Classification of Gayo Arabica coffee ethanol extract using FTIR-PCA

Z Akbar¹, R Idroes¹,²*, M Yusuf¹, T Karma¹, B Ginting¹, S Rahimah³, G M Idroes⁴, M Paristiowati⁵, and T E Tallei⁶

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia
² Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia
³ Department of Food Industrial Technology, Faculty of Agroindustrial Technology, Universitas Padjadjaran, Bandung, West Java, Indonesia
⁴ Department of Chemical Engineering, Faculty of Engineering, Universitas Syiah Kuala, Kopelma Darussalam, Banda Aceh 23111, Indonesia
⁵ Department of Chemistry Education, Universitas Negeri Jakarta, Jakarta, Indonesia
⁶ Department of Biology, Faculty of Mathematics and Natural Sciences, Sam Ratulangi University, Manado, Indonesia, 95115

*E-mail: rinaldi.idroes@unsyiah.ac.id

Abstract. The classification of the bean and powder ethanol extracts of Gayo Arabica coffee has been carried out using Fourier Transform Infrared (FTIR) and Principal Component Analysis (PCA). Coffee samples were obtained from 3 locations in Bener Meriah Regency, namely Pegasing, Celala, Jagong, and 3 locations in Aceh Tengah regency, namely Permata and Bandar and Wihpesam. Each extract was analyzed by FTIR at wavenumbers in the range of 4000 - 400 cm⁻¹. The obtained FTIR spectra were identified by PCA. The results showed that only the PCA plot of coffee powder extract showed a grouping pattern based on the sample location, namely Bener Meriah and Aceh Tengah. This showed that the ethanol extract of coffee powder could be used as a reference in the classification of coffee samples using FTIR-PCA.

1. Introduction
Gayo Arabica coffee grows in the Gayo Plateau, which includes three districts in Aceh Province, namely Aceh Tengah, Bener Meriah, and Gayo Lues. Geographically, this area is very suitable for coffee plantations because it is located at an altitude above 700 masl [1]. The uniqueness in Bener Meriah, the plantation land is located around the slopes of an active volcano.

The volcanic activity brings out unique minerals that change the composition of the surrounding soil [2]–[6]. This change also affects the metabolite content in plants that grow in this area [7], [8]. This can be used as a reference in authenticating coffee with non-volcano products. So, it can be avoided by counterfeiting.
Several identification methods are often used in organic samples, namely Mass Spectrometry [9–12], Uv-Vis [13–15], image processing [16], laser [17], [18], and FTIR [19]. Fourier Transform Infrared (FTIR) spectroscopy is the most used in metabolite identification in plant samples. This method can produce functional group information that represents the chemical compounds contained therein [20]. However, the direct interpretation of FTIR spectra is difficult because they have very complex patterns. Visually, the FTIR spectra of similar samples look the same. To solve this problem, a statistical method that can interpret complex data is needed [21]–[24].

One of the statistical methods that can be used to analyze complex data is Principal Component Analysis (PCA) [25], [26]. PCA can reduce the dimensions of big data. Data that have many variables can be interpreted into several simple variables. So, it is possible to explain trends in a data set (Gad, 2012).

PCA can be used to model plant differences which are closely related. The use of PCA for infrared spectra interpretation of plant samples has been widely used, including to distinguish coffee leaves collected from different climatic conditions [27], grain classification based on geographical differences, year of production and genotypic [28], identification of falsification [29], as well as forensic analysis [30]. In this study, the FTIR-PCA combination was used to see the differences in the ethanol extracts of the coffee beans and powder from the Aceh Tengah and Bener Meriah regions.

2. Materials and methods
2.1. Materials and tools
The tools used were maceration tools, rotary evaporator, FTIR (Shimadzu 50-IR Thermo Fischer), and unscramble X 10.4 software

2.2. Sample collection and pretreatment
Coffee samples were taken purposively at 3 locations in Aceh Tengah, namely Pegasing, Jagong, and Celala, and 3 locations in Bener Meriah namely Bandar, Permata, and Wih Pesam. The coffees obtained were skinned, washed, and dried. To obtain coffee powder samples, dry coffee beans were roasted at 200 °C until evenly black, then mashed to a powder, powdered then sifted with a 200 mesh sieve.

2.3. Ethanolic extraction
Extraction of coffee beans and powder samples using the maceration method with 96% ethanol solvent for 48 hours with occasional stirring. After 48 hours, the macerates were separated by filtration technique. Then the filtrate is placed in a rotary evaporator at 45 °C to obtain a thick extract.

2.4. FTIR analysis
FTIR analysis was carried out at the wavelength ranges of 400-4000 cm⁻¹. The measurements were made in two repetitions. The spectra obtained were interpreted by PCA.

2.5. Classification of samples with principal component analysis
Spectrum data used for analysis are all spectrum data in the wave number range 4000 - 400 cm⁻¹, PCA analysis is performed using The Unscramble 10.4 software.

