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In situ analysis of the Martian soil by gas chromatography: Decoding of complex chromatograms of organic molecules of exobiological interest

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Abstract

Gas chromatography–mass spectrometry (GC–MS) will be used in future space exploration missions, in order to seek organic molecules at the surface of Mars, and especially potential chemical indicators of life. Carboxylic acids are among the most expected organic species at the surface of Mars, and they could be numerous in the analysed samples. For this reason, a chemometric method was applied to support the interpretation of chromatograms of carboxylic acid mixtures. The method is based on AutoCovariance Function (ACVF) in order to extract information on the sample — number and chemical structure of the components — and on separation performance. The procedure was applied to standard samples containing targeted compounds which are among the most expected to be present in the Martian soil: *n*-alkanoic and benzene dicarboxylic acids. ACVF was computed on the obtained chromatograms and plotted versus retention time: peaks of the ACVF plot can be related to specific molecular structures and are diagnostic for chemical identification of compounds.

Keywords: Carboxylic acids; Martian soil; Chemometric method

1. Introduction

One of the main objectives of space exploration is to understand the events that led to the origin of life on Earth: evidence of abiotic chemistry and extinct or extant life is searched in extraterrestrial environments in order to shed light on how bio molecules can be synthesized by abiotic reaction in such environments [1–10].

At present, a major goal of the NASA-ESA Space Exploration Program is Mars, the planet which most closely resembles Earth [5–11]. In order to hunt for water's geological calling card, Mars robots (or rovers) are outfitted with geologic instruments rather than biologic life-detection instruments: the rover missions did indeed find minerals and rock formations that help to prove that Mars was once very wet, and therefore a favourable environment for the emergence and development of life [9–12]. This means knowing exactly where to look for possible traces of prebiotic chemistry, or organic compounds derived from extinct Martian biota: this will be the challenge of future explorations [11].

Amino acids are key compounds because they play an essential role in biochemistry: they have been detected in several meteorites [6–8]. Smaller molecules, such as carboxylic acids, can also be chemical indicators of life, since they could be metastable intermediates of organics under Martian oxidizing conditions. Thus, organic substances derived from Martian life, if it did or does exist, or from exogenous sources (meteorites, comets) may undergo oxidative diagenesis to yield alkane carboxylic acids from alkanes and benzene carboxylic acids from aromatic hydrocarbons [3]. These species

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could have been missed by the GC–MS experiment of the Viking probes, already dedicated to the search for organics at the Mars surface, which failed to detect organics in the soil at the ppb level [12]. Indeed, the used sample preparation procedure (i.e., heating and pyrolysis of the samples up to 500 °C) was not able to vaporise most of these polar species. Beyond the investigation of the surface, it must be noticed that the research also concentrates on subsurface analysis, as organics on the surface are most likely destroyed by oxidation, while they may be preserved in the subsurface, which was not investigated by the Viking probe [5,9,12]. Hence, with an appropriate sample preparation procedure, it seems that a future GC–MS experiment should have significant chances to find carboxylic acids, as the most probable organics present in the soil of Mars.

Gas chromatography is a flight-qualified technique for the analysis of organic molecules [12–22]. It has been successfully used in several space missions to Mars [4,9] and Venus [14], and has been selected for in situ analysis of Titan's atmosphere (Cassini–Huygens mission) [2,14–17] and in the Rosetta mission to explore comet 67P/Churyumov-Gerasimenko [16,18–25]. Whereas most of these missions are dedicated to the analysis of the gaseous atmospheric composition, in situ analysis of highly polar, thermally fragile compounds in a soil requires extraction from the mineral matrix (if necessary) and transformation into thermally stable volatile compounds prior to GC analysis [9,13]. This procedure (without extraction which is not required in this case) was first introduced in space GC for the Rosetta mission [21] and should be used in the future mission to Mars dedicated to the detection for organics [9,13].

Chromatograms resulting from such an analytical procedure could be very crowded with peaks because: (i) there could be numerous amino and carboxylic acids in the sample; (ii) other organic species could be present in the sample and analysed at the same time; (iii) artefacts could result from the chemical derivatization of the sample or decomposition of the stationary phase and thus interfere the chromatogram. In this case, it is very helpful to use a mathematical approach to deconvolve incompletely resolved chromatographic peaks and to interpret the chromatogram in order to extract all the analytical information hidden in it: in other words "decoding" the complex chromatogram [26].

