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Specific Heat of Beeswax and Thermal Analysis of Beeswax and Beeswax-Paraffin Mixtures

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Contents

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1.0 Introduction

Thermal analysis (D.T.A., T.G.A. and DSC) has been used to characterize the changes occurring in many products during temperature changes. These techniques can detect endo and exothermic reactions, phase changes or other occurrences which involve thermal energy changes. These methods can be used to characterize and identify materials and detect purity or composition changes.

The purity of beeswax is important both for liturgical reasons and economic reasons when one compares the cost of beeswax with petroleum waxes. Thermal analysis has been considered as a means of detecting adulteration. Mixtures of paraffin, carnuba and beeswax are frequently used in dental work and have been studied by workers in that area.

2.0 Review of Literature

Craig et al. (1968) studied the effect of addition of beeswax, ceresin and carnuba wax to paraffin. These waxes are added to paraffin to control its properties as a dental wax. They noted a distinct pre-melting transition at 61°C for carnuba with melting transitions at 76.4°C and 82.8°C. They found beeswax to have two incompletely resolved melting transitions at 50.7°C and 62.8°C. In their studies they used 25, 50 and 75% additions of paraffin to the natural waxes. While they note no significant change in the transition temperatures when beeswax was added to paraffin, they also observed that the 62.8°C transition disappeared when more than 50% paraffin was used. Craig et al. (1968) also studied the heats of transition for the natural waxes and paraffin mixtures.

3.0 Materials, Equipment and Methods

3.1 Thermal Analysis Apparatus

3.11 E.R.S.-constructed Differential Thermal Analysis Apparatus

The D.T.A. apparatus, described more fully in Engineering Specification 6836, consists of a cylindrical brass furnace block which holds the sample, reference, and temperature crucibles. These quartz crucibles, each approximately 38 mm long by 5 mm outside diameter, contain the test and reference materials. The three crucibles are located radially about a central heating core.

Sample and reference temperatures are monitored by immersing a fine gauge glass sheathed thermocouple to the midpoint of each crucible. The differential connection of sample and reference thermocouples provides the differential output, while a third thermocouple is used to monitor the temperature of the furnace block.

Linear temperature rates are achieved by utilizing a three-mode controller(a) and programmer(b) to regulate electrical power supplied to the furnace block cartridge heater. Temperature rates of 5.5°C per minute were standard.

3.12 Differential Scanning Calorimeter

A Perkin-Elmer DSC-2(c) was utilized. The unit was equipped with a sub-ambient dry box and intracoolers to allow sub-ambient operation and rapid cool-down. Aluminum volatile sample pans were used in all tests. Dry nitrogen purge gas was used in the dry box, while sample weights of 5 to 8 milligrams and scan rates of 20°C per minute were standard.

Whereas the D.T.A. thermograms plot the temperature differences that occur between sample and reference, the D.S.C. thermograms indicate the amount of energy necessary to hold both sample and reference at the same temperature.

(a) Micro-Thermac Model D30 Controller. Research Incorporated, P.O. Box 6164, Minneapolis, Minnesota 55424.

(b) Data-Trak Programmer, Model FGE 5110. Research Incorporated, P.O. Box 6164, Minneapolis, Minnesota 55424.

(c) Perkin-Elmer (Canada) Ltd., 8250 Mountain Sights, Montreal 308, Quebec.

The difference is significant as quantitative results are more easily obtained with the D.S.C. both for energy changes and specific heat.

3.13 Samples and Preparation

Waxes from several sources were tested in the two systems. Table 1 summarizes the various types of waxes and tests used.

TABLE 1

Waxes Investigated by Thermal Analysis

Type	Source/Trade Name	Tests Performed
Paraffin	Esso "ParoWax", Imperial Oil, Canada Ltd.	DTA, DSC
Paraffin	Scientific Products "Blue Ribbon"	DSC
Paraffin	International Waxes #4675 50 Salome Dr., Agincourt, Ontario.	DSC
Microcrystalline	Petrolite "Ultraflex White" Bareco Division, Petrolite Corp., Tulsa, OK.	DSC
Beeswax	Unprocessed Clean Cappings wax, Agriculture Canada, Apiculture Div., Ottawa.	DTA, DSC
Beeswax	Unprocessed Bulk Ungraded, Sample "A" Apiculture Div., Can. Ag.	DTA
Beeswax	Unprocessed Bulk Ungraded, Sample "B" Apiculture Div., Can. Ag.	DTA
Beeswax	American Domestic Processed, Grade 2 - water washed, carbon filtered cappings wax	DTA
Beeswax	Western Canadian Domestic Processed, Grade 1 - water washed, carbon filtered cappings wax	DTA

Mixtures of beeswax and paraffin were made up by melting and stirring together the two components and allowing the mixture to cool. Clean cappings wax from Agriculture Canada and Esso "Parowax" brand paraffin were used in all such mixtures. Concentrations of 1%, 5%, 10% and 50% paraffin were prepared and tested.

