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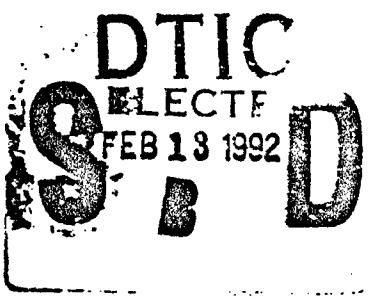

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ABSTRACT

The current method employed in the determination of the moisture content of activated carbon is the American Standard Test Method (ASTM) D-2867 (1976), using xylene extraction. However, this test is time-consuming and requires an elaborate experimental set-up. Furthermore, the ASTM has been found to be unsuitable for ASC/T carbon which contains triethylenediamine (TEDA). For this reason, alternatives to the ASTM were considered in this study. The ASTM method has been modified by replacing the extracting solvent xylene with toluene, to reduce the quantity of TEDA being collected with the water. Another alternative is the use of a convection oven where carbon samples were dried under three conditions: 150°C for 3 hours, 105°C for 3 hours and 105°C for 16 hours, and the moisture content results compared. This alternate method proves to be more efficient and the results obtained are comparable to that of the ASTM method. The optimum drying conditions for the accurate determination of moisture content on BPL, ASC and ASC/T carbons were determined to be 105°C for 60 minutes, 150°C for 90 minutes and 105°C for 90 minutes respectively. The last alternative considered was the use of a thermal analytical technique, namely Differential Scanning Calorimetry (DSC). It has been determined in this study that DSC can be used as an analytical tool for the determination of moisture content on carbons. However, better resolution of the DSC thermogram is required for precise measurements in moisture content determination.

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RÉSUMÉ

La méthode couramment utilisée dans la détermination du contenu en humidité des charbons de bois activés est "l'American Standard Test Method" (l'ASTM) D-2867 (1976), utilisant la méthode d'extraction avec le xylène. Cependant cette méthode prend beaucoup de temps et requière un montage élaboré. Par ailleurs, l'ASTM a été trouvé peu approprié pour le charbon ASC/T qui contient le triethylenediamine (TEDA). Pour cette raison, des méthodes alternatives à l'ASTM ont été considérées lors de cette étude. La méthode de l'ASTM a été modifiée en substituant le solvant d'extraction xylène par le toluene, pour réduire la quantité de TEDA qui était extrait avec l'eau. Une autre méthode alternative est l'emploi d'un four à convection où les échantillons de charbon de bois étaient séchés sous trois conditions: 150°C pour 3 heures, 105°C pour 3 heures et 105°C pour 16 heures et en comparant le résultat de la quantité d'humidité obtenue. Cette dernière méthode s'est montrée plus efficace et les résultats obtenus sont comparables à ceux obtenus avec la méthode de l'ASTM. Les conditions de séchages obtimum pour une détermination précise de la quantité d'humidité sur les charbons de bois BPL, AST et AST/T ont été déterminées être 105°C pour 60 minutes, 150°C pour 90 minutes et 105°C pour 90 minutes respectivement. La dernière méthode considérée à été l'emploi d'une technique aralytique thermale, c'est-à-dire la calorimétrie à balayage différentielle (DSC). Il a été démontré lors de cette étude que le DSC peut-être utilisé comme instrument analytique pour la détermination de la quantité d'humidité dans les charbons. Cependant, une meilleure résolution du thermogramme du DSC est requise pour des mesures plus précises pour la détermination de la quantité de l'humidité.

EXECUTIVE SUMMARY

The use of activated carbon in Canadian gas-mask canisters is governed by very strict specifications and requirements. One of the requirements is that the moisture content of the activated carbon cannot exceed 2%. The activated carbon employed in most gas-mask canisters is a base carbon which has been impregnated with copper, chromium and silver. After impregnation this carbon is called 'ASC Carbon'. Canada is currently employing an ASC/T carbon which is an ASC carbon further impregnated with an organic compound, triethylenediamine (TEDA), in the gas-mask canister. Water can be adsorbed on the surface of ASC carbon readily, and can reduce the performance of activated carbon in removing toxic materials from air. The 2% ceiling set for the moisture content on ASC carbon thus guarantees an adequate performance of the carbon.

The method currently employed in the determination of moisture content on carbon is the American Standard Test Method (ASTM) D-2867 (1976), using xylene extraction. This method is very time consuming and requires elaborate laboratory set-up. For this reason, the ASTM is not a good choice to be used as a quality assurance tool. Furthermore, it has been found that TEDA was also removed (along with water) in the xylene extraction, thus making the ASTM method not suitable for this purpose. The objective of this study was to analyze alternatives which can be used in the accurate determination of moisture content on carbon. The first task was an attempt to apply the ASTM extraction method to ASC/T carbon. This is accomplished by the replacement of xylene with toluene as the extracting solvent. The first alternative to the ASTM method considered was drying of the carbon samples by a forced convection oven. This method was simpler to use and has been found to yield results comparable to the ASTM method. The optimal drying conditions for BPL, ASC and ASC/T carbons were determined to be 105°C for 60 minutes, 150°C for 90 minutes and 105°C for 90 minutes respectively. Another alternative considered in this study was the use of a thermal analytical method known as the Differential Scanning Calorimetry (DSC). The results obtained demonstrated that DSC could be used as a quantitative tool in the determination of moisture content on carbon samples. For more accurate determination, a DSC with better resolution is required to improve the precision of the instrument.

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1.0 INTRODUCTION

Activated carbon (or charcoal) is a universal adsorbent for the removal of a variety of organic/inorganic contaminants, in both gaseous and aqueous phase. For military purposes, activated carbon has been used in the removal of a variety of air-borne toxic materials in the gas-mask applications. However, activated carbon has a very low adsorption capacity for a class of toxic chemicals which has low molecular weight and/or low boiling points, such as hydrogen cyanide (AC), cyanogen chloride (CK) and phosgene (CG). Thus, activated carbon is impregnated with copper, chromium and silver, to produce what is commonly referred to as ASC whetlerite (1), to enhance its chemical reactivity. It is believed that these chemical impregnants react or catalytically convert all the toxic vapors mentioned above into innocuous products. More recently an extra impregnant, triethylenediamine (TEDA), was added to the impregnating formula to increase CK protection, while prolonging the shelf-life of the impregnated carbon (2). This new carbon is designated as ASC/TEDA (or ASC/T) carbon.

Impregnated activated carbon (the ASC carbon), loses its chemical reactivity (i.e. performance reduction) easily in the presence of moisture. It is common experience that ASC carbon which has been exposed to open air for some time, cannot recover to its original chemical activity, even after the removal of water from the surface of the impregnated carbon. This phenomenon is called ageing. Thus, the impregnated carbon is preferably kept in a closed container to maintain the moisture content below 2% (by mass). This ceiling on the moisture content has been required by the Canadian Forces for years (3), and has been recently adopted by the United States, United Kingdom and Canada in an international purchase specification (4).

Since the performance of the impregnated carbon depends so much on the moisture content, the method employed in the determination of the moisture content on carbon is very important and should be strictly enforced. There exist several kinds of activated carbons, such as the ASC and the ASC/T mentioned above, and also the BPL carbon (the precursor base carbon for the ASC carbon, i.e. carbon which has no impregnation history). There are also various impregnated carbons obtainable from different manufacturers, such as Calgon Carbon Corporation (USA), Sutcliffe-Speakman (UK), Norit (Netherlands), and PICA (France). Furthermore, different companies utilize different carbonaceous precursors, which include coal, coconut shell and various other sources. It is therefore important to establish that a standard testing method can be employed for all activated carbons manufactured and impregnated differently, and from different precursor materials.

The standard method employed in the moisture content determination quoted in the international purchase specification originates from the American Standard Test Method (ASTM) D-2867 (1976), using xylene extraction. However, this ASTM method requires a minimum of six hours of the xylene extraction for each determination, which is very time consuming. The objective of this technical note is: i) to evaluate if this standard method of moisture determination using xylene extraction is optimised, and ii) to evaluate the merits of alternate methods which can be used to determine the moisture content of carbon and which may be as accurate as the ASTM method.

1.1 SCOPE OF THE PROJECT

It is obvious that an alternate method for the moisture determination could be as simple as measuring the mass difference before and after drying the carbon inside an oven. However, Canada has adopted ASC/T carbon as the adsorbent of choice to be used in the gas-mask canister. TEDA melts at about 160°C, and is known to sublime at as low as 40°C (5). Thus drying the carbon samples inside an oven at high temperature is not a good alternative. Furthermore, a suitable temperature and duration of the heating step has to be 'fine-tuned' to ensure that the results obtained are comparable to the ASTM method. As will be detailed later in this report, the problem of TEDA extracted from the ASC/T carbon also exists for the ASTM method.

Another alternate method which has been considered in the moisture determination in the course of this study was thermal analysis using a Differential Scanning Calorimetry (DSC) assembly. It has been demonstrated in the literature (6) that this method can detect the presence of water on carbon samples. However, no quantitative analysis using this analytical tool has ever been performed to date. Thus the second objective of this project is to determine if the DSC can be used as a quantitative tool for the moisture determination on carbon samples.

2.0 EXPERIMENTAL

The standard method quoted in the international purchase specification for activated carbon in the determination of the moisture content of activated carbon has been described in ASTM D-2867. This method is believed to produce the most accurate results. Moisture content on seven carbon samples and a control standard were determined using this standard method. The results were then used as standard references against which moisture determination obtained from other methods could be compared.

