The forensic analysis of soil organic by FTIR

R.J. Cox PhD[a], H.L. Peterson BS[b], J. Young BS[b], C. Cusik BS[b],
E.O. Espinoza Dr PH[a],[*]

[a]National Fish and Wildlife Forensic Laboratory, Ashland, OR 97520, USA
[b]Southern Oregon University, Ashland, OR 97520, USA

Abstract

In order to elucidate the discriminating power of various soil analytical techniques, over 100 soils samples were analyzed using conventional analysis (i.e., color, percent organic and density gradient) and a novel FTIR technique. The FTIR technique involves collecting a spectrum of a soil sample that has been oxidatively pyrolysed, and therefore all organic have been degraded. This spectrum is subtracted from the spectrum of the same sample that contained the organic prior to pyrolysis. This resultant IR spectrum represents the organic portion of the sample. The use of organic components increases the discrimination in soils that are otherwise similar. We have illustrated the usefulness of this technique by selecting four soil samples, which have identical Munsel color values but can be discriminated by subtractive ETIR. We propose that the ETIR spectra of the organic portion of soil serves a useful purpose in forensic investigations. Published by Elsevier Science Ireland Ltd.

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1. Introduction

Forensic soil characterization is particularly useful in wildlife criminal investigations, where large proportions of the infractions occur outdoors and soil is frequently transported from the crime scene. Commonly the analyst is asked to compare evidentiary soil collected from the suspect (i.e., shoes, clothes, etc.) against a geographical standard

collected at the crime scene. Current analytical methods allow forensic scientists to either conclude that the evidence did not share a common source with a standard or that the two soil types are similar in all analytical respects and cannot be excluded.

Forensic soil characterization has been comprehensively reviewed by Thornton [1] who points out that the uniqueness associated with soils has been unappreciated, largely due to the prevalent view that soil is an aggregate of inorganic compounds. Techniques presently used to characterize soil samples rely on either physical descriptors (i.e., color, density gradient, particle size determination, microscopy) or chemical analysis (i.e., elemental composition). These techniques, however, are not capable of probing the organic compounds found in soil, and it is this aspect that we wish to address in this paper.

An exclusionary hierarchy exists in the forensic examination of soil. If soil samples have different colors it is simple to deduce that they do not share a common provenance [2]. Sugita and Marumo [3] recently reviewed the validity of soil color, and conclude that if rigid statistical methods are employed, color can be used as an effective criterion for discriminating a soils origin. If the suspect sample cannot be excluded by this examination, the next analytical step is density gradient. If two soil samples have identical density gradients, we suggest examination by FTIR.

The ideal method of isolating organic compounds from soil would by extraction, where a solvent dissolves the organics components and leaves behind the insoluble inorganic salts. Attempts to carry out such extractions have been largely unsuccessful mainly because humic and fulvic acids, some of the main organic components of soil, are insoluble in most organic solvents [4]. An alternate approach, presented here, is not to isolate the organic materials but to eliminate them from the sample and to examine the soil before and after such elimination. The organic portion is thus inferred. We removed the organics from the soil samples by pyrolysis in air. Fourier Transform Infrared Spectroscopy (FTIR) lends itself to this type of analysis, in that the neat soil spectra can be collected and saved in a database, the soil organics are then removed and the spectra recollected. The resulting spectra, obtained by subtracting the pyrolized spectrum from its non-pyrolized counterpart, can be attributed solely to the organic portion of the soil. We have established that at moderate pyrolysis temperature (650°C) and times (15 min) the inorganic soil components remained unaltered while the organic portions were volatilized by pyrolysis. We have not attempted to identify the individual compounds in the organic portions, but have tentatively assigned several of the main bands found in the mid-IR region. It is the fingerprint region of the spectra (1600–400 cm^{-1}) that we have used for comparisons.

2. Experimental

Soil samples were collected from within a grid prepared by marking out a 7.5×7.5-m area in a field, located east of U.S. highway 5 near Ashland, OR. This 56.2-m^2 area was divided into 2.25-m^2 sections and one of these 2.25-m^2 sections was further divided into 16 equal parts. Approximately 25–30 g of topsoil was collected from each grid. The US Department of Agriculture classified the 56.2-m^2 area as 'Carney clay, 5 to 20% slopes'

[5]. This soil site will be referred to herein as the 'agricultural site'. Soil samples were also collected from eight distinct color layers from an excavation site several miles from the agricultural site. Soil samples were collected from the surface to 3.4 m below. This soil site is classified as 'Kubli loam, 0 to 30% slopes' [5], and will be referred to herein as the 'excavation site'. Sixty-five additional soil samples which were not classified were obtained from areas within a 32-km radius of the agricultural site.