3.14 Methods

Wax samples for the DTA apparatus are prepared by filling the quartz sample crucible with the molten wax to be tested, placing the crucible in the warm brass furnace block, and lowering the thermocouple into the molten sample. Cooling the furnace block back to the start temperature completes the loading procedure.

During a test, the furnace block assembly is heated at a predetermined programmed rate. The differential temperature signal between sample and reference is recorded against time. The furnace block temperature is monitored simultaneously to provide continuous temperature correlation for the differential signal.

Standard temperature range for most tests was $20^{o}C$ to $120^{o}C$ which covered the melting curves of the waxes studied.

Sample preparation and loading for the DSC apparatus consisted of trimming an appropriate sized piece of wax from a block of sample, and sealing it inside a volatile sample pan. After loading into the furnace, each sample was subjected to one heat-cool cycle to melt the sample and allow it to distribute evenly across the bottom of the sample pan.

A standard temperature range of $-10^{o}C$ to $+110^{o}C$ was used.

3.2 Specific Heat of Beeswax

The specific heat of beeswax was determined by two separate methods.

The classical method of mixtures was applied using an E.R.S. constructed calorimeter as one method, while a Perkin-Elmer DSC-2 differential scanning calorimeter was utilized for the other.

3.21 Apparatus and Equipment

3.211 E.R.S. Constructed Calorimeter

The unit is based on a 500 ml commercial Dewar flask, imbedded in a well-insulated wood box.

An equilibration chamber is placed on top of the calorimeter to isolate the mouth of the calorimeter from drafts, allow a place to hold sample material at constant temperature before testing, and provide a convenient mount for a stirring rod/motor assembly (Fig. 3).

Temperature Measurements

Two temperatures must be monitored during testing. Calorimeter water temperature is measured with a small commercial thermocouple(d) which has a rapid response time. The thermocouple is zero-referenced in an electronic zero-referencing unit(e), and the resulting output fed to a pre-amplifier(f). The amplified signal is then fed to a laboratory type strip chart millivolt recorder(g) where it is recorded continuously during testing.

The sample temperature before immersion is determined by reading a 0.1°C resolution thermometer placed in a beaker containing the sample under test.

(d) High Temperature Instruments Corp. #HT1-6-36GST
Union Hill Building, West Conshohocken, Pa. 19428.

(e) Zeref ice reference, Thermo Electric Co., Brampton, Ont.

(f) RdF Model 860 Heat Flow Meter, RdF Corp., Hudson, N.H.

(g) Riken Denshi Model SP-G5V, B.H. McGregor, Box 156, Stn. H, Toronto, Ont.

Mass of sample and mass of calorimeter water are determined by carefully weighing the amounts used. A top-load balance(h), capable of resolving to 0.01 g is used to weigh water and sample.

3.212 Differential Scanning Calorimeter

The measurement of specific heat with the D.S.C.(i) is accomplished by comparing the amount of energy necessary to change the temperature of known weights of reference and sample by the same amount. Since the ordinate scale of the system's recorder is calibrated in units of energy per unit time, this information is readily obtained. Sample and reference weights were accurately determined with a micro balance(j).

3.22 Samples and Preparation

All beeswax tested for specific heat was clean cappings wax obtained from Agriculture Canada, Apiculture Div., C.E.F., Ottawa. For the E.R.S. Calorimeter, beeswax is melted over a hotplate and poured into a number of lengths of glass tubing. After hardening, the wax "plugs" are ejected from the tubes, forming easy to handle rods of approximately 3/16" dia. by 3" long.

Approximately 20 of these rods are used as a sample during testing of the wax.

Sample preparation for the commercial DSC consisted of cutting a suitable sized sample from a block of wax. Average weights of wax samples were 5 to 6 milligrams. The samples were encapsulated in volatile sample pans during testing. A sapphire disc(k) of known specific heat was used as a reference material.

(h) Mettler P1210N balance, Mettler Instruments. Fisher Scientific Ltd., 1830 Walkley Rd., Ottawa.

(i) Perkin-Elmer (Canada) Limited, 8250 Mountain Sights, Montreal 308, Que.

(j) Mettler Model H16 , Fisher Scientific Co., 1830 Walkley Rd., Ottawa.

(k) Perkin-Elmer Specific Heat Kit, Part No. 219-0136, Perkin-Elmer Corp., 8250 Mountain Sights, Montreal 308, Que.

