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# CHARACTERIZATION OF MACADAMIA NUTS BY DIFFERENTIAL SCANNING CALORIMETRY FOR COUNTRY OF ORIGIN *

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## ABSTRACT

The U.S. Customs Service is frequently called upon to determine the country of origin of imported commodities. The results of this type of determination can affect the rate of applicable duty or the admissibility of a particular shipment. In the case of macadamia nuts, those nuts grown in South Africa are currently prohibited from entry under the terms of the U.S. Anti-Apartheid Act of 1986.

Differential scanning calorimetry (DSC) has been used to establish a set of parameters characterizing macadamia nuts grown in South Africa. These values are compared with those obtained from macadamia nuts of known origin and nuts from actual imported shipments. It has been demonstrated that DSC can be used as a screening technique for the identification of macadamia nuts grown in South Africa.

## INTRODUCTION

One major analytical problem frequently encountered in the laboratories of the U.S. Customs Service is that of determining the country of origin of an imported commodity. The origin affects the tariff classification and the rate of duty which may differ significantly, ranging from a very high rate to a zero rate. The latter would occur, for example, under the General System of Preferences which grants a number of tariff concessions to developing countries. Origin is also a determining factor in those instances where the United States, either unilaterally or in cooperation with other trading partners, has embargoed or sanctioned imports from a given country.

The U.S.A. grows macadamia nuts in Hawaii and also imports macadamia nuts from other countries. These nuts are grown in many countries of the world: Australia, Malawi, Zimbabwe, Brazil and several countries of Central America, and are thus subject to different rates of duty. Macadamia nuts are

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also produced in South Africa, and these are currently under embargo as a direct result of the Anti-Apartheid Act of 1986, which prohibits the importation into the U.S.A. of agricultural productions from South Africa along with other items of commerce.

The botanical literature on macadamia nuts indicate that there are two original varieties: "*Macadamia integrifolia*" having smooth nut shells and "*Macadamia tetraphylla*" having rough shells [1]. The macadamia nut was domesticated in Australia in 1858 and introduced to Hawaii in 1882. By 1980, 90% of the macadamia nuts in commerce were produced in Hawaii from cloned smooth shelled macadamia trees. It has been reported that South Africa has macadamia plantings of both the smooth and rough shell nuts [2].

Based on our previous work on determining the country of origin of pistachio nuts by DSC [3], the characterization of the macadamia nuts was carried out by DSC thermal profiling. Macadamia nuts were sampled in two forms, the ground nut meats and the extracted oil.

The DSC thermal curves for both forms were obtained for each of 55 macadamia nut samples. Of these, macadamia nuts of known origin were obtained from growers in four countries: Costa Rica, Guatemala, Australia and Malawi. Macadamia nuts also were purchased in three cities in South Africa and were assumed to have been grown locally. Forty-eight shipments of macadamia nuts imported into the U.S. were also sampled for use in this study.

The macadamia nuts were usually in the form of whole shelled nuts. Some samples showed evidence of salting which is preceded by roasting. From the macadamia nut literature, it was learned that roasting is accomplished by either cooking in coconut oil which contains an antioxidant or by dry roasting followed by the application of an oil coating containing an antioxidant [4]. Some of the nuts were labelled as being raw, and many did not indicate their state. This paper will describe a DSC method for country of origin determinations for this natural product.

## EXPERIMENTAL

Samples of the macadamia nuts weighing about 5 g were taken. This was usually two to three whole nuts or an eguivalent volume of pieces. These were chopped and then ground into fine fragments. The analytical samples for DSC weighing between 5 mg and 15 mg, and sealed in standard aluminum DSC sample pans, were taken at this point in triplicate. The remaining ground nut composite was then extracted with 25 ml of petroleum ether. The extract was filtered and the ether removed from the filtrate under flowing nitrogen. The resulting oil fraction was stored in a freezer until analysis. The oil fractions were defrosted and sampled for DSC at time of

analysis. The analytical samples were sealed in aluminum pans designed to hold liquids just prior to being run.

The DSC runs were made using a Perkin–Elmer (PE) DSC-2 in the heating mode from 230 K to 300 K at a rate of 5 K $min^{-1}$ under a dynamic nitrogen atmosphere. The prepared samples were taken at room temperature and placed directly into the cold DSC cell for shock cooling. They were allowed to equilibrate at 230 K and then the heating run was initiated. The results were collected and processed using the PE Thermal Analysis Data System (TADS) with the Partial Areas program which assumes that a flat baseline exists between the designated endpoints.