3. Results and discussion
3.1. FTIR spectra
Visually, all FTIR spectra showed similar functional groups from one sample to others (Figure 1). There were peaks of O-H (3500-3000 cm⁻¹), C-H (2800-2900 cm⁻¹), C=O (1650-1780 cm⁻¹), C=C (1500-1640 cm⁻¹), C-N (1200–1300 cm⁻¹) and C-O (1000–1100 cm⁻¹) functional groups which was identical to the spectral pattern of caffeine [31]. A slight change in absorption intensity was observed in powder samples where there were decreases in the intensity of C-N and C-O. The decreases were associated with the roasting process, which causes the release of those groups from the sample [32].
3.2. PCA plot

The classification of coffee ethanol extract using PCA is shown by plotting the values of the two-dimensional Principal Component (PC). The information obtained is the trend of the point pattern relative to others. The closer the point of one sample to another, the more similar the samples. In this case, it was the similarity of the FTIR spectra pattern.

The PCA plot of the coffee bean ethanol extract samples showed a very high diversity of 99% (PC-1 = 95%, PC-2 = 4%). However, the pattern between samples has not shown any similarity (Figure 2). On the other hand, the PCA plot of the coffee powder ethanol extract samples showed them otherwise. With a diversity of 100% (PC-1 = 97%, PC-2 = 3%), the PCA plot showed the fairly good classification of the samples into two groups, namely Aceh Tenga (blue group) and Bener Meriah (red group) (Figure 3). The differences in PCA plot patterns between bean and coffee samples indicated the effect of sample preparation on PCA results. It was estimated that there were differences in the extraction ability between the bean and powder samples to several compounds that were still bound in the coffee matrix. Coffee powder samples are easier to extract process, because to have a larger surface area than the coffee bean samples [33, 34].
Figure 2. PCA plot of the ethanol extract of Gayo coffee beans from Aceh Tengah and Bener Meriah.

Figure 3. PCA plot of ethanol extract of Gayo coffee powder from Aceh Tengah and Bener Meriah.

4. Conclusion
FTIR spectra of both the beans and coffee powder ethanol extracts showed a similar functional group, identical to the caffeine. There was a decrease in the intensity of the C-N and C-O peaks of the powder samples associated with the roasting process. The PCA plot showed the effect of sample preparation on PCA results. Only the PCA plot of coffee powder extract showed a grouping pattern based on sample locations, namely Bener Meriah and Aceh Tengah.

References
[1] Mawardo S, Hulupi R, Wibawa A and Wiryaputra S 2008 Panduan Budidaya dan Pengolahan Kopi Arabika Gayo (Aceh Kopi Forum)
[2] Jordán A, Zavala L M, Mataix-Solera J, Nava A L and Alanís N 2011 Effect of fire severity on water repellency and aggregate stability on Mexican volcanic soils CATENA 84 136–47
[3] Idroes R, Yusuf M, Alatas M, Subhan, Lala A, Saiful, Suhendra R, Idroes G M and Marwan 2018 Geochemistry of hot springs in the Ie Seu’um hydrothermal areas at Aceh Besar district,
[4] Idroes R, Yusuf M, Alatas M, Subhan, Lala A, Muhammad, Suhendra R, Idroes G M and Marwan 2019 Geochemistry of Sulphate spring in the Ie Jue geothermal areas at Aceh Besar district, Indonesia IOP Conf. Ser. Mater. Sci. Eng. **523** 012012

[5] Idroes R, Yusuf M, Alatas M, Subhan, Lala A, Muslem, Suhendra R, Idroes G M, Suhendrayatna, Marwan and Riza M 2019 Geochemistry of warm springs in the Ie Brûk hydrothermal areas at Aceh Besar district IOP Conf. Ser. Mater. Sci. Eng. **523** 012010

[6] Idroes R, Yusuf M, Saiful S, Alatas M, Subhan S, Lala A, Muslem M, Suhendra R, Idroes G M, Marwan M and Mahlia T M I 2019 Geochemistry Exploration and Geothermometry Application in the North Zone of Seulawah Agam, Aceh Besar District, Indonesia Energies **12** 4442

[7] Nuraskin C, Marlina, Idroes R, Soraya C and Djufri 2020 Rasayan J. Chem. **13** 18–23

[8] Nuraskin C A, Marlina, Idroes R, Soraya C and Djufri 2019 Res. J. Pharm. Technol. **12** 5247

[9] Estevam E, Griffin S, Nasim J, Zieliński D, Aszyk J, Oslowicka M, Dawidowska N, Idroes R, Bartoszek A and Jacob C 2015 Nat. Prod. Commun. **10** 1733–8

[10] Pratini S U T, Legendijk E L, de Weert S, Idroes R, Hertiandi T and den Hondel C Van 2015 Int. J. Appl. Res. Nat. Prod. **8** 1–13

[11] Earlia N, Muslem, Suhendra R, Amin M, Prakoeswa C R S, Khairan and Idroes R 2019 Sci. World J. **2019** 1–7

[12] Earlia N, Rahmad R, Amin M, Prakoeswa C, Khairan K and Idroes R 2019 Sains Malaysiana **48** 1019–24

