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COMPARISON OF VARIOUS GREEN COFFEES BY THERMOGRAVIMETRIC ANALYSIS/ATMOSPHERIC PRESSURE CHEMICAL IONIZATION MASS SPECTROMETRY (TGA/APCIMS). PART 2 *

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ABSTRACT

Coffee beans have been the subject of continuing analytical work at the Headquarters laboratory of the U.S. Customs Service. In this study of coffee beans by combined thermogravimetric analysis/atmospheric pressure chemical ionization mass spectrometry (TGA/APCIMS), negative ionization and photooxidation of the balance effluent prior to its entrance into the mass spectrometer will be used to differentiate between the major coffee varieties. The coffee beans will be compared by examining the ion abundance/temperature curves for selected ions and mass spectra for specific temperatures.

INTRODUCTION

Coffee beans have been the subject of continuing analytical work at the Headquarters laboratory of the U.S. Customs Service. Our interest in coffee beans stems from country of origin quotas on coffee and the problems associated with analytical measurements made on bulk commodities. There has been considerable published research on coffee beans, primarily utilizing extraction and distillation methods to separate fractions for analysis [1–8].

I have previously reported our work on green coffee beans utilizing Thermogravimetric Analysis/Atmospheric Pressure Chemical Ionization Mass Spectrometry (TGA/APCIMS) in the positive ionization mode to distinguish between coffee beans from different countries [9]. I concluded that this method was not the definitive analysis for determining the country of origin of green coffee beans. Based on other work in our laboratory, we realized that coffee bean variety might have a greater influence on the characteristics of the bean than place of growth. Therefore, this paper will deal with our efforts to distinguish between Robusta and Arabica coffees by negative mode TGA/APCIMS.

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EXPERIMENTAL

The details of the Perkin Elmer TGS-2 and Sciex TAGA 3000 interface have been published previously [10]. A modification to permit the photo-oxidation of the effluent from the TGS-2 balance within the interface was suggested by Hijazi and DeBrou [11]. This required the UV lamp from the Pen Ray SOG-2 ozone generator to be placed inside the interface with thermal and UV shielding outside. The UV lamp remained in place for all sample runs, whether or not it was operated. The experimental parameters are given in Table 1. Coffee beans of either known variety or known country of origin were obtained. The analytical samples were taken from 30 bean samples ground just prior to the TGA run.

In the TAGA 3000 negative ionization mode, the major reactant ion is the superoxide, O_2^-, which is formed through electron capture by oxygen. A series of other negative ion species is formed by dissociate electron capture by oxygen to form O^- which reacts with other compounds (CO_2, O_2, etc.) and with neutrals formed in the corona discharge (NO, NO_2, etc.).

In this ionization mode, typical product ions such as SO_2^-, SO_3^- and SO_4^- would result from SO_2. Mercaptans are known to ionize to M^{-1} and other organosulfur compounds can be ionized by photooxidation of the effluent prior to the corona discharge.

RESULTS

From the TGA curves, the percentage weight loss for the coffee samples averaged 7.5% with a range of 5.9–9.7%. The effective sample ionized was,

TABLE 1

Experimental conditions

TGS-2
Temperature program
50°C, Hold 1 min
50–200°C, Heat at 25 K min^{-1}
200°C, Hold 3 min
Purge gas
Balance chamber: nitrogen, 10 ml min^{-1}
Furnace tube: air, 90 ml min^{-1}
Sample weight: 1–2 mg
TAGA
Mass collection: 15–200 amu, 1 scan min^{-1}
Ionization mode: negative
Sweep gas: zero air, 900 ml min^{-1}
Inlet UV lamp: on or off

therefore, in the range from 0.07–0.14 mg. There were no notable features in the TGA curves; they all followed the profile of a gentle slope decreasing with increasing temperature.

Comparison of the weight normalized mass abundances for the same coffee run in both the positive and negative ionization modes indicates that the overall abundances were lower for the negative mode. This was evident for both background and sample runs. Although the presence of the UV lamp in the interface tube had no effect on the mass abundances when it was off, its operation for photooxidation of the effluent stream further reduced the mass abundances and some of the expected masses due to O_2^- clusters disappeared. However, the overall levels of mass abundances remained constant for a given set of conditions over time.

The mass abundance values were background corrected and weight normalized to the initial sample weight. Based on a statistical study of the variation in background during a run versus the variation from run to run, the background correction factor selected for an individual mass number was the abundance value for that mass averaged over the entire background run.

The analytical results will be presented in two parts. The designations indicate the negative ionization mode (NEG), the use of an oxidizing atmosphere in the furnace tube (OX), and the state of the UV lamp (OFF or ON).

