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► To cite this version:

Jérémy Jacob, Frédéric Delarue, Yoann Copard, Claude Le Milbeau, Laurent Grasset, et al.. Comparison between Rock-Eval® and temperature-programmed pyrolysis/mass spectrometry for the analysis of environmental and geological samples. *Journal of Analytical and Applied Pyrolysis*, 2023, pp.106078. 10.1016/j.jaap.2023.106078 . insu-04154836

HAL Id: insu-04154836

<https://insu.hal.science/insu-04154836v1>

Submitted on 7 Jul 2023

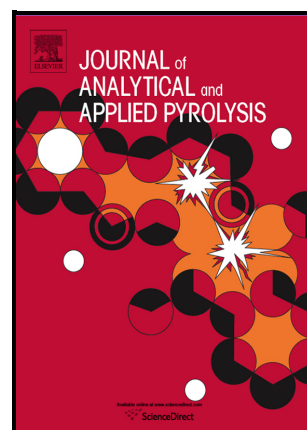
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Journal Pre-proof

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PII: S0165-2370(23)00222-X

DOI: <https://doi.org/10.1016/j.jaap.2023.106078>

Reference: JAAP106078

To appear in: *Journal of Analytical and Applied Pyrolysis*

Received date: 6 February 2023

Revised date: 1 July 2023

Accepted date: 4 July 2023

Please cite this article as: Jérémy Jacob, Frédéric Delarue, Yoann Copard, Claude Le Milbeau, Laurent Grasset and Patrick Brockmann, Comparison between Rock-Eval® and temperature-programmed pyrolysis/mass spectrometry for the analysis of environmental and geological samples, *Journal of Analytical and Applied Pyrolysis*, (2023) doi:<https://doi.org/10.1016/j.jaap.2023.106078>

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**Comparison between Rock-Eval® and temperature-programmed pyrolysis/mass spectrometry for
the analysis of environmental and geological samples**

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Abstract

Natural organic matter (OM) has a complex structure whose complete structural and chemical description remains a challenge. Rock-Eval® device constitutes a rapid and affordable method for obtaining key quantitative and qualitative parameters on OM. Previous studies on soil samples

proposed to deconvolute or to split into temperature slices Rock-Eval[®] S2 pyrograms in order to distinguish and quantify chemical fractions of increasing thermal lability. In order to provide support for such an assumption, this work proposes a methodological approach based on coupling a temperature-programmed pyrolyser to a standard mass spectrometer (Py-MS). In this manuscript, we compare results acquired by Rock-Eval[®] pyrolysis with those from Total Ion Current (TIC) traces obtained by Py-MS on a set of reference soil samples, completed by dissolved OM, source rock and coal samples, in order to test the extent to which this approach can be generalized. Our results show good quantitative and qualitative agreements between the two methods. This comparison is a prerequisite before going further and addressing the molecular significance of S2 pyrograms deconvolution through the examination of m/z fragments abundance curves.

Keywords:

Rock-Eval[®] pyrolysis, S2 deconvolution, organic matter, soil, environmental matrices, Py-MS

1. Introduction

First developed for oil and gas exploration [1-3], Rock-Eval[®] pyrolysis is a standardized method providing information about the amount and quality of organic matter (OM) in source and reservoir rocks. The version of Rock-Eval[®] released in 1996 (Rock-Eval Turbo 6[®]; RE6) allows a more accurate determination of the temperature of maximum release of organic compounds during the pyrolysis phase (TpS2, [4, 5]). The basic principle of this method is that a sample is subjected to increasing temperatures in a first oven under a stream of inert gas (pyrolysis) and then to phase of increasing temperatures in a second oven under oxidizing conditions (combustion). Organic compounds, CO and CO₂ released during the pyrolysis phase and CO and CO₂ released during the combustion phase are quantified continuously with a Flame Ionization Detector (FID) and with infrared cells (Fig. 1a). This results in five curves depicting the evolution of (1) organic compounds (S1 = vaporized compounds and

S2 = compounds released after the cracking of macromolecular structures); (2) CO (S3CO) and (3) CO₂ (S3) during pyrolysis (Fig. 1b) and (4) CO (S4CO) and (5) CO₂ (S4CO₂) during combustion, released over the time of analysis/temperature experienced by the sample). Integration of these curves over selected temperature ranges provides various indexes such as the Total Organic Carbon (TOC, wt.%), the Hydrogen Index (HI, mgHC/gTOC), the Oxygen Index (OI, mgCO₂/gTOC or OI RE6, mgO₂/gTOC), as well as the temperature of maximum release of organic compounds during S2 evolution (T_{max} or T_{pS2} in °C corresponding to T_{max} + ~41°C, to comply with previous versions of Rock-Eval® where the temperature sensor was more distant to the sample compared to RE6). Many studies on recent sediments for environmental and palaeoenvironmental purposes during the last 30 years have used these standard parameters [6-18].

During the last decade, there has been increasing interest in exploring the potential of Rock-Eval® pyrolysis for soil OM dynamics [19, 20] or fingerprinting [16] concerns, either through standard parameters, or by the development of a new index [17, 21-27]. These studies often relied on the analysis of large sets of samples in order to obtain statistics to interpret the significance of standard or underused Rock-Eval® parameters by comparison with data acquired with other techniques (Infra-Red and Near-Infra-Red Spectroscopy, elemental analysis, TG-DSC, NEXAFS, CPMAS ¹³C NMR...).

