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CHARACTERIZATION OF GREEN COFFEE BEANS BY COMBINED THERMOGRAVIMETRIC ANALYSIS/ATMOSPHERIC PRESSURE CHEMICAL IONIZATION MASS SPECTROMETRY *

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ABSTRACT

As a signatory to the International Coffee Agreement, the United States has set import quotas on green coffees from International Coffee Organization (ICO) member countries. Coffee from non-ICO countries has its own quota. The need has developed for the U.S. Customs Laboratory system to devise analytical methods useful in determining where coffee has been grown. This paper will discuss the application of combined thermogravimetric analysis/atmospheric pressure chemical ionization mass spectrometry to the characterization of green coffee beans as to country of origin.

INTRODUCTION

The coffee producers of the world have long attempted to regulate the supply and price of green coffee beans through the International Coffee Organization. This organization sets export quotas for each producing country and issues the "coffee stamps" which must be a part of the shipment's documentation. The United States is a signatory to the International Coffee Agreement and has set corresponding import quotas for ICO coffees. However, a country which has a coffee crop exceeding its export limit might attempt, by transshipment through a non-ICO country and false labeling, to circumvent that quota.

It falls on the U.S. Customs Service to sort out those imports which are legitimate non-ICO coffees from those that are not. What methods are available to carry out this task? Published accounts indicate that GC and GC–MS have been widely used to investigate the soluble fractions and the headspace of coffee beans [1–6]. Many of the compounds found are volatile and are produced or released during roasting. In addition, two DTA studies on green coffee beans were found in the literature: pressure DTA [7] and DTA–MS [8] which tracked the evolution of pyridine and furfural as a

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function of temperature. With these factors in mind and a deluge of coffee beans in the laboratory, thermogravimetric analysis coupled with atmospheric pressure chemical ionization mass spectrometry (TGA–APCIMS) was tried.

EXPERIMENTAL

The interfacing of the Perkin-Elmer TGS-2 and the Sciex TAGA 3000 has already been discussed in the literature [9]. Coffee bean samples of known origins were obtained (Table 1). Samples from actual import shipments were the "unknowns". Aliquots of the beans were ground in a Wiley mill. Both whole beans and ground beans were initially used in the TG runs. The whole beans proved to be too large for reproducible results. Therefore, all reported results will be from samples ranging in size from 2 to 5 mg of ground bean.

Both pyrolysis runs using nitrogen as the balance purge gas and oxidation runs using air were made. The oxidation runs were chosen for data analysis as they more closely approximated roasting conditions. The temperature program and instrumental factors used for the runs are shown in Table 2.

The mass spectral data from each sample run was processed as follows:

TABLE 1

Coffees of known origin

Columbian Arabica
Costa Rican Arabica
El Salvadorian Arabica
Ethiopian Arabica
Indonesian Arabica
Mexican Arabica
Nicaraguan Arabica
Ethiopian Djimma
Ethiopian H. Long Berry
Ethiopian Limnu
Indonesian Blue Sumatra
Indonesian Robusta
Philippine Excelsa

TABLE 2

Experimental conditions

TGS-2
Temperature program: Hold at 50°C for 1 min
Heat 25° min^{-1} to 50–200°C
Hold at 200°C for 3 min
Purge gas: air 100 ml min^{-1}

TAGA 3000
Mass scans: 15–250 amu, 1 scan per min
Positive mode
Sweep gas: zero air 900 ml min^{-1}

(1) for selected ions, the ion intensity values were weight normalized; (2) for each ion, the lowest normalized value of the run was then subtracted from the others to effect a background correction; (3) the resulting "Delta" values were plotted against the scan number corresponding to the TG temperature; (4) the curves thus produced were then compared.

DISCUSSION

The normalized intensities were plotted for both the knowns and unknowns. Comparisons were made based on the ion curves for four groups of samples: (1) a single coffee variety grown in one country; (2) different varieties grown in one country; (3) a single variety grown in the different countries; (4) the "unknowns" with the "knowns".