2.1 MATERIALS

The carbon samples tested include i) a BPL-grade ASC-base carbon Lot No. 937-YB, a base carbon for the preparation of ASC carbon, ii) an ASC carbon Lot No. 1048, which is over 10 years old, iii) an ASC carbon Lot No. 1746, recently procured (about 2 years old), and iv) an ASC/T carbon, Lot No. 947, containing about 1.5% of TEDA (by weight). All of these carbons were procured from Calgon Carbon Corporation, Pittsburgh, USA. The size of the carbon granules employed in this study is 12 to 30 US mesh. The chemical, triethylenediamine (TEDA) used for the impregnation of BPL and ASC charcoal was obtained 97% pure from Aldrich Chemical Co. The TEDA was used directly from the container without further purification. All carbons used were removed from the 220 litre (50 gallon) shipping drums and placed inside plastic containers (ca 500 g size) that sealed well. The carbon samples required for each test were then taken out from the plastic containers. This ensured that all the carbon samples used in the experiments were exposed to a similar controlled environment and were obtained from a single source.

Other chemicals such as xylene and toluene were all reagent grade obtained from Aldrich Chemical Co., Milwaukee, USA. They were used in all experiments without further purification.

2.1.1 Standard

Calgon BPL carbon Lot No. 937-YB was used as the control standard in all experiments. About 500 g of this carbon was added to a desiccator and was dried inside a forced convection oven for 3 hours at 150°C. The carbon was then placed in a series of small plastic containers and sealed well. Only one container was used for each experiment.

2.1.2 Specially-Prepared BPL/TEDA Carbon Samples

In order to construct a database, some TEDA impregnated carbons were custom-prepared in the laboratory. A BPL grade ASC-base carbon Lot No. 937-YB was employed as a starting material.

Two batches of BPL carbon were impregnated with approximately 10% TEDA. About 500 g of the BPL carbon was placed in a 2.2 litre vacuum desiccator and dried inside a forced convection oven at 150°C for three hours. The desiccator was then removed from the oven and a greased (with high vacuum silicone-based grease) lid was placed on the desiccator and the carbon was allowed to cool to room temperature. Once the carbon was cooled, the lid was removed and approximately 51 g of TEDA was accurately weighed and added to the

carbon (making up to ca 10% by weight of TEDA on carbon). The lid was quickly replaced on the desiccator and a vacuum at 1.33 Pa was applied to the desiccator for about one minute. The desiccator was then placed inside an oven for 2-3 days at 50°C for equilibration. This procedure was developed at DREO and an application for a patent has been filed (7). Once the impregnation process was complete (no visible presence of TEDA crystals), the carbon was removed from the desiccator and placed into a polypropylene container. This sample was designated as BPL/T/10/DRY.

Another sample, BPL/T/10/WET was prepared similarly as above, except that the BPL carbon used was not dried at all. About 50 g of TEDA (accurately weighed) was placed directly onto 500 g of the BPL carbon inside a vacuum desiccator. The greased lid was placed onto the desiccator and a vacuum also at 1.33 Pa was applied to the desiccator. The desiccator was then placed in the oven at about 60°C for 3 days. Once the impregnation was complete, the carbon was placed inside another polypropylene container ready for testing.

2.1.3 Specially-Prepared ASC/TEDA Carbon Samples

A sample, ASC/T/10 was prepared by impregnating Calgon ASC carbon Lot No. 1746 with TEDA. The procedure is identical to that described above in Section 2.1.2. The impregnated carbon was also stored in a polypropylene container.

2.2 MOISTURE CONTENT DETERMINATION

2.2.1 Xylene Method

This method was based on the ASTM D-2867 (1976) with some modifications to the experimental procedure. The experimental set up is shown in Figure 1. A round bottom flask was used as a container for the carbon and xylene, and stirred using a magnetic spin bar. A Glass-Col heating mantle was used to heat up the carbon and xylene mixture to a boil. A Mag-Mix was placed underneath the heating mantle and was used for stirring the solution. The rate of heating of the mantle was controlled by a Power Stat. The flask was attached to a Lurex 10 mL water trap followed by 300 mL water-cooled condenser. Pyrex ground-glass joints (size 24/40) were used at all connections. A drying tube filled with Drierite and Pyrex glass-wool was attached to the top of the condenser.

A typical experiment consisted of adding approximately 50 g (accurately weighed to the nearest mg) of carbon sample into the round bottom flask followed by 150 mL of xylene. Before the commencement of heating, the complete apparatus was wrapped with glass-wool and aluminum foil to maintain constant temperature throughout. A typical reflux step lasted about 6.5 hours. At the end of the extraction of water from the reaction mixture, the solution was allowed to cool. The mass of the water extracted (i.e. moisture content of the carbon sample) was deduced from the volume of the water collected inside the trap.

2.2.2 Toluene Method

The apparatus and procedure employed for this extraction is identical to that described for the xylene method except that 150 mL of toluene was used and less heating was required.

2.2.3 Oven Drying Method

This method involved the use of a Fisher Isotemp Oven 400 series (Model 438F) forced air convection oven in determining the moisture content of the carbon. Two temperatures were used: 105°C and 150°C. Carbon samples were dried inside the oven under the following conditions:

(i)	150°C for 3 hours	(Test A)
(ii)	105°C for 3 hours	(Test B)
(iii)	105°C for 16 hours	(Test C)

Ten duplicates for each carbon sample (using glass vials and matching lids) were carried out in each moisture determination. Approximately 4 grams of carbon granules (accurately weighed) were placed into each vial. The glass vials and the lids (separated) were then placed inside the oven. After the designated period of drying time, the lids were put back on the vials and were removed from the oven. They were then placed and cooled inside a vacuum desiccator. The mass of the 'dried' carbon samples were then obtained. The average moisture content of the carbon sample was assumed to be the mass loss from the carbon sample.

2.2.4 Differential Scanning Calorimetry Method

A Dupont Thermal Analyst 2100 operating with a 910 Differential Scanning Calorimeter (DSC) assembly was employed in the moisture determinations of all the carbons. A description of the equipment, the general operation and experimental uncertainties of the DSC will be detailed in another report (8). Approximately fifteen milligrams of carbon granules were placed inside a 40-μL aluminum pan with an aluminum cap. The samples were finely

crushed. The reference pan was provided with a similar but empty sample pan (with a cap). Experiments were carried out under a flow of nitrogen (100 mL/min). A temperature enthalpy analysis was carried out between 25°C and 600°C at a heating rate of 25°C/min. The data was stored on floppy disk and processed with a microcomputer.

2.2.5 Calibration of the DSC

In order to use the DSC as a quantitative tool in the moisture determination of carbon samples, the DSC curve indicating the enthalpy changes of the carbon sample has to be calibrated. Control standards were prepared for the three types of carbon used in this study (the BPL, ASC and ASC/T carbons). They were prepared as follows: the carbons were first dried in the forced air convection oven at 150°C for 3 hours and then the required amounts of water were added to the carbons to make up to the desired loading levels of 1% to 5% (w/w) moisture content. The containers of the carbons were then sealed and equilibrated at 50°C for 3 days.

2.3 PROFILES OF MOISTURE LOSS ON THE CARBON SAMPLES

2.3.1 Oven Drying

The profiles of the loss of water from the carbon versus time during oven drying at 105 and 150°C were obtained for the three types of carbons used in this study. The experiments were performed as follows. For each carbon sample, 18 glass vials with matching caps were used. About 4 grams of carbon (accurately weighed) were added into each of these 18 vials. These vials with the caps removed were then placed inside the oven preheated to the desired temperature (105 or 150°C) all at the same time (Time Zero). At the right time interval, two vials with their matching caps were removed, cooled and weighed at the following time intervals starting from time: zero, 30, 60, 90, 105, 120, 135, 150, 165, and 180 minutes for a total of 3 hours. The mass loss (moisture content) of the carbon sample at each time interval was then plotted against time to obtain the moisture profile.

3.0 RESULTS AND DISCUSSION

Based on the ASTM D-2867, the recommended way to determine the moisture content of carbon is by the six-hour xylene extraction method. With this study, several alternate methods were studied and compared with this standard method.

3.1 ASTM EXTRACTION METHODS

The results using the ASTM method are summarized in Table 1. In order to assess the accuracy of each test, a control carbon sample was used. This carbon standard was pre-dried at 150°C for several hours to ensure that the carbon was dry. As expected, the ASTM method gave a value of 0.0% for its moisture content.

As mentioned previously, the maximum allowable moisture content for respirator carbon is 2.0% (3,4). The results from the xylene extractions indicated that the BPL carbon and the BPL/T/10/WET have moisture content well above 2.0%. It is well known that carbon picks up moisture readily, especially BPL and ASC carbon. However, carbons which have been impregnated with TEDA appear to pick up less water for both BPL and ASC types, probably indicating the surface hydrophobicity that TEDA has created for the carbon. For this reason considerations were made in choosing an experimental procedure that would minimize the exposure of carbon samples to the atmosphere. The carbon was taken from the large shipping drums and placed in smaller 1L plastic containers. Then all the tests were carried out in the same day to avoid unnecessary exposure to air.

