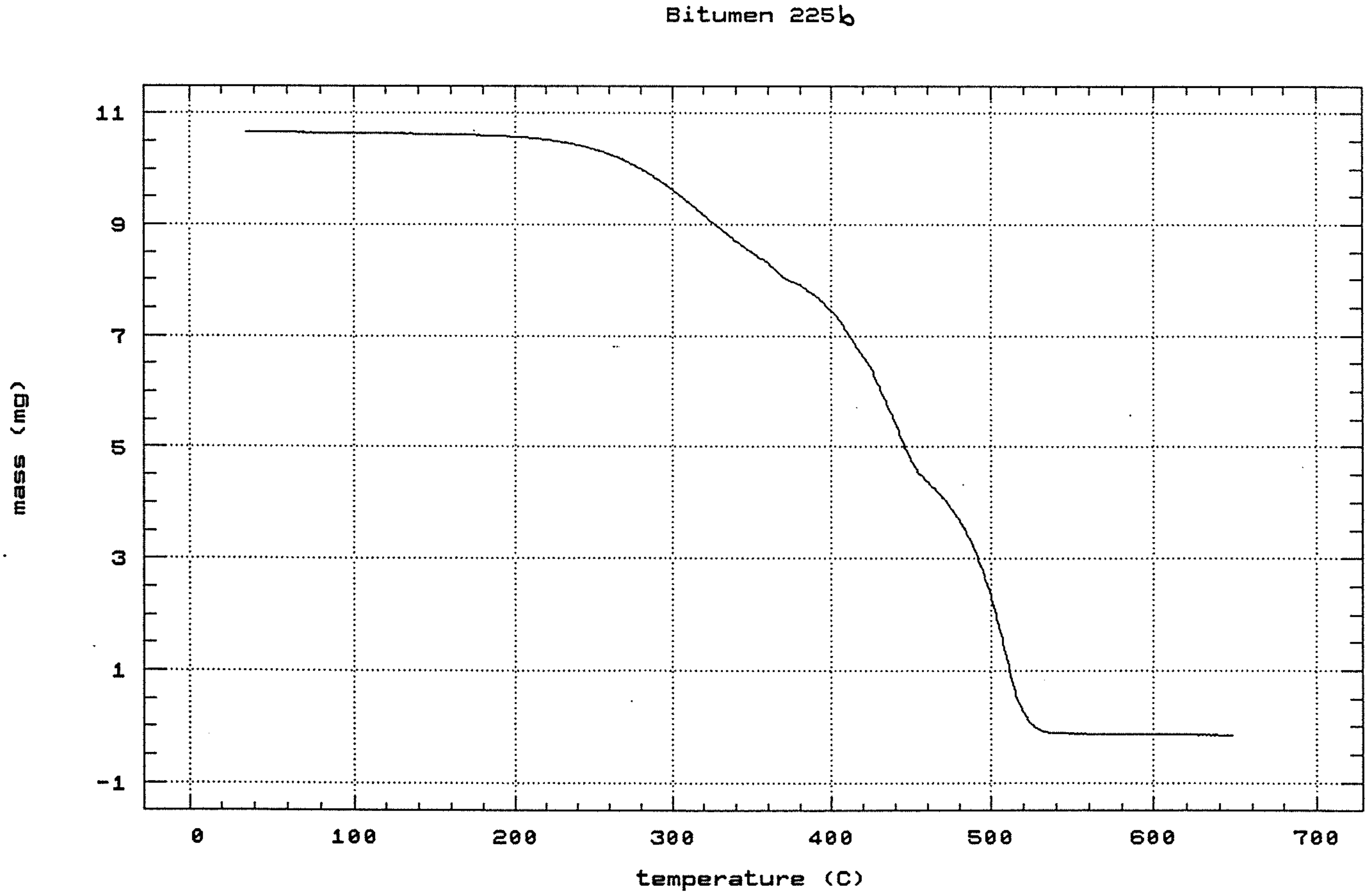


Figure 17. Thermogravimetric curves (air atmosphere), bitumen 225
Mass curve (two replicates)