3.23 Methods

3.231 E.R.S.-Constructed Calorimeter

The method of mixtures principle of calorimetry was applied to the tests. Known masses of water and sample were mixed, and initial and final temperatures monitored. After correcting final temperatures for the effects of ambient temperature on the calorimeter, the data was reduced by the following general equation:

$$Cp_{\text{SAMPLE}} \doteq \frac{(m\ Cp\ \Delta\ T)_{\text{CAL. }H_2O} + K(\Delta T)_{\text{CALORIM}}}{M\ (\Delta T)_{\text{SAMPLE}}}$$

Symbols Used:

K = constant of heat absorbed by calorimeter, as determined in calibration tests.

Cp = Specific Heat - calories per gram ^{o}C

ΔT = Temperature difference (^{o}C)

m = Mass (grams)

Test Procedure

A sample of wax (approx. 20 rods) is weighed and placed in a wide-mouth funnel, ready to be lowered into the calorimeter. A thermometer of 0.1^{o} resolution is placed among the rods to measure their temperature at the start of a test.

The calorimeter is then partially filled with an accurately weighed amount of ice water (250 g) and is capped with a foam plug to help insulate the top of the calorimeter. The stirring rod is started and the temperature of the water is recorded with a chromel-alumel thermocouple.

The temperature of the mixture is recorded for approximately 30 minutes, at which time the test is terminated.

Weights and temperature are then used to compute the value of Cp for each test.

Calibration Procedure

Since the thermocouple, calorimeter and stirring rod all absorb heat from the wax sample, it is necessary to determine a correction factor for the system that accounts for these losses.

By using a known quantity of water at a known temperature as a sample, and mixing this with the calorimeter water, a value for "K" may be obtained which expresses the number of calories lost per degree in the system.

Following a similar procedure to the beeswax testing, the various temperatures and masses are applied to the following general formula:

$$K = \frac{(m\ Cp\ \Delta T)_{SAMPLE} - (m\ Cp\ \Delta T)_{CAL.\ H_2O}}{\Delta T_{CALORIM}}$$

A value for K of 12.16 ± 1.35 was determined from the calibration runs using water as a calibration standard.

3.232 Differential Scanning Calorimeter

After calibrating the instrument for temperature and power over the temperature range of interest, the weighed sample pan and sapphire standard are loaded and run over the selected temperature range. The sapphire standard is then removed and the test repeated on the empty pan. These records are superimposed on one another on the chart paper. The sample to be tested is then sealed in the pan and the test repeated. The third record is superimposed on the same chart as the previous two traces.

The specific heat of the sample is obtained by determining the respective ordinate displacements of sapphire standard and sample at the selected temperature, and applying them to the formula:

$$\text{Specific Heat (Sample)} = \frac{\text{Amplitude (Sample)}}{\text{Amplitude (Reference)}} \times \frac{\text{Weight (Reference)}}{\text{Weight (Sample)}} \times \text{Specific Heat (reference)}$$

The specific heat of the sapphire standard used in these tests has been tabulated against temperature by the manufacturer, thus enabling precise determinations at selected temperatures.

4.0 Results and Discussion

4.1 Thermograms

Thermal analysis yielded well formed reproducible peaks on the samples tested.

The varieties of beeswax tested on the DTA apparatus showed very little difference between raw untreated waxes and refined waxes. The two peaks at 56°C and 68°C, apparent on the beeswax thermograms, remained quite constant in shape, relative size, and temperature (Figure 7). Thermograms obtained from cappings wax are representative of pure uncontaminated beeswax.

The DSC thermograms were in close agreement with the DTA results. The DSC study of three different paraffins and one microcrystalline wax showed differences between paraffins and large differences in peak magnitude between paraffin and microcrystalline wax (Figure 6). A major endotherm at 60°C characterized two of the three paraffins. A third showed a major peak at 54°C. Secondary peaks ranged from moderately strong at 38°C on one sample to 23°C and 45°C weak shoulders on the other two samples. The microcrystalline wax exhibited a totally different shaped endotherm, with a moderate rounded peak at 61°C. Mixtures of paraffin and beeswax (Figures 4 and 5) produced composite thermograms which, dependant on the relative amounts of each wax, showed most of the peaks of each separate wax. Since the paraffin endotherm at 60°C is much stronger than the 68°C beeswax endotherm, the paraffin peak became dominant at mixtures much in excess of 10% paraffin.

The small beeswax peak at 56°C is often indistinguishable from the very major paraffin peak at 60°C even at moderate paraffin contents (>5%), while at low concentrations the two are indistinguishable from each other and appear as one small peak. The lower temperature paraffin peak at 37°C is also indistinguishable at the 5% concentration level.

Good agreement was observed between results from the two systems used.

4.2 Specific Heat

4.2.1 E.R.S. Calorimeter

Beeswax Test Results

Three samples of clean cappings wax were selected, each containing approximately 20 rods, and weighing approximately 50 grams.