As stated earlier, the experimental procedure for the ASTM xylene method has been modified. These changes were made: (i) to reduce heat loss to the surroundings, the whole set-up was wrapped first with glass wool and then with aluminum foil; (ii) to ensure a more thorough stirring of the solution containing the xylene and carbon granules, a magnetic stirrer was used; and (iii) to maintain a more accurate temperature control of the experiment, a heating mantle was used. It has been observed that carbon impregnated with TEDA displayed a unique feature during the xylene extraction. During the extraction, it was observed that a white crystalline solid had condensed on the inside of the condenser and inside the water trap. The crystals were later determined to be TEDA. It also appeared that TEDA in the water trap was either dissolved in the water or had precipitated out, thus increasing the volume of water at the bottom of the water trap. (Note: TEDA is very soluble in water. Although no detailed experiment was done, it is believed that the volume expansion of water due to dissolved TEDA will be quite small.) This led to inaccurate measurement of the moisture content of the carbon, which depended on the volume of the water collected in the trap. This observation occurred mostly in carbon samples which have been impregnated with a large quantity of TEDA e.g. at 10% loading level.

To avoid this problem, another solvent, toluene, with a lower boiling point was employed. The ASTM experimental procedure was followed exactly. Toluene is in an analog of xylene but with a lower boiling point (110.6°C) and a lower azeotrope temperature when combined with water (85°C). Table 2 summarizes a comparison of both solvents.

TABLE 1: Moisture Content (% w/w) Analysis of Carbon Using ASTM and Oven Drying Methods

Carbon	TEDA Content % (w/w)	ASTM		OVEN DRYING METHODS		
		Xylene	Toluene	Test A 150°C 3 hrs	Test B 105°C 3 hrs	Test C 105°C 16 hrs
Control Standard Calgon BPL Lot No. 937-YB	0	0.0 ±0.0	0.0 ±0.0	0.15 ±0.03	0.07 ±0.03	0.08 ±0.03
Calgon BPL Lot No. 937-YB	0	3.2 ±0.2	3.0 ±0.4	3.15 ±0.11	3.33 ±0.20	3.49 ±0.27
DREO BPL/T/10/Dry	10	0.3 ±0.1	0.2 ±0.1	0.43 ±0.07	0.33 ±0.05	0.44 ±0.07
DREO BPL/T/10/Wet	10	4.0 ±0.7	3.1 ±0.3	3.95 ±0.05	3.42 ±0.09	3.43 ±0.05
Calgon ASC Lot No. 1048	0	2.0 ±0.4	1.7 ±0.2	1.71 ±0.07	1.52 ±0.05	1.60 ±0.05
Calgon ASC Lot No. 1746	0	0.8 ±0.1	0.4 ±0.1	0.57 ±0.09	0.40 ±0.07	0.48 ±0.05
DREO ASC/T/10	10	1.3 ±0.2	0.6 ±0.1	3.80 ±0.19	0.41 ±0.10	0.60 ±0.16
Calgon ASC/T Lot No. 947	1.5	1.7 ±0.1	1.3 ±0.3	1.79 ±0.04	1.28 ±0.18	1.38 ±0.09

TABLE 2: Comparison of Solvents Used in the ASTM Method

CHEMICAL PROPERTIES	XYLENE	TOLUENE
CHEMICAL STRUCTURE	C_8H_{10}	C_7H_8
BOILING POINT (°C)	139.1	110.6
DENSITY (g/mL)	0.8642	0.8669
SOLUBILITY IN WATER	insoluble	insoluble
SOLUBILITY OF TEDA IN THIS SOLVENT	insoluble	insoluble
AZEOTROPE WITH WATER:		
BOILING POINT (°C)	94.5	85.0
PERCENT COMPOSITION:	XYLENE H_2O	TOLUENE H_2O
IN AZEOTROPE	60.0 40.0	79.8 20.2
UPPER LIMIT	99.95 0.05	99.95 0.05
LOWER LIMIT	0.05 95.95	0.06 99.94
RELATIVE VOLUME OF LAYERS AT 20°C:		
UPPER	63.4	82.0
LOWER	36.6	18.0
SPECIFIC GRAVITY OF LAYERS :		
UPPER	0.868	0.868
LOWER	1.000	1.000
BOILING POINT OF WATER (°C)	100	100

The values for this chart were obtained from the CRC Handbook of Chemistry and Physics.

For carbons without TEDA impregnation, the toluene and the xylene extractions yield similar moisture results. However, the moisture content of TEDA-impregnated carbon was generally lower for the toluene extraction than for the xylene extraction.

3.2 OVEN-DRYING METHODS

The oven drying method was chosen as an alternative in determining the moisture content of the carbon samples, because of its simplicity. Three conditions were chosen: at 150°C for 3 hours (Test A), at 105°C for 3 hours (Test B) and at 105°C for 16 hours (Test C).

The results from Test Condition A and those obtained from xylene extraction are comparable, except for ASC carbon containing 10% TEDA. The moisture content obtained from oven-drying at 150°C is about three times higher than that obtained from the ASTM method using xylene extraction. This is in contrast with those values observed for BPL carbon containing 10% TEDA (wet or dry impregnation). The value of 3.8% for the moisture content on the ASC carbon containing 10% TEDA is considered too high, and this has been attributed to the co-desorption of TEDA from the carbon surface during the drying process. This is substantiated by the fact that during the preparation of this ASC carbon containing 10% TEDA, the ASC carbon was dried before the TEDA impregnation process, and therefore it would be expected that a value of 1.3% (from xylene extraction) would be more reasonable for moisture content.

It should be pointed out that the TEDA content of the carbon samples should be measured before and after the oven-drying procedures so that the true amount of water being removed from the carbon surface could be determined accurately. However, recent work at this laboratory and elsewhere (9) have shown that both the Canadian gravimetric method (5) and a methanol extraction method (4) for the quantitative analysis of TEDA are far from satisfactory. Calgon Carbon Corporation has been proposing a revised method for TEDA determination for their new impregnated carbon (10). Thus, this problem of the TEDA determination will be left as is until a better analytical method has been forged.

A lower temperature (105°C) was employed for Test Conditions B and C. The moisture content results from Test Conditions B and C are comparable, indicating that an extended drying period is not necessary. This observation will be elaborated later on in the section of the Moisture Loss Profiles. Furthermore, the results from Test Condition B compared more favourably with the toluene extraction values especially for carbons which have been impregnated with TEDA. It is not surprising to note that all test methods listed in Table 1 yielded similar results for carbons not impregnated with TEDA.

By comparing all the results so far, it seems that i) the ASTM method gives rise to more acceptable results using toluene rather than xylene extraction; ii) replacing the extraction methods (toluene or xylene) with an oven-drying method at suitable temperatures and duration is simpler and quicker; and iii) for activated carbons impregnated with about 1.5% TEDA, oven-drying at 105°C for 3 hours would yield reasonable results (comparable to ASTM toluene extraction method). This method is preferred because the trend is now to go with ASC carbons containing TEDA at levels no higher than 3%.

3.3 MOISTURE LOSS PROFILES OF CARBON SAMPLES

In order to understand the desorption process of water (or simply, the removal of moisture) from the carbon surface, the following experiments were performed to determine how fast the water was removed from several types of carbon samples at 150°C and 105°C.

Figure 2 shows the moisture loss profile of a BPL carbon (Calgon Lot No. 937-YB) at different drying temperatures. As shown in Table 1, this carbon contains an original moisture content of about 3%. It is immediately obvious from the figure that both temperatures remove water from the BPL carbon at about the same rate, assuming that the loss of moisture is linear between 0 and 20 minutes. Furthermore, both moisture loss profiles level off (i.e. not removing any more water) at about 30 to 40 minutes after the samples were placed inside the oven.

A major difference between drying at these two temperatures was observed for ASC carbon (Calgon ASC Lot No. 1746) as shown in Figure 3. The moisture content obtained for this carbon varied from one determination method to another, as is shown in Table 1. Obviously from Figure 3, the rate of moisture loss is faster for drying at 150°C than for 105°C. Furthermore, while the profile at 150°C seemed to level off after about 100 minutes of drying, the profile for 105°C seemed to be increasing even after 3 hours of drying. The reason for these observations is not obvious except that it seemed that drying at 105°C is not high enough a temperature to remove water from the carbon surface. This may be attributed to the strong ionic interaction between the metal impregnants and the adsorbed water molecules.

Figures 4 and 5 show the moisture loss profiles of the two specially impregnated carbons, the BPL/T/10/WET and BPL/T/10/DRY respectively. In both figures, the moisture loss was higher for drying at 150°C than at 105°C. For the BPL/T/10/WET sample, the profiles for both temperatures seemed to level off after about 30 to 40 minutes of drying. The final rise of 'moisture loss' after 150 minutes of drying was attributed to the beginning of the desorption of TEDA molecules from the carbon surface. The profiles

of the two temperatures observed for the BPL/T/DRY sample were very different from that of the BPL/T/WET sample. The 'levelling-off' was not observed, although there was also an initial sharp increase in mass loss for drying at 150°C. The observed difference may be attributed to the different ways by which the carbons were impregnated. In the preparation of the BPL/T/10/WET, the carbon was used as received, i.e. there is a surface layer of water already present on the carbon before the impregnation of TEDA. It would be easy to conjecture that during the impregnation, the TEDA molecules are displacing the water from the carbon surface and making them more labile, thus the water is easily and quickly removed from the carbon surface, as shown in Figure 4. There is no such displacement in the case of BPL/T/10/DRY carbon. However, the behaviour of binary adsorption systems (TEDA and water in this case) are difficult to predict, and more difficult to understand. The 'steady-state' percentages of moisture loss at 105 and 150°C after 3 hours of heating shown in Figure 5 for BPL/T/10/DRY were different from those reported in Table 1 (entry #3). This was attributed to the different batches of this specially-prepared carbon used in the profile experiment. e.g. the water may not have been completely driven off in the initial drying process.

