Application of Multi-Element Scanning Thermal Analysis (MESTA) Method in Tire Identification for Forensic Purposes

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Abstract

Traffic accidents or criminal cases may lead car to leave tire samples or tire marks on an accident scene or a criminal scene. Tire samples left in a scene can be a valuable source of information that links an accident or criminal scene to the suspected vehicle. However, it is difficult to analyze a tire sample in detail for forensic purposes by chemical method or spectroscopic method due to its low solubility in solvents and dark color. The objective of this study was to explore the feasibility of using the multi-element scanning thermal analysis (MESTA) for tire samples identification in forensic science.

In this study, 13 tire samples were collected randomly from various sources. Powder samples were scraped from tire surfaces by files. The scraped powder was analyzed by the MESTA method. The MESTA C, N and S thermograms in the three temperature regions, namely, 250-450 °C, 451-590 °C and 590-710 °C were chosen as the temperature interval for analysis. The result of statistical analysis shown that there is significant variations among the total C (carbon), N (nitrogen), S (sulfur) concentrations and peaks ratio to differentiate those tire samples. Totally, there are 12 parameters that can be used to distinguish one sample from others. Principal component analysis (PCA) and hierarchical clusters analysis (HCA) were performed for discriminating different tire samples. Results shown that the combination of MESTA and HCA can be a potential technique for distinguish tire samples that are from different sources.

Introduction

In traffic accidents or criminal cases, tires may leave their marks on the scenes. In addition to analyzing mark pattern, comparing the composition of the residuals from tire left may also help to link the suspected vehicle [1,2]. Information of tire residue can be a valuable evidence that links an accident or crime scene to the suspected vehicle [3,4]. Therefore, comparison of chemical properties between the recovered trace tire residues and the suspected vehicle is important for forensic identification purposes [1-4]. The common composition of tire rubber is consisted of (i) oil as part of the tire formulation, (ii) organic polymeric material, and (iii) carbon black [5]. It is difficult to analyze a tire sample by chemical or spectroscopic methods, other than its bulk elemental composition, due to its low solubility in solvents and carbon black interferes by absorbing substantial amounts of energy in the full range of spectrum. Few techniques have been developed for detailed tire sample chemical analysis: pyrolysis gas chromatographic mass spectrometry (Py-GC-MS) is one of them [1,2,6,7]. This technique has been used in the analysis and identification

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of polymers/copolymers and additives in the components of automobiles, tires, packaging materials, textile fibers, coatings, paints and other solid materials. The Py-GC-MS analysis of solid sample are under controlled conditions at elevated temperature (500-700°C) in the presence of an inert gas, then the pyrolytic products are separated by gas chromatography followed by mass spectrometry analysis. Theoretically, if two samples having same composition when they heated at the same rate to the same temperature for the same period of time, they will produce the same decomposition products. Using this technique, the polymer and their additives of a tire can be identified.

Another technique available for tire analysis is TGA-FTIR (thermogravimetric analysis coupled to a Fourier transform infrared spectrometer), which is a tool for identifying the volatiles evolved from materials heated in a flowing gas stream in a TGA furnace [8,9]. The temperature range of TGA furnace is 25-1200°C, which is typically operated with air or nitrogen atmosphere. Infrared spectra are taken in short time intervals during the heating program and stored on disk. The TGA weight loss vs. temperature curve from TGA controller is then plotted with an overlay plot of chosen infrared bands vs. temperature. The advantage of Py-GC-MS and TGA-FTIR method eliminate the need for pre-treatment by performing analyses directly on the solid sample. Here, we tried a novel technique (MESTA) on tires in order to explore its potential as complementary techniques.

Multi-element scanning thermal analysis (MESTA) has been developed for the analysis of organic matter of solid samples [10,11]. This technique is similar to the carbon scanning thermal analysis, except that it simultaneously determines volatilization and decomposition of carbon, nitrogen and sulfur compounds over a temperature range from ambient to 800°C. With the knowledge of co-volatilized/decomposed N and S, MESTA provided additional constraints for characterization of organic matter in comparison to carbon scanning thermal analysis. MESTA had been used in the analysis of biological carbon in sediment, soil samples. The purpose of this study is to test the possibility of applying MESTA to tire identification for forensic applications.