Each of the three samples was tested three times by the method described previously.

TABLE 2

Specific Heats of Beeswax Samples in cal/g°C

	Run 1	Run 2	Run 3	Mean
Sample 1	0.474	0.519	0.476	0.490
Sample 2	0.484	0.475	0.482	0.480
Sample 3	0.491	0.466	0.488	0.482

Arithmetic mean of all 9 tests = 0.484

Standard Deviation = 0.01321

4.22 Differential Scanning Calorimeter

The specific heat of clean cappings wax was determined in a Perkin-Elmer DSC-2 in accordance with the instruments' standard operating procedures.

Measurements were taken over two temperature ranges:

1) -3°C to + 17°C

2) +77°C to + 97°C

It was not possible to measure the specific heat in the 20°C to 75°C temperature range due to the marked slope of the thermogram in that region.

Two separate samples were tested, and specific heats calculated for both at six temperatures. The results are as follows:

TABLE 3

Specific heat of Beeswax as Influenced by Temperature,(cal/g°C)

Temperature (°C)	Test 1	Test 2	Mean
- 3	0.4055	0.4318	0.4187
+ 7	0.4413	0.4501	0.4457
+17	0.5234	0.4794	0.5014
+77	0.5066	0.5483	0.5275
+87	0.5270	0.5543	0.5407
+97	0.5346	0.5687	0.5517

5.0 Conclusions

Thermograms of beeswax varieties showed a repeatable form with a strong endothermic peak at 69°C and a shoulder at 57°C.

Paraffin types showed considerable variation, with a major endothermic peak occuring between 54°C and 61°C, while a second smaller endotherm varied in size and temperature,occurring between 23°C and 45°C.

Mixtures of a known type of paraffin in beeswax were detectable down to the 5% paraffin level. Careful comparison is necessary with standard curves produced from the pure materials for accurate detection.

Both thermal analysis systems produced excellent thermograms. For the DSC, availability of hermetically sealed disposable sample holders is a very significant advantage, as at higher temperatures, volatiles are lost from the wax.

Specific heat of beeswax, as determined using the E.R.S.-constructed calorimeter, ranged from 0.466 cal/gm-°C to 0.519 cal/gm-°C, with an arithmetic mean of all tests of 0.484 cal/gm-°C, over a temperature range of 2°C to 25°C.

The commercial D.S.C. apparatus yielded data at specific temperatures, unlike the E.R.S. calorimeter, which yielded data obtained over a range of temperature. The specific heats obtained from the DSC increased from 0.4187 cal/gm-°C at -3°C to 0.5517 cal/gm-°C at 97°C.

Very good agreement between the two methods was observed.

6.0 References

Craig, R.G., Powers, J.M. and Peyton, F.A. 1968. Differential thermal analysis and calorimetry of waxes. Proc. ACS Symposium on Analytical Calorimetry, San Francisco, Calif. Apr. 2-5.

Timbers, G.E. and Caron, J. 1969. Low cost differential thermal analysis. Eng. Spec. 6836. Engineering Research Service, Agriculture Canada, Ottawa, Ontario, K1A 0C6.