Lastly, the moisture loss profiles for the Calgon ASC/T (1.5% TEDA loading) carbon which is currently employed in the Canadian gas mask canister are shown in Figure 6. Once again the moisture loss is greater at the higher temperature of 150°C. Both curves exhibit a gradual increase of moisture loss over the 3 hour time period, which probably includes TEDA desorption also. Thus a lower drying temperature is advisable to minimize the loss of TEDA, which would confuse the moisture content data.

From these moisture loss profiles, it seemed that in the determination of moisture content of carbon samples: 1) drying the BPL carbon samples at 105°C for 60 minutes is more than adequate, 2) for ASC carbon, the oven-drying condition will be 150°C for about 90 minutes, and 3) for ASC/T carbon (containing about 1.5% TEDA), the optimum oven-condition is about 105°C for 90 minutes.

3.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC) RESULTS

For BPL and ASC carbons, it has been possible to correlate results from the ASTM method with the oven-drying methods in determining the moisture content of the carbons. However, for the ASC carbons impregnated with TEDA, such correlation did not exist. For this reason, the feasibility of DSC for this analytical purpose was attempted. Typical DSC curves are shown in Figures 7 to 9 for BPL, ASC and ASC/T carbons respectively. In general, an endothermic absorption peak (i.e. a 'dip' in the DSC curve which indicates that the direction of heat flow is towards the carbon sample) occurred between 60°C and 160°C for all carbons. This was

attributed to the heat required for the removal of water from the carbon surface, supported by the literature findings (6).

All carbons used in this analysis (BPL, ASC and ASC/T carbons) were pre-dried at 105°C for 3 hours. The carbon samples were stored inside glass vials fitted with ground-glass caps, and were weighed before and after the drying. Then accurately weighed water was added to the carbon, making up from 1 to 12% (by weight) of moisture on the carbon. Deionized, distilled water was used in these experiments. No trace analysis was performed on the water. It was assumed that any trace contaminant would not interfere with the DSC measurements at these water loading levels. These water-added carbon samples were then left inside the glass vials and allowed to equilibrate inside an oven at 50°C for 3 days. DSC measurements were performed on these water-treated carbon samples from 25°C to 600°C (except ASC/T carbons which were only measured up to 250°C). The size of the first endotherm peak (corresponding to the amount of heat absorbed) increases as the amount of moisture on the carbon increases, and this was observed for all the three carbons studied (as shown in Figure 7 to 9).

All observed DSC curves showed an initial dip (of about 0.5 J/g), indicating that the carbon samples were being heated. The endotherm corresponding to the moisture removal from the carbon surface started at 75°C and ended at around 160°C, with the peak maximum occurring at around 100°C. The DSC curve labelled 'DRY' for all three types of carbons consisted of a carbon sample which was only dried at 105°C for 3 hours, thus it would still contain a fair amount of water inside the structure.

For BPL carbon, as shown in Figure 7, all endotherms occurred at around 100°C, except the carbon sample containing 5% of water for which the peak maximum occurred at ca 125°C. The same shift of the endotherm was observed on repeated runs of the same batch of carbon. This is explained as follows: at higher moisture content (5% in this case), a higher percentage of the adsorbed water molecules would be situated inside the microstructure of the carbon. Since activated carbon itself is a poor conductor of heat, it would take more time for the heat to transfer from the carbon surface to the inner structure so that the water molecules can be evaporated and removed. Furthermore, the carbon sample was heated at a rate of 25°C/minute (therefore the temperature axis is also, in a sense, a time axis), a longer heating period would then imply a higher temperature at which the endotherm occurred. BPL carbon samples with added water as high as 20% by weight, showed an endotherm at ca 150°C, confirming this trend. This shift of the endotherm attributed to water removal, is not as pronounced in the cases for ASC and ASC/T carbons. In general, this endotherm occurred at ca 125°C for ASC and 150 °C for ASC/T carbons. This higher temperature (or longer heating period) at which the water is removed from the carbon surface is attributed to the stronger interaction between the water molecules and the metal impregnants

on the carbon surface, rather than the amount of water present. This explanation is based on: 1) the endotherm did not shift to higher temperature at higher loading level of water; and 2) because of the ionic nature of the metal impregnants, the sites on the carbon surface which are occupied by the metal offer stronger interaction to the water molecules because of their polar nature.

The moisture content of the carbon was then plotted against the heat absorbed in this endothermic change (i.e. the area underneath the endotherm on the DSC curve). The plots are shown in Figure 10 for all three carbons, which in general show a linear relationship. None of the regression lines passed through the origin, because the carbon which was labelled 'dry' was only dried at 105°C for 3 hours, and could still contain a substantial amount of water in the pore structures. Regression analysis using a first-order least squares fit was applied to all three relationships, and the following results were obtained:

BPL : $Y = -0.520 + 0.0702X$ $(R^2=0.997)$ [1]

ASC : $Y = -2.003 + 0.0729X$ $(R^2=0.990)$ [2]

ASC/T: $Y = -0.800 + 0.0914X$ $(R^2=0.978)$ [3]

Note that the linear regression used all the data up to 5% moisture only. The data corresponding to higher moisture content (e.g. 12% for ASC carbon) was put on the regressed line afterwards, and was not used in the regression model. This observation, combined with the very good regression coefficient (R^2) show that a reasonable linearity exists. Furthermore, this indicates that moisture content can be extrapolated from the regression model, if the heat absorbed (i.e. the area of the endotherm under the DSC curve) due to water removal is obtained by DSC measurement. The standard deviation associated with the determination of the area under the DSC curve has been estimated to be ± 15% (8). Thus, the moisture content on the carbon surface determined by DSC analysis would have an uncertainty of about ± 15%. This precision was not improved by using a slower rate of heating as was also confirmed by other researchers (6).

Notice that the slope has the following units:

(g of water) x 100%/(g of carbon) + (joule)/(g of carbon) [4]

Therefore, the reciprocal of the slope of the regression model will have a unit of joule/(100 g of water), and may be interpreted as the heat required to release the surface water (H_{water}). For the three carbons employed in this study, this amount of heat is equal to 79.09, 76.24 and 60.77 Joule/mole for BPL, ASC and ASC/T carbons respectively. The reason for assigning this as the heat associated with the release of surface water is because the value of 79 J/mole

obtained for BPL carbon is about two orders of magnitude lower than the heat of adsorption of water (H_{ads}) reported by Barton (11).

If the added water to all the carbon samples can be assumed to be a liquid water layer on the carbon surface (without any physical or chemical interaction with the surface), then the minimum heat required to remove it can be calculated as follows:

$$H_{vap} = (\text{g of water})(\text{specific heat of water})(\text{temp. change}) + (\text{g water})(\text{latent heat of vaporization}) \quad [5]$$

A sample calculation involving a carbon sample (normally about 16.5 mg in each DSC run from 25 to 100°C) with a 1% moisture content, and assuming that carbon did not pick up any appreciable amount of heat, is shown as follows:

$$\begin{aligned} H_{vap} &= 0.01 \times 0.0165 \times 1.00 \times (100-25) \\ &\quad + 0.01 \times 0.0165 \times 540 \ \text{cal} \\ &= 0.1015 \ \text{cal} \\ &= 0.424 \ \text{J} \end{aligned}$$

This calculation shows that the numbers calculated for H_{water} above probably corresponds to the heat of physical adsorption of water, i.e. water which is: i) not chemically adsorbed on the carbon surface; ii) not in the microporous structure of the carbon (which is difficult to remove); and iii) not labile enough to behave like liquid water.

Another interesting feature of Figure 10 is that it appears that water is more strongly 'physically-bound' to ASC carbon than on either BPL or ASC/T carbon. This is based on the difference of the slopes of the lines, and the intercept (on the x-axis). At 0% moisture (as was pointed out earlier, the carbon was not really 'dry' at 0% moisture), ASC carbon has a x-intercept of 25 J/g, while about 8 J/g for both BPL and ASC/T carbons. This probably indicates different levels of interaction between water and the carbon surfaces on these three carbons.

4.0 CONCLUSIONS

From this study it has been determined that the types of carbon (BPL, ASC or ASC/T), types of impregnant (inorganic or organic), and the method of impregnation (wet or dry) all have a profound effect on how strongly the carbon interacts with water on its surface. The trend seems to be that a higher amount of water is removed at higher temperatures (at the expense of other impregnants e.g. TEDA). For the BPL, ASC, and ASC/T carbon, all the methods of moisture determination appear to give comparable results.

It has also been demonstrated that the ASTM method using a six-hour xylene extraction is by no means optimized. It has been determined in this study that:

1) Toluene is a better solvent than xylene in the extraction, especially for ASC/T carbon.

2) The oven-drying method provides an accurate and simple alternative to the ASTM extraction method.

3) If the oven-drying method is adopted as the method of choice in the determination of moisture content in the future, then for BPL, ASC, and ASC/T carbons, the optimum drying conditions are 105°C for 60 minutes, 150°C for 90 minutes, and 105°C for 90 minutes respectively.

It has also been shown in this study that DSC can be used as an analytical tool in the determination of moisture content on the carbon surface, although the experimental error is estimated at ± 15%, this may be improved by the use of a DSC instrument with higher resolution.