In previous papers it has been demonstrated that a chemometric approach based on Fourier Analysis (FA) is a powerful tool for decoding a complex chromatogram, i.e., to extract all the information contained therein concerning the mixture — number of components, abundance distribution — and separation — separation performance, retention pattern [26–35]. In particular, its power lies in its ability to identify ordered retention patterns, singling them out from the complex chromatogram, which appears crowd with peaks randomly distributed throughout the chromatographic space [26,31–33]. The order — peaks appearing at repeated distances as a sequence (homologous series), or at constant distances located in different parts of the chromatogram — is related to specific chemical structure variations and can be used to identify the presence of such structures in the mixture [33–35].

The present work is a further application of the FA procedure focused on carboxylic acids, as chemical signature of life: in particular, the straight-chained homologous series of *n*-alkanoic acids is studied. In fact, the terms of homologous series of compounds presenting a non-random distribution of the number of carbon atoms are regarded as biomarkers, since they are indicators of the action of living organisms [9].

2. Theory

The chemometric approach, based on Fourier Analysis, studies the AutoCovariance Function (experimental ACVF, EACVF) that can be directly computed from the experimental chromatogram acquired in digitized form, using the following expression [24–27]:

$$\mathrm{EACVF}(t) = \frac{1}{M}\sum_{j=1}^{N-k}(Y_j - \hat{Y})(Y_{j+k} - \hat{Y}),$$

$$k = 0, 1, 2, \ldots M-1 \qquad (1)$$

where Y_j is the digitized chromatogram signal, $\hat{Y}$ its mean value, M the truncation point in the EACVF computation. The Autocorrelation Function (ACF), representing the ACVF normalized to the value computed at time 0, is more frequently used than the ACVF itself.

EACF represents the short and long term correlation between the positions of subsequent peaks. Information can be extracted from computation of the whole chromatogram (Eq. (1)), without handling any specific peaks.

The first part (short term correlation) describes the mean peak shape averaged over all the chromatographic peaks: a simplified procedure has been developed to extract information from this part of the ACVF by a simple graphical inspection [33]. The number of components m present in the mixture can be computed by the expression:

$$m = \frac{A_T^2(\sigma_a^2/a_a^2 + 1)}{\mathrm{ACVF}(0)2\sigma\sqrt{\pi}X} \qquad (2)$$

where ACVF (0) is the value of the AutoCovariance function at $t = 0$, A_T the total area and X the total time span of the chromatogram, σ_a/a_a is the peak area dispersion: all these values can be calculated directly from the digitized chromatogram. The mean σ value, representing separation performance, can be estimated from the EACF peak width.

The second part describes long term correlations [33–35]: if repeated constant interdistances are present in the chromatogram (i.e., arrows in the chromatogram reported in Fig. 1a), the EACF plot shows some positive peaks at the

