

ANALYSIS OF SOIL AGING FOR FORENSIC PURPOSES USING IR SPECTROSCOPY

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Abstract

For forensic purposes, sometimes, it is necessary to analyze the soil few years after the initial case has been closed. Soil can leave traces on any item such as shoes, car tires, clothes etc. In this paper 60 soil samples are analyzed. 48 soil samples were taken in three locations in the city of Tetovo in 2016. Three years later (in 2019) 12 additional soil samples from the same locations were collected. All samples were dried at 110 °C, and then their infrared spectra (IR) were recorded.

The infrared spectra were recorded on Fourier-transform infrared spectrophotometer Perkin-Elmer System 2000. The collected IR spectra we analyzed carefully analyzed in the part of the fingerprint region (in the range 1450-450) in order to examine the changes in the spectra which have resulted from the changes of the weather and the anthropogenic influence.

The detailed examination of all spectra showed that no visible changes were found in the newly collected spectra.

Keywords: soil, forensic chemistry, analytical chemistry

1. Introduction

The use of soil in forensic studies to date has shown that there is a strong link between soil and humans. The soil of the body or property of the person can be used as evidence in the form of traces in a number of criminal cases. As a type of evidence most often found in the form of traces, soil plays an important role in forensic examinations [1]–[4].

The studies have shown that soil usually contains 40–45% inorganic minerals, 5% organic minerals, 25% water and 25% and air [5]. The studies on agrogenesis and anthropogenesis in the changes on the physical and physicochemical properties of the soil are becoming increasingly relevant [6]–[8]. The complexity of the soil composition, however, provides an extremely large variety of soils. Actually, there is considerable variation among soil components even within a particular area where a pedogenic ally uniform soil is distributed, allowing us to differentiate soil samples [9].

In forensic science, when taking samples at the crime scene, researchers take care that the samples taken do not change over time, this is very important because in many cases it is necessary to take samples at the scene even after several years and to analyze with the evidence obtained at the time when the crime was committed, each time the question arises, how long a soil, after the sampling, can be stored without experiencing any change in chemical properties?

Many techniques are used in soil analysis for forensic purposes such as scanning electron microscopy, inductively coupled plasma, gas chromatography, X-ray diffraction, Raman spectroscopy and infrared spectroscopy [10]–[16].

In this paper the FTIR technique is used, this instrumental technique is based on the measurement of signals related to the interaction of infrared radiation with the analyzed samples. The advantage of infrared microscopy is that the method is not destructive. Alternatively, infrared microscopy in forensic science is commonly used for qualitative and quantitative analysis of microtexes such as soil analysis, paint particles, plastics, fibers, rubber and adhesives, etc. [17] Infrared spectroscopy (IR) is also used to identify minerals of inorganic origin and is a reliable method for forensic soil tests [18],[19].

2. Experimental

The samples were taken from three parks in the city of Tetovo, which are often visited by the inhabitants of the city. The location of these parks is shown in Figure 1a and Table 1.

Table 1. Locations of the parks from which the analyzed samples were taken.

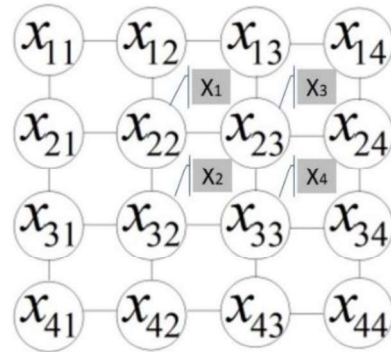
Labels	Location	The year in which the samples were collected and/or the number of samples	
		2016	2019
B	House of Culture	16 samples	4 samples
D	State University of Tetova	16 samples	4 samples
E	Mosha Pijade High School	16 samples	4 samples

In order to have representative samples whose quality would not depend on (1) the current conditions in the park, as well as on (2) possible short-term pollution, this part of the experiment was performed as follows:

- A total of 16 samples were taken from each park in 2016 and 4 additional samples in 2019 from the soil;
- All samples were collected from each location at a distance of one about one meter from the nearest sample (Figure 1b);
- The spatial arrangement of the samples is in the form of a matrix up to 4×4 samples
- Each of the samples was taken from the top layer of soil to a depth of about 10 cm.



a)



b)