Methods and Materials

Tire Specimen

Thirteen tire samples were collected from the used tire pool of a tire shop randomly. The manufactures and types of those tires were listed in Table 1. The collected tires were cleaned by tap water and dried on the outdoor concrete floor before sampling. Approximately 200mg tire powder was scraped from the surface of the tires by rasp. About 20mg of the scraped tire samples were subsampled and mixed with 80 mg of pure talc powder that was pre-treated in an 800°C furnace for one hour to get rid of any trace organic matter in the talc. The tire powder and talc powder were thoroughly mixed and ground for 30 minutes in an agate mortar. Mixing and grinding tire power with talc served two purposes: first, tire powder needed to be diluted to a desired concentration for MESTA and second, talc acted like micro beads, which enable the tire sample to be ground to very fine particles and thoroughly mixed with the inert talc, which is required for reproducible results of MESTA. For each MESTA measurement, 4mg of tire and talc mixture was placed into the sample compartment of a MESTA device. Three replicate MESTA measurements were performed for each sample.

Table 1 Information of the tire samples studied.

Sample no.	Manu-facturing Company	manu-facturing Place	tire type
1	Continential	USA	P215/60R16 94T
2	Bridgestone	USA	P215/70R15 97T
3	Bridgestone	Mexico	P205/55R16 89H
4	Delinte	China	P265/35R22 102W
5	Open country	Japan	P265/65R17 110G
6	Good Year	USA	P235/75R15 105S
7	Good year	USA	P225/75R16 104S
8	Michelin	USA	P205/60R16 91V
9	Supreme	Romania	P155/80R13 79I
10	SolusKH	Korea	P215/55R16 91H
11	Warrior	USA	P195/70R14 91T
12	General Altimax	Czech Republic	P175/65R15 84H
13	Corsa	Indonesia	P175/65R14 82H

The MESTA Procedure

The MESTA device first was described in 2007 by Hsieh [9,10]. This device has a quartz pyrotube, which is divided into a sample compartment and a combustion compartment. The combustion compartment is maintained at 1100°C with a furnace and constantly purged with 100%

ultra-pure grade O_2. The sample is placed in the sample compartment, constantly purged with a carrier gas, which was a mixture of 40% of pure oxygen and 60% of pure helium. During the analysis the sample is heated from ambient temperature to 800°C at a rate of 50°C/min. The volatilized and decomposed materials are carried by the carrier gas into the combustion compartment where their C (carbon), N (nitrogen) and S (sulfur) contents were oxidized to CO_2, NO_2 and SO_2, respectively. The oxidized gases then pass successively through detector for C [CO_2 analyzer (IR)], N [NO_2 chemiluminescent detector] and S [SO_2 chemiluminescent detector]. A PC based multi-channel data logger (National instruments Mult-iDQA 6034E, National Instruments Corporation, Austin, TX) is used to record the sample temperature, CO_2, NO_2 and SO_2 signals simultaneously. The flow rate of the carrier gas was 80 ml/min and that of the combustion compartment 350 ml/min. The proper sample sizes of C, N and S for the MESTA were in the range 10-200 µg. The C, N and S contents of a sample were quantified by using C, N and S calibration curves generated by various combinations of reagent grade cystine and potassium hydrogen phthalate [10].

Statistical Analysis

Principal component analysis (PCA) and hierarchical clusters analysis (HCA) were performed on the data obtained from MESTA to discriminate samples according to their C, N and S contents and the peak areas of the C, N and S thermograms. PCA represents the objects with the created variables which are linear combinations of the original variables [12]. Linear combinations of the variables forming principal components, then they are calculated along the directions of maximum variance and orthogonal to each other. The formation of groups of the study objects can be revealed by PCA [13]. HCA groups samples according to a similarity statistical parameter. Samples that have closely related properties are likely to be grouped closely from each other in the n-dimensional space represented by the n-original variables [14]. PAST, a free scientific data analysis software package with functions of univariate and multivariate statistics [15] was used to perform these statistical analyses.

Results and Discussion

The C, N and S concentrations of the tire samples determined from MESTA are listed in Table 2. These bulk elemental concentrations of tires do not have much discriminating power among the 13 samples because of the similarity of the chemical composition. The C, N and S thermograms of the MESTA, however, provide much more constrains for discriminating the tire samples. Typical MESTA C, N and S theromgrams of the tires are shown in Fig. 1 and 2 respectively. The peaks of the thermograms of the tire samples appeared from 250°C to 710°C and can be generally grouped into three temperature regions: I. 250-450°C, II 451-590°C and III 591-710°C.