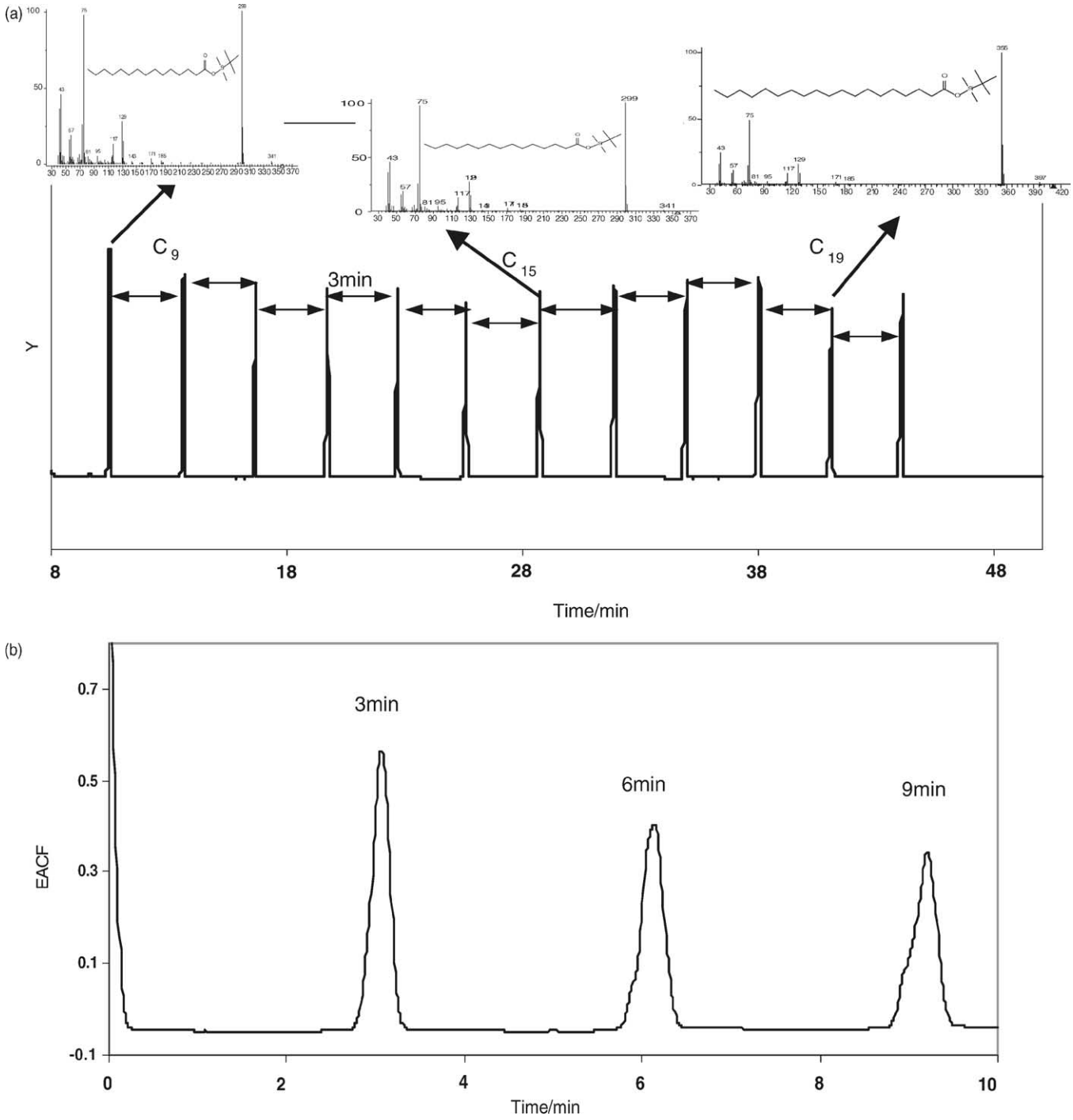

Fig. 1. (a) Chromatogram of a homologous series of *n*-alkanoic acids (containing from 9 to 20 carbon atoms). Inset: MS spectra of C9, C15 and C19 *n*-alkanoic acids. (b) EACF plot computed on this chromatogram.

corresponding interdistance values (peaks at 3, 6, 9 min in Fig. 1b). The result is that the EACF plot is much simpler than the original chromatogram and regularities in the retention pattern can be identified by simple visual inspection. Since repetitivities can be related to constant changes in the molecular structure (by comparison with proper standard compounds), the EACF peaks can be diagnostic for specific classes of compounds: the chemical composition of the mixture can be identified from the plot [20,24]. Information on quantitative composition of the samples can also be obtained, since the height of the EACF peaks is related to the abundance of repetitiveness in the chromatogram, i.e., the combination of the number of repeated peaks and their heights.

3. Experimental

3.1. Reagents

The analysed samples were standard solutions of *n*-alkanoic acids (containing from 7 to 20 carbon atoms), benzene carboxylic acids (1,2 and 1,3 benzenedicarboxylic, 1,2,3 and 1,3,5 benzenetricarboxylic), and amino acids (20 small molecules). The concentration of target molecules ranged from ppb to ppm for each component. All the standard compounds were purchased from Aldrich (99% min). *N*,*N*-Methyl-*tert*-butyl(dimethyl-silyl)trifluoroacetamide (MTBSTFA) and pyridine were obtained from Interchim (France) and from Fluka (France), respectively. 2-Propanol (99.8%) was purchased from Aldrich and dichloromethane from Riedel-de Haen (Germany).