The idea that the shape of the S2 pyrogram could provide pertinent information dates back to the eighties when authors proposed several shape indices derived from the S2 peak [2, 3, 6, 28]. This echoes the initial paradigm relating the increase in T_{max} values to the increased maturity experienced by petroleum source rocks interpreted as the sequential cracking of OM of increasing thermal maturity. For environmental samples (soils, sediments, peats, etc.), it has also been noted that varying T_{max} values correspond to the cracking of organic components of varying thermal stability [6]. From these considerations, several authors proposed to mathematically deconvolute multi-lobed S2 pyrolysis curves [16, 19, 20, 29, 30]. This was the rationale for proposing several indicators depicting the fate of OM in the environment. As an illustration, R400 and R330 ratios determine the contribution

of pyrolysates released from biopolymers (<400 °C) and those released from the most thermolabile OM (<330 °C) such as polysaccharides [17, 29], to the S2 signal.

Here we compare Rock-Eval® S2 pyrograms to those obtained by pyrolysis mass spectrometry (Py-MS) on a set of standard soil and geological samples. Py-MS is a type of Evolved Gas Analysis that was largely employed in the 90s for the molecular analysis of soil, dissolved and particulate marine and estuarine OM, dissolved aquatic humic substances, plants [31-46]. We used a temperature programmable pyrolyser connected to a standard single quadrupole mass spectrometer. This method is postulated to be a relevant means of obtaining molecular information in conditions comparable to those of RE6 pyrolysis. In this manuscript, the evolution of the Total Ion Current (TIC) with time/temperature is compared to S2 curves obtained by Rock-Eval® pyrolysis in terms of curve morphology, differences in temperature of maximum release, quantitative relationships and deconvolution. This step is a prerequisite before detailing the evolution of m/z abundance against temperature of pyrolysis in order to better understand the molecular significance of the Rock-Eval® S2 signal.

2. Materials and methods

2.1. Samples

The set of samples was primarily constituted by soil samples in order to compare the obtained results to those acquired by deconvolution or splitting into slices of the S2 signal, a method that has been, up to now, mostly applied to soil samples. Additional samples of global interest to the organic geochemistry community (peat, source rocks, coal and dissolved OM; Table 1) which display significant differences in RE6 parameters (TOC, HI, OI, Tmax) and in the shape of the S2 signal due to distinct sources, diagenesis and maturity, were added to the set of samples. This allows examining the extent to which the results obtained on environmental samples can be generalised to other types of samples. In addition, fossil OM can constitute a significant contribution to soil OM. The sample set is constituted

by a series of international standards that are well referenced [47-53]. "Elliott", "Vertisol" and "Chernozem" are soil samples provided by the International Humic Substances Society (IHSS), the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and Köln University, and CSIRO, respectively. Vertisol is a clay-rich soil. Chernozem is a sand-rich haplic soil (19% clay, 53% fine sand) from Northern Germany sampled at 20-60 cm depth, with a significant contribution of charred organic carbon (50% [49, 54]). "Elliott" is a silt loamy soil. "Pahokee" is a peaty soil from Florida (USA). "Suwannee" is dissolved OM (DOM) isolated by reverse osmosis from the Suwannee River (Florida, USA [48]). Both Suwannee and Pahokee are provided by IHSS. "Green" is a rock sample from the Green River Shale formation (Type I OM) provided by the USGS. "160000" is the standard provided by Vinci Technologies to calibrate RE6. "Pocahontas" is a low-volatile and highly aromatic bituminous coal, from Virginia, provided by the Argonne Laboratory [53]. All samples were ground to powder (~200 mesh size) in order to reduce sample heterogeneity.

2.2. Rock-Eval® pyrolysis

In order to compare the morphological features and TpS2 values of the S2 signal obtained during the pyrolysis phase, we analysed samples with the same RE6 temperature pyrolysis program (Bulk Rock/RecentSM program), whatever their nature: isothermal at 200 °C during 5 min, then an increase to 650 °C at 30 °C/min and a final cessation of heating during 3 min down to ~540°C. This corresponds to a pyrolysis time of 23 min. The combustion phase was performed in a second oven with the following temperature program: isothermal at 400 °C during 1 min and then increase to 700 °C at 30 °C/min, hold 5 min. Samples were analysed at least twice. The 160000 standard was analysed with a distinct temperature pyrolysis program since it is also used to calibrate the RE6 apparatus (Bulk Rock/Calib program): isothermal at 300 °C during 3 min, then an increase to 650 °C at 25 °C/min and a final decrease in temperature during 3 min. This corresponds to a pyrolysis time of 20 min. The combustion phase was conducted in a second oven with the following temperature program: isothermal at 400 °C during 1 min and then increase to 850 °C at 20 °C/min, hold 5 min.