Table 2 Total C, N, S concentrations of the 13 tested tire samples.

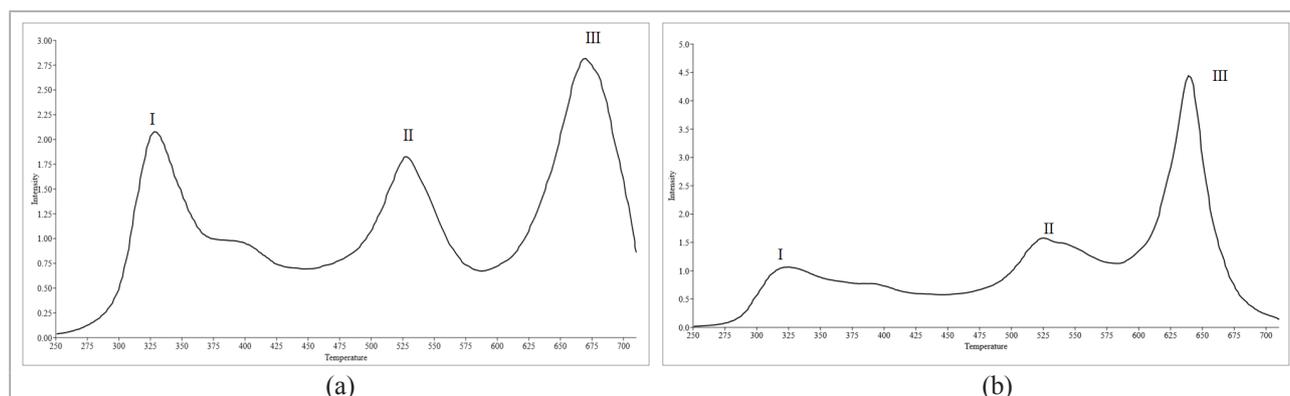| Sample.	C (mg /mg)	N (mg /g)	S (mg /g)
1	0.92 (± 0.02 , n=3)	5.8 (±0.1)	28 (±2)
2	0.92 (± 0.04 , n=3)	3.7 (±0.2)	30 (±2)
3	0.81 (± 0.02 , n=3)	4.6 (±0.1)	39 (±2)
4	0.93 (± 0.01 , n=3)	5.1 (±0.0)	23 (±2)
5	0.93 (± 0.03 , n=3)	3.4 (±0.0)	25 (±1)
6	0.90 (± 0.02 , n=3)	3.6 (±0.3)	19 (±3)
7	0.86 (± 0.04 , n=5)	3.2 (±0.2)	19 (±1)
8	0.86 (± 0.01 , n=4)	3.5 (±0.0)	28 (±2)
9	0.91 (± 0.02 , n=5)	5.9 (±0.3)	24 (±1)
10	0.93 (± 0.02 , n=4)	4.9 (±0.0)	24 (±1)
11	0.93 (± 0.02 , n=4)	4.7 (±0.2)	20 (±3)
12	0.86 (± 0.01 , n=5)	4.1 (±0.1)	24 (±1)
13	0.95 (± 0.02 , n=4)	4.3 (±0.0)	29 (±1)