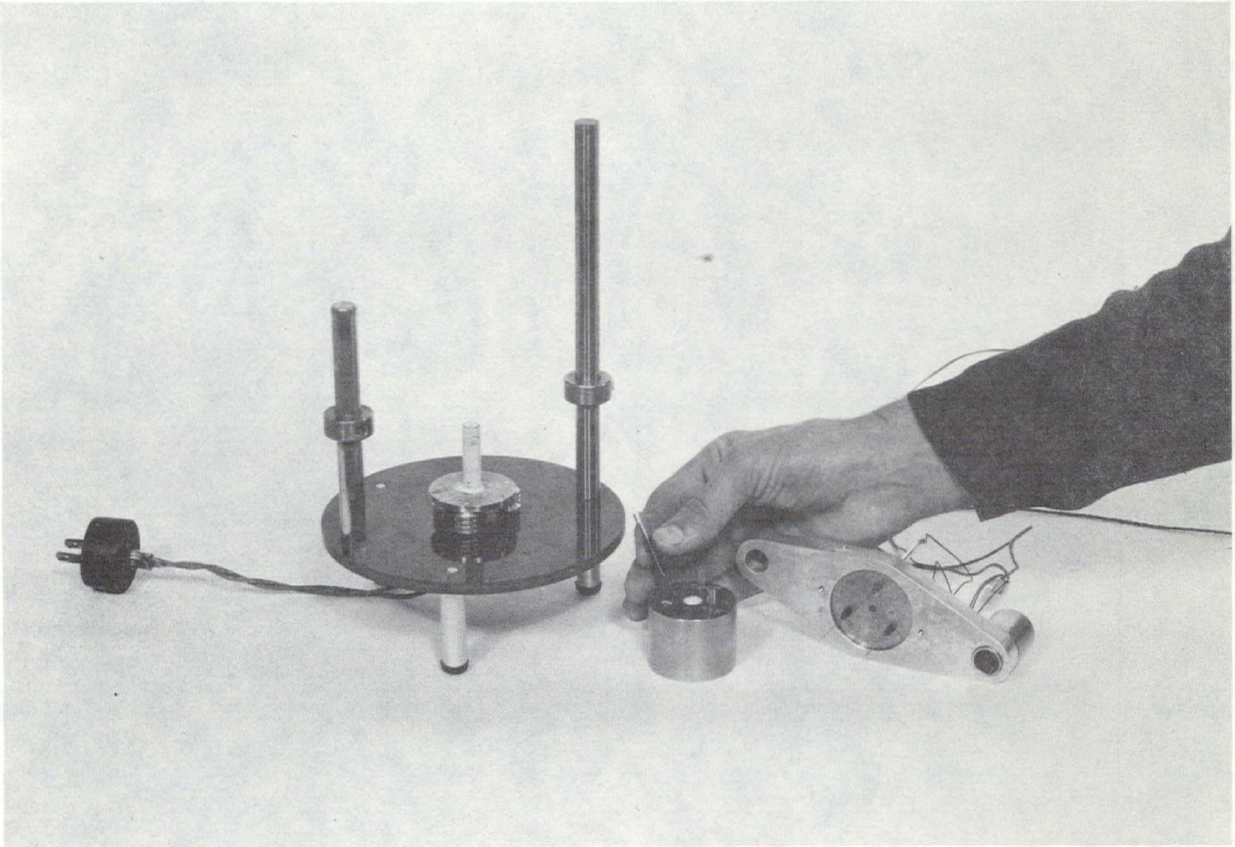


Figure 1. ERS-Constructed D.T.A. Apparatus.