Condition: NEG/OX/OFF

Twelve different coffees were run in air and the negative ionization mode. The UV source was off. From the masses collected over the range of 15–200 amu, four masses were profiled against changing temperature. These were $m/z = 33$ (HS^-), 46 (NO_2^-), 64 (SO_2^-), and 97 (furfural alcohol$^-$). These identifications were made based on expectations of ions formed in the negative mode and compounds found in coffee. Figures 1 and 2 illustrate the abundances for these masses for two Robusta coffee samples from Indonesia. There is agreement between the curves, following the trend that if $m/z = 46$ is high, the other curves will be high and, conversely, if $m/z = 46$ is low, the others will be low.

Comparing the Robusta coffees from Indonesia, Philippines, Uganda and Timor, the following observations can be made for the mass abundance versus scan number (S) curves:

$m/z = 33$ for a given scan number, the abundance of $m/z = 33$ is less or equal to $m/z = 46$

$m/z = 46$ two levels of response; high for Indonesia and Uganda, low for Philippine and Timor

$m/z = 64$ Indonesia and Uganda have significant responses, Philippine and Timor have zero response

$m/z = 97$ All have zero response until peak at $S = 8 \pm 1$.

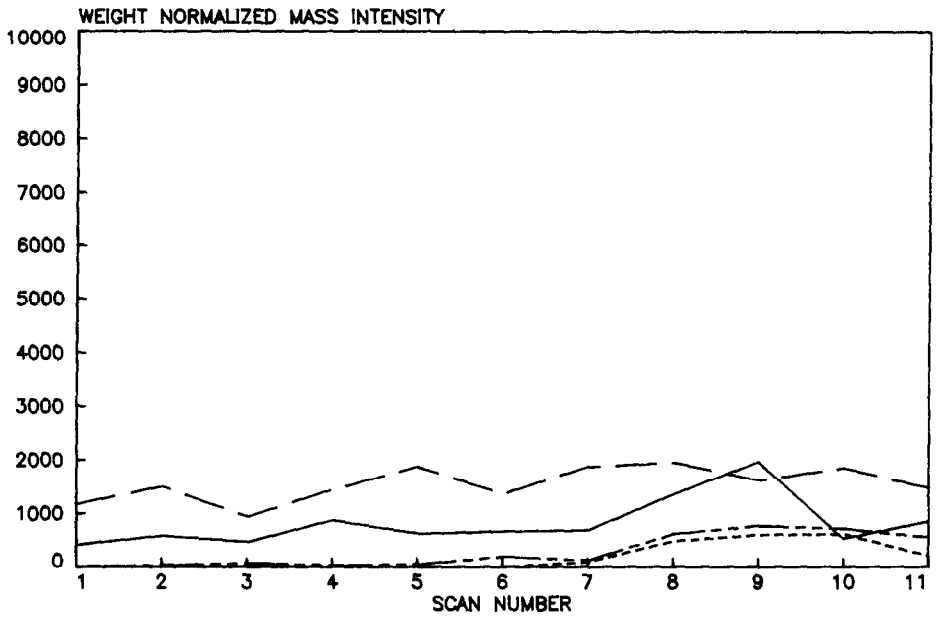

Fig. 1. Indonesian Robusta Coffee, NEG/OX/OFF, mass intensity as a function of time; $m/z = 33$ ——, $m/z = 46$ — — —, $m/z = 64$ —·—·—, $m/z = 97$ ------.