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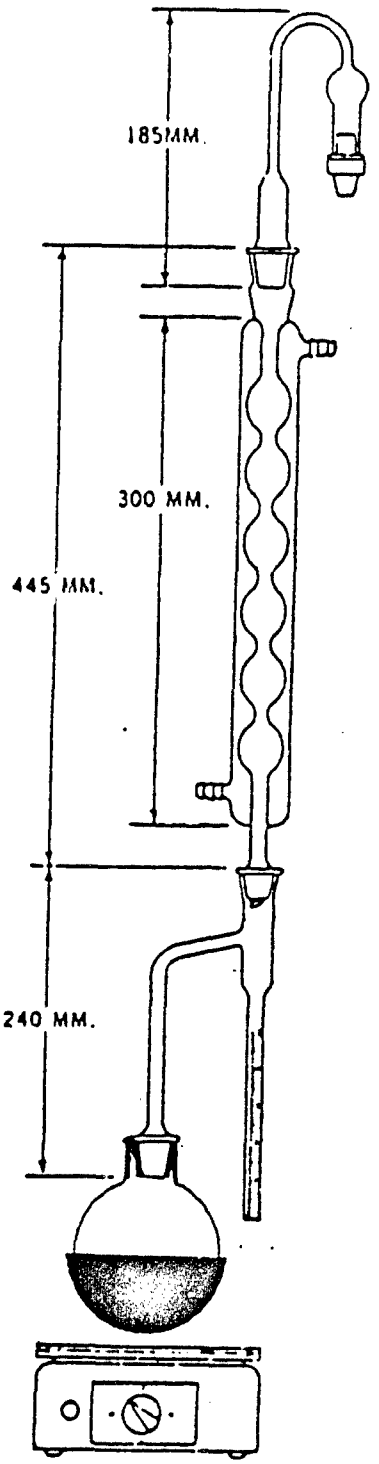

Figure 1: Modified ASTM Moisture Content Determination Apparatus.

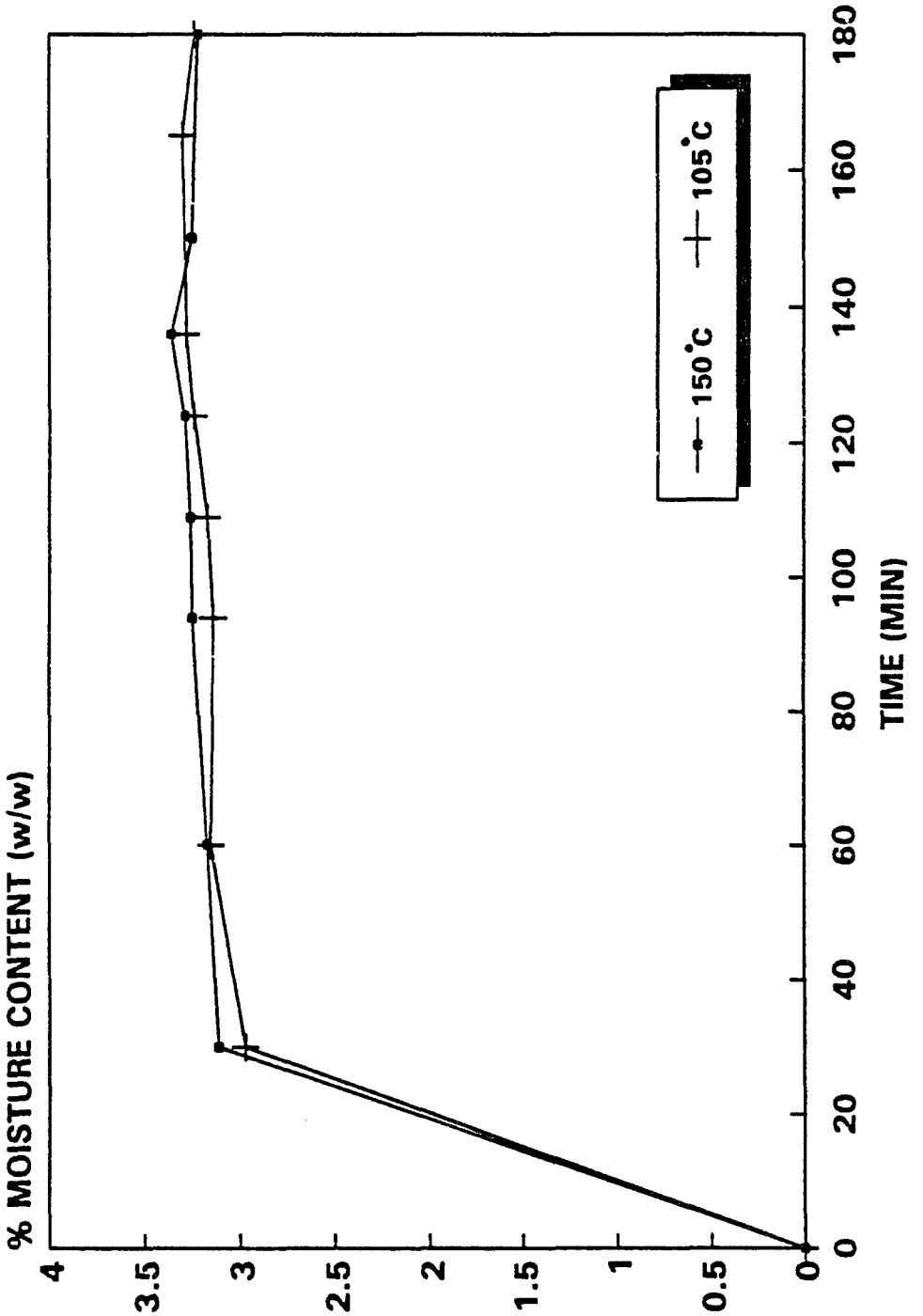

Figure 2: Moisture Loss Profiles of Calgon BPL Carbon.

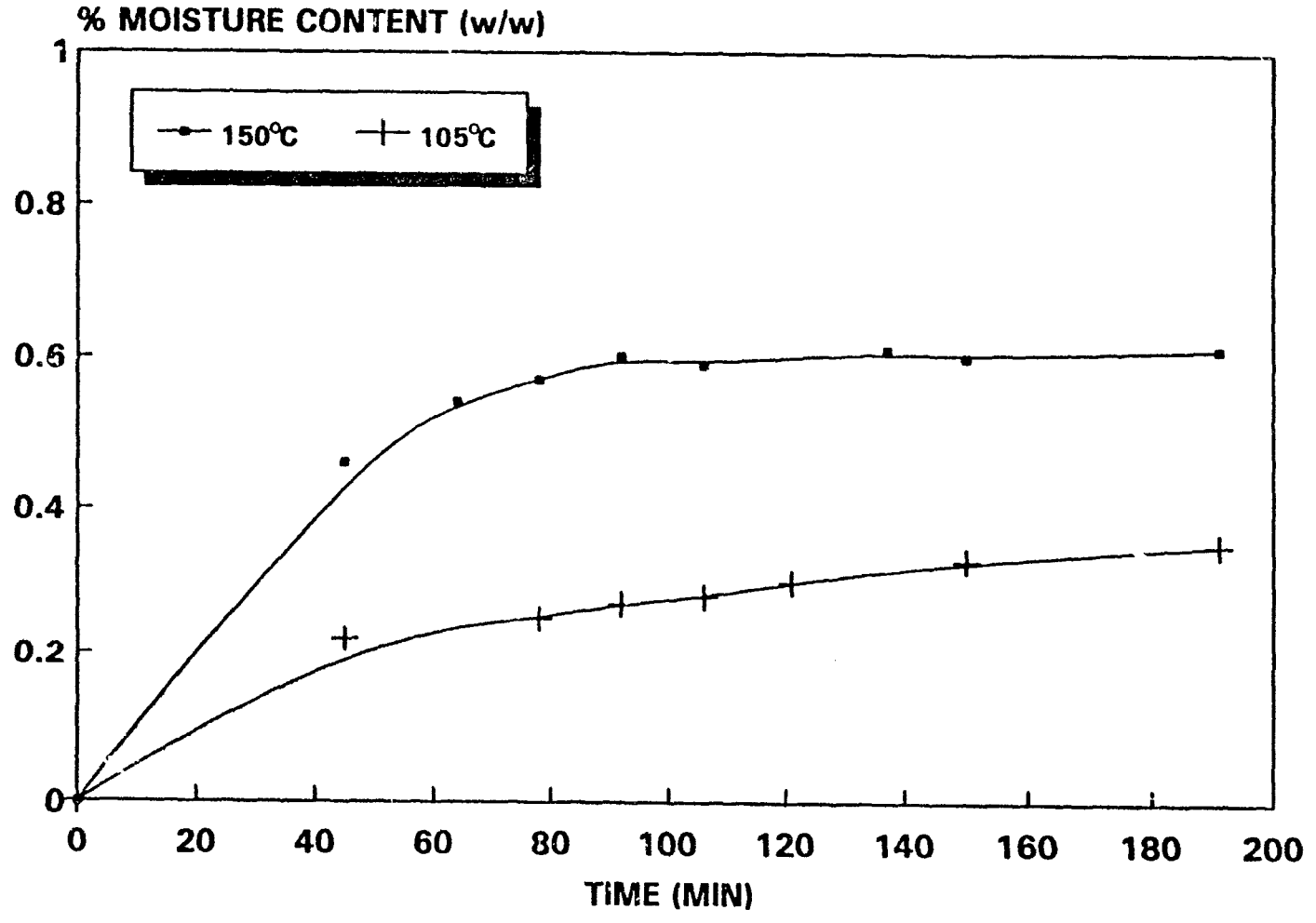

Figure 3: Moisture Loss Profiles of Calgon ASC Carbon.