## RESULTS AND DISCUSSION

The macadamia nut DSC curves were compared using the Partial Areas program on the PE TADS. The area was calculated between the temperatures of 250 and 290 K on the heating curves. The area was divided into four parts (designated A, B, C and D) using the valley between peaks to determine when a "transition" was finished. This profiling technique assumed that all the peaks were due to the melting of triglycerides in the oil portion of the sample. The validity of this assumption is based on the DSC profiling of pistachio nuts previously cited [3]. The ratio of area A to area B was used as the key characteristic for comparisons.

A second numeric quantity was calculated for each DSC curve—the total "heat of melting". This was taken as the total area under the DSC curve between the partial area end points divided by the sample weight, which resulted in a value with the units of cal $g^{-1}$. This value was used as the second variable ($X$) for the graphical characterizations where the A/B ratio was taken as the first variable ($Y$).

Table 1 details the average A/B ratio, its standard deviation and range for each of the three South African macadamia nut samples identified by the city of purchase. The values for the nut and oil ranges in this table should be compared with the results in Table 2 which gives representative A/B ratio data for other macadamia nut samples of known origin. In Table 2, the column designated "Match range" is an indication of whether the A/B ratio

TABLE 1

A/B area ratios for South African macadamia nuts

| Location | A/B ratio | A/B range |
|---|---|---|
| Capetown | $0.24 \pm 0.13$ | 0.06–0.40 |
| Johannesburg | $0.17 \pm 0.06$ | 0.09–0.25 |
| Pretoria | $0.23 \pm 0.04$ | 0.06–0.35 |

TABLE 2

A/B area ratios for macadamia nuts and oils of known origin

| Location | Form | A/B ratio | Match range? |
|---|---|---|---|
| Costa Rica Style III | nut | 0.43 | yes |
| | oil | 0.35 | yes |
| Malawi Style II | nut | 0.33 | yes |
| | oil | 0.38 | yes |
| Malawi Style IV | nut | 0.27 | yes |
| | oil | 0.33 | yes |
| Malawi Style VI | nut | 0.40 | yes |
| | oil | 0.43 | yes |
| Guatemala | nut | 0.57 | no |
| | oil | 0.43 | yes |
| Australia Style II | nut | 0.40 | yes |
| | oil | 0.47 | yes |

Match range for nuts 0.06–0.40
Match range for oils 0.22–0.47

for the sample fell within the range for the South African macadamia nuts of the same sample form. The range chosen reflects the extremes of the Capetown and Pretoria samples which had the broadest spread in values.

Figure 1 illustrates a DSC curve from a representative Capetown macadamia oil sample. When compared with Fig. 2, a DSC curve of the nut oil

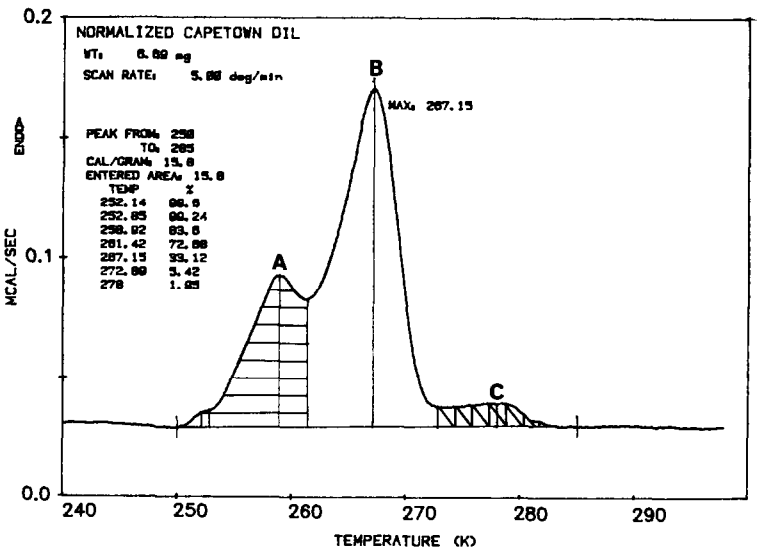


Fig. 1. DSC curve for macadamia nut oils from Capetown, South Africa. Heating program: 230–300 K at 5 K $min^{-1}$ in nitrogen.