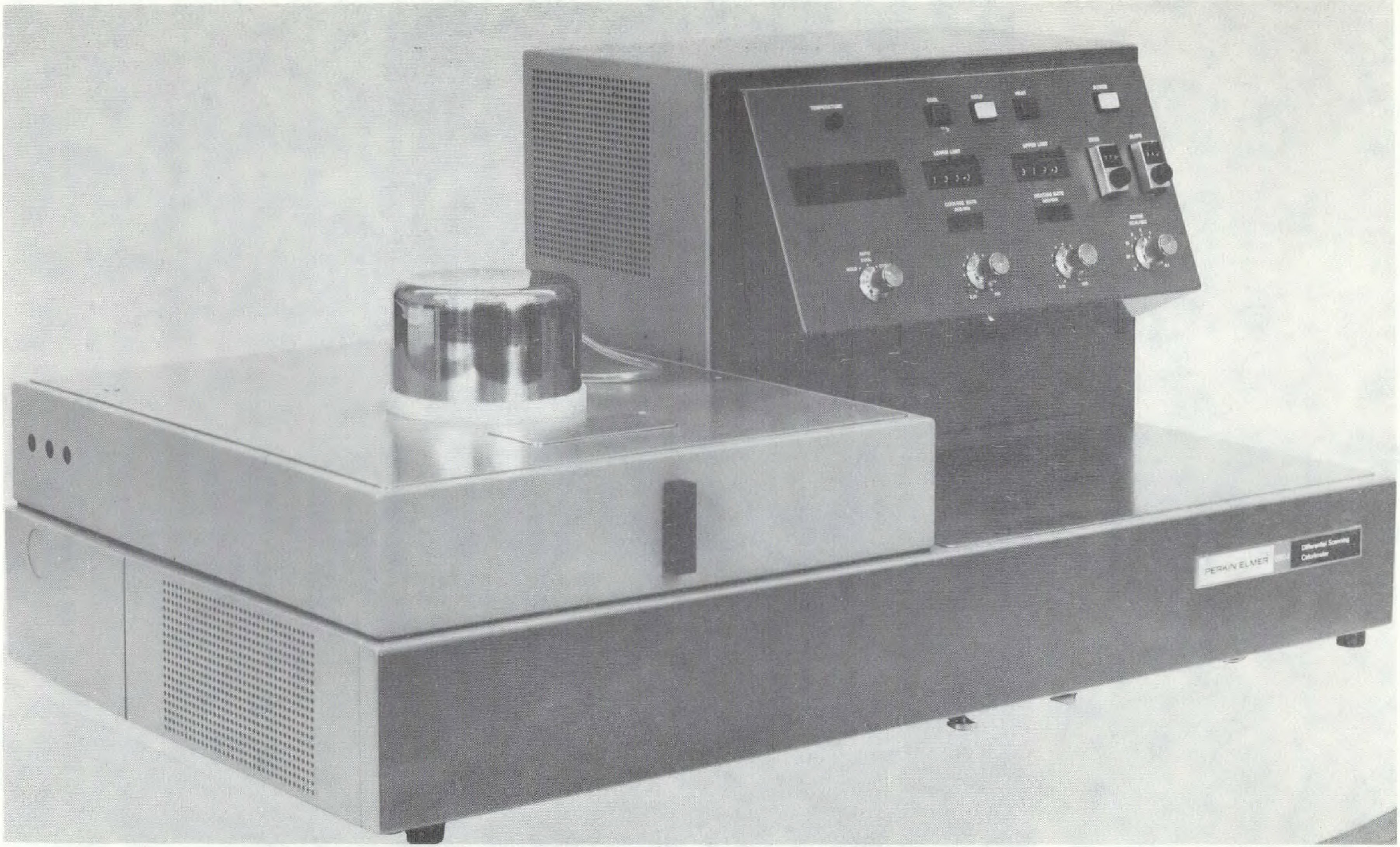


Figure 2. Perkin-Elmer DSC-2 Apparatus. Photo courtesy Perkin-Elmer Corp.

