Analytical Instrument and its Utilization in Soil Forensic: A Review

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Abstract

In the present paper, we give an overview on the importance of the analytical instrument used in the field of forensic science for the elemental analysis of soil evidence collected from the scene of occurrence. The forensic scientist must rely upon the elemental composition of major and trace elements for the soil sample comparison and discrimination. Variation in the composition of soil sample allows considerable discrimination through the instrumental technique even there is a little amount of sample. Through this paper, reviews on the techniques which are extensively used in forensic sciences have been reported. Report summaries based on soil analysis application and techniques employed for the elemental composition like X-ray fluorescence (XRF), SEM/EDX, inductively coupled plasma (ICP) spectrometry, and XRD. ATR-FTIR for mineral identification.

Key words: Forensic Science, ICP-, XRD, XRF, SEM/EDX, and Vibrational Spectroscopy, notably NIR and DRIFT.

Introduction

Soils matrix is composed of both organic and inorganic components and majority of examination methods of soil for its characterization and identification by a forensic soil scientist is based on the analysis of inorganic materials. (15) A soil sample is usually composed of more than just rock and minerals. Leaves, seeds, pollen, and other organic components are commonly present. Fourier transform infrared spectroscopy can be used to characterize the bulk soil organic components, such as plant fats and waxes, proteins, cellulose, and lignin.(15,20). Soil contains variety of elements and the elemental composition of soil is basically due to the rocks composition which comprise the earth crust. Environmental condition also effects the elements present in the soil. The earth crust contains elements such as sodium (Na), Calcium (Ca), Iron (Fe), potassium(k) and magnesium (Mg). In tropical condition climate area soil are produced with high contain of alumina and ferric iron oxide, in arid climate area gypsum and calcium carbonate are produced in soil. Sandy soil contains silica in higher concentration while clay soil contains silica in less amount, but contains alumina in higher concentration. In this paper, we have tried to explain the available analytical instruments for analysis of Soil evidence analysis.

Crystallography in Geology: Non-opaque minerals can be identified by the optical, crystallography. The crystal structure and mineral identification of the soil trace evidence can be determined by using different analytical instruments. Techniques which are used for identify minerals in the soil sample are such as scanning electron

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microscope/Energy dispersive X-ray spectroscopy (SEM/EDX), X-ray Florescence spectroscopy (XRF), X-ray powder diffraction (XRD).

Scanning electron microscope/Energy dispersive X-ray spectroscopy (SEM/EDX): Through SEM/EDX we can determine the elemental composition of a substance. In this process an electron beam is targeted on the sample and is used to excite an electron within the element present in the sample. Like in XRF, the X-ray emission spectra that are produced will have the maximum that correspond to the energies of particular electron transition and these transitions are associated with particular elements. The composition that are close to the surface of minerals can also be determined through SEM/EDX, as the SEM can magnify a sample up to 300,000x. [12] In SEM/E DX the SEM is to produce an image of the sample and serves as an excitation source by generating a beam of electron in a vacuum, whereas EDX detects and measures the electron induced X-ray emission allowing for qualitative analysis of the elements present in the sample [16]. In majority of soil examination through SEM/EDX involved either visual comparison of mineral morphological or individual mineral identification, rather than a bulk elemental analysis of a soil sample [6] but, both Cengiz et al [22] and Pye and Croft [14] prefer sample preparation methods for bulk elemental analysis of soil through SEM/EDX.

X-ray Diffraction Analysis: X-ray Diffraction (XRD) is one of the most important and reliable methods of identifying the composition of geological soil and other crystalline structures [5]. The method is based on the arrangement of atoms, ions, and molecules within a crystalline structure. X-ray diffraction is capable of distinguishing between, for example, pure carbon in graphite form and pure carbon in diamond form as the crystalline structures are different. The sample is analysed by passing X-rays through the crystal and measuring the angle of diffracted X-rays. The interpretation of X-ray diffractograms relies upon Braggs law, specifically the d spacing and the intensity. Each crystalline material has its own distinctive X-ray pattern which is compared to either a reference database or a pattern produced by a known mineral for identification [5]**.** If a simple comparison between samples is required then the X-ray diffractograms may be easily compared without identification.