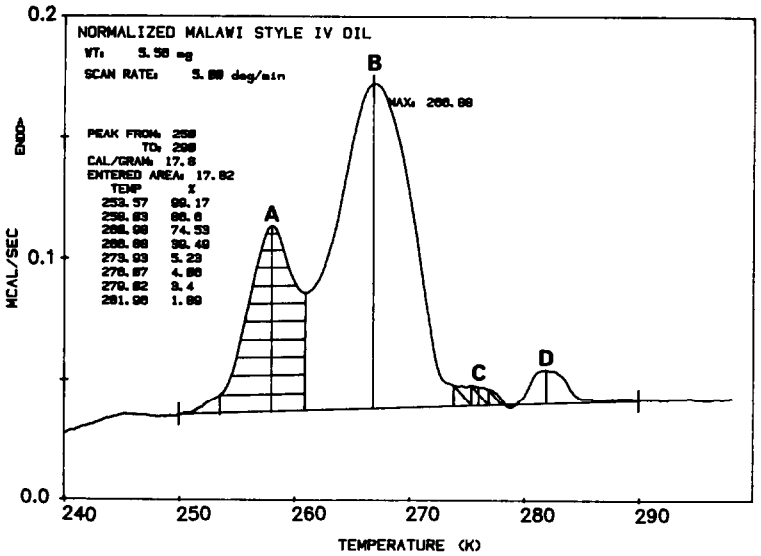


Fig. 2. DSC curve for macadamia nut oils from Malawi. Heating program: 230–300 K at 5 K $min^{-1}$ in nitrogen.

from Malawi, the similarity in A/B ratios between the Malawian and the South African samples is visually apparent.

Based on this single value comparison, it is clear that even with macadamia nuts of known origins, definitive distinctions between the South African nuts and the samples in question can not be made 100% of the time. A graphical method of data analysis was then utilized, in which the A/B ratio was plotted as the *Y*-coordinate and the heat of melting (cal $g^{-1}$) as the *X*-coordinate. Table 3 details the average heat of melting, its standard deviation, and the range for each of the three South African macadamia nut oils along with representative values from the known standard macadamia nut oils.

TABLE 3

Heats of melting for macadamia nuts

| Source | Heat of melting (cal $g^{-1}$) | |
|---|---|---|
| | Average | Range |
| Capetown | 16.34 ± 0.06 | 16.27–16.42 |
| Johannesburg | 16.15 ± 0.20 | 15.96–16.43 |
| Pretoria | 16.65 ± 0.06 | 16.57–16.70 |
| Malawi | 17.98 ± 0.55 | 17.31–18.63 |
| Guatemala | 17.62 ± 0.72 | 16.55–18.14 |
| Australia | 17.33 ± 0.26 | 17.07–17.59 |

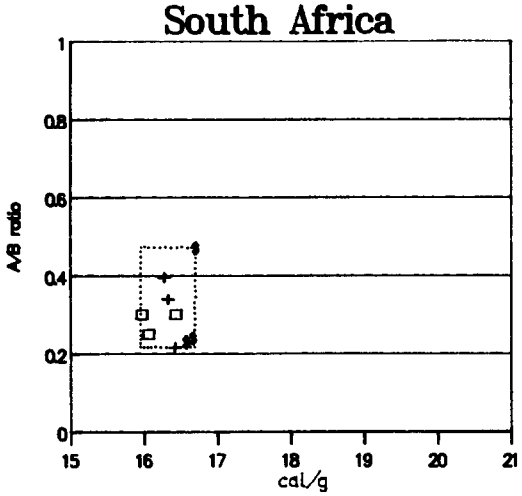


Fig. 3. A/B ratio vs. heat of melting plot for South African macadamia nut oils. The boxed area defines the limits of values attributed to macadamia nuts grown in South Africa. +, Capetown; □, Johannesburg; $, Pretoria.

Figure 3 illustrates the resulting plot for the South African macadamia samples. Each mark on the plot represents the average of 3 DSC replicate aliquots of a single extracted oil. Each nut source was sampled for three extractions. An area bounded by the box visually represents the segment of the plot defining the South African characteristics.