[13] Suhartono E, Thalib I, Aflianie I, Noor Z and Idroes R 2018 Study of Interaction between Cadmium and Bovine Serum Albumin with UV-Vis Spectroscopy Approach IOP Conf. Ser. Mater. Sci. Eng. **350** 12008

[14] Hasanah U, Sani N D M, Heng L Y, Idroes R and Safitri E 2019 Biosensors **9** 135

[15] Hasanah U, Setyowati M, Efendi R, Muslem M, Md Sani N D, Safitri E, Yook Heng L and Idroes R 2019 Biosensors **9** 60

[16] Suhartono E, Setiawan B, Santos P B, Idroes R and Indrawan M S 2019 Estimation of leaf antioxidant activity using image processing Journal of Physics: Conference Series vol 1374 (IOP Publishing) p 12057

[17] Hedwig R, Lahna K, Idroes R, Karnadi I, Tanra I, Iqbal J, Kwaria D, Kurniawan D P, Kurniawan K H, Tjia M O and Kagawa K 2019 Microchem. J. **147** 356–64

[18] Lahna K, Idroes R, Idris N, Abdulmadjid S N, Kurniawan K H, Tjia M O, Parasted M and Kagawa K 2016 Formation and emission characteristics of CN molecules in laser induced low pressure He plasma and its applications to N analysis in coal and fossilization study Appl. Opt. **55** 1731

[19] Suhartono E, Noor Z, Edyson, Budianto W Y and Idroes R 2019 Effect of chronic lead exposure on bone using ATR-FTIR spectroscopy AIP Conf. Proc. **2108** 020025

[20] Hasanah U, Setyowati M, Edwarsyah, Efendi R, Safitri E, Idroes R, Heng L Y and Sani N D 2019 Isolation of Pectin from coffee pulp Arabica Gayo for the development of matrices membrane IOP Conf. Ser. Mater. Sci. Eng. **523** 12014

[21] Idroes R, Noviandy T R, Maulana A, Suhendra R, Sasmita N R, Muslem M, Idroes G M and Irvanizam I 2019 Int. Rev. Model. Simulations **12** 373

[22] Idroes R, Husna I, Muslem, Mahmudi, Rusyana A, Helwani Z, Idroes G M, Suhendra R, Yandri E, Rahimah S and Sasmita N R 2019 Analysis of temperature and column variation in gas chromatography to dead time of inert gas and n-alkane homologous series using randomized block design IOP Conference Series: Earth and Environmental Science **364** (IOP Publishing) 12020

[23] Husna I, Rusyana A, Muslem, Idroes G M, Suhendra R and Idroes R 2020 Grouping of Retention Index on Gas Chromatography using Cluster Analysis IOP Conf. Ser. Mater. Sci. Eng. **796** 012064

[24] Idroes R, Japnur A F, Suhendra R and Rusyana A 2019 Kovats Retention Index analysis of flavor
and fragrance compound using Biplot Statistical method in gas chromatography systems IOP Conf. Ser. Mater. Sci. Eng. 523 12007

[25] Wahidah S, Khairi, Lelifajri, Idroes R, Rahmadi, Lala A, Mahmudi, Muslem and Japnur A F 2019 Analysis of mercury and its distribution patterns in water and sediment samples from Krueng Sabee, Panga and Teunom rivers in Aceh Jaya IOP Conf. Ser. Earth Environ. Sci. 364 12016

[26] Nadia Y, Ramli M, Japnur A F, Rusyana A, Idroes G M, Suhendra R, Sasmita N R, Tallei T E and Idroes R 2019 Simple combination method of FTIR spectroscopy and chemometrics for qualitative identification of cattle bones IOP Conference Series: Earth and Environmental Science vol 364 (IOP Publishing) p 12040

[27] Sanchez P, Pauli E, Scheel G, Rakoczevic M, Bruns R and Scarminio I 2017 J. Braz. Chem. Soc. 29 168–76

[28] Wadood S A, Guo B, Zhang X and Wei Y 2019 Geographical origin discrimination of wheat kernel and white flour using near infrared reflectance spectroscopy fingerprinting coupled with chemometrics Int. J. Food Sci. Technol. 54

[29] Guo L, Wu Y, Liu M, Ge Y and Chen Y 2018 J. Sci. Food Agric. 98 3057–65

[30] Kumar R and Sharma V 2018 Chemometrics in forensic science TrAC Trends Anal. Chem. 105 191–201

[31] Belay A, Kim H K and Hwang Y-H 2016 Luminescence 31 565–72

[32] Obeidat S M, Hammoudeh A Y and Alomary A A 2017 Журнал прикладной спектроскопии 84 977–81

[33] Gurak P D, De Bona G S, Tessaro I C and Marczak L D F 2014 Food Res. Int. 62 786–92

[34] Munawar AA, von Hörsten D, Wegener JK, Pawelzik E, Mörllein D 2016. Eng Agric Environ Food. 9(3):208–215.