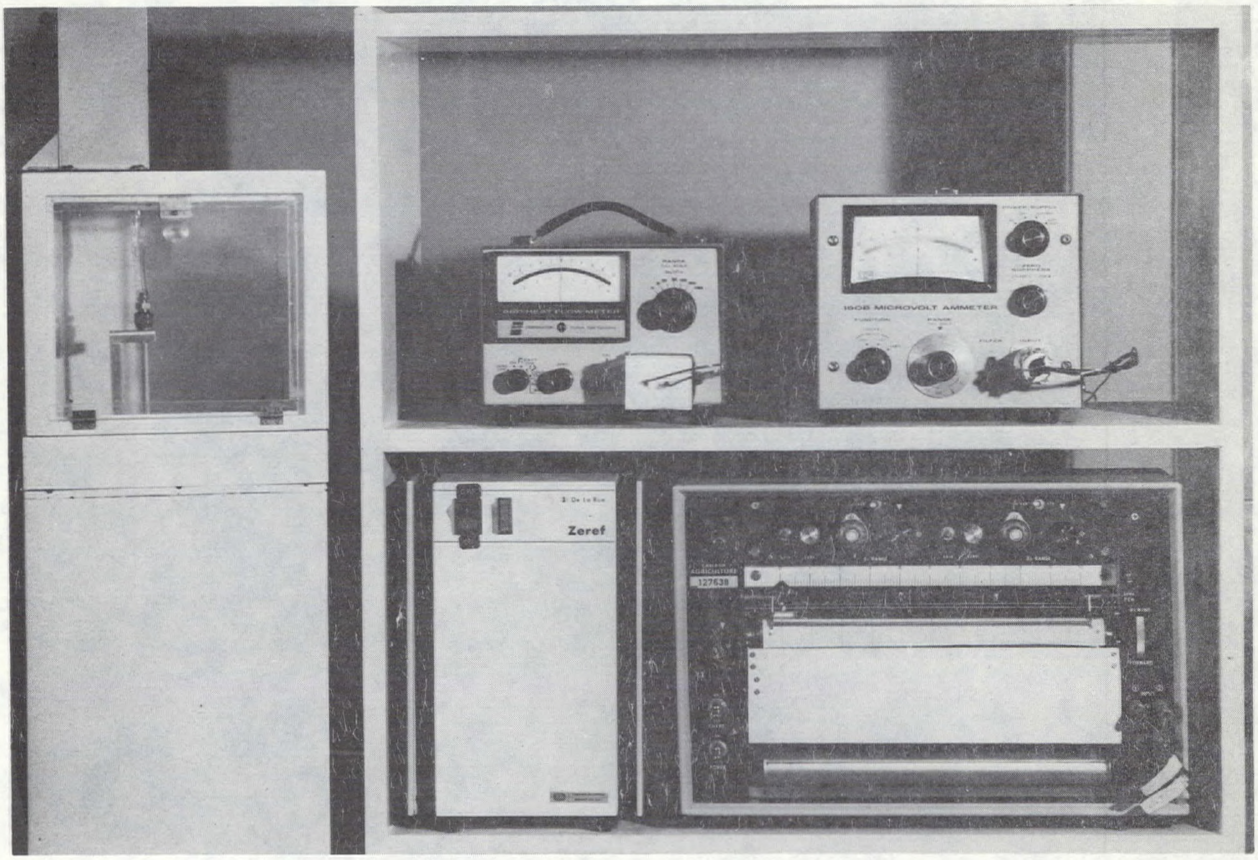
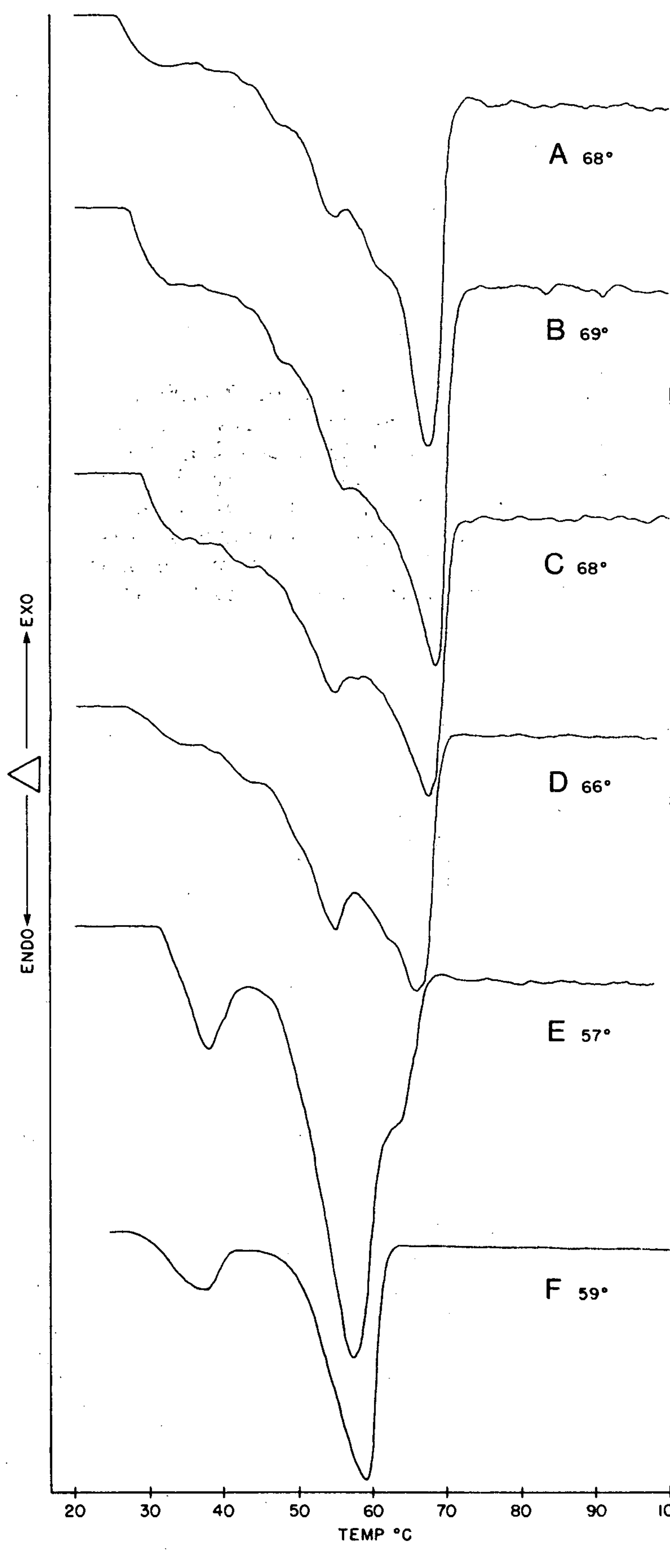


Figure 3. ERS-Constructed Calorimeter.

Figure 4. Thermograms of Paraffin-Beeswax Mixtures-ERS D.T.A. System.
A. Pure Beeswax (clean cappings wax)
B. 1% paraffin added to pure beeswax
C. 5% paraffin added to pure beeswax
D. 10% paraffin added to pure beeswax
E. 50% paraffin added to pure beeswax
F. Pure paraffin (Esso Brand "Parowax")