2.3. Pyrolysis-mass spectrometry

A Pyroprobe 5150 (CDS Analytical Inc.) pyrolyser was interfaced to a Trace1310 GC gas chromatograph (ThermoScientific) coupled to a single quadrupole ISQ7000 mass spectrometer (ThermoScientific). The Pyroprobe was operated under a constant flow of helium (1 mL/min) with the interface, transfer line and valve oven set at 300 °C during the analysis. Dried, crushed and homogenised samples were inserted in quartz tubes (CDS Analytical Inc.) between two plugs of glass wool. The temperature program set for the coil was similar to that of Rock-Eval® pyrolysis: 200 °C held for 5 min then an increase to 650 °C at 30 °C/min, except that this temperature was held 10 min. The Pyroprobe was interfaced to the Trace1310 GC through a split-splitless injector that was operated in splitless mode during 1 min and held at 300 °C, with a purge flow at 5 mL/min. The GC oven was set at 300 °C during the analysis (30 min) with a constant flow (1 mL/min), a split flow at 20 mL/min and a gas saver flow at 20 mL/min (after 2 min). The injector was directly connected to the transfer line (set at 300 °C) through a deactivated capillary column (id 0.1 mm, 60 cm length). Hence, the gas chromatograph only acted as an oven, allowing the additional transfer line constituted by the capillary column to remain at 300 °C. The mass spectrometer was operated in the electron ionisation (EI) mode at 70 eV and scanned from m/z 50 (to avoid interferences from light gases such as CO, N₂ and CO₂) to 450. The ion source was set at 240 °C. The analysis started after 3 min. Samples were analysed at least three times.

2.4. Data management

RE6 parameters and S2 curves were automatically recovered from RE6 results files (with the .R00 extension for method description and calculated parameters such as TOC, HI, OI and Tmax and the .S00 extension for S2, S3, S4... curves), and normalised to the sample weight with an in-house Excel Visual Basic macro. S2 pyrograms acquired by RE6 pyrolysis were recovered from the .S00 files and then copied into PeakFit© software (v4.06, AISN Software) for mathematical deconvolution into

Gaussian curves. TIC curves obtained by Py-MS were recovered by using "export to clipboard" function from the Chromatogram cell in QualBrowser/Xcalibur (ThermoElectron) and then pasting the copied data into an Excel sheet. The obtained TIC curves were then deconvoluted as for the S2 curves. Time of analysis was converted into temperature by using the temperature program equation over the temperature ramp (200 to 650 °C at 30 °C/min).

In the following, we will only use T_{max} values obtained by Rock-Eval pyrolysis for comparison purposes with previous literature. We will use T_{pS2} as the temperature effectively determined at the maximum of the S2 peak. T_{peak} values stand for the temperature determined either at the maximum of the Total Ion Current (TIC) curves acquired during programmed pyrolysis or at the maximum of the Gaussian curves resulting from mathematical deconvolution of S2 or TIC curves. T_{pS2} and T_{peak} values are hence directly comparable.

2.5. Potential caveats

74 analyses corresponding to 450 mg of sample and 32 mg of organic carbon were run in this study. No decrease was observed in the performance of the mass spectrometer. An initial point of concern was the short lifetime of the mass spectrometer filament that was finally not observed. For high amounts of samples (23 mg of 160000, not taken into account here) or for organic-rich samples (4 mg of Pocahontas and 3 mg of Green), saturation effects that may have affected the TIC curves were observed. In the operating conditions, the maximum amount of organic carbon in the samples to be analysed should be less than 1 mg, and optimally around 0.5 mg. Obviously, the quantitative relationships established here between the mass spectrometer response and RE6 parameters are strongly dependent upon the type of mass spectrometer, settings and performances. In the course of this study, a distinct quantitative response was observed after baking the mass spectrometer (ion source at 280 °C overnight compared to 240 °C in operation), and of course, notable differences after tuning the mass spectrometer. This study focuses on standards that had undergone homogenisation

procedures. Considering the low amount of material necessary for analysis, particular caution should be paid to sample homogeneity.

3. Results

3.1. Rock-Eval[®] pyrolysis

The mean and standard deviation of the main parameters calculated by RE6 on the set of samples are displayed in Table 2. TOC values ranged from low values (2-3 wt.%) in Elliott, Chernozem and Vertisol soils and in the 160000 standard up to 38 wt.% in Pahokee, 40 wt.% in Suwannee, and 51 wt.% in Pocahontas. TpS2 values ranged from 441 to 537 °C, which corresponds to Tmax values from 399 to 495 °C. HI values ranged from 74 to 872 mgHC/gTOC and OI values ranged from 10 to 299 mgCO₂/gTOC. Significant differences between our results and those from the literature are found for Pocahontas. From the H/C ratios published in the literature [53] one would expect IH values around 50 mgHC/gTOC instead of 280 mgHC/gTOC. This is due to the temperature program used (RecentSM) that underestimates TOC and hence artificially increases HI values. By using the "Pure Organic Matter Cycle", as advised in [5], TOC (88 wt.%) and HI (116 mgHC/gTOC) values of Pocahontas were in better agreement with the literature.

Fig. 2 represents S2 curves obtained for selected replicates of Elliott and Green standard samples. Curves for all samples are available in Fig. S1. Green S2 curves are characterized by a rather narrow peak shape whereas the S2 curves of Elliott samples, which exhibit lower TpS2 values, appear more complex with at least one shoulder.

3.2. Py-MS

3.2.1. Total Ion Current

Total Ion Current (TIC) signals obtained along the time of analysis are illustrated in Fig. 2 for Elliott and Green, and Fig. S1 for all standard samples. The signals can be interpreted as traces of the abundance of m/z fragments derived from compounds released by pyrolysis with increasing temperatures. As observed for the S2 signals, the peaks of TIC curves appear narrower and at higher temperatures for samples 160000, Green and Pocahontas compared to other samples (Fig. S1). At first glance, TIC curve shapes resemble those of S2 signals in each standard sample (Fig. 2; S1), with a slight shift in time (and hence temperature) of maximum organic compounds (for RE6) and fragments (for Py-MS) production observed for all samples. The temperatures corresponding to the peak of S2 (TpS2) and TIC (Tpeak Py-MS) curves are reported in Table 3.

