



HAL
open science

Rock-Eval 6 Technology: Performances and Developments

F. Behar, V. Beaumont, H. L. de B. Penteadó

► **To cite this version:**

F. Behar, V. Beaumont, H. L. de B. Penteadó. Rock-Eval 6 Technology: Performances and Developments. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2001, 56 (2), pp.111-134. 10.2516/ogst:2001013 . hal-02053894

HAL Id: hal-02053894

<https://ifp.hal.science/hal-02053894v1>

Submitted on 1 Mar 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Rock-Eval 6 Technology: Performances and Developments

F. Behar¹, V. Beaumont¹ and H.L. De B. Penteadó²

1 Institut français du pétrole, Division géologie-géochimie, 1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France

2 Cenpes, Petrobras Research Center, Citade Universitaria, Rio de Janeiro - Brazil

e-mail: francoise.behar@ifp.fr - valerie.beaumont@ifp.fr - hpenteadó@cenpes.petrobras.com.br

Résumé — Technologie Rock-Eval 6 : performances et développements — Le Rock-Eval 6 est la dernière version de la ligne de produits Rock-Eval, commercialisée par *Vinci Technologies* depuis 1996. Le présent article décrit la méthodologie développée à l'*IFP* pour l'obtention de données fiables et atteste la qualité des paramètres géochimiques acquis par le Rock-Eval 6. Les données ont été obtenues sur 147 roches mères provenant de bassins sédimentaires variés et présentant des matières organiques des différents types à différents stades de maturité.

Des corrélations intrinsèques, sur deux appareils Rock-Eval 6 différents, ont été réalisées et les données obtenues démontrent une excellente uniformité pour l'ensemble du jeu de paramètres Rock-Eval.

Le recouvrement complet du carbone total (CT) par le Rock-Eval 6 a été confirmé par comparaison avec l'analyse élémentaire.

Afin de vérifier la répartition du carbone (minéral et organique) réalisée par le Rock-Eval 6, des mesures du carbone minéral (MinC) et du carbone organique total (COT) ont été effectuées par des techniques alternatives.

Le carbone organique total mesuré par le Rock-Eval 6 a été comparé à ceux obtenus par l'appareil Leco pour les roches brutes, par l'analyse élémentaire pour les kérogènes, et par le calcul à partir du bilan de masse effectué après destruction de la matrice minérale et la concentration en carbone mesurée par analyse élémentaire sur les kérogènes ainsi obtenus pour les roches brutes.

Une bonne corrélation est obtenue pour toute la gamme de concentration (0-90 % en poids) lorsque l'on compare le Rock-Eval 6 et l'analyse élémentaire. La comparaison avec le Leco présente de plus importantes déviations, bien que le coefficient de corrélation soit satisfaisant.

Les kérogènes recouverts ont été soumis à l'analyse élémentaire et les quantités de carbone mesurées ont été comparées à celles obtenues par analyse Rock-Eval 6.

Pour un sous-ensemble de kérogènes, des pyrolyses préparatives ont été réalisées afin de confirmer la valeur de 83 % en poids pour le carbone organique contenu dans le pic S2 pour toutes les roches, quel que soit le type de la matière organique, et de vérifier la valeur absolue du pic S2.

Le carbone minéral mesuré par Rock-Eval 6 a été comparé à ceux obtenus par détermination de la perte de poids après traitement HCl, par la technique d'acidimétrie, et par le calcul à partir du TC, le bilan de masse obtenu lors de la préparation du kérogène et la concentration en carbone du kérogène. Une bonne corrélation est obtenue pour toute la gamme de concentration (0-12 % en poids) lors de la comparaison avec l'analyse élémentaire. De plus importantes déviations et un coefficient de corrélation satisfaisant sont obtenus pour la comparaison avec l'acidimétrie. La comparaison avec la détermination de perte de poids est médiocre.

En conclusion, une excellente fiabilité a été démontrée pour le COT et le MinC mesurés par Rock-Eval 6. En conséquence, il est désormais possible d'obtenir un bilan du carbone minéral et organique contenu dans une roche par une mesure unique. Des recommandations sont proposées concernant les échantillons de référence et les méthodes analytiques sélectionnées pour calibrer le Rock-Eval 6 sur une large gamme de carbone organique et minéral.

L'uniformité entre les valeurs de S_2 et de T_{max} mesurées par le Rock-Eval 2 d'une part, et le Rock-Eval 6 d'autre part, pour les roches brutes de type I et de type II a également été vérifiée. Une bonne corrélation a été obtenue pour le S_2 , bien que les valeurs mesurées par le Rock-Eval 2 soient d'une manière générale légèrement supérieures. Il a été démontré que ce point était lié au gaz vecteur (azote et hélium) en réalisant des analyses sous Rock-Eval 6 avec l'hélium comme gaz vecteur. La différence est de 5 à 10 % en poids relatif pour la plupart des échantillons étudiés. La corrélation des T_{max} présente une grande dispersion et en tendance générale, les valeurs de T_{max} obtenues par Rock-Eval 6 sont supérieures à celles obtenues par Rock-Eval 2, la différence augmentant avec la valeur du T_{max} . Ceci est dû au fait que le thermocouple régulant le four du Rock-Eval 2 est placé dans la paroi du four de pyrolyse : en conséquence, la détermination du T_{max} est dépendante du réglage et du calibrage de l'appareil. Une attention spéciale a été portée au contrôle de la température dans le Rock-Eval 6, où le thermocouple est directement placé sous la nacelle contenant l'échantillon, aboutissant à des mesures plus fiables.

Mots-clés : Rock-Eval, pyrolyse, COT, carbone minéral, potentiel pétrolier, caractérisation des kérogènes.

Abstract — Rock-Eval 6 Technology: Performances and Developments — *The Rock-Eval 6 apparatus is the latest version of the Rock-Eval product line, commercialized since 1996 by Vinci Technologies. The present work describes the methodology developed at IFP for reliable data acquisition and endorses the quality of geochemical parameters acquired with Rock-Eval 6. Data were obtained on 147 source rocks from various sedimentary basins, of different organic matter types and maturity stages.*

Intrinsic correlations for two different Rock-Eval 6 apparatus were performed and the obtained data set shows an excellent consistency and good reproducibility conditions for the whole set of Rock-Eval parameters.

Complete recovery of total carbon (TC) by Rock-Eval 6 was confirmed by comparison with elemental analysis.

In order to check the carbon partition (mineral vs. organic) determined by Rock-Eval 6, measurements of mineral carbon (MinC) and total organic carbon (TOC) were performed by alternative techniques.

TOC measured by Rock-Eval 6 was compared to that obtained either by: the Leco apparatus for bulk rocks; elemental analysis for kerogens; and calculation from the mass balance determined after destruction of mineral matrix and the carbon concentration determined by elemental analysis on recovered kerogens for bulk rocks. The results display a good correlation for the whole concentration range (0-90 wt% TOC), when comparing elemental analyses and Rock-Eval 6 for source rocks and kerogens. However, comparison of Rock-Eval 6 with Leco data leads to larger deviations while correlation factors are still good.

For a subset of kerogen samples, preparative pyrolysis was performed in order to confirm the value of 83 wt% for the organic carbon of the total S_2 peak for any rock with any organic type and to check the absolute value of the S_2 peak by gas chromatography analysis of pyrolysis by-product.

MinC measured with Rock-Eval 6 was compared to that determined by: weight loss after HCl treatment; the acidimetry technique; and calculation after TC, mass balance from kerogen isolation and organic carbon measurement on kerogen by elemental analysis. The results display a good correlation for the whole concentration range (0-12 wt% MinC), when comparing elemental analyses and Rock-Eval 6. However, comparison of Rock-Eval 6 with acidimetry data leads to larger deviations while correlation factors are still good while comparison with weight loss is poor.

As a whole an excellent reliability of TOC and MinC obtained by Rock-Eval 6 was demonstrated, and consequently, it is now possible to get at once the total organic and mineral carbon mass balance for a given rock. Recommendations are proposed regarding the standard samples and analytical methods selected for calibrating the Rock-Eval 6 over a large mineral and organic carbon range.

Consistency between S_2 and T_{max} measured by Rock-Eval 2 and Rock-Eval 6 for Types I and II bulk rocks was also checked. A good correlation was obtained for S_2 , even though S_2 values are slightly

higher when measured with Rock-Eval 2. It was demonstrated that this is due to carrier gas (nitrogen vs. helium) by running measurements with a Rock-Eval 6 under helium, the difference ranging from 5 to 10 relative wt% for most studied samples. For Tmax correlation, data are much more scattered and as a general trend Tmax obtained by Rock-Eval 6 are higher than Tmax obtained by Rock-Eval 2 and the difference increases with Tmax: this is due to the fact that the probe measuring the temperature in the Rock-Eval 2 is located in the oven wall, consequently Tmax determination is highly dependent on the setup and calibration of the apparatus. A special attention was given for temperature measurement in the Rock-Eval 6, where the probe is in contact with the crucible containing the sample, leading to much more reliable data.

Keywords: Rock-Eval, pyrolysis, TOC, mineral carbon, oil potential, kerogen typing.

INTRODUCTION

The Rock-Eval pyrolysis method has been extensively used for oil and gas exploration in sedimentary basins over the world. This technique uses temperature programmed heating of a small amount of rock (70 mg) or coal (30-50 mg) in an inert atmosphere (helium or nitrogen) in order to determine the quantity of free hydrocarbons present in the sample (S1 peak) and of those that can be potentially released after maturation (S2 peak). The Tmax value is a standardized parameter, calculated from the temperature at which the S2 peak reaches its maximum: this parameter is used as a maturity parameter for fossil organic matter. These parameters describe the quality of organic matter in the rock sample for exploration purpose. For a more complete diagnosis, total organic content (TOC) has to be determined together with the mineral carbon content (MinC). The latest version of the Rock-Eval product line, i.e. the Rock-Eval 6,

described by Lafargue *et al.* (1998), enables the determination of Rock-Eval parameters plus TOC and MinC as it is equipped with an oven for combustion of the rock residue after pyrolysis, and an infra-red cell ensuring the continuous monitoring of CO and CO₂ released during both pyrolysis and combustion. By studying the specific thermal decomposition of the carbonates during pyrolysis (Lafargue *et al.*, 1998), it is now possible to subtract from the total carbon curves during the pyrolysis and combustion stages, the contribution of the mineral carbon and to get a precise organic carbon profile. An important part of the present paper is dedicated to demonstrate the measurement accuracy for both organic and mineral carbon for a large concentration range (from less than 1 to 90 wt% for the organic carbon and less than 1 to 14 wt% for the mineral carbon) by intrinsic correlation between two Rock-Eval 6 apparatus and comparison with classical techniques (Leco for TOC; weight loss and acidimetry for MinC).

Rock-Eval 6 parameters

Total carbon (TC)	Total organic carbon (TOC) (1)	Mineral carbon (MinC)	Carbon content of the S2 peak	Tmax, S2
Source rocks + coals	i.o.m. + coals decarbonated source rocks	Source rocks	i.o.m. + coals	Source rocks
Elemental analysis (EA) combustion at 1300°C TC = [Σ(CO + CO ₂)] _{EA}	Elemental analysis (EA) combustion at 1000°C TOC = [Σ(CO + CO ₂)] _{EA}	1) Acidimetry 2) Weight loss after decarbonation	Preparative pyrolysis EA on the recovered pyrolysate C _{S2} = C _{gas} + C _{liquid}	Rock-Eval 2
	Source rocks			
	Mineral destruction EA on recovered i.o.m. (C _{i.o.m.}) TOC = [M1 x C _{i.o.m.}]/M2 M1 = i.o.m. mass M2 = initial SR mass			
	Decarbonated source rocks			
	Leco technique			

Figure 1
List of analytical methods selected for verifying the Rock-Eval 6 parameters.

As indicated in Lafargue *et al.* (1998), the pyrolysis furnace of the Rock-Eval 6 is able to reach a final temperature of 800°C instead of 600°C and the carrier gas helium in Rock-Eval 2 was replaced by nitrogen in Rock-Eval 6. Using the same set of rock samples as those used for carbon measurements, excluding coals, Rock-Eval parameters (*S2* and *Tmax*) obtained with Rock-Eval 6 are compared with those obtained with the Rock-Eval 2.

The main objective of this work is to add a metrological dimension to the previous paper presented by Lafargue *et al.* (1998) with:

- recalling of the Rock-Eval 6 method developed at *IFP* for bulk rocks and coals and isolated organic matter (i.o.m.) and description of the Rock-Eval 6 parameters and derived calculations;
- evaluation of the reproducibility of the Rock-Eval 6 parameters;
- verification of the organic carbon in the *S2* peak;
- comparison and validation of the Rock-Eval 6 parameters with those obtained by other techniques: the total carbon content (TC) with elemental analysis; the organic total content (TOC) with elemental analysis and Leco; the MinC with elemental analysis, weight loss estimation after decarbonation and acidimetry technique; and the *S2* and *Tmax* with Rock-Eval 2 apparatus.

The strategy and analytical methods involved in this work are summarized in Figure 1.