For the first case, a set of four Costa Rican grown Arabica coffees were compared. In Fig. 1, three of the four samples have curves which are similar in shape, for $m/z = 45$ (acetaldehyde H^+), the exception being the curve of OCOF 24. For $m/z = 80$ (pyridine H^+) (Fig. 2), OCOF 24 is again different from the other three samples. The same is true for $m/z = 117$ (indene H^+ or butyl acetate H^+) (Fig. 3). Finally, for $m/z = 29$ (ethyl fragment), there

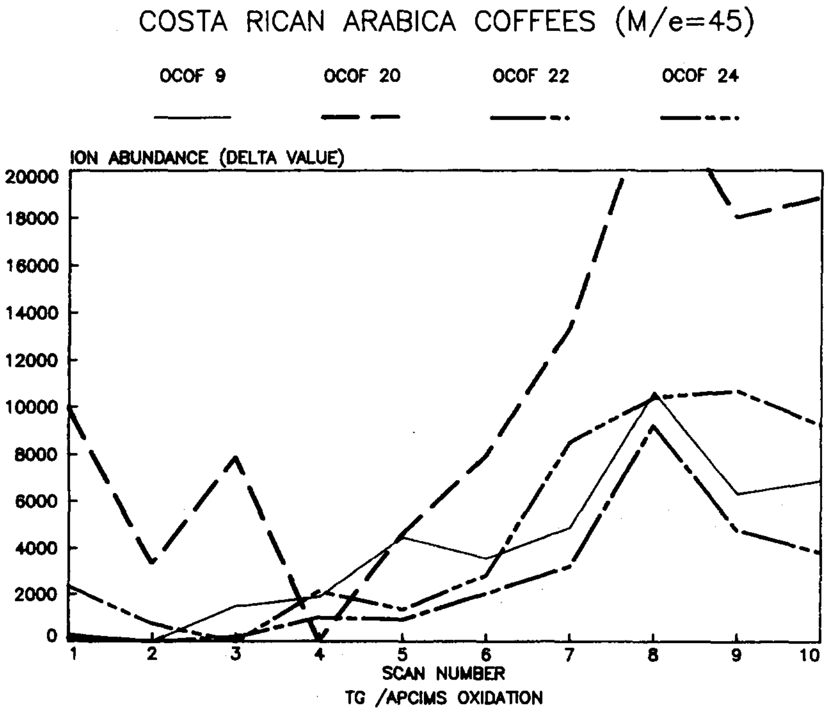

Fig. 1. Costa Rican Arabica coffees $m/z = 45$. OCOF 9 (——), OCOF 20 (— — —), OCOF 22 (— - —), OCOF 24 (— - - —).

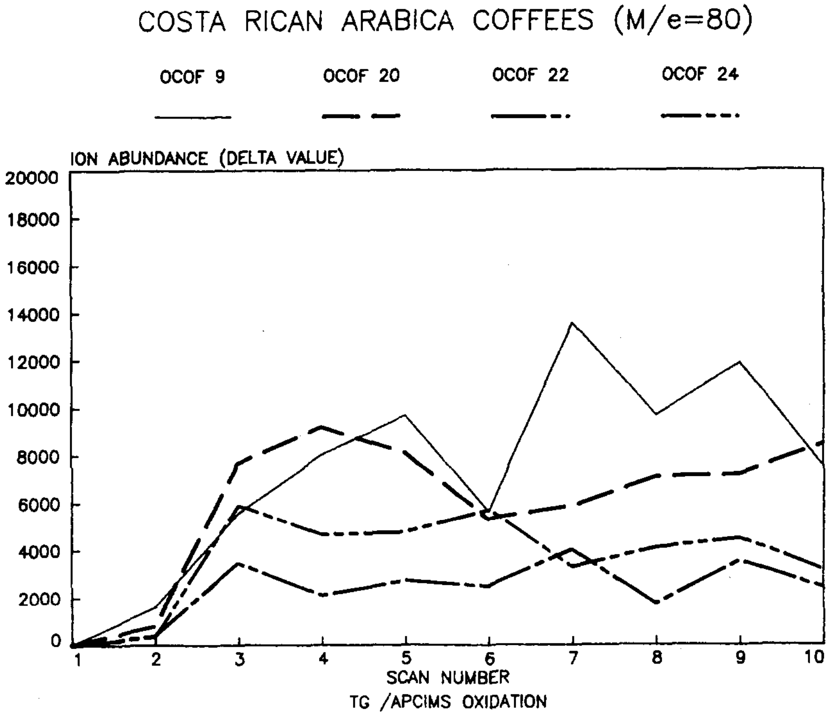

Fig. 2. Costa Rican Arabica coffees $m/z = 80$. OCOF 9 (———), OCOF 20 (— — —), OCOF 22 (— - —), OCOF 24 (— - - —).