Peak intensity of TIC from Py-MS increases with sample amount, as exemplified in the Elliott and Green standard samples (Fig. 2). The maximum intensity of the TIC curve (MaxInt) as well as the TIC peak area are reported together with sample weight and orgC (calculated from sample weight and TOC value) in Table S1 for the different replicate analyses of the eight standard samples.

3.3. Deconvolutions

Except for two standard samples (160000: 1 Gaussian curve and Vertisol: 3 Gaussian curves), mathematical deconvolution of S2 curves and TIC signal was best achieved by using 4 Gaussian curves (illustrated for Elliott and Green in Fig. 3). The Tpeak and % area values of deconvoluted fraction together with the r^2 of their sum compared to the original curve are provided in Table 4 for all standard samples.

4. Discussion

4.1. Nature of the standard samples

The set of standard samples affords a wide variety of TOC values, ranging from 2 to 51% (Table 2). Soil samples (Chernozem, Elliott and Vertisol) show the lowest TOC values whereas DOM (Suwannee),

peaty soil (Pahokee), low-volatile bituminous coal (Pocahontas) and Green exhibit a high C content. When plotted in a pseudo-van Krevelen diagram ([1, 55]; Fig. 4), standard samples can be separated into two populations: Green and 160000 are characterized by high HI values and low OI values. They are typical of Type I lacustrine-derived OM [56]. Conversely, Pahokee, Chernozem, Elliott, Vertisol and Suwannee are characterized by high OI values and low HI values and are considered as Type III terrestrial OM. Most standards display Tmax values lower than 435 °C, and should thus be considered as immature, except Green (449 °C) and Pocahontas (495 °C). All these results are in agreement with previous works [57- 59].

4.2. Reproducibility of Py-MS analyses

The response of the Py-MS signal remains rather stable in the course of the analyses. As illustrated in Fig. 2, for a given standard sample, the TIC signal appears remarkably reproducible when comparable amounts are analysed. For example, TIC curves obtained for Elliott with 23.10 and 21.35 mg on the one hand and with 16.7 and 14 mg on the other hand overlap in Fig. 2. The addition of a mass spectrometer to monitor the amount of fragments derived from pyrolysis does not appear to introduce additional biases in quantitation. Nevertheless, some minor differences can be observed in TIC traces of a single standard sample. For example, the TIC peak of the Green-3.28 mg sample displays a shoulder at higher temperatures that is not observed for lower amounts of Green samples. Slight differences in Py-MS response could be linked to possible sample heterogeneity.

4.3. Time and temperature lags between RE6 and Py-MS

Comparison of S2 curves with the evolution of TIC intensities showed a systematic delay in the maximum production of organic compounds or in fragment abundance (Fig. 2). This delay is partly due to the larger transit time from the pyrolysis tube to the mass spectrometer in Py-MS than from the

crucible to the FID in RE6. In addition, a yet unidentified temperature-related process may be invoked considering the lower $T_{\text{peak Py-MS}} / T_{\text{pS2}}$ difference observed for mature samples than for less mature samples (Table 3). Since $T_{\text{peak Py-MS}}$ was calculated from the time at which the maximum TIC signal was reached, it did not represent the temperature effectively experienced by the sample, contrary to T_{pS2} in RE6. This time lag was responsible for the difference in T_{pS2} and $T_{\text{peak Py-MS}}$ reported in Table 3. The average difference between $T_{\text{peak Py-MS}}$ and T_{pS2} is 26.8 ± 6.9 °C and there was a rather good agreement between the two temperatures over the set of standard samples ($r^2=0.94$; Fig. 5). In order to compare $T_{\text{peak Py-MS}}$ with T_{pS2} more directly in the following, $T_{\text{peak Py-MS}}$ was converted to a T_{pS2} equivalent using the following equation:

$$T_{\text{peak}_{\text{conv}}} = (T_{\text{peak Py-MS}} - 114.69)/0.8134$$

The correlation ($r^2=0.91$) was strongly impacted by the high temperature point (Pocahontas). Nevertheless, the correlation was still significant without this point ($r^2=0.75$). All T_{peak} values defined at the peak of individual m/z emission curves were converted into $T_{\text{peak}_{\text{conv}}}$ values with the same equation.

4.4. Quantitative response of Py-MS compared to RE6 pyrolysis

In order to evaluate the response of Py-MS to sample and carbon amount, each sample was analysed with varying weights. Results are given in Table S1 and in Fig. 6. In the course of this study, orgC amounts ranged from 11 to 2332 μg (Table S1). Although TIC signals were weak for a low amount of sample (for example, samples Elliott 0.431 mg = 11 μg orgC and Pocahontas 0.222 mg = 98 μg orgC in Table S1 and Fig. S1), they gave sufficient information and allowed surface integration. Conversely, for high amounts of sample and/or of orgC (for example Suwannee 3.2 mg = 1275 μg orgC and Pocahontas 5.3 mg = 2332 μg orgC; Table S1 and Fig. S1), a slight saturation of the detector is suspected. Fig. 6 compares the response of Py-MS to the orgC content of the samples, as determined

by RE6 (orgC amount equals sample weight divided by TOC; Table S1). For this purpose, the intensity at the peak of the signal minus the baseline height was determined. Similar results were obtained when the area of the TIC peak was taken into account.