1 SAMPLES

We have selected in the *IFP* rock collection 147 source rocks from various basins, representative of the three origin types: their main characteristics are given in Table 1.

TABLE 1

Geographic and kerogen type distribution of the 147 source rocks selected for the study

Country	Number of samples		Type	<i>Tmax</i> range (°C)
	Bulk rocks	i.o.m.		
Brazil	21	5	I	413-440
Brazil	27	26	I	436-448
Brazil	22	20	I	426-449
USA	11	12	I	427-468
West Africa	6	5	I	437-449
Canada	11	11	II	421-489
Germany	6	6	II	433-463
Middle East	8	8	II	414-444
West Africa	8	8	II	424-435
Thailand	14	13	III coal	424-474
USA	13	13	III coal	418-475

The rock selection was based on the availability of both bulk rocks and corresponding kerogens, the variability of the organic carbon content, the carbonate content and the organic matter type and its maturity stage.

Data given in Table 1 show that the samples which fulfill our conditions are biased to Type I organic matter.

2 EXPERIMENTAL

2.1 Rock-Eval 6 *IFP* Methods

A single method was developed in *IFP* in order to run any type of bulk source rock: it is called *Basic Method*. Another method called *Pure Organic Matter Method* was developed for the i.o.m. and coal samples. In this paragraph are given: a detailed description of the Rock-Eval 6 apparatus and of the calculated parameters; the *IFP* method for source rock analysis; the *IFP* method for organic matter analysis; and the Rock-Eval 2 technique.

2.1.1 Description of the Rock-Eval 6 Apparatus

The Rock-Eval method consists in estimating the petroleum potential of sedimentary rocks by heating samples in an open pyrolysis system under non-isothermal conditions. The released hydrocarbons are monitored by a flame ionization detector (FID), forming the so-called peaks *S1* (thermo-vaporized free hydrocarbons) and *S2* (pyrolysis products from cracking of organic matter). The method is completed by combustion (oxidation) of the residual rock recovered after pyrolysis up to 850°C, under artificial air (N₂/O₂; 80/20). During pyrolysis and combustion, released CO and CO₂ are monitored on line by means of an infra-red cell. This complementary data acquisition enables determination of the organic and mineral carbon content of samples, labeled TOC and MinC respectively.

The innovations of the Rock-Eval 6 are:

- micro-ovens heating up to 800°C for pyrolysis and 850°C for combustion with probes in contact with the sample, allowing a better temperature control;
- infra-red cells for on-line continuous recording of CO₂ and CO production during pyrolysis and oxidation;
- an automatic sequenced sampler with a capacity of 48 samples, which allows running 24 hours a day, 7 days a week.

Three of the four commercialized versions are presented in Figure 2. The “classic *S3*” version is not equipped with the additional oven for combustion of the pyrolysis residue. The other two versions are equipped with two ovens (pyrolysis and combustion): the same parameters are measured for both apparatus, but for the “Turbo” apparatus, the pyrolysis (25 min including cooling) and combustion (38 min) steps of two successive samples are run in parallel, thus, the

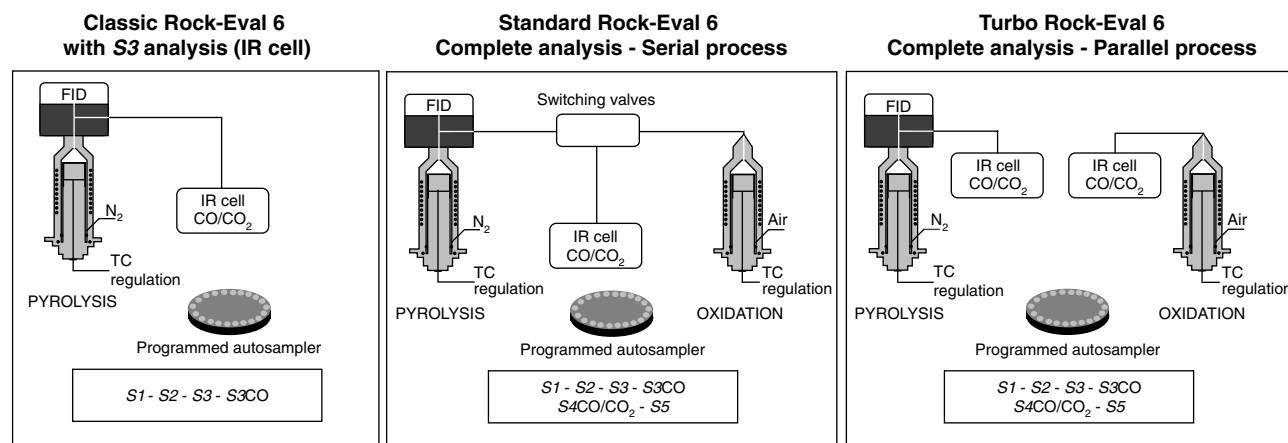


Figure 2

Presentation of the different Rock-Eval 6 versions commercialized by Vinci Technologies.

acquisition time is highly reduced. In fact, except for the first and the last samples of the same series, pyrolysis and combustion steps are run together. Consequently, the first and the last analyses last 63 min whereas the other lasts only 38 min.

Typical sample amount ranges from 50 to 70 mg for bulk rocks, from 10 to 30 mg for coals and from 5 to 15 mg for i.o.m. However, for high petroleum potential kerogens such as those of Type I, the sample amount can be reduced to 1-2 mg.

The initial weight has to be measured with a precision of 0.5 mg for bulk rocks and of 0.02 mg for kerogen and coals in order to obtain reliable Rock-Eval parameters (*i.e.* $S2 \pm 0.5$ mg/g rock, TOC and MinC ± 0.1 wt%).

Two different methods were used for running the bulk source rocks on the one hand and the i.o.m. and/or coals on the other. They are described in Figures 3a and 3b.

2.1.2 IFP Basic Method for Source Rocks

The method used for running bulk source rocks is called *Basic Method* and the corresponding pyrolysis and combustion conditions as well as integration conditions for the determination of the acquisition parameters are summarized in Figure 3a.

Acquisition and calculated parameters are given in Tables 2a and 2b respectively.

During the pyrolysis step, the recorded FID signal that corresponds to the petroleum potential is divided into two surfaces: $S1$ and $S2$, which are expressed in mg HC/g of initial rock. $S1$ corresponds to the quantity of hydrocarbons released during the isothermal temperature step at 300°C and represents the thermovaporized free hydrocarbons contained in the rock. $S2$ corresponds to the quantity of hydrocarbons released between 300° and 650°C and represents the hydrocarbons resulting from the cracking of sedimentary organic

matter. Assuming an average value of 83 wt% for the carbon content of the $S2$ surface whatever the organic matter type (Espitalié *et al.*, 1985a, 1985b, 1985c), it is possible to calculate the corresponding absolute organic carbon content of released hydrocarbons. The same calculation is done for the absolute organic carbon content of the $S1$ surface.

The total CO signal obtained during pyrolysis is split into two surfaces: the first one ($S3CO$) integrates the CO released from the beginning of measurements ($t = 0$, $T = 300^\circ\text{C}$) up to the temperature where a minimum of CO production is observed (between 450° and 600°C). When no minimum is detected, the integration limit is fixed at 550°C as default parameter. The second surface ($S3'CO$) starts at the upper limit defined for the previous surface and ends up at the end of the measurement. The $S3CO$ surface corresponds to the release of functions linked to organic matter and this signal will be integrated into the calculation of TOC. The $S3'CO$ is due to the reactivity of CO_2 released during the thermal decomposition of carbonates on the organic matter according to the so-called *Boudouard reactions*, producing two CO molecules, one with a carbon of organic origin integrated into the calculation of TOC, and the other one with a carbon of mineral origin integrated into the calculation of MinC.

During the oxidation stage, only one CO signal is integrated from beginning to end of the measurement and labeled $S4CO$. All the carbon contained in this CO is of organic origin.

In the same way, the CO_2 yield during the pyrolysis stage is split into $S3$, which corresponds to CO_2 released at the same time as the $S1$ peak added to that obtained between 300° and 400°C with an organic origin, and $S3'$, which is the CO_2 recorded between 400°C and the end of the measurement, with a mineral origin.

During the oxidation stage, the CO_2 production curve exhibits, when the rock contains carbonates, a minimum

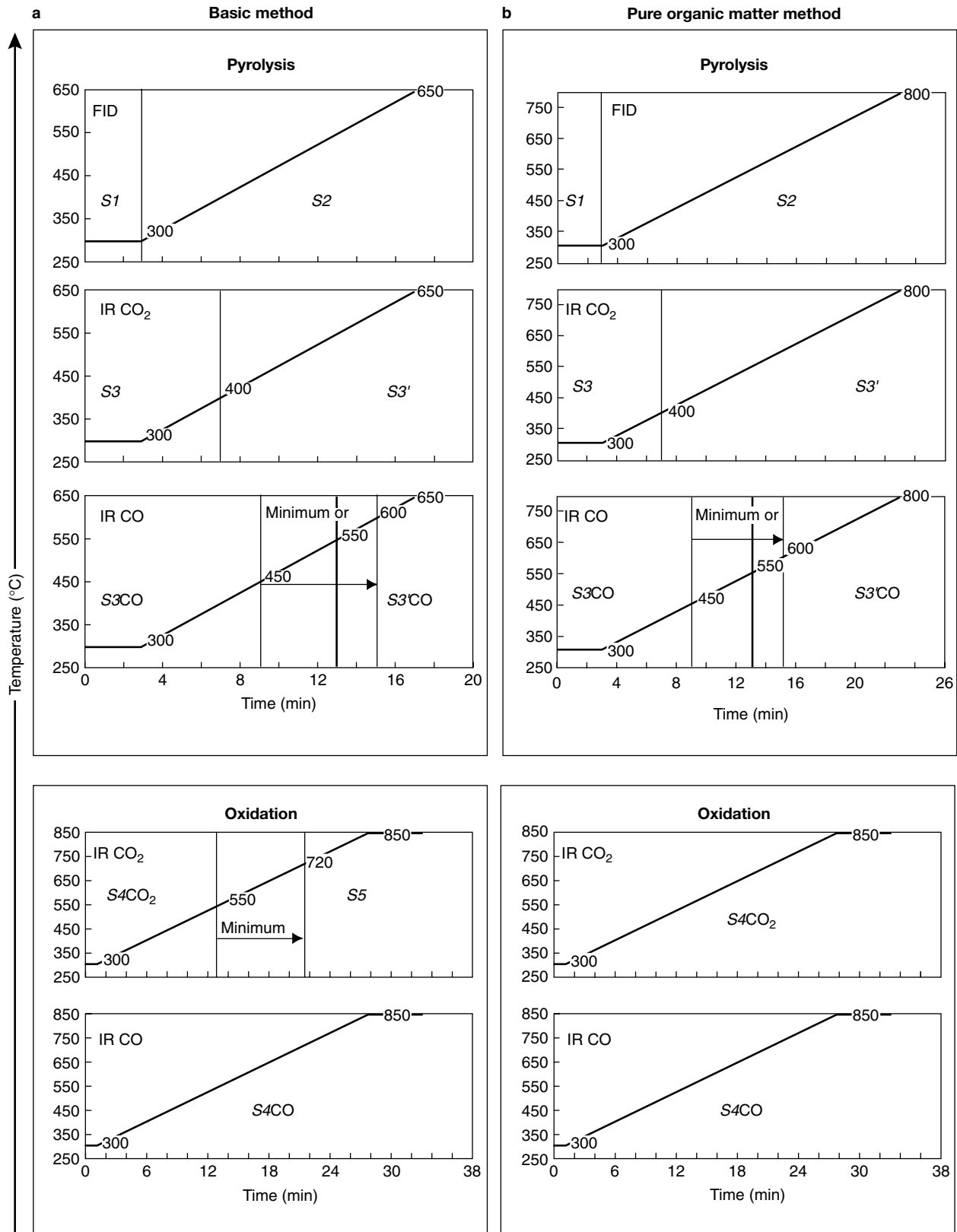


Figure 3

Description of the Rock-Eval 6 methods for source rocks (a) and pure organic matter (b).