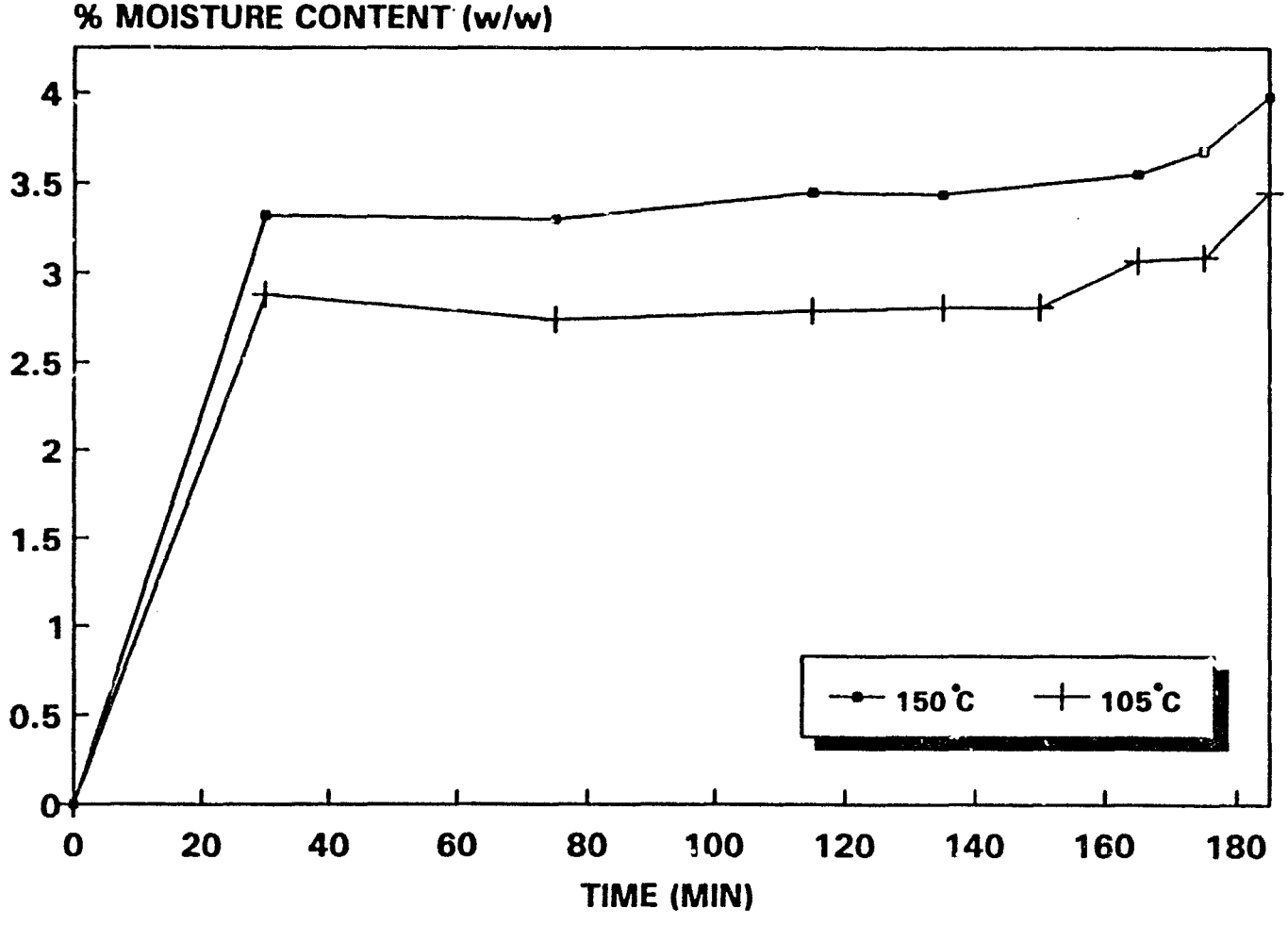

Figure 4: Moisture Loss Profiles of Specially Impregnated BPL/T/10/WET Carbon.

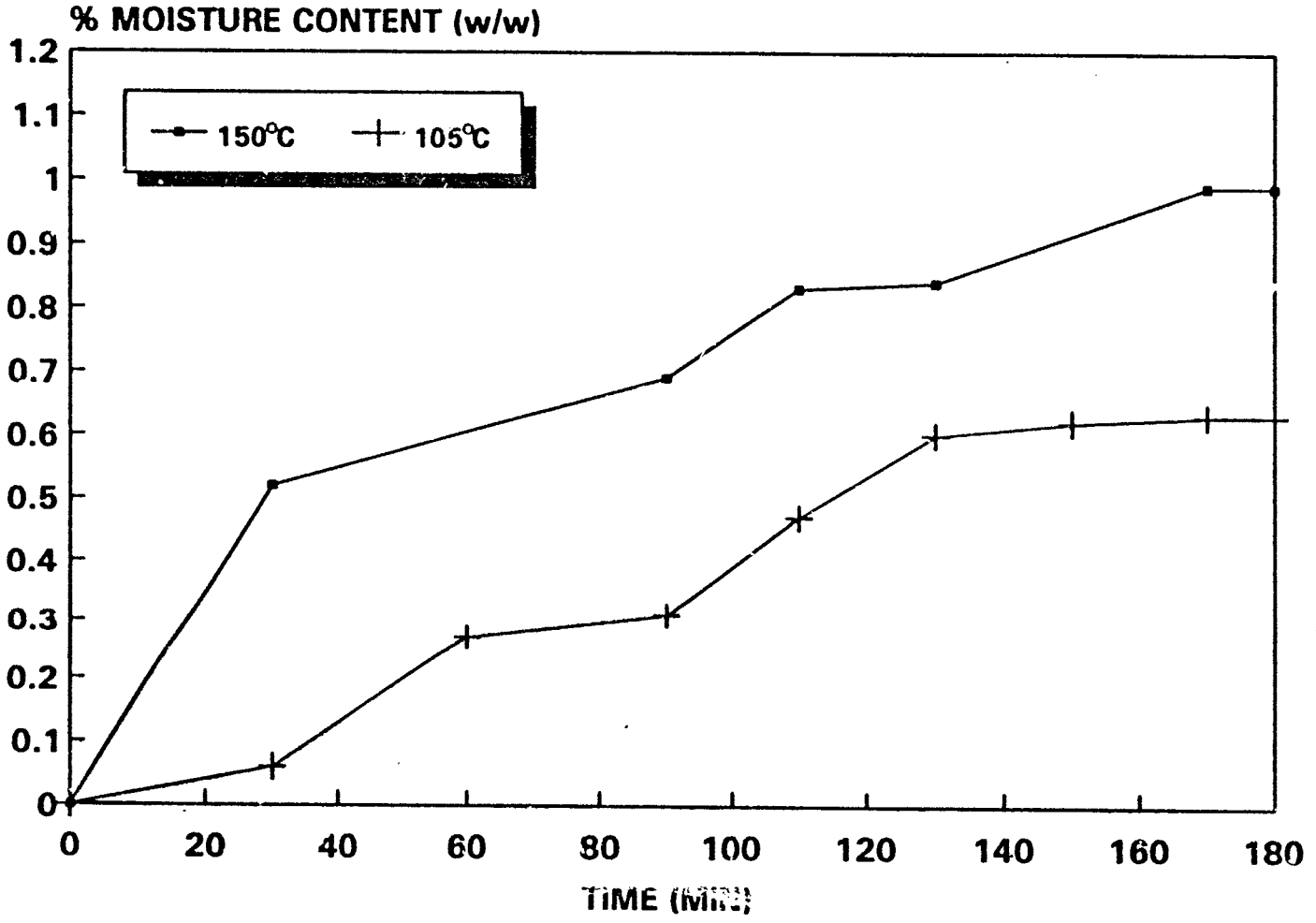

Figure 5: Moisture Loss Profiles of Specially Impregnated BPL/T/10/DRY Carbon.

