

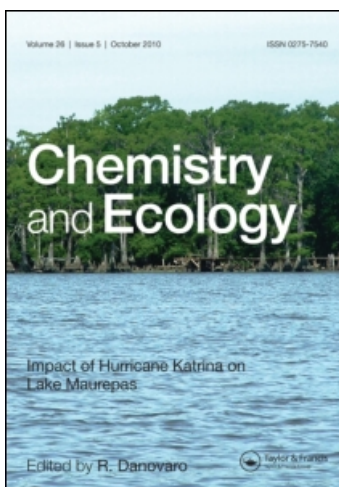
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## Direct laser desorption ionisation time-of-flight (TOF) mass spectrometry of soil organic matter for fast soil fingerprints

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Dissolved organic matter and water-extractable organic matter influence soil biological activity, affect the transport of metals and organic pollutants, and contribute to mineral weathering and podzolisation. An important part of soil organic matter (SOM) are humic substances (HS), the major sinks of organic carbon on Earth, found everywhere including Antarctica. HS and humic acids are isolated from soils using various extraction agents and isolated products are often characterised by mass spectrometry. In this work, detailed study of laser desorption ionisation of SOM and of humic acids directly from soils was performed. The micro-extraction procedure was optimised and the most suitable method was found to be direct ionisation of SOM from a soil after addition of a diluted NaOH solution. In this way, *in situ* release of adsorbed and bound SOM from soils is achieved and direct analysis by laser desorption ionisation time-of-flight mass spectrometry is possible without any tedious extraction procedure. The developed methodology enables fast screening of soil organic matter to obtain fingerprints and thus to follow the differences between soils from various environments. The developed procedure was applied to soil samples from several continents, including Antarctica, and to volcanic soils from the Canary Islands.

**Keywords:** soil; laser desorption ionisation; mass spectrometry; soil organic matter; fingerprints

### 1. Introduction

There is growing interest in and demand from both the civilian and military communities [1–3] for rapid field analysis of organic and inorganic compounds in the environment and especially in soil. This growing interest is also reflected in the forensic sciences, because soil represents an important ‘form’ of trace evidence [4].

Soil is a complex mixture in which soil organic matter (SOM) and water-extractable organic matter (WEOM) influence biological activity, affect the transport of metals and organic pollutants, and contribute to mineral weathering and podzolisation, although accounting for only a small proportion of the total organic matter in the soil [5–7]. SOM represents < 5% of the soil’s composition, and organic matter is usually located in the interior of soil aggregates [8]. Among SOM constituents, humic substances (HS) play an important role in geochemical and chemical

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processes, such as the transport and binding of inorganic and organic compounds [9]. SOM also influences C, N and other major element cycles in different ecosystems [10], not forgetting its importance in soil fertility. Because of this, maintaining SOM is an objective of many sustainable crop-production systems.

Soil analysis presents several problems, because soil is not a well-defined matrix and can change dramatically in terms of composition, structure and homogeneity, while, for example, the complex profile of the SOM itself must be considered. However, analytical instrumentation, in particular, mass spectrometry for the chemical characterisation of inorganic and organic parts of the soils has undergone important improvements.

Before chemical analysis of SOM or soil humic acids is carried out, the extraction of organic matter is usually performed. In the case of SOM, this may be viewed as consisting of non-humic and humic components [11]. For humic components, the standard extraction procedure is that described by the International Humic Substances Society (IHSS; <http://www.ihss.com>), although there are several other extraction procedures described in the literature [12–14]. In any case, extractions represent long-term and tedious procedures, which in the case of a high number of samples results in significant costs in terms of time, effort and money.

Chemical soil characterisation is done using different analytical technologies. In the case of SOM, different techniques such as elemental analysis, size-exclusion chromatography, nuclear magnetic resonance spectroscopy, vibrational spectroscopy, differential scanning calorimetry, pyrolysis and related techniques, capillary electrophoresis, mass spectrometry techniques, fluorescence spectroscopy, field flow fractionation and microscopy techniques have proven useful for studying HS at the molecular level and for the characterisation of HS [11,15–20].