For each standard sample, good agreement was observed between orgC and the response of Py-MS (i.e. the amount of fragments measured over the TIC peak). R^2 values range from 0.77 to 0.99. Each standard sample set displays distinct slopes for the orgC/Peak intensity relationship (Fig. 6). Type I samples (Green and 160000) show higher peak intensity relative to orgC compared to Type III samples. This distinct response of Py-MS depending on the type of sample can be more readily examined when the slope of the orgC/Peak intensity relationship for each standard sample is compared to its HI values (Table 5 and Fig. 7). The linear relationship between the slope of the orgC/Peak intensity linear regression and HI values ($r^2=0.8775$) suggests that the response of Py-MS to orgC depends on the degree of hydrogenation of OM. Samples displaying high HI values (and low OI values) have the best response by Py-MS. This could be notably due to the range of m/z analysed in the present settings because $m/z < 50$ amu were not taken into account. Therefore, light gases, as well as CO and CO₂ that are expected to be more abundantly released from soil samples (and more generally samples with high OI values) or that originate from carbonates, were not measured.

4.5. Deconvolution of S2 and TIC curves

Although the shape of S2 and TIC curves are considered comparable at first glance, a more robust mean of comparison lies in the confrontation of results from the mathematical deconvolution of both signals. Figure 8a and 8b compares the areas (as a percentage of the total area) and the Tpeak values obtained from the corresponding Gaussian curves of S2 and TIC signals. With some exceptions, the Tpeak values determined at the top of Gaussian curves obtained from the deconvolution of S2 signals are rather well correlated with those of the corresponding curves obtained from the deconvolution of the TIC signal ($r^2=0.8332$; Fig. 8a). Conversely, the agreement is poor when % areas of each Gaussian

curve are compared ($r^2=0.0626$; Fig. 8b). This poor agreement could result from two phenomenon: (1) from our experience (data not shown), several identically valuable (identical r^2 , same Tpeaks) solutions can be obtained by deconvolution of S2 or TIC curves with 4 Gaussian curves. In specific cases, this can lead to very distinct results in % areas and explain the main differences observed in Fig. 8b; (2) distinct response of the Rock-Eval FID and the mass spectrometer to the distinct chemical fractions that are recorded through time/temperature.

Conclusion

In order to unravel the complex chemical structure of environmental and geological natural OM, a simple, rapid and cost effective method based on temperature-resolved pyrolysis directly coupled to a mass spectrometer was used. Despite having been developed in standard conditions and with standard equipment, this approach provides quantitative and qualitative molecular information about environmental and geological OM. The results are quantitatively comparable to those obtained by Rock-Eval® pyrolysis, although some discrepancies are noted between the results of mathematical deconvolution of S2 and TIC curves. In order to use this method more routinely, standards should be developed to calibrate the signal and verify performances. These results constitute a prerequisite to discuss the molecular significance of Rock-Eval S2 pyrograms through a detailed examination of m/z abundance curves released by Py-MS.

Acknowledgments

The authors wish to thank David Curry, Thomas Gentzis and Joseph Curiale for their constructive comments on an earlier version of the manuscript and two anonymous reviewers. Rachel Boscardin at ISTO laboratory in Orléans is acknowledged for Rock-Eval® analyses. This work received financial

support from the OTARIE project (Région Centre Val de Loire, European Council through the FEDER fund) and from the Labex VOLTAIRE (ANR-10-LABX-100-01). The authors appreciated interactions with Benoit Auguin (Quad Service, France) from the initiation to the finalization of the project.

J. Jacob, F. Delarue and Y. Copard are indebted to J.R. Disnar for discussions on the scope and limitations of Rock-eval thermal analyses applied on soils, sediments and rocks. . M.F. Dignac and V. Grossi are thanked for their advice during data interpretation. E. Rowley-Jolivet is acknowledged for English language editing of the manuscript.

Tables

Table 1: List of samples analysed in the course of this study. GEOL = rock sample, COAL = coal sample, SOIL = soil sample, PEAT = peat sample and DOM = Dissolved Organic Matter.

Nature	Designation	Sample	Information	Source	Reference
SOIL	IHSS ELLIOT SILT LOAM SOIL - 1BS102M	Elliott	Silt loamy soil, Joliet, Illinois, USA	IHSS	http://humic-substances.org/source-materials-for-ihss-samples/ https://soilseries.sc.egov.usda.gov/OSD_Docs/E/ELLIOTT.html
SOIL	CHERNOZEM	Chernozem	Light sandy clay soil, Hildesheim, Germany	CSIRO (Australia)-U. KOLN (Germany)	[49]
SOIL	VERTISOL	Vertisol	Sandy clay soil, Urrbrae, South Australia	CSIRO (Australia)	[49]
PEAT	PAHOKEE PEAT SOIL - 2BS103P	Pahokee	Agricultural peat soil, Everglades, Florida, USA	IHSS	http://humic-substances.org/source-materials-for-ihss-samples/
DOM	IHSS SUWANNEE RIVER-1R101N	Suwannee	Dissolved OM isolated by reverse osmosis. Suwannee River, Georgia, USA.	IHSS	[48]
GEOL	USGS SGR-1b	Green	Green River Formation (Mahogany zone) Utah, USA	USGS (USA)	[47, 50, 51]
GEOL	IFP160000	160000	Unknown	Vinci Technologies (France)	
COAL	POCAHONTAS COAL	Pocahontas	Pocahontas, Buchanan County, Virginia, USA	ARGONNE LAB (USA)	[52]

Table 2: Main RE6 parameters for the set of eight standard samples.