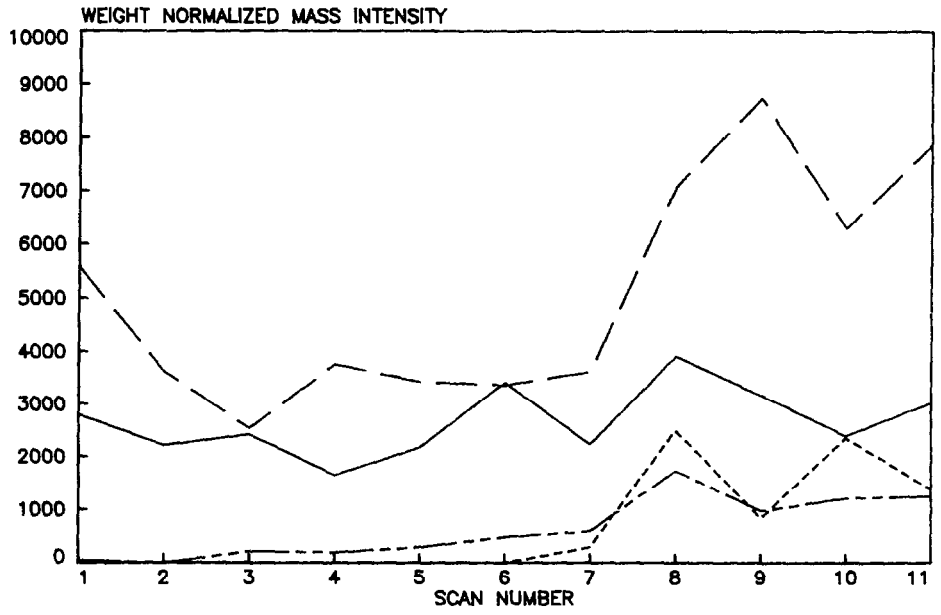

Fig. 2. Indonesian Robusta Coffee, NEG/OX/OFF, mass intensity as a function of time; $m/z = 33$ ——, $m/z = 46$ — — —, $m/z = 64$ —·—·—, $m/z = 97$ ------.

Comparing the Arabica coffees (Timor, Burundi, Costa Rica, Uganda, Angola and Kenya), the following observations were made of the mass abundance versus scan number (S) curves:

$m/z = 33$	high level	Burundi, Angola, Uganda Bugisu Peaberry, Kenya, $I_{33}/I_{46} \leq (\frac{1}{2})$; Costa Rica, $I_{33}/I_{46} \leq (\frac{1}{3})$
	low level	Timor, Uganda Bugisu AA
$m/z = 46$	high level	Burundi, Angola, Kenya, Uganda Bugisu Peaberry, Costa Rica
	low level	Timor, Uganda Bugisu AA
$m/z = 64$	zero level	Timor, Uganda Bugisu AA, Uganda Bugisu Peaberry, Costa Rica
	zero until $S = 8$	Angola, Burundi
	non zero	Kenya
$m/z = 97$	zero response until peak at $S = 10$ or 11, all except Timor (peak at $S = 8$)	

Under the same analytical conditions, 20 coffee samples were run and another type of data analysis was utilized. In this case, the nine most abundant masses were tabulated from the last mass scan ($S = 11$), TGA temperature 200°C. The mass abundances were background corrected and normalized to initial sample weight. The masses of 16, 32, 48 and 60 were not counted as these were present in all coffee samples. The mass numbers appearing in these nine most abundant peak tables were ranked as to the frequency of appearance by coffee variety. Table 2 presents those masses which appeared in 50% or more of the samples of a given variety. As can be seen, there are several peaks common to both groups. Eliminating those which appear in both the Robusta and Arabica coffees leaves the masses shown in Table 3. The list of mass identifications for both the "common" and "unique" masses appears as Table 4.

TABLE 2

Nine most abundant masses (NEG/OX/OFF)

Coffee variety	m/z								
Robusta	33	45	46	58	59	61	72	127	146
Arabica	33	45	46	58	59	72	92	100	

TABLE 3

Unique masses for coffee varieties (NEG/OX/OFF)

Coffee variety	m/z		
Robusta	61	127	146
Arabica	92	100	

TABLE 4

Mass fragment identification (NEG/OX/OFF)

m/z	Fragment
33	$(HS)^-$ Sulfide
46	$(NO_2)^-$ Nitrogen dioxide
59	$(C_2H_3O_2)^-$ Acetate
60	$(CO_3)^-$ Carbonate
61	$(HCO_3)^-$ Bicarbonate,
	$(C_2H_5S)^-$ Ethyl mercaptan, dimethyl sulfide
92	$(C_2H_5NO_3)^-$ Ethyl nitrate
127	$(C_6H_6O)O_2^-$ Phenol

Condition: NEG/OX/ON

The next set of coffee samples was analyzed under the influence of UV radiation. The nine most abundant mass tables for these coffee samples were developed from the mass scans. Proceeding as before, the "unique" masses for each variety were determined. These were $m/z = 47$, 50 and 62 for Robusta, and 59 for the Arabica. The tentative identities of some of these masses are listed in Table 5.

APPLICATION TO UNKNOWNS

A coffee of unknown variety from the Ivory Coast was run using the experimental conditions outlined. Comparison of the resulting nine most abundant mass tables with the "unique" masses was done for both NEG/OX/OFF and NEG/OX/ON runs. For the conditions of NEG/OX/OFF, this coffee sample could be identified as either Arabica or Robusta based on the presence of masses 92 and 61. Running this same Ivory Coast coffee under the conditions of NEG/OX/ON identified it as a

TABLE 5

Mass fragment identification (NEG/OX/ON)

m/z	Fragment
47	$(CH_3S)^-$ Methyl mercaptan
50	$(H_2O)O_2^-$ Water cluster
59	$(C_2H_3O_2)^-$ Acetate
62	$(NO_3)^-$ Nitrate
83	$(C_4H_3S)^-$ Thiophene
93	$(C_6H_7N)^-$ Ethyl pyrrole
	$(C_2H_5S_2)^-$ Dimethyl disulfide

Robusta on the strength of three matching masses (50, 47, 18). This result correlates well with the knowledge that Robusta Coffee is the primary variety grown in the Ivory Coast.