In mass spectrometry, different soft-ionisation techniques have been used to characterise SOM [11,16,17,21]. Among them, matrix-assisted laser desorption ionisation time of flight mass spectrometry (MALDI-TOF MS) and laser desorption ionisation time of flight mass spectrometry (LDI-TOF MS) allow the ionisation of molecules without promoting decomposition [17,22–25]. Recently, LDI-TOF MS fingerprints and multivariate analysis were used to characterise HA from different sampling sites (Antarctica, Brazil, Czech Republic, Mexico and the USA) and of different origin (plant, soil, peat and coal derived) [17,26,27]. The combination of MS and multivariate analytical tools allows us to extract and elucidate underlying information contained in the mass spectra of the humic acid (HA) samples, characterising them according to their origin. With a reasonable input of resources, LDI-TOF MS has the potential to generate extensive data based on HA in soil which may then be used for site-specific characterisation of soils, pollution and/or forensic purposes. Technologies such microprobe laser desorption/laser ionisation mass spectrometry ( $\mu\text{L}^2$  MS) [28], laser desorption laser photo ionisation time-of-flight mass spectrometry ( $\text{L}^2\text{TOF MS}$ ) [29] and laser desorption laser mass spectrometry [30] have been applied, for example, to determine and quantify aromatic pollutants in soils samples. However, to our knowledge, there are no citations in the literature concerning the direct analysis of soils by LDI-TOF MS. In this work, we investigate the possibility of using direct LDI-TOF MS, without isolating HA by extraction, for sensitive and rapid screening analysis to characterise SOM.

## 2. Materials and methods

### 2.1. Origin of soil samples and sampling sites

Canarian soil surface samples were collected at pine and laurel forests in Tenerife, in typical ecosystems of the Canary Islands. The sampling was carried out in a bare soil plot in the first 5 cm, at 10 randomly distributed sampling points. At each point, soil samples were collected manually,

mixed and air-dried at room temperature. The Canary Archipelago has a volcanic origin. Soils in Tenerife (Canary Islands) are classified as leptosols, vertisols and andosols, and the textures range from sand to loamy sand (IUSS Working Group WRB 2006). Although andosol soils have a high organic carbon content, in general, the soils of the Canary Islands are characterised by a low organic content, this being one of the main limitations for soil quality.

HA from Antarctic samples were extracted from soil sampled at Crepin Point (King George Island, South Shetland, Antarctica). The Antarctic soil samples were mainly of a sandy gravel-gravelly sand character. The procedure is described in detail elsewhere [24,26].

Garden soil, collected from an average garden (Brno, Czech Republic), was also analysed.

HA standards from the IHSS were Soil (1S102), Peat (1R103H) and Leonardite (1S104H) (<http://www.ihss.gatech.edu/>).

## 2.2. Sample preparation

Soil samples of different origin from the Canary Islands (Spain), Antarctica or the Czech Republic were ground in a glass mortar into a fine powder. Approximately 5 mg of powdered soil sample was placed in a micro vial and mixed with 100  $\mu$ L of diluted 0.1 M sodium hydroxide as the extractant and ultrasonicated for  $\sim$  10 min in an ultrasonic bath at room temperature.

HAs were extracted from the soil samples under study according to the procedure described by Gajdošová et al. [24].

## 2.3. Apparatus

The mass spectrometric experiments were carried out using an AXIMA CFR (Kratos Analytical, Manchester, UK) MALDI-TOF MS instrument equipped with a nitrogen laser emitting on 337 nm from Laser Science Inc. (Franklin, MA, USA). External calibration with sodium, potassium and bradykinine ions was used in the positive mode. Each mass spectrum was accumulated from spectra obtained from at least 200–500 laser shots. Mass spectra were measured in various modes depending on the analysed sample (linear positive, linear negative or reflectron negative modes), but generally, the spectra obtained with more signals were those measured in the linear positive mode.