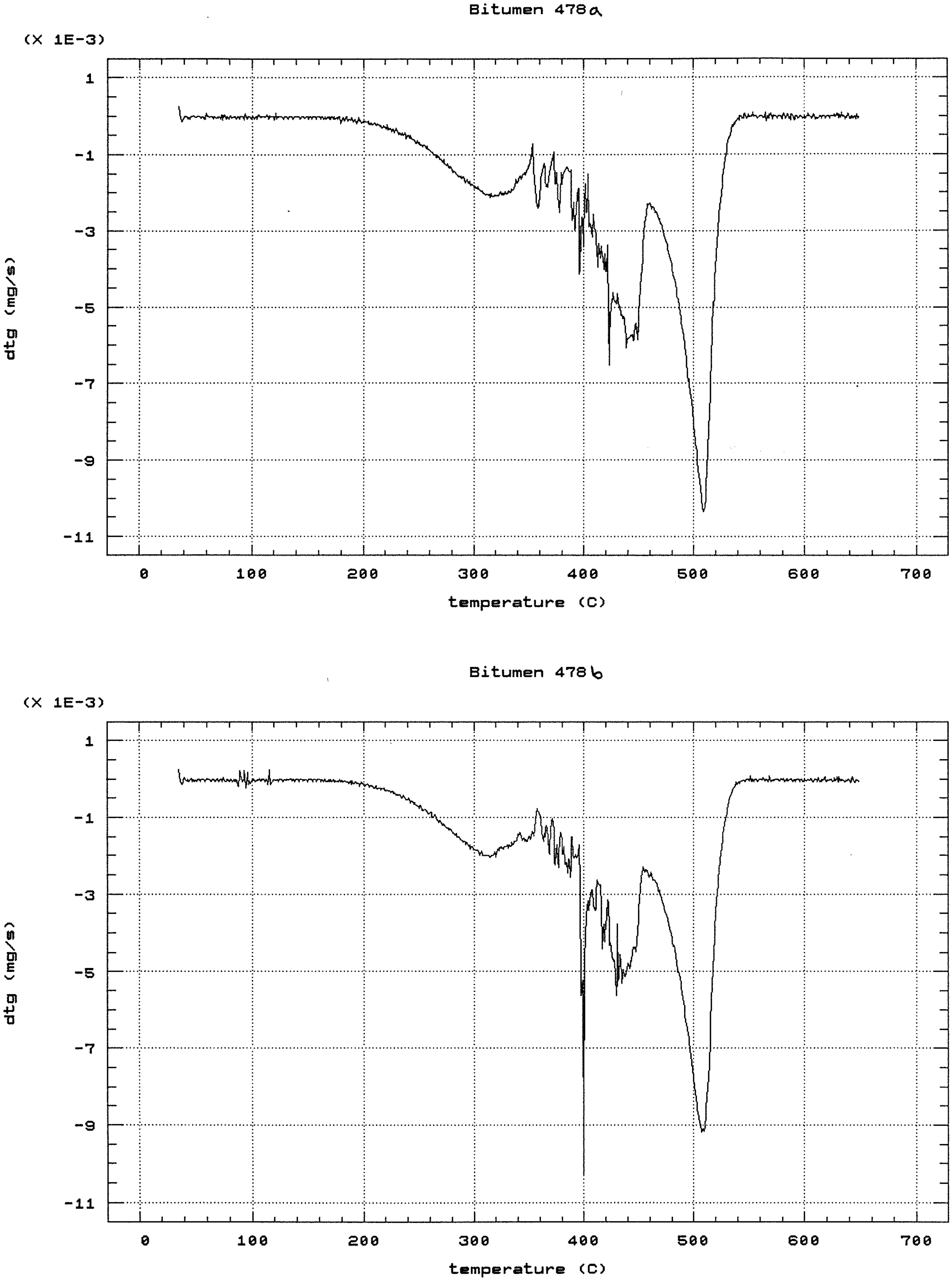


Figure 18. Thermogravimetric curves (air atmosphere), bitumen 478
First derivative of mass curves (two replicates)

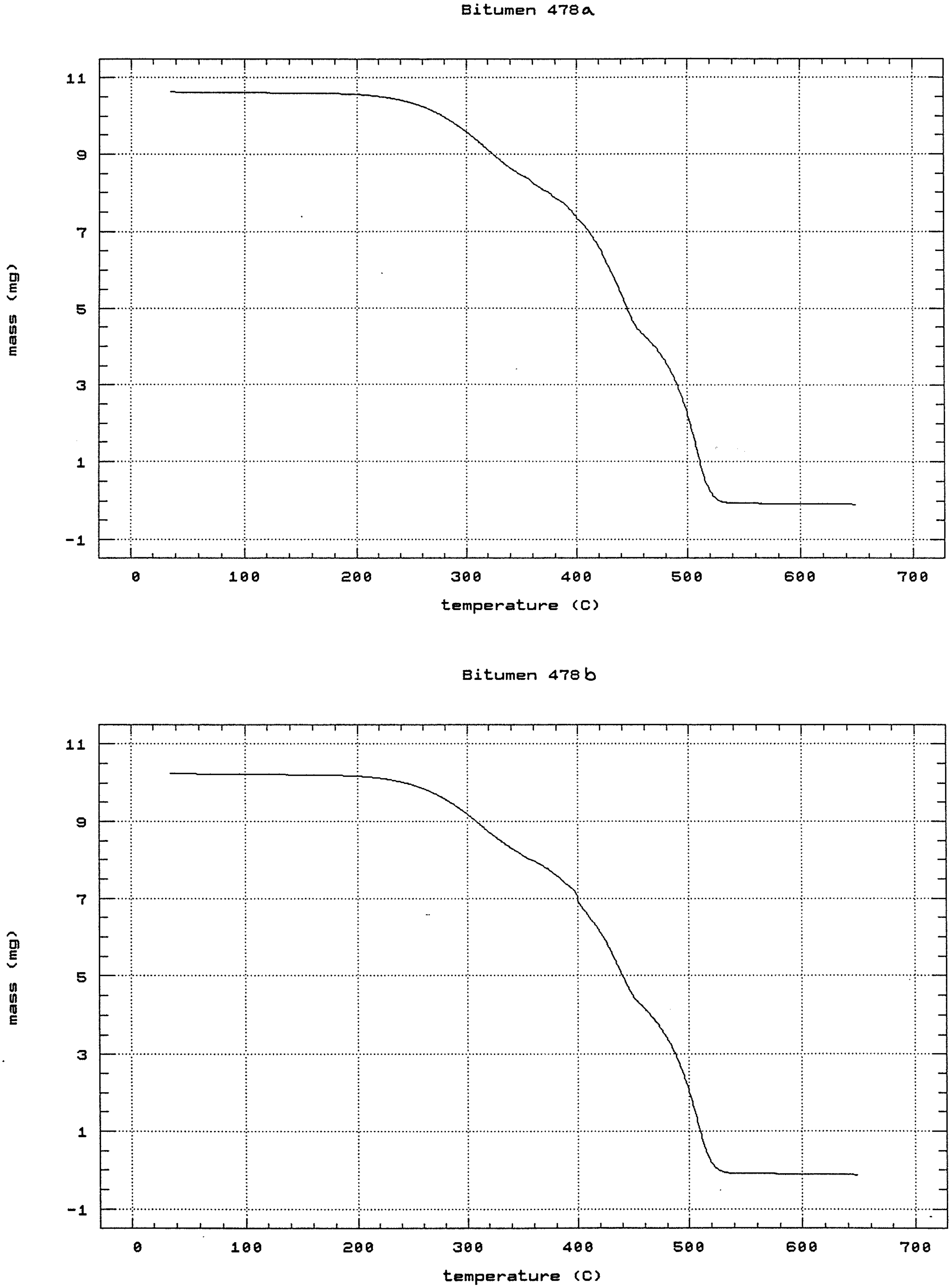


Figure 18. Thermogravimetric curves (air atmosphere), bitumen 478
Mass curve (two replicates)