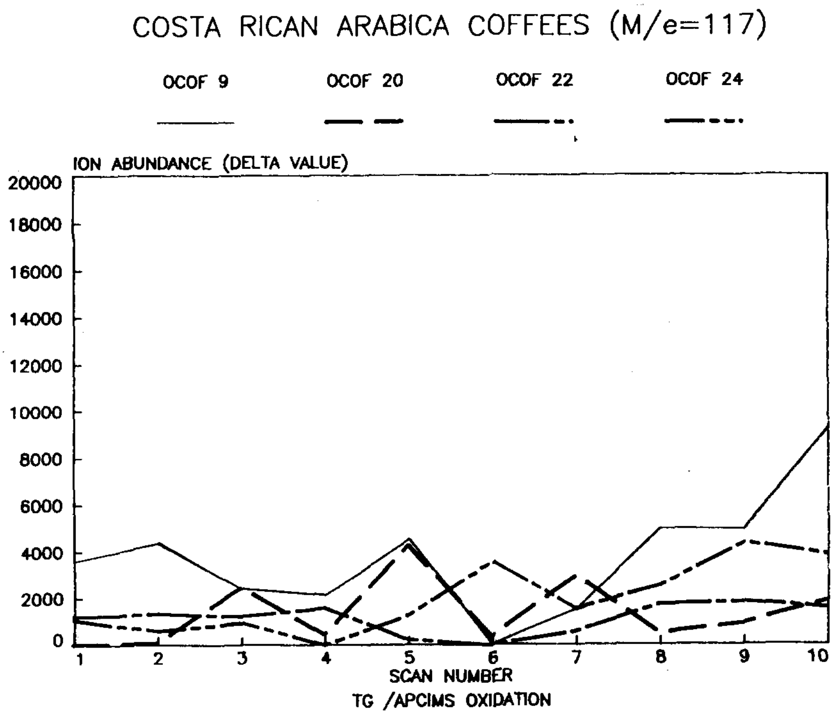

Fig. 3. Costa Rican Arabica coffees $m/z = 117$. OCOF 9 (———), OCOF 20 (— — —), OCOF 22 (— - —), OCOF 24 (— - - —).

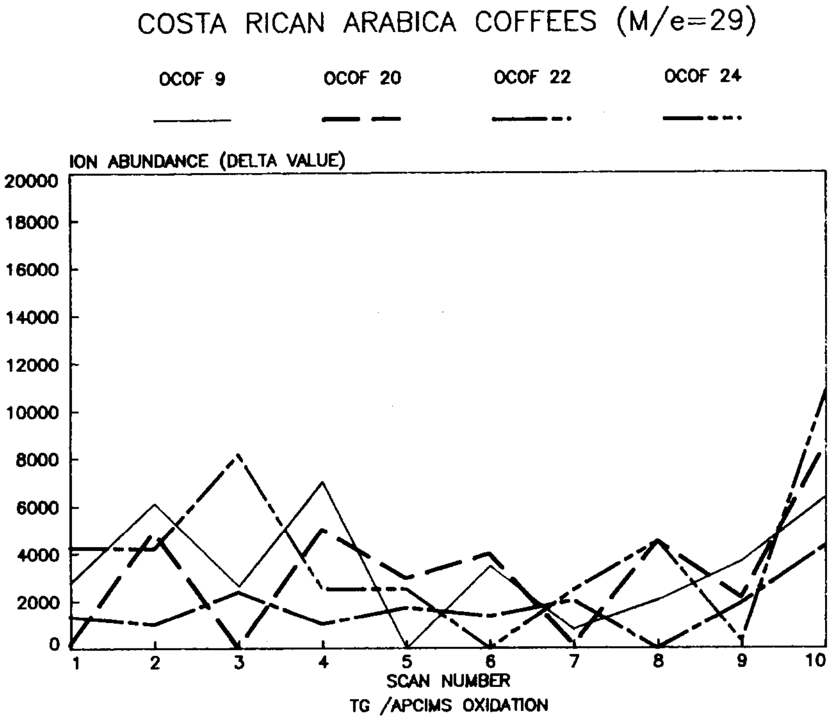

Fig. 4. Costa Rican Arabica coffees $m/z = 29$. OCOF 9 (——), OCOF 20 (— — —), OCOF 22 (— - —), OCOF 24 (— - - —).