Fig. 1 The C thermograms of MESTA obtained from tire sample 1 (a) and sample 5 (b). The decomposition peaks of each tire can be roughly grouped into three temperature regions: I (250-450°C), II (451-590°C) and III (591-710°C).
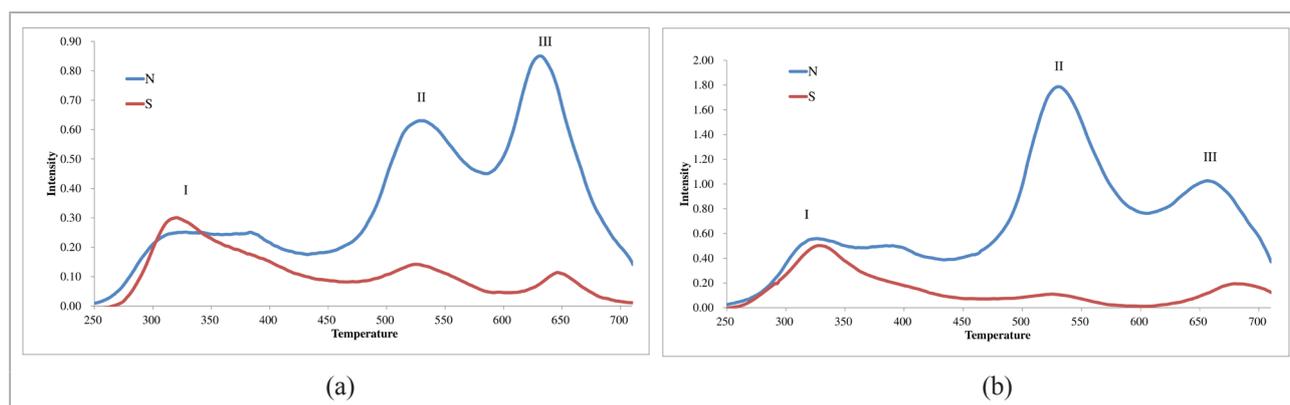

Fig. 2 The N and S thermograms of MESTA obtained from tire sample1 (a) and sample 5 (b). The decomposition peaks of each tire are grouped into three temperature regions: I (250-450°C), II (451-590°C) and III (591-710°C).

The MESTA of the 13 samples shown that their C thermograms have peaks appearing in similar temperature regions, all are close to the reported TGA-FTIR results [5]. The decomposition peaks of region I (250-450°C) contain two non-well separated peaks. The first part of region I (in the range between 250°C and 380°C) is due to the thermal decomposition of oil. The second part of region I (380-450°C) is from the thermal decomposition of polymers. Peaks of region II (450-590 °C) also produced from thermal decomposition of other polymers. Usually, there are two kinds of polymers in tires [5]. The peaks of region III range from 590°C to 710°C are attributed to oxidation of carbon black. We classified peaks of the MESTA thermograms into the three temperature regions for peak area analysis.

While all tires have similar MESTA decomposition temperature regions, their relative amounts of elements in each temperature region are different. Table 3 lists the integrated peak area within each of the temperature region, expressed as the percentage of the total peak area of each element in the three temperature regions. The results of Table 3 indicated that the C, N and S thermograms are quite reproducible quantitatively with small variation within triplicated measurements of each tire sample.

The analysis of C, N and S thermograms by area integrating of peaks shows that there are significant C, N, S constraints of the thermograms among samples (Table 2 and 3). There are 12 parameters available for discriminating one sample from others. We used the said 12 parameters of the

Table 3 The integrated peak area under each temperature region, expressed as the percentage (%) of the total peak area of each element under the three temperature regions (I, II and III) of the MESTA C, N and S thermograms of the13 tested tire samples. The values in the parentheses are the standard deviation of the means (n=3).