Sample	n=	TOC (wt.%)	HI (mgHC/gTOC)	OI (mgCO ₂ /gTOC)	Tmax (°C)	TpS2 (°C)
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		Average	Std Dev	Average	Std Dev	Std Dev	Std Dev	Average	Std Dev	Average	Std Dev
Elliott	4	2.47	0.07	135	3	196	6	406	5	448	5
Chernozem	5	1.67	0.04	97	2	205	10	418	5	460	5
Vertisol	5	2.67	0.09	71	3	165	6	426	4	468	4
Pahokee	7	38.13	0.27	193	15	171	8	427	2	469	2
Suwannee	5	39.57	0.34	108	2	296	10	397	3	439	3
Green	5	20.92	1.23	839	26	27	8	446	2	488	2
160000	11	3.3	0.05	381	17	26	2	415	1	459	1
Pocahontas	7	44.37	7.65	287	28	7	3	494	2	536	2

Table 3: Measured TpS2 (by RE6) and Tpeak (by Py-MS) values of the eight standard samples. The values are determined as the temperature of maximum production of organic compounds (TpS2) and as the maximum intensity reached by the Total Ion Current during pyrolysis (Tpeak Py-MS).

Sample	n=	TpS2 (°C)		Tpeak Py-MS (°C)		n=	Tpeak PyMS-TpS2 (°C)
		Average	Std Dev	Average	Std Dev		
Elliott	5	448	5	481	5	16	33
Chernozem	5	460	5	487	1	4	27
Vertisol	5	468	4	488	0	2	20
Pahokee	7	469	2	503	2	10	34
Suwannee	5	439	3	480	3	5	41
Green	5	488	2	504	2	4	16
160000	11	459	1	483	5	4	24
Pocahontas	7	536	2	556	4	3	20

Table 4: Main features of Gaussian curves obtained after deconvolution of S2 pyrograms provided by Rock-Eval® pyrolysis and of TIC signals (m/z 50-650) provided by Py-MS.

Sample	Fraction	Rock-Eval			Py-MS		
		Tpeak (°C)	Area (%)	r^2	Tpeak (°C)	Area (%)	r^2
Elliott	F1	321	13.8	0.998	345	17.8	0.999
	F2	390	34.2		394	7.3	
	F3	469	28.4		448	44.0	
	F4	504	23.6		512	30.9	
Chernozem	F1	342	22.9	0.999	344	10.0	0.998
	F2	415	27.5		415	29.1	
	F3	478	30.8		475	25.0	
	F4	537	18.7		527	35.8	

Vertisol	F1	398	46.6		368	27.2	
	F2	482	28.7	0.999	459	43.8	0.998
	F3	532	24.7		549	29.0	
Pahokee	F1	316	9.5		341	9.3	
	F2	395	43	0.999	405	24.7	0.997
	F3	478	42.1		478	41.7	
Suwannee	F4	571	5.4		544	24.3	
	F1	278	10		344	12.8	
	F2	376	37.5	0.999	416	33.2	0.999
Green	F3	462	29		484	34.1	
	F4	537	23.5		563	19.9	
	F1	319	3.7		434	32.3	
160000	F2	435	31.4	0.999	455	25.2	0.995
	F3	466	33.3		493	33.0	
	F4	500	31.5		584	9.5	
Pocahontas	F1	458		1	468		1
	F1	458	9		408	20.0	
	F2	491	13.3	0.998	514	16.2	0.997
	F3	540	54		541	25.1	
	F4	606	23.7		605	38.7	

Table 5: Values of the slope of the linear regression between orgC and maximum intensity (MaxInt) of the Py-MS signal as determined from Fig. 6 and HI values (Table 2) for the set of samples analysed.

Sample	Slope MaxInt vs orgC	HI (mgHC/gTOC)	
		Average	Std Dev
Elliott	0.0167	135	3
Chernozem	0.0124	97	2
Vertisol	0.0067	71	3
Pahokee	0.0167	193	15
Suwannee	0.0064	108	2
Green	0.0488	839	26
16000	0.0325	381	17
Pocahontas	0.0089	287	28