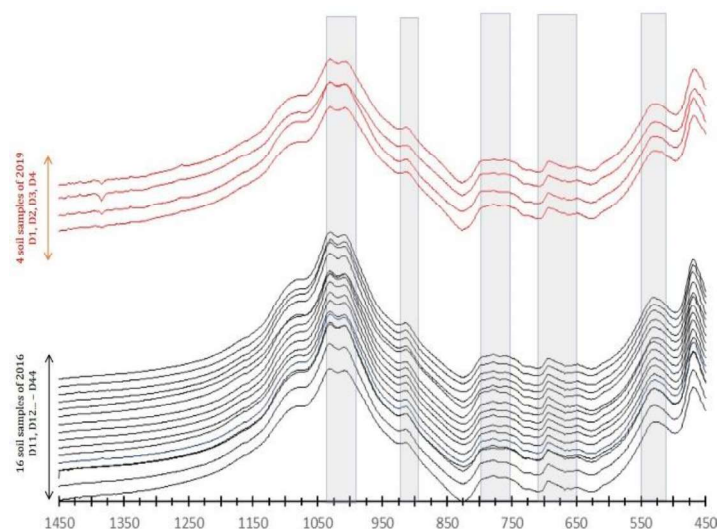
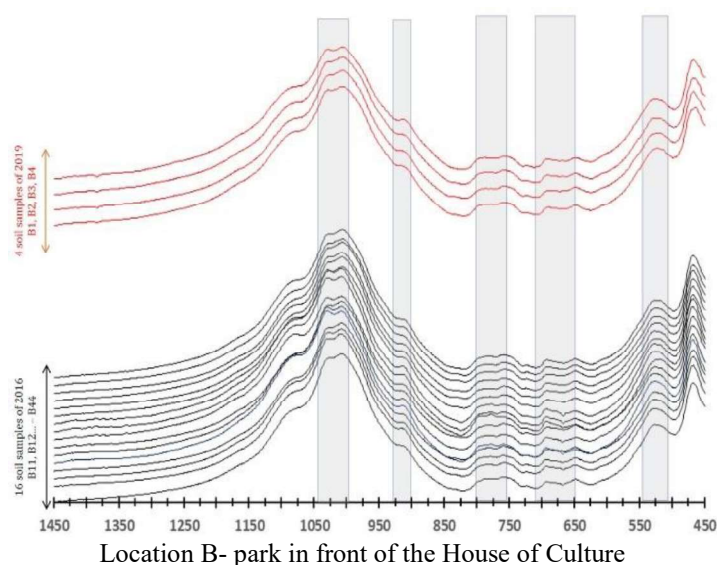
Figure 1. The parks from which the samples were taken and the scheme according to which the soil samples are taken, a) urban locations, b) Scheme according to which soil samples are taken, $x_1, \dots, x_4$ places of samples taken after 3 years.

Before the IR spectra were recorded the soil samples were prepared in a suitable way. The preparation of the samples involved removing the largest impurities using sieve. Then the samples were placed in a dryer for one hour at a temperature of 110 °C. The dried samples are then stored in a desiccator until further analysis. The dried samples were then used to record infrared spectra.

3. Results and discussion

The IR spectrum of the soil samples were recorded in the region between 4000–400 cm⁻¹. In this paper the spectra were analyzed only in the fingerprint region 1450–450 cm⁻¹, due to the fact that basic vibrations of the components present in the soil samples are mainly silicates or carbonates but can also include minor minerals components such as sulfates which might be more helpful for discrimination of the different samples.

On the following figure (Figure 2) all recorded spectra are presented. At the bottom of the figures the original 48 samples collected and recorded in 2016 are presented. At the top of this figure the samples collected in 2019 are presented (four additional samples from each location).