	C_I	C_{II}	C_{III}	N_I	N_{II}	N_{III}	S_I	S_{II}	S_{III}
1	35.8 (±0.4)	25.2(±0.4)	39.5(±0.2)	23.2(±2.0)	48.6(±1.9)	29.9(±2.7)	67.2(±0.4)	11.2(±0.4)	21.7(±0.5)
2	37.7 (±0.6)	24.4(±0.9)	38.2(±1.3)	27.2(±1.2)	44.0(±1.6)	29.0(±0.2)	67.4(±0.3)	10.3(±0.5)	22.1(±0.8)
3	37.6 (±1.5)	28.3(±0.7)	34.6(±1.8)	29.5(±1.4)	45.9(±3.2)	26.7(±0.5)	66.5(±1.2)	16.4(±0.4)	17.2(±0.4)
4	36.1 (±1.6)	27.8(±2.2)	36.2(±0.7)	26.3(±1.1)	44.2(±1.0)	28.6(±2.1)	74.2(±3.5)	16.2(±2.7)	12.7(±1.1)
5	29.1 (±0.6)	28.9(±2.6)	42.5(±2.7)	24.6(±1.6)	35.2(±1.7)	40.7(±0.2)	63.0(±0.4)	23.7(±1.2)	13.7(±1.4)
6	35.3 (±1.0)	23.0(±0.4)	41.4(±0.4)	27.8(±0.9)	40.2(±1.1)	32.3(±1.2)	74.2(±2.5)	10.2(±1.6)	15.5(±1.1)
7	35.9 (±0.5)	27.4(±0.7)	36.7(±0.8)	30.9(±1.5)	36.0(±0.6)	33.6(±0.9)	72.7(±2.5)	11.2(±2.5)	15.9(±0.3)
8	40.0 (±0.6)	26.5(±0.5)	33.5(±0.8)	28.9(±1.2)	47.8(±1.9)	23.3(±1.2)	67.7(±1.9)	10.7(±0.7)	21.5(±1.0)
9	40.3 (±0.8)	30.3(±1.3)	29.2(±1.0)	29.6(±0.3)	43.9(±1.1)	26.4(±1.2)	74.2(±2.3)	18.2(±2.3)	6.9(±0.9)
10	35.0 (±1.2)	25.8(±1.6)	39.3(±0.5)	30.0(±0.7)	38.9(±1.5)	31.1(±1.2)	65.7(±1.5)	16.1(±2.2)	18.4(±1.4)
11	33.5 (±1.0)	27.9(±0.8)	38.8(±0.5)	24.0(±1.7)	50.9(±0.7)	25.3(±0.9)	80.5(±2.8)	11.3(±1.3)	8.1(±1.4)
12	38.8 (±0.6)	26.4(±0.3)	35.4(±0.4)	32.6(±0.5)	33.4(±0.9)	34.3(±1.2)	81.1(±0.2)	11.3(±0.4)	7.8(±0.2)
13	31.1 (±0.9)	25.8(±0.3)	43.2(±0.9)	28.7(±1.1)	41.5(±0.7)	30.2(±1.9)	67.9(±0.4)	17.2(±0.3)	15.0(±0.8)

samples in the PCA and HCA analyses. The PCA is a non-parametric analysis and the answer is unique and independent of any hypothesis about data probability distribution [13]. The results of PCA using the 12 parameters of MESTA from13 samples with triplicate measurements are shown in Fig. 3. A distribution chart was generated from the first two principal components. The explained variances of the first two principal components (PC1 and PC2) are 36.16% and 32.05%, respectively, of the total. The combined variance explained by PC1 and PC2 accounting for 68.21% of the total variance. For most samples, triplicate measurements for each sample were classified into the same group. However, triplicate measurements of several other samples are scattered into different groups in the distribution plot. For example, sample 10 and 3, sample1 and 2, sample 4 and 9 are somewhat overlapping (Fig. 3). The loadings plots (Fig. 4 and 5) show that the ratios of C, N, S peaks are main factors that responsible for the classification whereas the C, N, S concentrations are not. The loading of PC1 mainly is contributed from C_I (-0.28), C_{III} (0.34), N_{III} (0.45), S_I (-0.54), S_{II} (0.32) and S_{III} (0.24) and that of PC2 contributed from N_{II} (0.51), N_{III} (-0.36), S_I (-0.48), S_{II} (-0.15) and S_{III} (0.58). From those results, discriminating power was estimated, in the order from high to low : $S_I > S_{III} \approx N_{III} > N_{II} > S_{II} > C_I \approx C_{III} > N_I \approx C_{II}$. This indicated that additive S in tires plays the most important factor in distinguishing the

tire samples, although its concentration was small compared to that of carbon. The ratio of N peaks also play more important role than ratio of C peaks for discrimination among tires.