Figure captions

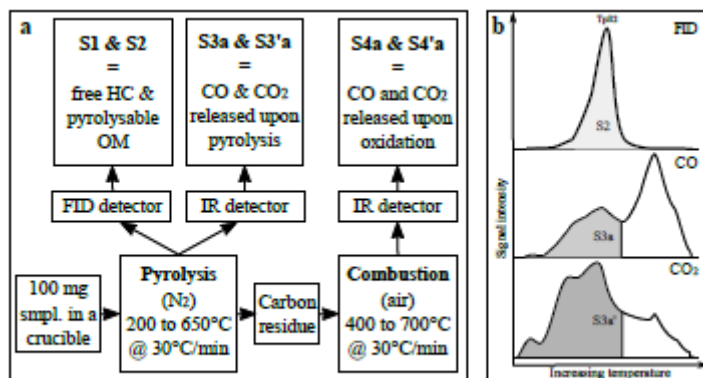


Figure 1: Basic principles of Rock-Eval® analysis and calculation. The sample first experiences temperature-programmed pyrolysis under a stream of N₂ (adapted from [5] and [20]). Carbonaceous compounds (S1 and S2) are quantified with a FID detector, and CO (S3CO) and CO₂ (S3) by infrared (IR) cells. Then, the carbon residue is progressively combusted under air and CO (S4CO) and CO₂ (S4 CO₂) are measured by infrared cells. Examples of curves obtained by FID, and IR cells during pyrolysis. Limits of S3a and S3a' are defined to exclude carbon from carbonates. To be comparable with previous data acquired on older versions of Rock-Eval®, T_{ps2} is corrected into T_{max} using the following equation: T_{max}=T_{ps2}-(TempFID-TempSTD) where TempFID is the temperature experienced in the crucible during 1600000 standard analysis and TempSTD is the T_{max} value of the 1600000 standard. TOC is the sum of carbon derived from Pyrolysable (PC) and Residual (RC) carbon calculated as follows: PC=(S1+S2)*83/1000+(S3CO)*12/280+(S3CO₂)*12/440 and RC=S4CO*12/280+S4CO₂*12/440. Hydrogen Index (HI) is calculated as follows: HI=S2*100/TOC. Oxygen Index (OI) is calculated as follows: OI=S3CO*100/TOC+S3*100/TOC

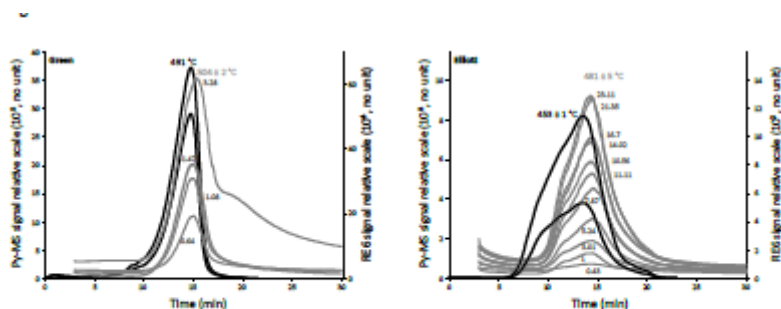


Figure 2: Evolution of FID (Rock-Eval[®], dark lines) and TIC (m/z 50-650) signals (Py-MS, grey lines) with time (min) for selected replicates of Elliott and Green samples. Mean and standard deviation of TpS2 (Rock-Eval[®]) and Tpeak (Py-MS) values are calculated according to Table 3. The weight of standard material used for analysis is indicated.

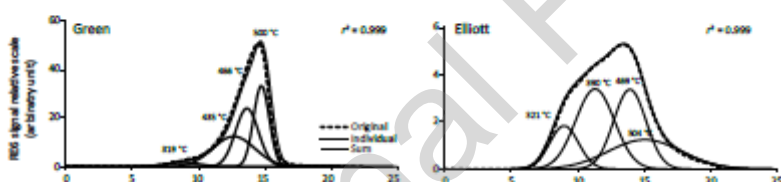


Figure 3: Deconvolution of S2 curves obtained by Rock-Eval[®] pyrolysis of Elliott and Green samples. Deconvolution of S2 curves of other samples are provided in Figure S2. The original S2 curve is indicated by a dotted line, individual Gaussian curves by a light black line and the result of the sum of individual Gaussian curves by a thick black line. The Tpeak values of each individual curve are indicated.

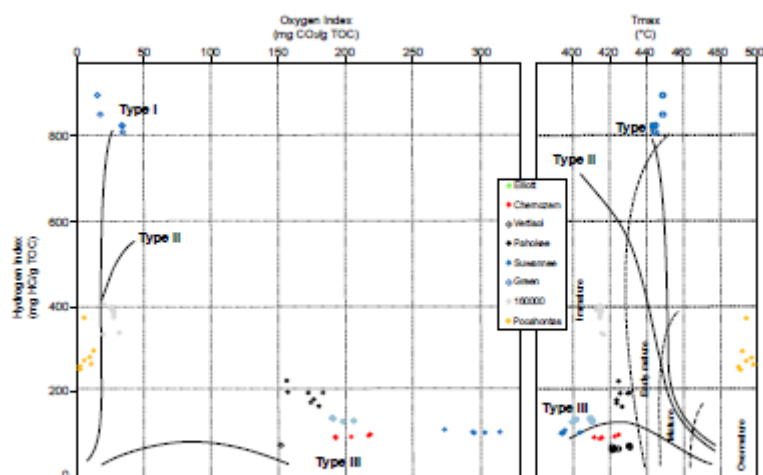


Figure 4: Pseudo-Van Krevelen diagram (Hydrogen Index vs Oxygen Index) and HI vs Tmax diagram for standard samples.

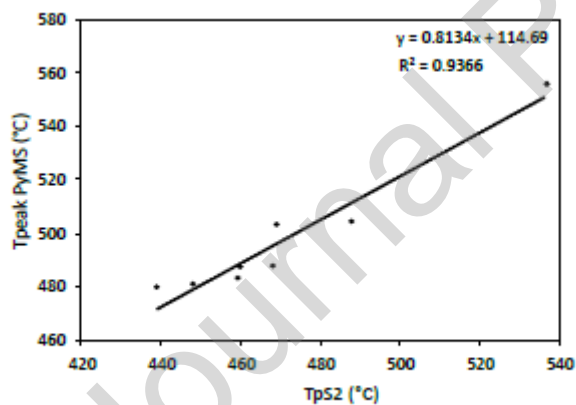


Figure 5: Comparison of Tpeak Py-MS (°C) determined at the maximum of TIC during Py-MS with TpS2 (°C) determined from RE6 (Table 3).