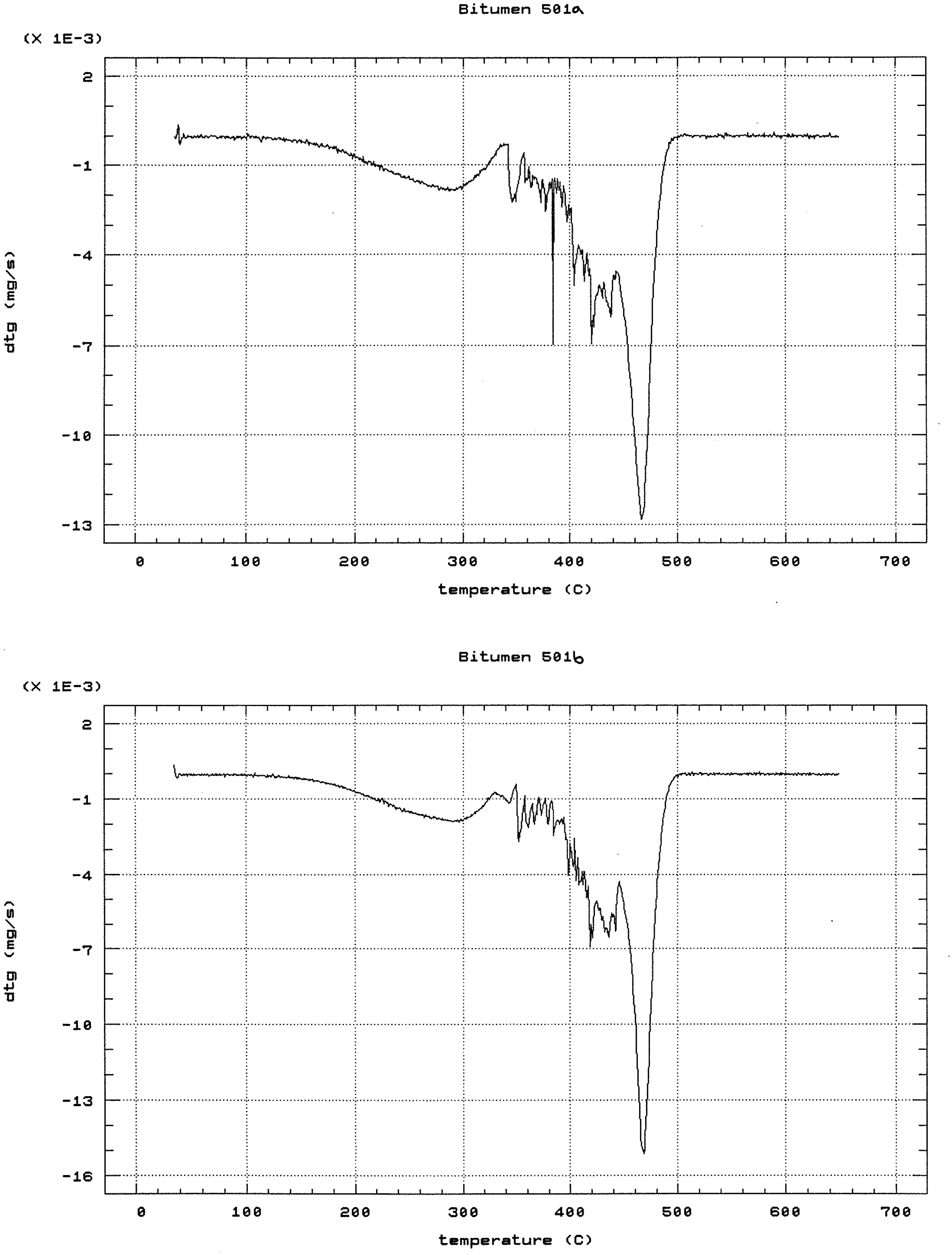


Figure 19. Thermogravimetric curves (air atmosphere), bitumen 501