### 2.3.1. Sample preparation method

One microlitre of either soil suspension or standard HA was deposited onto a sample plate and dried at room temperature before the analysis. One microlitre of matrix solution (in acetonitrile/0.1% aqueous TFA, 1:1) was added to 1  $\mu$ L of the soil-extractant suspension, pipetted onto a target plate and dried at laboratory temperature in a stream of air, and then introduced into the AXIMA CFR. The mass spectra were measured after the pressure had fallen below  $10^{-4}$  Pa.

## 3. Results

### 3.1. Micro-extraction of soil organic matter

Fast micro-extraction of the organic matter from the soil was studied using various extraction agents, starting from pure water, using aqueous solutions of ammonium or sodium hydroxide. For the extraction, different concentrations (0.001, 0.05, 0.1 and 1 M) of the extractants were mixed with  $\sim$  5 mg of fine-powdered soil sample (Supplementary Figure S1 – available online only).

### 3.2. Mass spectra measurements

The LDI-TOF MS measurement procedure was optimised in linear and/or reflectron positive or negative modes, respectively. Measurements in the negative mode yielded rather low-quality mass spectra; therefore in the remainder of this article, only results from positive ion modes are shown.

TOF mass spectra using LDI of the different soil-extractant suspensions show most of the signals corresponding to organic matter in the  $m/z$  range between 100 and 1000. It was shown that in the LDI mode only single-charged positive ions are observed. Comparison between the LDI mass spectra obtained for soil + water, soil + ammonium hydroxide (1 M) and soil + sodium hydroxide (1 M) are shown in Figure 1(A, B). Labelled peaks in the

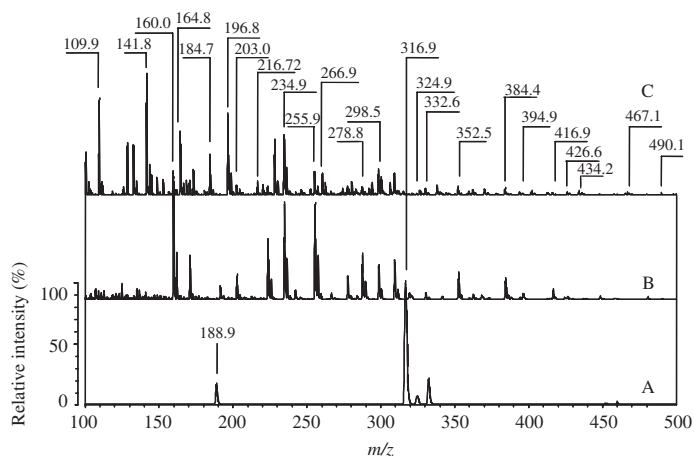


Figure 1. LDI-TOF MS obtained for Antarctic soil after addition of different extraction agents in the range of 'fulvic acids' 100–500  $m/z$ . (A) Soil + water, (B) soil + 1 M ammonium hydroxide, (C) soil + 1 M sodium hydroxide.

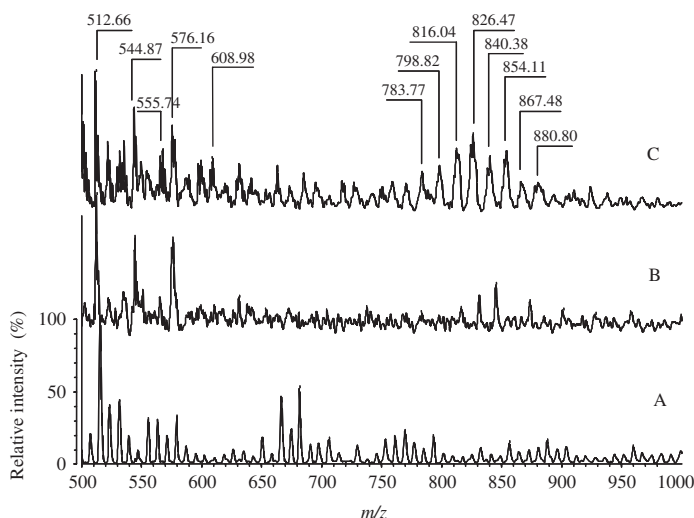


Figure 2. LDI-TOF MS obtained for Antarctic soil after addition of different extraction agents in the range of 'humic acids' 500–1000  $m/z$ . (A) Soil + water, (B) soil + 1 M ammonium hydroxide, (C) soil + 1 M sodium hydroxide.