The reference soil used for this study was a soil from Fontainebleau (Prolabo, France) of particle size ranging from 230 to 310 mm (volumic mass 1380 g l^{-1}). The spiked soil samples were prepared according to the procedure reported in [13]. An accurate amount (6×10^{-7} moles) of each organic acid was added to 6 g of sand and mixed to homogeneity: the obtained concentrations simulate those found in meteorites [8].

3.2. Extraction-derivatization procedure

The analytical procedure is based on organic solvent (2-propanol) extraction of organic compounds from the soil, followed by silanisation with *N*,*N*-methyl-*tert*-butyl(dimethylsilyl)trifluoroacetamide (MTBSTFA), as reported in [13]. To prevent the solvent evaporation, the extraction was performed in a sealed chamber: 6 g of soil were extracted with 6 ml of 2-propanol. In order to reduce the extraction time and make it compatible with space constraints (short analysis time and low energy consumption) sonication-assisted extraction was performed in an ultrasonic bath (Bransonic 12, Germany, frequency 48 kHz) at 60 °C.

After extraction, filtration and evaporation, the sample was submitted to the derivatization procedure: the reactant was *N*, *N*-methyl-*tert*-butyl(dimethyl-silyl)trifluoroacetamide MTBSTFA (30 μl) in pyridine (10 μl). This procedure is compatible with space constraints: it is a single-step reaction, allows water free conditions (important in the case of Mars exploration), it can be easily automated and integrated into space instrumentation [13]. The derivatized sample was submitted to GC analysis using a FID detector. In order to obtain chemical identification of the silylated derivatives GC–MS analysis was also performed.

3.3. Instrumentation

The analyses were performed with a CP-3800 gas chromatograph (Varian Inc., Les Ulis, France) equipped with a FID detector. The split/splitless injector operated at 300 °C (mean split ratio: 1:20) and the detector was heated at 300 °C. GC–MS analysis were obtained by using a Shimadzu QP5050 GC–MS instrument operating with a quadrupole detection mode. The detector operated at 270 °C. Helium was used as carrier gas for both the instruments; flow rate was 1.5 ml/min.

The GC column used was a CPSIL 5 CB capillary column (15 m × 0.25 mm, 0.25 μm) purchased from Varian-Chrompack (USA). Temperature-programmed analysis was performed increasing from 100 to 280 °C, at 3 °C/min. These temperature conditions were properly selected in order to obtain a homogeneous retention pattern, i.e., constant retention increments for subsequent terms of a homologous series [33–38]. The same column and the same temperature-programmed conditions were used in both the GC-FID and GC–MS experiments to obtain equivalent results.

4. Results

The proposed procedure has been tested on standard solutions of *n*-alkanoic acids (containing from 7 to 20 carbon atoms) and benzene carboxylic acids (1,2 and 1,3 benzenedicarboxylic, 1,2,3 and 1,3,5 benzenetricarboxylic); also 20 small amino acids were analysed, since they are the target molecules for the search of a exo/astrobiologic signature in Martian soil [9,11].

Standard mixtures containing normal saturated fatty acids (with carbon atom number ranging from 7 to 20) were analysed. It is well known that *n*-alkanoic acids are widely distributed in nature, in plants and living organisms: in particular the identification of a non-random distribution of the terms of the series can be regarded as a signature of biological origin [9]. After derivatization, the samples were submitted to GC analysis: a proper temperature program was applied to obtain constant interdistances between subsequent terms of the homologous series. The chromatogram of a standard mixture containing C9–C20 normal saturated fatty acids is reported in Fig. 1a (constant retention increments showed by arrows). The molecular structure of each peak was identified by comparison with retention times of standard compounds. MS spectra obtained from the GC–MS analysis are compared to reference data (MS spectra of C9, C15 and C19 *n*-alkanoic acids are reported in inset of Fig. 1a): they show characteristic features of low abundant molecular ion and dominate fragments due to fragmentation of the derivatizing group $[M^+–CH_3^+]$ and $[M^+–C_4H_9]^+$ [13,39,40]. The AutoCovariance Function was computed on the digitised signal (Eq. (1)) and plotted versus retention time increment (Fig. 1b): the EACF plot singles out well-shaped peaks at interdistance values of the constant retention increments present in the chromatogram. They correspond to the addition of a CH_2 group in terms of *n*-alkanoic acid series (3 min) and its multiple values (6, 9 min) due to retention repetition in the chromatogram. Therefore, under the applied experimental conditions, EACF peaks at 3–6–9 min are indicative of the presence of *n*-alkanoic acids in the analysed mixture.