First derivative of mass curves (two replicates)

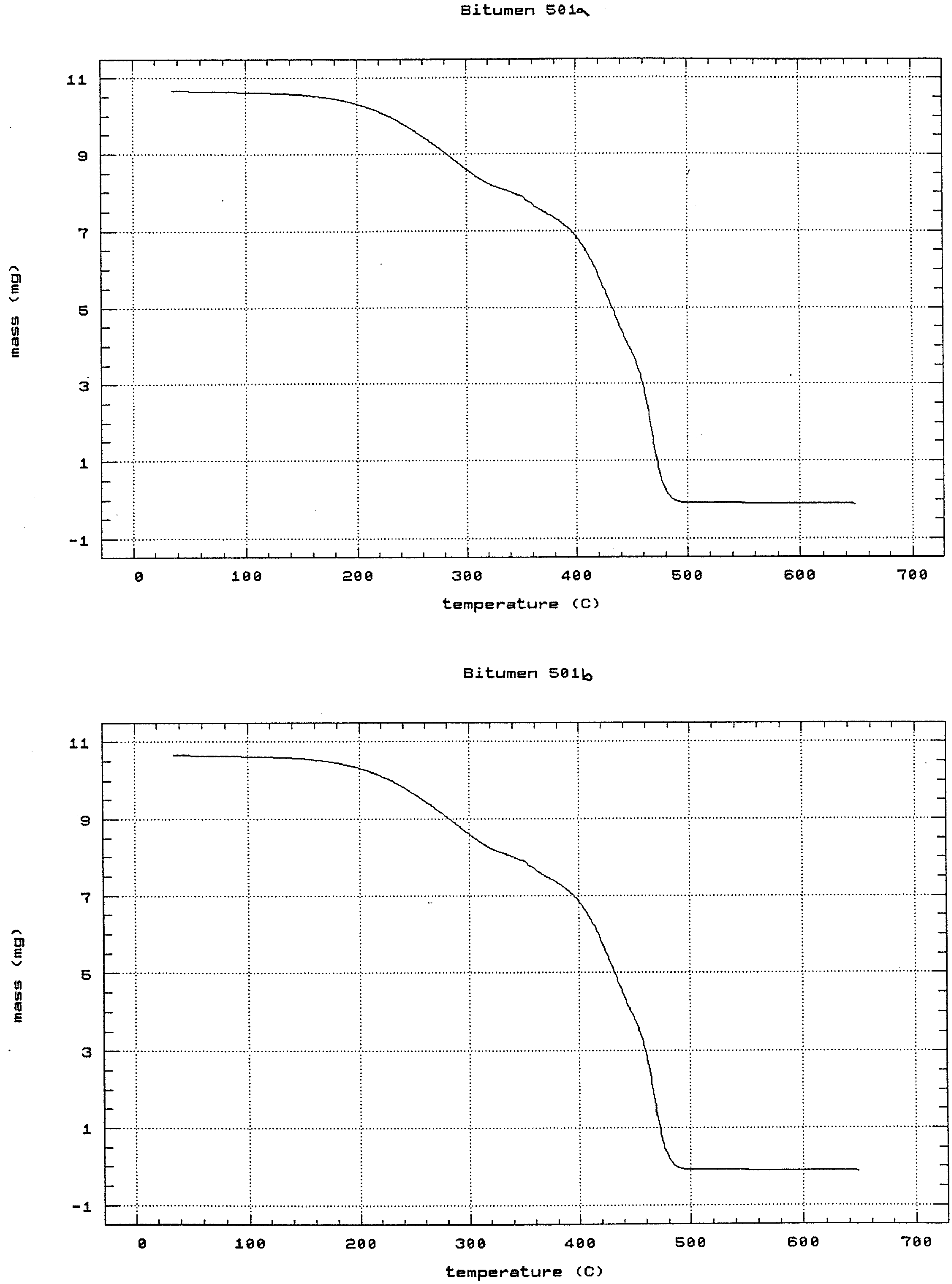
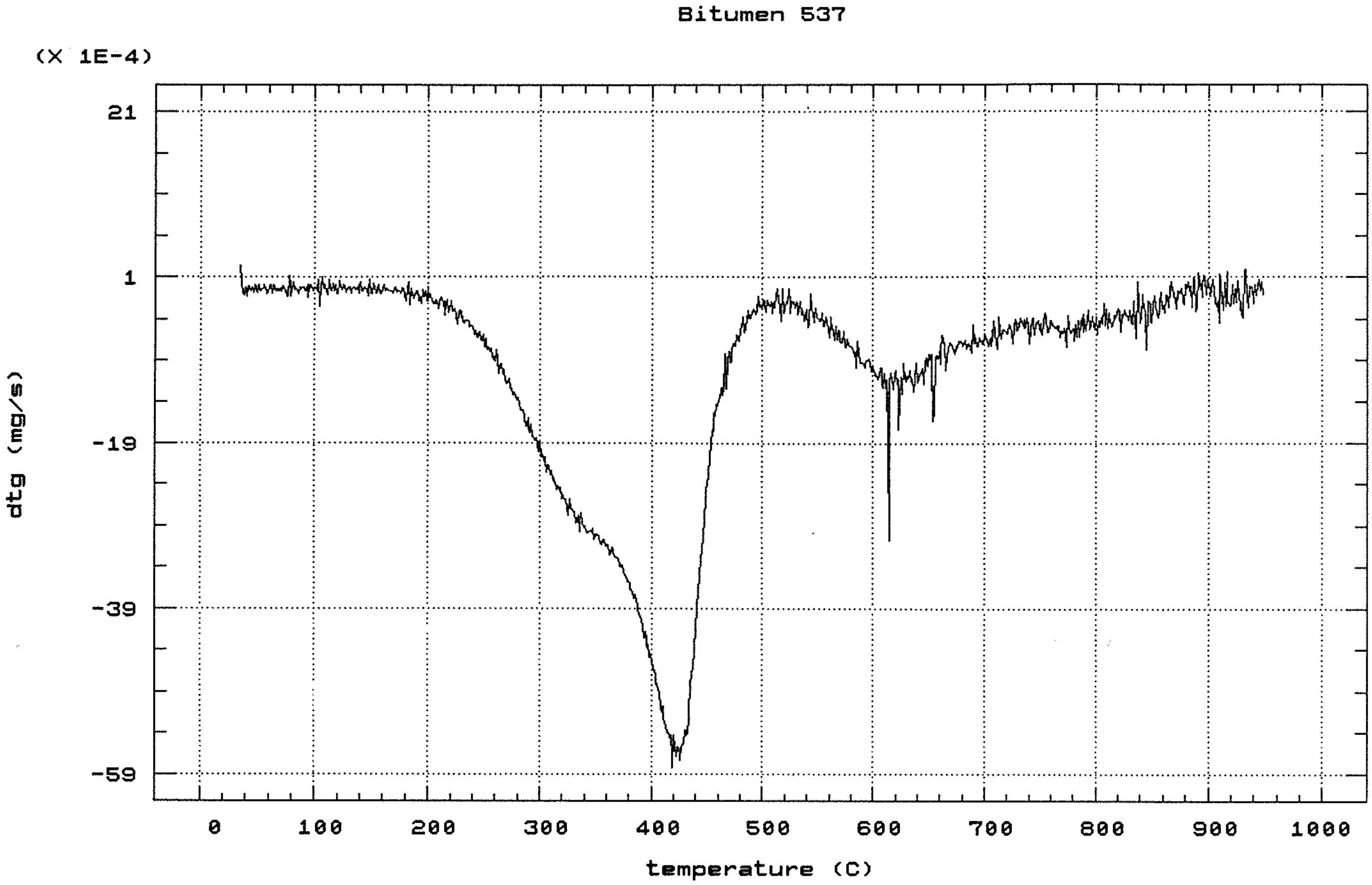