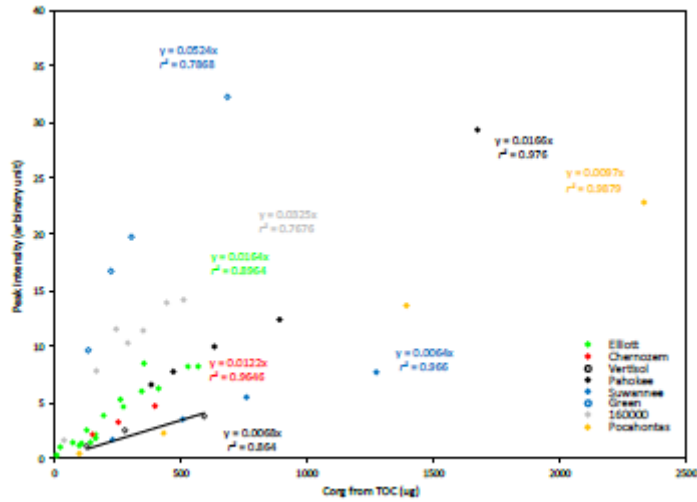


Figure 6: Comparison of the intensity of the TIC signal at maximum (MaxInt) during Py-MS with the amount of orgC in the standard samples as determined from the weight of sample analysed and the TOC determined by RE6.

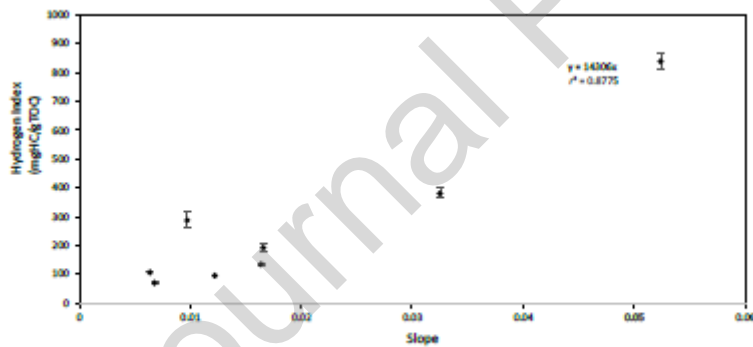


Figure 7: Comparison of HI values with the slope of the linear regression between orgC and maximum intensity (MaxInt) of the Py-MS signal (Table 5).

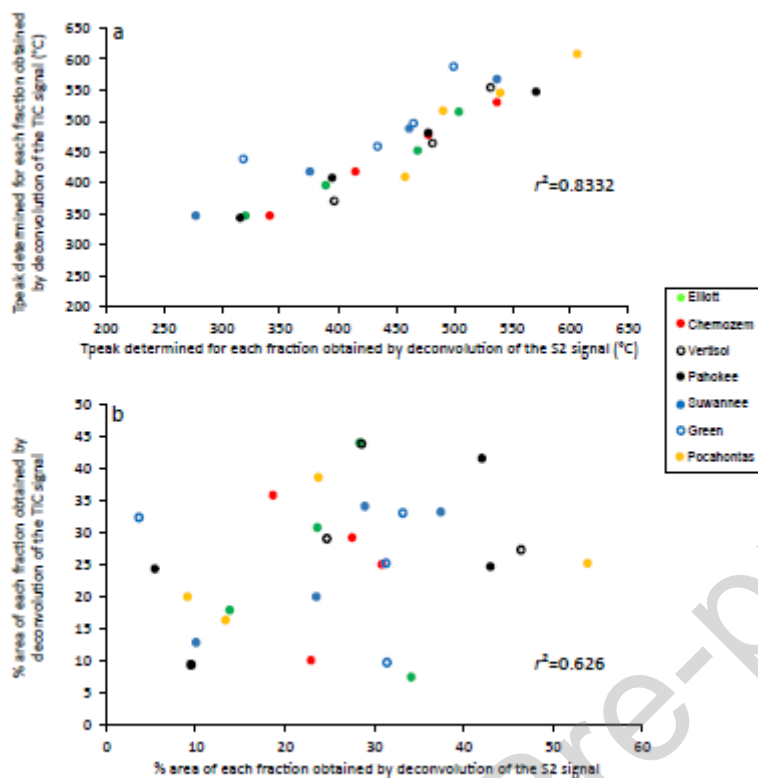


Figure 8: Comparison of Tpeak values (a) and % areas (b) of each pyrolytic fraction obtained after deconvolution of the S2 signal with that (calculated from time of analysis and corrected as described in 4.3.) of the corresponding fraction obtained after deconvolution of the TIC signal. Values are indicated in Table 4.

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CRedit authorship contribution statement

Jérémy Jacob: Conceptualization; Data curation; Formal analysis; Supervision; Writing- Original draft preparation. All authors: Methodology; Validation; Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Jacob reports financial support was provided by French National Research Agency. Jacob reports financial support was provided by European Research Council.

Highlights

- Environmental samples were submitted to both programmed Py-MS and Rock-Eval pyrolysis.
- A difference of temperature of maximum released is noted between the two methods.
- It results from distinct time of transit of pyrolysates to the detector.
- Py-MS results are quantitatively comparable to those of Rock-Eval pyrolysis.
- Py-MS response differs upon the type of organic matter.