XRD analysis was employed to define the mineralogy of each soil, to identify and quantify the dominant clay minerals present as well as to determine the amorphous content in each sample. Moore & Reynolds define a 'clay mineral' as the relatively small number of minerals that occur as grains and are less than 2µm in size [11]. The selection of soils with specific characteristics for subsequent analysis will be assisted by the knowledge of their mineralogy obtained through the XRD methods. Sample preparation is an important requirement for accurate analysis of soils by XRD. This is especially important for soils that contain finely divided colloids, which are poor reflectors of x-rays, as well as other materials such as iron oxide coatings and organic materials. Appropriate sample preparation techniques for soils have been described by Moore and Reynolds and are designed to remove undesirable substances as well as to obtain desirable particle size, orientation, and thickness [11]. In this work, each of the soils, were mixed with the use of a stainless-steel spatula. Those soils with a sample mass of greater than ca. 50g were split to attain a representative sub-sample. XRD analysis requires the soils to consist of extremely fine grains to achieve good signal-to-noise ratio, avoid spottiness and minimise preferred orientation. Conversely, excessive dry grinding can result in lattice distortion and changes of phase. Formation of an amorphous layer around individual grains has been known to occur as a result of excessive grinding [18]. In extreme cases, this can lead to strains on the crystal structure that cause XRD line broadening or the production of X-ray amorphous material [11]. Thus, sample preparation aimed to improve diffraction characteristics of the sample and to promote dispersion during size fractionation.

X-ray Florescence spectroscopy (XRF):

XRF is a popular technique in forensic geochemistry and uses a beam of primary radiation produced in an x-ray tube to excite a secondary x-ray emission from the sample. The emitted x-rays have a characteristic energy for each element, allowing for quantitative and qualitative elemental abundance analysis.

In an XRF instrumentation, X-rays produced by the X-ray tubes source are used to irradiate the sample. The interaction of the x-rays with the sample causes electron to be ejected from the atoms of the elements within the sample. Due to the ejected electrons, the elements present in the sample will emit fluorescent X-ray radiation with discrete energies that are characteristics of these elements. The XRF detects and measures the intensity of the emitted fluorescence allowing for qualitative analysis of the elements present in the sample [(19)] in geological laboratory several grams of the soil sample are required for the XRF analysis and the sample preparation involves either high temperature heating or high pressure compaction of finely grounded powder to produce fussed-glass or pressed-powder respectively[(13)] **Anjos et al**[(17)] used the pressed -powder sample preparation method then elementally examined the soil sample by XRF to determine the use of organic compost from recyclable urban garbage resulted in heavy metal contamination of both the soil and radishes growing in the soil. In a study by Rawlins and Cave [(3)] elemental abundance data for 19 elements, obtained by XRF analyses, was used to investigate the extent to which samples derived from the same geological parent material could be distinguished from each other. For 13 of the 19 individual elements, they found that on average, it was possible to discriminate between more than 80% of the samples within parent material groups, but when using the elements in combination, more than 99.8% of samples could be discriminated from one another. Hiraoka[(25)] used XRF to analyse soil sample collected from 110 different sites in the Kyoto district of Japan to predict unknown soil origins. Whilst trace evidence forensic laboratories may have access to a µXRF, the current methods using an XRF system are not suitable for forensic analysis of soil due to the sample preparation issues. In forensic term, a large amount of soil is required and the sample should be milled prior to producing fused – glass or pressed-powder disc. This sample preparation methodology which is currently used to prepare soil sample prior to analysis using XRF is destructive and would restrict any possible additional analyses a forensic or geological expert could conduct on the soil sample.

Inductively coupled plasma (ICP) spectrometry: ICP analysis requires the soil to be in solution. This can be achieved by digesting the powdered soil sample using either an acid or alkaline technique. An extremely high temperature plasma (up to 10,000^{0}C) generated by radio-frequency is used to atomise and ionise the soil solution. The elemental concentration of the soil sample is determined by either measuring the light emitted by the atoms and ions (atomic emission spectrometry- ICP-AES) or the ions are sorted by mass and measured (mass spectroscopy- ICP-MS). ICP analysis is extremely sensitive and can be used to measure up to 70 elements simultaneously. Some ICP systems have a laser ablation modification (LA-ICP) which allows for the analysis of solid samples without the need for digestion [(14)]**.** Numerous articles have presented the benefits of ICP analysis to determine the elemental composition of soils [(8,24)], however, most trace evidence forensic laboratories do not have access to an ICP. Further, ICP analysis only requires a small amount soil sample, which is of benefit for a forensic examination, however the need for the sample to be in solution means the process is destructive and would restrict any possible additional analyses a geological experts could conduct on the soil sample. Whilst LA-ICP is less destructive than traditional ICP, for bulk characterization of soils, the soil sample should be milled then compressed into a disc, again making the technique effectively destructive for further forensic testing.