Figure 19. Thermogravimetric curves (air atmosphere), bitumen 501
Mass curve (two replicates)



First derivative of mass curve

Mass curve

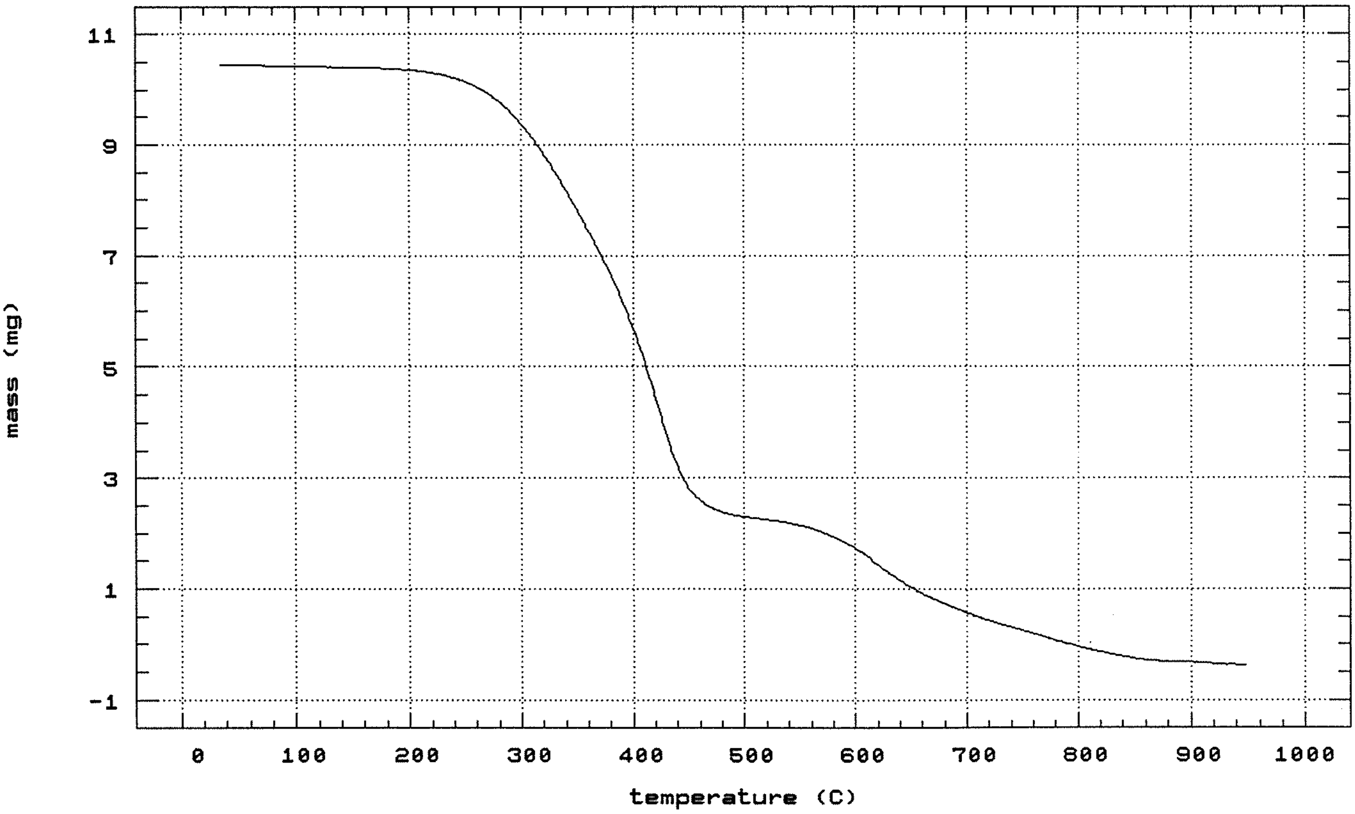
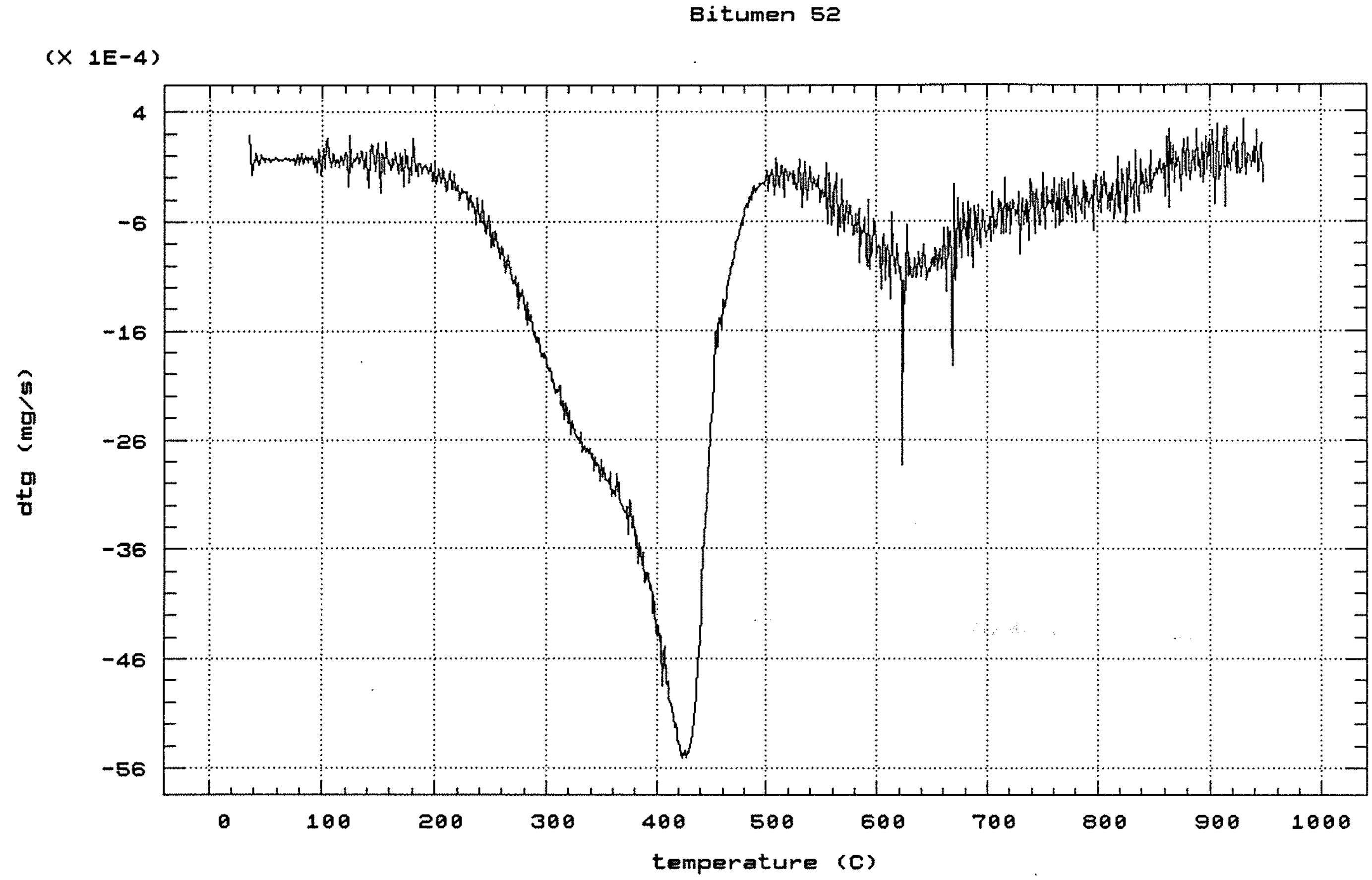