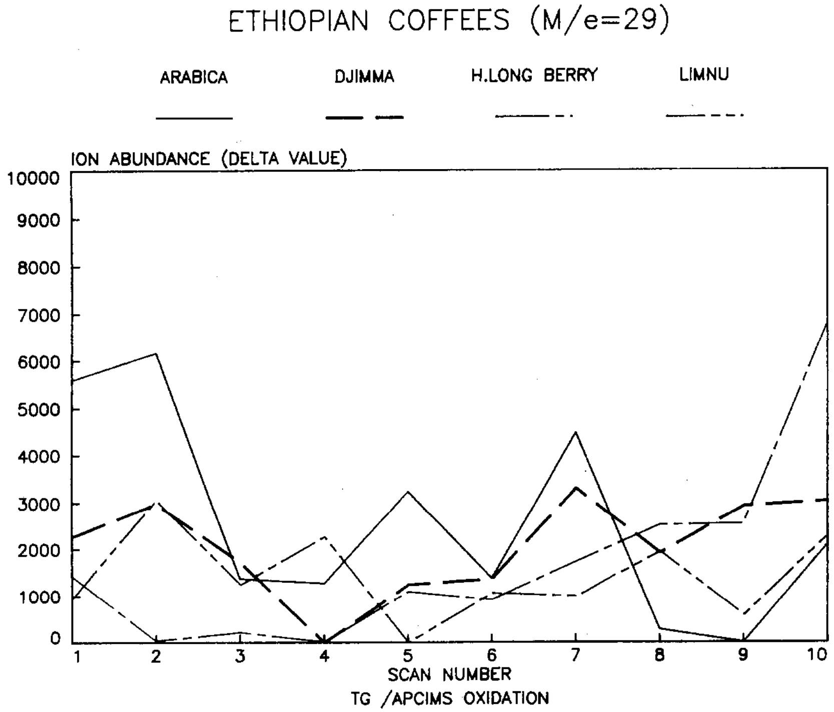

Fig. 5. Ethiopian coffees $m/z = 29$. Arabica (——), Djimma (— — —), H. Long Berry (— - —), Limnu (— - - —).

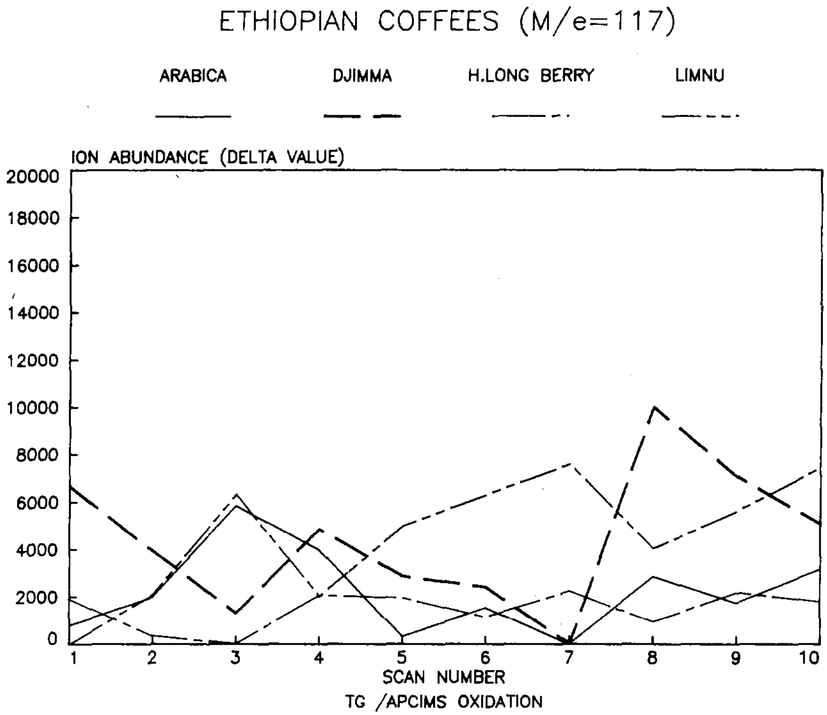

Fig. 6. Ethiopian coffees $m/z = 117$. Arabica (———), Djimma (— — —), H. Long Berry (— - —), Limnu (— - - —).