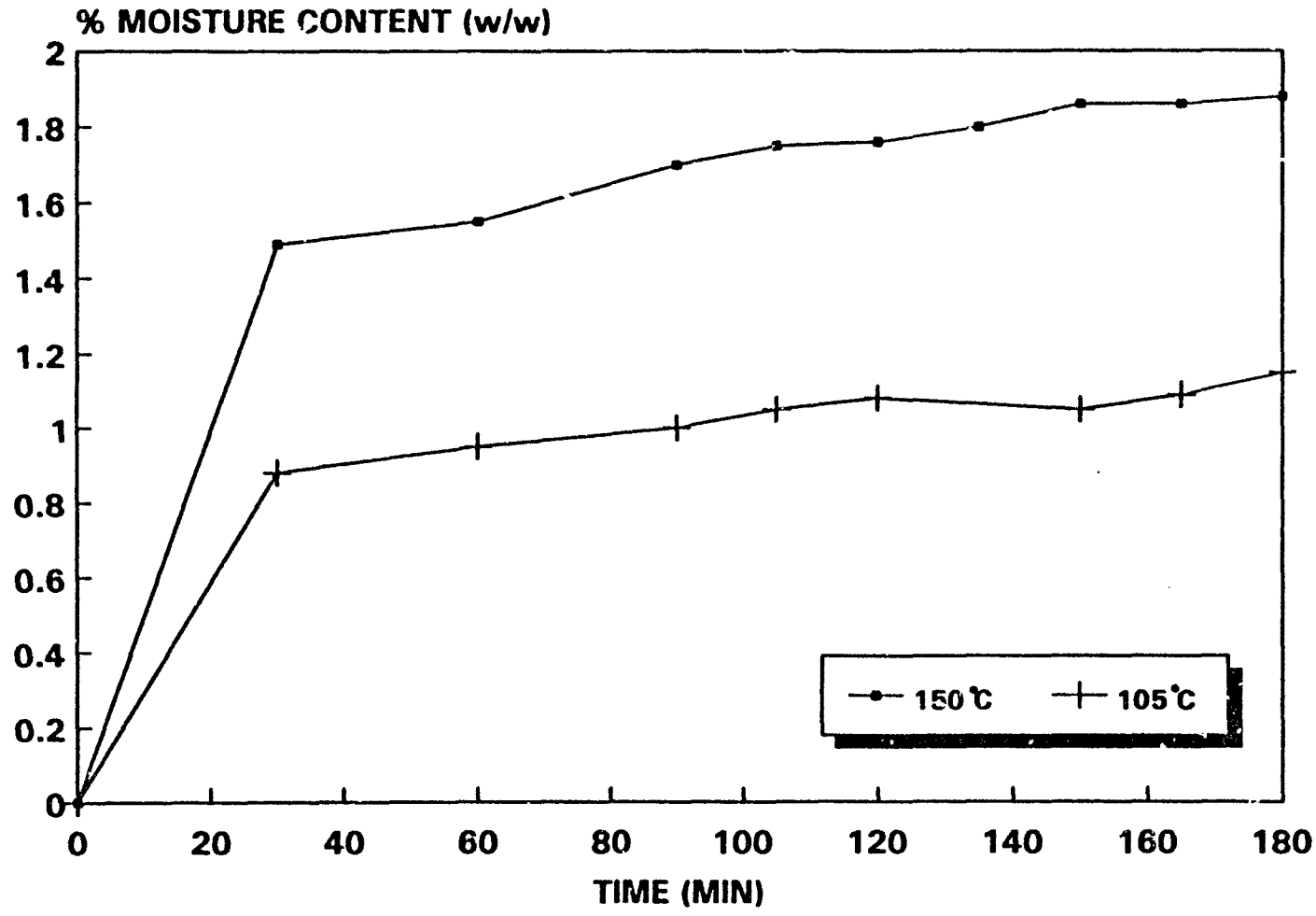

Figure 6: Moisture Loss Profiles of Carbon ASC/T (1.5% TEDA) Carbon.

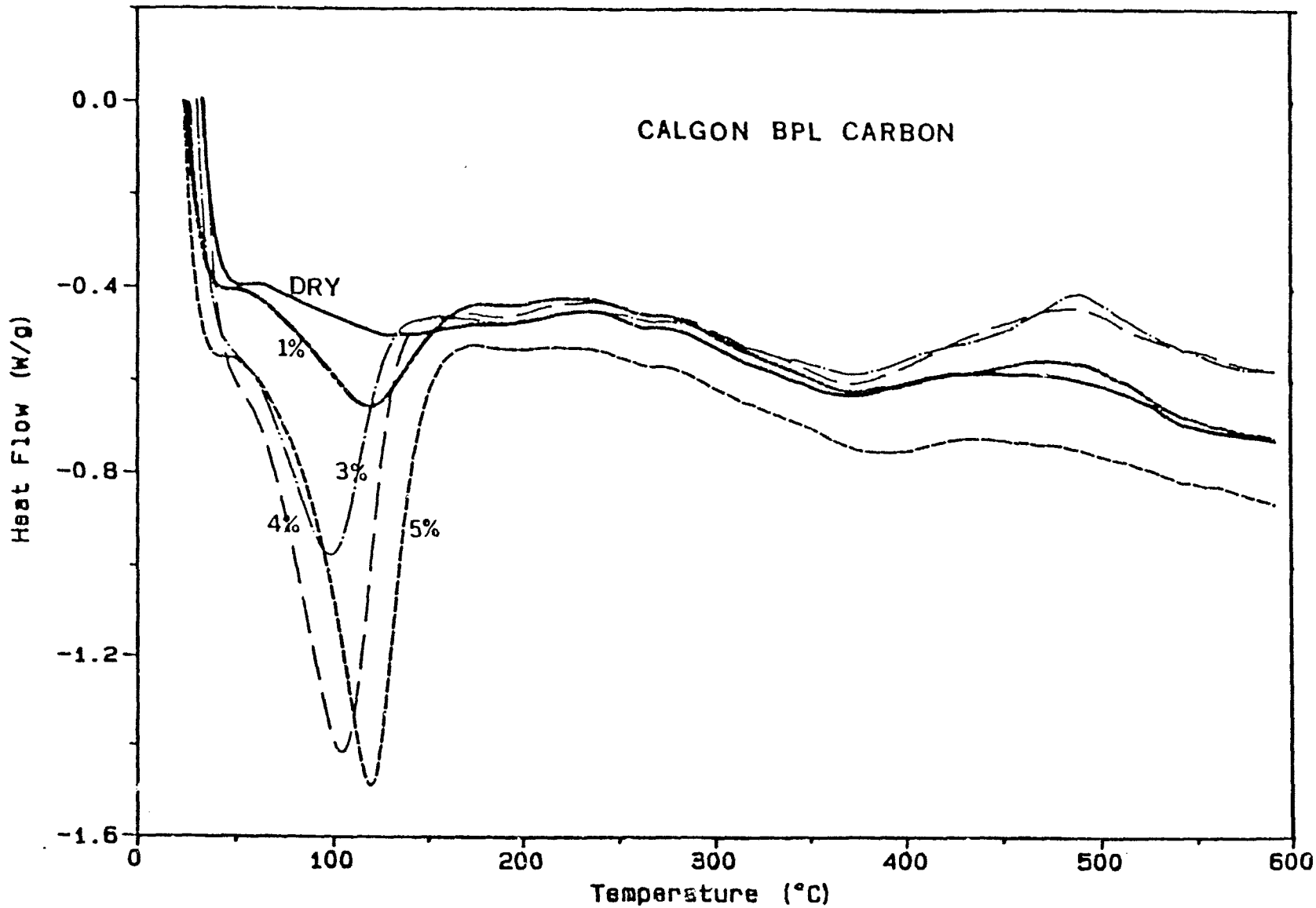

Figure 7: DSC curves for BPL carbon loaded with various water content.

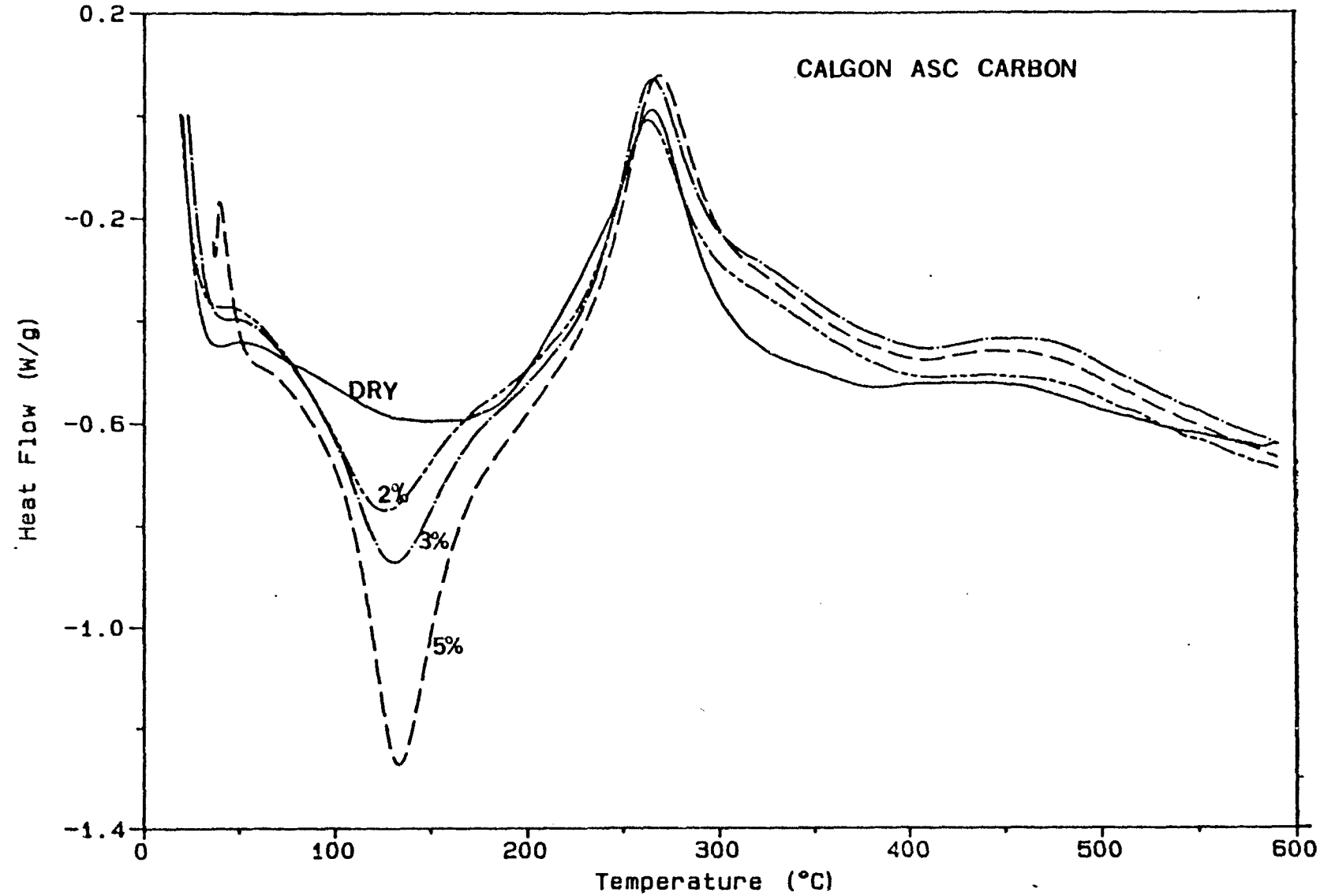

Figure 8: DSC curves for ASC carbon loaded with various water content.