Figure 20. Thermogravimetric curves (nitrogen atmosphere), bitumen 537



First derivative of mass curve

Mass curve

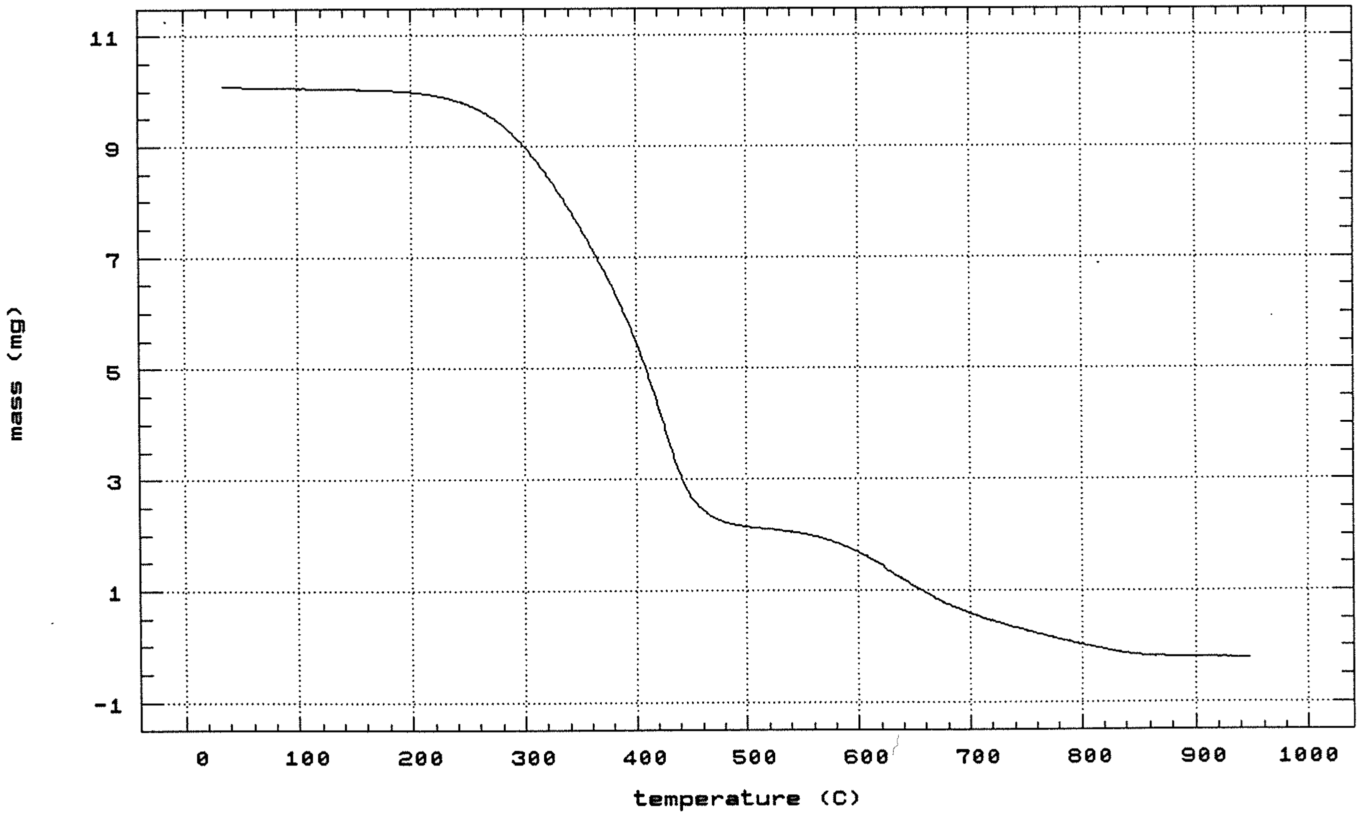
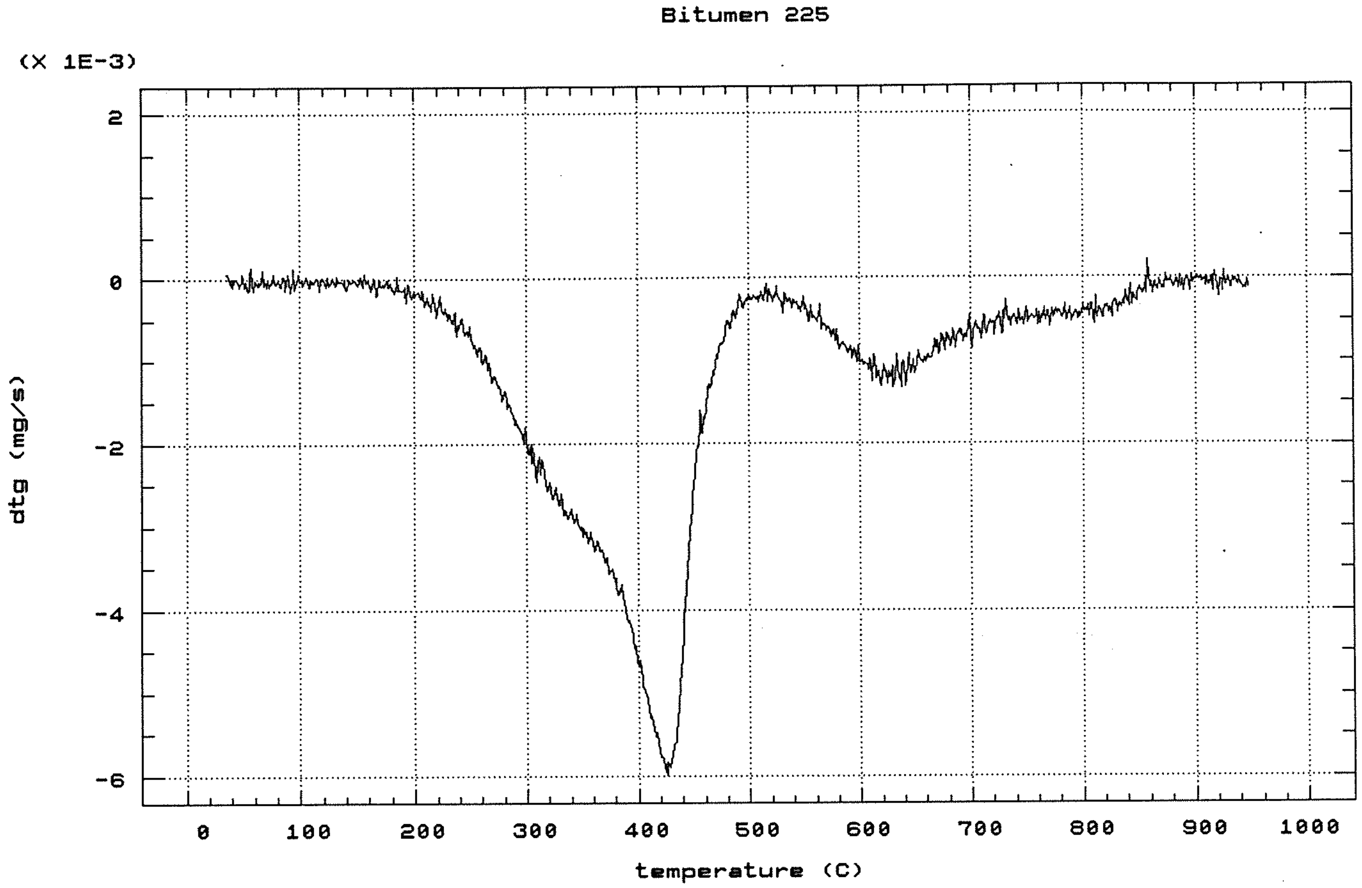