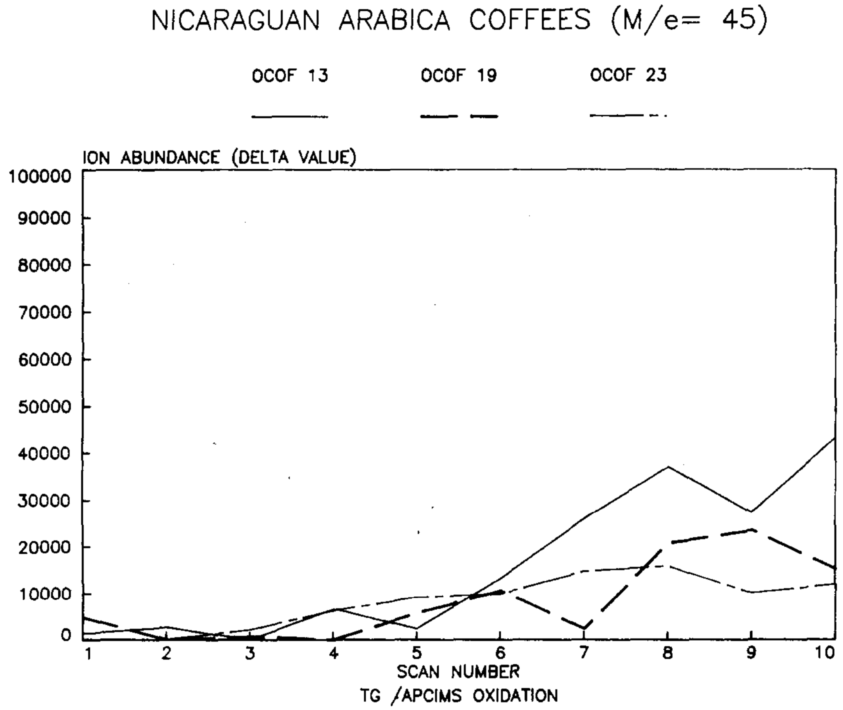

Fig. 7. Nicaraguan Arabica coffees $m/z = 45$. OCOF 13 (———), OCOF 19 (— — —), OCOF 23 (— - —).

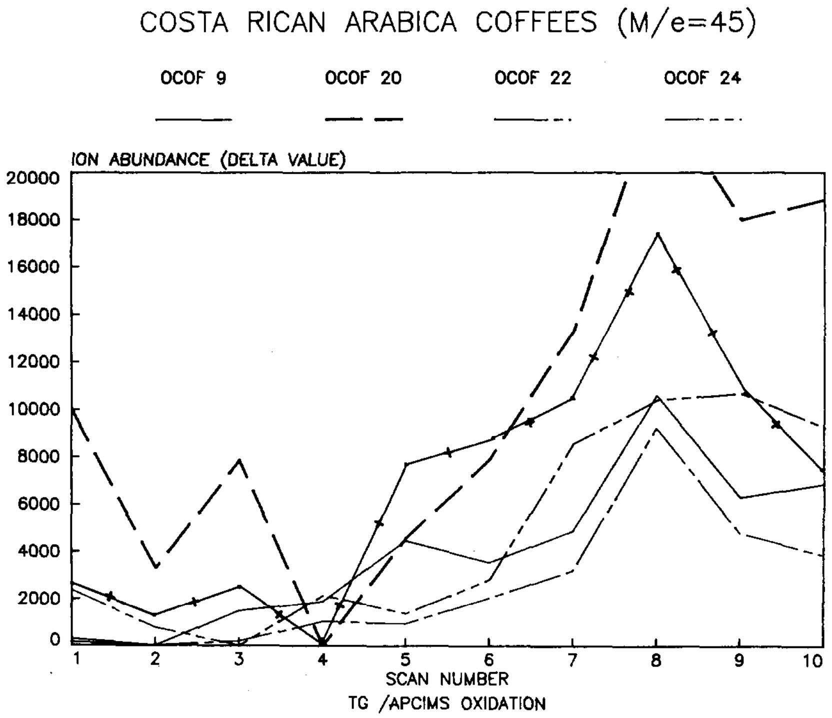

Fig. 8. Comparison of unknown with Costa Rican Arabica coffees $m/z = 45$. OCOF 9 (———), OCOF 20 (— — —), OCOF 22 (— - —), OCOF 24 (— - - —), OCOF 7 (unknown) (— + —).

appears to be little agreement among the curves (Fig. 4). It should be noted that six different types of Arabica coffee are grown in Costa Rica [10]. As this finer subdivision of plant type is not known for these samples, its effect on our curves can only be approximated.