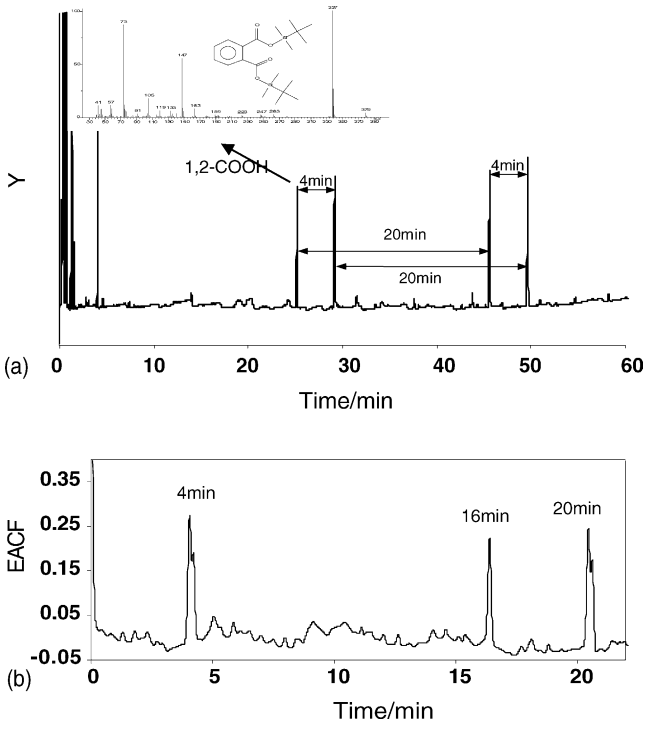

Fig. 2. (a) Chromatogram of a standard mixture of four benzene di- and tri carboxylic acids. Inset: MS spectrum of 1,2 benzene di-carboxylic acid. (b) EACF plot computed on this chromatogram.

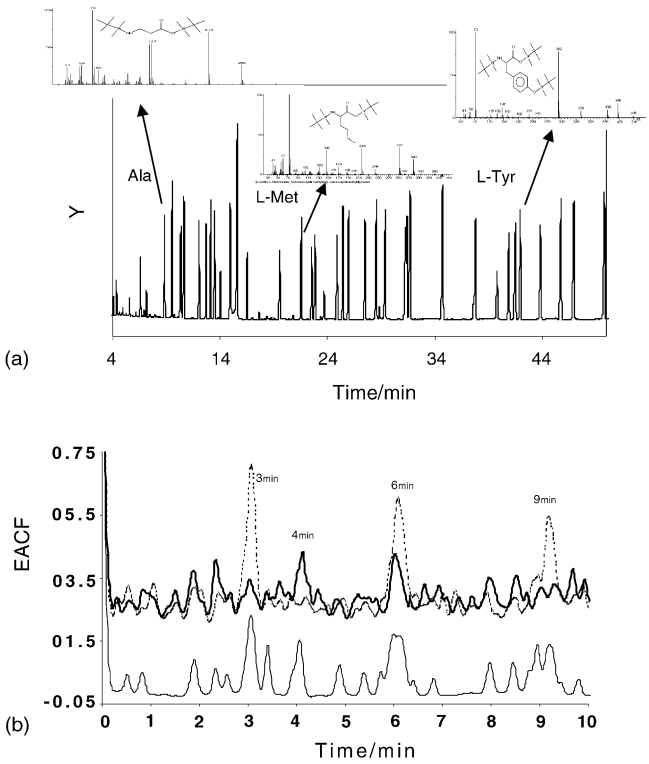

Fig. 3. (a) Chromatogram of a mixture of *n*-alkanoic, benzene carboxylic and amino acids. Inset: MS spectra of alanine, L-methionine and L-tyrosine. (b) EACF plot computed on the chromatogram. Lower trace: original mixture. Upper traces: bold line: mixture spiked with a triple amount of benzene carboxylic acids, dashed line: mixture spiked with a triple amount of *n*-alkanoic acids.