TABLE 2a
Acquisition parameters for the Basic Method

Acquisition parameters	Detector/Oven	Unit	Name
<i>S1</i>	FID/Pyrolysis	mg HC/g rock	Free hydrocarbons
<i>S2</i>	FID/Pyrolysis	mg HC/g rock	Oil potential
<i>TpS2</i>	–	°C	Temperature of peak <i>S2</i> maximum
<i>S3</i>	IR/Pyrolysis	mg CO ₂ /g rock	CO ₂ organic source
<i>S3'</i>	IR/Pyrolysis	mg CO ₂ /g rock	CO ₂ mineral source
<i>TpS3'</i>	–	°C	Temperature of peak <i>S3'</i> maximum
<i>S3CO</i>	IR/Pyrolysis	mg CO/g rock	CO ₂ organic source
<i>TpS3CO</i>	–	°C	Temperature of peak <i>S3CO</i> maximum
<i>S3'CO</i>	IR/Pyrolysis	mg CO/g rock	CO organic and mineral source
<i>S4CO₂</i>	IR/Oxidation	mg CO ₂ /g rock	CO ₂ organic source
<i>S5</i>	IR/Oxidation	mg CO ₂ /g rock	CO ₂ mineral source
<i>TpS5</i>	–	°C	Temperature of peak <i>S5</i> maximum
<i>S4CO</i>	IR/Oxidation	mg CO/g rock	CO organic source

TABLE 2b
Calculated parameters for the Basic Method

Calculated parameters	Unit	Formula	Name
<i>Tmax</i>	°C	$TpS2 - \Delta Tmax^*$	<i>Tmax</i>
PI		$\frac{S1}{(S1 + S2)}$	Production index
PC	wt%	$\frac{[(S1 + S2) \times 0,83] + \left[S3 \times \frac{12}{44} \right] + \left[\left(S3CO + \frac{S3'CO}{2} \right) \times \frac{12}{28} \right]}{10}$	Pyrolysable org. carbon
RC CO	wt%	$\frac{S4CO \times \frac{12}{28}}{10}$	Residual org. carbon (CO)
RC CO ₂	wt%	$\frac{S4CO_2 \times \frac{12}{44}}{10}$	Residual org. carbon (CO ₂)
RC	wt%	RC CO + RC CO ₂	Residual org. carbon
TOC	wt%	PC + RC	Total organic carbon
<i>S1</i> /TOC	mg HC/g TOC	$\frac{S1 \times 100}{TOC}$	
HI	mg HC/g TOC	$\frac{S2 \times 100}{TOC}$	Hydrogen index
OI	mg CO ₂ /g TOC	$\frac{S3 \times 100}{TOC}$	Oxygen index
OI CO	mg CO/g TOC	$\frac{S3CO \times 100}{TOC}$	Oxygen index CO
PyroMinC	wt%	$\frac{\left[S3' \times \frac{12}{44} \right] + \left[\left(\frac{S3'CO}{2} \right) \times \frac{12}{28} \right]}{10}$	Pyrolysis mineral carbon
OxiMinC	wt%	$\frac{S5 \times \frac{12}{44}}{10}$	Oxidation mineral carbon
MinC	wt%	PyroMinC + OxiMinC	Mineral carbon

* $\Delta Tmax$ is calculated when calibrating apparatus and results from the difference between *TpS2* of standard 55000 and its accepted *Tmax* (419°C) determined after Rock-Eval 2 measurements. $\Delta Tmax = Tps2_{std\ 55000} - Tmax_{accepted\ 55000}$

between 550° and 720°C. Thus, the $S4CO_2$ corresponds to the amount of CO_2 generated between 300°C and the temperature of the defined minimum (organic origin of carbon) and $S5$ corresponds to the counterpart up to the end of the measurement (mineral origin of carbon).

The calculations of the total organic and mineral carbon content are described in Table 2b and illustrated in Figures 4a and 4b.

The upper temperature of 650°C for pyrolysis of source rocks was chosen in order to obtain a complete $S2$ signal while a minimum of carbonates will decompose during this step. In these conditions, coals, which are generating late methane and contain few carbonates, will be preferentially analyzed under the organic matter method (pyrolysis up to 800°C).

2.1.3 IFP Acquisition Method for Coals and Isolated Organic Matter

As for source rocks, two steps are performed when running the method called *Pure Organic Matter*: pyrolysis and combustion. The final pyrolysis temperature is 800°C instead

of 650°C. Thus, it is not possible to have a direct comparison of the residual organic carbon for the two methods. The same is true for the CO_2 and CO total yields obtained during pyrolysis except for $S3$ and $S3CO$ which are quantified in the same temperature range (Fig. 3b).

Since i.o.m. does not contain minerals anymore, the total integrated signals for the FID, the CO and CO_2 during both the pyrolysis and oxidation stages give directly the value for the TOC as follows:

$$\begin{aligned} \text{TOC (\%)} = & [(0.83 * S1) + (0.83 * S2) \\ & + (12/44 * (S3 + S3' + S4CO_2)) \\ & + (12/28 * (S3CO + S3'CO + S4CO))] / 10 \end{aligned}$$

However, it is still possible to discriminate between the pyrolysable and residual organic carbon (PC and RC, respectively) because two distinct signals are recorded, one during pyrolysis and one during oxidation.

2.1.4 Comparison with Rock-Eval 2 Method

As said in the Introduction, one of the aims of the present study is to compare data acquired with the Rock-Eval 6 and

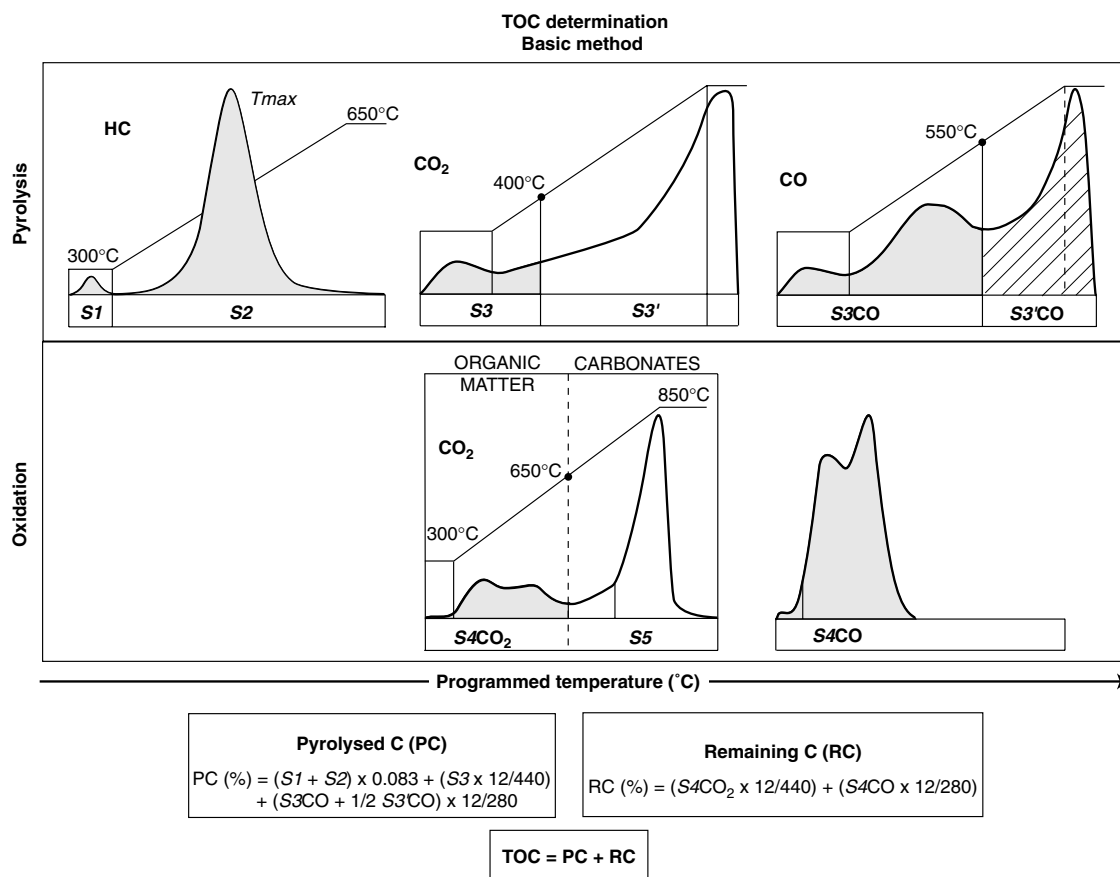


Figure 4a

Analytical procedure for calculating the TOC by Rock-Eval 6.

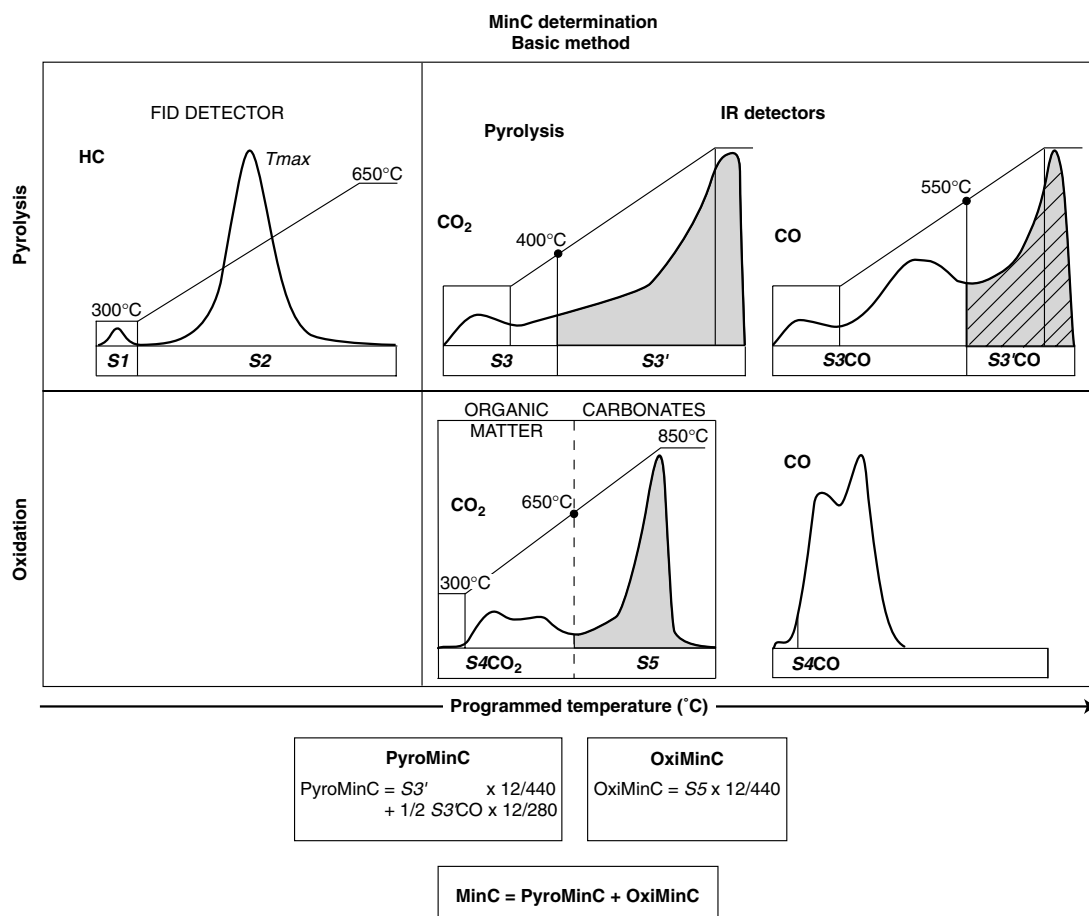


Figure 4b

Analytical procedure for calculating the MinC by Rock-Eval 6.

the previous technology, *i.e.* Rock-Eval 2 (Espitalié *et al.*, 1985a, 1985b, 1985c). The parameters measured in the Rock-Eval 2 are described in Figure 5 and compared to those determined by the Rock-Eval 6.

In the Rock-Eval 2, the probe is not in direct contact with the crucible but inserted in the oven wall. As a consequence, the recorded T_{max} is the oven temperature when the $S2$ peak maximum is reached, which is different from the effective temperature of the sample, and corrections were proposed by Espitalié *et al.* (1985a, 1985b, 1985c). In these conditions, the T_{max} reproducibility is highly dependent on the apparatus setup and calibration. In the Rock-Eval 6 the probe is in direct contact with the crucible, a precise measurement of the sample temperature is obtained when the $S2$ peak maximum is reached (T_{pS2}). The T_{max} is then calculated after T_{pS2} and ΔT_{max} which is the direct comparison of T_{pS2} of standard 55000 determined during calibration and its accepted T_{max} (established after Rock-Eval 2 measurements). The value of T_{pS2} being dependent on the rate of the pyrolysis, the T_{max} value is significant only for pyrolyses run at 25°C per minute.

The $S1$ peak is obtained in the same conditions for Rock-Eval 6 and Rock-Eval 2. However, as temperature is measured in the oven wall, the real sample temperature during this isothermal step is different from 300°C (20°C variations can be observed depending on apparatus setup). As a consequence, the $S1$ measured with Rock-Eval 2 can be different from the $S1$ measured with Rock-Eval 6.

For quantification of the $S2$ surface, pyrolysis is run between 300° and 600°C for Rock-Eval 2 (instead of 650°C for Rock-Eval 6). Thus, when the $S2$ surface is not completed at 600°C , an underestimation of this parameter should be expected (especially for mature Type III organic matter). As a whole, since the temperature measurement is different, comparisons of the $S1$ and $S2$ surfaces between the two apparatus may display inconsistencies. Nevertheless, the total amount $S1 + S2$ may be similar.

The carrier gas for the Rock-Eval 2 is helium and has been replaced by nitrogen in the Rock-Eval 6. In the present study, the influence of the carrier gas was studied with a Rock-Eval 6 run with helium as carrier gas on a reference sample.