$m/z$  region from 100 to 500 (Figure 1(A)) and 500 to 1000 Da (Figure 1(B)) are observed with relatively high intensities. Some inorganic species were also identified at  $m/z$  26.98 ( $\text{Al}^+$ ), 30.06 ( $\text{SiH}_2^+$ ), 23 ( $\text{Na}^+$ ), 30 ( $\text{K}^+$ ), 45.98 ( $\text{SiH}_2\text{O}^+$ ) and 103.95 ( $\text{Al}_2\text{O}_3\text{H}_2^+$ ). Comparison between the mass spectra of HA extracted from the Antarctic soil (Figure 2(A)) and those obtained using water, ammonium hydroxide and sodium hydroxide, shows a high coincidence between the mass spectra of HA and that obtained for the suspension of soil + sodium hydroxide (1 M).

The optimised extraction method using aqueous 1 M NaOH solution as the extractant was applied to the LDI-TOF MS screening analysis of Antarctic soil. Figure 2(A, B) shows the mass spectra measured in the linear positive mode for HA extracted using the IHSS procedure and the soil–NaOH suspension, respectively. LDI-TOF MS analysis of the soil–NaOH suspension yield in most intensive spectra in the  $m/z$  region 100–500, in comparison with mass spectra obtained for HA. Moreover, it may be noticed that mass spectra obtained for HA show more intensive peaks between  $m/z$  400 and 500. Mass spectra in the  $m/z$  range 500–1000 show no significant differences between spectra obtained for the soil–NaOH suspension and Antarctic HA isolated using the IHSS standard procedure. Peaks at the same  $[\text{M}+\text{H}]^+$   $m/z$  values were observed in mass spectra at: 128.9, 164.8, 164.9, 184.7, 189.9, 251.0, 255.6, 309.5, 310.1, 360.1, 362.4, 717.1, 718.3, 742.6, 745.1, 757.1, 759.2, 783.7, 785.1, 798.8, 799.0, 813.0, 813.3, 827.0, 826.4, 840.3, 841.0, 853.0, 854.1, 867.4, 881.3, 907.0, 911.0, 925.0 and 926.4. Surprisingly, even if a rather high concentration of NaOH was used, no substantial effect of sodium ions on the shape of the mass spectra was observed.

#### 4. Discussion

LDI-TOF MS was applied for the analysis of HA extracted from several soils of different origin (plant, garden, soil and coal derived) and precedence [23–25,31]. The soil sample was mixed with a small volume of 1 M NaOH, and the suspension was analysed by LDI-TOF MS. Detailed LDI-TOF MS was performed and selected results are shown in Figure 3(A)–(D). LDI-TOF MS measurement parameters were optimised according to soil origin. The mass spectra show coincidence in the presence of some peaks at various  $m/z$  values for very different samples [25,26,32]. Such coincidence was also observed here for direct laser ablation of soil, i.e. LDI of soil organic matter (cf. Figure 1). Instead of the presence of common peaks, the figures show the differences in the mass spectra fingerprints for volcanic, pine forest, laurel forest and garden soils. Peaks at almost the same  $[\text{M}+\text{H}]^+$   $m/z$  values were observed in the mass spectra of all humic acids, where 284.4, 310.3, 311.3, 326.3, 354.3, 370.3, 376.3, 409.2, 549.4, 605.4, 773.5, 787.5, 799.5, 813.5, 827.5, 841.6 and 855.6 Da are almost always present. The peaks with the highest intensity appeared in the  $m/z$  range 275–400 Da. There is a high degree of similarity between the mass spectra of different HA and the intensities of the individual peaks vary only a little. It was found that the  $m/z$  region 500–1000 is representative of the characterisation of the analysed soils. It can be noted that mass spectra in the range  $700 < m/z < 900$  obtained for the soil suspension with NaOH display similar fingerprints even if the resolution was lower, as present in the spectra of HA extracted from soil using the IHSS procedure (Figure 4 and Supplementary Figure S2 – available online only). Studying the isotopic patterns of all the peaks, it is evident that the charge of the ions observed equals one. This means that all  $m/z$  values are showing the real molecular mass of the organic matter analysed. This finding agrees well with the results of Gajdošová et al. [26,32] and Peña-Méndez et al. [17] for different HA. Moreover, Mugo and Bottaro [25] also described the presence of some of these peaks (with low  $m/z$  values) in their study of fulvic acids.