A standard mixture of benzene carboxylic acids was also submitted to the same analytical procedure: 1,2 and 1,3 benzene-di, 1,2,3 and 1,3,5 benzene-tri carboxylic acids. Structural elucidation of the detected peaks was based on retention times and on the study of MS spectra obtained in GC–MS analysis: the MS spectrum of 1,2 benzene-di carboxylic acid is reported in inset in Fig. 2a [13,41]. From these data it is possible to relate constant interdistances repeated in the chromatogram (arrows in Fig. 2b) to specific molecular structural effects: the retention time increment of 4 min is due to the isomerisation effect and that of 20 min to the addition of a carboxylic group, under the reported experimental conditions. The EACF plot computed on the chromatogram (Fig. 2b) singles out such repetitivities showing well-shaped peaks at 4–16–20 min, which are diagnostic of benzene carboxylic acids.

The proposed procedure was tested on more complex mixtures containing possible interfering components: this is the case of amino acids, the key organic molecules ubiquitous to living systems. They also yield MTBSTFA derivatives eluting in the same chromatographic space as those of carboxylic acids. Fig. 3a reports the chromatogram obtained from a standard mixture of *n*-alkanoic and benzene carboxylic acids and 20 amino acids. The EACF method was applied both to characterize the mixture/separation properties (first part of the EACF plot) and to extract information on the chemical composition of the mixture (second part of the EACF plot) by using the procedure described elsewhere [26–30] and widely applied in GC space analyses [20,23–25]. The estimated number of components present in the sample, *m*, was 44 ± 7: this value shows a good agreement with the effective number of components, 43, present in the standard mixture. The reliability in estimating mean peak standard deviation, i.e., the analytical separation performance, was checked by comparing the σ_{EACF} value with the $\sigma_{PeakFit}$ value, independently estimated by using PeakFit software (Jandel Scientific): exactly the same value 0.7 s was obtained with both procedures.

A simple inspection of the EACF plot (Fig. 3b, lower trace) makes it possible to extract information on the chemical composition of the sample: the EACF plot clearly shows the peaks at 3–6–9 min, diagnostic for *n*-alkanoic acids, and that at 4 min corresponding to benzene carboxylic acids. The same results are also obtained by chemical identification of peaks of the standard compounds on the basis of their retention times and their MS spectra from GC–MS analysis (i.e., spectra of alanine, L-methionine and L-tyrosine are reported in inset in Fig. 3a) [13,39–41]. The EACF peaks were also confirmed by spiking the mixture with a triple amount of *n*-alkanoic and benzene carboxylic acids: the EACF plots computed on the spiked sample chromatograms (Fig. 3b, upper traces) show that the interdistance values coincide exactly and reveal an

increase of peak height, compared to the original mixture. The presence of diagnostic peaks can easily be singled out on the basis of a GC-FID chromatogram, despite the complexity of the chromatogram and the presence of interfering compounds. It must be underlined that the identification of *n*-alkanoic and benzenecarboxylic acids can be obtained by this study, but the structure elucidation of each peak present in the chromatogram is far to be achieved.

The described procedure was also tested on soil samples spiked with carboxylic acids: the aim of the study was to check the reliability of the method in presence of complex interfering compounds, such as organic matter usually present in soil (i.e., saturated and unsaturated hydrocarbons, oxygenated compounds, nitriles, amines, *N*- and *O*-heterocycles) [42]. Samples were prepared by adding given amounts of carboxylic acids to a representative soil (Fontainebleau sand). This sand is relatively free of organic contamination and was washed with concentrated sulphuric acid prior to use. The soil was extracted according to the procedure reported in [13] to yield a quantitative extraction of amino and carboxylic acids from soil under water free conditions. A soil sample was spiked with a mixture of *n*-alkanoic and benzene carboxylic acids (18 compounds): after the extraction and derivatization procedures, the sample was submitted to GC analysis (chromatogram in the inset in Fig. 4). Twenty peaks can be detected in the chromatogram and the EACF procedure estimates 30 components: it is clear that interfering compounds are co-extracted from the soil and by-products are obtained by the derivatization procedure. Despite such interference, the peaks diagnostic of *n*-alkanoic and benzene carboxylic acids can be simply identified in the EACF plot (Fig. 4): peaks at 3, 6, 9 min reveal the presence of *n*-alkanoic acids, the peak at 4 min reveals benzenecarboxylic acids and those at 1 and 7 min correspond to the simultaneous presence of both classes. Such results are confirmed by chemical identification of peaks on the basis of their retention times and MS spectra from GC–MS analysis.