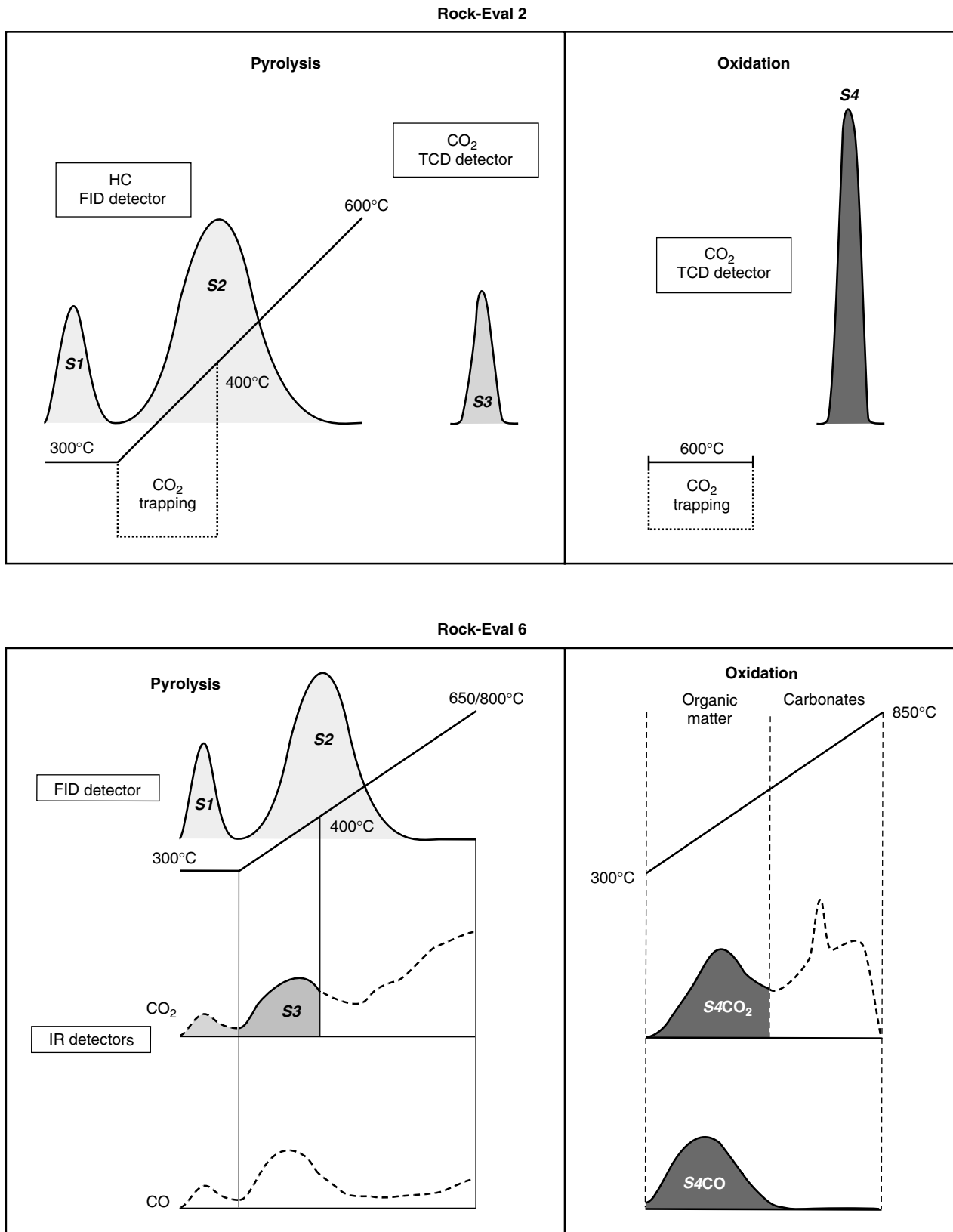


Figure 5

Comparison between Rock-Eval 2 and Rock-Eval 6 pyrolysis conditions.

The Rock-Eval 2 is equipped with a catharometer detector for measurement of CO₂ released during pyrolysis. This gas is not recorded continuously: it is trapped from the beginning of pyrolysis up to 400°C (Fig. 5). Then, it is released and quantified at once. This value can be directly compared to the S3 surface measured by Rock-Eval 6.

The CO curve is not recorded at all, thus preventing any comparison with Rock-Eval 6 for CO data.

With the standard version of the Rock-Eval 2, it is not possible to determine the total organic carbon. However, Rock-Eval 2 can be equipped with a “carbon module” which enables to oxidize the residual rock after pyrolysis. In that case, it is assumed that carbonate decomposition has not yet started at 600°C.

In the present study, the available Rock-Eval 2 was not equipped for TOC measurements. Moreover, analyses were run in the Geochemistry Section in *Petrobras* (Brazil) where only Types I and II samples are usually analyzed. Thus, the two series of coals selected for the present study were not included in these comparisons.

2.2 Verification of the TOC for Bulk Rock, Isolated Organic Matter and S2 Peak

As indicated in the Introduction (Fig. 1), the TOC measured by Rock-Eval 6 was verified through alternative techniques on bulk source rocks and i.o.m. (kerogen). For kerogens, a direct comparison was done between the TOC measured by the Rock-Eval and the carbon content measured as the CO₂ amount recovered after oxidation at 1000°C and quantified by the use of a thermal conductivity detector. For bulk source rock, the TOC can be estimated by combining the TOC measured on the corresponding i.o.m. and the ratio between the initial amount of rock before mineral destruction and that of the i.o.m. after this acidic treatment. The TOC measured by Leco on decarbonated rocks can be also compared to that obtained by Rock-Eval 6. Finally, the TOC content of the S2 peak was determined on kerogen samples of various organic matter types through preparative pyrolysis.

In this section are described the procedure for mineral destruction; the elemental analyses; the Leco apparatus; and the preparative pyrolysis technique for the recovery of the C₆⁺ S2 peak.

2.2.1 Isolated Organic Matter Preparation

The sample amount for each kerogen (i.o.m.) preparation depends on the initial TOC of the bulk rock. For low TOC samples (< 2 wt%), at least 50 g are submitted to acidic treatment whereas less than 10 g are needed for samples with higher TOC. i.o.m. was prepared according to the protocol developed by Durand and Nicaise (1980), *i.e.* by successive acid treatments (HCl and HF) under inert atmosphere (N₂) at

80°C followed by water washings. Special care is given to washings in order to ensure dissolution of newly formed fluorosilicates, and that would interfere with elemental analyses of kerogens. Recovered kerogens are dried at 100°C under nitrogen flow, ground, weighed, and stored. Besides isolated matter, pyrite and heavy metal oxides, if present, are recovered by this procedure and quantified by elemental analyses.

2.2.2 Elemental Analyses

All the elemental analyses were done by an external specialized laboratory.

For i.o.m., the following elements were estimated in wt% of the sample: C, H, N, O, total S and Fe. Ashes (combustion residues) were weighed in order to crosscheck the obtained data. All determinations were doubled or tripled according to preset reproducibility criteria.

C, H and N were determined on one aliquot of the kerogen by use of a thermal conductivity detector on gases resulting from combustion at 1000°C. O is measured on a different aliquot by pyrolyzing the kerogen under nitrogen flow: pyrolysis gases are reduced on carbon into carbon monoxide, which is oxidized in carbon dioxide and finally quantified by coulometry. Total S (including pyritic and organic S) is obtained by oxidation of a third aliquot of kerogen and quantification of sulfur dioxide by coulometry. The determination of Fe is necessary to calculate the amount of pyrite (FeS₂) in the sample and, by mass balance, the mineral and organic sulfur. This analysis is done on a fourth aliquot by mineralization of the sample in a mixture of nitric and sulfuric acids, then quantification of Fe is done by atomic absorption.

In Table 3 are given duplicate data of all measured elements on four aliquots of a kerogen selected in the *IFP* data base together with the standard deviation and relative error (wt%) of the average values. The sum (Σm) of average values is not equal to 100 wt% due to the contribution of elements which were not analyzed but present at very low concentrations. Thus, presented data were not normalized data and the raw carbon determined by elemental analysis can be directly compared to that measured by Rock-Eval 6.

Once the organic carbon content of the i.o.m. is known, it is possible to determine the absolute amount of organic carbon in the source rocks (C₀) before acidic digestion by the following equation:

$$C_0 = (\text{IOM} * C_{\text{i.o.m.}}) / R_0$$

with:

- C₀ calculated organic carbon of the initial source rock
- R₀ initial weight of bulk rock before kerogen isolation
- IOM mass of the i.o.m. and/or pyrite recovered after acidic treatment
- C_{i.o.m.} carbon content of the i.o.m.

TABLE 3

Duplicate elemental analyses on four aliquots of the same kerogen and calculation of the standard deviation and relative error for the average values

	C(a)	C(b)	C(m)	H(a)	H(b)	H(m)	N(a)	N(b)	N(m)	O(a)	O(b)	O(m)	S(a)	S(b)	S(m)	Fe(a)	Fe(b)	Fe(m)	Σm
1	60.75	60.78	60.8	6.26	6.21	6.2	1.51	1.50	1.5	8.28	8.21	8.3	12.65	12.66	12.7	8.10	8.60	8.4	97.8
2	60.66	60.77	60.7	6.32	6.36	6.3	1.53	1.57	1.6	8.53	8.36	8.5	12.56	12.83	12.7	8.40	8.15	8.3	98.0
3	60.18	60.13	60.2	6.36	6.27	6.3	1.49	1.48	1.5	8.52	8.39	8.5	12.18	12.83	12.5	7.80	8.25	8.0	97.0
4	60.52	60.36	60.4	6.30	6.30	6.3	1.58	1.47	1.5	8.87	8.83	8.9	12.44	12.40	12.4	8.50	8.40	8.5	98.0
Std deviation			0.29			0.04			0.03			0.25			0.13			0.20	
Rel. error (%)			0.5			0.7			1.7			3.05			1.0			2.2	

This calculated C_0 can be directly compared to TOC determined either by Leco or Rock-Eval 6 techniques on the bulk rock.

The i.o.m. comprises the insoluble residue, *i.e.* kerogen and free petroleum products, *i.e.* bulk rock extracts. Unfortunately, all available i.o.m. samples were stored after solvent (dichloromethane, DCM) extraction and in most cases, the extract yield is unknown. However, we have corrected the carbon content by taking into account at least the carbon contained in the *SI* peak measured by Rock-Eval 6. Since the weight of this extract is always very small, the correction was very minor except for samples with accumulated petroleum which were systematically excluded for this type of correlation.

Since C_0 is the only parameter which enables to check the TOC value measured by Rock-Eval 6, it was necessary to determine the accuracy of its measurement. For this purpose, a bulk rock available in large amount was selected in the *IFP* data base. Several tests of organic matter isolation for the two sizes of reactor used for kerogen preparation were run. Then, for each aliquot of bulk rock, the insoluble organic matter was weighed and submitted to elemental analyses for triplicate carbon measurements. The resulting average value was used to calculate the C_0 .

Results given in Table 4 show that the i.o.m. recovery does not depend on the initial amount of source rock: the same yield is obtained when 50 or 10 g are treated and the relative error on that estimation is only 1.5%. The accuracy

TABLE 4

Relative error for C_0 estimation

R_0 (g)	i.o.m.		C(a) (%)	C(b) (%)	C(c) (%)	C(m) (%)	C_0 (%)
	(g)	(%)					
50.6100	5.5685	11.0	60.51	61.50	61.22	61.1	6.7
50.2164	5.6473	11.2	61.40	60.34	60.54	60.8	6.8
50.2658	5.3766	10.7	60.66	59.65	60.99	60.4	6.5
10.0789	1.1172	11.1	59.87	60.15	60.77	60.3	6.7
10.0899	1.1283	11.2	61.46	61.36	60.99	61.3	6.9
10.0007	1.1130	11.1	60.83	60.68	60.88	60.8	6.8
10.0012	1.1190	11.2	60.80	61.02	61.32	61.0	6.8
10.0008	1.1188	11.2	60.66	60.77	61.13	60.9	6.8
10.0016	1.1024	11.0	60.18	60.13	59.73	60.0	6.6
10.0008	1.1067	11.1	60.52	60.36	60.61	60.5	6.7
10.0010	1.1146	11.1	60.94	60.78	60.18	60.6	6.8
10.0011	1.1466	11.5	60.35	60.31	59.92	60.2	6.9
10.0036	1.1283	11.3	60.63	60.82	60.12	60.5	6.8
10.0012	1.1173	11.2	59.80	60.01	nd	59.9	6.7
10.0028	1.1001	11.0	60.71	60.54	nd	60.6	6.7
10.0006	1.1242	11.2	59.25	60.87	60.69	60.3	6.8
Average value		11.1	60.5	60.6	60.6	60.6	6.7
Standard deviation		0.2	0.6	0.5	0.5	0.4	0.1
Relative error (%)		1.5	0.9	0.8	0.8	0.6	1.6

of carbon measurement by elemental analysis is excellent since the relative error on triplicate sets is 0.6%. The resulting C_0 calculated value is given with an error of 1.6%.

In conclusion, C_0 is precisely determined and thus can be used as a reliable parameter for checking the TOC measured by Rock-Eval 6.