3. Methods

3.1. Soil preparation

Each 25–30 g sample was dried in a microwave oven at 100°C for 30 min. A light grinding in a mortar followed and the sample was then filtered through a coarse sieve to remove large structures such as leaves, twigs and rocks. Approximately 5 g of each filtered sample was reground, passed through a 0.05-mm mesh sieve, and then stored in a closed glass vial pending further examination.

3.2. Color classification

Each sample was matched to a color in the Munsell Color Chart [2] and assigned a Munsell value. A second examiner confirmed each color assignment.

3.3. Organic content

The organic content was determined following Thornton's method [1], by weighing a portion of each sample on an analytical balance, heating for 15 min at 650°C in a muffle furnace and then reweighing the pyrolized sample. Additional heating and reweighing ensured no further weight loss. The percent of organic content was calculated from the weight loss on heating.

3.4. FTIR spectroscopy

Each soil sample was pressed into a KBr pellet and the spectra were collected on a Nicolet 5SXC FTIR, using Nicolet Omnic software. Care was taken to ensure that each pellet was translucent. Each KBr pellet was then reground in a mortar, placed in a glass vial and heated for 15 min at 650°C in a muffle furnace to decompose the organic components. After cooling, the samples were again pressed into pellets, and the IR spectra collected. The spectra obtained after pyrolysis were subtracted from their counterparts obtained before pyrolysis. The resultant subtracted spectra represented the absorption by the organic components of soil.

Table 1
Soil color (pre and post-pyrolysis) and percent organic of the experimental agricultural site[a]

		A	B	C	D	B
1	Natural color	10YR 3/2	10YR 4/2	10YR 4/2	10YR 4/3	10YR 4/3
	Post color	7.5YR 4/6	7.5YR 4/6	7.5YR 4/6	7.5YR 4/6	7.5YR 4/6
	Percent organic	10.3%	10.6%	10.5%	8.9%	8.9%
2	Natural color	10YR 4/2	10YR 4/2	10YR 4/3	10YR 4/2	10YR 4/2
	Post color	7.5YR4/6	7.5YR4/6	7.5YR4/6	7.5YR4/4	7.5YR4/6
	Percent organic	11.9%	9.5–18.3%	10.3%	12.1%	11.3%
3	Natural color	10YR 3/2	10YR 4/2	10YR 4/2	10YR 4/2	10YR 4/3
	Post color	7.5YR 2.5/1	7.5YR 4/4	7.5YR 4/6	7.5YR 4/6	7.5YR 4/6
	Percent organic	10.6%	11.9%	9.2%	15.8%	11.9%
4	Natural color	10YR 4/2	10YR 4/2	10YR 4/2	10YR 4/3	10YR 4/3
	Post color	7.5YR 4/6	7.5YR 4/4	7.5YR 4/6	7.5YR 4/6	7.5YR 4/6
	Percent organic	11.5%	11.9%	9.7%	12.0%	8.4%
5	Natural color	10YR 4/2	10YR 4/2	10YR 4/2	10YR 4/3	10YR 4/3
	Post color	7.5YR 4/6	7.5YR 4/4	7.5YR 4/6	7.5YR 4/6	7.5YR 4/6
	Percent organic	10.6%	10.8%	9.6%	15.6%	9.5%

[a] Each square (i.e., C2) represents a 1.5×1.5-m area. B2 represent the results of 16 soil samples.

4. Results

4.1. Color

Table 1 represents the 56.2-m^2 area surveyed at the agricultural site. It includes the Munsell Color assignment before and after pyrolysis, and the percent of organic present for each of the 2.25-m^2 sections. These values show that the soil colors both before and after pyrolysis are indistinguishable within the agricultural site.

Table 2 exhibits the data from the excavation site in which eight samples were taken at each identifiable level to a maximum depth of 3.4 m. Of the eight layers, five horizons exhibit a different color and three have the same color (2.5YR 6/6) prior to pyrolysis. The post pyrolysis color of the excavation site shows five different soil colors.

Table 2
Soil color (pre and post-pyrolysis) and percent organic of the excavation site

Horizon	Depth (m)	Natural color	Post color	Percent organic
1	Surface	10YR 4/2	10YR 4/3	11.1
2	0.6	2.5YR 4/4	7.5YR 4/6	7.2
3	1.2	2.5YR 6/6	7.5YR 4/6	6.4
4	1.5	2.5YR 6/6	7.5YR 4/6	5.5
5	2.1	10YR 4/4	7.5YR 5/8	9.8
6	2.4	2.5YR 6/4	7.5YR 5/6	4.3
7	2.7	2.5YR 5/3	7.5YR 5/6	7.4
8	3.4	2.5YR 6/6	7.5YR 3/6	6.4

Thus color is a useful tool to exclude soils that do not share a common color and therefore a common source [6]. Soil samples that can not be differentiated using color need to be submitted to a more rigorous analysis to exclude common provenance.