We also use HCA, another statistical tool to build a hierarchy of clusters among tires [13]. HCA of MESTA data obtained from 13 tire samples with three replicates is shown in Fig. 6. The dendrogram was obtained by the calculation of similarity by the un-weighted pair group method with arithmetic average (UPGMA) and with Gower similarity index [16]. Gower similarity index is a distance measure that averages the difference over all variables, each term normalized for the range of that variable. The results showed that the distance between intra-samples (min. value about 0.05) is smaller than that of inter-samples (min. value about 0.17), as such that the triplicate of each sample is not mixed with other samples. This result indicated that the constraints provided by MESTA of the 13 tested tires can be completely distinguishable from one another by HCA. Although the bulk C, N and S concentrations are not significant as discriminators in PCA, the triplicates of two samples among 13 were mixed with each other if the bulk C, N and S concentrations were not included in the HCA. Therefore, all 12 parameters are needed to be included in HCA to completely discriminate all 13 tire samples.
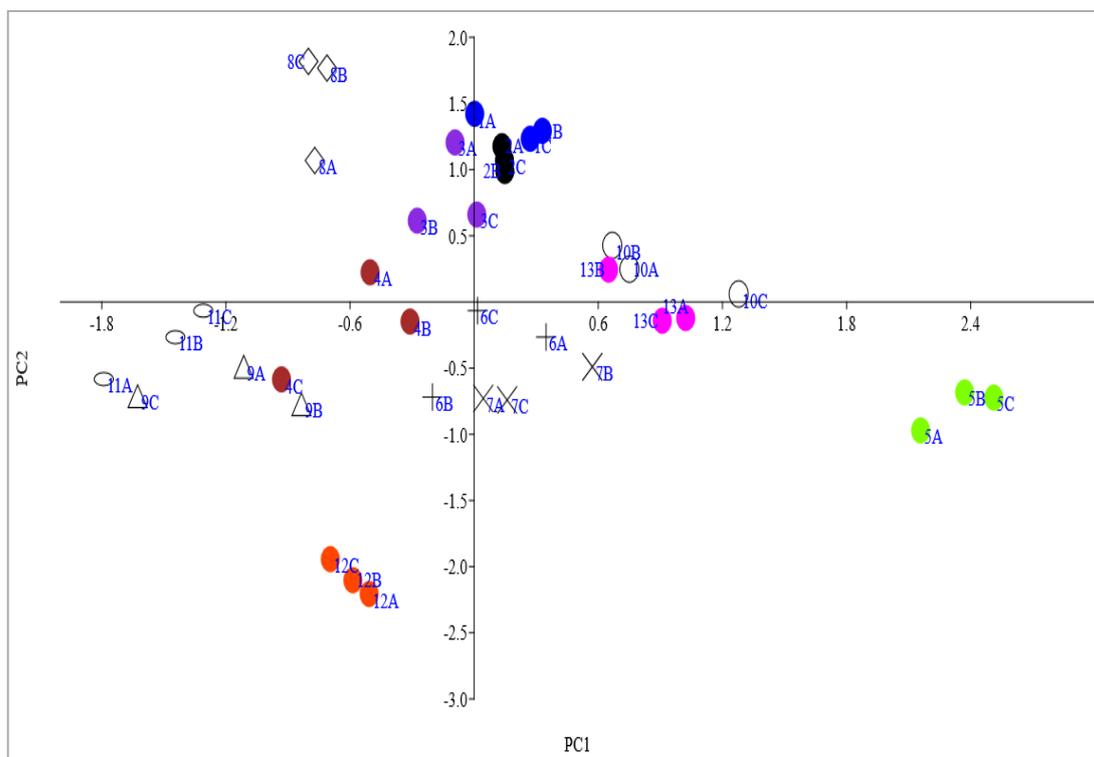
Fig. 3 Principle Component Analysis (PCA) scatter plot for MESTA data from13 samples with triple replicates, A, B and C denote triplicate measurements, respectively. PC1 and PC2 are responsible for 36% and 32% of total variance respectively.
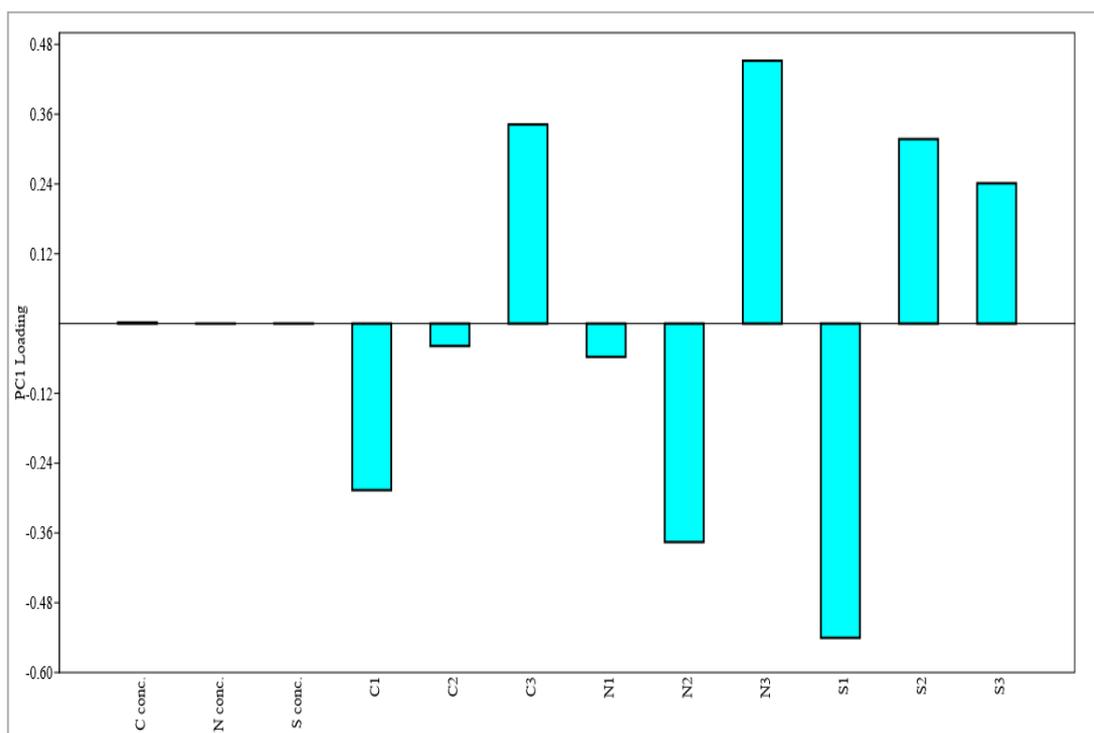