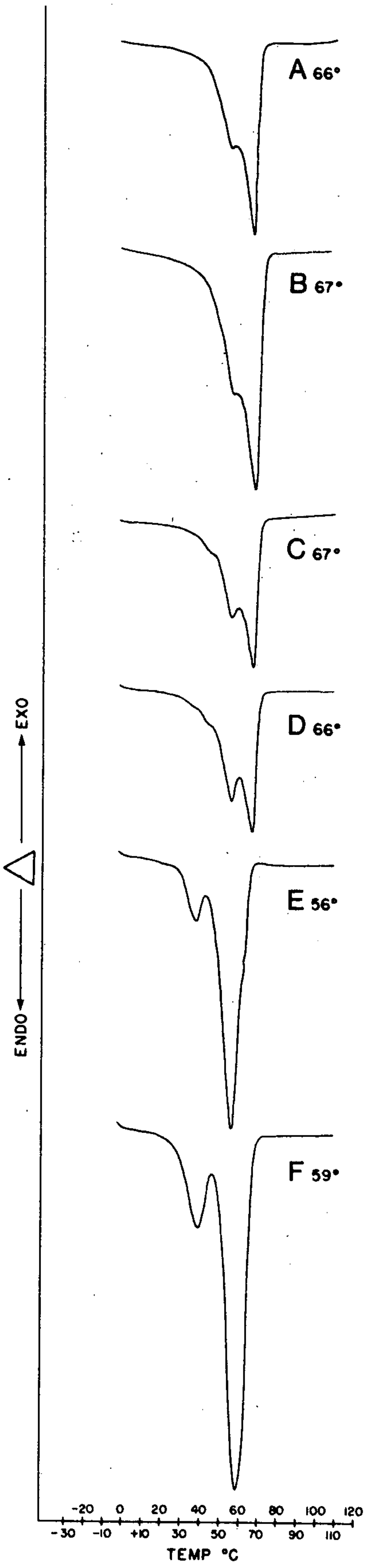


Figure 5. Thermograms of Paraffin-Beeswax Mixtures-Perkin-Elmer DSC-2

A. Pure Beeswax (clean cappings wax)
B. 1% paraffin added to pure beeswax
C. 5% paraffin added to pure beeswax
D. 10% paraffin added to pure beeswax
E. 50% paraffin added to pure beeswax
F. Pure paraffin (Esso brand "Parowax")

Figure 6. Thermograms of Paraffin Varieties-Perkin-Elmer DSC-2

A. Esso Brand "Parowax" Paraffin

B. Petrolite Brand "Ultraflex White" Microcrystalline

C. Scientific Products Brand "Blue Ribbon" Paraffin

D. International Waxes Brand "4675" Paraffin

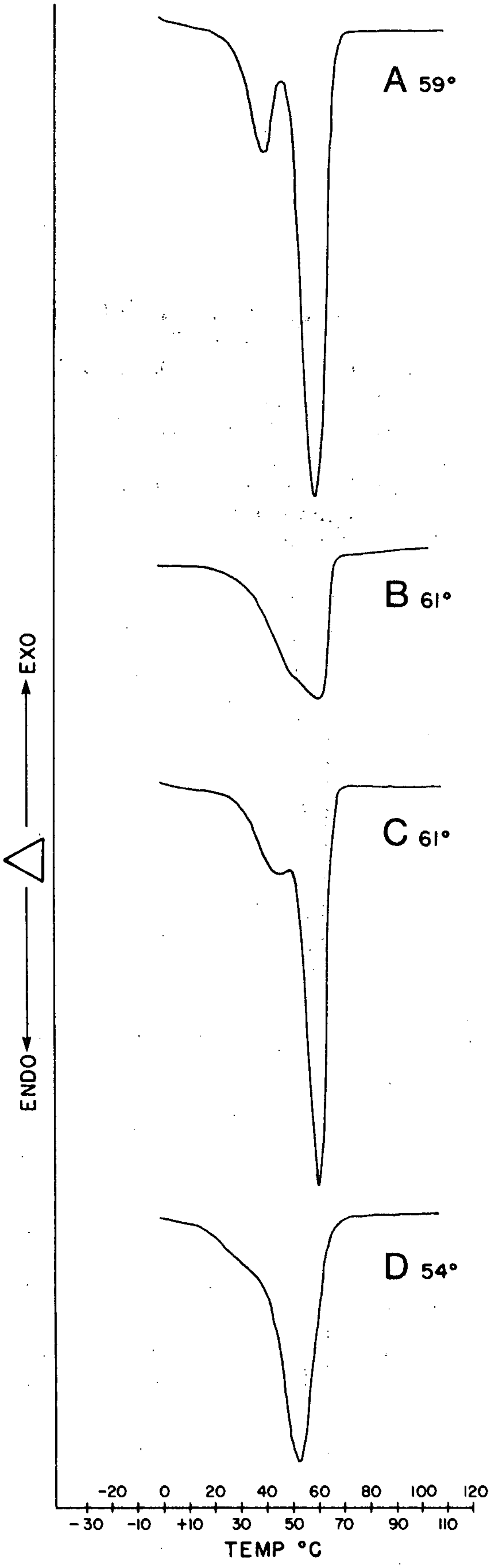


Figure 7. Thermograms of Beeswax Varieties - ERS D.T.A. System
A. Untreated bulk wax, Sample A
B. Untreated bulk wax, Sample B
C. Western Canadian Domestic Grade 1
D. American Domestic Grade 2
E. Clean Cappings Wax (Pure Beeswax)