4.2. Organic content

Table 1 shows the percent organic content as determined by pyrolysis. The values range from a low of 8.4% to a high of 18.3%, and even within the 16 samples collected from the 2.25-m^2 in subplot areas (B2 in Table 1) the values ranged from 9.5% to 18.3%.

The percent organic is therefore a reflection of the conditions under which organics have been incorporated or deleted from the experimental area. In our experience the wide range of 6 percent organic in this study makes this analytical technique a poor choice for inferring common provenance in forensic comparisons.

Table 2 lists the percent organic in the excavation site. The values, as would be anticipated, show a higher organic content in the surface soil than in the underlying layers.

4.3. FTIR spectroscopy

Our initial observations confirmed the suggestion by Thornton [1] that the FTIR spectrum of untreated soil is dominated by the inorganic components and exhibits undifferentiable spectra. This similarity was found to be consistent for all the samples we investigated and spectral differentiation was only possible by the thermal subtraction technique described above.

A spectrum of montmorillonite, a ubiquitous soil component, was obtained before and after pyrolysis and is shown in Fig. 1a, confirming that the thermal treatment of 650°C does not degrade this compound. This same stability was shown for iron oxide, silicon dioxide and, calcium carbonate (data not shown).

A 'synthetic soil' was prepared by adding 10% of Trizma (tris(hydroxy-methyl)aminomethane) to iron oxide and the subtraction spectrum was obtained by the method described in the experimental section. The identity of this spectrum with that of pure Trizma, shown in Fig. 1b, demonstrates the ability of the technique to obtain an accurate spectrum of the organic portion of such a synthetic soil. A similar experiment substituting cystine for Trizma also resulted in a spectrum of pure cystine. This indicates that the subtracted spectrum is accurate, reliable and may assist in inferring the organic components in natural soils. A representative soil subtraction spectrum is shown in Fig. 1c.
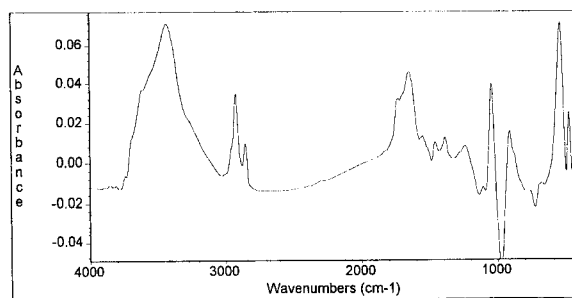
4.4. Organic spectra peak assignment

Several workers [4,7–10] have investigated the infrared spectroscopy of soil humic compounds and on the basis of these works, band assignments have been made. Fig. 1c is a typical soil subtraction spectrum and exhibits absorption bands at 3400, 2925, 2858
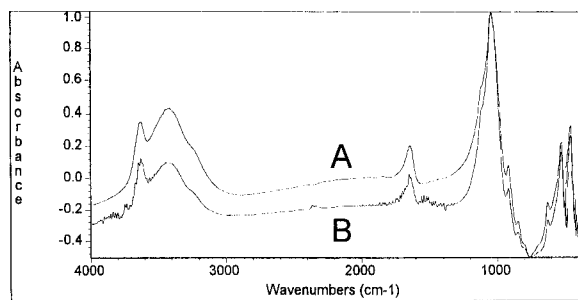
(a)
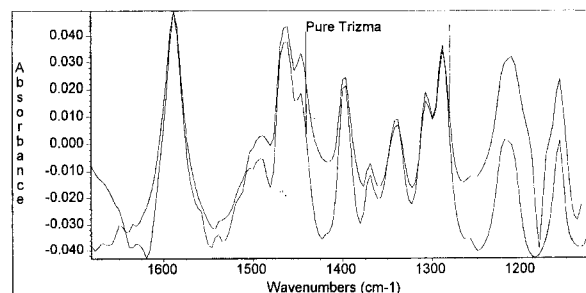
(b)

(c)

Fig. 1. FTIR spectra of montmorillonite (a) and Trizma (b) before and after pyrolysis (c). Subtraction spectra obtained for a typical soil.

and 1730 cm^{-1} which are characteristic to soil humic compounds. The sharp band at 1050 cm^{-1} can be assigned to the Si–O stretch, which has not been completely eliminated in our subtraction process. A strong band at 547 cm^{-1} that is invariably seen in our spectra has not been assigned.