Different coffee varieties grown in one country usually show more diver-

TABLE 3

Sample matches for masses 29,45,60,80,95,117

Unknown	Country	No. of ions matched [a]
OCOF 3	Costa Rican Arabica	2
OCOF 5	Costa Rican Arabica	3
OCOF 6	Costa Rican Arabica	2
OCOF 7	Costa Rican Arabica	5
OCOF 25		0
OCOF 26	Costa Rican Arabica	3
OCOF 27	Indonesian Arabica	2
OCOF 28	Costa Rican Arabica	2

[a] Maximum number of matches = 6.

TABLE 4

Sample matches for masses 33,60,97,111

Unknown	Country	No. of ions matched [a]
OCOF 3	Indonesian Robusta	2
OCOF 5	Indonesian Robusta	2
OCOF 6	Indonesian Arabica	2
OCOF 7	Indonesian Robusta	3
OCOF 25	Nicaraguan Arabica	2
OCOF 26	Nicaraguan/Costa Rican Arabica	3
OCOF 27	Nicaraguan/Indonesian Arabica	2
OCOF 28	Costa Rican Arabica	3

[a] Maximum number of matches = 4.

TABLE 5

Masses studied

m/z	Compound
29	Ethyl fragment$^+$
33	Methanol H^+
45	Acetaldehyde H^+
60	Trimethyl amine H^+, propyl amine H^+
69	Furan H^+, isoprene H^+
80	Pyridine H^+
83	Methyl furan H^+
93	Glycerol H^+
95	Phenol H^+, 2-vinyl furan H^+
97	Furfural H^+
111	Catechol H^+
117	Indene H^+, butyl acetate H^+
125	*o*-Methoxyphenol H^+
149	Coumarin H^+

TABLE 6

Sample matches for all 14 masses

Unknown	Country	No. of ions matched [a]
OCOF 3	Indonesian Robusta/Costa Rican Arabica	4/4
OCOF 5	Costa Rican Arabica/Indonesian Robusta	5/4
OCOF 6	Indonesian Arabica/El Salvadorian Arabica/ Costa Rican Arabica	3/3/3
OCOF 7	Costa Rican Arabica/Indonesian Robusta	7/5
OCOF 25	Nicaraguan Arabica/Costa Rican Arabica	3/3
OCOF 26	Costa Rican Arabica/Nicaraguan Arabica	5/4
OCOF 27	Indonesian Arabica/Indonesian Robusta/ Nicaraguan Arabica/Costa Rican Arabica	4/3/3/3
OCOF 28	Costa Rican Arabica/Nicaraguan Arabica	5/4

[a] Maximum number of matches = 14.

sity than that shown by the Costa Rican samples. This second case is demonstrated by Figs. 5 and 6 for $m/z = 29$ and 117, respectively, for four Ethiopian coffee varieties. For the third case, a single coffee variety grown in different countries, we compared three Arabica coffees grown in Nicaragua with those from Costa Rica. One of the Nicaraguan grown coffee samples, OCOF 19, was consistently different from the other two samples. In comparison with the Costa Rican samples, the curves for $m/z = 45$ were judged to be similar in shape. Figure 7 illustrates that the intensity is different, however.

For the purpose of determining the country of origin of the unknowns, the fourth case, six ions of interest were initially chosen. The ion abundance curve for the unknown was compared with the known curves as illustrated in Fig. 8. The curves that matched in intensity and shape were considered indicative of possible matching origin. Table 3 lists the unknowns along with the coffee which has the most matching ion curves for the selected ions.

In order to test whether the selection of the ions made a significant difference in the country identified as the origin of the unknown, two more sets of ions were tabulated, plotted and compared. Table 4 indicates that, based on four ions, the identifications change. Finally, the fourteen masses shown in Table 5 were all used to provide curves for matching. Table 6 details the possibility of an unknown coffee matching more than one known coffee.

CONCLUSION

The application of thermogravimetric analysis/atmospheric pressure chemical ionization mass spectrometry to green coffee beans has provided us with several insights into the relationship between coffee variety and country of origin. First, we have seen that the oxidation products of green coffee beans are a complex mixture, and that some of these compounds are volatile at low temperatures and some form during the oxidation process. Second, based on comparisons of ion abundance curves, intracountry variations for a single variety of coffee are less than intercountry variations. Third, intercountry variations for a single coffee variety are less than intervariety variations. Fourth, unknown coffees can be matched to known coffees for country of origin based on various combinations of 14 ions with varying degrees of certainty. Finally, we have concluded that further work on the subject of green coffee beans by TGA/APCIMS is necessary, utilizing the negative ionization mode to highlight the sulfur-containing oxidation products.

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