Organic Examination: That being said, infrared spectroscopy has been used by geologists as a method to predict the organic carbon content, the presence of nutrients and trace metals, the pH, the redox potential, and the conductivity of soil sample as well as to identify the presence of minerals in soil sample[(23)]**.** By predicting these parameters, the soil scientist may be able to recommend procedures to improve soil quality.

Fourier transform infrared spectroscopy: Fourier transform infrared spectroscopy (FTIR) can be used to determine the chemical composition of a sample. Organic materials are composed of atoms bonded together in a specific manner unique to that material. The absorption of infrared light by a sample result in frequencies generated from bending and stretching of bonds between atoms or group of atoms.

The resulting absorption or reflection of wavelengths is unique for a material. Alternatively, the IR spectra could be used to compare samples or standards to determine similarities or difference. There are two main methods geologists use to present a soil sample to the FTIR spectrometer: the manufacture of potassium bromide (KBr) discs and the use of a Diffuse Reflectance infrared Fourier transform spectroscopy (DRIFTS) holder. KBr is an IR inactive salt. The preparation of a KBr disc involves finely grinding a quantity of KBr with a sample of milled soil. The soil needs to be milled and the KBr mixture finely ground to remove the scattering effects from large crystals. The mixture is then placed in a KBr die set and pressure applied creating in a translucent, indurate disc. The KBr method requires a very small amount of soil sample, approx. 1.5mg. The KBr disc is analysed using transmission spectroscopy. The DRIFTS method of IR analysis involves placing the soil sample in a sample holder and the spectrum is collected on the bulk sample. The DRIFTS sample method utilises reflectance IR spectroscopy.

In a forensic trace evidence laboratory transmission FTIR with a microscope attachment and attenuated total reflectance (ATR) FTIR are commonly used for comparison of typical samples-including paints, fibres, rubbers, tapes, adhesives, and other miscellaneous materials. [1, 7].

Attenuated Total Reflectance (ATR) FTIR: ATR-FTIR is particularly useful to the forensic scientist as the examination requires little or no sample preparation, only a very small sample is required, and the non-destructive nature of the analysis means that the sample is still available for further testing. ATR is an FTIR sampling technique that enables samples to be examined directly without further preparation. A beam of infrared light is passed through the ATR crystal such that it reflects off the internal surface in contact with the sample. This reflection forms a wave that extends into the sample. The beam is then collected by a detector as it exits the crystal. There has been limited work using ATR-FTIR for the examination of soils, and very little ATR-FTIR soil comparisons work in a forensic context. In 2004, linker[21] proposed the use of ATR-FTIR to determine the nitrate concentration in soils. Weinger et al[4] in 2009, expanded on this work and proposed the use of ATR-FTIR for the identification of silicates, phosphates, nitrates, and carbonates, while Madejova [10] concentrated on identifying clay minerals. Schulz and Baranska[9] examined plant metabolites using ATR-FTIR to determine the quality parameters in horticulture and agriculture crops. This work could be used to form the foundation of work on the organic humic content of soil sample. Morrison et al[2] used ATR-FTIR as part of a wider soil examination process to examine the soil organic matter and the mineral composition for the discrimination of soil from urban areas around Scotland. The research to date shows that IR examination can provide information on both the organic and inorganic components of a soil sample. As both the KBr and DRIFTS FTIR examination have limitation in a forensic context and ATR-FTIR is a technique commonly available in forensic trace evidence laboratories which requires no sample preparation.

Discussion

The analytic techniques initiated by forensic experts have continued to expand in complexity and improve in reliability. Many new analytic tools have been applied to analytical problems in almost all areas of the field, and the technology continues to open new areas of research. Over the last two decades, a new analytical tool has been developed. Forensic examiners continue to be concerned about conducting unequivocal identification of toxic substances in such a manner that the results can withstand a legal challenge. The problems of substance abuse, designer drugs, increased potency of therapeutic agents, and widespread concern about pollution and the safety and health of workers present challenges to the analyst's skills. Today investigators have a wide range of analytical tests and sophisticated equipment with which to study microscopic pieces of evidence collected at such crime scenes. As disgruntled individuals and terrorists continue to use fire and explosives to disrupt society, forensic chemists will go on developing methods for identifying the persons responsible for such events.

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