Figures 4, 5, and 6 represent the results of the Malawi, Guatemala, and other standards as compared to the South African "box". It can be seen that

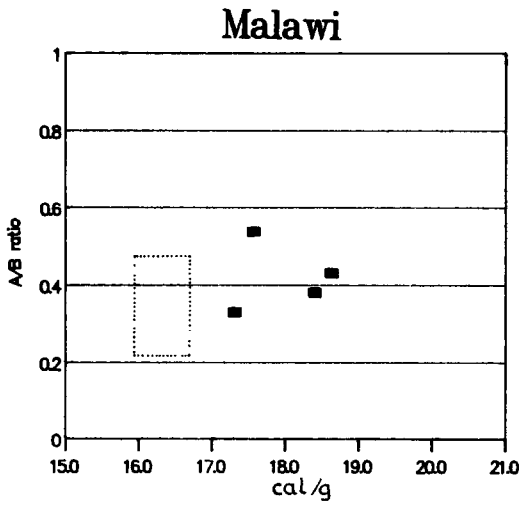


Fig. 4. A/B ratio vs. heat of melting plot for Malawi macadamia nut oils (known origin). The box represents South African values.

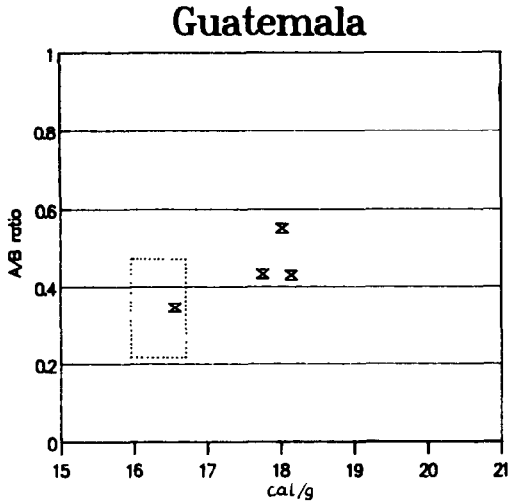


Fig. 5. A/B ratio vs. heat of melting plot for Guatemala macadamia nuts oils (known origin). The box represents South African values.

the standard macadamia nut oils from Malawi are clearly distinguishable from the South African. Likewise, the Australian, Zimbabwian and Brazilian samples have values falling outside those of South Africa. One of the Guatemala standards included in Fig. 4 falls into the area designated for South African macadamias. There is some question on the authenticity of this standard, and it probably should be treated as a sample rather than as a standard. A single value appears in Fig. 6 for the Costa Rican standard.

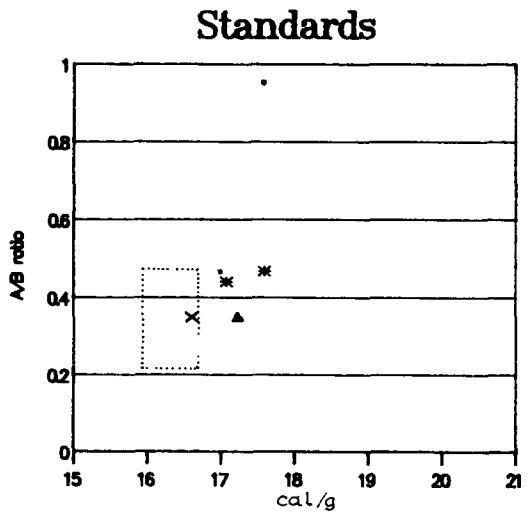


Fig. 6. A/B ratio vs. heat of melting plot for other known macadamia nut oils. The box represents South African values. *, Australia; •, Zimbabwe; ×, Costa Rica; ▲, Brazil.

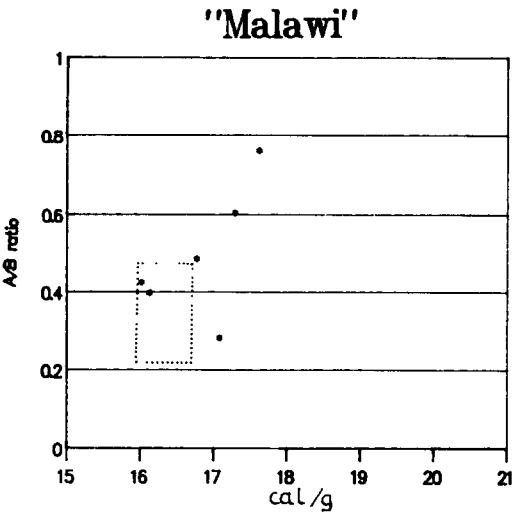


Fig. 7. A/B ratio vs. heat of melting plot for oils from six imported nut Shipments labelled "Product of Malawi". The box represents South African values.