Figure 21. Thermogravimetric curves (nitrogen atmosphere), bitumen 52



First derivative of mass curve

Mass curve

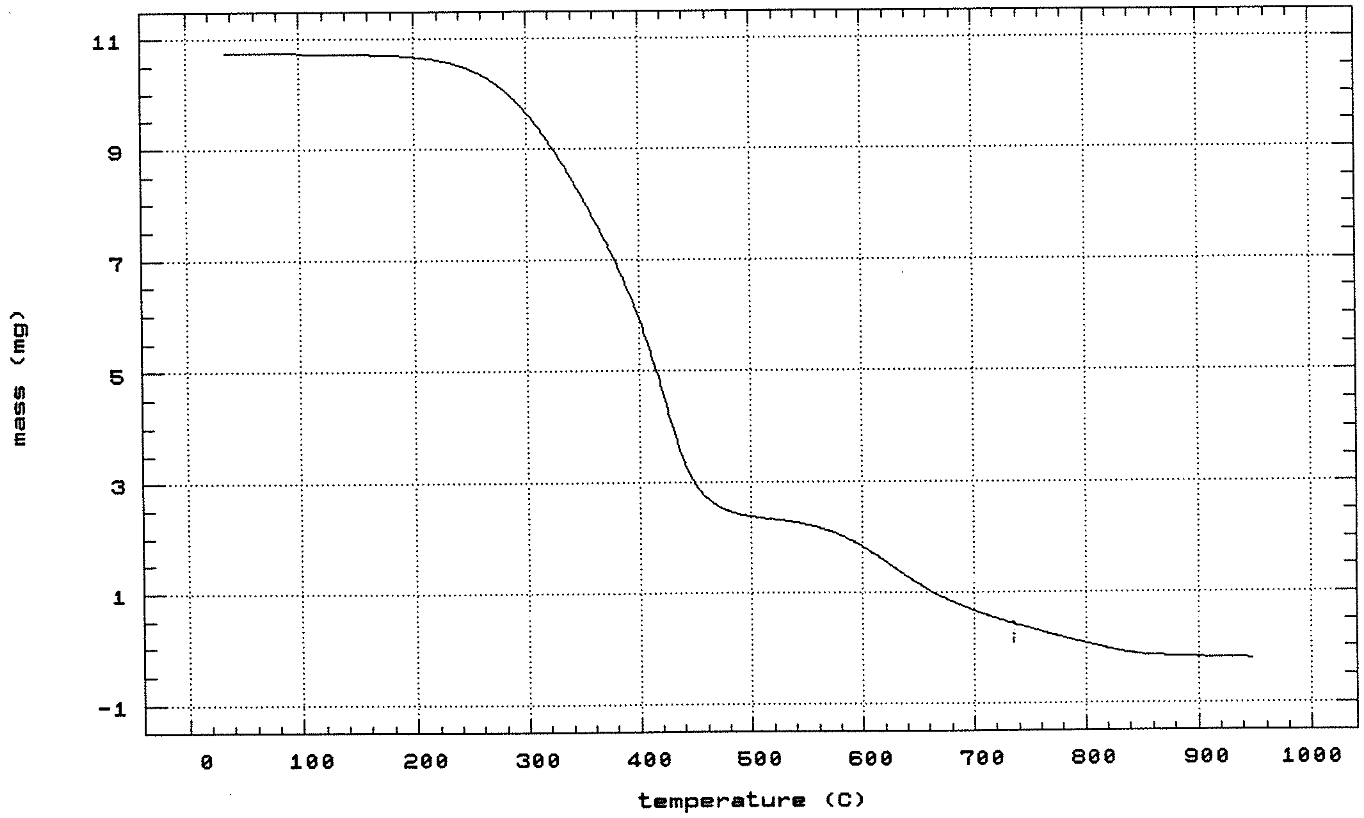
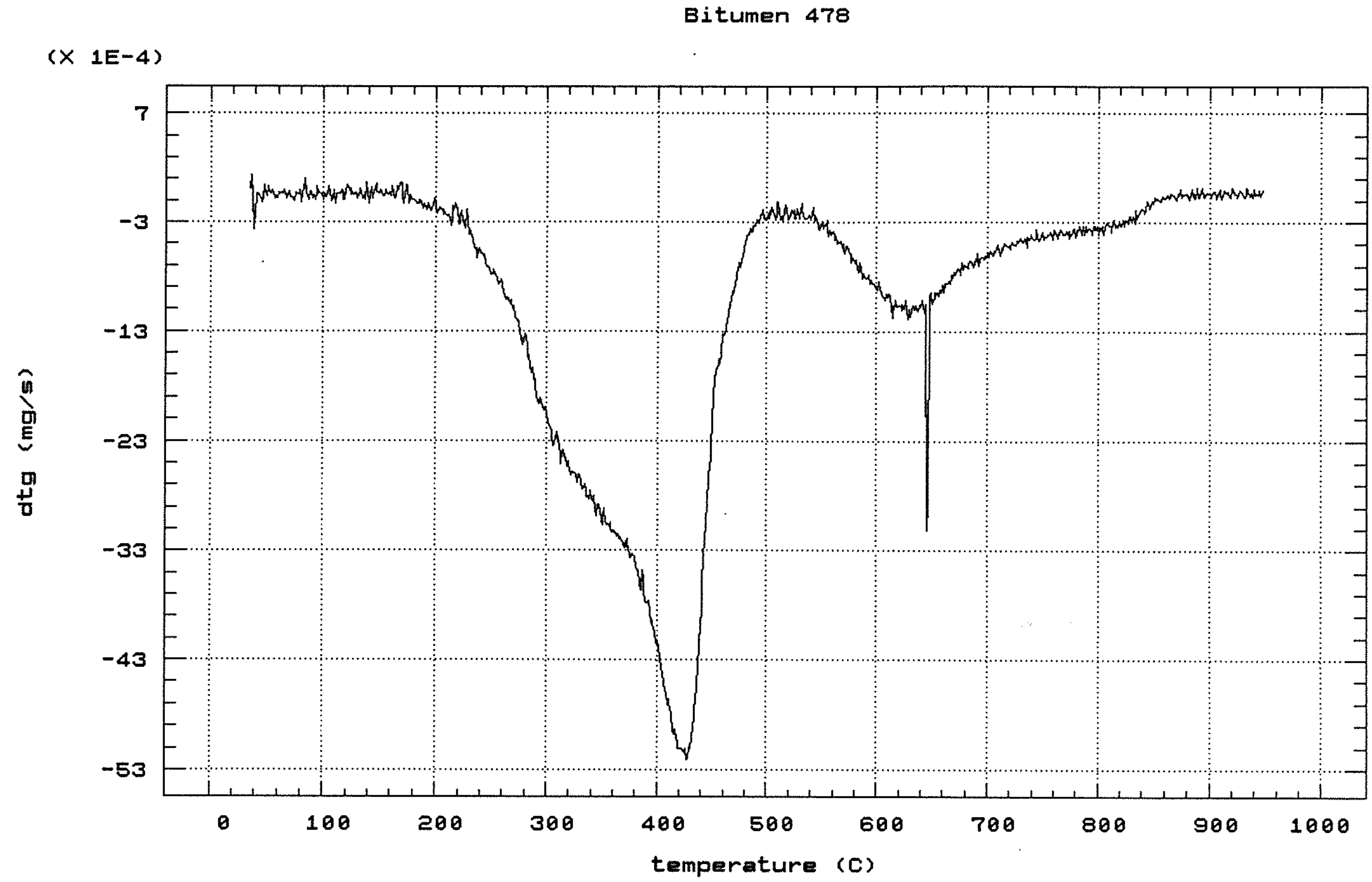