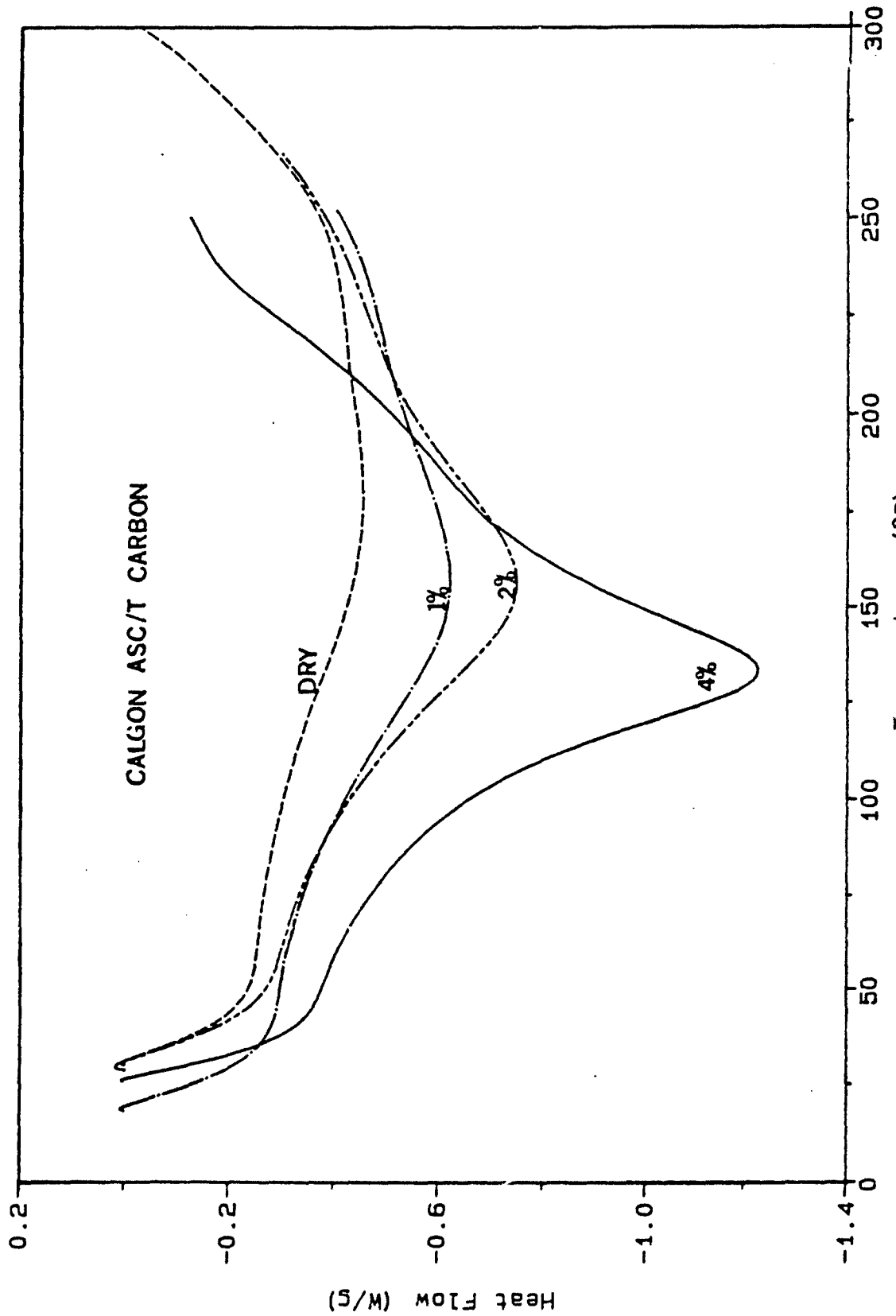

Figure 9: DSC curves for ASC/T carbon loaded with various water content.

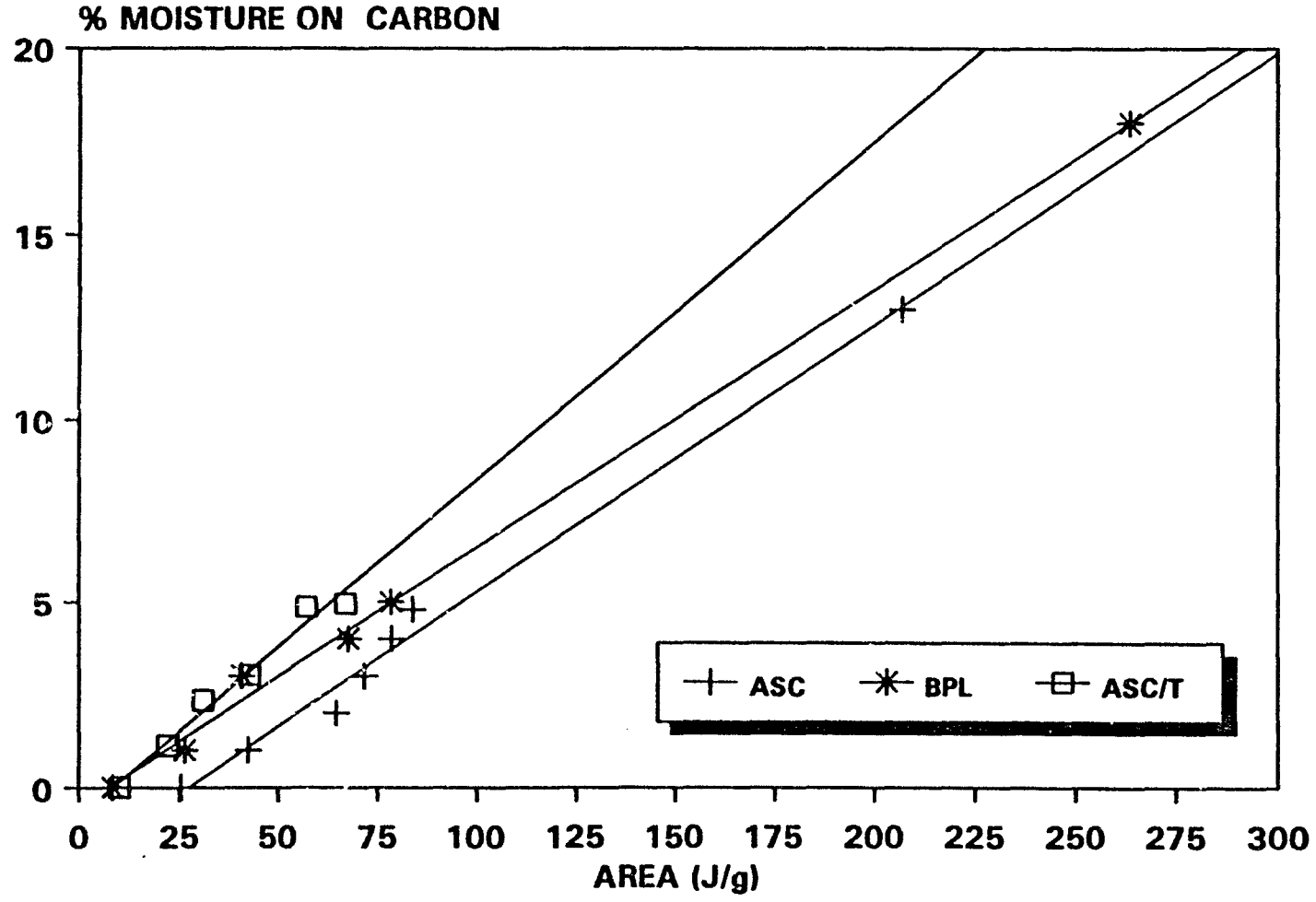

Figure 10: Relationship Between Moisture Content and the Heat Absorbed by water under the DSC Curves.

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The current method employed in the determination of the moisture content of activated carbon is the American Standard Test Method (ASTM) D-2867 (1976), using xylene extraction. However, this test is time-consuming and requires an elaborate experimental set-up. Furthermore, the ASTM has been found to be unsuitable for ASC/T carbon which contains triethylenediamine (TEDA). For this reason, alternatives to the ASTM were considered in this study. The ASTM method has been modified by replacing the extracting solvent xylene with toluene, to reduce the quantity of TEDA being collected with the water. Another alternative is the use of a convection oven where carbon samples were dried under three conditions: 150°C for 3 hours, 105°C for 3 hours and 105°C for 16 hours, and the moisture content results compared. This alternate method proves to be more efficient and the results obtained are comparable to that of the ASTM method. The optimum drying conditions for the accurate determination of moisture content on BPL, ASC and ASC/T carbons were determined to be 105°C for 60 minutes, 150°C for 90 minutes and 105°C for 90 minutes respectively. The last alternative considered was the use of a thermal analytical technique, namely Differential Scanning Calorimetry (DSC). It has been determined in this study that DSC can be used as an analytical tool for the determination of moisture content on carbons. However, better resolution of the DSC thermogram is required for precise measurements in moisture content determination.

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