4.5. Thermal analysis

Differential Thermal Analysis (DTA) is a technique which records the physical/ chemical transition of a material and a reference, against time as the two samples are subjected to identical heating or cooling at a precisely controlled rate. DTA was used in this study to confirm that the soil organics were being completely oxidized under the experimental conditions.

In a DTA scan a thermal event such as a melt, a glass transition, or decomposition is recorded as a peak or large variation in the smooth trace during the heating cycle. Fig. 2 shows a trace of a DTA scan during a heating cycle from 25°C to 1500°C of a typical soil sample and of the cooling cycle of the same material down to 200°C, both at the same scan rate (40°C/min) performed in air. The heating cycle exhibits an exotherm beginning at about 300°C and ending at about 500°C. The cooling curve, on the other hand, shows no thermal event in this temperature range. A repeat of this experiment, carried out under a nitrogen atmosphere did not show the event occurring between 300°C and 500°C on heating. This temperature range is in agreement with our observations obtained by heating the sample in a muffle furnace for the determination of organic content, and suggests that the organic compounds in the soil are completely removed by oxidation.

4.6. Four sample tests

From samples analyzed for this exercise four samples were encountered that had different geographic provenance but coincidentally had the same Munsell Color
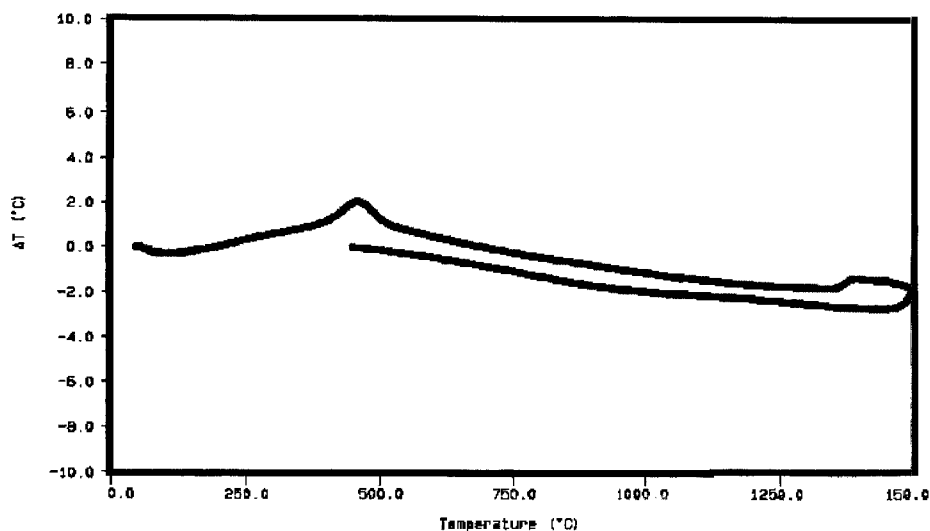