This calculation was not done for coals in which the MinC was less than 1 wt% because for these samples the TC measured by elemental analysis corresponds to the organic carbon and thus can be directly correlated to the Rock-Eval 6 data. The same is true for kerogens for which the organic carbon measured by elemental analysis was labeled C_k . For these coals and kerogens, besides carbon content measurement, determination of the oxygen content was of special interest when plotting a HI/OI (hydrogen index vs. oxygen index) diagram as a function of the organic matter and maturity stage (Espitalié *et al.*, 1985a, 1985b, 1985c). Unfortunately, the selected kerogens were prepared a long time ago (some weeks to some years ago) and had undergone chemical alteration resulting in a systematic increase of their oxygen content and as a counterpart in the decrease of the carbon percentage. Consequently, kerogens were resubmitted to elemental analyses in parallel with Rock-Eval 6 analysis.

Our experimental correlation could have been done between the new oxygen content and the yield of CO and CO₂ but it would obviously have no geochemical meaning. However, since our kerogens were prepared at various times in the past, it was possible to quantify this chemical artifact vs. time and to propose recommendations for future coal and kerogen storage.

Data on Type II kerogens are reported in Table 5. They clearly show that for less than three to four years, the H/C has not significantly changed whereas the atomic ratio O/C may increase between 20% and 60%. When the storage time is

doubled (8 years), the O/C ratio is multiplied by between 2 and 6 and the H/C ratio is significantly increased.

As a consequence, it was not possible to compare the S3 peak measured by Rock-Eval 2 and Rock-Eval 6 because most of samples selected in this study were provided by Petrobras and the Rock-Eval 2 analyses were performed at various times in the past. Since all Rock-Eval 6 analyses were done this year, alteration of our kerogen set precludes any S3 comparison between Rock-Eval 2 and Rock-Eval 6 in the framework of the present study.

TC, which corresponds to the sum of the organic and mineral carbon, was also determined by elemental analysis on most of selected bulk rocks. In that case, the rock sample was submitted to a combustion at 1050°C. This temperature being much higher than that of the Rock-Eval 6 program, this measurement is a very good crosscheck of the TC. Knowing TC and C_0 , it is possible to determine the theoretical value for mineral carbon content (MinC₀) which can be directly compared to MinC measured by Rock-Eval 6.

2.2.3 Determination of Organic Carbon by the Leco SC-444 Equipment

The Leco SC-444 analyzer, equipped with infra-red detectors, was designed to measure carbon and sulfur content in a large variety of organic materials such as coal, coke and oil, as well as in inorganic materials including soil, cement and limestone.

An amount of 0.25 g is placed in a crucible made of porous porcelain, which is introduced into the combustion furnace. The samples are burned in an oxygen atmosphere at 1350°C, with a constant oxygen flow. Reduced carbon and sulfur contained in the sample are oxidized, thus producing CO₂ and SO₂. These gases are then swept from the sample and carried to the analyzer. After passing through two tubes containing magnesium perchlorate for the retention of

TABLE 5
Influence of time on H/C and O/C atomic ratios for kerogens of three different series of type II during storage under ambient air

Date 1	Date 2	Δt (months)	H/C atomic ratio		O/C atomic ratio		
			1	2	1	2	2/1
29/11/96	16/03/00	40	1.17	1.19	0.115	0.146	1.27
			1.05	1.07	0.066	0.091	1.38
			0.89	0.91	0.036	0.046	1.28
			0.86	0.89	0.062	0.076	1.23
19/06/97	29/02/00	32	1.11	1.10	0.215	0.266	1.24
			1.10	1.13	0.171	0.235	1.37
			0.79	0.79	0.057	0.089	1.56
24/03/92	29/02/00	95	1.28	1.31	0.084	0.181	2.15
			1.05	1.17	0.065	0.248	3.82
			0.85	0.97	0.057	0.190	3.33
			0.60	0.79	0.070	0.412	5.89
			0.58	0.76	0.075	0.302	4.02

humidity, and by one flow controller, CO₂ and SO₂ are measured by two specific infra-red detectors. Measured concentrations (expressed in percentages or parts per million) are calculated by a software which takes into account sample weight, calibration and humidity values. In this paper, C concentrations measured by Leco analyzer are expressed in percentages and labeled C_{leco}.

2.2.4 Preparative Pyrolysis

Preparative pyrolysis experiments were carried out in order to recover the C₆-C₁₄ and C₁₄⁺ fractions of the S2 peak and measure their composition. The knowledge of their carbon content is important for the calculations of organic carbon by Rock-Eval 6.

The preparative pyrolysis device is a cylindrical mini-furnace coated with gold to avoid wall effects, as described in previous publications (Behar and Pelet, 1985; Behar *et al.*, 1989). 20-30 mg of kerogen loaded on a gold rod were introduced into the pyrolysis chamber under argon flow. After a preliminary heating at 300°C for 3 min, the temperature was raised up to 600°C at a rate of 25°C/min, with a temperature program similar to classical Rock-Eval pyrolysis. Effluents were swept away and condensed, along with the carrier gas, in a trap cooled with liquid nitrogen. After pyrolysis completion, the pyrolysate was recovered by addition of solvent in the trap at room temperature, resulting in argon elimination and loss of C₁-C₅ products.

Two pyrolysis experiments were needed for the quantification of the C₆⁺ fraction. The first pyrolysate was recovered with *n*-pentane and fractionated by liquid chromatography into saturates and aromatics (Behar *et al.*, 1989). The recovered solutions were injected as such into a gas chromatograph for their quantification by the FID, previously calibrated with an external standard (saturated C₁₅-C₂₅ distillation cut). Previous molecular analyses of these fractions have enabled to assign carbon content values to the C₆-C₁₄ saturate and aromatic fractions (Behar *et al.*, 1991, 1997) which are respectively 85 and 91 wt%.

The second pyrolysate was recovered in DCM. After solvent evaporation, the C₁₄⁺ fraction was quantified by weighing and submitted to elemental analysis.

For the estimation of the hydrocarbon gas content of the S2 peak, the gas composition from previous studies (Behar *et al.*, 1997) was assigned for each organic matter type (listed in Table 6). The hydrogen content of the C₂-C₅ is an average value (82 wt%) considering that the carbon content is 80 wt% in C₂ and 83 wt% in C₅.

The organic carbon content of the S2 peak (OC (S2)) is calculated as follows:

$$\text{OC (S2)} = Xa * 0.75 + Xb * 0.82 + Xc * 0.85 \\ + Xd * 0.91 + Xe * Ye$$

where Xa and Xb are respectively the C₁ and C₂-C₅ proportions indicated in Table 6, Xc and Xd are respectively

the proportions of the C₆-C₁₄ saturates and aromatics quantified by gas chromatography, Xe is the C₁₄⁺ yield determined by weight and Ye its carbon content measured by elemental analysis.

TABLE 6

Proportion (wt%) of C₁ and C₂-C₅ gas in the S2 peak for standard immature kerogens (after Behar *et al.*, 1997)

Kerogen type	C ₁ (wt%)	C ₂ -C ₅ (wt%)
Type I	2	8
Type II	3	8
Type III	16	13

2.3 Verification of the MinC for Bulk Rocks

Two methods were used for verifying the MinC measured by the Rock-Eval 6: the acidimetry technique and the estimation of the weight loss after carbonate destruction.

2.3.1 Acidimetry Method

The mineral carbon labeled MinC_{ac} can be determined by acidimetry by submitting the bulk rock to HCl acid treatment (Bierner *et al.*, 1978). Typically, 50 to 400 mg of rock are added to a solution of HCl 2N and heated at 80°C during 30 min. After cooling to room temperature, a sodium hydroxide solution at 1.33N is added up to reach a pH equal to 7. The quantity of sodium hydroxide added is automatically measured and enables the calculation of the quantity of carbonates that were dissolved in the acidic solution (after pH variation). After this measurement, the samples are washed, dried and weighed. Theoretically, the weight loss MinC_{wt} must correspond to the carbonate content determined by acidimetry. In the present study, we will present a comparison between both measurements.

2.3.2 Estimation of Weight Loss after Carbonate Destruction

An amount of 0.25-0.26 g of rock sample is placed in a small crucible made of filtering porcelain. Samples are treated with HCl (50%) at room temperature for 24 h for total elimination of carbonates. Afterwards, samples are washed with hot distilled water. One hour later, they are washed with cold distilled water at least four times for elimination of chlorides. The samples are then dried in an open hood under bulb light at 80°C. After total drying, the decarbonated samples are weighed for the calculation of the insoluble residue and carbonate content.

The insoluble residue (IR) corresponds to the fraction of the sample not eliminated by HCl treatment (*i.e.* non-carbonate minerals and organic matter). To calculate IR, the following formula is used:

$$\text{IR (\%)} = \text{MI/MS} * 100$$

where MI is the mass of the insoluble residue, and MS is the mass of the rock sample before acid treatment. The carbonate content is given by subtracting IR% from 100%.

In conclusion, based on all the experimental methods described above the following equations and correlations can be done:

– for bulk rocks:

$$\text{TOC} + \text{MinC} = \text{TC}$$

$$\text{TOC} = C_0$$

$$\text{TOC} = C_{\text{leco}}$$

$$\text{MinC} = \text{MinC}_0$$

$$\text{MinC} = \text{MinC}_{\text{ac}}$$

$$\text{MinC} = \text{MinC}_{\text{wt}}$$

$$T_{\text{max}_{\text{RE2}}} = T_{\text{max}_{\text{RE6}}}$$

$$S_{\text{RE2}} \leq S_{\text{RE6}}$$

– for pure organic matter (coals and isolated kerogens):

$$\text{TOC} = C_k$$

$$T_{\text{max}_{\text{RE2}}} = T_{\text{max}_{\text{RE6}}}$$

$$S_{\text{RE2}} \leq S_{\text{RE6}}$$

3 RESULTS AND DISCUSSION

3.1 Rock-Eval 6 Data: Reproducibility

A subset of 109 samples was analyzed by the Standard and the Turbo Rock-Eval 6 which are available in *IFP*: for both apparatus, each analysis was carefully checked in terms of surface integration and search of the real minimum of CO and CO₂ curves.

During the two to three months' duration of data acquisition, two reference samples were regularly analyzed. The first one is the well-known 55000 source rock (used as a standard for Rock-Eval analysis) and the second one, labeled 46190, is a Toarcian Shale source rock from the Paris Basin. Sample 46190 has a TOC of 7.5 wt%. These two references enable to calibrate the Rock-Eval 6 for a large carbon range (1-10 wt%) which covers the values usually encountered by organic geochemistry laboratories. It is worth noting that in the 55000 sample, the *SI* value is very low, *i.e.* 0.1 mg/g; this

TABLE 7

Data accuracy for source rock and kerogen standards analyzed by Turbo and Standard Rock-Eval 6 apparatus

		TOC	PC	RC	S2	HI	OI	OI CO	Tmax	MinC
		(wt %)			(mg/g)	(mg/g C)			(°C)	(wt%)
Turbo basic 55000 Source rock n = 43	Mean value	2.8	0.8	2.0	8.7	308	36	16	422	4.2
	Standard deviation	0.04	0.02	0.03	0.20	6	6	2	1	0.0
	Max value	2.9	0.8	2.1	9.1	319	49	19	424	4.2
	Min value	2.7	0.7	2.0	8.2	297	25	13	419	4.1
	Relative error (%)	1.3	2.4	1.2	2.3	1.8	17.7	9.4	0.3	0.6
Turbo basic 46190 Source rock n = 23	Mean value	7.5	3.6	3.9	42.0	559	29	17	423	3.0
	Standard deviation	0.08	0.06	0.04	0.66	5	6	1	2	0.1
	Max value	7.7	3.8	4.0	43.7	571	39	19	427	3.2
	Min value	7.4	3.5	3.8	40.7	550.	15	12	420	2.9
	Relative error (%)	1.1	1.7	1.0	1.6	0.9	19.7	7.3	0.4	1.9
Standard basic 55000 Source rock n = 28	Mean value	2.9	0.8	2.1	8.7	298	40	16	420	4.3
	Standard deviation	0.04	0.01	0.03	0.13	4	4	1	1	0.1
	Max value	3.0	0.8	2.2	8.9	305	55	18	422	4.5
	Min value	2.8	0.8	2.1	8.3	290	35	14	419	4.2
	Relative error (%)	1.3	1.2	1.5	1.5	1.3	10.3	6.0	0.2	1.6
Standard basic 46190 Source rock n = 22	Mean value	7.9	3.8	4.1	43.5	553	32	18	421	3.2
	Standard deviation	0.06	0.05	0.04	0.54	4	2	1	1	0.1
	Max value	8.0	3.9	4.2	44.5	561	36	19	422	3.8
	Min value	7.7	3.7	4.0	42.4	545	29	16	420	3.1
	Relative error (%)	0.8	1.2	0.9	1.3	0.8	5.0	4.5	0.2	4.3
Standard MO 55000 Kerogen n = 16	Mean value	49.9	17.7	32.2	148.8	299	39	121	412	nd
	Standard deviation	1.25	0.68	1.42	8.83	20	2	15	1	nd
	Max value	51.3	19.3	34.3	156.9	330	44	156	414	nd
	Min value	46.6	16.9	29.0	121.9	243	36	99	409	nd
	Relative error (%)	2.5	3.8	4.4	5.9	6.6	5.4	12.1	0.4	nd
Standard MO 46190 Kerogen n = 16	Mean value	51.6	28.6	23.0	304.2	590	24	73	418	nd
	Standard deviation	0.39	0.70	0.68	6.65	13	1	20	2	nd
	Max value	52.5	29.7	24.2	315.3	605	28	115	421	nd
	Min value	50.7	27.4	21.8	292.0	566	22	49	414	nd
	Relative error (%)	0.8	2.4	2.9	2.2	2.1	6.3	26.8	0.5	nd

choice was done because samples are usually stored at room temperature in open air. Consequently, the $S1$ value decreases with time by vaporization of free hydrocarbons and this parameter cannot be reliable on a long duration that is necessary for a standard use.