Fig. 4 The PC1 loadings (Y axis) vs. the 12 MESTA parameters (X axis). The values of loading indicate that relative % peak areas of C, N, S thermograms in the three temperature regions.
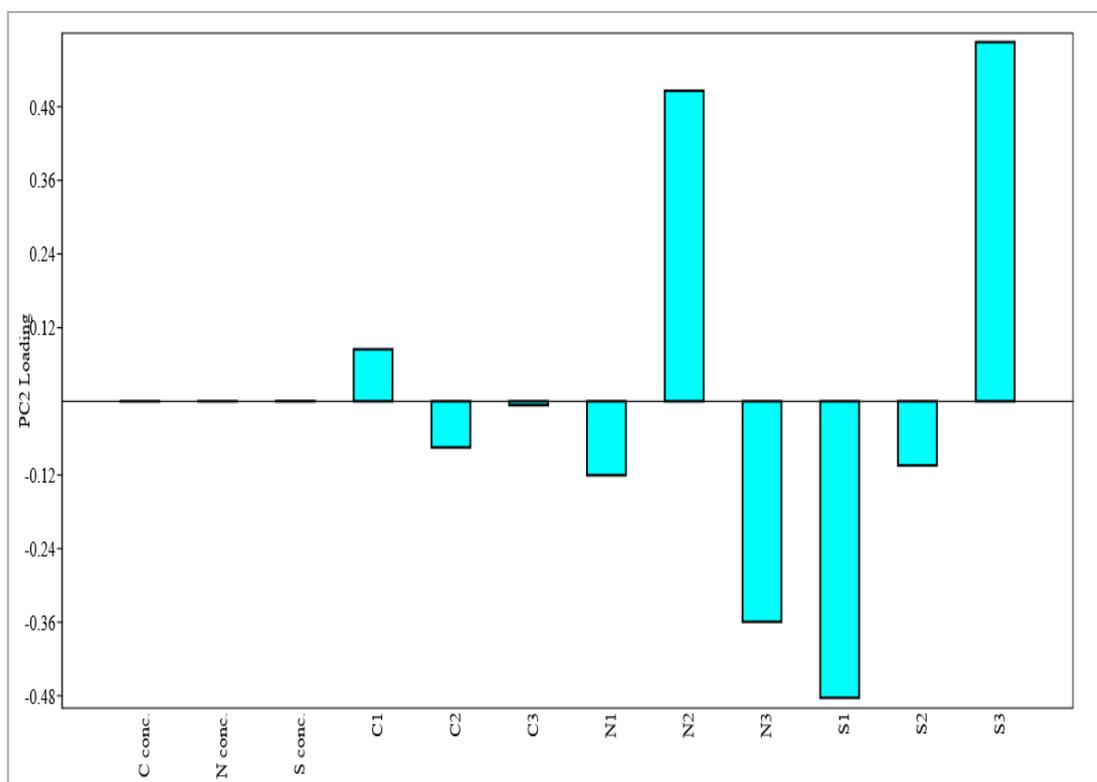
Fig. 5 The PC2 loadings (Y axis) vs. the 12 MESTA parameters (X axis). The values of loading indicate that the relative % peak areas of C, N, S thermogram in the three temperature regions.
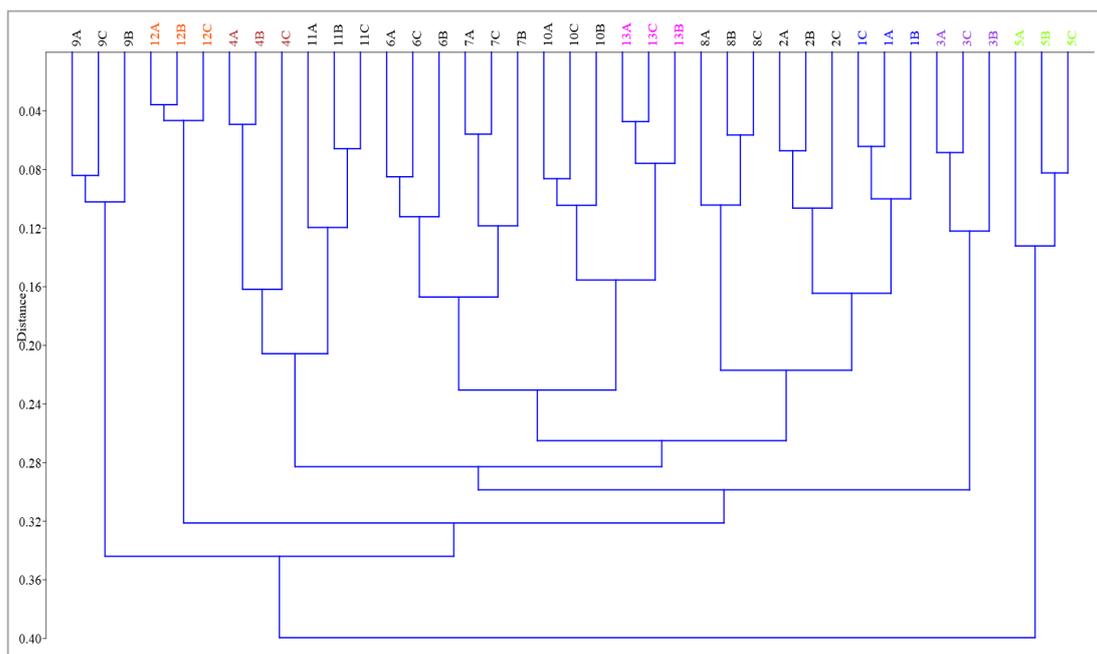