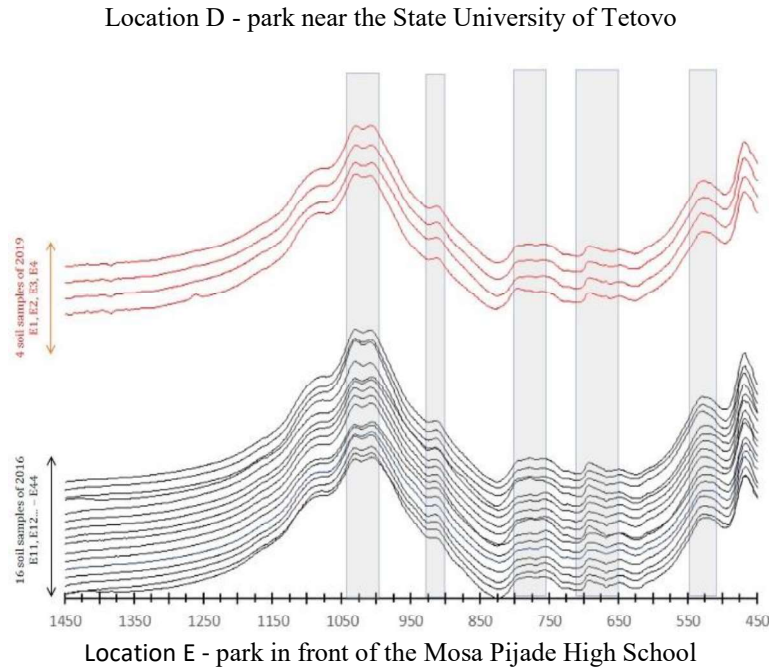


Figure 2. Spectra from FTIR, from the locations in the three parks of the city of Tetovo, in black the spectra from the samples taken in 2016 while in red the samples taken in 2019.

In all samples of urban locations, the park in front of the House of Culture (label B), the park near the State University of Tetovo (label D) and the park in front of the Mosa Pijade High School (label E) we will discuss the specific signals of the infrared spectra. Critical observation of the spectra of the first 16 samples and the additional 4 samples taken three years later for each location shows that the information obtained from the most intense region where the bands emanating from the stretching vibrations are strong bands close to 1000 to 1050 cm^{-1} for silicates [20],[21]. Estimation of the relative amount of Si-O-Si and Si-O-Al bonds developed during their formation [22] can be explained by the published spectra of well-crystallized individual minerals. This information could be extracted from the signals obtained below 600 cm^{-1} . The dioctahedral layer silicates containing octahedral aluminum all have strong bands in the 520 to 540 cm^{-1} region, which are absent in the ferruginous forms and in trioctahedral minerals [23]–[25]. In soil these stretching vibrations arise from the combination of minerals and are usually not very diagnostic of the specific minerals present, but the model is representative of the soil and may be useful for discrimination. Usually vibrations below 900 cm^{-1} can be used to identify similar minerals such as calcite, aragonite and dolomite [26],[27]. Some minerals, such as quartz, can be identified by their deformation vibrations which are weak. The band for these vibrations could be found in the region around 800 cm^{-1} and 780 cm^{-1} , and for albite at around 730 cm^{-1} and 650 cm^{-1} [28],[29].

4. Conclusion

Fourier-transform infrared spectroscopy is a powerful tool for studying soils and characterizing inorganic ions and minerals on the earth's surface. The results presented here are based on the analysis of infrared spectra of the samples for urban soils from (1) the park in front of the House of Culture (label B), (2) the park near the State University of Tetovo (label D) and (3) the park in front of the Mosa Pijade High School (label E). From the analysis of soil similarity with changing

atmospheric conditions over three years show that, climatic conditions and the anthropogenic influence do not have induce significant change on the composition of these soils.

The detailed analysis of the infrared spectra presented here shows that for forensic purposes we cannot find any difference between the originally collected spectra and those collected three years later.