For both reference samples, organic matter isolation was performed in order to determine the Rock-Eval data accuracy on kerogens. These latter were extracted with DCM, thus the $S1$ cannot be quantified.

The statistical calculations on reference samples 55000 and 46190 (bulk rocks and kerogens) for Turbo and Standard Rock-Eval 6 available at IFP are reported in Table 7 for parameters listed and defined in Tables 2a and 2b.

Basic and pure organic matter methods were used for source rocks and kerogens respectively. For rock data, the TOC is slightly overestimated by the Standard Rock-Eval 6 which leads, as a counterpart, to an underestimation of the HI, since the average $S2$ values are the same. A less pronounced overestimation is also observed for MinC. $S2$ measurements show no difference between the two apparatus. Finally, $Tmax$ is slightly lower when measured with the Standard Rock-Eval 6.

In terms of absolute variations, the reproducibility is excellent for TOC, PC, RC, MinC, $S2$ and HI measured by the

two apparatus with less than 2.5% for the relative error. However, for all parameters except MinC, accuracy is higher for the standard 46190 than for the 55000. This is true for both sets of data measured on source rocks and on isolated kerogens. In contrast, the relative error for MinC, although small, is doubled in comparison to that measured on the 55000 sample. These observations suggest that the data accuracy depends more on the sample itself, *i.e.* its organic and/or mineral heterogeneity, than on the absolute concentration or value of the parameters measured by Rock-Eval 6. The total carbon (TOC + MinC) values measured by the two apparatus were also compared to those obtained by elemental analysis (TC). Data reported in Table 8 show that values obtained with Standard Rock-Eval 6 are closer to TC and thus, data measured with Turbo Rock-Eval 6 are slightly underestimated.

TABLE 8
Comparison of the total carbon contents
for the two standards measured by Rock-Eval 6
and elemental analysis

Source rock	Turbo Rock-Eval 6	Standard Rock-Eval 6	Elemental analysis
55000	7.0 ± 0.1	7.2 ± 0.2	7.3 ± 0.3
46190	10.5 ± 0.1	11.1 ± 0.2	11.5 ± 0.3

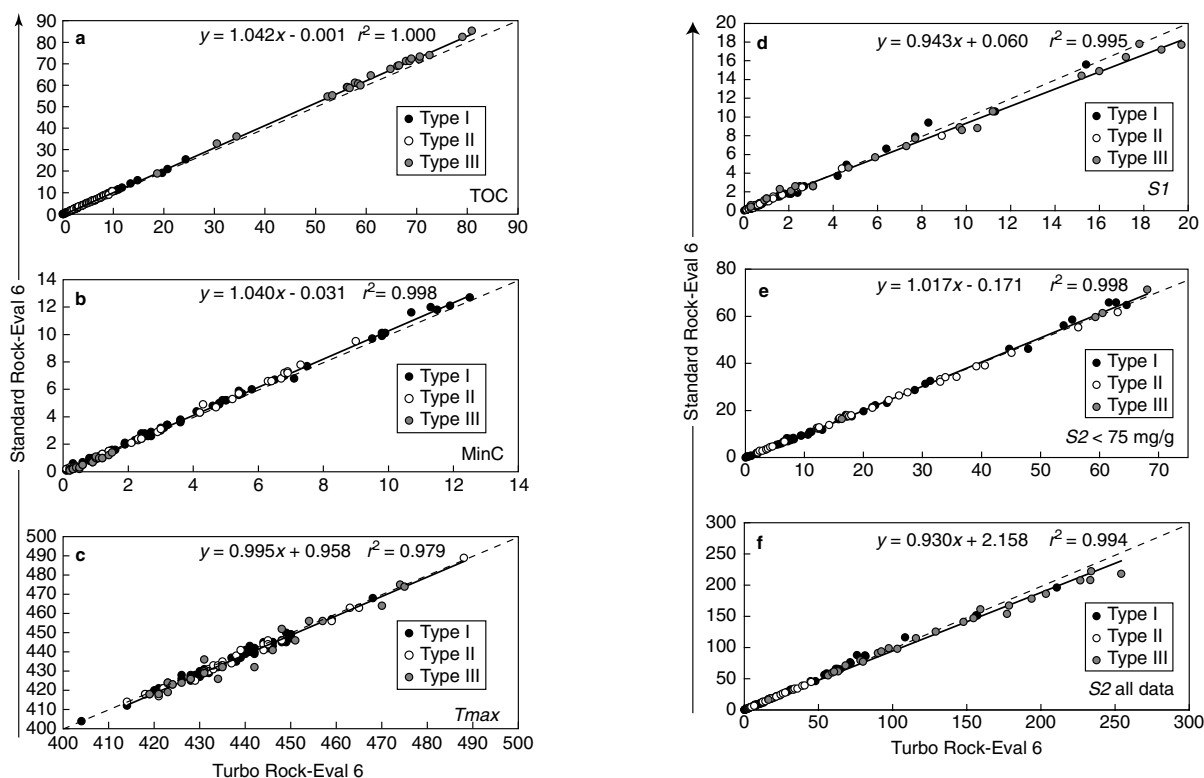


Figure 6

Correlation between Standard Rock-Eval 6 and Turbo Rock-Eval 6 analyses:

(a) TOC; (b) MinC; (c) $Tmax$; (d) $S1$; (e) $S2 < 75$ mg/g; (f) $S2$ all data.

Type I samples. The observed difference may be due to a slight underestimation of the S2 peak measured on kerogens by Rock-Eval 6: this point is discussed further.

For all samples, whatever the organic matter type, the total C₆⁺ pyrolysate represents by far the major fraction of the total pyrolysate with more than 70 wt%. Thus, as the yield and the carbon content of that fraction were determined experimentally for each sample, the carbon content of the total pyrolysate can be accurately determined. The average values found for the three series of kerogens are very similar: 84.2 wt% for Type I, 82.1 and 82.2 wt% for Types II and III samples. The average carbon content is 82.8 wt% which is similar to that proposed by Espitalié *et al.* (1985a, 1985b, 1985c). This study confirms the validity of the coefficient 83 wt% used for TOC calculation.

3.3 Rock-Eval 6 Data: Comparison with Other Methods

3.3.1 Total Carbon in Source Rocks

A total number of 89 samples among the 147 selected were submitted to elemental analyses for a direct measurement of the TC. The comparison between the TC (*i.e.* TOC + MinC) measured by Rock-Eval 6 and elemental analyses is given in Figure 7a for all samples and in Figure 7b for TC values lower than 15 wt%. The correlation obtained with all samples is excellent and matches the 1 × 1 correlation for the total

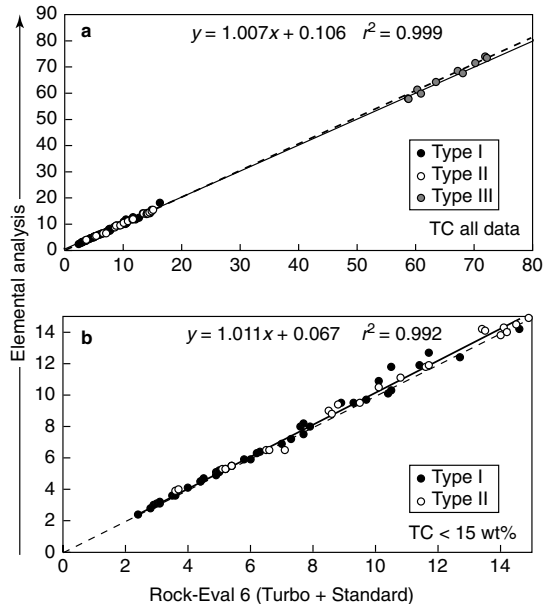


Figure 7

Correlation between Rock-Eval 6 (average values between Standard Rock-Eval 6 and Turbo Rock-Eval 6) obtained on source rocks for: (a) TC and TC determined by elemental analysis for all data; (b) TC and TC determined by elemental analysis for data below 15 wt%.

carbon concentration from 2 to 75 wt%. For lower concentrations, the correlation is still very good but the r^2 is slightly lower, with a value of 0.992 instead of 0.999. Consequently, absolute quantification of the total carbon by Rock-Eval 6 can be done with a very good accuracy for a very large concentration range.

3.3.2 TOC in Source Rocks

As explained in Section 2, the TOC measured on bulk rocks by the Rock-Eval 6 was compared to C₀ calculated by mass balance after mineral matrix destruction and elemental analyses of the recovered i.o.m. and TOC measured by the Leco method (C_{leco}).

Figure 8a displays the comparison of Rock-Eval 6 TOC and C₀ for all samples, TOC values lower than 15 wt% are displayed in Figure 8b. For all samples, the correlation is almost perfect since it matches the 1 × 1 correlation with an

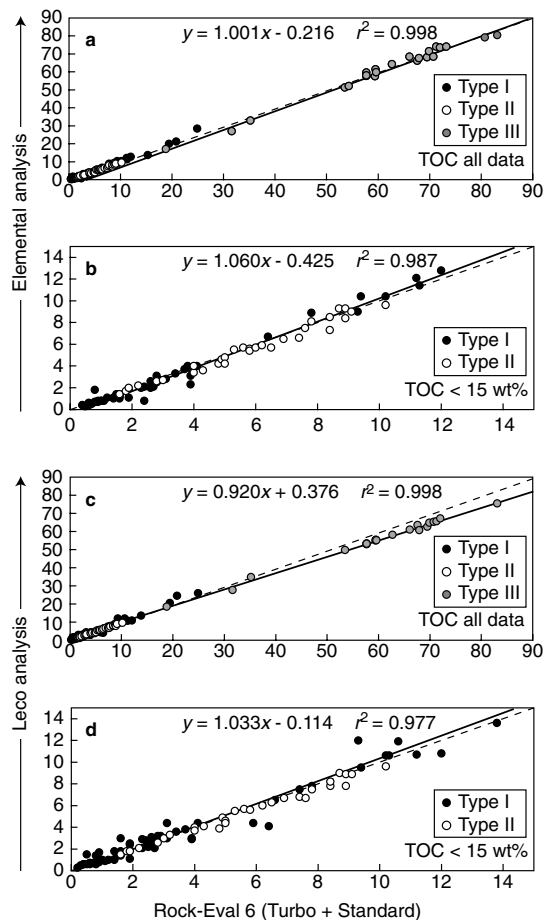


Figure 8

Correlation between Rock-Eval 6 (average values between Standard Rock-Eval 6 and Turbo Rock-Eval 6) obtained on source rocks for: (a) TOC and calculated C₀ for all data; (b) TOC and calculated C₀ for values lower than 15 wt%; (c) TOC and Leco data for all samples; (d) TOC and Leco data for values lower than 15 wt%.

r^2 at 0.998. For low carbon concentration, the correlation is still excellent even if a slight underestimation is observed for Rock-Eval 6 data. Consequently, the good match of the Rock-Eval data with C_0 validates the absolute quantification of the TOC for a very large organic carbon concentration range, *i.e.* from 0.1 to 80 wt%. It is worth noting that the correlation is still good for very high organic carbon concentration when measured on coals.

A comparison is done with TOC determined by Leco, a very nice correlation ($r^2 = 0.998$) is obtained but with a larger deviation from the 1×1 correlation for TOC above 20% (Fig. 8c). For samples with TOC lower than 15 wt% (Fig. 8d), data are more scattered than in the comparison with elemental data. In fact, the Leco measurement is expected to be less precise than C_0 because prior to this analysis carbonates have to be removed: during this step, a part of the organic carbon may be hydrolyzed and lost in the aqueous phase and floating organic particles may be lost when washing the sample for eliminating the salts formed during decarbonation (especially for coals).

In conclusion, because of the need of a decarbonation step prior to Leco measurement, C_0 data are more precise than those obtained by Leco and as a direct consequence Rock-Eval 6 data are also more reliable than Leco ones.

3.3.3 Mineral Carbon in Source Rocks

Prior running bulk rocks containing carbonates, the MinC was quantified on decarbonated rocks. Results, shown in Figure 9, clearly indicate that MinC values do not exceed 0.2 wt% on carbonate-free rocks. Nevertheless, this value even low does not mean that some residual carbonates are still present after acidic attack because no S5 signal was recorded. This 0.2 wt% value corresponds to the S3' signal, which was assigned to MinC contribution in the Basic Method.