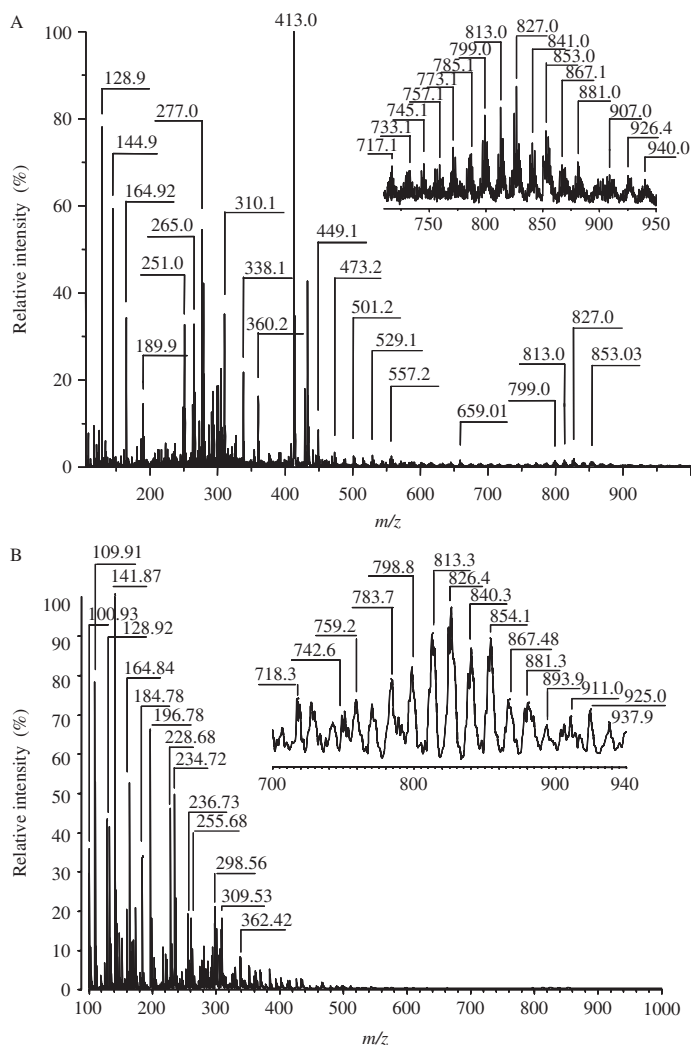


Figure 3. Comparison of LDI-TOF MS of extracted soil humic acids with micro *in situ* extraction using soil + sodium hydroxide solution. (A) LDI-TOF MS for HA extracted from Antarctic soil. (B) LDI-TOF MS for soil + sodium hydroxide (1 M).

## 5. Conclusions

It was found that a micro-extraction of soil humic acid with diluted sodium hydroxide and without any isolation of SOM gives reliable and characteristic mass spectra fingerprints for SOM.

Characteristic mass spectra fingerprints enable us to classify soils and detect specific compounds corresponding to their origin.