References

- [1]. B.D. Lee, T.N. Williamson, R.C. Graham, Identification of stolen rare palm trees by soil morphological and mineralogical properties, *Journal of Forensic Sciences*, 47 (2002).
- [2]. M. H. a. K. J. Walsh, "Pollen on grass clippings: putting the suspect at the scene of the crime," *Journal of Forensic Sciences*, vol. 46, no. 4, 2001.
- [3]. L. A. Daugherty, "Soil science contribution to an airplane crash investigation," *Journal of Forensic Sciences*, Ruidoso, New Mexico, vol. 42, no. 3, 1997.
- [4]. N. Petraco and T. Kubic, "A density gradient technique for use in forensic soil analysis," *Journal of Forensic Sciences*, vol. 45, no. 4, 2000.
- [5]. S. D. Kalev, G. S. Toor, The Composition of Soils and Sediments, *Green Chemistry*, 339-357, 2018, <https://doi.org/10.1016/B978-0-12-809270-5.00014-5>
- [6]. A. Imeson, Desertification, Land Degradation and Sustainability, Wiley, 2012. DOI:10.1002/9781119977759
- [7]. C. Boix-Fayos, A. Calvo-Cases, A.C. Imeson, M.D. Soriano-Soto, Influence of soil properties on the aggregation of some Mediterranean soils and the use of aggregate size and stability as land degradation indicators, *CATENA* 44 (1) (2001) 47–67. [https://doi.org/10.1016/S0341-8162\(00\)00176-4](https://doi.org/10.1016/S0341-8162(00)00176-4)
- [8]. Y.T. Delelegn, W. Purahong, A. Blazevic, B. Yitaferu, T. Wubet, H. Göransson, D.L. Godbold, Changes in land use alter soil quality and aggregate stability in the highlands of northern Ethiopia, *Sci. Rep.* 7 (1) (2017) 13602 DOI:10.1038/s41598-017-14128-y
- [9]. R. Sugita, Y. Marumo *Forensic Science International* 83, 201-210(1996), [https://doi.org/10.1016/S0379-0738\(96\)02038-5](https://doi.org/10.1016/S0379-0738(96)02038-5)
- [10]. R.M. Morgan, P.A. Bull, Data interpretation in forensic sediment and soil geochemistry, *Environ. Forensics*, 7 (2006) 325–334.
- [11]. K. Pye, D. Croft, Forensic analysis of soil and sediment traces by scanning electron microscopy and energy-dispersive X-ray analysis: An experimental investigation, *Forensic Sci. Int.*, 165 (2007) 52–63.
- [12]. L. Reidy, K. Bu, Murrell, G. James, V. Cizdziel, Elemental fingerprinting of soils using ICP-MS and multivariate statistics: A study for and by forensic chemistry majors, *Forensic Sci. Int.*, 233 (2013) 37–44.
- [13]. P.M. Medeiros, B.R.T. Simoneit, Gas chromatography coupled to mass spectrometry for analyses of organic compounds and biomarkers as tracers for geological, environmental, and forensic research, *J. Sep. Sci.*, 30 (2007) 1516–1536.
- [14]. A. Ruffella, P. Wiltshireb, Conjunctive use of quantitative and qualitative X-ray diffraction analysis of soils and rocks for forensic analysis, *Forensic Sci. Int.*, 145 (2004) 13–23.
- [15]. B.W. Kammrath, A. Koutrakos, J. Castillo, C. Langley, D. Jones, Morphologically-directed Raman spectroscopy for forensic soil analysis, *Forensic Sci. Int.*, 285 (2018) 25–33.
- [16]. X. Xu, C. Du, F. Ma, Y. Shen, J. Zhou, Forensic soil analysis using laser-induced breakdown spectroscopy (LIBS) and Fourier transform infrared total attenuated reflectance spectroscopy (FTIR-ATR): Principles and case studies, *Forensic Sci. Int.*, 310 (2020) 110222.
- [17]. Brenda Woods, Chris Lennard, K. Paul Kirkbride, and James Robertson, "Reinstating Soil Examination as a Trace Evidence Sub-discipline -Chapter 7," in *Soil in Criminal and Environmental Forensics*, Netherlands, Cham, Switzerland, 2012, pp. 107 -120
- [18]. Janina Zieba-Palus and Maria Kala, "Forensic Analytics," in Chapter 11, Springer, 2012

- [19]. Brooke A. Weinger M.S. John A. Reffner Ph.D. Peter R. De Forest D. Crim, "A Novel Approach to the Examination of Soil Evidence: Mineral Identification Using Infrared Microprobe Analysis," *Journal of Forensic Sciences*, vol. 54, no. 4, 2009.
- [20]. Farmer V. C. and Russell, J. D. The infrared spectra of layer silicates. *Spectrochimica Acta*, 20,1149-1173 (1964)
- [21]. Wilson, M. J., Russell, J. D., Tait, J. M. et al. Macaulayite, a new mineral from North-East Scotland. *Mineralogical Magazine*, 48,127-129(1984)
- [22]. Mitchell, B. D, V. C. Farmer, and W. J. McHardy,. Amorphous inorganic materials in soils. *Advances in Agronomy* 16:327. New York: Academic Press (1964)
- [23]. V.Stubiean, R. Roy, Isomorphous substitution and infrared spectra of the layer lattice silicates. *Am. Mineralogist* 46 :32. (1961).
- [24]. V. Stubiean, R. Roy, A new approach to the assignment of infrared absorption bands in layer silicates. *Z. Krist.* 115:200 (1961)
- [25]. V. Farmer, The infrared spectra of talc, saponite and hectorite. *Mineral. Mag.* 31 :829 (1958)
- [26]. W.B. White in *The Infrared Spectra of Minerals*, Mineralogical Society, London, 1974, pp. 227-284.
- [27]. J.D. Russell and A.R. Fraser in *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods*, London, 1994, pp. 11-67.
- [28]. R.Chester, R. N. Green, The infrared determination of quartz in sediments and sedimentary rocks. *Chemical Geology*, 3, 199-213. (1968)
- [29]. J. P. Coates, IR analysis of toxic dusts. Analysis of collected samples of quartz and asbestos. Part 1. *American Laboratory* (Fairfield, Connecticut, USA), 9,105-108,110-111. (1977)