Some samples were also obtained by adding to the reference soil a standard mixture containing only even terms of the *n*-alkanoic acids, i.e., C10–C14 or C16–C20 terms.

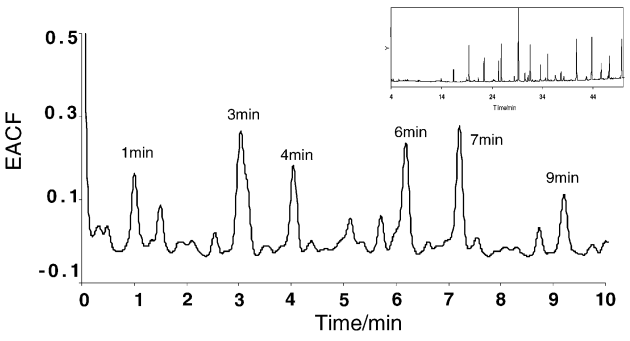

Fig. 4. EACF plot computed on the chromatogram of a soil spiked with a mixture of *n*-alkanoic and benzene carboxylic acids. Inset: Chromatogram of the spiked soil.

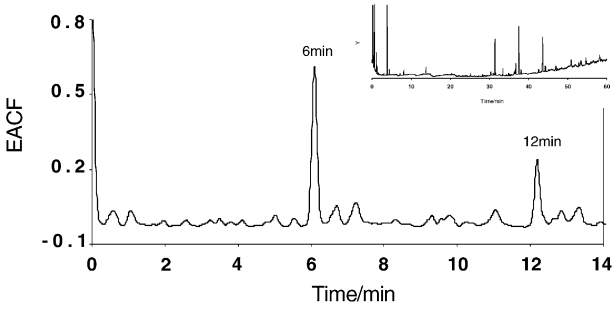

Fig. 5. EACF plot computed on the chromatogram of a soil spiked with a mixture of odd terms (C16–C20) of *n*-alkanoic carboxylic acids. Inset: Chromatogram of the spiked soil.

Molecular distributions displaying a marked odd-over-even or even-over-odd dominancy are characteristic indicators of the action of living organisms, since they are the result of the acetate pathway almost universally followed in synthesizing straight-chain carbon compounds [5,6,9]. Alkanoic acids are typically synthesized by almost all organisms from C2 units as a homologous series reaching C30 with a marked dominance of even-over-odd carbon numbers.

When the standard soil is spiked with a mixture of C16–C20 *n*-alkanoic acids, the EACF plot computed on the obtained chromatogram (Fig. 5) clearly shows peaks only at 6 and 12 min: these peaks correspond to retention increments for the addition of two CH_2 groups in *n*-alkanoic acids, i.e., only the biosynthetic odd-even terms of the series are present in the sample.

5. Conclusions

The EACF chemometric procedure proves to be a helpful method to efficiently extract the largest amount of useful information from the raw chromatogram using a simple data processing: this result is particularly relevant for interpreting chromatograms recovered from space missions.

Information on the presence of specific chemical classes of compounds in the sample can be obtained by handling the simple FID signal, without any data acquisition on MS spectra: in contrast with the original chromatogram which is very crowded with peaks, the ACVF plot retains all the information on the nature and relative abundance of the compounds present in the mixture in a much simpler plot. The application of the EACF method to the FID signal, even if it does not allow a chemical identification of all the mixture components, is particularly powerful in identifying the presence of an ordered distribution of terms of a homologous series. This is particularly relevant for exo/astrobiology since it can be considered a biochemical signature of extinct and/or extant life in extraterrestrial environments. It is clear that the reliability of the method is closely dependent on the accuracy of the previous steps of the analytical procedure, i.e., extraction and derivatization of the analytes.

The procedure can be extended to identify chemical structures of different compounds present in complex samples: it will be available for future, more refined searching processes devoted to specific topics, i.e., nucleic acids, peptides, role of chirality, effect of photosynthesis.

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