While this falls within the characteristic values for South African, it is unknown if this one sample truly reflects the characteristics of macadamia nuts grown in Costa Rica.

Imported macadamia nuts from actual shipments are shown in Figs. 7–9. Of the samples labelled "Product of Malawi", two have values comparable to the South African. Those labelled "Product of Australia" were clearly

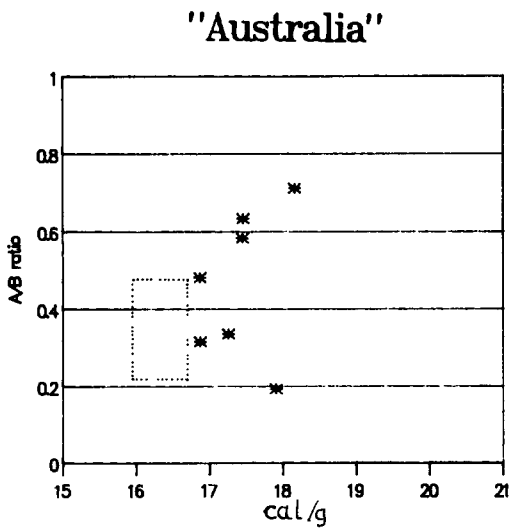


Fig. 8. A/B ratio vs. heat of melting plot for oils from seven imported nut shipments labelled "Product of Australia". The box represents South African values.

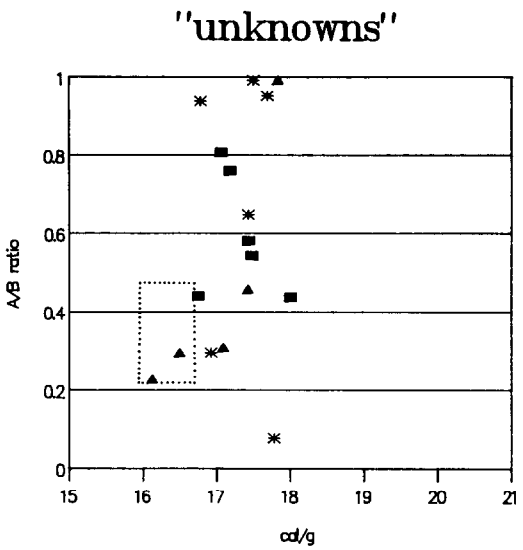


Fig. 9. A/B ratio vs. heat of melting plot for oils from thirteen imported nut shipments with no country of origin. The box represents South African values. ■, Samples A–F; *, samples G–L; ▲, samples M–G.

distinguishable under this method. Finally, the samples of unknown origin are shown in Fig. 9. Three of these could be considered as suspect and would need more information before the final determination of country of origin. It is possible that the samples which fall into the South Africa "box" may have been from South Africa. However, the majority of the imported samples were clearly distinguishable from the South African oils.

Based on visual comparison of the DSC curves, the tabulated A/B ratios, and the $X$–$Y$ representations, it can be seen that there is a difference between the South African macadamia nuts and most of the other samples. This difference may be attributed to the variety of the nuts themselves. The relative distribution of the triglycerides in the macadamia nut oils appears to vary sufficiently to distinguish between the rough and smooth shelled varieties. The fact that some imported nut samples resemble the South African nuts may be a reflection of the variety of the nuts. At the time of this writing, we are attempting to ascertain the variety of macadamia nuts grown in Malawi to test the validity of this conclusion.

It was observed that the DSC runs of the ground nut composite samples generally showed more variation from sample to sample that did the extracted oil samples and less variation than an equivalent number of samples taken from whole nuts. This is entirely expected and reflects the sampling problem inherent is using milligram size samples to reflect a less than perfectly homogeneous product.

## CONCLUSIONS

DSC, coupled with graphical data analysis, has been shown to have potential as a useful technique for the characterization of macadamia nuts. The drawback of small sampling sizes can be overcome by taking larger composite samples or extractions for analysis.

The results have been shown to correlate with information obtained from the literature on the varieties of macadamia nuts and their respective growing areas. While the DSC profile of these nuts is not currently sufficient by itself to assign the country of origin, further work is proceeding to refine this screening tool. There is need for more standards and specific varietal information about those standards.

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