Figure 22. Thermogravimetric curves (nitrogen atmosphere), bitumen 225



First derivative of mass curve

Mass curve

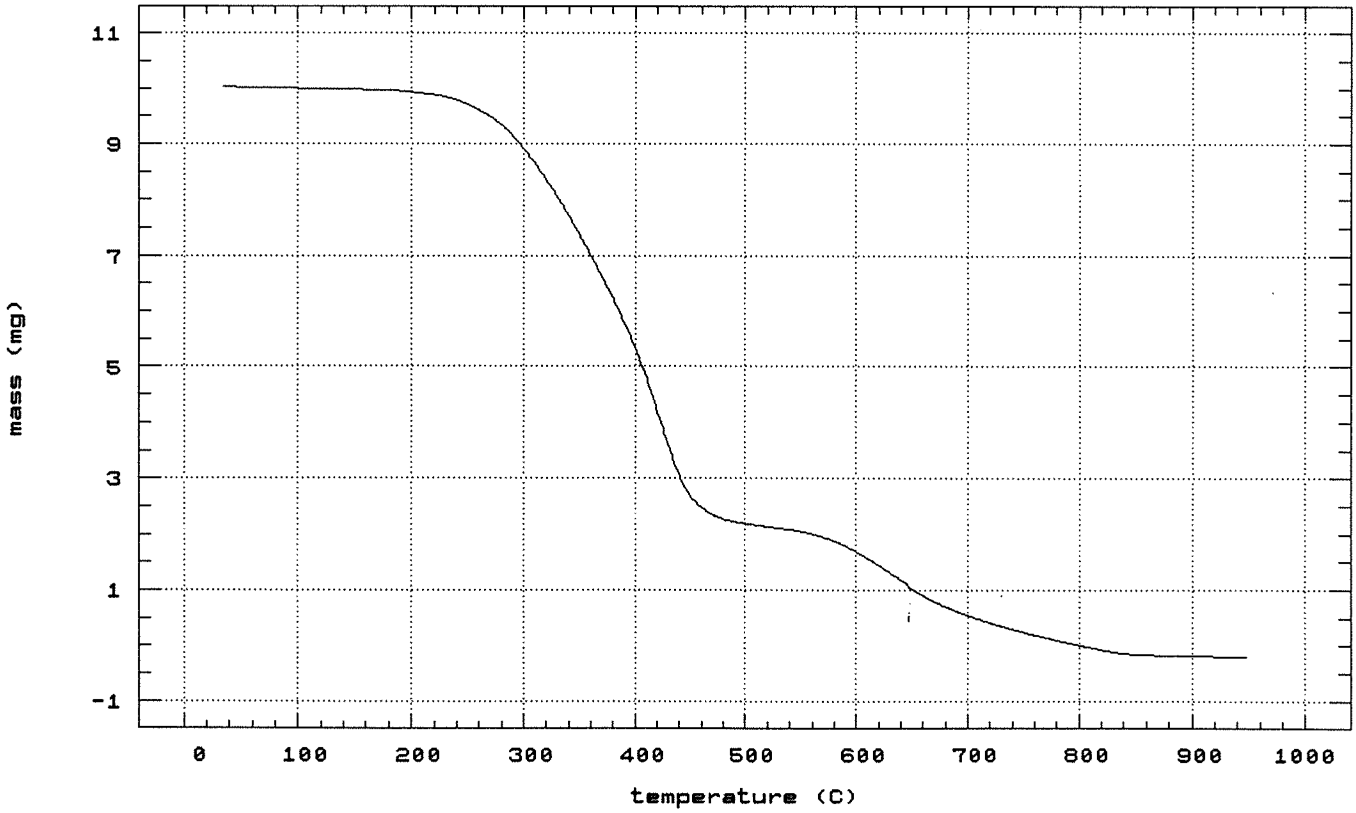


Figure 23. Thermogravimetric curves (nitrogen atmosphere), bitumen 478

10. PHYSICAL ADHESION

During the course of this work we became aware of earlier data (G.F.A. Ball, unpublished data) comparing the adhesion of bitumen 537 and a 1989 180/200 bitumen (which met the specifications of TNZ M/1). The procedure used in that work was based on that of the Vialit test currently used for adhesion agent approval. The two procedures are described here.

Procedure 1 (from Ball) - Galvanised iron plates (20 x 20 cm) were coated with a film of bitumen (40g) and allowed to stand (2 hours) in a constant temperature room (21°C). One hundred washed and air-dried chippings, also at 21°C, were placed individually on each plate and rolled in. The prepared plates were allowed to stand at 21°C for 24 hours (to allow good bond formation) and were then placed in a 21°C water bath for a further 22 hours. After this time, plates were removed (four at a time) at intervals and tested as for the standard Vialit test. Results for this work are presented in Table 9. Although there is some variation, both bitumens are seen to have given very similar adhesion values.

Procedure 2 (after Ball) - To compare results of our procedure with those of Ball, another test was carried out using bitumens 537 and 225. Ball's procedure was followed except that the plates were not immersed in water and were tested at intervals timed from the addition of the chip, i.e. without an initial "bond formation" period. The results (Table 9) show that both bitumens give comparable values although the results are all near the 100% mark.

Table 9. Physical adhesion test data.

Procedure 1 (from Ball): 24-hours bond formation followed by 22 hours water immersion at 21.0°C ±0.5

Bitumen	Percentage of Chips Retained
537	75.5
"1989"	77.8

Procedure 2 (after Ball): immediate testing after rolling, without 24-hour bond formation at 21.0°C ±0.5

Bitumen	Percentage of Chips Retained at Specified Times					
	0.25	0.5	1	4	8	24 Hours
537	n.d.	n.d.	95	100	95	98
225	100	97	98	100	100	100

n.d. = not determined

11. CONCLUSIONS

The physical properties (as measured according to TNZ M/1), elemental analyses, nmr spectra, IR spectra, asphaltene content, and DSC thermograms of the 1986 and 1991 Safaniya bitumens are very similar, and do not support the contention that the old and new materials are significantly different. This is also borne out by the results of the simple adhesion test that was carried out.

Although the molecular weight of the 1986 bitumen is lower than those of the 1991 bitumens, the spread of results between these materials is too large to confidently conclude that this difference is significant.

The thermogravimetric analyses carried out in air show clear differences between the eight Safaniya bitumens studied. The weight losses in air at such high temperatures are related to a complex combination of pyrolysis and oxidative decomposition reactions. The differences in the weight loss data are thus difficult to interpret in terms of the original bitumen composition, although no apparent trend or pattern differentiates the pre-1990 samples from the later bitumens.

No significant difference in the composition of the 1986 and 1991 bitumens is obvious from the results presented here, although only a very small sample of the total bitumen production over that period has been studied.

In addition, the binder actually used in the field is almost always modified with adhesion agents, fluxes and cutters, and the effects of these additives have not been considered here.

Bitumen-aggregate adhesion is a property determined not only by the properties of the bitumen, but also by the mineralogical characteristics (and physical state) of the aggregate. All are significant factors in determining bonding efficiency.

12. RECOMMENDATIONS

- Given that the bitumen being produced in New Zealand appears to be consistent in terms of its chemical composition, work that establishes the number and exact circumstances surrounding reported stripping failures is necessary. This will allow common contributory factors or combinations of factors to be identified.

- To provide rapid answers to the immediate problem, efforts should be directed towards development of a method for the direct, realistic, empirical comparison of physical adhesion of different bitumens.

  Such a procedure would be used simply as a research tool, and thus would not require the refinements and scale of investment previously made to establish the Vialit test currently used for determining the relative effectiveness of adhesion agents.

  Such research should complement the research project "Adhesion Properties of Bitumen for Chipsealing" (PR3-0057), currently being undertaken by Works Central Laboratories.

- The inclusion of some form of chemical characterisation (such as thermogravimetry or infrared analysis) should be considered as an adjunct to the routine TNZ M/1 testing carried out under the current bulk bitumen programme. This would provide a database for the comparison of bitumens, and allow detection of trends or sudden changes.

13. REFERENCES

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