Fig. 6 Hierarchical cluster analysis (HCA) of the MESTA data from the 13 tire samples with three replicates. The dendrogram was obtained by calculating the distance with the un-weighted pair group method and with the arithmetic average (UPGMA) of a Gower distance function [15].

Pyrolysis gas chromatographic mass spectrometry (Py-GC-MS) [7] and TGA-FTIR had been used in characterization of tire samples [9]. The study showed that TGA-FTIR may not be a good method for quantitation of components in tires [9] because of poor reproducibility. Py-GC/MS is a good technique to identify polymers, to determine the structural characterization of copolymers, to analyze volatile compounds and to determine the additive in the tire [6,7,17]. Although MESTA cannot identify the chemical components as detailed as Py-GC-MS, it is a simple technique for characterization the tire samples. In addition, the data obtained from MESTA can be analyzed easily by PCA and HCA, which leads to a convenient procedure. We concluded, therefore, in this study that MESTA is a promising tool for the characterization and discrimination of tire sample or mark residues in forensic cases.

Conclusion

This is the first time using multi-element scanning thermal analysis (MESTA) in the car tire sample analysis. Results shown that the combination of MESTA and HCA can be a potential technique for distinguish tire samples that are from different sources. In this study we only analyzed the scraped tire sample, we may try to analyze tire mark sample in the future.

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