Since the TC determined by elemental analysis represents the sum of the organic and mineral carbon, it is possible to get a calculated value for the mineral carbon MinC_0 by

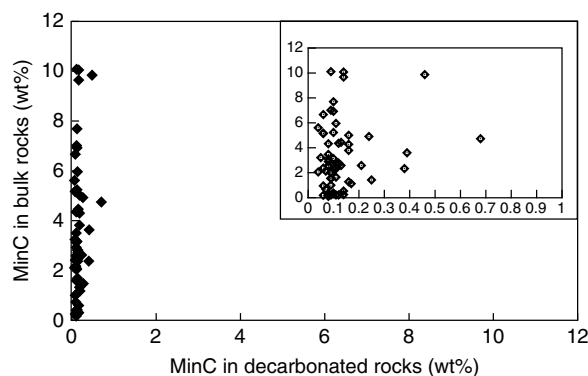


Figure 9

MinC values obtained by Rock-Eval 6 on decarbonated rocks.

subtracting the C_0 value from TC. MinC_0 can be directly compared to MinC determined by Rock-Eval 6 as shown in Figure 10a. A good correlation with $r^2 = 0.983$ is obtained; however, an underestimation is observed with Rock-Eval 6 which seems more pronounced for carbon concentration lower than 4%.

When the same comparison is done with the acidimetry method as indicated in Figure 10b, the r^2 factor drops from 0.983 to 0.933 and an overestimation with Rock-Eval 6 is observed for values higher than 4 wt%. The measurement of carbonate concentration by the acidimetry method can be erroneous as non-carbonate minerals can be dissolved by HCl and mistaken for carbonates. Moreover, in an IFP internal report published by Bienner *et al.* (1978), the authors clearly indicated that this method is less precise than the CO_2 volumetric estimation.

Finally, the correlation between MinC measured by Rock-Eval 6 and that estimated by the weight loss during decarbonation is very poor as indicated in Figure 10c.

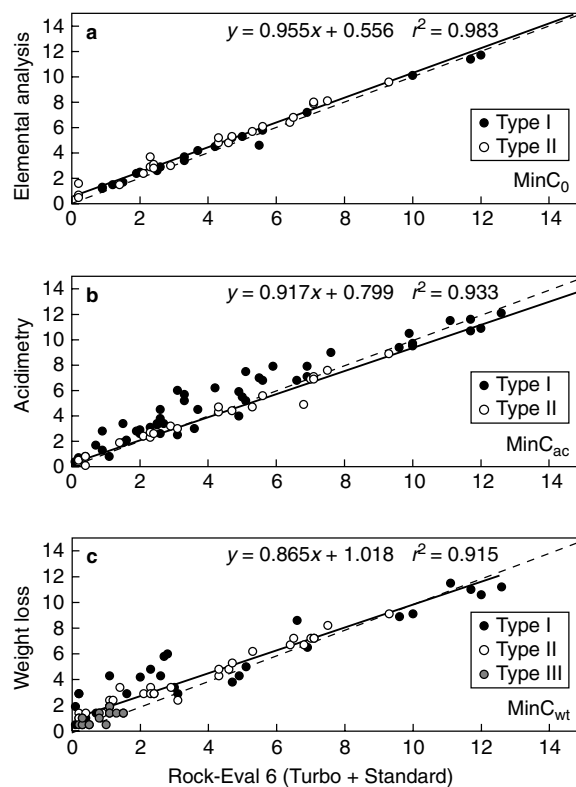


Figure 10

Correlation between Rock-Eval 6 (average values between Standard Rock-Eval 6 and Turbo Rock-Eval 6) obtained on source rocks for: (a) MinC and $(\text{TC} - C_0)$ determined by elemental analysis for all data; (b) MinC and MinC determined by acidimetry; (c) MinC and the weight loss during decarbonation.

3.3.4 TOC on Isolated Kerogens

On a large subset of source rocks (86 samples), kerogen was prepared and then submitted to Rock-Eval 6 pyrolysis and elemental analyses (C_k). For Type III samples, both coals and clays were submitted to acidic treatment in order to recover the corresponding kerogens. The correlation of the TOC measured by the two methods (Fig. 11) presents an r^2 of 0.958 and matches the 1×1 straight line, but data are more scattered than those given in Figure 8b for bulk rocks. We have observed that in contrast to bulk rocks and coals, elemental analyses data obtained on isolated kerogens were less precise. This can be explained by the presence of pyrite in most Types I and II samples, which is concentrated in the organic matter recovered after mineral destruction. In that case, since the sample aliquot amount for elemental analyses is lower than 0.5 mg for the C, H and N measurements, whereas the sample aliquot amount is from 1 to 5 mg for Rock-Eval, these aliquots may contain different proportions of pyrite, thus causing the observed deviation.

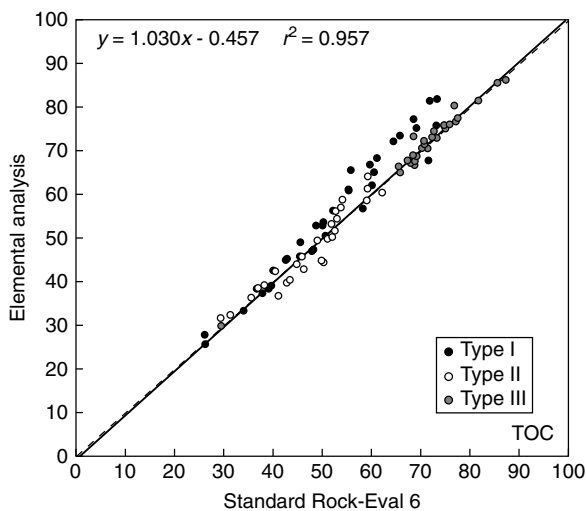


Figure 11

TOC correlation measured on isolated kerogens by Standard Rock-Eval 6 and elemental analysis.

A systematic underestimation by Rock-Eval 6 is observed for Type I kerogens with TOC higher than 50 wt%. However, the difference between the two methods never exceeds 10 wt%. It is worth noting that this difference was not observed for Type III samples when comparing the TC values determined on the initial coals (Fig. 7a) nor when comparing the TOC determined on the isolated kerogen from coals (Fig. 11). The value proposed at 83 wt% for the carbon content of the S2 peak is slightly lower than that found as the average value for Type I series (Table 7). By applying the specific value of 84.3 wt% proposed in Table 7 for Type I samples, the TOC values given by the Rock-Eval 6 increase

only by near 1 wt%. We have also checked that the FID was not saturated for these kerogens by decreasing the initial sample amount. Similar S2 signals were obtained for different sample amounts (Table 10).

TABLE 10
Influence of the sample amounts on the FID response
for a subset of Type I kerogens

Kerogen	C_k (%)	Weight (mg)	S2 (mg/g)	TOC (%)	RC (%)
Green River Shale	81.4	5.16	609	70.3	18.1
		2.77	623	71.2	18.2
		1.89	621	71.0	17.2
Green River Shale	81.8	5.42	625	71.1	18.4
		2.71	647	73.3	17.8
		1.31	630	71.6	17.8
Green River Shale	60.9	5.26	469	53.2	13.5
		2.89	474	53.2	12.9
		1.56	466	52.6	12.5

When comparing the total pyrolysate recovered by preparative pyrolysis (S2 from S2 analyzer, reported from Table 9) and the S2 measured with Rock-Eval 6 for Type I kerogens (Table 11), discrepancies increasing with S2 values are observed between the two methods for samples with S2 values higher than 400 mg/g. TOC (labeled b) calculated in substituting the Rock-Eval 6 S2 values by the S2 values calculated after preparative pyrolysis results (S2 from S2 analyzer) leads to values adequate with TOC measured by elemental analysis (labeled a) (Table 11).

This suggests that hydrocarbon effluents produced during pyrolysis of Type I kerogen samples do not undergo a complete combustion in the flame of the FID in the standard conditions (H_2 30 ml/min; air 270 ml/min) defined for routine analysis. In order to test this hypothesis we have measured the S2 value of the sample labeled 7 with different flame conditions by changing the H_2 flow. Based on ten measurements for each H_2 flow tested, Figure 12 displays that S2 yields can be increased by slight variations of flame conditions. For a H_2 flow of 28 ml/min, an average S2 value of 667 mg/g was obtained, the corresponding calculated TOC is 77.8 wt%. A precise adjustment of flame conditions such as a complete combustion is achieved was not attained. Figure 12 also shows that even though higher yields are obtained with non-standard flame conditions data are more dispersed. Fluctuations of the answers with the H_2 flow are not explained. It is worthy to note that analyses of standard 55000 with the different flame conditions tested in this study were leading to constant S2 yields.

As a consequence, Rock-Eval 6 analysis of very rare kerogen samples with S2 values higher than 400 mg/g is not reliable. TOC values measured for those samples have to be

TABLE 11

Comparison of TOC measured on Type I kerogens by: a) elemental analysis;
b) Conjugation of S2 analyzer data for total pyrolysate (given in Table 9)
and CO and CO₂ effluents measured by infrared with Rock-Eval 6 (PC from IR and RC); c) Rock-Eval 6

Sample label	S2 (mg/g)		$\Delta S2$ (mg/g)	PC (wt% from HC)		PC (wt% from IR)	RC (wt%)	TOC (wt%)		
	S2 analyzer	Rock-Eval 6	S2 analyzer vs. Rock-Eval 6	S2 analyzer	Rock-Eval 6	Rock-Eval 6	Rock-Eval 6	(a) Elemental analysis	(b) S2 analyzer	(c) Rock-Eval 6
1	119	115	4	9.9	9.6	2.1	35.7	46.7	47.6	47.4
2	201	179	22	16.7	14.9	0.9	20.3	38.2	37.9	36.1
3	280	302	-22	23.2	25.3	1.3	47.9	76.0	72.4	74.4
4	393	383	10	32.6	31.8	1.8	38.9	75.7	73.3	72.5
5	558	463	95	46.3	38.5	3.3	12.6	60.9	62.2	54.4
6	632	538	94	52.5	44.8	1.9	25.1	78.4	79.5	71.8
7	721	584	137	59.8	48.5	3.2	19.2	81.4	82.2	70.9
8	745	614	131	61.8	51.1	2.0	19.2	81.8	83.0	72.3

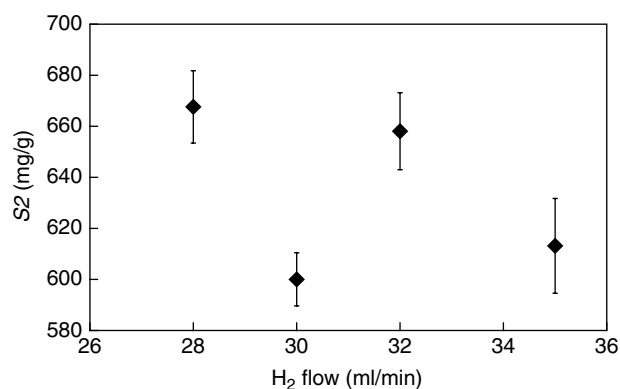


Figure 12

S2 yields for a Type I kerogen vs. FID flame conditions: each symbol displays average value for ten measurements; error bars give the standard deviation.

checked by elemental analysis. In case of discrepancy between TOC obtained by elemental analysis on one hand and Rock-Eval 6 analysis on the other hand, the TOC value determined by Rock-Eval 6 will not be valid.

3.3.5 Comparison of Rock-Eval 6 and Rock-Eval 2 Data

As mentioned in Section 2, the comparison of S2 and Tmax from Rock-Eval 6 and Rock-Eval 2 was done for Type I and Type II source rocks: this represents around 70 samples. For the S2 peak, the correlation given in Figure 13a is good, with S2 values systematically higher for the Rock-Eval 2 but the difference with Rock-Eval 6 does not exceed 5 relative wt% for values higher than 80 mg/g and 10 relative wt% for values ranging between 20 and 80 mg/g. For Tmax values, the correlation given in Figure 13b displays a deviation between Rock-Eval 2 and Rock-Eval 6 increasing with

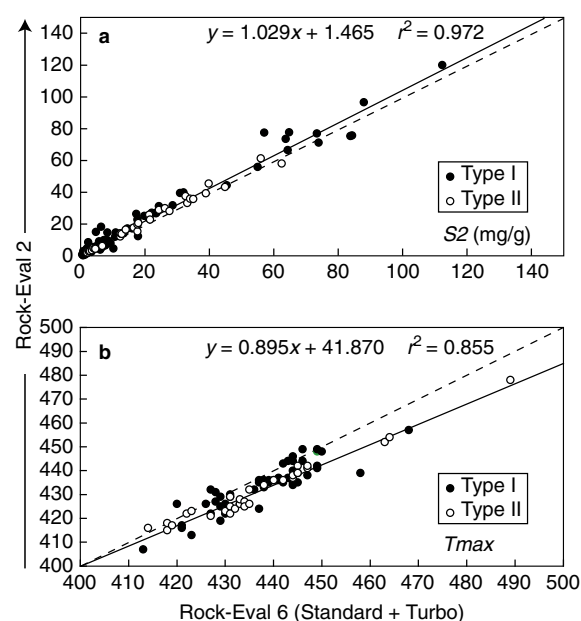


Figure 13

Correlation between Rock-Eval 2 and Rock-Eval 6 data: (a) S2 (mg/g); (b) Tmax.