In an attempt to see how this methodology would handle a variety of coffee other than the ones it was based on, two other coffees were sampled; an Ethiopian H. Long Berry coffee and a Philippine Excelsa coffee. Under the conditons of NEG/OX/OFF, the H. Long Barry matched the Robusta with a mass of 61 while the Excelsa resembled the Arabica with a double match of masses 92 and 100. These coffees were also run under NEG/OX/ON but showed no clear distinction as neither set of unique masses appeared in their tabulation of nine most abundant masses.

The Excelsa coffee is not in the same botanical group as the Arabica and Robusta coffees but may share some characteristics with the Arabica. The Ethiopian H. Long Berry coffee has its origins in Ethiopia, and is an older strain of Arabica coffee. It becomes apparent that a clear match would not be expected when this strain is compared to an Arabica, as the Arabica profile is based on contemporary crossbred Arabica coffees [12,13].

DISCUSSION

From the results presented, several observations can be made. First, under the experimental conditions used, the major mass fragments tended to have an m/z less than 100. Second, for a given ionization mode, the predominant masses were essentially the same for both major varieties of coffee, Robusta and Arabica. Third, there were some masses which tended to appear in one variety or the other on a frequency basis of greater than 50%.

When methodology based on pattern matching of this sort is applied to coffee samples, it must be recognized that varieties, other than the two on which the patterns are based, may give confusing or contradictory results. Therefore, other corroborating information must be taken into account before assigning variety based on the results obtained by this method.

The problem of fingerprinting a bulk commodity such as coffee beans is complicated by several factors. One of the first problems we noted was that our "standard" coffees had year to year variation, reflecting differences in growing season and handling. Second, the effect of storage on a natural product such as coffee has the potential to change the profile being monitored. Third, the inhomogeneity of the samples was illustrated by the range of percent weight loss recorded from duplicate runs. This is due to the composition of the analytical sample and reflects the effect of varying amounts of different bean parts as well as particle sizes in the ground sample.

CONCLUSION

In conclusion, we have shown that despite several definite sampling related factors, Arabica and Robusta coffees can be distinguished from each other based on the nine most abundant masses collected by the negative ionization of the effluent from a temperature programmed oxidation. The on and off photooxidation modes help further to point up differences between the two varieties.

REFERENCES

1 R. Tressl and R. Silwar, J. Agric. Food Chem., 29(51) (1981) 1789.
2 O.G. Vitzthum and P. Werkhoff, Z. Lebensm. Unters. Forsch., 160 (1976) 277.
3 O.G. Vitzthum and P. Werkhoff, in G. Charalambous (Ed.), Analysis of Food and Beverages, Headspace Techniques, Academic Press, New York, 1978, p. 121.
4 O.G. Virtzthum and P. Werkhoff, J. Agric. Food Chem., 23(3) (1975) 515.
5 R. Tressel, Proceedings of the ASIC 8th Colloquim, Abidjan, 1977, p. 115.
6 W. Rahn and W.A. Konig, J. High Res. Chromatogr., July (1978) 68.
7 G.M. Singer and W. Lijinsky, J. Agric. Food Chem., 24(3) (1976) 550.
8 J.Th. Heins, H. Maarse, M.C. ten Noever de Brawn and C. Weurman, J. Gas Chromatogr., Nov. (1966) 395.
9 S.M. Dyszel, in A. McGhie (Ed.), Proceedings of the 13th NATAS Conference, Sept. 23–26, 1984 Philadelphia, PA, 51.
10 S.M. Dyszel, in B. Miller (Ed.), Thermal Analysis, Proceedings of the 7th ICTA, John Wiley, Chichester, 1982, 272.
11 N.H. Hijazi and G.B. Debrou, Trans. Tech. Sect., J. Pulp Paper Sci., 8 (1982) TR 100.
12 M. Sivertz, Coffee—Origin and Use, Sivetz Coffee, Inc., Corvallis, OR, 1984, p. 6.
13 B. Rothfas, Coffee Production, Gordian-Max-Riech, GmGH, Hamburg, 1980, pp. 39, 40.