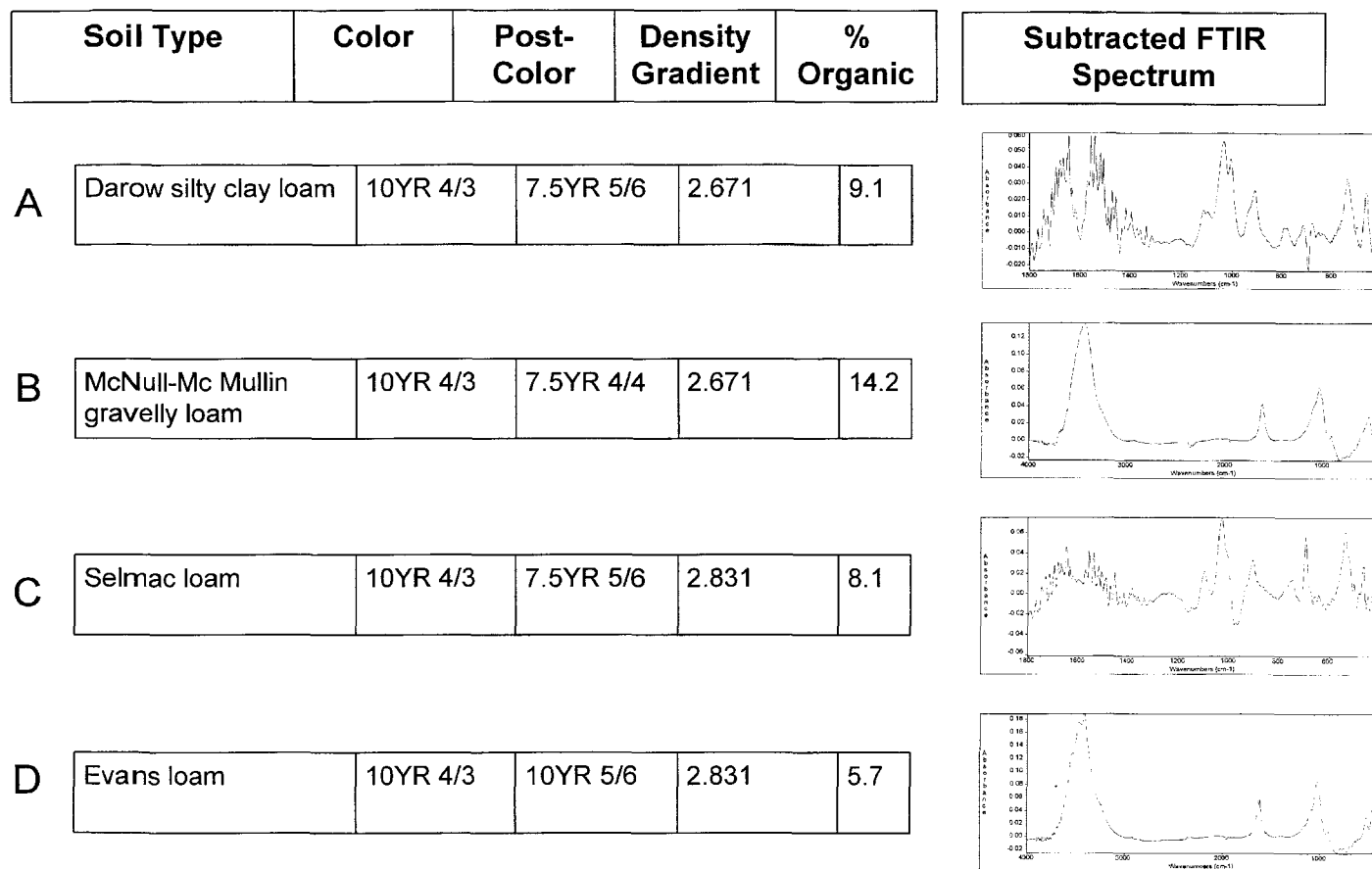Fig. 2. A DTA trace of a typical soil (heating and cooling).

	Soil Type	Color	Post-Color	Density Gradient	% Organic	Subtracted FTIR Spectrum
A	Darow silty clay loam	10YR 4/3	7.5YR 5/6	2.671	9.1	
B	McNull-Mc Mullin gravelly loam	10YR 4/3	7.5YR 4/4	2.671	14.2	
C	Selmac loam	10YR 4/3	7.5YR 5/6	2.831	8.1	
D	Evans loam	10YR 4/3	10YR 5/6	2.831	5.7	

Fig. 3. All data collected for four random soils that had identical Munsell color values.

assignment. Fig. 3 exhibits the pre- and post-pyrolysis color, the density gradient, the percent organic and the FTIR-subtracted spectra of these four soils.

These four soils illustrate how, using techniques available to the forensic scientist, including the FTIR subtractive method described in this paper, soils which on initial observation have identical color but were in fact obtained from different geographic locations, could be differentiated. For example soils A and B in Fig. 3 have identical post pyrolysis colors and density gradient values. The percent organic values are quite different, however, we have shown that this parameter can show large variations over very short distances. The subtracted spectra, however, are dissimilar suggesting that these two samples are indeed differentiable. Samples B and D on the other hand have very nearly identical subtraction spectra. The differences in their post pyrolysis colors and their density gradient values can however, differentiate them. Samples A and C have identical post pyrolysis colors, similar organic content and although the subtraction spectra are similar, density gradient determination suggests they can be their differentiable.

When using these analytical parameters, one or more of the results can discriminate each soil. We propose that the FTIR spectra of the organic portion of soil serves a useful purpose in forensic investigations.

5. Conclusions

Analysis of over 100 soil samples has been completed. We have examined each with respect to color, density, organic content, and subtractive FTIR. The use of a subtractive FTIR technique after thermal degradation has allowed us to examine and compare the IR spectra of the organic portion of soil. When color is inconclusive, the soil organic component analyzed by FTIR is a technique that allows discrimination within evidentiary samples. We propose that the FTIR spectra of the organic portion of soil serves a useful purpose in forensic investigations.

Acknowledgements

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