Tmax, higher Tmax are recorded with Rock-Eval 6. This fact is intrinsic to the differences between the two Rock-Eval versions, in conditions for temperature measurement described in Section 2.1.4 (probe location), superposed to the carrier gas effect.

Indeed, the differences between these two techniques for estimating S2 are:

- the final pyrolysis temperature (650°C for the Rock-Eval 6 and 600°C for the Rock-Eval 2);
- the carrier gas (nitrogen and helium respectively).

A higher pyrolysis temperature is not the right factor for explaining the S_2 differences since lower values are measured by Rock-Eval 6.

We have checked the influence of the carrier gas by running reference source rocks (sample 46190) with the Rock-Eval 6 (standard version), using helium or nitrogen. First, we have studied the influence of the sample amount on S_2 and T_{max} values when pyrolysis is done under helium or nitrogen (Table 12). For sample amounts between 5 and 78 mg the S_2 responses are very homogeneous with nitrogen as carrier gas: values are comprised between 42.0 and 44.3 mg/g (Fig. 14a). In contrast, under helium the S_2 response increases from 36.6 to 47.8 mg/g for the same range of initial amounts (Fig. 14b). For this sample, S_2 values obtained under nitrogen on one hand and helium on the other hand are convergent when the product of S_2 by amount of sample is around 800. For T_{max} , systematically higher values are obtained under nitrogen. As a general trend, T_{max} increases with sample size. Displayed data are mean values obtained on three measurements for helium and three to fifteen measurements for nitrogen. Standard deviations obtained for measurements under nitrogen are lower, especially for T_{max} values.

In conclusion, more reliable data are obtained under nitrogen: this point is very important for kinetic studies. A comparative kinetic study was also run on reference sample 46190. Data obtained at heating rates ranging from 1° to 25°C/min are displayed in Table 13. With helium as carrier gas, it is observed that the S_2 yield increases with the heating rate and thus, it is not possible to get consistent data. In contrast, similar values are obtained whatever the heating rates are when using N_2 (according to theoretical expectations). Another appreciable consequence of running

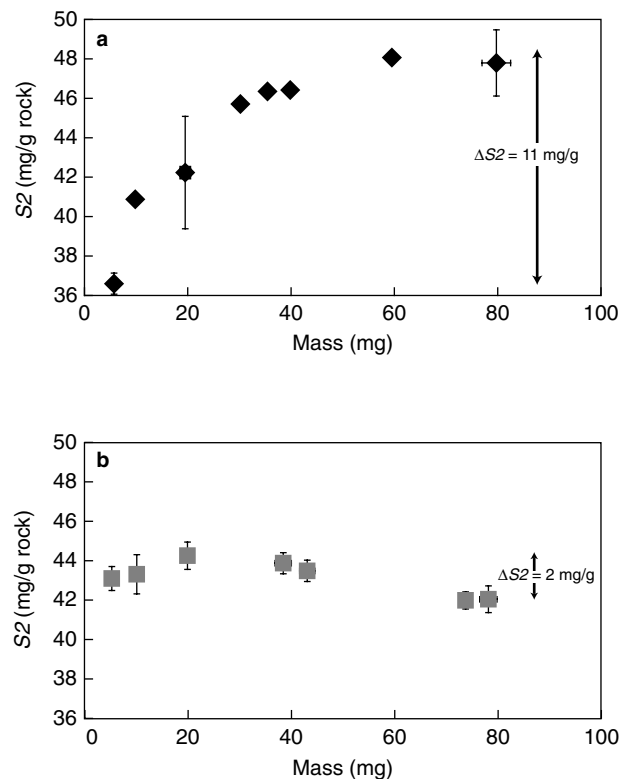


Figure 14

Influence of the carrier gas on the S_2 peak measured by Rock-Eval 6: (a) carrier gas = helium; (b) carrier gas = nitrogen.

samples under nitrogen is that the whole system is less sensible to micro gas leaks and thus data are more reproducible.

TABLE 12

Influence of the initial sample amount on the S_2 and T_{max} parameters from pyrolysis under nitrogen and helium flow with Rock-Eval 6 on sample 46190

Sample amounts (mg)	Carrier gas	S_2 (mg/g)	Standard deviation	T_{max} (°C)	Standard deviation	$S_2 \times$ amount
5.30	Nitrogen	43.1	0.6	415	0	228
5.80	Helium	36.6	0.5	411	2	212
10.13	Nitrogen	43.3	1	417	0	439
10.03	Helium	40.6	0.2	413	0	407
19.93	Nitrogen	44.3	0.7	419	1	883
19.59	Helium	42.2	2.9	415	2	827
38.48	Nitrogen	43.9	0.5	421	1	1689
35.50	Helium	46.4	0.1	414	2	1647
43.13	Nitrogen	43.5	0.6	421	1	1876
39.90	Helium	46.4	0.3	415	1	1851
73.78	Nitrogen	42.0	0.4	423	1	3099
79.81	Helium	47.8	1.7	418	4	3815

TABLE 13
Estimation of the S_2 peak by Rock-Eval 6
under helium and nitrogen for various heating rates

°C/min	46190 source rock	
	S_2 (He)	S_2 (N ₂)
25	47.0	42.7
15	44.2	43.0
10	43.6	42.1
5	41.0	43.0
2	38.4	42.3
1	35.3	42.1

Whatever, the correlations observed in Figures 13a and 13b for both S_2 and T_{max} values do not preclude comparison of data obtained by Rock-Eval 2 and those obtained by Rock-Eval 6 for confident geochemical interpretation.

CONCLUSION

The new version of the Rock-Eval technique, *i.e.* the Rock-Eval 6, was commercialized for the first time in 1996. Its main new technology was focused on a better measurement of temperature along the heating program, and a specific measurement of carbon oxide effluents which enables discrimination between mineral and organic carbon. The aim of our study was to determine the accuracy of the different parameters determined by the Rock-Eval 6 and to crosscheck the quality of quantitative values by other independent techniques.

In terms of reproducibility, two standards were analyzed regularly during two to three months on both Rock-Eval 6 equipment available in our laboratory: the first one is the Turbo version and the second one a Standard version. The relative error for S_2 , TOC, HI, PC, RC, MinC and T_{max} was found to be lower than 2.5 wt% for both apparatus. S_1 was not analyzed because of its very low content in our standards. The relative error is higher for OI and OI CO and a specific study is in progress for improving the measurement of these two parameters.

After checking of the data reproducibility, 147 bulk rocks, including two series of coals, were selected from the *IFP* rock collection. All the analyses were duplicated on our two apparatus. The comparison of the whole set of Rock-Eval parameters, including the S_1 , from both apparatus demonstrates a very good intra-laboratory reproducibility.

For checking the absolute carbon measurement by Rock-Eval 6, the TC of almost 100 bulk rocks, including the two series of coals, was determined by elemental analyses. The correlation between the two methods was found excellent and almost fits the 1 × 1 straight line all along the investigated carbon range from 2 wt% to values higher than 80 wt%. This means that the Rock-Eval 6 technique is as

accurate as the elemental analysis for measurement of the total carbon on a very large concentration range.

For the specific determination of the total organic carbon (TOC), results obtained with Rock-Eval 6 were compared to C_0 which is a calculated value based on the yield of organic matter recovered after mineral destruction and on the carbon content of this organic matter. It was shown that C_0 is a very reliable parameter because its estimation is given with a relative error of 1.6 wt%. The quality of the correlation between TOC and C_0 from less than 0.5 to more than 80 wt% demonstrates the reliability of TOC measurements with Rock-Eval 6. Comparison with Leco data (C_{leco}) was not as spectacular because the analytical protocol for Leco analysis includes an acidic attack followed by several water washings that may lead to loss of organic material.

Knowing the TC and C_0 , the mineral carbon $MinC_0$ is obtained by difference. $MinC_0$ was compared to $MinC$ determined by Rock-Eval 6. Although the correlation displays an $r^2 = 0.983$, there is a slight underestimation by Rock-Eval 6 but it is not significant enough to shift the TC value estimated by this technique compared to that obtained by elemental analysis. In contrast, a poor correlation is obtained when comparing the Rock-Eval 6 $MinC$ and the value obtained by acidimetry method ($MinC_{ac}$) which cannot be considered as a reliable technique for calibrating this parameter.

For organic carbon measurement on pure organic matter, *i.e.* isolated kerogens, the correlation between Rock-Eval data and elemental analysis is still excellent for kerogens from Types II and III organic matter. However an underestimation between 5 and 10 relative wt% of Rock-Eval 6 results to elemental analysis is observed for Type I immature samples.

In conclusion, for total, organic and mineral carbon determination on source rocks and coals, Rock-Eval 6 is a powerful technique. Very accurate data can be obtained at once for complete ranges for both organic and mineral carbon: 0 to 90 wt% and 0 to 12 wt% respectively within one hour. We recommend to select three or four samples on which TC, C_0 and $MinC$ are known as standards for checking these parameters at least once a week. Therefore, following this methodology, it is no more necessary to calibrate these parameters by other methods, which means a significant reduction in the experimentation time.

Finally, it was demonstrated that for Types I and II source rocks, S_2 and T_{max} measured by Rock-Eval 2 and Rock-Eval 6 are fully consistent. However, a slight underestimation of the S_2 is observed for Rock-Eval 2. This effect is linked to the change of carrier gas from helium to nitrogen in Rock-Eval 6 which is justified by acquisition of more robust data.

The T_{max} correlation is characterized by scattered data due to the position of the probe in the Rock-Eval 2, which implies less accuracy compared to Rock-Eval 6. A special attention was given for temperature measurement on Rock-Eval 6 leading to much more reliable data.

ACKNOWLEDGEMENTS

Special thanks are expressed to T. Lesage, F. Le Bihan, R. Martinez, C. Leblond and B. Jarry for all the analyses undertaken at IFP. T. Lesage is also acknowledged for drawing the figures of the present paper. D. Pillot and F. Marquis are acknowledged for their devotedness in developing the Rock-Eval 6.

We would also like to express our gratitude to Dr. Luiz Antonio Freitas Trindade, head of the Geochemistry Section at the *Petrobras R&D Center*, for authorization and encouragement in running Rock-Eval 2 analyses for this study. Special thanks are due to Ligia Jeremias Lemos de Aquino and Marcelo Santos Lima, laboratory technicians responsible for the Rock-Eval 2 analyses undertaken in the geochemical laboratories in Rio de Janeiro, Brazil.

REFERENCES

- Behar, F. and Pelet, R. (1985) Pyrolysis-Gas Chromatography Applied to Organic Geochemistry, Structural Similarities Between Kerogens and Asphaltenes from Related Rock Extracts and Oils. *J. Anal. Appl. Pyr.*, 8, 173-187.
- Behar, F., Saint-Paul, C. and Leblond, C. (1989) Analyse quantitative des effluents de pyrolyse en milieu ouvert et fermé. *Rev. Inst. fr. Pét.*, 44, 3, 387-397.
- Behar, F., Ungerer, P., Kressmann, S. and Rudkiewicz, J.L. (1991) Thermal Evolution of Crude Oils in Sedimentary Basins: Experimental Simulation in a Confined System and Kinetic Modelling. *Rev. Inst. fr. Pét.*, 46, 2, 151-181.
- Behar, F., Vandenbroucke, M., Tang, Y., Marquis, F. and Espitalié, J. (1997) Thermal Cracking of Kerogen in Open and Closed Systems: Determination of Kinetic Parameters and Stoichiometric Coefficients for Oil and Gas Generation. *Org. Geochem.*, 26, 5/6, 321-339.
- Bienner, F., Laporte, J.L. and Espitalié, M. (1978) Méthodes de dosage dans les roches du carbone minéral et organique mises au point et pratiquées dans la Division Géologie IFP. *IFP report*, No. 22330.
- Durand, B. and Nicaise, G. (1980) Procedure for Kerogen Isolation, *Kerogen*, Durand, B. (ed.), Éditions Technip, 35-53.
- Espitalié, J., Deroo, G. and Marquis, F. (1985a) La pyrolyse Rock-Eval et ses applications. *Oil & Gas Science and Technology*, 40, 5, 563-579.
- Espitalié, J., Deroo, G. and Marquis, F. (1985b) La pyrolyse Rock-Eval et ses applications. *Oil & Gas Science and Technology*, 40, 6, 755-783.
- Espitalié, J., Deroo, G. and Marquis, F. (1985c) La pyrolyse Rock-Eval et ses applications. *Oil & Gas Science and Technology*, 41, 1, 73-89.
- Lafargue, E., Marquis, F. and Pillot, D. (1998) Rock-Eval 6 Applications in Hydrocarbon Exploration, Production and Soils Contamination Studies. *Oil & Gas Science and Technology*, 53, 4, 421-437.

Final manuscript received in February 2001