The methodology can be used for forensic purposes or for the fast characterisation of soil samples. Direct LDI combined with TOF MS provides information for the characterisation and differentiation of soils through their organic matter mass spectra fingerprint. The methodology described here has small sample requirements and minimum sample pre-processing. The approach developed enables high throughput analysis and characterisation through mass spectra fingerprints of soils of different origins and precedence.

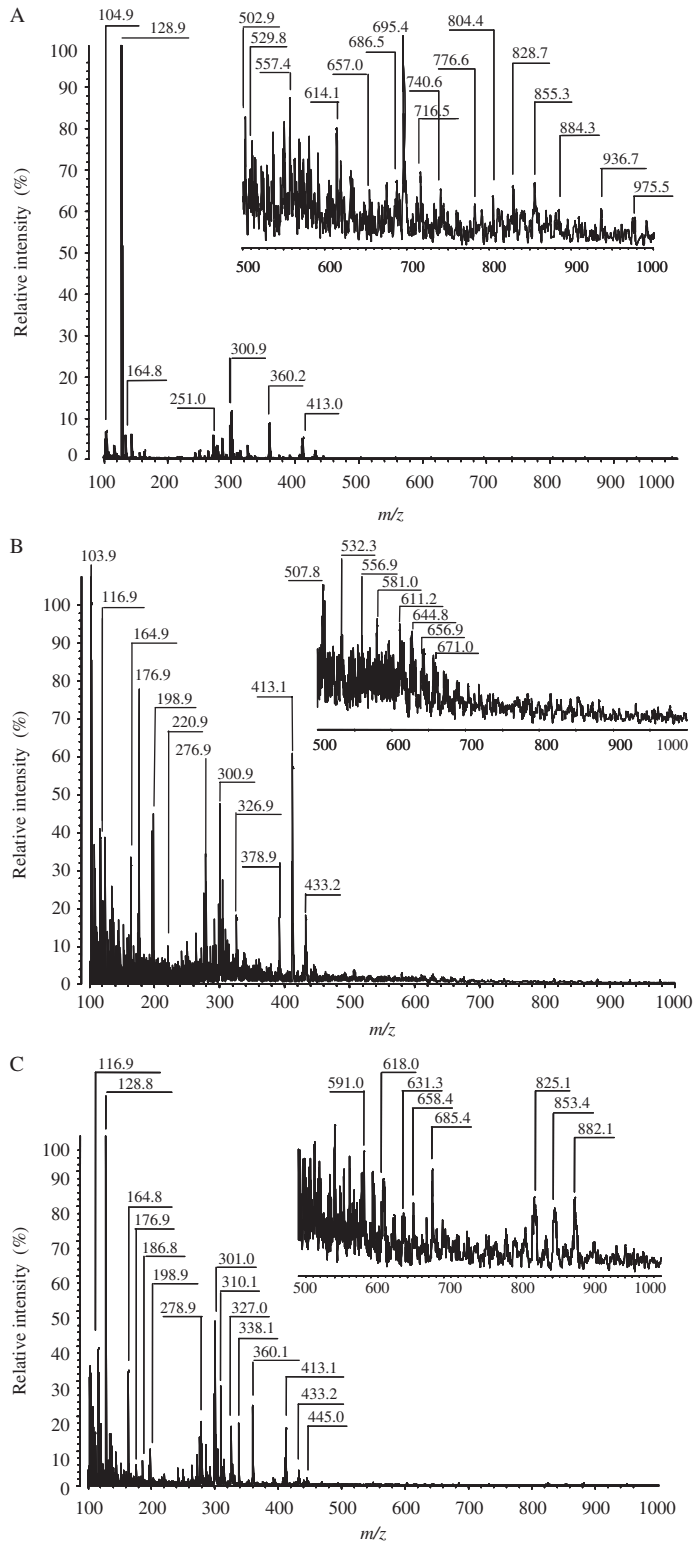


Figure 4. Examples of LDI-TOF MS obtained for the analysis of soil of different origin after addition of sodium hydroxide (1 M). (A) Volcanic soil, (B) pine forest, (C) laurel forest.



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